

REACTIVITIES OF STABLE ROTAMERS:  
STUDIES IN SOME 9-(2-SUBSTITUTED-  
6-METHYLPHENYL)FLUORENE DERIVATIVES

1985

Shigeru Murata

To my family

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Chapter I  
General Introduction

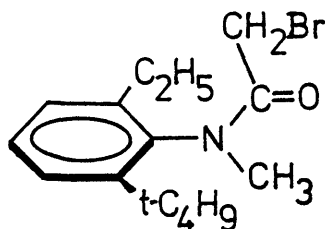
## I General Introduction

The concept of rotational isomerism, which was established by Mizushima and his co-workers in the dipole moment and vibrational studies of 1,2-dichloroethane in 1930's, was developed in all fields of chemistry during the last fifty years.<sup>1</sup> Combined with a large development of nuclear magnetic resonance spectroscopy, the physical organic chemists performed the systematic studies on the observations of rotational dynamic processes<sup>2</sup> and detections of weak interactions governing conformational distributions.<sup>3</sup>

In the field of the organic reaction mechanism, many works have been done on the theoretical and experimental studies of the differences in reactivities of conformational isomers. Curtin and Hammett showed that the distribution of reaction products from conformational isomers was dependent not only on the equilibrium constant but on the difference of the activation energies for reaction of each conformer, if the rotational barrier of conformers was much less than the activation energies of the reaction.<sup>4</sup> The differences in reactivities of conformational isomers have been studied in the systems of 4-*t*-butylcyclohexyl and 3,5-dimethylcyclohexyl derivatives, which are known to exist practically in a single conformer because of the large equilibrium constant. However, since there are the cases that the differences in reactivities

of conformational isomers reach more than  $10^4$ , for example, the dehydration of rotamers of di-*t*-butyl-*o*-tolylmethanols,<sup>5</sup> in a more precise sense the study on the differences in reactivities of conformational isomers should be performed in the research of each conformer independently.

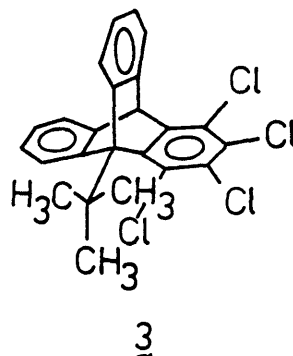
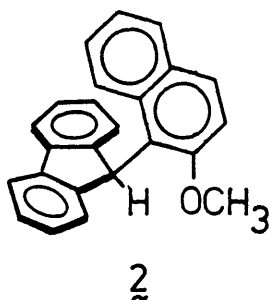
It was the isolation of rotational isomers that could realize the idea. Though Christie and Kenner reported the optical resolution of 2,2'-dinitrodiphenyl-6,6'-dicarboxylic acid more than 60 years ago,<sup>6</sup> the isolation of rotational isomers involving the tetrahedral carbon atoms was achieved only in 1970's.<sup>3a</sup> The pioneering work on the reactivities of stable diastereomeric rotational isomers was done by Chupp and Olin.<sup>7</sup> They isolated stable rotamers of 2'-*t*-butyl-2-bromo-6'-ethyl-*N*-methyl acetoanilides (1) and showed the large difference of their reactivities in the bimolecular



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nucleophilic substitution reaction with pyridine. Ōki and his co-workers reported that the hydrogen at 9-position of the ap-conformer of 9-(2-methoxy-1-naphthyl)fluorene (2) was lithiated over  $10^3$  times faster than that of the sp-conformer.<sup>8</sup> Moreover they also showed that in radical

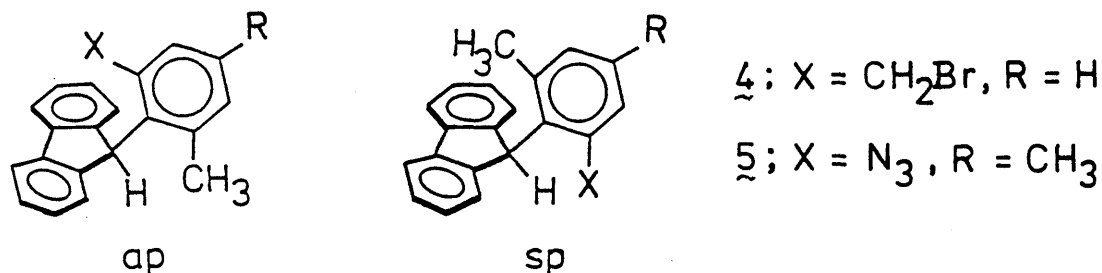




halogenations of 9-*t*-butyl-1,2,3,4-tetrachlorotriptycene (3) *±*sc-methyls was 1.6 times more reactive than the *ap*-methyl.<sup>9</sup> These results can be understood as in the conformationally fixed systems the weak interaction which involves steric and electronic participations of the neighbouring group is amplified and becomes to be observed explicitly. Therefore the studies of reactivities of stable rotational isomers could contribute highly to the investigation of weak interactions which governs organic reactions.

In 9-arylfluorenes (4) and (5), particularly, it is expected that the functional group X on the ortho position exists on a very different environment between the rotational isomers. The functional group of the one isomer is situated right over the fluorene ring, and thus its reactivities would be much influenced by the  $\pi$ -electrons of the fluorene ring, while that of the other isomer would have a less influence of the fluorene  $\pi$ -electrons but a possibility to interact with the 9-hydrogen of fluorene. In this thesis, according to the IUPAC nomenclature,<sup>10</sup> the rotational isomer with a functional group in anti position against the 9-hydrogen of fluorene is

called an ap-conformer, and in syn position called an sp-conformer.



In the independent investigation by Siddall,<sup>11</sup> Ford<sup>12</sup>, and Ōki,<sup>13</sup> 9-arylfluorenes have barriers to rotation around the C<sub>9</sub>-C<sub>Ar</sub> bond of more than 24 kcal/mol, which is high enough to isolate the rotational isomers at room temperature, if the aryl group is either 2,6-disubstituted phenyl or 2-substituted 1-naphtyl group.

The author synthesized and separated two pairs of the rotational isomers in 9-(2-substituted-6-methyl)phenylfluorene systems and investigated the differences in reactivities of isomers. One of them is a nucleophilic substitution reaction of the isomers of 9-(2-bromomethyl-6-methyl)phenylfluorene (4).<sup>14</sup> Since it is well known that in a unimolecular reaction (S<sub>N</sub>1 reaction) a cationic intermediate is involved and a bimolecular reaction (S<sub>N</sub>2 reaction) is much sensitive to steric effects, the research of the differences in reactivities of the rotamers would reveal the electronic and steric effect of the fluorene ring explicitly. The results

are discussed in Chapter 2.

The other is a photochemical reaction of rotational isomers of 3,5-dimethyl-2-(9-fluorenyl)phenyl azides (5).<sup>15</sup> In the photolysis of these azides, the conformationally fixed nitrenes should be generated. The direct observation of these nitrenes by means of some spectroscopic techniques and the structural analysis of photoproducts would elucidate the interaction of these reactive monocentric diradical intermediates with the fluorene moiety. The results are discussed in Chapter 3.

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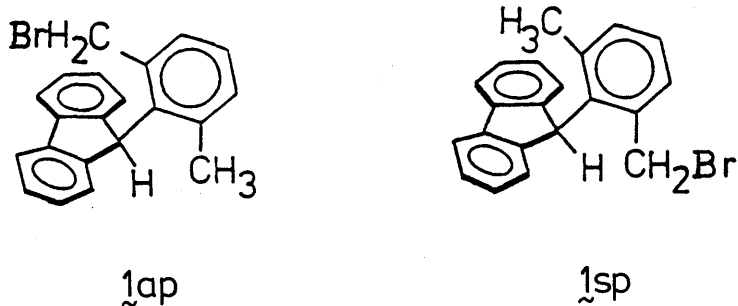
## Chapter II

### Nucleophilic Substitution Reactions of 9-(2-Bromomethyl-6-methylphenyl)fluorene Rotamers

## II Nucleophilic Substitution Reactions of 9-(2-Bromomethyl-6-methylphenyl)fluorene Rotamers

### 2-1 Introduction

The title compounds (1) were synthesized and separated into ap- and sp-rotamers by Nakamura and Ōki in 1974.<sup>1</sup> As pointed out in the previous section, the bromomethyl group of each rotamer is situated in a very different environment. Therefore the author is much interested in investigating the differences in reactivities of the bromomethyl group of 1<sub>ap</sub> and 1<sub>sp</sub>.



A nucleophilic substitution reaction of alkyl halides is one of the reactions of which mechanisms have been most studied in detail. Since the reactivities of alkyl halides to nucleophiles are known to be very sensitive to the structural change of the substrates, the investigation of reactivities toward various nucleophiles will serve to reveal the steric and electronic participations of the substituent groups on the reaction center. A typical example reported by Kevill and

Degenhardt on the reactivities of the allyl chlorides to some nucleophiles is shown in Table I.<sup>2</sup>

The purpose of the studies discussed in this chapter is to elucidate the differences in the environment of the bromomethyl group of **1ap** and **1sp**, that is, the differences of the steric and electronic effects of the fluorene ring on the reactivities of the functional group. The author studies the differences in the reactivities of **1ap** and **1sp** toward the various nucleophiles quantitatively and isolates the reaction products to determine their structures. According to the classification of the nucleophiles advanced by C. K. Ingold, the results are shown in two separate sections; unimolecular ionizing reactions involving forced ionizations with silver salts are discussed in section 3 and bimolecular substitution reactions with nucleophiles are in section 4.

## 2-2 Preparation and rotational barrier of 9-(2-bromomethyl-6-methylphenyl)fluorene rotamers

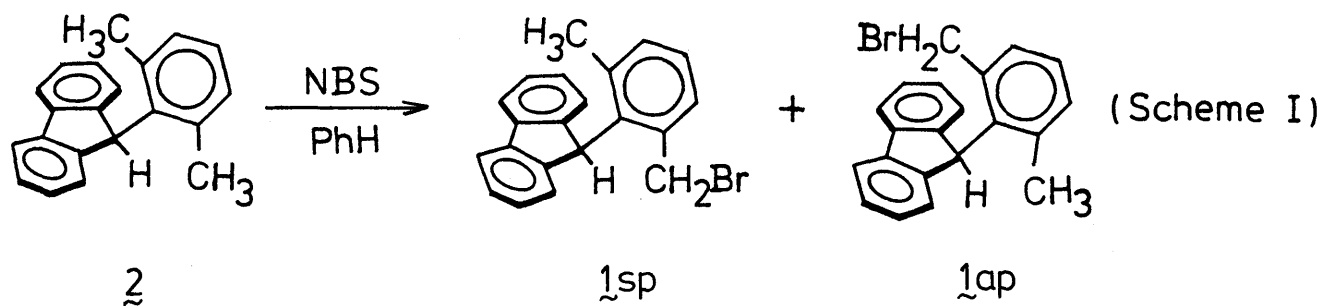
Before discussions on the reactivities of **1**, the preparation of these rotamers and the measurement of their rotational barrier should be stated. As described by Nakamura and Ōki,<sup>1</sup> **1** was synthesized from the bromination of 9-(2,6-dimethylphenyl)fluorene (**2**) by N-bromosuccinimide (NBS). The separation of the rotational isomers of **1** was performed by means of a chromatography on silica gel or a preparative



Table I. Relative Rates of Allylic Chlorides under Various Conditions

substituent	KI in		NaOEt in		EtOH		AgNO <sub>3</sub> in		AgNO <sub>3</sub> in		AgClO <sub>4</sub> in		HCO <sub>2</sub> H
	acetone	EtOH	EtOH	EtOH	CH <sub>3</sub> CN	EtOH	CH <sub>3</sub> CN	EtOH	CH <sub>3</sub> CN	EtOH	CH <sub>3</sub> CN	EtOH	
$\alpha$ -methyl	0.02		0.06		3.3		5.3	187	2230				5670
$\beta$ -methyl	1.6		1.03		1.3		2.2						0.5
cis- $\gamma$ -methyl	8.4		5.2				15						
trans- $\gamma$ -methyl	1.6		4.4		16		19	321	1000				3550
none (allyl)	1.0		1.0		1.0		1.0	1.0	1.0				1.0

liquid chromatographic apparatus equipped with  $\mu$ -porasil column, which used hexane as an eluent. The sp-form ( $\downarrow$ sp) was eluted first and the ap-form ( $\downarrow$ ap) follows (Scheme I).



Assignment of the stereochemistry of the rotamers was performed by taking the ring current effect of the fluorene ring in  $^1\text{H}$ NMR spectra into account. In  $\downarrow$ ap, the bromomethyl group is in the shielding area of the benzene ring, while the methyl group is in the deshielding area. In contrast, the bromomethyl group in  $\downarrow$ sp is in the deshielding and the methyl group is in the shielding. Therefore in  $\downarrow$ sp the methyl and the methylene protons should show a large difference in chemical shifts, while those in  $\downarrow$ ap should show a small difference.

The activation energy for the rotation around the  $\text{C}_9\text{-C}_{\text{Ar}}$  bond of  $\downarrow$ ap was 27.1 kcal/mol, reported by Nakamura and Ōki.<sup>1</sup> Putting the rate constants reported in their paper into the Eyring equation, the activation parameters for the conversion of the ap-isomer to the sp are obtained, which are shown in Table II together with the free energy of activation and the

Table II. Kinetic Parameters for the Conversion of  
 $\text{lap}$  to  $\text{lsp}$

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$$\Delta H^\ddagger = 26.3 \text{ kcal/mol}$$

$$\Delta S^\ddagger = -9.3 \text{ e.u.}$$

$$\Delta G^\ddagger_{353} = 29.6 \text{ kcal/mol}$$

$$k_{353} = 3.5 \times 10^{-6} \text{ sec}^{-1}$$

$$K^a) = 3.6 \pm 0.2$$

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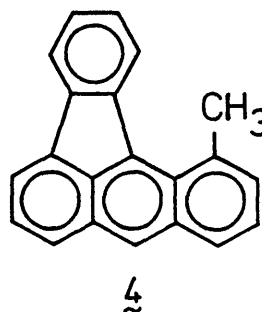
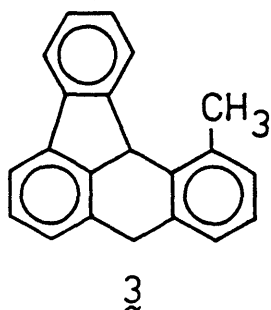
a) The equilibrium constant,  $[\text{sp}]/[\text{ap}]$ , was invariant throughout the temperature range examined.

calculated rate constant at 353K. The barrier to rotation in 9-(2,6-dimethylphenyl)fluorene (**2**) was reported to be more than 25 kcal/mol, which was too high to be measured by the dynamic NMR studies.<sup>3</sup> The present results conform with this prediction. Calculated from the rates of rotation at 80°C, the time necessary for conversion of e.g. 5% of  $\text{lap}$  to  $\text{lsp}$  at this temperature is ca.  $1.4 \times 10^5$  sec. The value gives the author the guarantee that the interconversion of the rotamers in the course of the reactions need not be considered, because the nucleophilic substitution reactions studied in this chapter are carried out at the temperature below 80°C and in not so long a reaction time.<sup>4</sup>

It should be noticed that the equilibrium constant,  $K$ , is 3.6, meaning that  $\lambda_{sp}$  is more stable than  $\lambda_{ap}$ . Moreover the equilibrium constant is found to be invariant throughout the temperature range examined, which suggests that the equilibrium is controlled by the entropy. It may be explained in terms of the restriction of the conformations in the bromomethyl group and imperfections of the solvent shell in  $\lambda_{ap}$ . Since the bromine atom is too large to direct toward the fluorene ring, the freedom for rotation of the bromomethyl group is reduced in  $\lambda_{ap}$ . Formation of a solvent shell cannot be completed with the solvent molecules in  $\lambda_{ap}$  because of the steric effect of the fluorene moiety.

#### 2-3 Ionizing reactions of 9-(bromomethyl-6-methylphenyl)-fluorene rotamers

Preliminary experiments of heating the isomer of  $\lambda$  in trifluoroacetic acid showed that  $\lambda_{ap}$  reacted at a pseudo-first order rate constant of  $1.4 \times 10^{-5} \text{ sec}^{-1}$  at  $62^\circ\text{C}$ , while  $\lambda_{sp}$  did not react with a measurable rate under the same conditions.<sup>5,6</sup> The product of the reaction of  $\lambda_{ap}$  were dependent on the concentration. If the concentration was high, a mixture of polymers which could be formed by an intermolecular Friedel-Crafts reaction was obtained. If the concentration was lowered, however, two identifiable products were obtained; 12-methyl-8,12b-dihydrobenz[a]aceanthrylene (3) and 12-methyl-



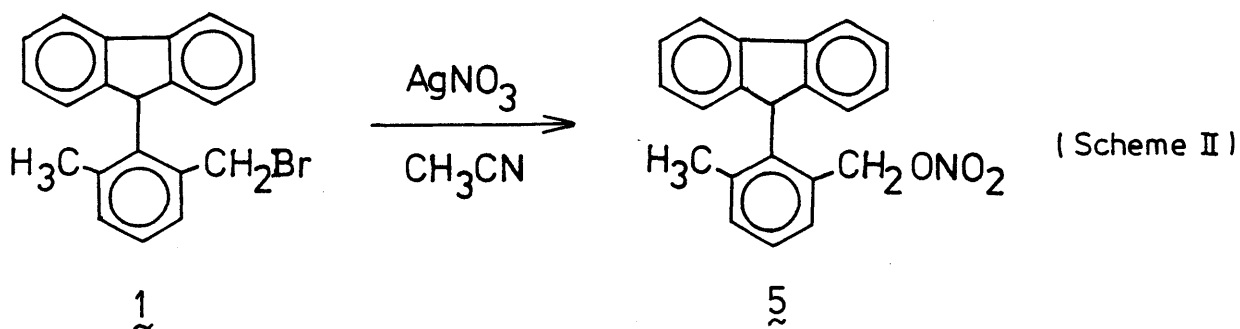
benz[a]aceanthrylene (4). The formation of 3 was rationalized by considering the ionization at the bromomethyl group and the intramolecular Friedel-Crafts cyclization. Since the amount of 4 could be reduced appreciably if the reaction was carried out under nitrogen, 4 seemed to be formed from 3 by dehydrogenation with air in the course of the reaction. In order to get further informations on the differences in the ionizing reactivities of 1ap and 1sp, the author carried out the forced ionization reactions with silver salts and the solvolysis in some ionizing solvents.

#### Reaction with silver nitrate

Silver salts are often used for forced ionization of organic halides. Though it is known that the addition of silver salts increases the unimolecular character of the substitution reactions, the reaction mechanism is not well understood because of the complexity derived by the catalytic action of the precipitated silver halide and the diversity of the reaction products. Pocker and Wong found the reaction of neopentyl or 1-adamantyl halides with silver nitrate to be of 2.5th order.<sup>7</sup> Kevill and his co-workers reported some

detailed investigations on the reaction of allyl chlorides with silver nitrate.<sup>2</sup> It is suggested that the reaction proceeds with the intermediacy of ion pairs. In spite of these difficulties and the limited solubility to the organic solvents, silver nitrate is the most handy reagent for the ionization of organic halides.

To a solution of halide 1ap or 1sp in acetonitrile, silver nitrate in acetonitrile was added at 25°C. Both isomers gave the corresponding nitrate esters, 5ap and 5sp, in good yields (Scheme II). The structures of these compounds



were identified by the characteristic IR absorptions of the nitrate group. It should be noted that in the forced ionization of the halide (1ap) by silver nitrate no cyclized product (3) was detected at all. Probably the nucleophilicity of the nitrate anion is so high that the ion pair is collapsed by the nucleophilic attack of the anion before the internal rotation which is necessary for the ring closure.

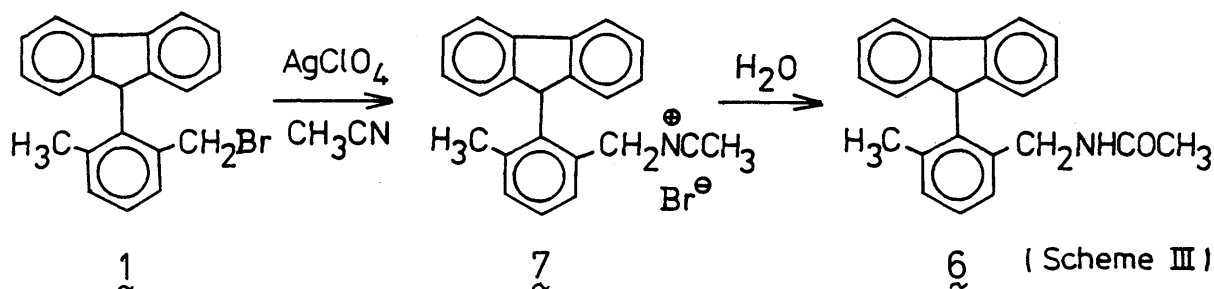
The difference in the reactivity of the rotamers, 1ap and 1sp, with silver nitrate was determined by the competitive

reaction. The relative reaction rate,  $k_{sp}/k_{ap}$ , was obtained to be 5.9 at 25°C. The relative reactivity of benzyl bromide used as a reference compound under the same conditions,  $k_{bz}/k_{sp}$ , was 0.36.

#### Reaction with silver perchlorate in acetonitrile

In order to lower the nucleophilicity of the counter anion, silver perchlorate was used. Though Kevill and Degenhardt presumed the reaction of allyl chlorides with silver perchlorate to be a pure  $S_N1-Ag^+$  reaction,<sup>2</sup> the mechanism of the reaction was known to be very complicated. Pocker and Kevill reported that in the reaction of 2-octyl halides with silver perchlorate the kinetic order of the reaction with respect to the silver salt was dependent on the concentration of the silver salt.<sup>8</sup> Since silver perchlorate has a good solubility in many organic solvents, the author investigated the reactions of the halides (1) with silver perchlorate in some poorly nucleophilic solvents.

The reaction of 1ap and 1sp with silver perchlorate in acetonitrile gave, after treatment of the reaction mixture with water, the corresponding acetamide derivative, 6ap and 6sp, respectively (Scheme III). The formation of these products were understood in terms of the Ritter type reactions,<sup>9</sup> that is, the formation of N-alkylnitrilium ion, 7ap and 7sp, by the nucleophilic attack of acetonitrile to the ion pair, followed by hydrolysis with the addition of water.



As is the case with the reaction with silver nitrate, no cyclization product (3) was found from  $\lambda_{ap}$  at all. The results suggest that acetonitrile is so nucleophilic in the case of the forced ionization of  $\lambda_{ap}$  with silver perchlorate that the reaction of the ion pair with acetonitrile is more favored process than the cyclization to give 3. The relative reactivity of the rotamers,  $k_{sp}/k_{ap}$ , was 1.3 at 60°C. Furthermore the reaction of benzyl bromide under the same conditions afforded N-benzylacetamide, and the relative reactivity,  $k_{bz}/k_{sp}$ , was 0.21.

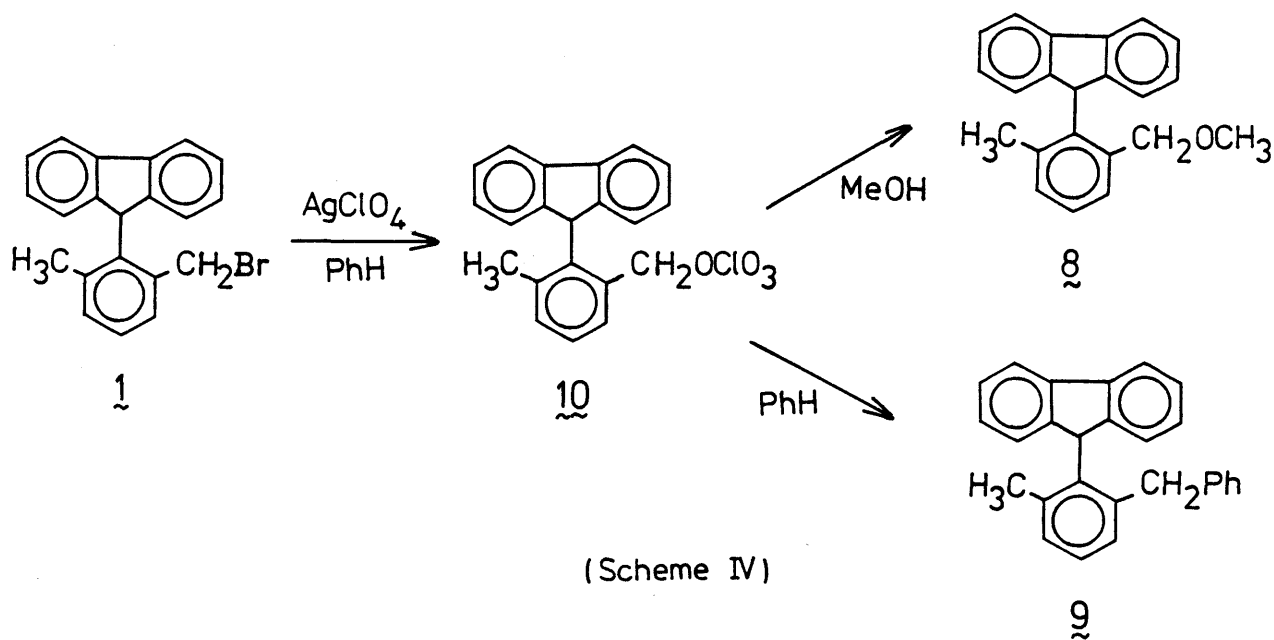
#### Reaction with silver perchlorate in benzene

On addition of silver perchlorate in benzene to a solution of halide  $\lambda_{ap}$  or  $\lambda_{sp}$  at 22°C, the reaction occurred rapidly to produce silver bromide precipitate. After 2-3 hr at this temperature the addition of methanol afforded 9-(2-methoxymethyl-6-methylphenyl)fluorene with the retained conformation,  $\lambda_{ap}$  and  $\lambda_{sp}$ , together with 9-(2-benzyl-6-methylphenyl)fluorene,  $\lambda_{ap}$  and  $\lambda_{sp}$ , respectively. If the reaction mixture, however, allowed to stand for 23 hr at 22°C



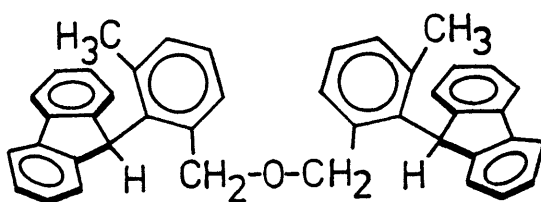
before the treatment with methanol, 2sp was obtained as a sole product from the reaction of 1sp, while the reaction of 1ap afforded mainly 2ap with a small amount of the cyclized products, 3 and 4.

