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The Photochemical Rearrangements of *N*-Acetyl Diphenylamine and *N*-Acetyl Carbazole

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The photochemical reactions of *N*-acetyl diphenylamine and *N*-acetyl carbazole in solution have been studied. *N*-Acetyl diphenylamine and *N*-acetyl carbazole undergo the photo-Fries-rearrangement by means of 2537Å irradiation. The reaction products consist of the *ortho*- and *para*-isomers, plus corresponding amines transformed through the deacetylation of the original compounds. The quantum yields in the early stages of the rearrangement were measured under various conditions by spectrophotometry. The reaction mechanism has been discussed on the basis of the relation between the rate constants of the rearrangement and the odd π electron densities obtained from simple Hückel MO calculations.

Recently, the photo-Fries-rearrangements have been extensively stidied.[1-18] There are two mechanisms which have been proposed for the photo-Fries-rearrangement. One is a molecular pathway, involving a bridged intermediate proposed by

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1) J. C. Anderson and C. B. Reese, *Proc. Chem. Soc.*, **1960**, 217.

2) J. C. Anderson and C. B. Reese, *J. Chem. Soc.*, **1963**, 1781.

3) H. Kobsa, *J. Org. Chem.* ,**27**, 2293 (1962).

4) D. Elad, *Tetrahedron Lett.*, **1963**, 873.

5) D. Elad, D. V. Rao and V. I. Stenberg, *J. Org. Chem.*, **30**, 3252 (1965).

6) W. M. Horspool and P. L. Parson, *J. Chem. Soc.*, **1965**, 5162.

7) R. A. Finnegan and A. W. Hagen, *Tetrahedron Lett.*, **1963**, 365.

8) R. A. Finnegan and J. J. Matice, *Tetrahedron*, **21**, 1015 (1965).

9) R. A. Finnegan and D. Knutson, *J. Amer. Chem. Soc.*, **89**, 1970 (1967).

10) D. Bellus, P. Hrdlovic and Z. Manasek, *J. Polym. Sci.*, *Part B*, **4**, 1 (1966).

11) D. Bellus and P. Hrdlovic, *Chem. Rev.*, **67**, 599 (1967).

12) G. M. Coppinger and E. R. Bell, *J. Phys. Chem.*, **70**, 3479 (1966).

13) H. Shizuka and I. Tanaka, This Bulletin, **41**, 2343 (1968).

14) H. Shizuka, *ibid.*, **42**, 52 (1969).

15) H. Shizuka, *ibid.*, **42**, 57 (1969).

16) H. Shizuka and I. Tanaka, *ibid.*, **42**, 909 (1969).

17) H. Shizuka, T. Morita, Y. Mori and I. Tanaka, *ibid.*, **42**, 1831 (1969).

18) M. R. Sandner, E. Hedaya and D. J. Trecker, *J. Amer. Chem. Soc.*, **90**, 7249 (1968).

Anderson and Reese[2] or a concerted, symmetry-allowed process proposed by Sander *et al.*[18] The other is a radical mechanism, as has been proposed by Kobsa,[3] by Finnegan *et al.*,[7-9] and by Shizuka *et al.*[13-17]

In the study of the photochemical reactions of acetanilide and phenyl acetate, it has been shown that, in the liquid phase, the photo-Fries-rearrangement occurs *via* the predissociation by the intersystem crossing $^3\sigma_0(\text{N-C})\leftarrow S_1(\pi\pi^*)$, forming pair radicals which recombine efficiently in a solvent cage into the original substance, *o*- and *p*-isomers.[13-15,17]

The photochemical reactions of acetanilide have been exmained in the vapor phase at 120°C and in a rigid matrix at -196°C, but no photochemical rearrangement was observed in either case.[16] Bellus *et al.* have reported that the radiolysis of phenyl esters in solution yielded the same products as those of the photo-Fries-rearrangement and involved the radical mechanism due to homolytic fission.[19]

On the other hand, the photocyclization of diphenylamine to carbazole has been reported.[20-24] Therefore, the photochemical reaction of *N*-Acetyl diphenylamine may be expected to be either a photo-Fries-rearrangement or a photocyclization.

