at 80° (0.1 mm): mp 100–102°; ir (CCl_4) 3040, 2980, 2945, 1575, 1468, 1438, 1413, 1286, 1200, and 1088 cm^{-1}; nmr ($CDCl_3$) δ 1.80 (3 H, d, J = 1.2 Hz), 4.50 (2 H, s), 5.78 (1 H, q, J = 1.2 Hz), and 7.2–7.6 ppm (4 H, m); mass spectrum *m/e* (rel intensity) 194 (34), 162 (12), 161 (100), 153 (18), 135 (59), 134 (15), 121 (11), 90 (15), 77 (12), 59 (12), and 45 (12).

Anal. Calcd for $C_{10}H_{10}S_2$: C, 61.81; H, 5.19; S, 33.01. Found: C, 61.75; H, 5.13; S, 33.18.

To a solution of 97 mg (5.0 mmol) of the above olefin in 50 ml of ethanol was added 388 mg of palladium-on-carbon catalyst (Matheson). The flask was equipped with a magnetic stirrer and placed under 1 atm of hydrogen. After 12 hr, 300 mg of catalyst was added, and the material was hydrogenated for an additional 12 hr. The catalyst was removed by filtration with the aid of Celite and washed with hot methanol, and the solvent was removed under reduced pressure. The residue contained starting olefin and **29** (13% yield) that was collected from glpc (LAC-446): ir (CCl_4) 3060, 2962, 2905, 1470, 1440, 1410, 1372, 1238, 1152, and 1000 cm^{-1}; nmr ($CDCl_3$) δ 1.29 (3 H, d, J = 7 Hz), 2.36–3.40 (3 H, m), 3.74 (1 H, d, J = 15 Hz), 4.18 (1 H, d, J = 15 Hz), and 7.0–7.7 ppm (4 H, m); mass spectrum *m/e* (rel intensity) 196 (100), 155 (19), 154 (64), 153 (72), 150 (25), 136 (24), 135 (57), 121 (22), 91 (15), 78 (10), 77 (22), 45 (14), 44 (12), 40 (13), and 39 (13).

Anal. Calcd for $C_{10}H_{12}S_2$: C, 61.18; H, 6.16; S, 32.66. Found: C, 61.27; H, 6.22; S, 32.86.

2,3-Benzo-1,5-dithiaspiro[5.5]undecane (31).—Mercaptole **31** was prepared in 74% yield from 9.2 g (0.104 mol) of cyclohexanone and 15.6 g (0.10 mol) of *o*-α-toluenedithiol by the same procedure described for the preparation of **7**: bp 120–124° (0.07 mm); ir (CCl_4) 3065, 2940, 2860, 1570, 1470, 1450, 1272, 1120, and 1012 cm^{-1}; uv (cyclohexane) 231 nm (ϵ 6000), 263 (469); nmr ($CDCl_3$) δ 1.4–2.0 (10 H, m), 3.71 (2 H, s), and 6.95–7.4 ppm (4 H, m); mass spectrum *m/e* (rel intensity) 237 (15), 236 (100), 203 (57), 193 (21), 154 (10), 153 (26), 147 (15), 123 (84), 121 (26), 81 (12), 78 (10), and 45 (10).

Anal. Calcd for $C_{13}H_{16}S_2$: C, 66.05; H, 6.82; S, 27.13. Found: C, 65.91; H, 6.89; S, 26.98.

cis-**2,3-Benzo-1,5-dithiabicyclo[5.4.0]undecane (32).**—The identification of **32** is based slowly on spectral data: ir (CCl_4) 3050, 2910, 2840, 1470, 1443, 1408, 1268, and 1005 cm^{-1}; mass spectrum *m/e* (rel intensity) 226 (30), 203 (10), 155 (17), 154 (70), 153 (100), 124 (12), 123 (19), 122 (11), 121 (17), 109 (10), 81 (17), 77 (22), 45 (12), 41 (12), 40 (13), and 39 (19).

2,3-Benzo-1,4-dithiaspiro[4.5]decane (33).—Mercaptole **33** was prepared in 55% yield from 2.60 g (26 mmol) of cyclohexanone and 3.55 g (25 mmol) of 1,2-benzenedithiol by the procedure described for the preparation of **7**: bp 120–123° (0.25 mm); ir (CCl_4) 3040, 2910, 2840, 1440, 1254, 1112, 1005, and 975 cm^{-1}; uv max (cyclohexane) 238 nm (ϵ 12,100), 273 (3070), 292 (2220), 302 (2100), and 312 (1600); nmr (CCl_4) δ 1.3–1.9 (6 H, m), 2.1–2.4 (4 H, m) and 7.05 ppm (4 H, m); mass spectrum *m/e* (rel intensity) 222 (45), 179 (100), 166 (17), 153 (8), 81 (8), and 77 (7).