Pocker and Kevill reported that organic perchlorate could survive for some time in a nonpolar solvent such as benzene.<sup>10</sup> The reaction of 1 with silver perchlorate in benzene is very rapid to produce the corresponding perchlorates, 1Qap and 1Qsp. In a short reaction time, these perchlorates (1Q) are present in the solution and react on addition of methanol to give the methyl ether (8) (Scheme IV). Since the perchlorate,  $\text{ROClO}_3$ , is thought to be in equilibrium with the ion pair,  $\text{R}^+\text{ClO}_4^-$ , the intermolecular Friedel-Crafts reaction with benzene should take place; the reaction of 1Qap and 1Qsp give 2ap and 2sp, respectively. In the case of 1Qap, the intra-



molecular Friedel-Crafts reaction to afford the cyclization products, 3 and 4, can compete with the intermolecular process. As shown in Table III, the formation of the cyclized products becomes relatively favored as the temperature is raised, though it does never become a main reaction.

Mention should be made of the unique product detected in a small amount when the reaction mixture from 1sp and silver perchlorate in benzene was treated with methanol after a few hours. Based on the spectroscopic data and the elemental analysis, the product was identified as bis[sp-2-(9-fluorenyl)-3-methylbenzyl]ether (11). The ether (11) could



11

not be found after the reaction period of 23 hr. This product (11) is derived from water which is present within the reaction system, because careful drying of silver perchlorate and benzene decreased the amount of 11.

If a small amount of water was deliberately added during the reaction of 1sp with silver perchlorate in benzene, the formation of the corresponding benzyl alcohol (12sp) was detected together with the dimeric ether (11). However, an

Table III. Dependence of Distribution of Products in the Reaction of  $\lambda$ ap with Silver Perchlorate in Benzene

reaction conditions		products <sup>a)</sup>			
temperature (°C)	duration (h)	$\lambda$ ap	$\lambda$	$\lambda$	$\lambda/3+4$
70	0.7	4.22	1.0	0.28	3.2
50	2.0	5.23	1.0	0.07	4.9
20	23	13.1	1.0	0.14	11.5

a) The product distribution is shown in relative amounts, taking the amount of  $\lambda$  as reference.

attempted coupling of the benzyl alcohol ( $12_{sp}$ ) in the presence of concentrated sulfuric acid in tetrahydrofuran did not give any of  $11$  but led to the formation of polymers. And an attempt of the Williamson synthesis of  $11$  from  $1_{sp}$  and  $12_{sp}$  in N,N-dimethylformamide in the presence of silver oxide was unsuccessful. The difficulties of the formation of  $11$  under the above conditions led to the author to believe that the facile formation of  $11$  in the reaction of  $1_{sp}$  with silver perchlorate was to take place on the precipitated silver bromide surface where water and the benzyl alcohol ( $12_{sp}$ ) were strongly absorbed. It should be noted that if the reaction occurred in solution, the concentration of water and the benzyl alcohol ( $12_{sp}$ ) would be prohibitively low. The disappearance of the ether ( $11$ ) in the reaction products after 23 hr must be ascribed to the possibility that  $11$  is cleaved by perchloric acid formed as a result of the Friedel-Crafts reaction. No such ether was detected from the reaction of  $1_{ap}$  under the same conditions. It would be explained in terms of a large steric hindrance in the  $ap$ -conformation to form the dimeric ether.

The relative reaction rate,  $k_{sp}/k_{ap}$ , was obtained to be 1.6 on the decay process of the perchlorates,  $10_{ap}$  and  $10_{sp}$ , which were formed instantly by the addition of silver perchlorate to the halides,  $1_{ap}$  and  $1_{sp}$ , respectively. The reaction of benzyl bromide under the same conditions afforded

diphenylmethane. The perchlorate derived from benzyl bromide and silver perchlorate, however, reacted rapidly with solvent; a half-life period of ca. 3.6 min at 22°C. The relative reactivity of benzyl bromide with  $\text{Isp}$ ,  $k_{\text{bz}}/k_{\text{sp}}$ , was ca. 34.<sup>11</sup>

Reaction with silver perchlorate in 1,1,1,3,3,3-hexafluoro-2-propanol (HFP) and trifluoroacetic acid (TFA)

These solvents are known to be little nucleophilic.<sup>12</sup> Therefore, in these solvents, the reaction with solvent molecules is prohibited. If the halides are ionized by the use of silver perchlorate in these solvents, the practically pure unimolecular reaction processes of the ion pair will be expected without the nucleophilic attack of anion or solvent molecules. Since silver perchlorate is not appreciably soluble in these solvents, the reaction had to be carried out in heterogeneous systems.

The suspension of silver perchlorate in a solution of the halide  $\text{Iap}$  or  $\text{Isp}$  in HFP containing ca. 5% (v/v) chloroform for solubility of the substrate was vigorously stirred at room temperature. The precipitate of silver bromide was gradually formed. In the reaction of  $\text{Isp}$ , after the disappearance of the material, the reaction mixture was treated with methanol to afford the methoxy derivative ( $\text{Qsp}$ ), together with many unidentified polymeric products. When the reaction was carried out at 50°C, only polymers resulted. It would be reasonable to think that the corresponding perchlorate ester

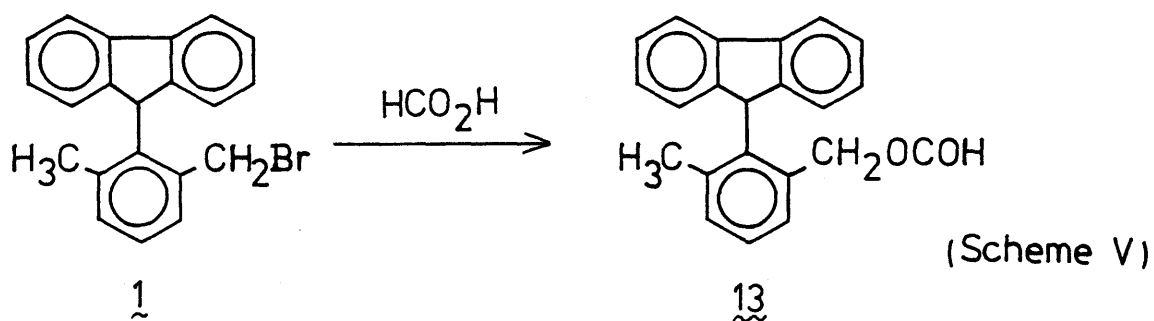
( $1Q_{sp}$ ) survived until methanol was added, but that the fate of the ester in equilibrium with the perchlorate ion pair was merely the polymerization in HFP. On the other hand,  $1ap$  reacted to give the cyclized compound (3) in a good yield under the same conditions. These results were thought to indicate that if the ion pair was forced to produce without the nucleophilic anions and solvent molecules,  $1ap$  cyclized intramolecularly very easily whereas  $1sp$  gave only polymers which could be formed by an intermolecular Friedel-Crafts reaction. The life period of the ion pair generated from the forced ionization of  $1sp$  with silver perchlorate in HFP would not be long enough to make the internal rotation which is necessary to form the cyclized product (3).<sup>13</sup> At extreme dilution to prevent from the intermolecular processes, the intramolecular cyclization of the ion pair derived from  $1sp$  may be possible in principle, though it is not practicable. The relative reactivity of the halide rotamers (1) in this heterogeneous reaction,  $k_{sp}/k_{ap}$ , was found to be 0.78.

The similar situation was observed in the heterogeneous reaction of 1 with silver perchlorate in TFA, where the relative reactivity,  $k_{sp}/k_{ap}$ , was 0.94 at 25°C. It should be emphasized that in the forced ionization with silver perchlorate  $1ap$  is more reactive than the  $sp$ -isomer ( $1sp$ ) only in poorly nucleophilic solvents such as HFP and TFA, and that the cyclized compounds, 3 and 4, are the sole products of  $1ap$

in these solvents.

### Solvolytic reactions

It was pointed out in the previous sections that the role of solvent was important to determine the relative reactivity in the ionizing reactions of the rotamers (1). In order to obtain the further information on this point, the author investigated the solvolytic reactions of 1 in various ionizing solvents. At the outset, solvolysis in formic acid was studied. Formic acid is known to one of the ionizing solvents in which solvolytic reactions are close to  $S_N1$ , but it has a comparable nucleophilicity to acetic acid.<sup>14</sup> A solution of halides 1<sub>ap</sub> or 1<sub>sp</sub> was heated at 42°C in formic acid containing 8% (v/v) chloroform for solubility of the substrate to give the corresponding formate, 13<sub>ap</sub> or 13<sub>sp</sub>, in a good yield, respectively (Scheme V). The cyclization product (3)



could not be detected at all from the reaction of 1<sub>ap</sub>. These results indicate that formic acid is so nucleophilic that the substitution reaction is more favored process than the intramolecular cyclization. The pseudo-first order rate constants

of the reaction of  $\text{lap}$  and  $\text{lsp}$  under these conditions were obtained as  $7.7 \times 10^{-6} \text{ sec}^{-1}$  and  $1.2 \times 10^{-5} \text{ sec}^{-1}$ , respectively. Thus the relative rate,  $k_{\text{sp}}/k_{\text{ap}}$ , is 1.6, which means that  $\text{lsp}$  is more reactive than  $\text{lap}$  in formic acid.

In a 1:1 (v/v) mixture of TFA and chloroform, the initial rate of disappearance of  $\text{lap}$  was determined according to the first order kinetics. However, the rates were dependent on the concentration of the substrate; at 86 mM the rate constant was  $1.4 \times 10^{-5} \text{ sec}^{-1}$  at  $60^\circ\text{C}$ , whereas it was  $9.3 \times 10^{-6} \text{ sec}^{-1}$  at 48 mM at the same temperature. The products were only unidentified polymers which were undoubtedly formed by intermolecular Friedel-Crafts reactions. Under the same conditions,  $\text{lsp}$  was recovered as well as benzyl bromide. The relative rate,  $k_{\text{sp}}/k_{\text{ap}}$ , was less than 0.05.

At 2 mM in TFA containing 3% (v/v) chloroform, however,  $\text{lap}$  disappeared with a half life of 50-60 min at  $60^\circ\text{C}$  to give the two cyclized products, **3** and **4**. The drastic changes of the solvolytic reactions in the lowered concentration of  $\text{lap}$  in TFA should be due to the retardation of intermolecular processes and the stabilization of the cation in the more polar solvent with only 3% chloroform. Heating a solution of  $\text{lap}$  at 2 mM in HFP containing 2% (v/v) chloroform at  $55^\circ\text{C}$  also showed the disappearance of the substrate with a half life of 30-40 min. The main product in this reaction was **3**, and only a trace amount of **4** was detected. Under these conditions,  $\text{lsp}$

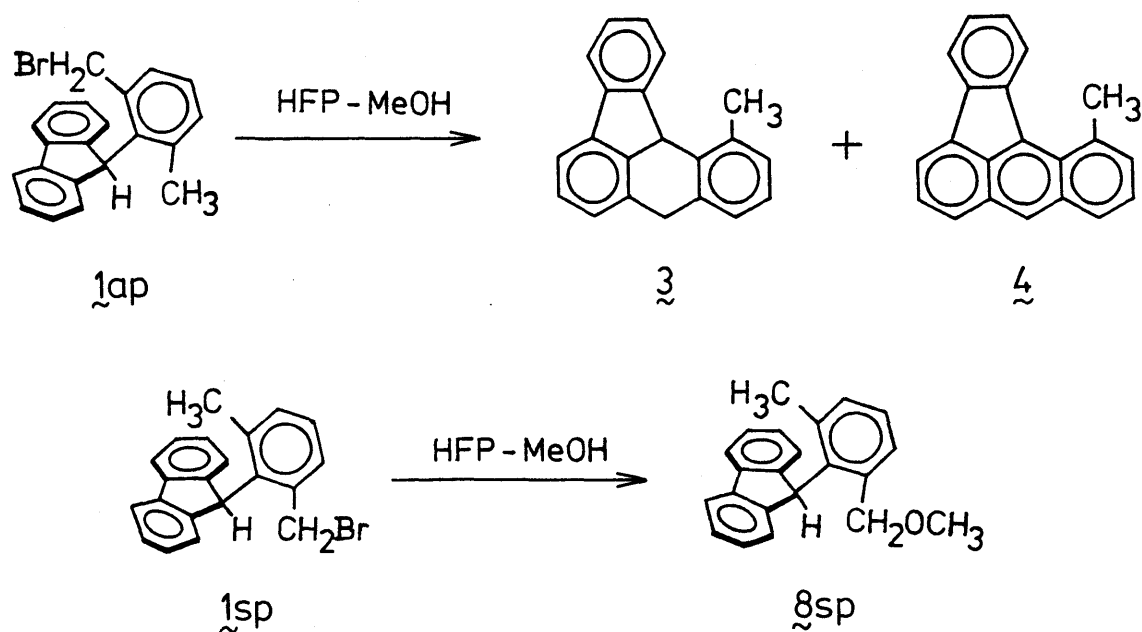


was recovered, the relative reactivity,  $k_{sp}/k_{ap}$ , being less than 0.05.

How should these results be explained, that is, the more ionizing solvents such as TFA and HFP show no reaction of  $\text{lsp}$  while in formic acid the solvolysis product is obtained? In TFA and HFP  $\text{lsp}$  should ionize to the ion pair as well as in formic acid. Taking into account that the more ionizing solvents are less nucleophilic,<sup>14</sup> it would be reasonable to think that in TFA or HFP the ion pairs return to the covalent species rather than to give a reaction product because of their poor nucleophilicity. The measurable solvolysis rate is generally less than the true ionizing rate because of the presence of the internal return. Thus it should be noted that the inertness of  $\text{lsp}$  in TFA and HFP does not necessarily lead the conclusion that  $\text{lsp}$  is much less reactive in the ionizing solvents than  $\text{lap}$ . The comparison of the reactivities in poorly nucleophilic solvents is usually carried out in the presence of the small amount of the nucleophile with a low nucleophilicity; trifluoroacetolysis in the presence of sodium trifluoroacetate and solvolytic reaction in HFP containing 3% (v/v) water were investigated.<sup>12b,15</sup>

If the inertness of  $\text{lsp}$  in TFA and HFP is due to the internal return, a TFA or HFP solution containing a nucleophile should show some reactivities of  $\text{lsp}$ . Thus the author studied the reaction in HFP containing 5% (v/v)

chloroform and 3% (v/v) methanol. When a 1.8 mM solution of halide  $\underline{1ap}$  or  $\underline{1sp}$  in the above solvent was heated at 40°C,  $\underline{1ap}$  afforded the cyclized product ( $\underline{3}$ ) together with a small amount of its dehydrogenated compound ( $\underline{4}$ ), while  $\underline{1sp}$  afforded the corresponding methoxy compound ( $\underline{8sp}$ ) in a good yield. The rate constants of decrease in the amount of  $\underline{1ap}$  and  $\underline{1sp}$  were obtained according to the first order kinetics to be  $1.4 \times 10^{-4} \text{ sec}^{-1}$  and  $2.5 \times 10^{-5} \text{ sec}^{-1}$ , respectively. The relative reactivity,  $k_{sp}/k_{ap}$ , is 0.18. It should be noted that  $\underline{1ap}$  did not give  $\underline{8ap}$  to a measurable degree (Scheme VI). It would be reasonable to think that the ion pairs formed from  $\underline{1ap}$  in HFP are so tight that they react intramolecularly with the benzene



(Scheme VI)

ring of the fluorene rather than with external nucleophile.

Under the same conditions in TFA (containing 5% chloroform and 3% methanol, 40°C, 1.8 mM) the rate constants were found to be  $2.5 \times 10^{-5} \text{ sec}^{-1}$  and  $5.1 \times 10^{-6} \text{ sec}^{-1}$ , respectively, for  $\lambda_{ap}$  and  $\lambda_{sp}$ . The relative reactivity,  $k_{sp}/k_{ap}$ , was 0.19. Although  $\lambda_{ap}$  gave the cyclized products (3) and (4), the methoxy compound ( $\delta_{sp}$ ) could not be obtained from  $\lambda_{sp}$  in TFA-CHCl<sub>3</sub>-CH<sub>3</sub>OH. The products from  $\lambda_{sp}$  were similar to those of the polymers obtained by the reaction of  $\lambda_{sp}$  in TFA or HFP with silver perchlorate. The failure in affording  $\delta_{sp}$  in TFA-CHCl<sub>3</sub>-CH<sub>3</sub>OH must be attributed to the reduction in effective concentration of methanol in the solution because of the protonation.

In HFP or TFA containing a small amount of methanol,  $\lambda_{ap}$  was ca. five times more reactive than  $\lambda_{sp}$ . Since in both rotamers it would be reasonable to consider that the ionization is the rate determining step in these solvents, the larger ionizing reactivity of  $\lambda_{ap}$  than  $\lambda_{sp}$  in such poorly nucleophilic solvents was confirmed at this stage.

#### Role of solvent molecules in ionization

The relative reactivities,  $k_{sp}/k_{ap}$ , obtained in the ionizing reactions are summarized in Table IV. In TFA or HFP, the ionization of  $\lambda_{ap}$  is faster than that of  $\lambda_{sp}$ . As expected, this difference is thought to be attributed to the  $\pi$ -participation of the fluorene ring to the cationic center

Table IV. Relative Reactivity of  $\text{I}_{\text{ap}}$  and  $\text{I}_{\text{sp}}$  under Ionizing Conditions

reaction conditions	temperature (°C)	relative reactivity ( $k_{\text{sp}}/k_{\text{ap}}$ )
$\text{AgNO}_3$ in $\text{CH}_3\text{CN}$	25	5.9
$\text{AgClO}_4$ in $\text{C}_6\text{H}_6$ <sup>a)</sup>	22	1.6
$\text{HCO}_2\text{H}$ <sup>b)</sup>	42	1.6
$\text{AgClO}_4$ in $\text{CH}_3\text{CN}$	60	1.3
$\text{AgClO}_4$ in $\text{TFA}$ <sup>c), d)</sup>	25	0.94
$\text{AgClO}_4$ in $\text{HFP}$ <sup>c), d)</sup>	14	0.78
$\text{TFA-3\% MeOH}$ <sup>c)</sup>	40	0.19
$\text{HFP-3\% MeOH}$ <sup>c)</sup>	40	0.18

a) Reaction of the corresponding perchlorate ester,  $\text{I}_{\text{Qap}}$  and  $\text{I}_{\text{Qsp}}$ , with benzene

b) Containing 8% (v/v) chloroform

c) Containing 5% (v/v) chloroform

d) Heterogeneous reactions

formed by the ionization of  $\text{lap}$ . The table shows, however, the ionization reaction of the ap-form is slower than the sp-form in acetonitrile, in benzene and in formic acid. Thus it should be noticed that solvent plays an important role in controlling the relative reactivities in the ionization of the rotamers of  $\text{l}$ .

The ionizing reactions investigated in this section are classified into three categories. The first is the forced ionization with silver nitrate in acetonitrile, where the relative reactivity,  $k_{\text{sp}}/k_{\text{ap}}$ , showed the largest value. Since a nitrate ion participates in the rate determining step of this reaction because of its large nucleophilicity,<sup>7</sup> one of the factors controlling the relative reactivity should be steric hindrance for the nucleophile to attack the reaction center. On the ap-conformation this steric effect is very severe as shown in the following section. The second category comprises the forced ionization with silver perchlorate in acetonitrile, the decomposition of the perchlorate ester in benzene and the solvolytic reaction in formic acid. Though each isomer shows nearly equal reactivities in these reactions, the sp-isomer is significantly more reactive than the ap-isomer. The third is the ionizing reaction in TFA and HFP, where  $\text{lap}$  shows the large reactivities than  $\text{fsp}$ . Moreover in these reactions the cyclized compounds,  $\text{3}$  and  $\text{4}$ , are obtained from  $\text{lap}$  in a good yield.

The cation formed by the ionization reaction can be surrounded by solvent molecules to form a solvation shell. The difference in the solvation of the cation derived from the halide,  $\downarrow$ ap or  $\downarrow$ sp, is that in the ap-conformation at least one of the solvent molecule cannot participate in the solvation because of the steric effect of the fluorene ring. In other words, the benzene ring of the fluorene moiety participates in completing the solvent shell in the ap-form. It can be termed the  $\pi$ -participation. Which of them plays a more important role in the stabilization of the cation, the  $\pi$ -participation or the solvation with solvent molecules? It would control the relative reactivities in the ionizing reaction of  $\downarrow$ ap and  $\downarrow$ sp. Namely if a solvent molecule is more basic than the benzene ring of the fluorene,  $\downarrow$ sp can be more reactive than  $\downarrow$ ap, as is the case with the ionizing reaction in acetonitrile, in benzene and in formic acid.<sup>16</sup> If the basicity of the solvent molecule is lower than the benzene ring of the fluorene,  $\downarrow$ ap can be more reactive than  $\downarrow$ sp. It should be the reason why in poorly nucleophilic solvents such as TFA and HFP  $\downarrow$ ap showed the larger reactivities than  $\downarrow$ sp.

#### 2-4 Reactions of 9-(2-bromomethyl-6-methylphenyl)fluorene rotamers with nucleophiles

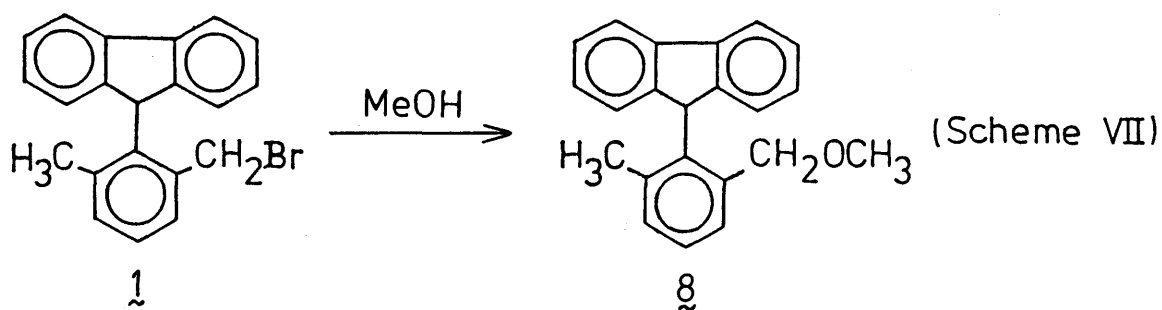
Bimolecular nucleophilic substitution reactions ( $S_N2$  reactions) are known to be space-demanding reactions in their

transition states. Therefore the relative reactivities,  $k_{sp}/k_{ap}$ , are expected to be large in their reactions because of the severe steric hindrance of the fluorene moiety to the reaction center of the ap-form. The author carried out the solvolytic reactions in a nucleophilic solvent and the substitution reactions with some nucleophiles in order to reveal the differences in the steric environment around the bromomethyl groups of  $\text{lap}$  and  $\text{lsp}$ .

#### Solvolytic reaction in methanol

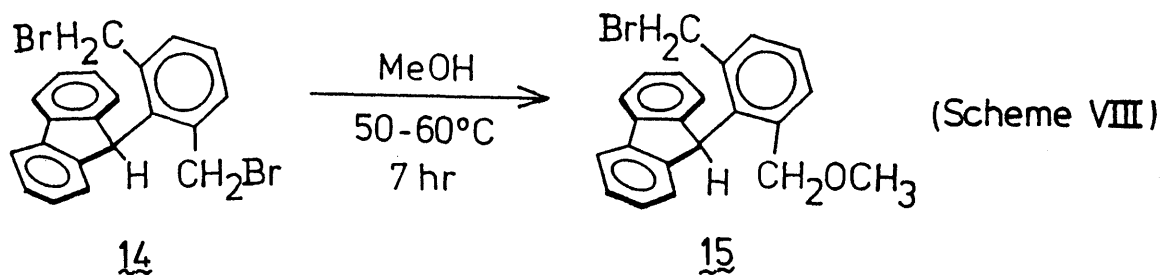
Since methanolysis of alkyl halides is an autocatalytic reaction, only the initial reaction rates should be considered or a base with less nucleophilicity should be added to scavenge protons produced by the reaction, if one wishes to discuss the reaction rates quantitatively. Furthermore it should be noted that benzyl halides such as the title compounds are known to react in both  $S_N1$  and  $S_N2$  fashions in solvolytic reactions because of the complicated steric and electronic effects of the  $\alpha$ -phenyl group and the substituted groups.<sup>17</sup>

A solution of halides ( $\text{l}$ ) was heated at 52°C in methanol containing 2% (v/v) chloroform for solubility of the substrates to give the corresponding methoxy compounds,  $\text{gap}$  and  $\text{gsp}$  (Scheme VII). The reaction obeyed the pseudo-first order rate law until ca. 20% completion. The rate constants of the reaction of  $\text{lap}$  and  $\text{lsp}$  were obtained as  $3.2 \times 10^{-6}$



$\text{sec}^{-1}$  and  $9.2 \times 10^{-5} \text{ sec}^{-1}$ , respectively. The relative rate,  $k_{\text{sp}}/k_{\text{ap}}$ , is 29, which means much larger reactivity of the sp-form than the ap-form in contrast to the ionizing reactions reported in the previous section.

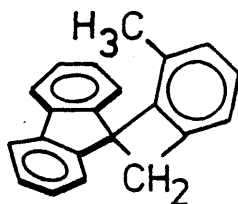
The large difference in reactivities of the two bromomethyl groups demonstrated separately in the methanolysis of 9-[2,6-bis(bromomethyl)phenyl]fluorene (14). This compound, obtained in the bromination of 9-(2,6-dimethylphenyl)fluorene (2) for a long time, possesses a diastereotopic pair of bromomethyl groups, which are expected to have large different reactivities from each other. Indeed, heating a solution of 14 in methanol containing 2% (v/v) chloroform at 50–60°C for 7 hr afforded ap-9-(2-bromomethyl-6-methoxymethylphenyl)-fluorene (15) as a sole product (Scheme VIII).