In the case of *N*-Acetyl carbazole, it has also been predicted that its photochemical reaction may occur through the photo-Fires-rearrangement or though a photochemical isomerization such as *N*-acetyl pyrrole,[25] since *N*-acetyl carbazole has a *N*-$COCH_3$ group like acetanilide and since the nitrogen atom is present in such a five-membered ring as that of *N*-acetyl pyrrole. It has been shown that *N*-acetyl pyrrole upon 2537 Å irradiation in both the liquid and vapor phases, converts to an intermediate *via* the lowest excited singlet state and is subsequently changed to 2-acetyl pyrrole or to the ground state of the original substance; its isomerization mechanism involves a molecular pathway.[25] For these reasons, it seemed that it would be interesting to ivestigate the photochemical reactions of *N*-acetyl diphenylamine and *N*-acetyl carbazole. This paper will report on the photochemical reactions of these compounds at 2537 Å in the liquid phase, and will also include a discussion of the photo-Fries-rearrangement.

Experimental

The experimental procedure and solvents were almost the same as those previously described.[13-17] *N*-Acetyl diphenylamine and *N*-acetyl carbazole were prepared by treating the corresponding amines with acetic anhydride and were purified by repeated recrystallizations from ligroin.

A low-pressure mercury lamp with a Vycor glass filter was used as the 2537 Å radiation source, while a mercury xenon lamp with a diffraction grating was used as the 2800 Å range radiation source. Actinometry was carried out in a reaction cell (quartz) using a ferric oxalate actinometer solution.[26] The light intensity at 2537 Å and at 2800 Å were 4.9×10^{14} photon·sec^{-1}·ml^{-1} and 2.4×10^{14} photon·sec^{-1}·ml^{-1} respectively.

The mixture of the photo-products after a long irradiation at 2537 Å was condensed by an evaporator, separated by column chromatography (silica gel), and purified by repeated recrystallizations from ligroin. The components of the photoproducts were determined by thin-layer chromatography. The reaction products were identified by means of UV, IR, mp, and elementary analysis. The quantum yields in the early stages of the photochemical reaction were determined spectrophotometrically.

Results and Discussion

Reaction Products. *a) N-Acetyl Diphenylamine (N-Ace DA).* Figure 1-1 shows the sepctral change of the cyclohexane solution of *N*-Ace DA. The absorption band (246 mμ) of *N*-Ace DA decreased, and new bands with maxima at 227, 288, 320, and 381 mμ appeared as the irradiation time increased; the spectrum had two isosbestic points, at 238 and at 265 mμ.

The reaction products were separated from *N*-Ace DA by column chromatography and were crystallized after a long irradiation at 2537 Å on a highly-concentrated solution of *N*-Ace DA. It was comfirmed by thin-layer chromatography that the photoproducts comprised three compounds; 2-acetyl diphenylamine (2-Ace DA), 4-acetyl diphenylamine (4-Ace DA), and diphenylamine (DA). They were identified by means of UV, IR, mp, and elementary analysis in comparison with authentic samples. Neither *N*-acetyl carbazole (*N*-Ace CA) not any carbazole derivative was obtained from the irradiated solution. Therefore, it can be said that a photocyclization of *N*-Ace DA such as that of DA did not occur, but that the photo-Fries-rearrangement did occur. Figure 1-2 shows the absorption spectra of 2-Ace DA, 4-Ace DA,

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[19] D. Bellus, K. Schaffner, and J. Hoigne, *Helv. Chim. Acta*, **51**, 1980 (1968).

[20] C. A. Parker and W. J. Barnes, *Analyst*, **82**, 606 (1957).

[21] E. J. Bowen and J. H. Eland, *Proc. Chem. Soc.*, **1963**, 202.

[22] K. H. Grellmann, G. H. Shermann, and H. Linschitz, *J. Amer. Chem. Soc.*, **85**, 1881 (1963).

[23] H. Linschitz and K. H. Grellmann, *ibid.*, **86**, 303 (1964).

[24] H. Stegemeyer, *Naturwissenschaften*, **53**, 582 (1966).

[25] H. Shizuka, E. Okutsu, Y. Mori and I. Tanaka, *Molecular Photochem.*, **1**, 135 (1969).

[26] C. A. Parker, *Proc. Roy. Soc.* (London), **220A**, 104 (1953).