Anal. Calcd for $C_{12}H_{14}S_2$: C, 64.81; H, 6.35; S, 28.84. Found: C, 65.03; H, 6.42; S, 29.08.

cis-**3,4-Benzo-2,5-dithiabicyclo[4.4.0]decane (34).**—To a solution of 416 mg (2.81 mmol) of *cis*-1,2-cyclohexanedithiol[3] in 50 ml of ethanol was added 393 mg (2.75 mmol) of cuprous oxide. The mixture was heated under reflux for 40 hr, cooled, and filtered. The red cuprous salt was dried and dissolved in 25 ml of quinoline containing 5 ml of pyridine. *o*-Dibromobenzene (589 mg, 2.5 mmol) was added and the mixture was heated under reflux for 12 hr. The solution was cooled and poured into a stirred mixture of ice and hydrochloric acid. The mixture was stirred 2 hr and extracted with ether. The ether extracts were washed with 3 *N* HCl, 10% $NaHCO_3$, and water and dried ($MgSO_4$). After removal of the solvent, the product (14% yield) was collected by glpc: ir (CCl_4) 3060, 2940, 2860, and 1460 cm^{-1}; nmr (CCl_4) δ 1.4–2.2 (8 H, m), 3.3–3.7 (2 H, m), and 6.9–7.1 ppm (4 H, m); mass spectrum *m/e* (rel intensity) 222 (100), 179 (27), 153 (23), 142 (35), 140 (80), 96 (19), 81 (59), 80 (20), 79 (10), 77 (12), 41 (13), and 39 (12).

Anal. Calcd for $C_{12}H_{14}S_2$: C, 64.82; H, 6.35. Found: C, 65.29; H, 6.49.

Registry No.—**3,** 4479-55-4; **5,** 4410-13-3; **7,** 14198-71-1; **8,** 31443-07-9; **9,** 31443-08-0; **12,** 7133-39-3; **14,** 31443-10-4; **15,** 31443-11-5; **19,** 7216-19-5; **23,** 14198-73-3; **24,** 31443-14-8; **28,** 6247-53-6; **29,** 31443-21-7; **30,** 31442-16-0; **31,** 31443-17-1; **32,** 31443-18-2; **33,** 7127-65-3; **34,** 31443-19-3; 3-butene-1,2-dithiol trithiocarbonate, 31443-20-6.

Photocyclization of Acrylanilides[1]

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Ultraviolet irradiation of acrylanilides (I) has been found to afford a cyclization product, 3,4-dihydrocarbostyrils (II); *e.g.*, methacrylanilide (Ib) in *n*-hexane gives IIb in a quantum yield of 0.26 and *N*-methylmethacrylanilide (Id) gives IId in a quantum yield of 0.24. The sensitizing and quenching studies suggest that the reaction occurs *via* an excited singlet state and that the formation of an enol precursor IV is less favorable. Their quantum yields tend to decrease with increasing solvent polarity, which is attributable to an increase of the efficiency of intersystem crossing with increasing the polarity of solvent.

It is known that the photolysis of *N*-phenylacylamides undergoes acyl migration to *o*- and *p*-acylanilines,[2–4] but that acrylanilides with an α,β-unsaturated acyl group photocyclize[5] without rearrangement except in the case of benzanilides which give both rearranged and cyclized products.[6]

Ultraviolet irradiation of *N*-allylanilines affords mainly anilines together with small amounts of ortho and para rearranged products.[7] However, *N*-allylaniline gives a cyclized product, *i.e.*, quinoline, in the presence of oxidizing agents such as $FeCl_3 \cdot 6H_2O$. Similarly, photolysis of aryl acrylates gives *o*- and *p*-acrylphenols without cyclization to lactones.[8]

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[1] Contribution No. 168.

[2] (a) For the review of the photo-Fries rearrangement see D. Bellus and P. Hrdlovic, *Chem. Rev.*, **67**, 599 (1967); (b) J. C. Anderson and C. B. Reese, *J. Chem. Soc.*, 1781 (1963); (c) H. Kobsa, *J. Org. Chem.*, **27**, 2293 (1962); (d) R. A. Finnegan and A. W. Hagen, *Tetrahedron Lett.*, 365 (1963); (e) Y. Ogata, K. Takagi, and I. Ishino, *Tetrahedron*, **26**, 2703 (1970).

[3] (a) H. Shizuka, *Bull. Chem. Soc. Jap.*, **42**, 52, 57, 909 (1969); (b) H. Shizuka and I. Tanaka, *ibid.*, **41**, 2343 (1968).

[4] (a) D. Elad, D. V. Rao, and V. I. Stenberg, *J. Org. Chem.*, **30**, 3252 (1965); (b) D. V. Rao and V. Lamberti, *ibid.*, **32**, 2896 (1967); (c) J. S. Bradshaw, R. D. Knudsen, and E. L. Loveridge, *ibid.*, **35**, 1219 (1970).