### Reaction with alkoxide ions

When the differences in the reactivities of nucleophilic substitution reactions of the rotamers,  $\text{lap}$  and  $\text{isp}$ , are discussed quantitatively, it must be kept in mind that using a strong base as a nucleophile should be unsuitable. This is because the use of a strong base may cause deprotonation at the 9-position of fluorene. The base-catalyzed isomerization of rotational isomers of 9-arylfluorenes was already noted.<sup>4</sup> Thus if the halides ( $\text{l}$ ) is treated with a strong base, deprotonation from the 9-position of fluorene should be expected to compete with nucleophilic substitution reaction. Indeed, treatment of  $\text{isp}$  with ca. 10 equivalents of sodium methoxide in methanol containing 2% (v/v) chloroform at 25°C afforded the corresponding methoxy compound ( $\text{isp}$ ) and a small amount of the isomerized compounds,  $\text{lap}$  and  $\text{isp}$ . Furthermore in the reaction mixture the unique hydrocarbon was isolated, which was characterized by its  $^1\text{H}$ NMR spectroscopy where the proton at the 9-position of fluorene was absent. This compound was assigned to a spiro compound, 6-methylspiro-[benzocyclobutene-1(2H),9'-[9H]fluorene] ( $\text{l6}$ ), the formation



16

of which was rationalized in terms of deprotonation at the 9-position of fluorene followed by an intramolecular nucleophilic substitution reaction. Under the same conditions, the reaction of  $\lambda$ ap afforded the spiro compound ( $\lambda$ 6) mainly. The reaction conditions and product distributions in the reaction of  $\lambda$  with sodium methoxide are summarized in Table V.

As shown in the table, rotational isomerization of the material are observed in the reaction course at 25°C. Since this isomerization should proceed via deprotonation at the 9-position of fluorene,<sup>18</sup> it would be reasonable to think that the intramolecular substitution reaction to give  $\lambda$ 6 is slower than the deprotonation at this temperature. However at 50°C the rate of the intramolecular reaction is comparable with that of the deprotonation, so that the isomerization cannot be observed in the reaction at this temperature. In the ap-form the nucleophilic substitution reaction of methoxide ion is so much retarded for the steric reason that the deprotonation process becomes the main reaction. The mechanism of the formation of the isomerized methoxy compound ( $\lambda$ 8) is not clear. Two processes are probably involved; the isomerization of the halide followed by the  $S_N2$  reaction and the  $S_N2$  reaction followed by the isomerization of the resulting product.

The relative rate of disappearance of the halide,  $k_{sp}/k_{ap}$ , was obtained to be 1.2 in the reaction with sodium methoxide at 50°C. The further quantitative discussion on

Table V. Conditions and Distribution of Products in the Reaction of 1 with sodium methoxide in methanol<sup>a)</sup>

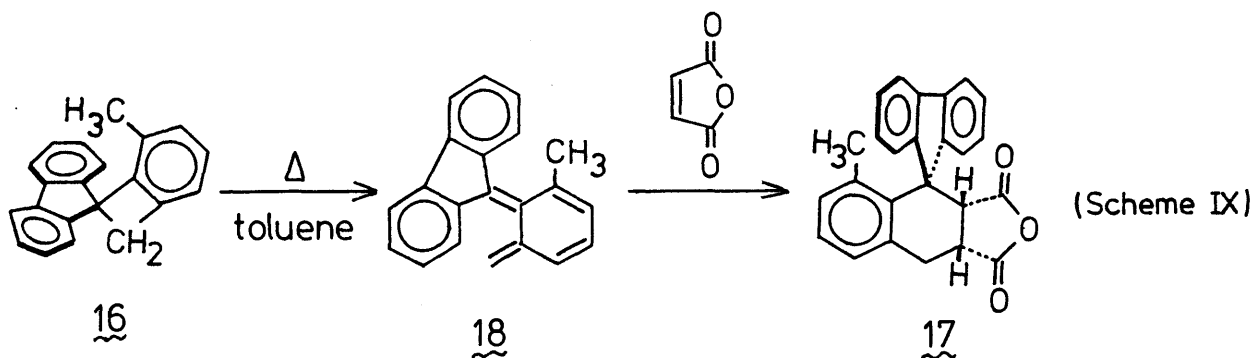
reaction conditions			products (%) <sup>b)</sup>			
temperature (°C)	duration (min)	substrate	conversion	isomerization	gap	gap 16
25	500	lap	58	8	trace	6 86
		lsp	72	4	trace	78 19
50	80	lap	88	0	5 trace	95
		lsp	94	0	7	72 20

a) Containing 2% (v/v) chloroform

b) Normalized to 100%

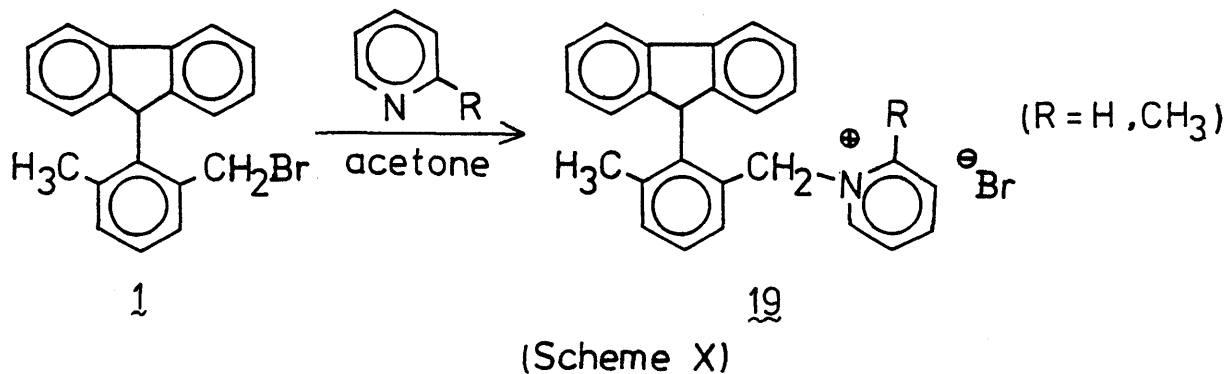
this reactions was ceased because of the complicated reaction mechanism derived by the presence of the deprotonation process.

t-Butoxide is known to be a stronger and less nucleophilic base than methoxide.<sup>19</sup> Thus the deprotonation is expected to be a preferential process in the reaction of **1** with this base. Treatment of either **1ap** or **1sp** with potassium t-butoxide in t-butyl alcohol afforded quickly the spiro compound (**16**) as a sole product. Furthermore the spiro compound (**16**) was also prepared by treating either **1ap** or **1sp** with sodium hydride at 55°C in tetrahydrofuran containing a small amount of N,N-dimethylformamide. The facile formation of the compound (**16**), which contained a benzocyclobutene moiety, was a surprise for the author because benzocyclobutenes are usually prepared by special techniques.<sup>21</sup> Benzocyclobutenes are known to be pyrolyzed to give o-quinone dimethides which can be trapped by a dienophile.<sup>20</sup> Recently this reaction has been used for syntheses of natural products.<sup>21</sup> When a solution of **16** in toluene with maleic anhydride was heated at 135°C, the author was able to isolate a Diels-Alder adduct (**17**) (Scheme IX). The formation of adduct (**17**) explicitly showed the generation of the o-quinone dimethide (**18**) in spite of its sterically unfavorable structure, and afforded a chemical evidence to support the structure of **16**.



### Reaction with pyridine bases

The Menshutkin reaction of benzyl halides with pyridine bases were investigated in detail by Baker and Nathan.<sup>22</sup> They pointed out that these reactions were pure bimolecular substitution reactions.<sup>22b</sup> Since the basicities of pyridines are not so high, it is expected that deprotonation at the 9-position of fluorene is unimportant in the reaction. Indeed, the halides (**1**) reacted with pyridine or 2-methylpyridine in acetone at 35°C with neither isomerization nor formation of the spiro compound (**16**). The sole product of this reaction was the pyridinium salt with a retained conformation, **19ap** and **19sp** (Scheme X).<sup>23</sup>



The second order rate constants of the reaction of the halides ( $\text{I}$ ) with the pyridines are summarized in Table VI, together with the results of benzyl bromide used as a reference compound. The rate constants of benzyl bromide is in good agreement with that reported.<sup>24</sup> The relative reaction rate,  $k_{\text{sp}}/k_{\text{ap}}$ , was found to be 22 for the reaction with pyridine, and 35 for the reaction with 2-methylpyridine. The significant effect of the 2-methyl substitution on the relative reactivity is thought to reflect that the controlling factor in determining the relative reactivity is the steric effect.

As shown in Table VI,  $\text{I}_{\text{sp}}$  is 4.0 and 6.0 times more reactive than benzyl bromide in the substitution reaction with pyridine and 2-methylpyridine, respectively. The rate enhancement of the  $\text{S}_{\text{N}}2$  reaction by substitution of the ortho alkyl group is already known.<sup>25</sup> The ortho alkyl group is believed to contribute to the stabilization of the transition state for the  $\text{S}_{\text{N}}2$  reactions by the attractive interaction derived from the van der Waals force.

## 2-5 Conclusion

As the author expected, 9-(2-bromomethyl-6-methylphenyl)-fluorene rotamers,  $\text{I}_{\text{ap}}$  and  $\text{I}_{\text{sp}}$ , showed contrasting reactivities to the various nucleophiles. In ionizing reactions involving forced ionizations with silver salts and

Table VI. The Second Order Rate Constants of the Menschutkin Reactions of  $\lambda$  and Benzyl Bromide with Pyridines<sup>a)</sup>

	pyridine	2-methylpyridine
$\lambda_{ap}$	$3.9 \times 10^{-5}$	$6.1 \times 10^{-6}$
$\lambda_{sp}$	$8.5 \times 10^{-4}$	$2.3 \times 10^{-4}$
benzyl bromide	$2.1 \times 10^{-4}$	$3.8 \times 10^{-5}$
relative rate ( $k_{sp}/k_{ap}$ )	22	35

a) These reactions were carried out in acetone at 35°C.

solvolytic reactions, it was noted that solvent played an important role in determining the relative reactivities of rotamers. The sp-form was more reactive than the ap-form in the forced ionization with silver perchlorate in acetonitrile, in the decomposition of the perchlorate ester in benzene and in solvolysis in formic acid. These reactions showed that the relative reactivities,  $k_{sp}/k_{ap}$ , were found to be 1.3-1.6 and the main reaction product was the substituted compound by the solvent. In poorly nucleophilic solvents, on the contrary, the reaction of  $\lambda_{ap}$  was faster than  $\lambda_{sp}$ . These reaction of  $\lambda_{ap}$  afforded the cyclized compounds derived from the intramolecular Friedel-Crafts reaction, 3 and 4. Thus it is concluded that in the ap-conformation the ionization is accelerated by the  $\pi$ -participation of the benzene ring of the fluorene moiety, though it can be observed in the limited cases, that is, in the reaction conditions without nucleophilic counter anions and in little nucleophilic solvents. The accelerations of solvolysis rates derived from the through-space  $\pi$ -participation were reported in anti-7-norbornenyl systems<sup>26</sup> and in [2.2]-p-cyclophanylethyl derivatives.<sup>27</sup> The  $\pi$ -participation of the benzene ring to the cationic center, which is demonstrated in this chapter, can be regarded as a novel example in this field.

In the bimolecular substitution reactions, the sp-form was more reactive than the ap-form without exception. The low



reactivities of  $\lambda_{ap}$  is rationalized in terms of the high energy transition state in the ap-form because of the steric effect. The typical  $S_N2$  reaction showed that the relative reaction rate,  $k_{sp}/k_{ap}$ , was around 30, which was found to be dependent on the steric effects of nucleophiles. It is rather a surprise that  $\lambda_{ap}$  reacts with nucleophiles with a measurable rate under the same conditions as  $\lambda_{sp}$ , since the bromomethyl group of the  $\lambda_{ap}$  is situated right above the fluorene ring so that the attack of nucleophiles appeared to be hindered very seriously. Taking into consideration that the rotation of the bromomethyl group of  $\lambda_{ap}$  is not restricted, the reactivities of  $\lambda_{ap}$  to nucleophiles is explained in terms of the possibility that the nucleophiles attack the bromomethyl group from the direction parallel to the fluorene ring. Furthermore, the use of a strong base as a nucleophile is not suitable for the purpose of this studies, because deprotonation at the 9-position of fluorene competes with nucleophilic substitutions.

Thus the author could demonstrate the differences in environment of the bromomethyl groups of the rotamers,  $\lambda_{ap}$  and  $\lambda_{sp}$ , through the quantitative investigations of their reactivities to various nucleophiles.

## EXPERIMENTAL

Spectral measurements  $^1\text{H}$ NMR spectra were recorded on a Hitachi R-20B spectrometer operating at 60 MHz or on a Varian EM-390 spectrometer operating at 90 MHz. IR and UV spectra were obtained with a Hitachi IR-260-30 spectrometer and a Hitachi UV-340 spectrometer, respectively. High resolution mass spectra were recorded on a JEOL D-300 machine.

9-(2-Bromomethyl-6-methylphenyl)fluorenes (lap) and (lsp)  
To a boiling solution of 2.5 g (9.3 mmol) of 9-(2,6-dimethylphenyl)fluorene (2)<sup>28</sup> in 100 mL of benzene was added 2.5 g (14 mmol) of N-bromosuccinimide and 170 mg of benzoyl peroxide in small portions during a period of 17 h. After filtration, the solvent was removed by evaporation and the residue was submitted to chromatography on silica gel (Wakogel C-200), which used hexane as an eluent. The sp-form (lsp) was eluted first and the ap-form (lap) followed. The separation of the isomers was more conveniently performed by using a Waters System 500 preparative liquid chromatographic apparatus,  $\mu$ -porasil and hexane. In a typical run, 17% of lsp and 6% of lap were obtained with 40% of the recovered starting material. The ap-form, colorless needles, mp 125-126°C;  $^1\text{H}$ NMR ( $\text{CDCl}_3$ )  $\delta$  2.70(3H,s), 3.37(2H,s), 5.52(1H,s), 7.0-8.0(11H,m); Found: C, 72.40; H, 4.74; Br, 23.06%. Calcd for  $\text{C}_{21}\text{H}_{17}\text{Br}$ : C, 72.22; H, 4.91; Br, 22.88%. The sp-form, colorless granules,

mp 115-116°C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  1.12(3H,s), 4.83(2H,s), 5.60(1H,s), 6.8-7.9(11H,m); Found: C,72.37; H,4.76; Br,23.06%. Calcd for  $\text{C}_{21}\text{H}_{17}\text{Br}$ : C,72.22; H,4.91; Br,22.88%.

Reaction of 1 with silver nitrate in acetonitrile To a solution of 22 mg (0.06 mmol) of 1ap in 2 mL of acetonitrile, 10 mg (0.06 mmol) of silver nitrate in 1.0 mL of acetonitrile was added. The whole was allowed to react for 30 min at 50°C. The reaction mixture was filtered and the filtrate was evaporated. Recrystallization of the residue from ethanol afforded 20 mg (90%) of ap-2-(9-fluorenyl)-3-methyl-benzyl nitrate (5ap) as colorless granules, mp 128°C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  2.75(3H,s), 4.22(2H,s), 5.56(1H,s), 7.0-8.0(11H,m); IR (KBr disk) 1617, 1280, 875  $\text{cm}^{-1}$ ; Found: C,75.97; H,4.97; N,4.30%. Calcd for  $\text{C}_{21}\text{H}_{17}\text{NO}_3$ : C,76.12; H,5.17; N,4.23%.

1sp similarly gave sp-2-(9-fluorenyl)-3-methylbenzyl nitrate (5sp): colorless granules, mp 104°C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  1.16(3H,s), 5.32(1H,s), 5.80(2H,s), 7.0-7.9(11H,m); IR (KBr disk) 1628, 1278, 842  $\text{cm}^{-1}$ ; Found: C,76.19; H,5.03; N,4.18%. Calcd for  $\text{C}_{21}\text{H}_{17}\text{NO}_3$ : C,76.12; H,5.17; N,4.23%.

Reaction of 1 with silver perchlorate in acetonitrile The reaction was carried out similarly as above except using silver perchlorate instead of silver nitrate. The reaction mixture was treated with 5% aqueous lithium chloride. Ether was added and the mixture was filtered to remove insoluble materials. The ether layer was separated and the aqueous

layer was extracted with ether. The combined ether layer was washed with water, dried on magnesium sulfate and evaporated. The residue was recrystallized from hexane-ethanol. 1ap gave ap-9-(2-acetamidomethyl-6-methylphenyl)fluorene (6ap) in a 50% yield: colorless granules, mp 188°C;  $^1\text{H}$ NMR ( $\text{CDCl}_3$ )  $\delta$  1.46(3H,s), 2.73(3H,s), 3.23(2H,d,J = 6.3 Hz), 4.1(1H,br,s), 5.54(1H,s), 7.0-8.0(11H,m); IR (KBr disk) 3270, 1640, 1550  $\text{cm}^{-1}$ ; Found C,84.23; H,6.24; N,4.37%. Calcd for  $\text{C}_{23}\text{H}_{21}\text{NO}$ : C,84.37; H,6.46, N,4.28%.

1sp gave sp-9-(2-acetamidomethyl-6-methylphenyl)fluorene (6sp) in a 70% yield: colorless granules, mp 194°C;  $^1\text{H}$ NMR ( $\text{CDCl}_3$ )  $\delta$  1.13(3H,s), 1.96(3H,s), 4.76(2H,d,J = 5.4 Hz), 5.37(1H,s), 5.7(1H,br,s), 6.8-8.0(11H,m); IR (KBr disk) 3240, 1635, 1550  $\text{cm}^{-1}$ ; Found: C,84.17; H,6.31; N,4.28%. Calcd for  $\text{C}_{23}\text{H}_{21}\text{NO}$ : C,84.37; H,6.46; N,4.28%.

Reaction of 1 with silver perchlorate in benzene The reaction was carried out similarly with that in acetonitrile except that benzene was used as solvent at 22°C. After 2-3 h the reaction mixture was treated with methanol to afford the methoxy compound with the retained conformation (8) (see below) together with the corresponding benzyl derivative (9). When the reaction mixture was allowed to stand overnight at this temperature, the latter was mainly obtained. 1ap afforded 12-methyl-8,12b-dihydrobenz[a]aceanthrylene (3) and 12-methylbenz[a]aceanthrylene (4), which were characterized in

the section of the reaction in trifluoroacetic acid, together with ap-9-(2-benzyl-6-methylphenyl)fluorene (2ap). The product distributions are shown in Table III. 2ap: colorless granules, mp 143°C;  $^1\text{H}$ NMR ( $\text{CDCl}_3$ )  $\delta$  2.67(2H,s), 2.69(3H,s), 5.54(1H,s), 6.5-7.9(16H,m); Found: C,93.76; H,6.22%. Calcd for  $\text{C}_{27}\text{H}_{22}$ : C,93.60; H,6.40%.

1sp afforded sp-9-(2-benzyl-6-methylphenyl)fluorene (2sp) as a sole product in a 64% yield: colorless granules, mp 105°C;  $^1\text{H}$ NMR ( $\text{CDCl}_3$ )  $\delta$  1.10(3H,s), 4.37(2H,s), 5.45(1H,s), 6.8-7.9(16H,m); Found: C,93.50; H,6.20%. Calcd for  $\text{C}_{27}\text{H}_{22}$ : C,93.60; H,6.40%.

Formation of bis[sp-2-(9-fluorenyl)-3-methylbenzyl] ether (11) (see below) was detected during the reaction but this compound subsequently reacted under the reaction conditions to afford sp-9-(2-benzyl-6-methylphenyl)fluorene (2sp).

9-(2-methoxymethyl-6-methylphenyl)fluorenes (8ap) and (8sp) To a solution of 25 mg (0.07 mmol) of 1ap in 0.4 mL of chloroform and 5 mL of methanol, was added a solution of 56 mg (0.27 mmol) of silver perchlorate in 2 mL of methanol. The mixture was allowed to stand for 10 min at room temperature in dark. Silver bromide was removed by filtration and the filtrate was poured into water. The mixture was extracted with dichloromethane. The extract was washed, dried and evaporated to give ap-9-(2-methoxymethyl-6-methylphenyl)-fluorene (8ap) as colorless granules, mp 118°C;  $^1\text{H}$ NMR ( $\text{CDCl}_3$ )

$\delta$  2.56(3H,s), 2.71(3H,s), 3.14(2H,s), 5.48(1H,s), 6.9-8.0 (11H,m); Found: C,88.11; H,6.66%. Calcd for  $C_{22}H_{20}O$ : C,87.96; H,6.71%.

Similarly, sp-9-(2-methoxymethyl-6-methylphenyl)fluorene (8sp) was obtained from 1sp: colorless oil;  $^1H$ NMR ( $CDCl_3$ )  $\delta$  1.12(3H,s), 3.44(3H,s), 4.76(2H,s), 5.56(1H,s), 6.8-7.9 (11H,m); MS found  $M^+ = 300.1497$ .  $C_{22}H_{20}O$  requires  $M^+ = 300.1512$ .

Bis[sp-2-(9-fluorenyl)-3-methylbenzyl] ether (11) A mixture of 15 mg of 1sp in 2.6 mL of benzene and 17.8 mg of silver perchlorate in 1.7 mL of benzene containing ca. 10  $\mu$ L of water was stirred for 30 h at room temperature and then was heated at 50°C for 30 min. To the cooled mixture, 3.5 mL of methanol and then 5% aqueous lithium chloride were added. Silver salts were removed by filtration and the organic products were collected. Preparative TLC on silica gel (3:1 hexane-benzene) afforded ca. 4 mg of the desired ether (11), and small amounts each of sp-9-(2-hydroxymethyl-6-methylphenyl)fluorene (12sp) (see below) and sp-9-(2-methoxymethyl-6-methylphenyl)fluorene (8sp). 11: colorless granules, mp 192-193°C;  $^1H$ NMR ( $CDCl_3$ )  $\Delta$  1.12(6H,s), 4.98(4H,s), 5.64(2H,s), 6.8-7.9(22H,m); Found: C,91.23; H,5.88%. Calcd for  $C_{42}H_{34}O$ : C,90.94; H,6.18%.

9-(2-Hydroxymethyl-6-methylphenyl)fluorene (12sp) To a solution of 60 mg (0.17 mmol) of 1sp in 6 mL of acetone was

added a solution of 106 mg (0.51 mmol) of silver perchlorate in 1 mL of water. The mixture was stirred for 10 min at room temperature in dark, and then warmed at 50°C for 10 min. After silver bromide was removed by filtration, the reaction product was precipitated by addition of water and extracted with ether. The extract was washed with water, dried and evaporated. The residue was developed on a preparative TLC plate (1:4 hexane-benzene) to give 40 mg (81%) of sp-9-(2-hydroxymethyl-6-methylphenyl)fluorene (12sp): colorless needles, mp 74-75°C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  1.12(3H,s), 1.8(1H,br,s), 5.02(2H,s), 5.59(1H,s), 6.8-7.9(11H,m); Found: C, 88.17; H, 6.21%. Calcd for  $\text{C}_{21}\text{H}_{18}\text{O}$ : C, 88.08; H, 6.34%.

Solvolysis of 1 in formic acid A solution of 29 mg of 1ap in 3 mL of chloroform and 20 mL of formic acid was heated at 50-60°C for 24 h and poured into water. The organic materials were extracted with ether and the ether extract was washed and dried. After evaporation of the solvent, the residue was developed on a preparative TLC plate (1:2 hexane-benzene) to give ap-2-(9-fluorenyl)-3-methylbenzyl formate (13ap) in a 80% yield: colorless granules, mp 106°C,  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  2.75(3H,s), 3.97(2H,s), 5.53(1H,s), 6.9-8.0(12H,m); IR (KBr disk) 1716, 1178  $\text{cm}^{-1}$ ; Found: C, 84.02, H, 5.50%. Calcd for  $\text{C}_{22}\text{H}_{18}\text{O}_2$ : C, 84.05; H, 5.77%.

Similarly, 1sp afforded sp-2-(9-fluorenyl)-3-methylbenzyl formate (13sp) in a 80% yield: colorless oil;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$

1.12(2H,s), 5.37(1H,s), 5.54(2H,s), 6.8-8.0(11H,m),  
8.14(1H,s); IR (neat) 1722, 1150  $\text{cm}^{-1}$ ; MS found  $M^+ = 314.1314$ .  
 $\text{C}_{22}\text{H}_{18}\text{O}_2$  requires  $M^+ = 314.1307$ .

Reaction of 1 in trifluoroacetic acid (TFA) A solution of 33 mg of 1ap in 1.5 mL of chloroform was added to 25 mL of TFA. The whole solution was heated at 60°C for 6 h. The mixture was poured into water and then extracted with chloroform. After the usual treatment, the products were purified by silica gel TLC plate (hexane) to afford 8 mg (32%) of 12-methyl-8,12b-dihydrobenz[a]aceanthrylene (3) as colorless needles, mp 180-181°C;  $^1\text{H}$ NMR ( $\text{CDCl}_3$ )  $\delta$  2.48(3H,s), 3.99(1H,d,J = 16.4 Hz), 4.14(1H,dd,J = 16.4, 2.3 Hz), 4.80(1H,d,J = 2.3 Hz), 6.9-8.1(10H,m); Found: C,94.23; H,5.78%. Calcd for  $\text{C}_{21}\text{H}_{16}$ : C,93.99; H,6.01%.

The product was always accompanied by 12-methyl-benz[a]-aceanthrylene (4) which was eluted before the dihydro compound (3). Preparation of the dehydrogenated compound (4) is described below. The concentration of 1ap in TFA plays an important role in determining the yield of the cyclized products. Heating a 50-80 mM solution of 1ap in a 1:1 mixture of TFA and chloroform, which was convenient for the routine  $^1\text{H}$ NMR measurement, afforded only polymers.

1sp did not apparently react under the similar conditions. Heating a solution of 20 mg of 1sp in 0.1 mL of chloroform and 0.4 mL of TFA at 62°C for 40 h gave only the



recovered starting material.

12-methylbenz[a]aceanthrylene (4) A solution of 6 mg of 12-methyl-8,12b-dihydrobenz[a]aceanthrylene (3) in 1 mL of benzene was mixed with 6 mg of 2,3-dichloro-5,6-dicyano-p-benzoquinone in benzene. The mixture was stirred for 1 h at room temperature and then heated at 50°C for 1 h. The hydroquinone produced in the reaction was removed by passing the solution through a column of 200 mg of silica gel. The filtrate and washings (1:1 hexane-benzene) were combined and evaporated to give the dehydrogenated compound (4) in an almost quantitative yield: orange oil;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  3.17(3H,s), 7.2-8.5(11H,m); UV (EtOH)  $\lambda_{\text{max}}$  ( $\log \epsilon$ ) 260 nm (4.54), 366 (3.40), 430 (3.65); MS found  $M^+ = 266.1106$ .  $\text{C}_{24}\text{H}_{14}$  requires  $M^+ = 266.1095$ .