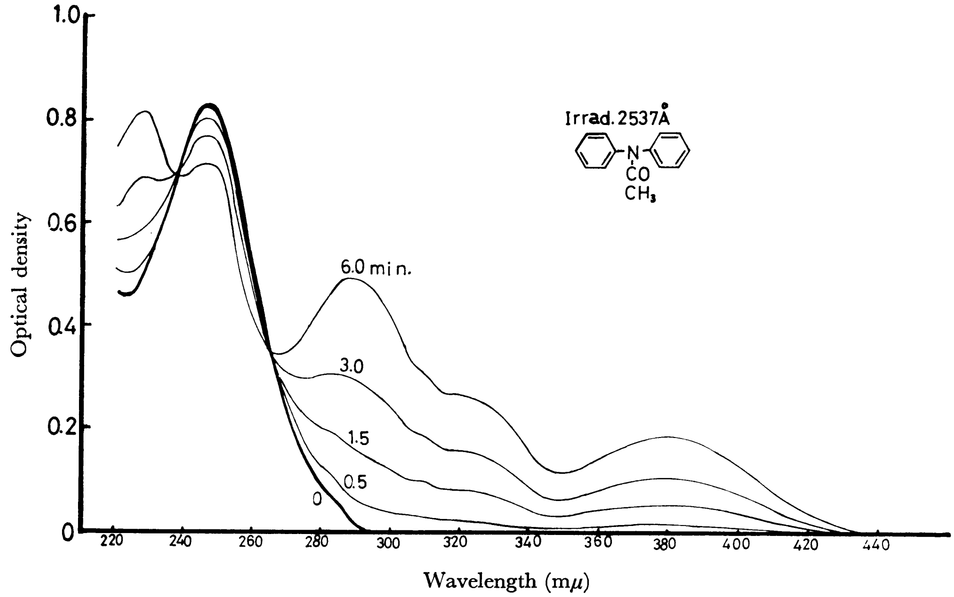

Fig. 1-1. Spectral change of cyclohexane solution of *N*-Ace DA with lapse of irradiation time at 2537 Å. Numbers refer to time in minutes.

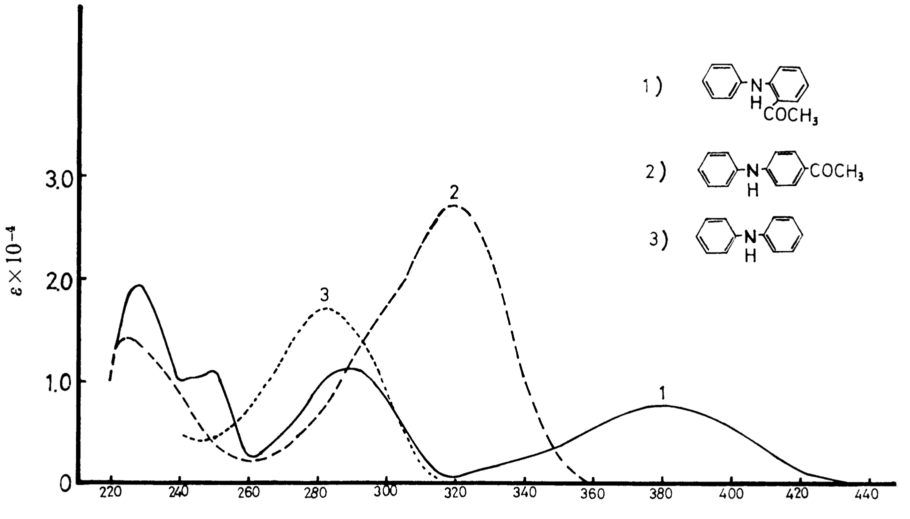

Fig. 1-2. Absorption spectra of the photo-products from *N*-Ace DA: 1) 2-Ace DA, 2) 4-Ace DA, and 3) DA.

and DA respectively in a cyclohexane solution.

b) N-Acetyl Carbazole (N-Ace CA). The spectrum of the cyclohexane solution of *N*-Ace CA changed by 2537 Å irradiation is shown in Fig. 2-1.

The reaction products of *N*-Ace CA at 2537 Å were identified by the same procedure as was used for *N*-Ace DA. The photochemical reaction of *N*-Ace CA yielded 1-acetyl carbazole (1-Ace CA), 3-acetyl carbazole (3-Ace CA), and carbazole (CA). Figure 2-2 shows the absorption spectra of these products. In view of the above facts, the photochemical rearrangement of *N*-Ace CA seems to be a photo-Fries-reaction and not to be analogous to the photochemical isomerization of *N*-acetyl pyrrole, which gives only the product (2-acetyl pyrrole).[25]

The quantum yields for the formation of these photoproducts were measured spectrophotometrically. The molar extinction coefficients of the original compounds and the photoproducts are summarized in Table 1.

