4 + 5 →

6

$$\xrightarrow[\text{anisole}]{\text{CH}_3\text{MgI}} 3$$

by decomposition of the reaction mixture with sulfuric acid and neutralization of the product with sodium bicarbonate, gave 3 in 47% yield. Recrystallization from acetonitrile gave an analytically pure sample, mp 187–188°. *Anal.* Calcd for $C_{20}H_{29}NO_2$: C, 76.15; H, 9.27; N, 4.44. Found: C, 75.83; H, 9.24; N, 4.45. λ_{max}^{EtOH} 225 mμ (ϵ 20,700), 280 mμ (ϵ 9880).

The nmr spectra of 3 and 6 are summarized in Table I. The use of trifluoroacetic acid as the solvent for 3 caused general downfield shift of absorption for 3 relative to 6 and consequently a protonation splitting of the N-methyl absorption to a doublet.

Table I. Summation of Nmr Spectra of 3 and 6[a]

Type of proton	6 δ	Rel area	3 δ	Rel area
Aromatic	6.78 (m)	(1)	6.47 (m)	(2)
	6.86 (m)	(1)		
C-1	4.22 (s)	(2)	4.52 (m)	(2)
C-3	2.80 (m)		3.73 (br, m)	(2)
		(4)		
C-4	2.80 (m)		2.64 (br, m)	(2)
N-CH₃	2.41 (s)	(3)	3.19 (d)	(3)
gem-di-CH₃	. . .	. . .	1.43 (s)	(3)
			1.51 (s)	(3)
ω-CH₃	0.82 (m)	(3)	0.91 (t)	(3)

[a] The spectrum of 6 was determined in pyridine solution, and that of 3 in trifluoroacetic acid. Values are given in parts per million relative to TMS as an internal standard: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad.

We have similarly prepared analogs of 3 where the C_5H_{11} side chain in the aromatic ring was replaced by CH_3, $CH(CH_3)(CH_2)_4CH_3$, $CH(CH_3)(CH_2)_{11}CH_3$, and $CH(CH_3)$-c-C_6H_{11}. Satisfactory analytical and spectral data were obtained for all of these compounds. When the side chain was CH_3, two coumarins 7 and 8 were isolated from the Pechmann condensation. The only differences in the nmr spectra in trifluoroacetic acid of 7 and 8 are in the absorption positions of the aromatic methyl and aromatic protons. The absorptions in 7 are at 2.37 ppm (aromatic methyl) and a splitting of the aromatic protons at 6.71 and 6.8 ppm,

whereas in 8 they are at 2.74 and 6.97 ppm, respectively.

7

8
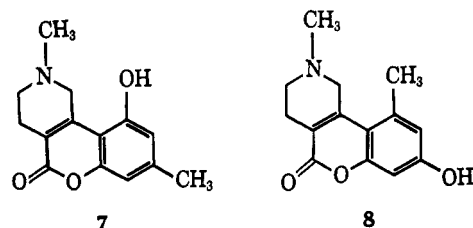
The investigation of these and other analogs of the tetrahydrocannabinols is being continued, and the detailed results of our biological and chemical findings will be reported elsewhere.

H. G. Pars, F. E. Granchelli, J. K. Keller, R. K. Razdan
*Organic and Medicinal Chemistry Laboratories
Research and Development Division, Arthur D. Little, Inc.
Cambridge, Massachusetts*

Conjugated Dienes as Quenchers for Excited Singlet States of Aromatic Hydrocarbons[1]

Sir:

In recent study of photosensitized reactions of conjugated dienes, we have noted marked discrepancies between predicted and measured quantum yields when aromatic hydrocarbons are used as sensitizers.[2] Furthermore, the isomerization of piperylene (1,3-pentadiene) sensitized by benzene is accompanied by formation of a number of photoadducts of the diene to benzene. The reactions are probably related to other photoaddition reactions of benzene reported recently.[3]

These observations were disturbing because we have used piperylene to measure the efficiency of intersystem crossing of similar hydrocarbons.[4] We now find that the deviations are due to interactions (including reactions) between excited singlet states of the aromatic hydrocarbons and the dienes in their ground states. The processes are easily monitored by observing quenching of fluorescence of the sensitizer molecules. We present results of experiments using systems in which little or no chemical reaction occurs between the