Reaction of 1 in 1,1,1,3,3,3-hexafluoro-2-propanol (HFP)  
A solution of 10 mg of lap in 0.3 mL of chloroform and 15.6 mL of HFP was heated at 50-55°C for 4 h. The reaction product was similarly treated as above to give 12-methyl-8,12b-dihydrobenz[a]aceanthrylene (3) in a 65-75% yield. The dehydrogenated compound (4) was detected only in a trace amount. Under the similar conditions lsp was completely recovered.

Reaction of 1 with silver perchlorate in TFA or HFP A heterogeneous mixture of 10 mg of lap in 0.6 mL of chloroform and 15.6 mL of HFP and ca. 3 equivalent of silver perchlorate

was stirred at 20°C for 5 h. The mixture was treated with methanol to decompose any of the possible perchlorate still present. After the usual treatment, 3 mg (40%) of 12-methyl-8,12b-dihydrobenz[a]aceanthrylene (3) was obtained. No methoxy compound (8ap) was detected. Similar treatment of 1sp afforded sp-(2-methoxymethyl-6-methylphenyl)fluorene (8sp) in a 30% yield. No cyclized product (3) was obtained. Reaction of 1 with silver perchlorate in TFA was performed similarly as above.

Reaction of 1 in TFA-CH<sub>3</sub>OH-CHCl<sub>3</sub> or HFP-CH<sub>3</sub>OH-CHCl<sub>3</sub>  
The reaction was similarly carried out as for those without methanol, except 3% (v/v) methanol was added to TFA or HFP prior to the mixing. 1ap afforded 12-methyl-8,12b-dihydrobenz[a]aceanthrylene (3) and its dehydrogenated compound (4) in both systems. Though 1sp gave sp-9-(2-methoxymethyl-6-methylphenyl)fluorene (8sp) in HFP, only polymers were obtained in TFA.

Solvolysis of 1 in methanol      A solution of 29 mg of 1sp in 3 mL of chloroform and 20 mL of methanol was heated at 50-60°C for 24 h and then was poured into water. The mixture was extracted with ether and the extract was dried. After evaporation of the solvent, the residue was submitted to TLC (1:2 hexane-benzene) to afford sp-9-(2-methoxymethyl-6-methylphenyl)fluorene (8sp) in a ca. 95% yield. Similar treatment of 1ap showed the presence of the starting material (35%) as

well as ap-9-(2-methoxymethyl-6-methylphenyl)fluorene (8ap) (55%), of which  $^1\text{H}$ NMR spectrum was identical with that of an authentic sample, after 70 h heating.

ap-9-(2-Bromomethyl-6-methoxymethylphenyl)fluorene (15)

A solution of 46 mg of 14<sup>29</sup> in 0.5 mL of chloroform and 30 mL of methanol was heated at 50–60°C for 7 h and the solvent was evaporated. The residue was developed on a preparative TLC plate (3:1 havane-benzene) to give 6 mg of the recovered material and 25 mg (58%) of the desired product (15) as colorless granules, mp 91–92°C;  $^1\text{H}$ NMR ( $\text{CDCl}_3$ )  $\delta$  3.38(2H,s), 3.44(3H,s), 4.73(2H,s), 5.57(1H,s), 7.1–8.0(11H,m); Found: C, 69.43; H, 4.99; Br, 21.34%. Calcd for  $\text{C}_{22}\text{H}_{19}\text{BrO}$ : C, 69.67; H, 5.05; Br, 21.07%.

6-Methylspiro[benzocyclobutene-1(2H),9'-[9H]fluorene]

(16) A solution of 140 mg (0.40 mmol) of a ca. 1:1 mixture of lap and lsp in 3.5 mL of tetrahydrofuran was mixed with a suspension of 60 mg (2.5 mmol) of sodium hydride in 3.5 mL of tetrahydrofuran. To the mixture was added 0.7 mL of N,N-dimethylformamide and the whole was stirred for 3 h at 55–60°C under a nitrogen atmosphere. After being cooled, the mixture was treated with 7 mL of ether containing 1.4 mL of methanol. Water was added and the organic layer was separated. The organic layer and ether extracts of the aqueous layer were combined, and washed successively with dilute hydrochloric acid and aqueous sodium hydrogencarbonate. The combined

solution was dried and evaporated. The residue was purified by a preparative TLC (4:1 hexane-benzene) to give 80 mg (75%) of the desired product (16) as colorless granules, mp 93°C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  1.49(3H,s), 3.65(2H,s), 6.9–7.9(11H,m); Found: C, 94.28; H, 5.83%. Calcd for  $\text{C}_{21}\text{H}_{16}$ : C, 93.99; H, 6.01%.

8'-Methyl-3',4-dihydrospiro[9H-fluorene-9,1'(2'H)-naphthalene]-cis-2',3'-dicarboxylic anhydride (17) A solution of 85 mg (0.32 mmol) of 16 and 40 mg (0.41 mmol) of maleic anhydride in 0.5 mL of toluene was sealed in a tube under a nitrogen atmosphere and heated in a boiling xylene bath for 2 d. The reaction mixture was cooled and the precipitate was collected. Washing the crystals with benzene afforded 45 mg of the desired product (17) whereas the mother liquor afforded 25 mg of the starting material after evaporation followed by TLC separation (3:1 hexane-benzene). The yield was 55%: colorless granules, mp 235–236°C;  $^1\text{H NMR}$  ( $\text{DMSO}-d_6$ )  $\delta$  1.02(3H,s), 3.4–4.4(4H,m), 6.9–8.1(11H,m); IR (KBr disk) 1860, 1780  $\text{cm}^{-1}$ ; Found: C, 82.04; N, 4.69%. Calcd for  $\text{C}_{25}\text{H}_{18}\text{O}_3$ : C, 81.95; H, 4.95%.

Reaction of 1 with sodium methoxide To a solution of 20 mg (57  $\mu\text{mol}$ ) of 1ap or 1sp in 0.4 mL of chloroform and 28.6 mL of methanol, was added 1 mL of a methanolic solution of sodium methoxide, which was prepared by adding 0.13 g of sodium to 10.0 mL of methanol. After the solution was heated at appropriate temperatures. The reaction mixture was cooled

and diluted with chilled water. The mixture was acidified with dilute hydrochloric acid and was extracted with dichloromethane. The organic layer was washed, dried and evaporated. The residue in chloroform-d showed the presence of the spiro compound (16) and the methoxy compound (8) in addition to the starting materials. The product distribution is summarized in Table V.

Reaction of 1 with potassium t-butoxide To a solution of 5 mg (14  $\mu$ mol) each of 1ap and 1sp in 14 mL of t-butyl alcohol, was added 1 mL of a solution of potassium t-butoxide (280  $\mu$ mol) in t-butyl alcohol, of which concentration was determined by titration. After 30 min, the mixture was treated in a usual manner. No products other than the spiro compound (16) were detected with  $^1\text{H}$ NMR and TCL.

1-[2-(9-Fluorenyl)-3-methylbenzyl]-2-methylpyridinium bromide (19:R  $\equiv$  CH<sub>3</sub>) A solution of 20 mg (57  $\mu$ mol) of 1sp in 0.3 mL of acetone containing 50  $\mu$ L (510  $\mu$ mol) of 2-methylpyridine. The mixture was stirred for 2 h at 35°C. The precipitate was collected and washed with acetone to give 12 mg (48%) of the desired compound (19sp:R = CH<sub>3</sub>) as colorless granules, mp 227°C (decomp.);  $^1\text{H}$ NMR (DMSO-d<sub>6</sub>)  $\delta$  1.12(3H,s), 2.96(3H,s), 5.50(1H,s), 6.39(2H,s), 6.7-9.2(15H,m); Found: C,73.30; H,5.18; N,3.33; Br,18.06%. Calcd for C<sub>27</sub>H<sub>24</sub>NBr: C,73.30; H,5.47; N,3.18; Br,18.06%.

Though similar reaction of 1ap carried out for 3 d under

a nitrogen atmosphere afforded the desired compound ( $\underline{19ap}$ :R =  $\text{CH}_3$ ), the compound was obtained as fine crystals when a solution of  $\underline{1ap}$  in 2-methylpyridine allowed to stand overnight at room temperature: colorless granules, mp  $210^\circ\text{C}$  (decomp.);  $^1\text{HNMR}$  ( $\text{DMSO}-d_6$ )  $\delta$  1.81(3H,s), 2.83(3H,s), 4.40(2H,s), 5.77(1H,s), 6.6-8.5(15H,m);  $^1\text{HNMR}$  ( $\text{CDCl}_3$ )  $\delta$  2.04(3H,s), 2.79(3H,s), 4.75(2H,s), 5.62(1H,s), 7.1-8.3(15H,m); Found: C,71.59; H,5.42; N,3.11; Br,17.87%. Calcd for  $\text{C}_{27}\text{H}_{24}\text{NBr}\cdot 1/2\text{H}_2\text{O}$ : C,71.84; H,5.58; N,3.10; Br,17.70%.

1-[2-(9-Fluorenyl)-3-methylbenzyl]pridinium bromide ( $\underline{19}$ : R  $\equiv$  H) The reaction of  $\underline{1}$  with pyridine was carried out similarly as described for the reaction of 2-methylpyridine.  $\underline{19sp}$ (R = H): colorless granules, mp  $216^\circ\text{C}$  (decomp.);  $^1\text{HNMR}$  ( $\text{DMSO}-d_6$ )  $\delta$  1.04(3H,s), 5.46(1H,s), 6.38(2H,s), 6.7-9.2(16H,m); Found: C,73.40; H,5.25; N,3.32; Br,18.90%. Calcd for  $\text{C}_{26}\text{H}_{22}\text{NBr}$ : C,72.90; H,5.18; N,3.27; Br,18.65%.  $\underline{19ap}$ (R = H): colorless granules, mp  $189^\circ\text{C}$  (decomp.);  $^1\text{HNMR}$  ( $\text{CDCl}_3$ )  $\delta$  2.79(3H,s), 5.05(2H,s), 5.60(1H,s), 7.0-8.2(16H,m); Found: C,71.02; H,4.92; N,3.14; Br,18.22%. Calcd for  $\text{C}_{26}\text{H}_{22}\text{NBr}\cdot 1/2\text{H}_2\text{O}$ : C,71.40; H,5.30; N,3.20; Br,18.27%.

Determination of rates of reactions A) Solvolysis A solution of 6.0 mg ( $17\mu\text{mol}$ ) each of  $\underline{1ap}$  and  $\underline{1sp}$  and 2.9 mg of fluorene, which served as an internal reference in the analysis, in solvent was heated at appropriate temperatures. The aliquot was syringed out at appropriate intervals and the

materials were analyzed with the use of a Waters M-6000A high pressure liquid chromatograph (HPLC) which was equipped with a UV detector. The reaction obeyed the pseudo-first order rate law until 20-30% completion. The reaction rates of lap in 1:1 TFA-CHCl<sub>3</sub> at the concentration of 48 and 86 mM at 60°C were determined by monitoring the decrease of the starting material using cyclohexane as an internal standard with the use of <sup>1</sup>HNMR after heating the solution in an NMR tube at appropriate intervals.

B) the Menshutkin reaction To a solution of 12.5 mg (36  $\mu$ mol) of lap or lsp in 0.18 mL of dry acetone containing a small amount of dichloromethane or 1,2-dichloroethane in an NMR tube, was added 0.18 mL of a solution (0.190 M) of pyridine and the tube was placed in an NMR probe at 35°C. The decrease in the amount of the halide (l) was measured by taking the signal intensity of the added dichloromethane or 1,2-dichloroethane as an internal standard. The reaction obeyed the second-order rate law until 15-20% completion. The reaction of l with 2-methylpyridine was monitored similarly except that the excess of an acetone solution (1.0 M) of the base was used. Pseudo-first order rate constants thus obtained gave the second-order rate constants.

Competitive reactions A typical procedure follows. To a solution of 6.0 mg (17  $\mu$ mol) of lap, the same amount of lsp and 2.9 mg of fluorene in 1 mL of acetonitrile was added a

solution of 3.0 mg (17  $\mu$ mol) of silver nitrate. The mixture was stirred for 40 min at 25°C. An excess amount of aqueous lithium chloride was added and the precipitate was removed by filtration. The amount of unreacted starting material was measured with the use of HPLC. Fluorene which had been added to the original mixture served as an internal standard. The relative reactivity,  $k_{sp}/k_{ap}$ , was calculated by applying the following equation,

$$k_{sp}/k_{ap} = \log \frac{[sp]}{[sp]_0} \bigg/ \log \frac{[ap]}{[ap]_0}$$

where subscript 0 denotes the initial concentration. In the cases of other competitive reactions, the solvent systems quoted in the independent reactions for the respective rotamers were used. In the reaction of **1** with sodium methoxide, 2-methylnaphthalene was used as an internal reference.



## References and Notes

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- (7) (a) Poker, Y.; Wong, W. H. J. Am. Chem. Soc. 1975, 97, 7097. (b) Poker, Y.; Wong, W. H. ibid. 1975, 97, 7105.
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(11) The reason why the low reactivities of the perchlorates formed from the halides (1) relative to benzyl bromide in benzene is not known at the present stage. However it would be reasonable to think that the perchlorates derived from 1 is so strongly absorbed on the silver bromide surface, as suggested in the formation of the dimeric ether (11), that the frequency of the attack of solvent molecules is much reduced.

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Wallace, T. W. J. Chem. Soc., Perkin Trans. 1 1974, 415.
- (21) For example, see Kametani, T.; Matsumoto, H.; Honda, T.;  
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(b) Baker, J. W.; Nathan, W. S. J. Chem. Soc. 1935, 519.

(23) The salts with the ap-conformation were much more soluble in various solvents than the sp. The ap-salt was obtained as colorless crystal when the solution of lap in pyridine or 2-methylpyridine allowed to stand overnight at room temperature.

(24) The second order rate constants of the reaction of benzyl bromide with pyridine and 2-methylpyridine at 35°C were calculated to be  $3.4 \times 10^{-4} \text{ Lmol}^{-1}\text{sec}^{-1}$  and  $4.6 \times 10^{-5} \text{ Lmol}^{-1}\text{sec}^{-1}$ , respectively, from the kinetic parameter reported by Baker: ref 22.

(25) Charlton, J. C; Hughes, E. D. J. Chem. Soc. 1956, 855.

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Chapter III

Photochemical Reactivities of

3,5-Dimethyl-2-(9-fluorenyl)phenyl Azide

Rotamers

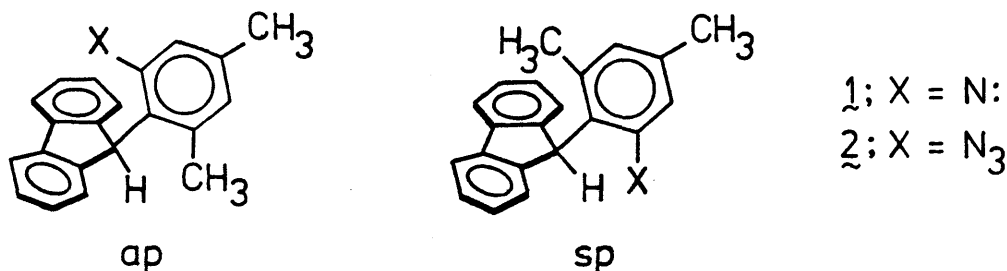
### III Photochemical reactivities of 3,5-dimethyl-2-(9-fluorenyl)-phenyl azide rotamers

#### 3-1 Introduction

Nitrenes are electroneutral and electron-deficient reactive intermediates, which were first proposed by Tiemann in 1891.<sup>1</sup> The monovalent nitrogen in nitrenes has six valence electrons, and these species can exist in two kinds of spin states; the singlet state and the triplet state. It is known that the latter which has two nearly equivalent half-occupied orbitals has a lower energy than the former. The most convenient method of the generation of aryl nitrenes is the photochemical decomposition of aryl azides. The decomposition of aryl azides produces aryl nitrenes in the singlet state and then the spin state is rapidly converted to the triplet ground state, which is termed the intersystem crossing, if no chemical reactions take place from the singlet state.

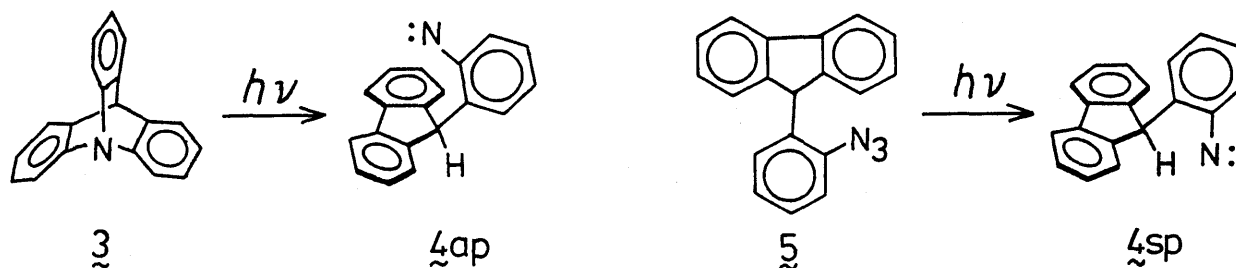
In the previous chapter, the author showed the significant interactions between the carbenium ion formed from the ionization of the bromide and the  $\pi$ -electrons of the fluorene ring situated underneath. In this chapter, the interactions of nitrenes with the  $\pi$ -electrons are investigated by the use of the conformationally fixed aryl nitrenes  $1_{ap}$  and  $1_{sp}$ , generated by the photolysis of the corresponding azides  $2_{ap}$  and  $2_{sp}$ . Two kinds of interactions may be expected in this system. One of them is the interaction of the vacant  $\pi$ -

orbital of arylnitrene in the singlet state with the highest occupied molecular orbital of the fluorene ring. This interaction is thought to be in the same category as the interaction described in the previous chapter. The other is the interaction of the electron in the half-occupied orbital of arylnitrene in the triplet state with the lowest unoccupied molecular orbital of the fluorene ring. This interaction would result in the delocalization of one of the parallel spins onto the fluorene moiety.



The research for the conformationally fixed azides **2ap** and **2sp** may serve to solve the problem derived from the photochemistry of 1-azatriptycene (**3**). Sugawara and Iwamura studied in detail the photorearrangement of 1-azatriptycene (**3**) and found a cleavage of the two carbon-nitrogen bonds resulting in the formation of o-(9-fluorenyl)phenylnitrene (**4**).<sup>2</sup> The phenylnitrene derivative **4** was independently generated by the photolysis of o-(9-fluorenyl)phenyl azide (**5**), and thus the intermediacy of **4** in the photolysis of **3** was unambiguously established. They noted, however, a slight

difference in the behavior of the nitrenes (4) generated from the photolysis of 3 and 5.<sup>2</sup> For example, the field positions of the X,Y transition of the triplet nitrenes were slightly different in the ESR spectra obtained at cryogenic temperature. The product distributions in the photoreactions of 3 and 5 in fluid solutions were significantly different. They explained these results in terms of the difference in conformation of the nitrenes (4) generated from the two precursors. From 3, generation of ap-nitrene (4ap) is expected by assuming the least motion principle for the ring opening. On the other hand, from 5, which is known to have



mainly the sp-conformation in the ground state,<sup>3</sup> sp-nitrene (4sp) should be produced. The generation of conformationally fixed nitrenes 4ap and 4sp and the research for the differences in their reactivities may provide a direct evidence for this postulate.

The author shows in section 3 the contrasting behaviors of the nitrenes 4ap and 4sp generated from the corresponding azides 2ap and 2sp at cryogenic temperature, involving direct



observations of these nitrenes by the use of ESR and UV absorption spectra. Moreover the photochemical reactivities of the azides  $\mathcal{Z}_{ap}$  and  $\mathcal{Z}_{sp}$  in fluid solutions are discussed in section 4.

### 3-2 Preparation and rotational barrier of 3,5-dimethyl-2-(9-fluorenyl)phenyl azide rotamers

The title compounds were synthesized in the following manner. 3,5-Dimethyl-2-(9-fluorenyl)aniline ( $\mathcal{G}$ ) was obtained by the Lewis acid-catalyzed thermal rearrangement of N-(9-fluorenyl)-3,5-xylidine and separated into the stable rotational isomers,  $\mathcal{G}_{ap}$  and  $\mathcal{G}_{sp}$ , by means of column chromatography on silica gel. They were converted separately to the corresponding azides,  $\mathcal{Z}_{ap}$  mp 121-122°C and  $\mathcal{Z}_{sp}$  mp 113-114°C, by the Sandmeyer reaction (Scheme I). Assignment of the conformation of the rotational isomers was readily made by  $^1\text{H}$ NMR spectroscopy by considering the ring current effect of the fluorene ring. In  $\mathcal{Z}_{ap}$ , the methyl group at 3-position occupies the deshielding area and, therefore, shows up at  $\delta$  2.63. In contrast, since the methyl group in  $\mathcal{Z}_{sp}$  is situated in the shielding zone, we observe the signal of this methyl group at  $\delta$  1.06.

The isomerization rates of the azides have been determined in decalin at 40-69°C, and the results for equilibration starting from ap-azide ( $\mathcal{Z}_{ap}$ ) are summarized in

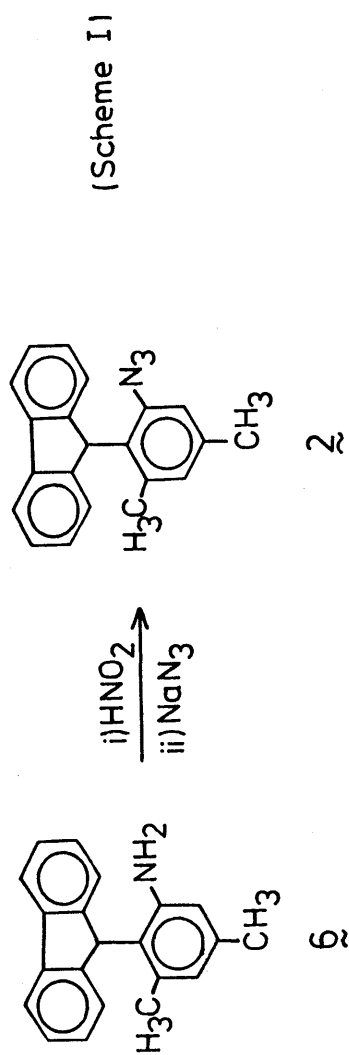
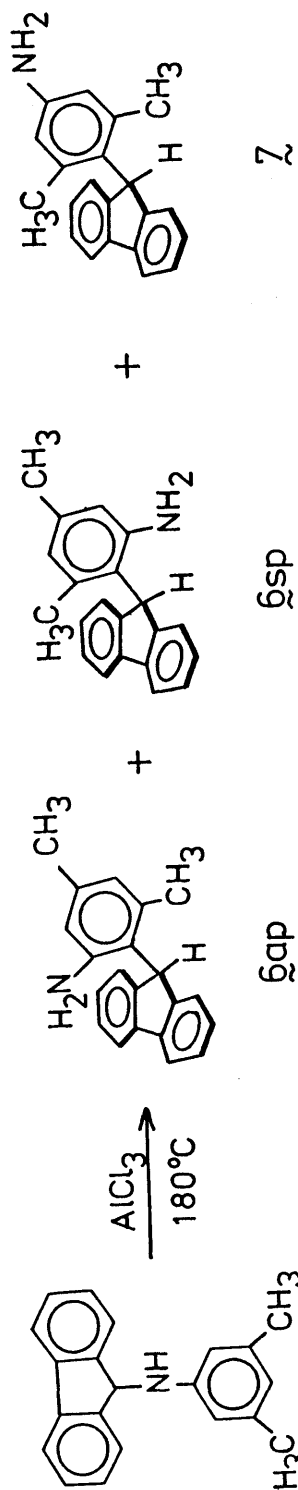


Table I. The azide group was thermally stable in this temperature range. When the data are treated according to the Eyring equation, the author obtains the activation parameters for the conversion of the ap-isomer to the sp, together with the free energy of activation and the calculated rate constant at 300K as given in Table II.

It is found in Table I that the equilibrium constant,  $K$ , is moderately large, meaning that  $2_{sp}$  is more stable than  $2_{ap}$ . The significant temperature dependence of the equilibrium constant indicates that this equilibrium is mainly controlled by the enthalpy factor. The thermodynamic parameters obtained according to equation,  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln K$ , are shown together in Table II. The high population of the sp-conformation is already reported for o-(9-fluorenyl)phenyl azide (5) and explained in terms of the electronic repulsion between the azide group and the fluorene ring.<sup>3</sup>

From the rotational barrier, we can calculate that the time required for the conversion of e.g. 5% of the ap-azide to the rotational isomer at 27°C in solution, is  $9.1 \times 10^3$  sec. Since the photoreactions discussed in the subsequent sections were carried out at the temperature below 27°C and in the very short reaction time, absence of the interconversion of the starting material in the course of the reaction was guaranteed.<sup>4</sup>

Table I. Isomerization rates of  $\lambda_{ap}$  and equilibrium constants in decalin

temperature ( $^{\circ}\text{C}$ )	k ( $\times 10^5 \text{s}^{-1}$ )	K = (sp)/(ap)
40.3	3.02	(12.4)*
56.7	19.1	10.9
61.2	30.6	10.4
68.8	66.8	9.78
80.2	—	9.14

\* This value was obtained indirectly from the other thermodynamic parameters.

Table II. Kinetic and thermodynamic parameters for the conversion of  $\lambda_{ap}$  to  $\lambda_{sp}$

$\Delta H^{\ddagger} = 22.5 \text{ kcal/mol}$	$\Delta H^{\circ} = -1.70 \text{ kcal/mol}$
$\Delta S^{\ddagger} = -7.6 \text{ e.u.}$	$\Delta S^{\circ} = -0.42 \text{ e.u.}$
$\Delta G^{\ddagger}_{300} = 24.8 \text{ kcal/mol}$	$\Delta G^{\circ}_{300} = -1.57 \text{ kcal/mol}$
$k_{300} = 5.38 \times 10^{-6} \text{ sec}^{-1}$	$K_{300} = 14.0$

### 3-3 Spectroscopic and chemical behavior of 3,5-dimethyl-2-(9-fluorenyl)phenylnitrene rotamers at cryogenic temperatures

#### Detection of triplet nitrenes by ESR spectroscopy

Since Smolinsky and Wasserman reported the first observation of the ESR spectrum of triplet phenylnitrene in 1962,<sup>5</sup> this technique has proven to be a standard method for studying nitrenes. Irradiation of 2ap with a high pressure mercury lamp in a methylcyclohexane glass at 4.2K produced an intense signal at 6722 gauss in X-band ESR spectrum (Figure I). This signal is assigned to the X,Y transition of triplet 3,5-dimethyl-2-(9-fluorenyl)phenylnitrene ( $D = 0.9735 \text{ cm}^{-1}$ ,  $E = 0.000 \text{ cm}^{-1}$ ).<sup>6</sup> The parameter,  $D$ , is the value related to the distance between two parallel spins. Since  $D$  is known to be proportional roughly to the reciprocal of the third power of the distance, the smaller value means the more delocalized parallel spins. The parameter,  $E$ , reflects the cylindrical symmetry of the diradical species. In the case of nitrenes, two molecular orbitals occupied by two parallel spins are nearly equivalent, so that  $E$  is almost zero in general.