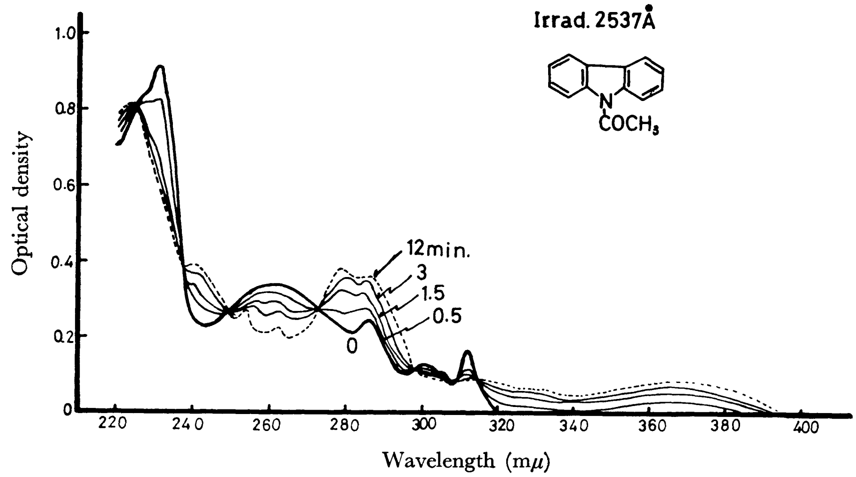

Fig. 2-1. Spectral change of cyclohexane solution of *N*-Ace DA at 2537 Å.

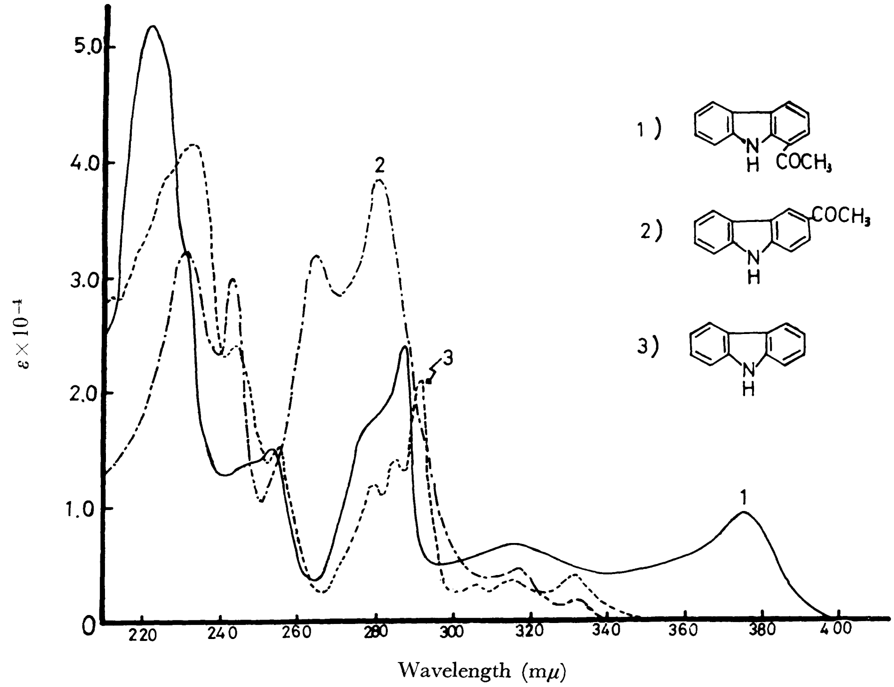

Fig. 2-2. Absorption spectra of the photo-products from *N*-Ace CA: 1) 1-Ace CA, 2) 3-Ace CA, and 3) CA.

Effect of Irradiation Time, Concentration, and Triplet Quencher on Quantum Yields. The quantum yields were measured under various condition; the results are shown in Fig. 3 and in Table 2.

The quantum yield for 2-Ace DA formation from *N*-Ace DA at 2537 Å did not change with the variation in the *N*-Ace DA concentration ($<\sim 10^{-3}$ mol/*l*), as is shown in Fig. 3. The photo-Fries-rearrangement of *N*-Ace DA is an intramolecular reaction, as has been proposed by several workers.[1,2,13,15,17] The addition of piperylene as a triplet quencher ($E_T=2.48$ eV)[13,17,27-29] did not affect the quantum yield for this isomerization in the concentration range from 10^{-4} to 5×10^{-2} mol/*l*, as is shown in Fig. 3(c). Dissolved oxygen had scarcely any effect on the quantum yields. Similar results were obtained regarding the quantum yields

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27) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

28) P. E. Eaton and W. S. Hurt, *J. Amer. Chem. Soc.*, **88**, 5038 (1966).