[5] (a) P. G. Cleveland and O. L. Chapman, *Chem. Commun.*, 1064 (1967); (b) O. L. Chapman and W. R. Adams, *J. Amer. Chem. Soc.*, **89**, 4243 (1967); (c) O. L. Chapman and W. R. Adams, *ibid.*, **90**, 2333 (1968).

[6] B. S. Thyagarajan, N. Kharash, H. B. Lewis, and W. Wolf, *Chem. Commun.*, 614 (1967).

[7] Y. Ogata and K. Takagi, *J. Org. Chem.*, **35**, 1642 (1970).

[8] (a) H. Obara and H. Takahashi, *Bull. Chem. Soc., Jap.*, **40**, 1012 (1966); (b) H. Obara, H. Takahashi, and H. Hirano, *ibid.*, **42**, 560 (1969); (c) H. Obara, H. Takahashi, and J. Onodera, *Kogyo Kagaku Zasshi*, **72**, 309 (1969).

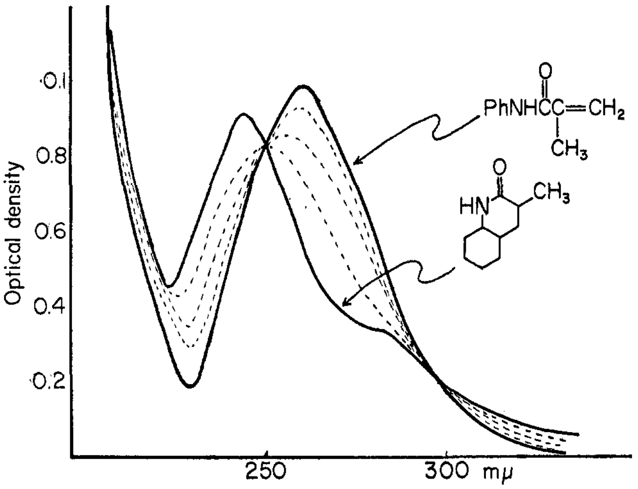


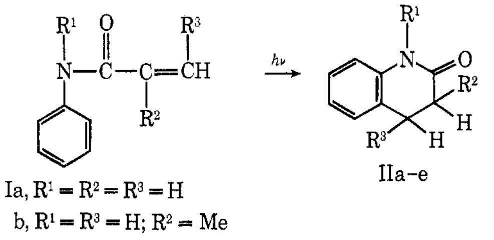
Figure 1.—Spectral changes of methacrylanilide in ethyl ether with lapse of the time on irradiation with 2537-Å light (at room temperature).

N-Allyl- and *N*-benzylanilines are easily oxidized to the corresponding conjugated imines, *i.e.*, *N*-allylideneaniline and *N*-benzylideneaniline, respectively;[9] hence the photocyclization of *N*-allylaniline to quinoline by $FeCl_3$ may proceed through oxidation to *N*-allylideneaniline. Also an α,β-unsaturated aromatic imine such as *N*-cinnamylideneaniline was observed to undergo cyclization.[10] These facts suggest for the photocyclization of acrylanilides a pathway involving α,β-unsaturated aromatic imines.

The present paper proposes a mechanism for the photocyclization of some acrylanilides and presents a discussion on the solvent effect and the nature of the excited state.

Results and Discussion

Uv irradiation of acrylanilide (Ia) in benzene (10^{-2} *M*) afforded 3,4-dihydrocarbostyril (IIa, 4.0%) together with a small amount of aniline and some other products. The identification of products was done by their melting points, ir, uv, and glc in comparison with the authentic samples.



IIa-e

Ia, $R^1 = R^2 = R^3 = H$
b, $R^1 = R^3 = H$; $R^2 = Me$
c, $R^1 = R^2 = H$; $R^3 = Ph$
d, $R^1 = R^2 = Me$; $R^3 = H$
e, $R^1 = Me$, $R^2 = R^3 = H$

The spectrum of the solution of methacrylanilide changed markedly on irradiation with 2537-Å light as shown in Figure 1. The absorption maximum at 260 mμ of Ib decreased and a new band with a maximum at 240 mμ of IIb appeared with two isosbestic points at 250 and 297 mμ as the reaction proceeded.

Photolysis of *N*-methylmethacrylanilide (Id) in benzene (2×10^{-2} *M*) gave *N*-methyl-3-methyl-3,4-dihydrocarbostyril (IId, 57.0%) and a small amount of *N*-methylaniline. Its identity was established as follows. The nmr spectrum of the product (IId) showed aromatic protons (τ 3.0, m, 4 H), NCH_3 (τ 6.75, s, 3 H), methyl and methine protons (τ 7.3, m, 3 H), and CCH_3 (τ 8.56, d, 3 H). The characteristic carbonyl absorption of lactam (liquid film) was observed at 1660 cm^{-1}.