Under these conditions, however, no signal characteristic of triplet species was observed in irradiation of 2sp. The starting material was consumed as efficiently as 2ap, but all attempts to detect the triplet 1sp were unsuccessful at several temperatures and in some other matrices. The author could observe the triplet nitrene with sp-conformation in the

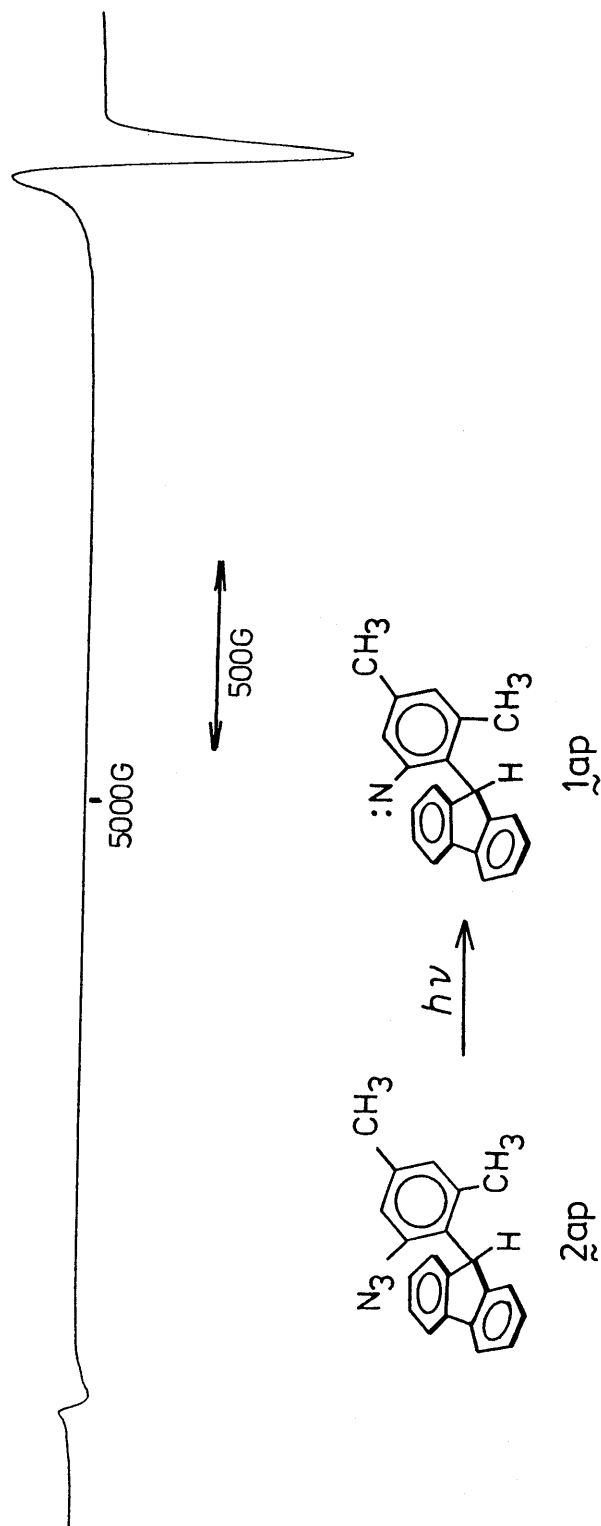


Figure 1. ESR spectra obtained by irradiation of 2ap in a methylcyclohexane glass at 4.2K. The microwave frequency was 9.2236 GHz. The intense signal at ca. 6700G was assigned to the X,Y transition of triplet 1ap. The weak signal at ca. 3300G was due to a contaminating radical.

photolysis of 9-deuterio derivative ( $2'sp$ ) at 14K. The effect of the 9-deuterium substitution on the resonance magnetic field is not conceivable. The signal due to the X,Y transition appeared at 6745 gauss (  $D = 0.9823 \text{ cm}^{-1}$ ,  $E = 0.000 \text{ cm}^{-1}$  ), which was shifted to higher field by 23 gauss compared with that of the triplet nitrene with ap-conformation.

The triplet nitrenes with ap- ( $1ap$ ) and sp- ( $1'sp$ ) conformations both showed a linear Curie plot in the temperature range 14-85K, indicating that these species had triplet ground states. Triplet nitrenes  $1ap$  and  $1'sp$  showed different thermal stability;  $1ap$  which survived at 105K was slightly more stable than  $1'sp$ . The latter disappeared rapidly at 100K: a stability comparable to that of parent phenylnitrene. The resonance position of the X,Y transition and zero-field parameters for various triplet nitrenes are collected in Table III. Previously Sugawara and Iwamura postulated that triplet nitrene  $4$  with the lower-field X,Y transition generated from 1-azatriptycene ( $3$ ) had the ap-conformation and  $4$  with higher-field transition from the azide  $5$  had the sp-conformation.<sup>2a,2c</sup> This assignment is in agreement with the present results. The probable explanation of a smaller D-value of the ap-conformation is that the interaction of the p-orbital at the nitrenic center with the  $\pi$ -system of the fluorene ring may result in the delocalization of one of the parallel spins.<sup>8</sup>

Table III. ESR fields and zero field parameters for various triplet o-(9-fluorenyl)phenylnitrenes at 4.2K

precursor of nitrene	resonance <sup>a</sup>		
	field (gauss)	shift <sup>b</sup> (gauss)	$\frac{D}{P}$ (cm <sup>-1</sup> )
phenyl azide	6824	0	1.012 <sup>c</sup>
1-azatriptycene (3)	6730	-94	0.9764
9-(2-azidophenyl)fluorene (5)	6750	-74	0.9838
ap-3,5-dimethyl-2-(9-fluorenyl)- phenyl azide (2ap)	6722	-102	0.9735
sp-3,5-dimethyl-2-(9-deuterio-9- fluorenyl)phenyl azide (2'sp)	6745	-79	0.9823

a) The microwave frequency was normalized at 9.2196 GHz.

b) The negative values correspond to downfield shifts relative to the signal position of phenylnitrene.

c) The agreement with the literature data<sup>7</sup> is excellent.



## UV absorption spectroscopy during the irradiation of azides at 77K

In order to detect the triplet nitrenes independently and other singlet intermediary species that were not found by ESR, UV spectra were obtained after irradiation of **2ap** and **2sp** at 77K with a high pressure mercury lamp. In the photolysis of **2ap** in an EPA glass, absorptions at 309 and 340 nm increased with irradiation (Figure 2). The band at 309 nm is assigned to the ap-nitrene (**1ap**).<sup>9</sup> The broad absorption at 340 nm is clearly assigned to azanorcaradiene derivative (**8**), since this band closely resembles the norcaradiene derivative (**2**) isolated from the photorearrangement of hydrocarbon triptycene.<sup>10</sup> Moreover, as shown in a subsequent section, this spectrum was observed by the irradiation of **2ap** at room temperature and changed in the presence of base to absorptions assigned to the azepine derivative (**10**), which was the isolated product. Azanorcaradiene (**8**) is thought to be formed by intramolecular addition of the nitrene to the double bond of the fluorene ring lying underneath (Scheme II).

On the other hand, in the irradiation of **2sp** under similar conditions, the absorptions at 367, 426 and 554 nm were obtained. The broad band at 554 nm is assigned to o-quinoid imine derivative (**11**), which is formed by the hydrogen migration from the 9-position of the fluorene moiety to the nitrenic center. This characteristic band was also observed

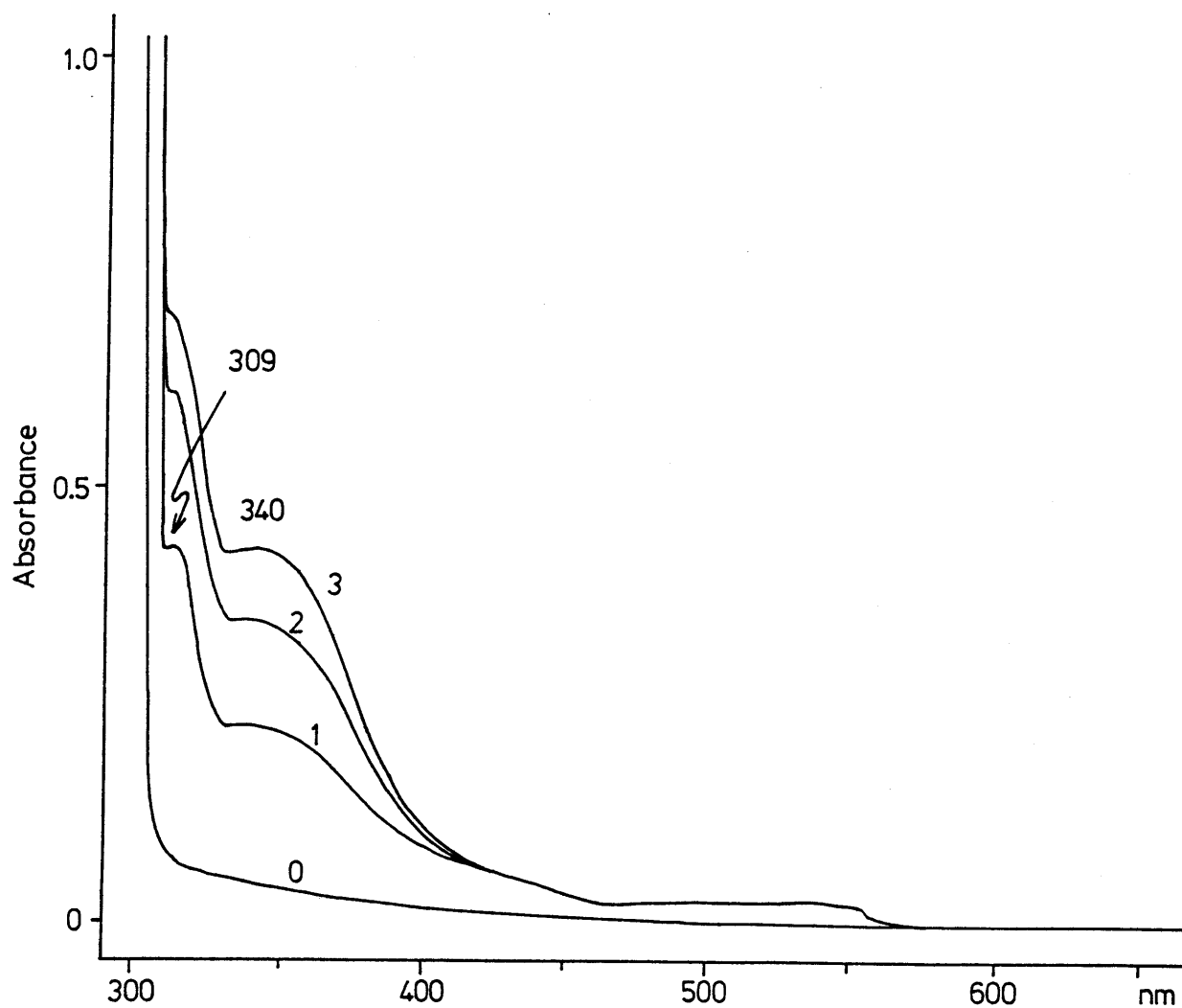
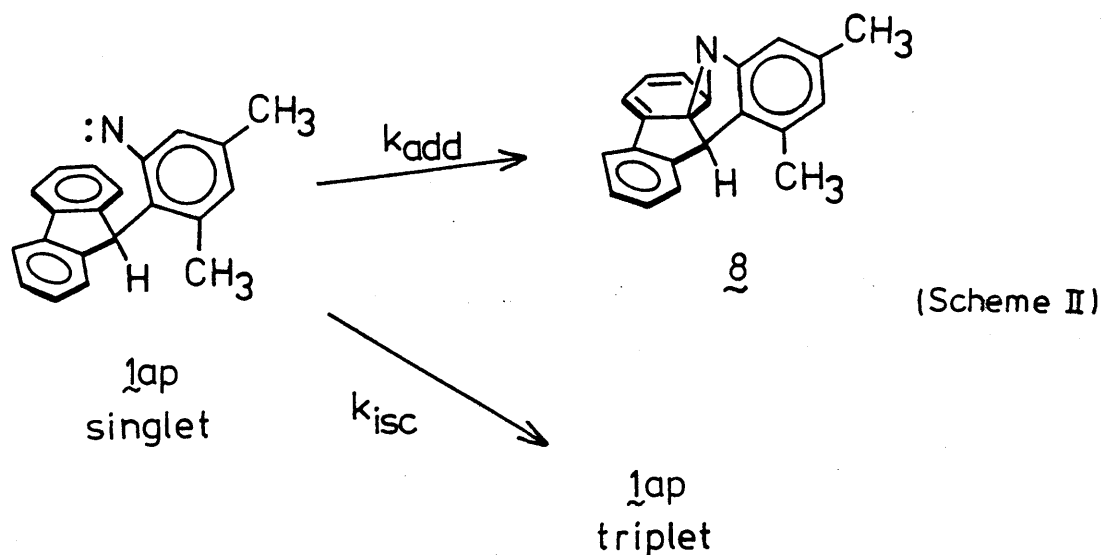


Figure 2. UV absorption spectra obtained by irradiation of 2ap in an EPA matrix at 77K. The spectra were recorded at (0) 0, (1) 5, (2) 10 and (3) 16 minutes after continuous irradiation.



in the photolysis of *o*-(9-fluorenyl)phenyl azide (5),<sup>2b</sup> in which the position of the band was at 507 nm. A bathochromic shift of 47 nm is noted for the dimethyl derivative (11). If the *o*-quinoid species has a planar conformation, the replacement of the hydrogen at 3-position in the benzene ring with the methyl group should cause a hypsochromic shift, because the non-bonding interaction of the methyl group and peri-hydrogen of the fluorene ring seriously decreases the planarity. The opposite tendency would indicate that the *o*-quinoid species essentially had a conformation with a twisted double bond and rather 1,4-biradical character.<sup>11</sup>

When the irradiation was continued, the absorption at 554 nm started to disappear and the intensity of peaks at 367 and

426 nm increased with isosbestic points at 439 and 620 nm (Figure 3). When the sample solution was allowed to warm to room temperature and aerated, it was a bright yellow color with absorptions at 358, 377 and 419 nm. The UV spectrum resembles closely that of indeno[k,1]acridine.<sup>12</sup> The product could be isolated by means of chromatography and identified as 10,12-dimethylindeno[k,1]acridine (13) as predicted. The o-quinoid imine (11) is considered to photocyclize conrotatorily to give dihydroindenoacridine (12) which then was oxidized by air to provide the final product (13) (Scheme III).

Comparing with the case of the irradiation of o-(9-fluorenyl)phenyl azide (5), the absorbance of photogenerated o-quinoid species was more intense and the photocyclization of 11 occurred smoothly. The remarkable reactivity of 1sp is probably due to the easy access of the nitrenic center to the 9-hydrogen of the fluorene unit compared with the nitrene generated from 5. The repulsive non-bonding interaction of the methyl group at 3-position with the  $\pi$ -electron of the fluorene ring appears to be responsible. The irradiation of 9-deuterio derivative (2'sp) under these conditions gave essentially the same results as the unlabeled material, although the author could not confirm the generation of the triplet nitrene (1'sp) in the UV spectrum because of the interference by the broad and intense absorptions due to o-

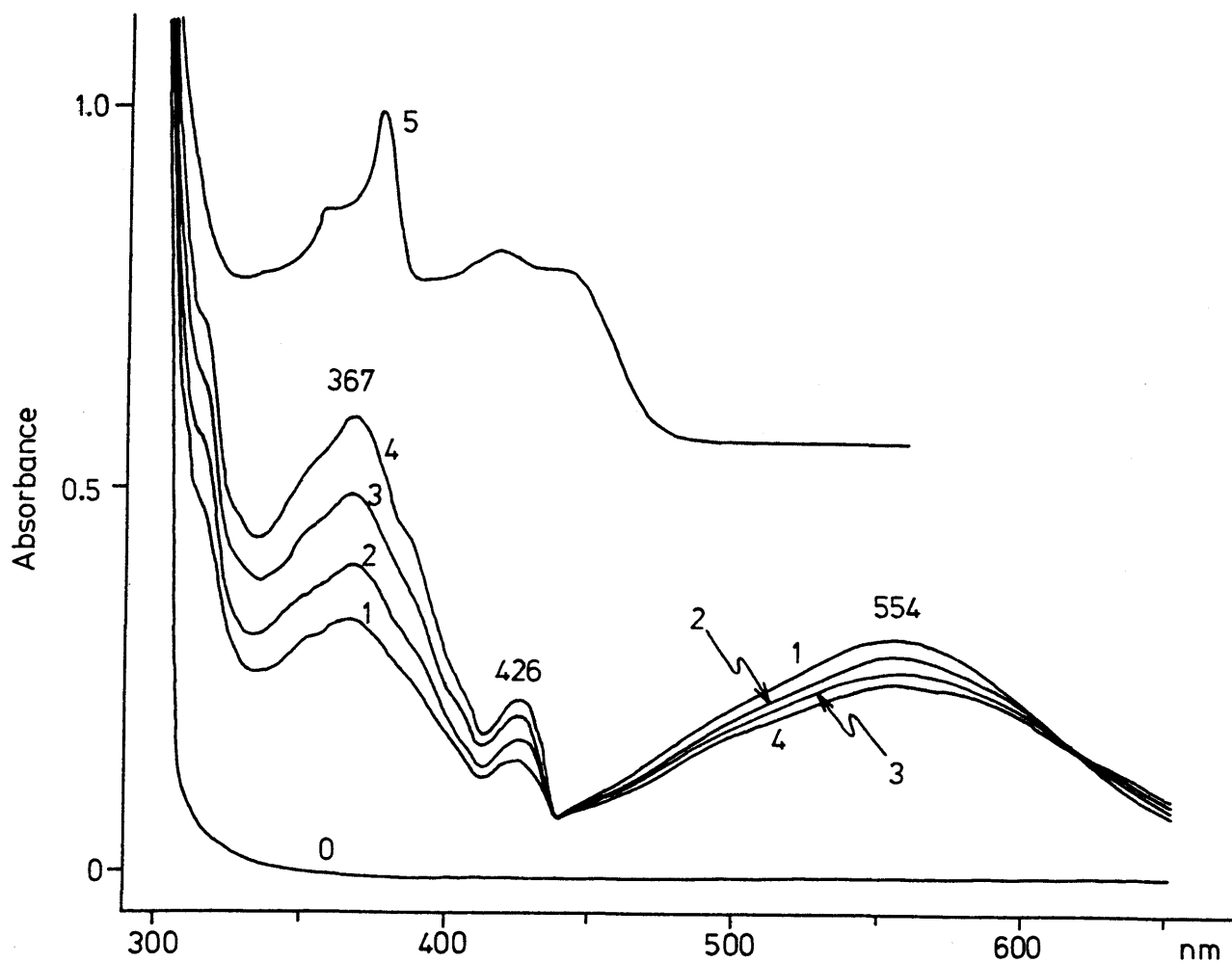
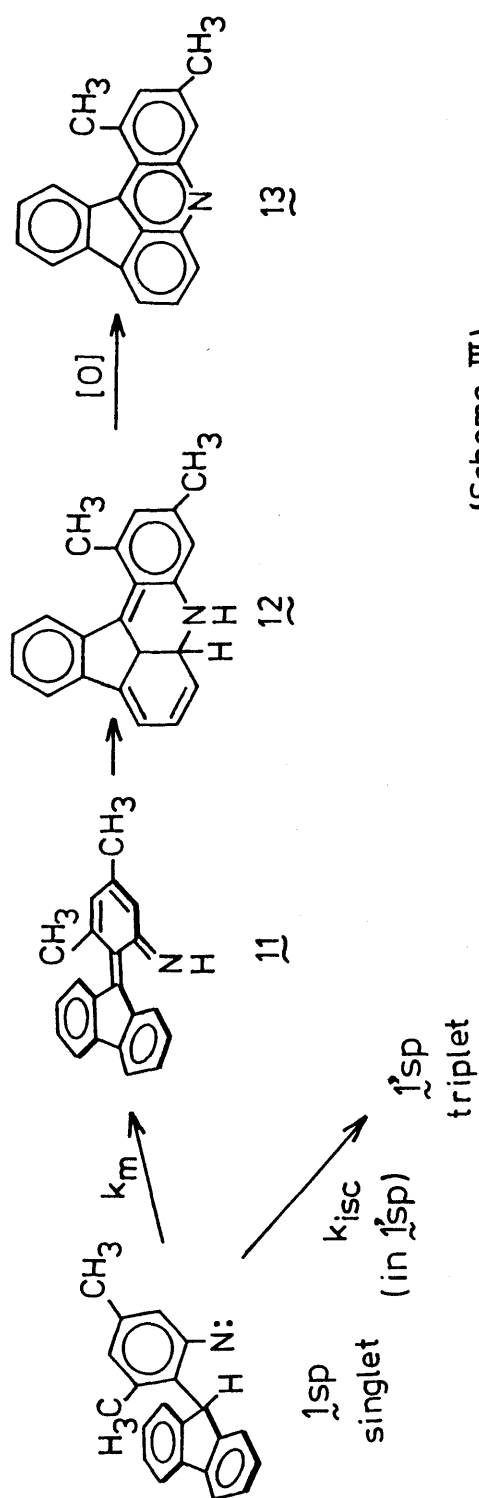


Figure 3. UV absorption spectra obtained by irradiation of 2sp in an EPA matrix at 77K. The spectra were recorded at (0) 0, (1) 13, (2) 20, (3) 31 and (4) 46 minutes after continuous irradiation. Spectrum (5) was recorded after the sample solution was allowed to warm to ambient temperature and aerated. This spectrum is shifted upward by 0.55 of absorbance for clarity.



(Scheme III)

quinoid imine (11) and its photocyclized product (12).

Different behaviors between nitrene rotamers at cryogenic temperature

The conformationally fixed nitrenes generated by the irradiation of 2ap and 2sp showed the remarkable contrast of the ESR and UV absorption spectroscopic and chemical behaviors at cryogenic temperatures. The behaviors of the ap- and sp-nitrenes corresponded to those of the nitrene generated from 1-azatriptycene (3) and of o-(9-fluorenyl)phenylnitrene, respectively.<sup>2</sup> The expectation of two conformations of the nitrenes generated from precursors, 3 and 5, which was proposed by Sugawara and Iwamura, was now clearly verified. The different behavior between the rotamers is explained in terms of the different competition between the singlet reactions and intersystem crossing to the triplet nitrene in each rotamer. In the singlet 2ap, the addition to the double bond of the fluorene ring is a favorable reaction path, since the nitrenic center is located right above the fluorene ring. Intersystem crossing to triplet 2ap can compete with the singlet reaction to give the triplet ESR signals. On the other hand, in the singlet 2sp, the hydrogen at the 9-position of fluorene is so close to the nitrenic center that the exclusive reaction is a 1,4-migration of the hydrogen.<sup>13</sup> The latter reaction is too rapid for the intersystem crossing process to be competitive. The replacement of the hydrogen

with deuterium retards the 1,4-migration and allows intersystem crossing to the triplet to compete with the 1,4-migration. The remarkable isotope effect suggests to the author the operation of the tunneling through a potential barrier in this process. Tunneling in proton-transfer reactions in solution has two general features:<sup>14</sup> nonlinear Arrhenius plots and anomalous isotope effects beyond the classical limitations. The maximum primary isotope effect in the absence of the tunneling mechanism is given by Equation 1,

$$k_H/k_D = \sqrt{2} \exp(\Delta E/RT) \quad (1)$$

where  $k_H$  and  $k_D$  are the rate constants for hydrogen and deuterium abstraction, respectively, and  $\Delta E$  is the difference in zero-point energy between the C-H and C-D bonding. Assuming that the migration of the hydrogen in  $1sp$  is expressed as a one-dimensional reaction along a linear path,  $\Delta E$  is calculated from the difference of stretching frequencies,  $\Delta\nu$ , between C-H and C-D bond,  $\Delta E = h\Delta\nu N_A/2$ , in which  $h$  is the Plank constant and  $N_A$  is the Avogadro number. If we assume  $\Delta E = 350 \text{ cm}^{-1}$  (1.00 kcal/mol), the maximum isotope effect in the absence of tunneling is obtained as  $9.8 \times 10^2$  even at 77K. At this temperature the migration of deuterium in 9-deuterio nitrene ( $1'sp$ ) must be slow enough to compete with the intersystem crossing, allowing the triplet nitrene to be observed even though in a very weak intensity.



The large value of the maximum primary isotope effect calculated without tunneling mechanism at cryogenic temperatures prevents us from concluding that this process occurs by tunneling of the hydrogen atom. The above assumption is, however, not valid in the case of the reaction in fluid solutions at room temperature. As shown in a subsequent section, the author estimates the deuterium isotope effect on the migration of 9-hydrogen in  $\text{lsp}$  to be 1.84, which is much smaller than the value, 7.6, calculated with the above equation at 298K.

Unfortunately, since the author has no technique to determine the absolute rate constant of the hydrogen migration in  $\text{lsp}$ , the author cannot prove a tunneling mechanism at the present stage.