29) E. Y. Y. Lam, D. Valentine and G. S. Hammond, *ibid.*, **89**, 3482 (1967).

TABLE 1. MOLAR EXTINCTION COEFFICIENTS

Substance	Solvent	λ (mμ)	ε ($\times 10^{-4}$)
N-Ace DA	CH	246	1.18
	EtOH	237	1.05
2-Ace DA	CH	288	1.13
		381	0.78
	EtOH	287	1.06
		383	0.75
4-Ace DA	CH	320	2.71
	EtOH	342	2.87
DA	CH	282	1.74
	EtOH	285	2.03
N-Ace CA	CH	263	1.62
		313	0.88
	EtOH	262	1.69
		312	0.66
1-Ace CA	CH	287	2.39
		374	0.94
	EtOH	287	1.91
		372	0.84
3-Ace CA	CH	280	3.87
		332	0.19
	EtOH	286	2.98
		350	0.22
CA	CH	291	2.17
		331	0.42
	EtOH	293	1.61
		336	0.32

CH: cyclohexane EtOH: ethanol

TABLE 2. QUANTUM YIELDS FOR THE PRODUCT FORMATIONS OF *N*-Ace DA AT 2537 Å AND 20°C

Substance	Solvent	Φ_O	Φ_P	Φ_{NH}	Φ_Σ
N-Ace DA	CH	0.20	0.096	0.048	0.344
	EtOH	0.15	0.064	0.045	0.259
N-Ace CA	CH	0.10	0.09	0.06	0.25
	EtOH	0.07	0.05	0.05	0.17

Φ_O, Φ_P, and Φ_{NH} are the quantum yields for the formations of 2-Ace DA, 4-Ace DA, and DA, and those for the formations of 7-Ace CA, 3-Ace CA, and CA, respectively.

$\Phi_\Sigma = \Phi_O + \Phi_P + \Phi_{NH}$

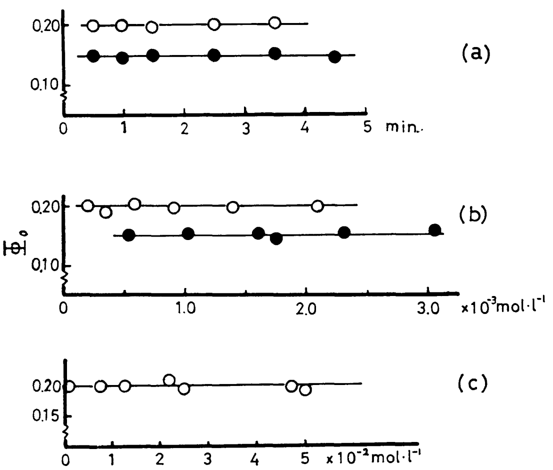


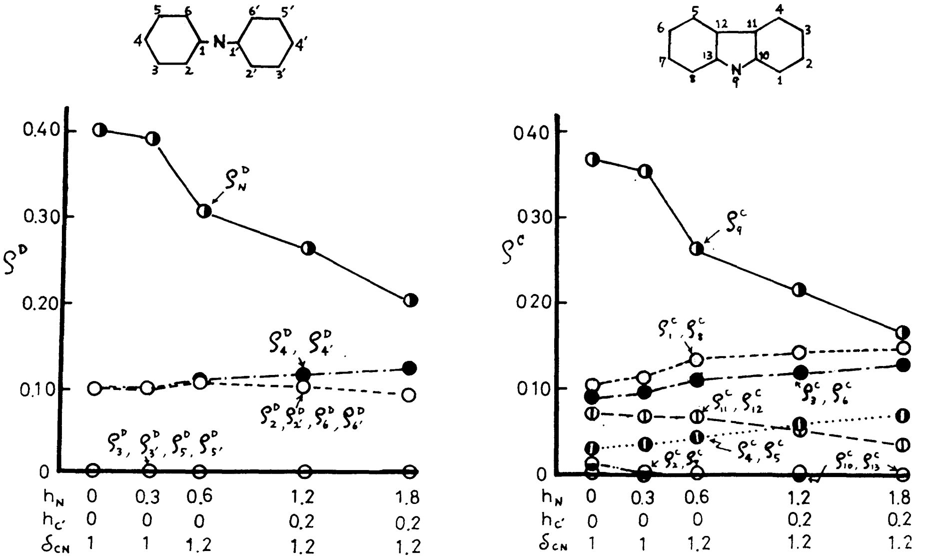
Fig. 3. Dependence of the quantum yield for the formation of 2-Ace DA at 2537 A.
(a) on irradiation time.
(b) on the concentration of *N*-Ace DA.
(c) on the concentration of piperylene as a triplet quencher.
○: in cyclohexane
●: in ethanol