(1) Mechanisms of Photochemical Reactions in Solution. XLII. For part XLI see A. J. Fry, R. S. H. Liu, and G. S. Hammond, *J. Am. Chem. Soc.*, in press.
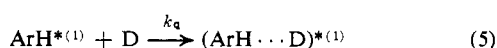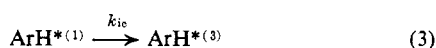(2) Unpublished results from this laboratory.
(3) R. Srinivasan and K. A. Hill, *J. Am. Chem. Soc.*, **87**, 4653 (1965); G. Koltzenburg and K. Kraft, *Tetrahedron Letters*, 389 (1965); *Angew. Chem. Intern. Ed. Engl.*, **4**, 981 (1965); J. G. Atkinson, D. E. Ayer, G. Büchi, and E. W. Robb, *J. Am. Chem. Soc.*, **85**, 2257 (1963); D. Bryce-Smith and J. E. Lodge, *J. Chem. Soc.*, 695 (1963); K. E. Wilzbach and L. Kaplan, *J. Am. Chem. Soc.*, **88**, 2066 (1966).
(4) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

sensitizer and the diene. Piperylene (a mixture of cis and trans isomers) and 1,3-cyclohexadiene were used as quenchers, and fluorescence measurements were made with an Aminco-Bowman spectrofluorometer. In general the experiments were performed with samples sealed in tubes after degassing by conventional freeze–thaw techniques. Figure 1 shows the fluorescence spectra of solutions of naphthalene in benzene containing varying amounts of piperylene. Figure 2 shows representative plots of relative fluorescence intensity vs. diene concentration.

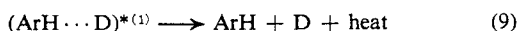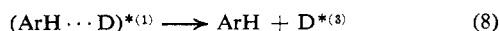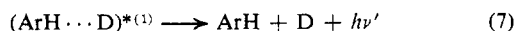The following mechanism is consistent with the results.

$$\text{ArH} \xrightarrow{h\nu} \text{ArH}^{*(1)} \tag{1}$$

$$\text{ArH}^{*(1)} \xrightarrow{k_f} \text{ArH} + h\nu \tag{2}$$

$$\text{ArH}^{*(1)} \xrightarrow{k_{ic}} \text{ArH}^{*(3)} \tag{3}$$

$$\text{ArH}^{*(1)} \xrightarrow{k_{ds}} \text{ArH} \tag{4}$$

$$\text{ArH}^{*(1)} + \text{D} \xrightarrow{k_q} (\text{ArH}\cdots\text{D})^{*(1)} \tag{5}$$
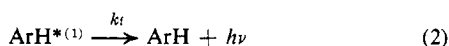
$$\frac{1}{\phi_f} = 1 + \frac{k_{ic} + k_{ds}}{k_f} + \frac{k_q[\text{D}]}{k_f} \tag{6}$$

The sums of the quantum yields for fluorescence and intersystem crossing are not known accurately enough to allow assessment of the importance of radiationless decay, reaction 4, but it is included for the sake of completeness. Combination of values reported for quantum yields of fluorescence and values of k_f estimated from the oscillator strengths for first absorption bands with our present data allows us to estimate values of k_q. Table I shows data for interesting examples.

Table I. Calculated Rate Constants for the Quenching of Aromatic Hydrocarbon Excited Singlets by Conjugated Dienes

Hydrocarbon	Diene	k_q, l. mole^{-1} sec^{-1}
Naphthalene	Piperylene	1.2×10^8
Naphthalene	1,3-Cyclohexadiene	2.2×10^9
1-Methylnaphthalene	Piperylene	5.1×10^7
1-Methylnaphthalene	1,3-Cyclohexadiene	1.4×10^9

Since little chemical reaction occurs in the examples given, it is clear that the excited complexes are loose enough so that permanent adduct formation is not a necessary consequence of reaction 5. Possible schemes for decay of the excited complex include the following.