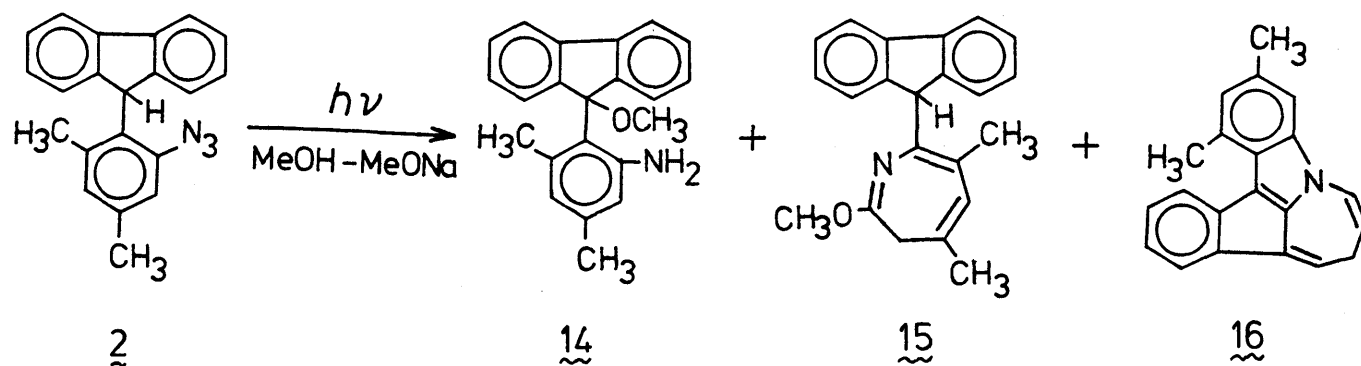
### 3-4 Photoreactions of 3,5-dimethyl-2-(9-fluorenyl)phenyl azides in fluid solutions

The author has studied the photoreactions of **2** in methanol containing sodium methoxide, in diethylamine and in acetonitrile in the presence of tetracyanoethylene.<sup>15</sup> In this section, the photoreactions are discussed in reference to those of well-documented aryl nitrenes<sup>16</sup> and the reactivities of the two rotamers are compared.

Photoproducts in methanol containing a small amount of sodium methoxide

A solution of azide 2ap or 2sp in methanol containing 8% (v/v) ether for solubility of material was irradiated with a low pressure mercury lamp under nitrogen atmosphere. In the presence of a small amount of sodium methoxide ( $5.7 \times 10^{-3}$  M), three reaction products were obtained after separation by chromatography (Scheme IV). The product distribution is shown in Table IV. The methoxyamine (14) was characterized by its  $^1\text{H}$ NMR spectroscopy, in which the proton at 9-position of the fluorene ring was absent and the methoxy signal appeared at  $\delta$  2.77. In IR spectrum the antisymmetrical and symmetrical stretching frequencies of  $\text{NH}_2$  group were observed at 3470 and  $3360\text{ cm}^{-1}$ , respectively. On the analogy of related compounds,<sup>17</sup> the rotational barrier around the bond connecting the fluorene with the benzene ring should be high enough to distinguish the rotational isomers of 14 by  $^1\text{H}$ NMR. The author could, however, find 14 only in the sp-conformation at room temperature. Strong intramolecular hydrogen bond of the amino group with 9-methoxy group seems to favor the sp-conformation exclusively. The formation of the methoxyamine (14) is rationalized by the conjugate addition of methanol to the o-quinoid imine (11).

The second photoproduct was identified as 3H-azepine derivative (15).<sup>18</sup> The  $^1\text{H}$ NMR spectrum of 15 at room temperature is shown in Figure 4. The line shape of the spectrum was much dependent on temperature. At  $-40^\circ\text{C}$ , two



(Scheme IV)

Table IV. Photoproducts in methanol containing sodium methoxide

substrate	yield (%)		
	<u>14</u>	<u>15</u>	<u>16</u>
2ap	9	8	70
2sp	40	22	29
2'sp	24	23	32

27°C, [substrate]<sub>0</sub> = 3.7 × 10<sup>-4</sup>M, [MeONa]<sub>0</sub> = 5.7 × 10<sup>-3</sup>M

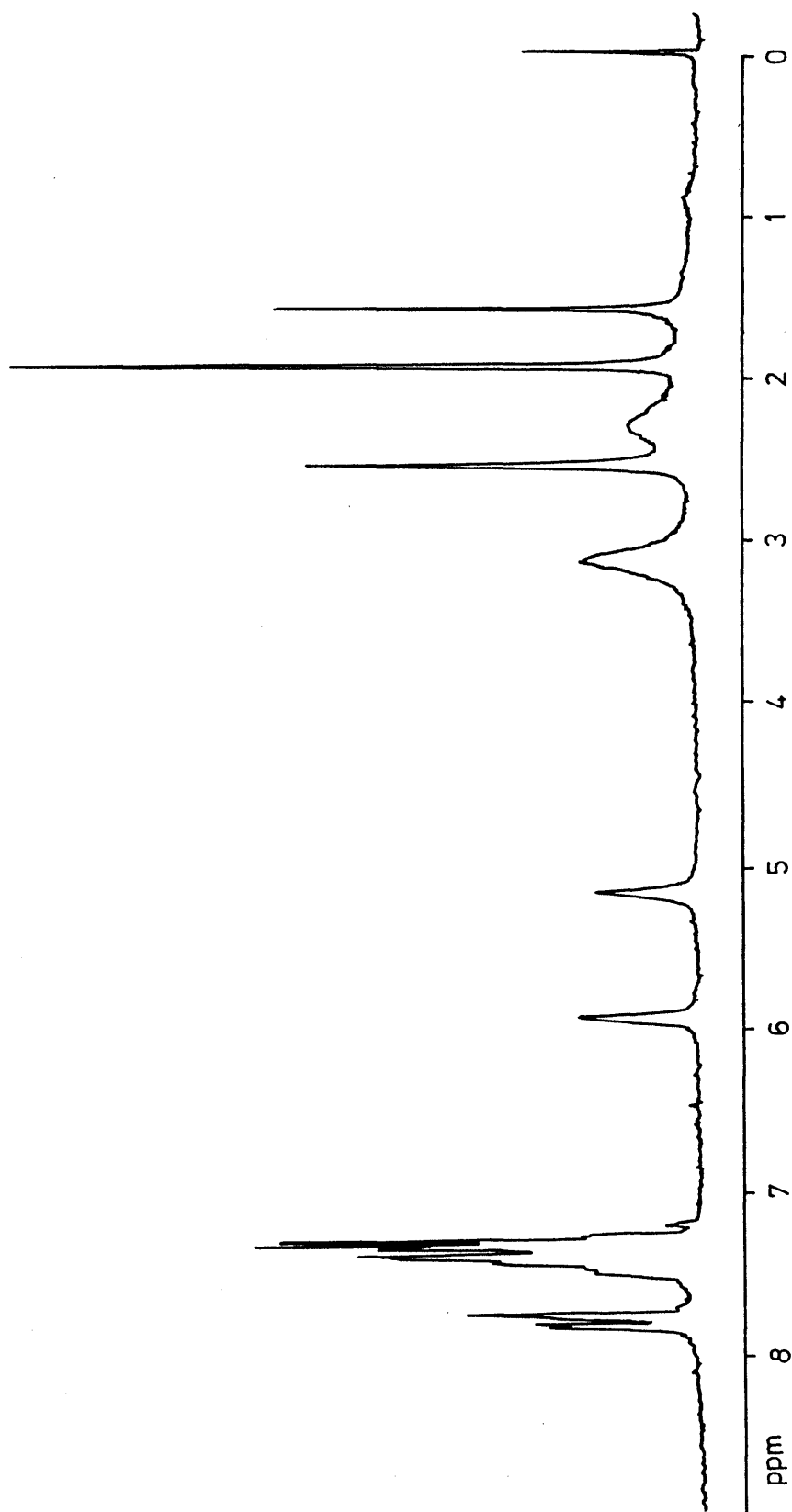
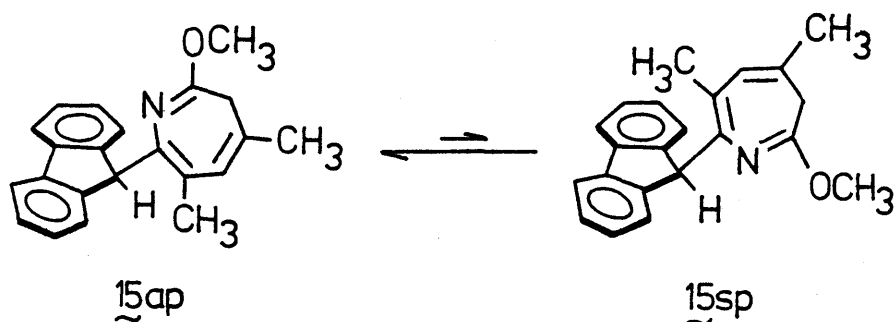


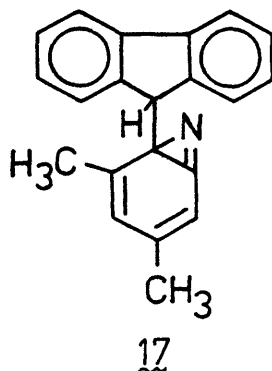
Figure 4. 100MHz <sup>1</sup>H NMR spectrum of 15 obtained in CDCl<sub>3</sub> at 25°C. The sharp peaks at δ 0.0 and 1.6 are due to tetramethylsilane and a contamination water, respectively.

sets of signals due to the presence of two isomers were observed in a 9.1:1 ratio which was hardly dependent on temperature. The conformation of the major and minor isomers is easily assigned by considering the ring current effect of the fluorene ring; the methoxy signals of the major and minor isomers are at  $\delta$  3.00 and 3.85, respectively. Since these two



signals coalesced at 7°C in the 100 MHz  $^1\text{H}$ NMR, the rate and activation energy for the rotational isomerization at the coalescence temperature are estimated as  $18.7 \text{ sec}^{-1}$  and 14.7 kcal/mol.<sup>19</sup> This is the first example of measurement of the rotational barrier on the fluorene derivative with 7-membered ring at the 9-position. The considerable decrease of the barrier height compared with other 9-arylfluorenes is rationalized by the loss of planarity and rigidity of the 3H-azepine ring at the 9-position.<sup>24</sup>

The formation of 15 is explained in terms of the well-known "benzazirine" reaction of arylnitrenes.<sup>16,25</sup> The intermediate benzazirine leading to 15 should be 17, which is formed by attack of the nitrenic center to the substituted



ortho carbon. This is contrary to the usual tendency that ortho substituted phenyl azides undergo ring expansion involving migration of the unsubstituted ortho carbon.<sup>21</sup>

The other azepine (16) is assigned to the dimethyl derivative of the compound obtained by the photorearrangement of 1-azatriptycene (3) under similar conditions.<sup>2a,2c</sup> The <sup>1</sup>HNMR data are consistent with the structure. This product is thought to be derived from the azanorcaradiene (8), which is in equilibrium with 1H-azepine (18) to give 16 by the base-promoted isomerization. The rate of the process to the final product (16) was dependent on the kind and concentration of bases. If triethylamine was used instead of sodium methoxide in a similar concentration ( $6.3 \times 10^{-3}$  M), the author could detect the precursor of 16 by means of reversed phase HPLC, though it could not be isolated. The UV absorption of the precursor was obtained on an almost colorless irradiated solution. The spectrum ( $\lambda_{\text{max}}$  352 nm) closely resembled that of azanorcaradiene, 8, which was obtained in the EPA matrix at 77K. When the solution was allowed to stand at room

temperature, the absorption at 352 nm decreased in the half-life period of ca. 40 min and the peaks at 359 and 430 nm appeared with an isosbestic point at 380 nm (Figure 5). The final spectrum was fully consistent with that of azepine, 16. From these results it is concluded that the azanorcaradiene (8) should be the precursor to 16 though it is not known whether 8 leads to 16 directly or via the short-lived 1H-azepine (18). In the photolysis of phenyl azide in diethylamine, 1H-azepine is detected as a relatively long-lived transient,<sup>9a,26</sup> and as shown subsequently the author obtained the adduct of tetracyanoethylene with 18. The transient spectrum with the peak at 352 nm, however, can not be assigned 18, since the 1H-azepine derivatives are usually colored to yellow or orange which should have the absorption at longer wavelength.<sup>27</sup>

It would be reasonable to consider that the azepine (16) was produced specifically from the ap-nitrene (1ap) and the methoxyamine (14) was specifically from the sp-nitrene (1sp) by reference to the UV spectrum at cryogenic temperature. The product distributions shown in Table IV, however, are not fully in line with this expectation. The methoxyamine (14) is formed in the photoreaction of the ap-nitrene (1ap) even though in a low yield, and 16 is obtained in considerable yield from the sp-nitrene (1sp). It should be emphasized that, in contrast with the stereospecific behaviors at

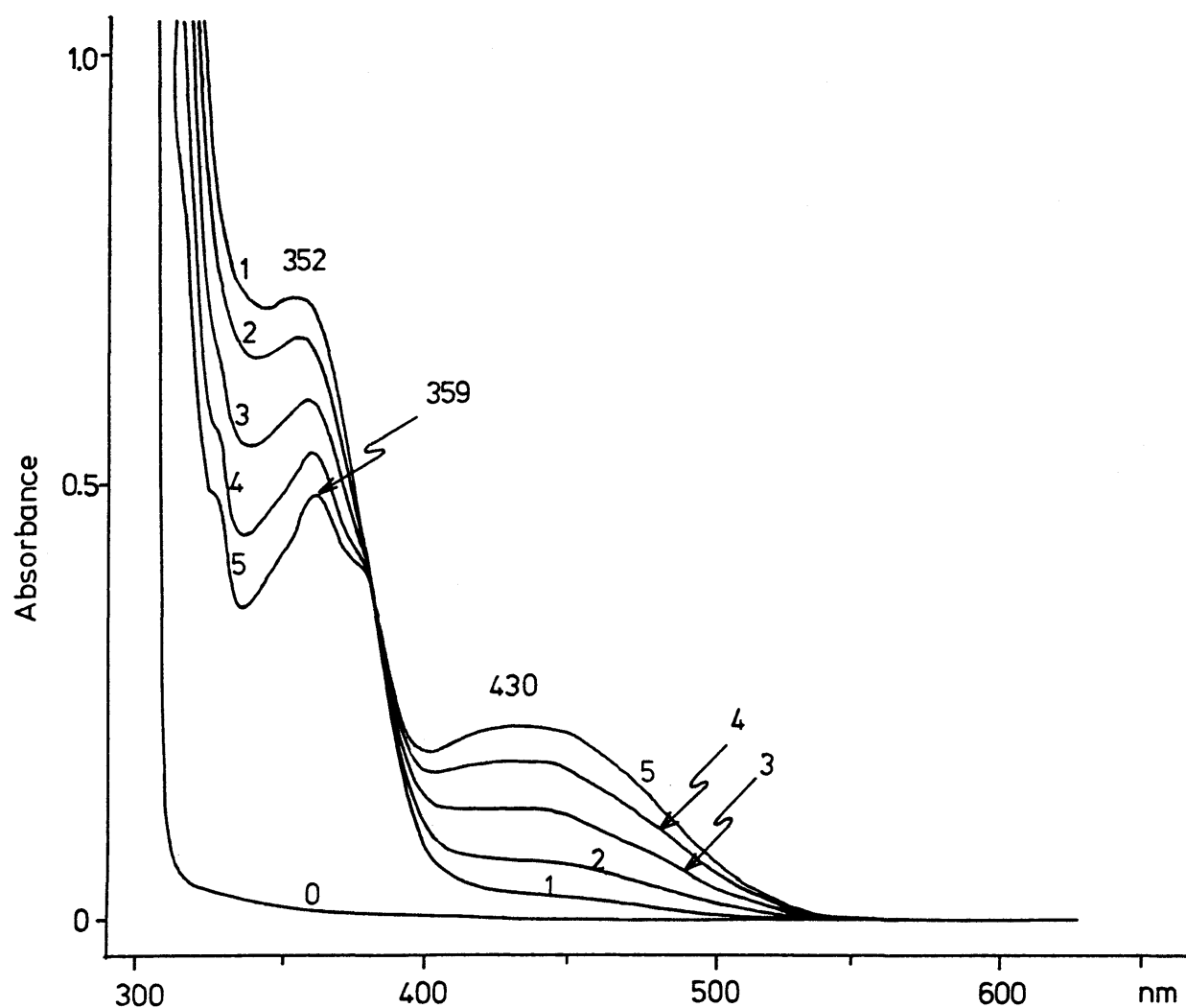


Figure 5. Change of UV absorption spectra obtained by irradiation of 2ap in methanol-ether (94:6) containing triethylamine at 25°C. The spectra were recorded (0) before irradiation and after irradiation of 25 seconds and standing at 25°C for (1) 5, (2) 16, (3) 43, (4) 89 and (5) 400 minutes.



cryogenic temperature, the crossover of the products from 2ap and 2sp is observed in the photolysis in a fluid solution at room temperature.

The dependence of the product distributions on the reaction temperature and on the concentration of the base is shown in Tables V and VI, respectively. The loss of

Table V. Temperature dependence of the photoproducts in methanol containing sodium methoxide

substrate	temperature (°C)	yield (%)		
		14	15	16
2ap	27	9	8	70
	0	9	8	78
	-70	<5	5	51
2sp	27	40	22	29
	0	43	24	17
	-70	49	15	8

[substrate]<sub>0</sub> =  $3.7 \times 10^{-4}$ M, [MeONa]<sub>0</sub> =  $5.7 \times 10^{-3}$ M

Table VI. Dependence of the photoproducts in methanol on the concentration of the added base

substrate	base	yield (%)		
		14	15	16
2ap	none	<5	0	0
	MeONa, $5.7 \times 10^{-4}M$	10	5	79
	MeONa, $5.7 \times 10^{-3}M$	9	8	70
	MeONa, $4.4 \times 10^{-2}M$	<5	16	71
	Et <sub>3</sub> N, 0.63M	10	0	70
2sp	none	27	0	0
	MeONa, $5.7 \times 10^{-4}M$	36	6	29
	MeONa, $5.7 \times 10^{-3}M$	40	22	29
	MeONa, $4.4 \times 10^{-2}M$	36	26	24
	Et <sub>3</sub> N, 0.63M	37	0	28

27°C, [substrate]<sub>0</sub> =  $3.7 \times 10^{-4}M$

specificity in products is also observed even at low temperature, though the yield of the azepine (16) obtained from the sp-rotamer (2sp) is lowered appreciably. It is shown in Table VI that the azepine (15) is formed only in the presence of methoxide ion though the yield does not depend on the concentration linearly.<sup>28</sup> Irradiation of phenyl azide in methanol is reported to give 2-methoxy-3H-azepine in 11% yield.<sup>29</sup> A failure to form 15 in the absence of sodium methoxide might be explained in terms of low concentration of the intermediate benzazirine (17) and/or decrease of the rate of formation as a result of the reduced electrophilicity of 17 by the alkyl substituents.

In order to have a clue to disclosing the mechanism for the photoreaction of 2ap and 2sp in a methanolic solution, the author carried out laser-flash photolysis experiments and determined the absolute rates of some processes.<sup>30</sup> In the photolysis of 2ap, the rate of formation of the azanorcaradiene (8) was found to be  $7.1 \times 10^5 \text{ sec}^{-1}$  by monitoring the increase of absorbance at 340 nm (Figure 6). No absorption was observed even after  $2\mu\text{s}$ , at 550 nm where the o-quinoid imine (11) should absorb, though the methoxyamine (14) derived from 11 was obtained as a minor product by the preparative photolysis of 2ap (*vide supra*). For 2sp, the absorption at 550 nm was formed at a rate faster than the time resolution ( $10^8 \text{ sec}^{-1}$ ) of this method and decreased at  $2.6 \times$

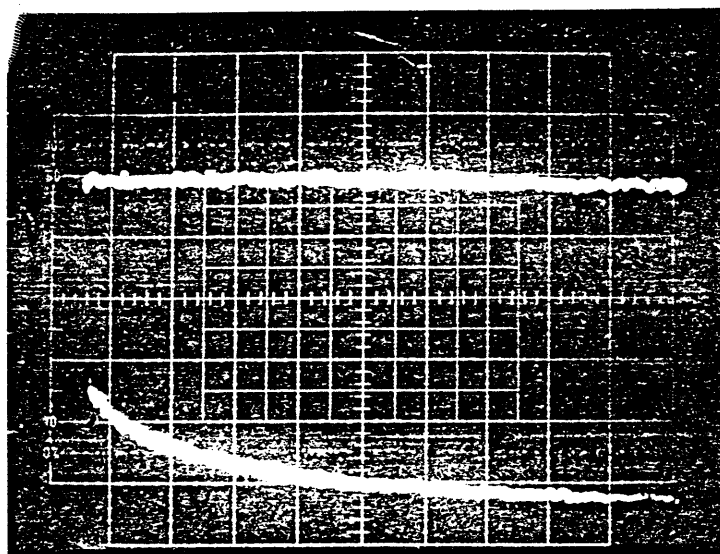


Figure 6. The lower curve represents the rise of an absorption at 340 nm after irradiation of 2ap in methanol-ether. (One division is 500 ns.) The curve fits the single exponential equation. The upper line shows the  $I_0$  level. The fluctuation of  $I_0$  is less than 1%.

$10^3 \text{ sec}^{-1}$ . The rate of the decay of this absorption is assigned to the reaction of o-quinoid imine (11) with methanol to give 14. When the 9-deuterio derivative (2'sp) was irradiated, though the rate of formation of 11 was still too fast to be measured, the absorbance at 550 nm due to a laser pulse was only 68% of that of 2sp. The deuterium isotope effect on the 1,4-migration of 9-hydrogen of the fluorene ring in 2sp is concluded to be responsible for the decreased concentration of the o-quinoid imine (11). The author notes in Table IV that, in the product distribution in the irradiation of 2'sp, the yield of the methoxyamine (14) was extremely diminished. It is reasonable to assume that the concentration of 11 is proportional to the fraction of the 1,4-migration among the whole reaction path,  $k_m/(k_m + k_o)$ , where  $k_m$  shows the rate of the 1,4-migration and  $k_o$  means the total rate of the other reactions. Moreover, the value can be regarded as the ratio of 14 to all the reaction products, which is easily obtained from Table IV; 0.44 for 2sp and 0.30 for 2'sp. The ratio of these two values, 0.68, should indicate the ratio of the concentration of o-quinoid imine (11), which is sufficiently consistent with the value obtained from the difference of the absorbance described above, 0.68. From Equation 2,

$$\frac{k_m^D}{k_m^D + k_o} \cdot \frac{k_m^H + k_o}{k_m^H} = 0.68 \quad (2)$$

where  $k_m^H$  and  $k_m^D$  stand for the rates of the 1,4-migration for  $2sp$  and  $2'sp$ , respectively, and  $k_m^H/(k_m^H + k_o)$  is equal to 0.44, we obtain the deuterium isotope effect for the 1,4-migration at 25°C as  $k_m^H/k_m^D = 1.84$ .

In solution chemistry, a wide range of the deuterium isotope effect is reported for the hydrogen transfer reactions from solvents to radicals<sup>31</sup> and triplet carbenes.<sup>32</sup> In contrast with the remarkable effect in the matrix, the rather small isotope effect in the hydrogen migration from the 9-position to the nitrenic center was obtained in a fluid solution at room temperature. It seems to indicate the modest breaking of carbon-hydrogen bond in the transition state.

The mechanism to explain the formation of the three products in the reaction of the conformationally fixed nitrenes,  $1ap$  and  $1sp$ , generated from the corresponding azides is summarized in Scheme V. As pointed out previously, the author has to explain the crossover of the reaction products, namely, the formation of  $14$  from  $1ap$  and of  $16$  from  $1sp$ . An interconversion process between the rotational isomers has to intervene in the course of the reaction. Moreover, the rate of interconversion should be comparable to the reaction rate



of the nitrenes, that is, in the range  $10^5$ - $10^6$  sec<sup>-1</sup>.<sup>33</sup>

Since the isomerization of the starting azides under these conditions is negligible as discussed in the second section, there remain four potential intermediates participating in the interconversion process. These are the excited azides ( $2^*$ ), the singlet nitrenes ( $1$ ), the o-quinoid imine ( $11$ ) and the benzazirine intermediate ( $17$ ). Since the C<sub>9</sub>-C<sub>Ar</sub> single bond in question is not involved in the excitation, the rotational barrier should not be different from that of the ground state. Aryl azides do not fluoresce and their excited state potential energy curves are nearly dissociative. Moreover, no isomerization was observed in unreacted azides under irradiation. Therefore an azide in the excited state ( $2^*$ ) is not a good candidate. Though the rotational barrier of the singlet nitrene ( $1$ ) is thought to be slightly lower than that of the azide ( $2$ ) for steric reasons, the value should not be lower than 16.4 kcal/mol which is the value of 9-(2-methylphenyl)fluorene.<sup>23</sup> Thus the rate of isomerization at room temperature of the singlet nitrenes ( $1$ ) is expected to be slower than  $10^1$ - $10^2$  sec<sup>-1</sup>. If the isomerization between the rotamers takes place in these time scale, the reaction of the nitrenes should proceed stereospecifically since the rates of the reactions are much faster than that of the isomerization. The singlet nitrenes ( $1$ ) are therefore excluded from the intermediates responsible



for the crossover of the products. If the o-quinoid imine (11) is in equilibrium with the singlet nitrene, it is possible for 1sp to isomerize to the rotational isomer. The yield of the azepine (16) should extremely decrease in the photolysis of the 9-deuterio derivative (2'sp). It is not the case as shown in Table V. Moreover, this mechanism alone can not explain the formation of 14 from the ap-nitrene (1ap).

The benzazirine (17) is a much more stable closed-shell isomer of the singlet nitrene (1) and the only intermediate responsible for the crossover of the products. The estimation of the rotational barrier in 17 is difficult, but it is reasonable to expect a considerable decrease of the barrier because of the loss of rigidity in the benzazirine ring and the change of the hybridization of the atom attached to the fluorene ring. The isomerization of 17 would be fast enough to compete with the reactions. It is known that 9-alkyl-fluorenes have a very low rotational barrier.<sup>34</sup>

The crossover of the photoreactions of the conformationally fixed azides can now be rationalized by the rotational isomerization of the intermediate benzazirine during the course of the reaction. It should be pointed out that the product distributions are determined not only by the rate of each process but also by the concentrations of the intermediary species, that is, the singlet nitrene (1), the benzazirine (17) and o-quinoid imine (11). Therefore, the

effect of temperature on the product distribution is complicated, though it appears as shown in Table V that the crossover of the products decreases probably due to considerable retardation of the isomerization rates of all processes at low temperatures.