for the product formations from *N*-Ace CA at 2537 Å. The quantum yields decreased in a polar solvent, as is shown in Table 2. However, the variation in the rearrangement quantum yields with the solvent was smaller than that of acetanilide.[14)] The dependences of the quantum yields of *N*-Ace DA and *N*-Ace CA on the solvent resemble those of phenyl acetate and *p*-substituted phenyl acetates.[17)] As was described in a previous paper,[17)] they may be due to the fact that *N*-Ace DA and *N*-Ace CA have no hydrogen atom to form hydrogen bonds with a proton acceptor. In the photo-Fries-rearrangement of acetanilide, a hydrogen-bond formation between the lowest excited singlet state in acetanilide and ethanol causes the decrease in the rearrangement quantum yields of acetanilide.[14)] Sandner *et al.* have reported that the quantum yield of the photo-Fries product from any given ester did not vary with the solvent.[18)] Their finding differs from ours. These differences might be caused by the experimental conditions; Sandner *et al.* performed the photochemical rearrangement of *p*-tolyl acetate in a very high concentration (0.556 mol/*l*) and with a very long irradiation (28—136 hr).

The primary process of the photo-Fries-rearrangement occurs from the lowest excited singlet state, as has been shown by Shizuka and Tanaka.[13)] In the cases of *N*-Ace DA and *N*-Ace CA, their primary processes are the same as those described before, because these is no dependence of the rearrangement quantum yields on piperylene and dissolved oxygen, which are triplet quenchers, and no effect of the excitation wavelengths from 2537 to 2800 Å on the quantum yields.

The photo-Fries-rearrangements of *N*-Ace DA and *N*-Ace CA are similar to those of acetanilide[13—15)] and phenyl acetate.[17)] It may be assumed that their reaction mechanism involves the predissociation forming pair radicals and a subsequent recombination reaction between the pair radicals in a solvent cage.

Relations between the Rearrangement Quantum Yields and the Odd π Electron Densities. The recombination reaction between the pair



(a) (b)

Fig. 4. Odd π electron densities of diphenyl amino (a) and carbazolyl (b) radicals as functions of h_N, $h_{C'}$, and δ_{CN}.
See the foot note.*2

radicals consists of a back reaction and of *o*- and *p*-rearrangements in a solvent cage. It has been shown that the rates of this recombination reaction in a solvent cage are proportional to the odd π electron densities of the anilino or phenoxy radical.[15,17]

The approximate odd π electron densities (ρ) of diphenyl amino and carbazolyl radicals were obtained from a simple Hückel MO calculation using the various values of Coulomb integrals (α) and resonance integrals (β). Figure 4 (a) and (b) show the odd π electron densities*1 of the diphenyl amino and carbazolyl radicals respectively.

The h_N parameter, which is equal to 0.6, is an appropriate value in the valency state of a nitrogen atom such as that of the pyridine molecule.[30–32] It is assumed that the valency state of the nitrogen atom in the case of the diphenyl amino or carbazolyl radical is nearly the same as that of pyridine, since the odd π electron on the nitrogen atom is considered to migrate to the benzene ring of their radicals. Therefore, we took the h_N value (0.6) in the present estimation. The relation between the quantum yields (Φ) and the odd π electron densities (ρ) is as follows:

N-Ace DA:

$$k_O^D : k_P^D = \frac{1}{4}\Phi_2^D : \frac{1}{2}\Phi_4^D \qquad (1)$$

$$= 1:0.96$$

$$\rho_2^D : \rho_4^D = 0.11037 : 0.11438 \qquad (2)$$

$$= 1 : 1.04$$

$$k_O^D : k_P^D \approx \rho_2^D : \rho_4^D \qquad (3)$$

N-Ace CA:

$$k_O^C : k_P^D = \frac{1}{2}\Phi_1^C : \frac{1}{2}\Phi_3^C \qquad (4)$$

$$= 1 : 0.9$$

$$\rho_1^C : \rho_3^C = 0.13498 : 0.11243 \qquad (5)$$

$$= 1 : 0.83$$

$$k_O^D : k_P^C \approx \rho_1^C : \rho_3^C \qquad (6)$$

where k_O and k_P are the rate constants of the *ortho*- and *para*-rearrangements respectively.