No photorearrangement of Ia–e to *o*- and *p*-acrylanilides was observed. Furthermore, cinnamylanilide (Ic) and *N*-methylacrylanilide (Ie) undergo neither cyclization nor rearrangement, but polymerization alone.

Solvent Effect.—The photocyclization is much affected by the nature of solvents used. Table I lists the yields of photoproducts of methacrylanilide (Ib) and *N*-methylmethacrylanilide (Id) in acetonitrile, methanol, 2-propanol, acetone, *n*-propyl bromide, diethyl ether, benzene, and *n*-hexane as solvents. Apparently, the ratio of products depends on the nature of the solvent polarity.

Table I

Photolysis of Methacrylanilide in Various Solvents[a]

Solvent	Dielectric constant	Viscosity, cP (25°)	Recovered,[b] %	Product, %	Quantum yield
CH_3CN	37.5	0.33	89.4	None	
CH_3OH	32.6	0.55	96.6	None	<0.01
$(CH_3)_2C{=}O$	20.7	0.30	80.6	None	
i-PrOH	18.3	1.76	96.0	None	
n-PrBr	8.1	0.46	60.1	22.3	
EtOEt	4.34	0.24	55.5	24.3	0.23
C_6H_6	2.28	0.65	53.4	33.0	
n-C_6H_{14}[c]	1.09	0.29	17.7	63.5	0.26

[a] Concentration of 4.0×10^{-2} *M* except for the case of *n*-hexane. [b] Irradiation time 8 hr with a 300-W light high-pressure Hg lamp in a Pyrex tube. [c] Concentration of 9.0×10^{-5} *M* with irradiation time 5 min.

The quantum yield for the formation of IIb did not increase even in acetone, which is known as an efficient triplet sensitizer. This result suggests that the reaction does not proceed *via* an excited triplet state. The effect is ascribed to an increase of the rate of intersystem crossing by increasing the spin orbital coupling in polar solvents, because the quantum yields do not correlate with any other factors such as viscosity, hydrogen-bonding ability, etc.

Reaction Multiplicity.—For the clarification of multiplicity in the cyclization the following quenching and sensitizing experiments were carried out.

A plot of the ratio of the quantum yields of Ib in the absence and presence of quencher (1,3-pentadiene) (Φ_0/Φ) against the quencher concentration shows the independence of Φ_0/Φ on the quencher concentration, which means the lack of quenching (Figure 2). No sensitization by acetophenone (E_T = 73.6 kcal/mol) and benzophenone (E_T = 68.5 kcal/mol) was observed under conditions in which over 99% of incident light of wavelength longer than 330 mμ was absorbed. Although the phosphorescence of benzophenone was not quenched by Ib and Id, those of acetophenone and acetone were efficiently quenched by Ib and Id; hence

[9] Y. Ogata, A. Kawashaki, and S. Suyama, *J. Chem. Soc. B*, 805 (1969).
[10] Y. Ogata, and K. Takagi, *Tetrahedron*, **27**, 1573 (1971).

the energy transfer from the latter sensitizer to substrates (Ib and Id) is probable (Table II). Therefore, the cyclization occurs *via* an excited singlet state, but not *via* an excited triplet state. Additionally, the sensitization study indicates that the triplet energy of Ib and Id is between 68.5 and 74 kcal/mol.

TABLE II

QUENCHING OF SENSITIZER PHOSPHORESCENCE BY ANILIDES

Sensitizer	E_T, kcal/mol	Anilides (M)	I_{rel}[c]
Benzophenone,	68.5	None	1.00
1.0×10^{-3} M,		MAA (1×10^{-4})[a]	1.08
λ_{max} 442 mμ		NMAA (1×10^{-4})[b]	1.05
Acetophenone,	76.3	None	1.00
1.0×10^{-2} M,		MAA (1×10^{-3})	0.28
λ_{max} 414 mμ		NMAA (1×10^{-3})	0.35
Acetone,	78	None	1.00
0.2 M,		MAA (1×10^{-2})	0.29
λ_{max} 440 mμ		NMAA (1×10^{-2})	0.30

[a] MAA, methacrylanilide. [b] NMAA, *N*-methylmethacrylanilide. [c] I_{rel} is the relative intensity of the phosphorescence maximum. Excitation wavelength is 280 mμ for acetone, 350 mμ for acetophenone, and 360 mμ for benzophenone.

Emission Spectra.—Excited states of anilides were examined by means of their fluorescence emission spectra in various solvents as listed in Table III. The emission maxima shift bathochromically in polar solvents. This fact indicates that the lowest excited singlet state is π–π*, as observed with other anilides.[3] Therefore, the fluorescence may be due to the emission in falling from S_1 (π–π*) to S_0.