It is sometimes inferred that a zwitterionic intermediate intervenes during the addition of a nitrene to double bonds.<sup>35</sup> If it applies to ap-nitrene ( $\text{1ap}$ ) intermediate  $\text{19}$  would be formed, although it can not be detected. When  $\text{2ap}$  was photolyzed in cyclohexane in the presence of triethylamine, the azepine ( $\text{16}$ ) is obtained only in a trace amount. The solvent effect is presumably due to decreased stability of  $\text{19}$  in a nonpolar solvent.<sup>36</sup> The zwitterionic intermediate is also assumed in the photoreaction of 1-azatriptycene ( $\text{3}$ ) on the basis of the kinetic evidence.<sup>2b</sup>

The author should point out, finally, a remarkable difference of the reaction of the sp-nitrene ( $\text{1sp}$ ) in matrices and fluid solutions. While indenoacridine ( $\text{13}$ ) was exclusively obtained in the matrix, it could not be detected at all in the methanolic solution. In solution, the intermediate is estimated to have a short life-time of ca.  $10^{-4}$  sec at room temperature, and therefore the photocyclization can not compete with the capture of  $\text{11}$  by methanol.

Photoproducts in diethylamine

The photochemistry of aryl azides in secondary amines is well-documented.<sup>16</sup> A solution of the azides **2ap** or **2sp** in diethylamine was irradiated with a low-pressure mercury lamp under nitrogen atmosphere. After chromatographic separation, the author could isolate three reaction products (Scheme VI). The product distribution and its dependence on the reaction temperature are shown in Table VII and Table VIII, respectively.

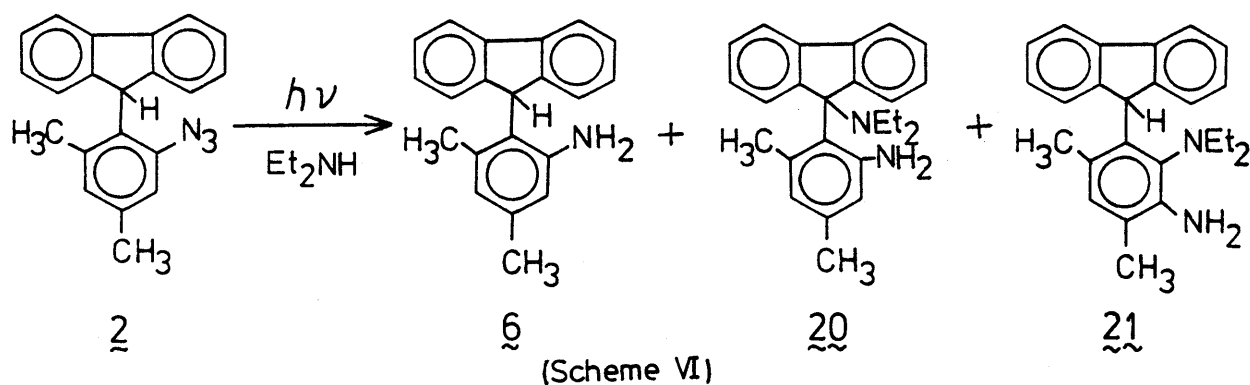


Table VII. Photoproducts in diethylamine

substrate	<b>2ap</b>	yield (%)		
		<b>6sp</b>	<b>20</b>	<b>21</b>
<b>2ap</b>	65	0	0	16
<b>2sp</b>	11	42	10	15

27°C, [substrate]<sub>0</sub> = 3.6 × 10<sup>-4</sup>M

Table VIII. Temperature dependence of the photoproducts in diethylamine

substrate	temperature (°C)	yield (%)			
		$\xi_{ap}$	$\xi_{sp}$	20	21
2ap	27	65	0	0	16
	0	59	0	0	31
	-30	37	0	0	51
2sp	27	11	42	10	15
	0	8	36	13	19
	-30	5	15	20	27

$$[\text{substrate}]_0 = 3.6 \times 10^{-4} M$$

The main product obtained was the corresponding amines,  $\xi_{ap}$  and  $\xi_{sp}$ . While the reaction of the ap-nitrene ( $1_{ap}$ ) proceeded stereospecifically, the ap-amine was obtained from the sp-nitrene. It is generally established that amines are derived from triplet nitrenes. The irradiation of 2 in the presence of oxygen or 1,3-pentadiene in diethylamine gave no or a trace of the amine ( $\xi$ ). The result is not incompatible with the above mechanism.

The second product was obtained only from the photolysis of the sp-azide ( $2_{sp}$ ) and assigned to the diamine (20). The product is the diethylamino analogue of the methoxyamine ( $14$ )

obtained in methanol. The diamine (20) was characterized by the lack of the 9-hydrogen of the fluorene ring in its  $^1\text{H}$ NMR spectrum, and present exclusively in the sp-conformation probably due to the stabilization by the intramolecular hydrogen bond. The o-quinoid imine (11) formed by the 1,4-migration of the hydrogen to the nitrenic center in the sp-nitrene (1sp) is considered to have reacted with the solvent to give 20.

The last product was assigned to the o-diamine (21), of which the  $^1\text{H}$ NMR showed a single aromatic proton on the benzene ring at  $\delta$  6.55. This compound is expected to have a high rotational barrier around the  $\text{C}_9\text{-C}_{\text{Ar}}$  bond enough to isolate the isomers even at room temperature. In the photoreaction products, however, we could find the o-diamine (21) only with the sp-conformation, which showed in the  $^1\text{H}$ NMR spectrum a characteristically high field signal of the methyl group experiencing the shielding of the fluorene ring at  $\delta$  0.95. o-Diamines are also known to be formed from benzazirine intermediates. In general o-diamines are formed on irradiation of condensed aromatic azides in the presence of secondary amines.<sup>37</sup> The o-diamine (21) was the first example obtained by the photoreaction of a phenyl azide derivative.<sup>38</sup> No azepine derived from benzazirine intermediate could be isolated from the photoreaction of the azides (2) in diethylamine; if any were present, the yield should be less

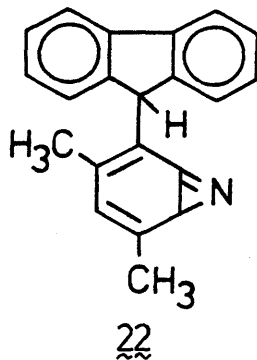
than 5%.

It is well-known that photolysis of ortho-substituted aryl azide in diethylamine leads to oxidizable intermediates and gives pyridine derivatives and 2H-azepin-2-ones.<sup>21</sup> From the photolysis under similar conditions of o-(9-fluorenyl)-phenyl azide (5) the corresponding pyridine derivative was obtained.<sup>2c</sup> In the reaction of the azides (2), however, the author was not able to obtain any product derived from an oxygen-sensitive intermediate. These results are in agreement with the reactions of 2-mesityl-5-methylphenyl azide and ascribed to a large steric effect.<sup>21</sup>

The azepine (16) formed by the internal addition of the ap-nitrene (1ap) to the fluorene ring was not obtained in diethylamine. It is probably due to the lowered polarity of the solvent which would cause the destabilization of zwitterionic intermediate (19) described in the previous section. The intersystem crossing to the triplet nitrene becomes relatively efficient and its reaction to the corresponding amine predominates in diethylamine.

As indicated in the photoreaction in methanol, crossover of the reaction products was also noted; formation of the ap-amine (6ap) from the sp-azide (2sp) took place in diethylamine and the reaction was one-way from the side of the sp-conformation. It may be reasonable to assume that the intermediate responsible for the crossover of the products

should be benzazirine which has a relatively low rotational barrier. The benzazirine intermediate leading to the o-diamine (21) should now be 22, which has a different structure



from that in methanol, 17. The benzazirine (22) formed from the singlet sp-nitrene (1sp) seems to be much less stable than that from the ap-nitrene because of a serious steric repulsion between the fluorene ring and the methyl group. Therefore, the rate of interconversion of the sp-conformer of 22 to the ap-conformer should be much faster than the back-reaction. In the reaction in diethylamine, the interconversion along the faster direction alone can compete with the electrophilic reaction of 22 with diethylamine, which is presumably the reason why the crossover of the photoreaction products was observed only in the sp-azide (2sp). On the whole, the crossover observed in the reaction in diethylamine was less than that in methanol containing a small amount of sodium methoxide. The trend is thought to be partially due to the higher rotational barrier of 22 than that of 17, though the author should also consider the difference of the reaction

rate of the benzazirines with the nucleophile.

The author has found an interesting temperature dependence of the product distributions as shown in Table VIII. The yield of the diamines, 20 and 21, which were derived from the singlet nitrene, increased considerably at low temperature at the expense of the amines (6) (*vide infra*).

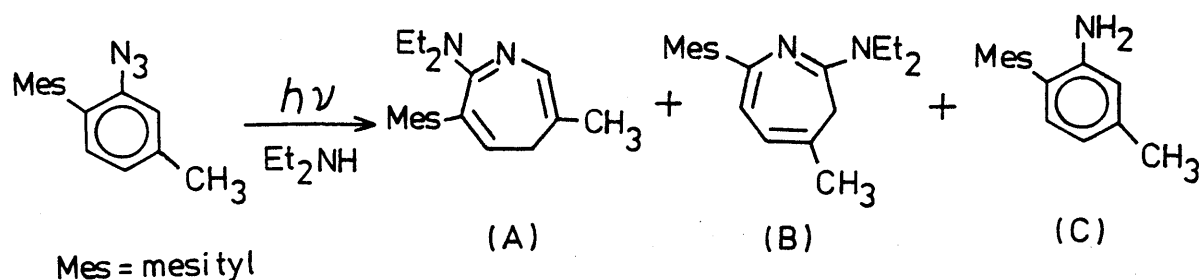
As shown above, the nitrenes (1) showed remarkably different reactivities in diethylamine from those in methanol. The reaction scheme for the formation of the products is shown in Scheme VII. In reference to other aryl nitrenes, the reactivity of 1 in diethylamine differs considerably from that in methanol in the presence of sodium methoxide. The results appear to be explained by assuming that the steady-state concentration of the singlet nitrene, which is in equilibrium with the benzazirine, is higher in methanol than in diethylamine. There are three possible bases for the assumption. One is a lower reactivity of the triplet nitrene (1) in methanol and the presence of an equilibration of the singlet and triplet nitrenes.<sup>39,40</sup> The alkyl substituents on the benzene ring may lower the energy of the singlet nitrene because of their electron-donating ability, and therefore the singlet state can be in equilibrium with the triplet state. The second basis is the effect of solvent on the energy level of the singlet state and the rate of intersystem crossing. It is established that the use of lone-pair carrying solvents





such as tetrahydrofuran and dioxane results in stabilization of the singlet nitrene in equilibrium with a benzazirine.<sup>36b,41</sup> The solvent polarity effect on the rate of intersystem crossing is studied for a similar monocentric diradical, diphenylcarbene, where the rate is higher in the less polar solvents.<sup>42</sup> For a third is mentioned the slightly higher nucleophilicity of diethylamine than methoxide ion,<sup>43</sup> though it may be questionable to apply the order of nucleophilicity in  $S_N2$  reactions to the nucleophilic reactions with a benzazirine intermediate.

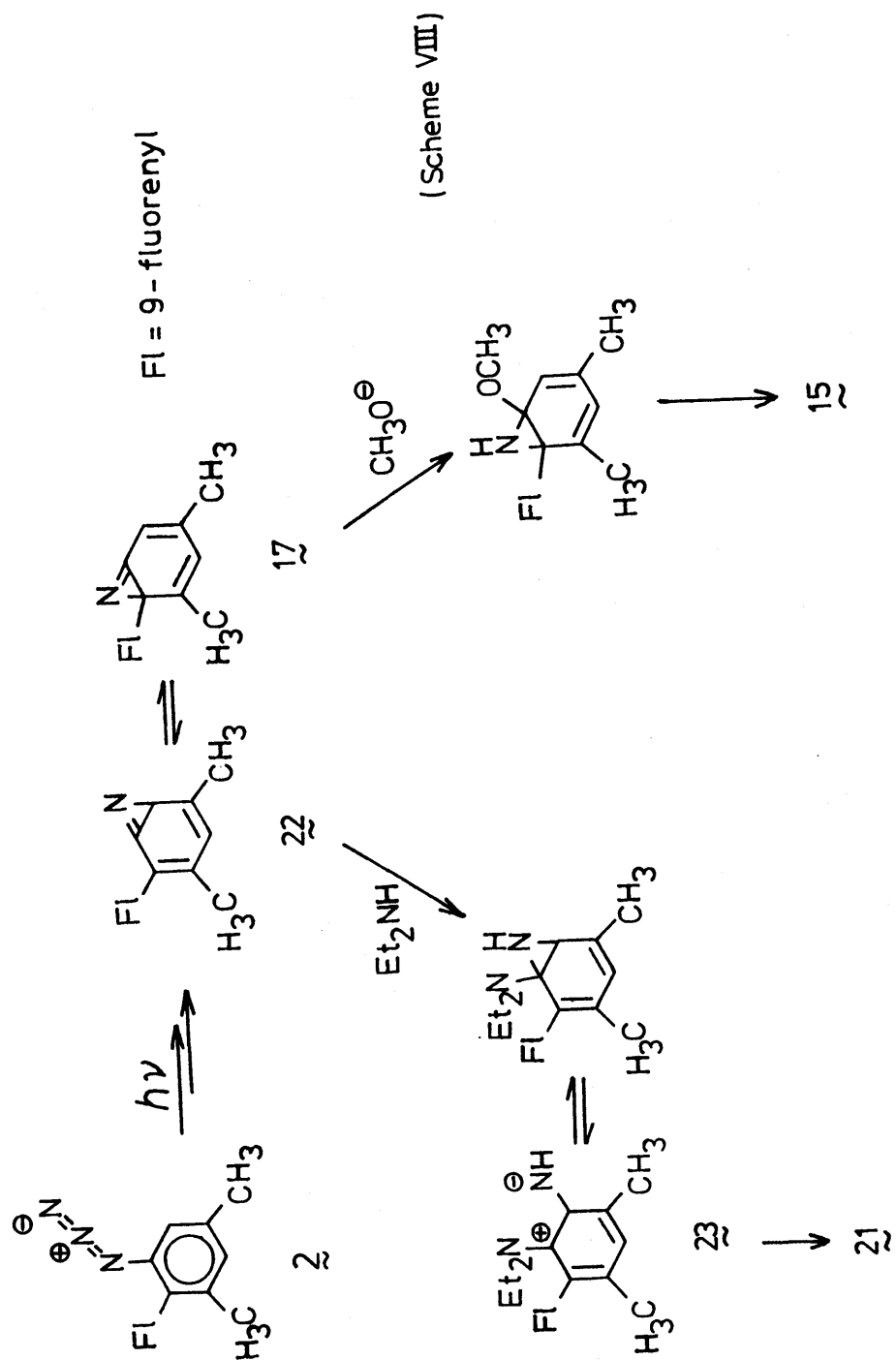
The singlet nitrene in methanol is, therefore, thought to have such a long lifetime that the benzazirine intermediate of structure **22** can isomerize to **17**. Moreover, the strong nucleophile, diethylamine, attacks **22**, while methoxide ion reacts selectively with **17** for the stereochemical reasons. As discussed by Sundberg and his co-workers, it would be reasonable to consider that the initially generated benzazirine has the structure, **22**, as the result of this predominant conformation in the precursor azide (**2**).<sup>21</sup> An interesting solvent effect on the benzazirine structure which reacts with amines is reported in the photoreaction of 2-mesityl-5-methylphenyl azide in diethylamine. Only in this solvent, 4H-azepine (A), which is derived from the benzazirine formed by the attack of the nitrenic center to the unsubstituted ortho carbon atom, is obtained in a 47% yield,



and the 3H-azepine (B) formed by the attack at the substituted carbon is obtained in a 10% yield with the corresponding amine (C) in a 16% yield. However in diethylamine-tetrahydrofuran (1:9) B is exclusively obtained in a 39% yield with the amine in a 19% yield.

Once the attack of nucleophiles occurs and the benzazirine ring is expanded to the azepine derivative, the product structure is determined from its stability since azepines are believed to be the products of kinetic control.<sup>16a,16b</sup> It would be reasonable to think that the serious non-bonded repulsion between the fluorene ring and the diethylamino group in the azepine derived from 22 with diethylamine results in shifting the equilibrium toward the zwitterion (23) to give the o-diamine (21) (Scheme VIII).

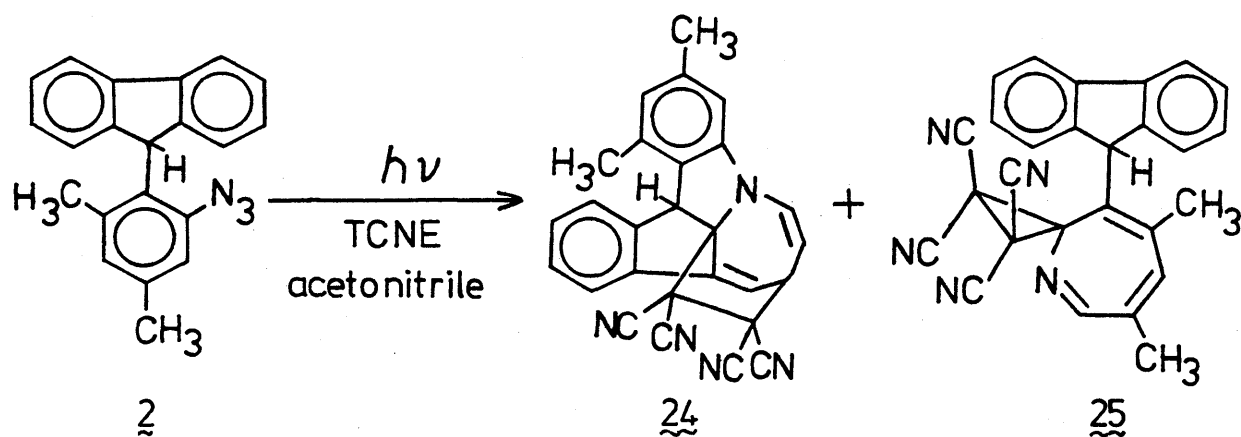
Finally the author has to refer to the reactivity of the triplet nitrenes (1) in two solvents. The low reactivity in methanol is rationalized by two reasons. First the availability of abstractable hydrogens in this solvent molecule may be so low that the process to the corresponding



amine is unfavorable. Secondly the rate of dimerization to the azo compound, which is a usual reaction of triplet nitrenes in methanol, would be seriously reduced in the azide (1) since the reaction center is sterically covered against the approach of another bulky attacking reagent. In diethylamine, it is well-known that triplet nitrenes are effectively reduced to the corresponding amines, though the mechanism of this process is not entirely established.<sup>44</sup> Though the alkyl substitution on the benzene ring of phenylnitrene has a tendency to increase the yield of the corresponding amine,<sup>45</sup> the reason for the extremely high yield of the amine from 1 is not known at the present stage. The decrease of the yield of the triplet product at lower temperature as shown in Table VIII would be explained by the retardation of this process and the decrease of the triplet concentration because of the shift of the equilibrium of the singlet nitrene to the benzazirine.

Photoproducts in acetonitrile in the presence of tetra-  
cyanoethylene (TCNE)

The photolysis of a solution of azide 2ap or 2sp in the presence of the three equivalents of TCNE under nitrogen atmosphere gave two adducts (Scheme IX) to which structures 24 and 25 were assigned. They are the dimethyl derivatives of the adducts obtained by the irradiation of o-(9-fluorenyl)-phenyl azide (5) under similar conditions.<sup>2c</sup> In Table IX, the



(Scheme IX)

Table IX. Photoproducts in acetonitrile in the presence of tetracyanoethylene(TCNE)

substrate	yield (%)	
	24	25
2ap	44	24
2sp	12	11

27°C, [substrate]<sub>0</sub> = 4.0 × 10<sup>-4</sup>M, [TCNE]<sub>0</sub> = 1.2 × 10<sup>-3</sup>M

yields of the two adducts obtained in the photoreaction of 2ap and 2sp, are shown. In this reaction, we obtained no photoproduct derived from the o-quinoid imine intermediate (11), indicating that 11 could not be externally trapped by TCNE.<sup>46</sup> The low yields of the adducts in the photolysis of 2sp seemed to indicate that 11 reacted with TCNE to give no isolable products.

The adduct (24) is regarded as the 1H-azepine derivative (18) trapped externally with TCNE. Though 24 should be formed from the ap-nitrene (1ap), it was also obtained in large amount by the irradiation of 2sp. The other adduct (25) is the analogue of the TCNE adduct of 2-nitrenobiphenyl, for which the structure has recently been determined by the X-ray crystallographic analysis.<sup>47</sup> Though this adduct appears to be formed via the isomerization of singlet nitrene to azacycloheptatetraene rather than benzazirine, the mechanism has not been fully explored yet. We could find the adduct (25) only in the sp-conformation, which showed in <sup>1</sup>HNMR a signal of the methyl group at  $\delta$  1.02.

Note that in the photoreaction in acetonitrile containing TCNE the product crossover between the rotational isomers was also observed as was the case in methanol and in diethylamine.

### 3-5 Conclusion

The conformationally fixed nitrenes generated by the

photolysis of rotamers of 3,5-dimethyl-2-(9-fluorenyl)phenyl azide, 2<sub>ap</sub> and 2<sub>sp</sub>, showed a remarkable contrast not only at cryogenic temperature, but also in fluid solutions at room temperature. These results provided the first example demonstrating differences in spectroscopic behaviors and reactivities between the defined conformers of a nitrene.<sup>48</sup>

The behaviors of the ap- and sp-nitrenes, 1<sub>ap</sub> and 1<sub>sp</sub>, were parallel to those of the nitrenes generated from 1-azatriptycene (3) and of o-(9-fluorenyl)phenylnitrene (2), respectively. Thus the author was able to obtain evidence for the assumption proposed by Sugawara and Iwamura that the nitrenes generated from the two precursors, 3 and 5, differed conformationally.

In matrices at cryogenic temperatures, the ap- and sp-nitrenes showed fully stereospecific behaviors. In fluid solutions, however, the photoproduct derived from 2<sub>ap</sub> by addition of the nitrene to the double bond of the fluorene ring was obtained in the photolysis of 2<sub>sp</sub>, and that derived from 2<sub>sp</sub> by a conjugate addition of solvent to the o-quinoid imine (11) was detected in the irradiation of 2<sub>ap</sub>. The author concluded that the crossover of the photoreactions was due to the rotational isomerization of the intermediate benzazirine during the course of the reaction in fluid solutions.

In addition, the author should point out some interesting reactivities of the nitrene (1) in view of aryl nitrene and



different behaviors of  $\text{I}$  in methanol in the presence of sodium methoxide and in diethylamine, for example, an extremely high yield of the aniline ( $\text{6}$ ) in diethylamine and a difference of the structure of the benzazirine intermediate in the two solvents. Though the author explained these matters in terms of the larger stabilization of the singlet nitrene in methanol than in diethylamine, they must involve the interesting problems in the field of the solution chemistry of aryl nitrenes.

## EXPERIMENTAL

Spectral measurements  $^1\text{H}$ NMR spectra were recorded on a Varian EM-390 spectrometer (90 MHz), a JNM-FX-100 spectrometer and a JNM-GX-400 spectrometer.  $^{13}\text{C}$ NMR spectra were obtained with a JNM-GX-400 spectrometer operating at 100.5 MHz. IR and UV spectra were recorded on a Hitachi 295 spectrometer and a Cary 17 absorption spectrophotometer, respectively. Low and high resolution mass spectra were obtained with a JEOL D-300 machine. ESR spectra were measured on a Varian E-112 spectrometer (X-band microwave unit, 100 kHz field modulation) equipped with an optical transmission cavity and an Oxford cryomagnetic system or an Air Products LTD-3-100 liquid helium transfer system. The microwave frequency was measured with a Takeda Riken 5201M frequency counter and the X,Y band positions of triplet nitrenes were read with the aid of a Varian E-500 NMR gaussmeter. Time-resolved absorption spectra were obtained by the use of an excimer laser (Lambda Physik EMG 500) and the monitoring light source for the transient absorption spectra (an EG & G FX-265 UV xenon lamp).

Photolysis Irradiation in the ESR and UV measurements was carried out with an Ushio USH-500D 500-W high-pressure mercury lamp. The UV absorption spectra at 77K were obtained by the irradiation of the sample which was cooled in a liquid nitrogen Dewar vessel with a transparent window and placed in

the sample chamber of a spectrometer. Preparative photolysis in fluid solutions was carried out with a NORMAG TNN 15/32 15-W low-pressure mercury lamp or an sp-3 3-W "pen-light" containing mainly 254 nm (SEN Tokushu Kogen Co., Ltd.).

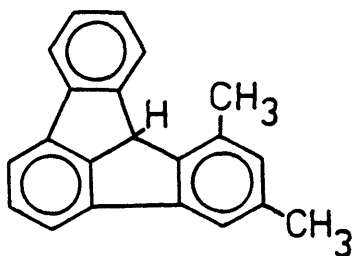
N-(9-Fluorenyl)-3,5-xylylidine To a solution of 3.0 g (12.2 mmol) of 9-bromofluorene<sup>49</sup> in 30 mL of 2-propanol was added 1.9 g (15.7 mmol) of freshly distilled 3,5-xylylidine and 1.2 g (14.6 mmol) of sodium acetate. The mixture was refluxed with stirring for 30-40 min. After rapid filtration of the hot suspension followed by cooling, the colorless precipitate was collected by filtration, washed with cold 2-propanol and dried to afford 3.0 g (86%) of N-(9-fluorenyl)-3,5-xylylidine as colorless granules, mp 126-127°C; <sup>1</sup>HNMR (CDCl<sub>3</sub>) δ 2.25(6H,s), 3.85(1H,brs), 5.67(1H,s), 6.48(2H,s), 7.2-7.8(8H,m); IR (KBr disk) 3360 cm<sup>-1</sup>; MS found M<sup>+</sup> = 285.1524. C<sub>21</sub>H<sub>19</sub>N requires M<sup>+</sup> = 285.1517.