The rate constants (k) of the *o*- and *p*-rearrangements were proportional to the odd π electron densities on the radicals, as are shown in Eqs. (3) and (6). These results lend some support to the radical mechanism for the secondary processes in the photo-Fries-rearrangement as has been tentatively suggested by Kobsa[3] and has been shown by Shizuka *et al.*[15,17] On the other hand, Sandner

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*1 The odd π electron densities were obtained from the square of the coefficient of the atomic orbital in the highest-occupied molecular orbital, ϕ_7.

*2 $\alpha_N = \alpha_C + h_N\beta_{CC}$, $\alpha_{C'} = \alpha_C + h_{C'}\beta_C$, $\beta_{CCN} = \delta_{CN}\beta_{CC}$ where α_C: Carbon atom Coulomb integral, α_N: Nitrogen atom Coulomb integral. $\alpha_{C'}$: Coulomb integral of the carbon atom next to the nitrogen atom, β_{CC}: carbon-carbon resonance integral, β_{CN}: carbon-nitrogen resonance integral, h_N, $h_{C'}$, and, δ_{CN}: parameters of α_N, $\alpha_{C'}$, and, β_{CN} respectively.

30) C. A. Coulson and J. Jacobs, *J. Chem. Soc.*, **1949**, 1983.

31) S. F. Mason, *ibid.*, **1958**, 674.

32) R. D. Brown, *ibid.*, **1959**, 3451.

et al. have proposed that the photo-Fries-rearrangement originates from an upper singlet state and proceeds to the products by a molecular pathway that is independent of its reaction environment.[18)] Considering Sandner *et al.*'s formulation, which involves a concerted, symmetry-allowed process, it may be predicted that the quantum yield for the product formations in the photo-Fries-rearrangement is medium-independent and the *ortho/para* ratio is wavelength-dependent. However, the quantum yields for the product formations in the early stages of the photochemical reaction are medium-dependent[14),17)] and are also dependent on the reaction phase.[16)],[*3]

If the photo-Fries-rearrangement had occurred through a molecular pathway, the rearrangement products would be obtained in the vapor phase, since the photoisomerization of benzene[33)–38)] or *N*-acetyl pyrrole,[25)] which involves a molecular pathway, yields the corresponding isomers even in the vapor phase. On the basis of the study of the benzene photosensitization of acetanilide,[13)] the solvent effect on the rearrangement quantum yields,[14)] and the effect of the excitation wavelength on the yields,[14)] it is not reasonable that the photo-Fries-rearrangement originated from the upper excited singlet state, as has been proposed by Sandner *et al.*[18)] The results obtained in the present work are consistent with the mechanism of the photo-Fries-rearrangement proposed by Shizuka *et al.*[13)–17)]

The estimations of the dissociation and the back reaction quantum yields of *N*-Ace DA and *N*-Ace CA were carried out as is described below. It is reasonable to consider that the rate constant of the back reaction, k_B, is also proportional to the odd π electron density at the position of the nitrogen atom, because the recombination rate constants, k_O, k_P, and k_B, are parallel to the odd π electron densities, ρ_O, ρ_P, and ρ_N respectively.[15),17)]

N-Ace DA:

$$\frac{k_B^D}{k_O^D} = \frac{\Phi_B^D}{(1/4)\Phi_O^D} = \frac{\rho_N^D}{\rho_2^D} = \frac{0.30747}{0.11035} \approx 2.8 \qquad (7)$$

$$\Phi_B^D \approx 0.14$$

N-Ace CA:

$$\frac{k_B^C}{k_O^C} = \frac{\Phi_B^C}{(1/2)\Phi_O^C} = \frac{\rho_N^C}{\rho_1^C} = \frac{0.26368}{0.13498} \approx 2.0 \qquad (8)$$

$$\Phi_B^C \approx 0.10$$

The dissociation quantum yields (Φ_{dis}) are given by:

$$\Phi_{dis}^D = \Phi_\Sigma^D + \Phi_B^D \approx 0.48 \qquad (9)$$

$$\Phi_{dis}^C = \Phi_\Sigma^C + \Phi_B^C \approx 0.35 \qquad (10)$$

The recombination ratios (γ) between the pair radicals are quite high, just as in the cases of acetanilide[15)] and phenyl acetate.[17)]

$$\left.\begin{aligned} \gamma^D &= \frac{\Phi_O^D + \Phi_P^D + \Phi_B^D}{\Phi_{dis}^D} = 0.91 \\ \gamma^C &= \frac{\Phi_O^C + \Phi_P^D + \Phi_B^D}{\Phi_{dis}^C} = 0.81 \end{aligned}\right\} \qquad (11)$$