TABLE III

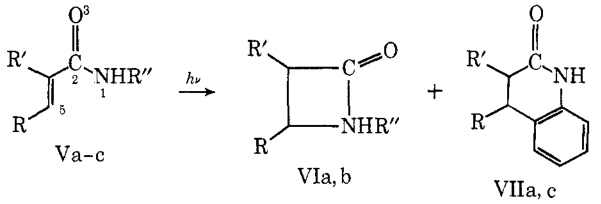
FLUORESCENCE SPECTRA OF METHACRYLANILIDE AT 290 mμ

	Fluorescence (at room temperature)	
Solvent	λ_{max}	I_{rel}[a]
n-Hexane	318	0.1
Ethyl ether	320	1.0
Methanol	328	2.4

[a] I_{rel} is the relative intensity of the fluorescence maximum. The concentration was adjusted so that the optical density at 290 mμ is 0.400.

Our attempt to examine phosphorescence emission in various rigid glasses at 77°K failed. However, the lowest triplet electronic state may also be π–π* in view of the less efficient photoreduction of anilides by isopropyl alcohol and the π–π* character of the lowest triplet state reported with acetanilide.[3]

Reaction Pathways.—α,β-Unsaturated amides were reported to be photocyclized to the corresponding β-lactams and/or the corresponding dihydrocarbostyrils.[5]



Va-c VIa,b VIIa,c

a, R = R′ = R″ = Ph

b, R = R′ = Ph; R″ = H

c, R = R′ = Me; R″ = Ph

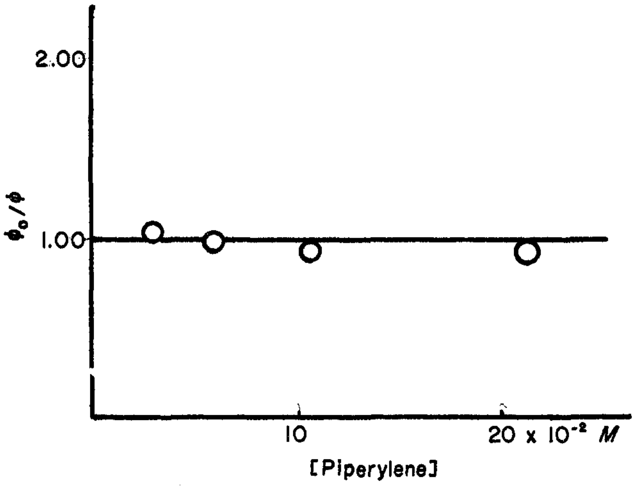
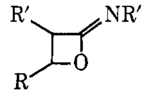


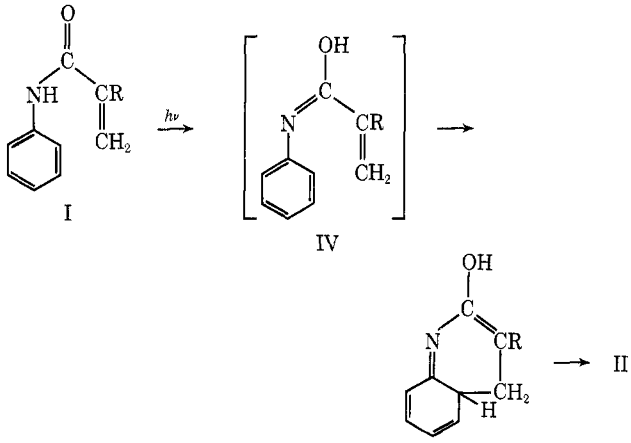
Figure 2.—Stern–Volmer plot of the quenching of methacrylanilide by piperylene in ether at room temperature.

The β-lactam formation from Va and Vb was predicted by means of HMO calculations,[5] but the predicted formation of iminolactone VIII from Vb was incorrect. Hence bonding between 1 and 5 atoms is preferred to that between 3 and 5 atoms. The 1,5 bonding may occur by way of enolization as shown in Scheme I (one-electron transfer of a nonbonding electron on N to the excited carbonyl oxygen atom[11-13] followed by proton migration). Moreover, our HMO calculations indicate that 1,5 bonding of the enol intermediate of the amide (Vb) is more favorable than the 1,3 bonding on excitation; *i.e.*, the 1,5 bond order is equal to +0.06370 and the 1,3 bond order to +0.03876 on excitation (Scheme I).



VIII

SCHEME I



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(11) (a) S. G. Cohen and J. B. Guttenplan, *J. Amer. Chem. Soc.*, **89**, 164 (1967); (b) S. G. Cohen and H. M. Chao, *ibid.*, **90**, 165 (1968); (c) S. G. Cohen and J. B. Guttenplan, *Tetrahedron Lett.*, 5353 (1968); (d) S. G. Cohen, M. D. Daltzman, and J. B. Guttenplan, *ibid.*, 4321 (1969); (e) S. G. Cohen and G. I. Cohen, *J. Phys. Chem.*, **72**, 3782 (1968).