$$(\text{ArH}\cdots\text{D})^{*(1)} \longrightarrow \text{ArH} + \text{D} + h\nu' \tag{7}$$

$$(\text{ArH}\cdots\text{D})^{*(1)} \longrightarrow \text{ArH} + \text{D}^{*(3)} \tag{8}$$

$$(\text{ArH}\cdots\text{D})^{*(1)} \longrightarrow \text{ArH} + \text{D} + \text{heat} \tag{9}$$

$$(\text{ArH}\cdots\text{D})^{*} + \text{D} \longrightarrow \text{ArH} + \text{dimer} \tag{10}$$

In all experiments to date no shifted fluorescence, such as would be expected from (7), has been observed. If reaction 8 is important, photoproducts characteristic of diene triplets should be produced even under conditions where intersystem crossing (reaction 3) is unimportant. Solutions containing 1-methylnaphthalene and varying concentrations of 1,3-cyclohexadiene were irradiated at 3130 A. In solutions containing the high-

est concentrations of the diene the yields of diene dimers were too small to measure by our vapor chromatographic analysis; thus reaction 10 is unimportant under these conditions. With 0.21 M diene, however, the dimers formed in sensitized reactions[5] were produced in a quantum yield of 0.027. If diene triplets are produced only by energy transfer from naphthalene triplets, the quantum yield should be given by

$$\phi_{\text{dim}} = \frac{\phi_f \phi_{ic}}{\phi_{fo}} \left(\frac{k_{\text{dim}}[\text{cyclohexadiene}]}{k_{\text{dim}}[\text{cyclohexadiene}] + k_d'} \right) \tag{11}$$

where ϕ_f = quantum yield of fluorescence, ϕ_{fo} = quantum yield of fluorescence with no added quencher, ϕ_{ic} = quantum yield of sensitizer triplets in the absence of singlet quenching, k_{dim} = rate constant for addition of diene triplets to diene, and k_d' = rate constant for decay of diene triplets.

The function within the parentheses has been determined using benzophenone as a sensitizer and has a value of 0.88 with 0.21 M cyclohexadiene. The value of ϕ_{ic} for 1-methylnaphthalene, determined using low concentrations of piperylene,[4] is 0.5, and ϕ_f/ϕ_{fo} is 0.054 in the presence of 0.21 M diene. The calculated value of ϕ_{dim} is 0.024, in excellent agreement with the measured value.

We conclude that dienes facilitate nonradiative $S_1 \rightarrow S_0$ decay of aromatic hydrocarbons. Fortunately, the process is usually negligible in a range of concentrations of the dienes high enough to ensure completely efficient scavenging of sensitizer triplets by the dienes. Consequently, the triplet counting experiments reported earlier[4] still have the significance originally attached to them. Further quenching experiments and an account of our study of the addition compounds formed from aromatic hydrocarbons and dienes will be reported in detail in the near future.

(5) D. Valentine, N. J. Turro, Jr., and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 5202 (1964).
(6) National Science Foundation Predoctoral Fellow, 1964 to present.
(7) National Institutes of Health Postdoctoral Fellow, 1965–1966.
(8) National Institutes of Health Predoctoral Fellow, 1965 to present.

Leonard M. Stephenson,[6] David G. Whitten[7]
George F. Vesley,[8] George S. Hammond
*Contribution No. 3377, Gates and Crellin Laboratories
of Chemistry, California Institute of Technology
Pasadena, California*
Received May 21, 1966

Homogeneous Asymmetric Catalysis

Sir:

We wish to report a novel example of nonenzymatic homogeneous asymmetric catalysis. To our knowledge this is the second such catalytic system with the first being the addition of hydrogen cyanide to aldehydes in the presence of quinine alkaloids.[1-3]

N-(2-Phenyl-2-hydroxyethyl)-4-methylthiazolium bromide[4] (I) was converted to its d-10-camphorsul-

(1) G. Bredig and P. S. Fiske, *Biochem. Z.*, **46**, 7 (1912).
(2) G. Bredig and M. Minaeff, *ibid.*, **249**, 241 (1932).
(3) V. Prelog and M. Wilhelm, *Helv. Chim. Acta*, **37**, 1634 (1954).
(4) R. Breslow, *J. Am. Chem. Soc.*, **80**, 3719 (1958).