3,5-Dimethyl-2-(9-fluorenyl)anilines (6ap) and (6sp) A mixture of 1.0 g (3.50 mmol) of N-(9-fluorenyl)-3,5-xylylidene, 1.0 g of anhydrous aluminum chloride and 10 mL of 3,5-xylylidine was heated at 180°C for 20 h under an argon atmosphere. To the cooled reaction mixture was added 20 mL of 5% aqueous sodium hydroxide. The organic material was extracted with benzene and the extract was washed and dried over magnesium sulfate. The solvent and excess 3,5-xylylidine were removed under reduced pressure. The residue was developed on a silica

gel column (Wakogel C-200) with hexane-benzene (1:1). The ap-form ( $\zeta_{ap}$ ), 420 mg (42%), was eluted first and the sp-form ( $\zeta_{sp}$ ), 130 mg (13%), followed. The ap-form, oil;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  2.17(3H,s), 2.48(2H,brs), 2.57(3H,s), 5.40(1H,s), 6.10(1H,s), 6.56(1H,s), 7.2-7.9(8H,m); IR (KBr disk) 3450, 3350  $\text{cm}^{-1}$ ; MS found  $M^+ = 285.1524$ .  $\text{C}_{21}\text{H}_{19}\text{N}$  requires  $M^+ = 285.1517$ . The sp-form, colorless granules, mp 137-138°C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  1.05(3H,s), 2.21(3H,s), 3.83(2H,brs), 5.28(1H,s), 6.29(1H,s), 6.57(1H,s), 7.2-8.0(8H,m); IR (KBr disk) 3360, 3300  $\text{cm}^{-1}$ ; MS found  $M^+ = 285.1492$ .  $\text{C}_{21}\text{H}_{19}\text{N}$  requires  $M^+ = 285.1517$ . Elution with benzene gave 3,5-dimethyl-4-(9-fluorenyl)aniline ( $\zeta$ ) as colorless needles, mp 138-139°C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  0.99(3H,s), 2.56(3H,s), 3.29(2H,brs), 5.37(1H,s), 6.15(1H,s), 6.50(1H,s), 7.2-7.9(8H,m); IR (KBr disk) 3410, 3320  $\text{cm}^{-1}$ ; MS found  $M^+ = 285.1517$ .  $\text{C}_{21}\text{H}_{19}\text{N}$  requires  $M^+ = 285.1517$ .

3,5-Dimethyl-2-(9-fluorenyl)phenyl azides ( $\zeta_{ap}$ ) and ( $\zeta_{sp}$ )  
To a cooled solution of 500 mg (1.75 mmol) of ap-3,5-dimethyl-2-(9-fluorenyl)aniline ( $\zeta_{ap}$ ) in 22 mL each of dioxane and 6N sulfuric acid was added in portions at 0-5°C a solution of 125 mg (1.81 mmol) of sodium nitrite in 4 mL of water. The reaction mixture was stirred for 15 min at this temperature to obtain a yellow homogeneous solution. The cooled diazonium salt solution was added dropwise to a solution of 1.5 g of sodium azide in 8 mL of water warmed to 40-50°C in advance.

After the addition, the reaction mixture was allowed to stand for 10 min and cooled. The organic materials were extracted with ether and the extract was washed with dilute aqueous sodium hydroxide and dried on magnesium sulfate. The solvent was removed under reduced pressure with the temperature below 50°C to avoid extensive isomerization of the product. The residue was developed on a silica gel column with hexane. After elution of 36 mg (7%) of isomeric sp-azide (4sp) (see below), the ap-form was eluted. The yield was 300 mg (55%): colorless granules, mp 121-122°C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  2.27(3H,s), 2.63(3H,s), 5.24(1H,s), 6.63(1H,s), 6.94(1H,s), 7.2-7.9(8H,m); IR (KBr disk) 2090  $\text{cm}^{-1}$ ; MS  $m/z$  (%) 311( $\text{M}^+$ , 21), 283( $\text{M}^+ - \text{N}_2$ , 71), 282(100), 268(45); found  $\text{M}^+ = 311.1415$ .  $\text{C}_{21}\text{H}_{17}\text{N}_3$  requires  $\text{M}^+ = 311.1421$ . 1,3-Dimethylindeno[*j,k*]fluorene (26) was obtained (44 mg, 9%) as a by-product which was eluted between



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the ap- and sp-azides in the chromatography. When an aqueous sodium azide solution was added to the diazonium salt solution, 26 was obtained in a larger amount at the expense of the azides. 26: colorless granules, mp 61-62°C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )

$\delta$  2.41(3H,s), 2.78(3H,s), 5.16(1H,s), 6.95(1H,s), 7.2-8.0(8H,m);  $^{13}\text{C}\{^1\text{H}\}$ NMR ( $\text{CDCl}_3$ )  $\delta$  21.3, 21.5, 55.5, 118.6, 118.7, 120.1, 121.9, 126.2, 126.6, 127.2, 128.9, 129.8, 134.8, 137.4, 139.3, 139.6, 143.3, 144.8, 145.1, 147.3, 160.7; MS  $m/z$  (%) 268( $\text{M}^+$ , 77), 253( $\text{M}^+ - \text{CH}_3$ , 100); found  $\text{M}^+ = 268.1271$ .  $\text{C}_{21}\text{H}_{16}$  requires  $\text{M}^+ = 268.1252$ .

Aniline 6sp afforded sp-3,5-dimethyl-2-(9-fluorenyl)-phenyl azide (4sp) as a sole product in a 40% yield: colorless powder, mp 113-114°C;  $^1\text{H}$ NMR ( $\text{CDCl}_3$ )  $\delta$  1.06(3H,s), 2.31(3H,s), 5.74(1H,s), 6.57(1H,s), 6.97(1H,s), 7.2-7.9(8H,m); IR (KBr disk) 2110  $\text{cm}^{-1}$ ; MS found  $\text{M}^+ = 311.1418$ .  $\text{C}_{21}\text{H}_{17}\text{N}_3$  requires  $\text{M}^+ = 311.1421$ .

Deuteration of 3,5-dimethyl-2-(9-fluorenyl)aniline (6)  
To a solution of 620 mg (2.17 mmol) of the amine (6)<sup>50</sup> in 35 mL of dry ether was added slowly 12 mL (19.6 mmol) of n-butyllithium solution in hexane (1.60 M) at 0°C. After the addition, the reaction mixture was stirred for 15 h at room temperature, cooled in an ice bath and quenched by the slow addition of 10 mL of deuterium oxide. The organic layer was separated and the water phase was extracted with ether. The combined extract was washed with water, dried on magnesium sulfate and evaporated to give sp-3,5-dimethyl-2-(9-deuterio-9-fluorenyl)aniline (6'sp) in a quantitative yield. The Sandmeyer reaction of 6'sp as described above gave the sp-azide-9-d (4'sp), in which the deuterium isotope purity was found

by an NMR integration of the remaining 9-h compound to be higher than 98.5%.

Rates of rotational isomerization      The pure ap-azide (2ap) was dissolved in decalin ( $3.2 \times 10^{-3}$  M) and the solution was transferred into glass capillaries and then sealed. The solution was heated in an appropriate boiling solvent bath. The decrease of 2ap and the increase of 2sp were monitored by the use of a Waters M-6000A high pressure liquid chromatograph (HPLC) on a  $\mu$ -Porasil column with hexane-dichloromethane (5.5:1) elution. The equilibrium constant, K, was obtained at each temperature by heating the solution for a long enough time (at least 50 half-lives). Assuming the first order reaction, the rate constant, k, was obtained by the following equation,

$$kt = \frac{K}{K + 1} \ln \left( \frac{1 + x}{1 - x/K} \right)$$

where x is the ratio of the amount of 2sp to that of 2ap at time t. The plot gave good straight lines. Putting k's into the Eyring equation, we obtained the activation parameters.

Photolysis at cryogenic temperatures      A) ESR measurements at 4K      The azides were dissolved in methylcyclohexane (ca.  $5 \times 10^{-3}$  M) and the solution was degassed in a quartz cell by three freeze-thaw cycles. The sample was cooled in a pre-cooled ESR cavity and irradiated.

B) UV absorption spectral measurements at 77K The azides were dissolved in EPA (ca.  $1.1 \times 10^{-4}$  M), and the solution was transferred to a quartz cell of 1.0 cm optical length and degassed by three freeze-thaw cycles. The spectra were recorded at an appropriate interval after irradiation. The preparative experiment was carried out in the similar manner. The degassed solution of 2.5 mg (8  $\mu$ mol) of 2sp in 5 mL of EPA was irradiated in a quartz cell at 77K. The solution was colored immediately to red-violet and the irradiation was continued until the color completely disappeared to give a blue-green fluorescent solution (for 40-60 min). After the irradiation, the sample was allowed to stand overnight at ambient temperature on exposure to air. The obtained yellow solution was evaporated and the residue was separated by the use of GLPC with chloroform eluant to give 36% of the recovered starting material and 10,12-dimethylindeno[k,l]acridine (13) in a 29% yield based on the reacted material. 13: yellow needles, mp 148-149°C;  $^1\text{H}$ NMR ( $\text{CDCl}_3$ )  $\delta$  2.59(3H,s), 3.21(3H,s), 7.36(1H,s), 7.40(1H,dd,J = 7.6, 7.0 Hz), 7.46(1H,dd,J = 7.3, 7.0 Hz), 7.79(1H,dd,J = 8.5, 6.5 Hz), 7.88(1H,d,J = 6.5 Hz), 7.95(1H,d,J = 7.3 Hz), 8.01(1H,s), 8.05(1H,d,J = 8.5 Hz), 8.47(1H,d,J = 7.6 Hz); UV (EPA)  $\lambda_{\text{max}}$  ( $\log \epsilon$ ) 358 nm (3.45), 377 (3.70), 419 (3.50); MS  $m/z$  (%) 281( $\text{M}^+$ , 100), 266( $\text{M}^+ - \text{CH}_3$ , 4); found  $\text{M}^+ = 281.1223$ .  $\text{C}_{21}\text{H}_{15}\text{N}$  requires  $\text{M}^+ = 281.1205$ .



Photolysis in fluid solutions      Solutions of the azide in the concentration of ca.  $4 \times 10^{-4}$  M were prepared and purged with nitrogen for 5-10 min. Irradiation was carried out under a nitrogen atmosphere. The reaction was monitored by HPLC on a  $\mu$ -Porasil column with hexane-dichloromethane (5:1) or on a  $\mu$ -Bondapak C<sub>18</sub> column with methanol-water (5:1) elution. The irradiation was stopped when 80-90% of the material was consumed. Yields of the products based on the reacted material were determined by HPLC after the correction of absorptivities. The resulting solution was worked up by the following procedures.

A) In methanol in the presence of sodium methoxide      A solution for the photoreaction was prepared by the addition of 150 mL of methanol containing 20 mg of dissolved sodium to the solution of 20 mg (64  $\mu$ mol) of azide (2) in 12 mL of ether. The photolyzed solution was concentrated under reduced pressure and diluted with chloroform. The solution was washed with water until the water phase was neutral, dried over magnesium sulfate and evaporated. The residue was separated by the use of GLPC to give three products, which were further purified by Lobar column chromatography with dichloromethane eluants. The yield of products is shown in Table IV; 9-(2-amino-4,6-dimethylphenyl)-9-methoxyfluorene (14), oil; <sup>1</sup>HNMR (CDCl<sub>3</sub>)  $\delta$  1.16(3H,s), 2.15(3H,s), 2.77(3H,s), 6.12(1H,s), 6.45(1H,s), 7.2-7.7(8H,m); IR (Nujol) 3470, 3360 cm<sup>-1</sup>; MS m/z

(%) 315( $M^+$ , 67), 283(86), 282(100); found  $M^+$  = 315.1612.  $C_{22}H_{21}ON$  requires  $M^+$  = 315.1622. 4,6-Dimethyl-7-(9-fluorenyl)-2-methoxy-3H-azepine (15), oil;  $^1H$ NMR ( $CDCl_3$ ) at 22°C  $\delta$  1.92(3H,s), 2.37(3H,brs), 2.51(2H,s), 3.07(3H,brs), 5.15(1H,s), 5.91(1H,s), 7.2-7.8(8H,m). At -50°C  $\delta$  1.92(3H,brs), 2.40/0.81(3H,s), 2.51(2H,brs), 3.00/3.84(3H,s), 5.19/4.78(1H,s), 5.95/5.66(1H,s), 7.2-7.8(8H,m) (the signals for the major and minor conformers are indicated before and after the slant lines, respectively.);  $^{13}C\{^1H\}$ NMR ( $CDCl_3$ ) at -45°C  $\delta$  20.1, 23.8, 37.8, 51.6, 53.9, 119.5, 119.6, 124.2, 126.6, 126.6, 126.8, 126.9, 141.4, 142.6, 147.3, 151.1; MS m/z (%) 315( $M^+$ , 100), 300( $M^+-CH_3$ , 26), 284( $M^+-OCH_3$ , 15); found  $M^+$  = 315.1615.  $C_{22}H_{21}ON$  requires  $M^+$  = 315.1622. 1,3-Dimethyl-4b-aza-7H-benz[a]indeno[c,d]azulene (16), orange granules, mp ca. 115°C(decomp.);  $^1H$ NMR ( $CDCl_3$ )  $\delta$  2.37(3H,s), 2.76(3H,s), 3.70(2H,ddd,  $J$  = 4.7, 4.7, 1.8 Hz), 4.57(1H,tdd,  $J$  = 9.9, 4.7, 0.8 Hz), 6.14(1H,td,  $J$  = 4.7, 0.8 Hz), 6.58(1H,td,  $J$  = 1.8, 9.9 Hz), 6.69(1H,s), 6.82(1H,s), 6.8-7.6(4H,m); UV ( $CH_3OH-CH_2Cl_2$ , 9:1)  $\lambda_{max}$  ( $\log \epsilon$ ) 325 nm (3.39), 359 (3.46), 375sh (3.40), 424 (3.14); MS found  $M^+$  = 283.1317.  $C_{21}H_{17}N$  requires  $M^+$  = 283.1361.

B) In diethylamine The photoreaction in diethylamine was carried out in a small photoreaction vessel (12 mL) with a pen-light under nitrogen bubbled continuously through the solution. The irradiated solution was evaporated and the

residue was treated in the same manner described in methanol to give three photoproducts. The yield is shown in Table VII. The amines (6) were identified by comparing with the authentic samples. 9-(2-Amino-4,6-dimethylphenyl)-9-diethylaminofluorene (20), oil;  $^1\text{H}$ NMR ( $\text{CDCl}_3$ )  $\delta$  0.92(6H,t,J = 7.0 Hz), 1.08(3H,s), 2.14(3H,s), 2.16(2H,m), 2.69(2H,m), 6.05(1H,s), 6.39(1H,s), 7.2-7.8(8H,m);  $^{13}\text{C}\{^1\text{H}\}$ NMR ( $\text{CDCl}_3$ )  $\delta$  16.1, 20.5, 23.5, 44.8, 79.3, 116.3, 119.5, 120.5, 123.1, 126.2, 127.1, 128.0, 136.5, 138.0, 140.9, 147.4, 149.9; MS m/z (%) 356( $\text{M}^+$ , 26), 284( $\text{M}^+ - \text{Et}_2\text{N}$ , 100), 282(43); found  $\text{M}^+$  = 356.2270.  $\text{C}_{25}\text{H}_{28}\text{N}_2$  requires  $\text{M}^+$  = 356.2253. 9-(3-Amino-2-diethylamino-4,6-dimethylphenyl)fluorene (21), colorless needles, mp ca. 235°C(decomp.);  $^1\text{H}$ NMR ( $\text{CDCl}_3$ )  $\delta$  0.95(3H,s), 1.24(6H,t,J = 7.2 Hz), 2.15(3H,s), 3.33(4H,m), 4.13(2H,brs), 5.67(1H,s), 6.55(1H,s), 7.2-7.9(8H,m);  $^{13}\text{C}\{^1\text{H}\}$ NMR ( $\text{CDCl}_3$ )  $\delta$  15.7, 17.2, 17.8, 49.5, 49.5, 119.9, 121.3, 124.1, 126.6, 127.1, 127.5, 131.0, 136.5, 137.3, 140.9, 142.8, 148.1; MS m/z (%) 356( $\text{M}^+$ , 100), 327( $\text{M}^+ - \text{Et}$ , 12), found  $\text{M}^+$  = 356.2268.  $\text{C}_{25}\text{H}_{28}\text{N}_2$  requires  $\text{M}^+$  = 356.2253.

C) In acetonitrile in the presence of TCNE A solution of 20 mg (64  $\mu\text{mol}$ ) of the azide and 26 mg (200  $\mu\text{mol}$ ) of TCNE in 160 mL of acetonitrile was irradiated. The photolyzed solution was evaporated and the residue was extracted with a small amount of chloroform. The extract was filtered through the tube packed with cotton. The two adducts, 24 and 25, were

obtained by the separation and purification in the same manner as described for methanol. The yield of the adducts shown in Table IX was determined by the integration of  $^1\text{H}$ NMR in the crude reaction mixture, based on the reacted material determined by HPLC; 1,3-dimethyl-4c,7-tetracyanoethano-4c,12b-dihydro-4b-aza-7H-benz[a]indeno[c,d]azulene (24), colorless needles, mp ca. 190°C(decomp.);  $^1\text{H}$ NMR ( $\text{CDCl}_3$ )  $\delta$  2.27(3H,s), 2.67(3H,s), 3.63(1H,dd,J = 8.5, 7.6 Hz), 4.97(1H,dd,J = 8.5, 8.5 Hz), 5.34(1H,s), 6.41(1H,s), 6.59(1H,d,J = 8.5 Hz), 6.70(1H,s), 6.86(1H,d,J = 7.6 Hz), 7.4-7.7(4H,m); MS m/z (%) 411( $\text{M}^+$ , 12), 284(36), 283( $\text{M}^+$ -TCNE, 100), 282(69), 268(25); found  $\text{M}^+$  = 411.1480.  $\text{C}_{27}\text{H}_{17}\text{N}_5$  requires  $\text{M}^+$  = 411.1483. 6,8-Dimethyl-9-(9-fluorenyl)-1,1,2,2-tetracyano-4-spiro[2,6]nona-4,6,8-triene (25), colorless granules, mp ca. 205°C(decomp.);  $^1\text{H}$ NMR ( $\text{CDCl}_3$ )  $\delta$  1.02(3H,s), 2.28(3H,s), 4.96(1H,s), 6.79(1H,brs), 7.1-7.8(8H,m), 8.21(1H,d,J = 1.8 Hz); MS m/z (%) 411( $\text{M}^+$ , 54), 347(44), 346( $\text{M}^+$ -HC(CN) $_2$ , 100), 282(35); found  $\text{M}^+$  = 411.1455.  $\text{C}_{27}\text{H}_{17}\text{N}_5$  requires  $\text{M}^+$  = 411.1483.

Time-resolved absorption spectroscopy An undegassed solution of the azide ( $4.8 \times 10^{-5}$  M) in methanol-ether (92:8) was irradiated at 25°C in a 1 x 1 x 4 cm quartz cell with a 248 nm pulse from an excimer laser with a pulse width of 12 ns and output energy of 50 mJ/cm $^2$ . In the observation of decomposition rate of the o-quinoid species (11), a steady light source was used as a monitor light.

## References and Notes

- (1) Tiemann, F. Ber. 1891, 24, 4162.
- (2) (a) Sugawara, T.; Iwamura, H. J. Am. Chem. Soc. 1980, 102, 7134. (b) Sugawara, T.; Nakashima, N.; Yoshihara, K.; Iwamura, H. Ibid. 1983, 105, 859. (c) Sugawara, T.; Iwamura, H. Ibid. 1985, 107, 1329.
- (3) Tukada, H.; Iwamura, M.; Sugawara, T.; Iwamura, H. Org. Magn. Reson. 1982, 19, 78.
- (4) It is indicated that the rates of interconversion of the rotational isomers in 9-arylfluorene systems are accelerated in basic media: (a) Ōki, M.; Saito, R. Chem. Lett. 1981, 649. (b) Saito, R.; Ōki, M. Bull. Chem. Soc. Jpn. 1982, 55, 3267. Moreover, when a solution of **2** in methanol containing sodium methoxide or in diethylamine was allowed to stand in the dark at room temperature, **2** was consumed to give the product derived from the o-quinoid imine intermediate (**11**), namely **14** or **20**. This was thought to cause another trouble. Though the initial rate of the reaction in the dark was larger than that of rotational isomerization, the reaction was confirmed still to be too slow to compete with the photoreactions carried out under our conditions. Moreover, the barrier to interconversion between the amine rotamers,  $\epsilon_{ap}$  and  $\epsilon_{sp}$ , has been obtained to be ca. 27 kcal mol<sup>-1</sup>. The conformational stability of **6** is larger than that of **2**.

(5) (a) Yager, W. A.; Wasserman, E.; Cramer, R. M. R. J. Chem. Phys. 1962, 37, 1148. (b) Smolinsky, G.; Wasserman, E.; Yager, W. A. J. Am. Chem. Soc. 1962, 84, 3220.

(6) Two parameters, D and E, which are called zero-field splitting parameters, are calculated from the following equations.

$$H_x^2 = (H_o \pm D \mp E)(H_o \mp 2E)$$

$$H_y^2 = (H_o \pm D \pm E)(H_o \pm 2E)$$

$$H_z^2 = (H_o \pm D)^2 - E^2$$

where  $H_x$ ,  $H_y$  and  $H_z$  show the corresponding transitions and  $H_o$  means the resonance field of a free electron, assuming that the anisotropy of g-value of nitrenes is negligible;  $g_x = g_y = g_z = g_e = 2.0023$ . The upper part of the double signs in the equations corresponds to the transitions in a higher field, and the lower corresponds to the transitions in a lower field. In the case of nitrenes, the all transitions in a lower field and the z transition in a higher field are not observed in general. Moreover since E is nearly zero,  $H_x$  is equal to  $H_y$  in nitrenes.

(7) (a) Wasserman, E.; Smolinsky, G.; Yager, W. A. J. Am. Chem. Soc. 1964, 86, 3166. (b) Moriarty, R. M.; Rahman, M. Ibid. 1966, 88, 842. (c) Chapman, O. L.; Sheridan, R. S.; LeRoux, J. P. Ibid. 1978, 100, 6245.

(8) In order to disclose the origin of such a slight but

significant difference of resonance fields between conformational isomers, the author carried out the calculations on the ap- and sp-rotamers of o-(9-fluorenyl)-phenylnitrene (4) with INDO-UHF. In these calculations, however, the evidence that the difference of resonance field should be due to the delocalization of p-electron at the nitrenic center over the  $\pi$ -system of the fluorene ring. In order to obtain more accurate information of the spin distributions on nitrenes 4, a calculation with more rigorous methods containing geometry optimization and electron configuration mixing would be required.

(9) It is well-known that, when irradiated at 77K, phenyl azide shows a broad absorption between 300 and 420 nm. This band is assigned to triplet phenylnitrene. Recently Schuster pointed out, however, that the absorption was likely to be due to the singlet intermediate: (a) Schrock, A. K.;

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(16) The photochemistry of aryl nitrenes in solutions has been reviewed; for example, (a) Iddon, B.; Meth-Cohn, O.;



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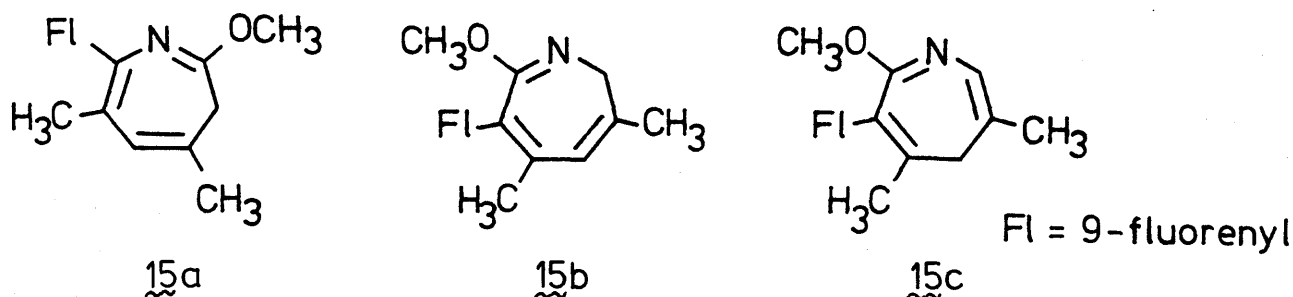
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(18) A comment on the assignment of the 3H-azepine structure  
in 15 should be added. Though three possible structures were



feasible from the  $^1\text{H}$ NMR spectrum, we chose 15a for the four following reasons. First, the 3H-azepine framework as shown in 15c is rare, although there are some precedents for this type of substitution pattern as reported by Sundberg and his co-workers for the photoproducts of o-azidobiphenyl and 2-mesityl-5-methylphenyl azide: ref 20 and 21. There is no report of the isolated 2H-azepine derivative like 15b. Secondly, at  $-50^\circ\text{C}$ , though the olefinic proton in 15 was

observed at  $\delta$  5.95 for the major conformer and  $\delta$  5.66 for the minor conformer in the  $^1\text{H}$ NMR, the signals of one methyl group and one methylene group did not separate into those due to each conformer. It indicates that the two groups are situated so nearly on the axis of rotation around the C-fluorenyl bond that the difference of chemical shifts between the rotamers can not be observable. These results seem to exclude the structure 15c. For a third, we could obtain the  $^{13}\text{C}$ NMR at  $-45^\circ\text{C}$  to identify the signals of the only major conformer, 15ap. The methylene carbon appeared at  $\delta$  37.8, which was very close to the value of the parent 2-methoxy-3H-azepine,  $\delta$  33.5: ref 22. Finally, it is empirically known that the  $^1\text{H}$  chemical shift of the 9-hydrogen of the fluorene moiety is sensitive to the substituent lying closely. In the minor conformer (15sp), the proton was observed at  $\delta$  4.78, a value shifted to higher field by 0.41 ppm compared with that of 15ap. The large high field shift indicates that in 15sp there is not such a large substituent as methyl or methoxy group near the hydrogen. This situation is similar to the case of 9-(2-methylphenyl)fluorene: ref 3 and 23. These results support the structure 15a.

(19) The value is for the process from the major to the minor isomer, calculated according to the graphical method of Jaeschke et al.: Jaeschke, A.; Muensch, H.; Schmid, H. G.; Friebolin, H.; Mannschreck, A. J. Mol. Spectrosc. 1969, 31,

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(20) Sundberg, R. J.; Brenner, M.; Suter, S. R.; Das, B. P. Tetrahedron Lett. 1970, 2715.

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(24) This decrease of the barrier height may be explained by the replacement of the ortho hydrogen by the lone pair on nitrogen atom. The author could not decide the question at the present stage, since the barriers to rotation around the C<sub>9</sub>-C<sub>Ar</sub> bond of 9-arylfluorenes with nitrogen atom at the ortho position, e.g. 2-(9-fluorenyl)pyridines, were unknown.

(25) It is the hot issue which of benzazirine and azacycloheptatetraene should be the stable isomer and reactive intermediates for amines. In this thesis, the author describes the intermediate tentatively as the benzazirine derivative.

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\* not discussed in this thesis

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