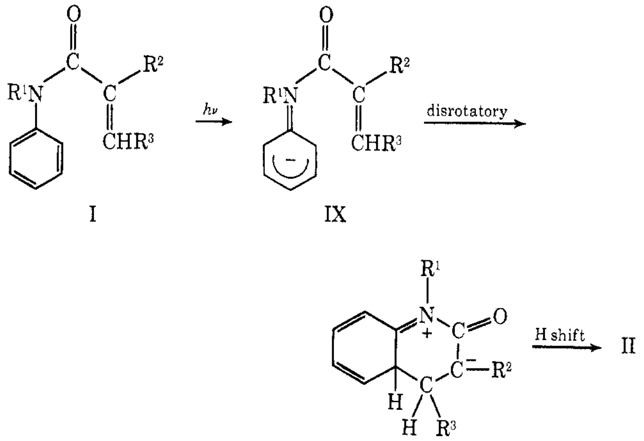
(12) A. Padwa, W. Eisenhardt, R. Gruber, and D. Pashayan, *J. Amer. Chem. Soc.*, **91**, 1857 (1969).

(13) P. J. Wagner and A. E. Kempanen, *ibid.*, **91**, 3085 (1969).

However, this scheme is unlikely, because (i) two isosbestic points at 250 and 297 mμ in Figure 1 indicate that the I → II photoconversion is void of a competitive or consecutive reaction; (ii) the *N*-methyl compound (Id, without N–H bond) cyclizes in high yield (Table I); and (iii) the esr signal of biradical could not be detected.

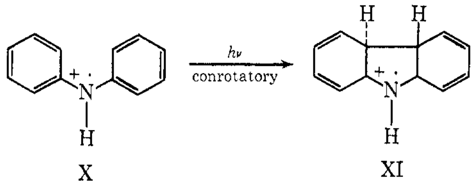
An alternative mechanism is presented in Scheme II, which involves formation of a charge-transfer intermediate (IX) indicated by the 250-mμ light absorption of the anilino ring followed by the seven-π-electrocyclic reaction in a disrotatory motion.

SCHEME II



This electrocyclization fits the Woodward–Hoffmann rule,[14] because most concerted reactions occur by way of a singlet state. Cyclization of a system of odd electrons ($n - 1$) of which IX is an example follows the rules for a system of even electrons (n) which has one more electron, if the highest occupied molecular orbitals are operative.

Thus, a five-π-electron system such as the radical cation of diphenylamine (X) cyclizes in a conrotatory motion to a hydrocarbazol species (probably trans ion XI) as a result of symmetry-allowed excited-state process.[15]



Experimental Section

Ir spectra were measured by the method of liquid film (or KBr disk) with a Perkin-Elmer ir spectrophotometer, Model 337; uv spectra were measured by a Hitachi double-beam spectrophotometer, Model 124; nmr spectra were measured by a Japan Electron Optic Laboratory Co. C60 HL high resolution nmr instrument. Quantitative analysis of photolysates was done by a Yanagimoto gas chromatograph with a flame ionization detector, Model GCG-550F, employing a 1.0 m × 2.5 mm column packed with PEG 20 M (5.0 wt %) on Chamelite CS of 80–100 mesh using N_2 as a carrier gas at 120–240°.

Materials.—Anilides[16] were prepared by the condensation of anilines and acyl halides in yields of 40–60%: acrylanilide (Ia),[16] mp 104° (lit.[16] 104–105°); methacrylanilide (Ib),[16] mp 86° (lit.[16] 87°), λ_{max}^{ether} 260 mμ (log ε 3.95); cinnamic anilide (Ic),[16] mp 154–156°, λ_{max}^{MeOH} 293 mμ; *N*-methylacrylanilide (Ie),[16] mp 74–75° (lit.[16] 75°), λ_{max}^{ether} 245 mμ; *N*-methylmethacrylanilide (Id),[16] mp 57° (lit.[16] 57°), λ_{max}^{ether} 242 mμ (log ε 3.85). Authentic 3,4-dihydrocarbostyril (IIa)[17] was prepared by $AlCl_3$-catalyzed intramolecular alkylation of β-chloropropionylanilide at 130–140° (45%), mp 165–166° (lit.[17] 165–166°), λ_{max}^{MeOH} 250 mμ (log ε 4.07).

Commercial *n*-hexane was purified by rectification after treatment with H_2SO_4, NaOH, and Na, bp 34.0–34.5°. Ethyl alcohol was rectified by treatment with concentrated H_2SO_4 and KOH, $AgNO_3$, and a silica gel column.