These results indicate that the recombination reaction between the pair radicals occurs efficiently in a solvent cage. From these results, it can be said that the photochemical rearrangement of *N*-Ace DA and *N*-Ace CA can be explained by a mechanism similar to those of acetanilide and phenyl acetate described in previous papers.[13)–17)]

In general, the quantum yields for the product formations in the photo-Fries-rearrangement are parallel to the odd π electron densities described above. There are some exceptions in the case of *N*-Ace CA. The values of $\rho^C{}_{11}$, $\rho^C{}_{12}$, $\rho^C{}_4$, and $\rho^C{}_5$ on the carbazolyl radical (see Fig. 4(b)) are not very small. However, no shift of the acetyl group to their positions by UV light could be observed. The non-occurrence of the shift to the positions 11 and 12 may be understood from the fact that their positions are blocked by phenyl groups. It is well known that the photo-Fries-rearrangements of *p*-substituted phenyl acetate[3),17)] and *p*-substituted acetanilide[15)] do not take place at the *p*-positions on their molecules, but at the *o*-positions. For both the 4 and 5 positions, it may be assumed that a transient complex formed in the recombination reaction between pair radicals has an unstable structure because of the lack of resonance energy compared with that of the *o*- or *p*-position. Finally, the reaction schemes of *N*-Ace DA and *N*-Ace CA at 2537 Å in the liquid phase are as follows:

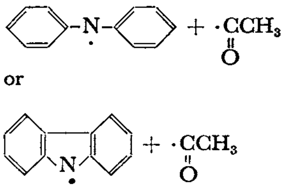
$$S_0 + h\nu \longrightarrow S_1(\pi\pi^*) \qquad (12)$$

$$S_1(\pi\pi^*) \xrightarrow{k_s} S_0 \qquad (13)$$

$$S_1(\pi\pi^*) \xrightarrow{k_f} S_0 + h\nu' \qquad (14)$$

$$S_1(\pi\pi^*) \xrightarrow{k_c} T_1(\pi\pi^*) \qquad (15)$$

$$S_1(\pi\pi^*) \xrightarrow{k_{dis}}$$



(16)

[*3] We examined the photochemical reaction of phenyl acetate in the gas phase at 2537 Å and at room temperature. The rearrangement products were not observed.

33) K. Shindo and S. Lipsky, *J. Chem. Phys.*, **45**, 2292 (1966).

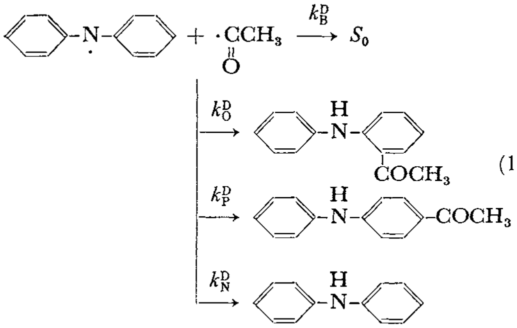
34) F. Mellows and S. Lipsky, *J. Phys. Chem.*, **70**, 4076 (1966).

35) H. R. Ward, J. S. Wishnok and P. D. Sherman, Jr., *J. Amer. Chem. Soc.*, **89**, 162 (1967).

36) L. Kaplan and K. F. Wilzback, *ibid.*, **89**, 1030 (1967).

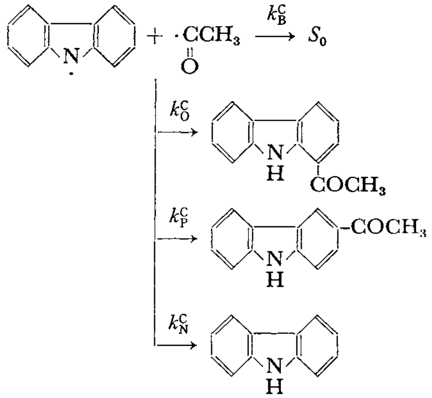
37) K. E. Wilzback, A. L. Harkness and L. Kaplan, *ibid.*, **90**, 1116 (1968).

38) See the review on *Photochemical Reactions of Benzene and its Derivative.* which was described in *Denkikagaku*, **36**, 628 (1968) by I. Tanaka and H. Shizuka.


N
CCH3
O
k_B^D
S_0
k_O^D
k_P^D
k_N^D
H
N
COCH3
-COCH3

(17)

or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-COCH3

(17′)