Light Source.—The irradiation was carried out using a Halos 300-W high pressure Hg lamp, which emits 3650–3663-Å light, and a Halos low-pressure Hg lamp emitting exclusively 2537-Å light.

Irradiation Procedure.—All experiments were carried out in a cylindrical quartz tube (20 × 150 and 10 × 200 mm) or a Pyrex tube (10 × 200 mm) under N_2 atmosphere except for preparative experiments.

Photolysis of Ia.—A solution of benzene (1 l.) containing Ia (2.0 g) was irradiated with a high-pressure Hg lamp for 150 hr at room temperature. Nitrogen was bubbled through the solution during the irradiation. The concentrated reaction mixture was chromatographed on a 20 × 450 mm column slurry packed in benzene with 100-mesh silica gel (Mallinckrodt), using benzene (500 cc) and then benzene–3% acetone (500 cc) as eluents. Fractions 30–40 (each 7 ml) were IIa (35 mg, 4%): mp 164–166°; λ_{max}^{MeOH} 250 mμ; ν_{max} 3170 (NH), 1680 (amide I, C═O), 1280, 1250 (amide III, CN), 2850, 2925 ($-CH_2-$), 3030, 1600, 1500 (aromatics), 1700–2000, 750 (ortho substitution); nmr spectrum showed aromatic protons (τ 3.0, m, 4 H), methylene protons (τ 7.3, A_2B_2 type, m, 4 H), NH (τ 0.4, 1 H). Fractions 56–70 were Ia (1.35 g), λ_{max}^{MeOH} 270 mμ, mp 104°.

Photolysis of Ib.—A solution of benzene (1 l.) containing Ib (1.80 g) was irradiated under N_2 with a high-pressure Hg lamp for 80 hr at room temperature. After irradiation, the solution was worked up as above. The concentrated reaction mixture was chromatographed on a 20 × 450 mm column slurry packed in benzene with 100 mesh silica gel (Mallinckrodt), using benzene (800 ml) as an eluent. Fractions 56–70 (each 7 ml) were IIb (1.09 g, 60.8%): mp 129–130°; λ_{max}^{MeOH} 250 mμ (log ε 3.93); ν_{max} 3175, 3070 (NH, cyclic lactam), 1680 (amide I, C═O), 1285 (amide III, CN), 3030, 1600, 1500 (aromatics), 1700–2000, 760 (monosubstitution), 2850, 2925 ($-CH_2-$, CH_3).

Photolysis of Id.—A solution of benzene (1 l.) containing Id (2.8 g) was irradiated under N_2 with a high-pressure Hg lamp for 80 hr at room temperature. After concentration by evaporation, the product mixture was chromatographed on a 20 × 450 mm column slurry packed in benzene with 100 mesh silica gel (Mallinckrodt), using benzene (800 cc) as an eluent. Fractions 43–68 (each 7 ml) were IId as a liquid (1.59 g, 57.0%): red-brown liquid; λ_{max}^{MeOH} 250 mμ (log ε 4.04); ν_{max} 1660 (amide I, C═O), 1230, 1305, 1115 (amide III, CN), 3050 (RCH, CH_2), 3020, 1580, 1450 (aromatics), 1700–2000, 765 (ortho substitution); nmr spectrum showed aromatic protons (τ 3.0, m, 4 H), NCH_3 (τ 6.75, s, 3 H), methylene and methine protons (τ 7.3, m, 3 H), CCH_3 (τ 8.56, d, 3 H). Fractions 77–100 were starting material (0.82 g).

Determination of Quantum Yield for Formation of 3,4-Dihydrocarbostyrils.—The quantum yields were determined by means of a liquid-phase chemical actinometer using potassium ferrioxalate at 15°. A low-pressure Hg lamp without filter was used as a light source, and produced 3,4-dihydrocarbostyrils were determined by uv spectrophotometry. A general procedure was as follows. A solution of 0.1–0.2 m*M* Ib in *n*-hexane was placed in a square quartz cell (path length 1 cm), degassed by four freeze–thaw cycles on a vacuum line, and sealed. A solution of 6.0 m*M* potassium ferrioxalate in 0.1 *N* H_2SO_4 was placed in an actinometer cell (path length 1 cm). Irradiation was continued for 5 min. The number of molecules of produced IIb in a cell was determined spectrophotometrically. The conversion of anilides (I) is less than 10% in all runs. The light intensity absorbed by the reactant was determined by the procedure reported by Parker and Hatchard.[18] The quantum yield was calculated from these data.

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Quenching Studies.—A solution (each 8 ml) containing a given concentration (4.0×10^{-2} *M*) of anilides and varying concentrations of 1,3-pentadiene was placed in a 10 × 150 mm Pyrex tube, degassed by four freeze–thaw cycles on vacuum line, and sealed. The tubes were irradiated by a Halos 300-W high-pressure Hg lamp on a rotating turntable apparatus immersed in a running water bath at 15°. The products were analyzed by glc.

Sensitizing Studies.—The irradiation was carried out for 50 hr at a 2:1 molar ratio of sensitizers to anilides. A Halos 300-W high-pressure Hg lamp with Toshiba UV-35 filter, which cut off light shorter than 3300 Å, was used as a light source.

Fluorescence and Phosphorescence Emission Studies.—The fluorescence spectra were measured on a Hitachi MPF-2A fluorescence spectrophotometer and the phosphorescence spectra were measured on the same apparatus with phosphorescence attachments. All phosphorescence spectra were recorded using EPA (ethyl ether–isopentane–ethanol, 5:5:2 volume ratio) as solvent. The solvent was checked for emission at each time when a spectrum was recorded. No interference due to emission of solvent was observed. The solutions contain *ca.* 10^{-3}–10^{-1} *M* solute and they formed clear glasses without microcrystals at 77°K.

Registry No.—Ia, 2210-24-4; Ib, 1611-83-2; Id, 15796-89-1; IIa, 553-03-7; IIb, 31883-79-1; IId, 31883-80-4; benzophenone, 119-61-9; acetophenone, 98-86-2; acetone, 67-64-1; *n*-hexane, 110-54-3; ethyl ether, 60-29-7; methanol, 67-56-1.

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Cycloaddition of Benzyne to Substituted Cyclopentadienes and Cyclopentadienyl Grignard Reagents

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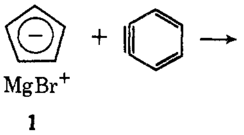
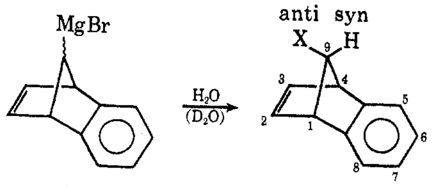
Benzyne was generated from 2-bromofluorobenzene and magnesium in tetrahydrofuran and added to isomeric mixtures of methylcyclopentadienes, 1,3-, 1,4-, and 2,5-dimethylcyclopentadienes, trimethylsilylcyclopentadienes, and *tert*-butylcyclopentadienes to give mixtures of substituted benzonorbornadienes whose isomeric distributions resembled those of the starting cyclopentadienes. Benzyne also was added to the corresponding cyclopentadienylmagnesium chlorides to give mixtures in which a 2-substituted benzonorbornadiene was always the major component. The intermediacy of 9-benzonorbornadienylmagnesium chlorides was demonstrated by stereospecific incorporation of one atom of D into the benzonorbornadienes by deuterolysis. The Grignard reactions may be described as $\pi^2s + \pi^4s$ cycloadditions, and their orientational selectivities are best explained by steric requirements in the transition state for cycloaddition.

The instability of benzyne makes it one of the most reactive dienophiles known in [2 + 4] cycloaddition and also makes it highly susceptible to nucleophilic addition, the ene reaction, insertion in carbon–hydrogen bonds, and other cycloadditions.[1] Additions of benzyne to cyclopentadiene and to cyclopentadienylmagnesium bromide (**1**) were first reported by Wittig and Knauss[2] to produce benzonorbornadiene (3,1,4-dihydro-1,4-methanonaphthalene) in 66 and 21% yields, respectively. Recently we[3] communicated that 9-benzonorbornadienylmagnesium bromide (**2**) was an intermediate in the addition of benzyne to **1** because deuterolysis of the reaction mixture produced benzonorbornadiene-*anti-9-d* (**4**). We described our results as the first well-established $\pi^2s + \pi^4s$ cycloadditions involving all-carbon anions. This paper describes additions of benzyne to cyclopentadienyl Grignards carried out to determine the influence of substitution on the course of cycloaddition. Concurrently, additions of benzyne to mixtures of isomeric substituted cyclopentadienes were investigated as control experiments for the Grignard cycloadditions.



1



2

3, X = H
4, X = D

Of the wide variety of methods available for generation of benzyne,[1] only organoalkali and organomagnesium routes appeared likely to be compatible with the cyclopentadienyl anion. The reaction of 2-bromofluorobenzene with magnesium in THF (tetrahydrofuran) was chosen because of its previous success in cycloadditions of benzyne to cyclopentadienyl-[2,3] and indenylmagnesium bromide,[3,4] because of the ease of preparation and the ionic character of cyclopentadienyl Grignard reagents, and because of failure in preliminary experiments to produce cycloadducts from cyclopentadienyllithium, *o*-dihalobenzenes, and alkyllithiums.

Results

Diene Cycloadditions.—All additions to dienes were carried out by generating benzyne from 2-bromofluorobenzene and magnesium in a refluxing THF solution about 1 *M* in the diene. The benzonorbornadienes produced in 45–65% yields were isolated by distillation and/or glpc. Several side products were

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