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.

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

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

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

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

$$\mathrm{ArH}^{*(1)} + \mathrm{D} \xrightarrow{k_q} (\mathrm{ArH}\cdots\mathrm{D})^{*(1)} \tag{5}$$

$$\frac{1}{\phi_f} = 1 + \frac{k_{ic} + k_{ds}}{k_f} + \frac{k_q[\mathrm{D}]}{k_f} \tag{6}$$

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 | $1.2 \times 10^8$ |
| Naphthalene | 1,3-Cyclohexadiene | $2.2 \times 10^9$ |
| 1-Methylnaphthalene | Piperylene | $5.1 \times 10^7$ |
| 1-Methylnaphthalene | 1,3-Cyclohexadiene | $1.4 \times 10^9$ |

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.

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

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

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

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

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 highest 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

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

where $\phi_f$ = quantum yield of fluorescence, $\phi_{fo}$ = quantum yield of fluorescence with no added quencher, $\phi_{ic}$ = quantum yield of sensitizer triplets in the absence of singlet quenching, $k_{\mathrm{dim}}$ = 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 $\phi_{ic}$ for 1-methylnaphthalene, determined using low concentrations of piperylene,[4] is 0.5, and $\phi_f/\phi_{fo}$ is 0.054 in the presence of 0.21 *M* diene. The calculated value of $\phi_{\mathrm{dim}}$ 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.

**Acknowledgment.** This work was supported by the Directorate of Chemical Services, Air Force Office of Scientific Research, Contract No. AF 49 (638)-1479. We are indebted to Mr. Ronald S. Cole, who has made observations related to those reported above.

(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:*

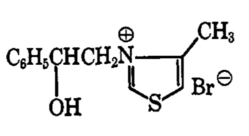
We wish to report a novel example of nonenzymatic homogeneous asymmetric catalysis. To our knowledge this is the second such catalytic system with the first being the addition of hydrogen cyanide to aldehydes in the presence of quinine alkaloids.[1–3]

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

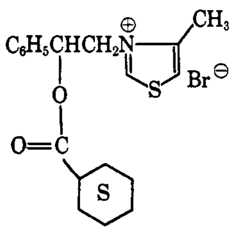
(1) G. Bredig and P. S. Fiske, *Biochem. Z.*, **46**, 7 (1912).
(2) G. Bredig and M. Minaeff, *ibid.*, **249**, 241 (1932).
(3) V. Prelog and M. Wilhelm, *Helv. Chim. Acta*, **37**, 1634 (1954).
(4) R. Breslow, *J. Am. Chem. Soc.*, **80**, 3719 (1958).

fonate and fractionally crystallized to a constant rotation ($[\alpha]^{25}_{546}$ +82.5° (*c* 1.55, ethanol)).[5] The bromide was regenerated by the use of an ion-exchange column to give (+)-I, $[\alpha]^{25}_{546}$ +76.3° (*c* 1.29, ethanol).

Treatment of (+)-I with cyclohexanecarboxylic acid anhydride and pyridine gave a 77% yield of (+)-N-[2-phenyl-2-(cyclohexanecarboxylate)ethyl]-4-methylthiazolium bromide (II), $[\alpha]^{25}_{546}$ +83.0° (*c* 1.50, ethanol).



I



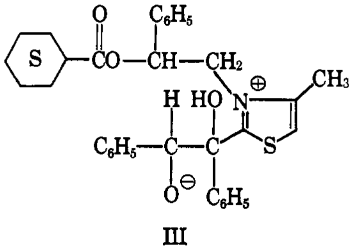
II

Using II as a catalyst in the benzoin condensation[4] with a 10:1 molar ratio of benzaldehyde to catalyst and a 1:1 molar ratio of triethylamine to catalyst, in methanol at ambient temperature, a precipitate of 0.52 g of benzoin (theory, 1.046 g) was obtained. This material was purified by chromatography on silica gel and showed a rotation of $[\alpha]^{25}_{546}$ +2.0° (*c* 2.0, $CHCl_3$) (optical purity 0.77%).[6]

The mother liquors from the reaction mixture were evaporated and purified by chromatography on silica gel to give 98.4 mg of benzoin, mp 123–131°. This material showed the following rotations, $[\alpha]^{25}_{546}$ (optical purity given in parentheses): +34.8° (*c* 0.79, acetone) (23.5%), +56.2° (*c* 1.04, $CHCl_3$) (21.5%), +112.5° (*c* 0.51, $CS_2$) (22.4%). An ORD curve of this material in *n*-hexane was consistent with that of benzoin with an optical purity of 22%.[7] This material had an infrared spectrum identical with that of authentic benzoin and showed only one spot on tlc.

In a separate experiment in which N-benzyl-4-methylthiazolium chloride was used as a catalyst, a measured amount of (+)-benzoin was added to the reaction mixture. After the aforementioned purification process all of the optically active benzoin was accounted for, principally in the mother liquor fraction.

The observed asymmetric catalysis was predicted on the basis of a "Lapworth-type" mechanism for benzoin condensation. The asymmetry presumably is induced during the formation of species III.



III

**Acknowledgment.** This work was supported by a grant from the National Institutes of Health.

---

(5) Rotations were determined on a Zeiss photoelectric precision polarimeter.

(6) E. G. Rule and J. Crawford, *J. Chem. Soc.*, 138 (1937).

(7) P. Preiswerk, *Helv. Phys. Acta*, 7, 203 (1933).

**John C. Sheehan, D. H. Hunneman**
*Department of Chemistry, Massachusetts Institute of Technology*
*Cambridge, Massachusetts 02139*

*Received May 7, 1966*

---

## The Fate of the 1-([2.2]Paracyclophanyl)methylcarbonium Ion. A Double-Barrelled Ring Expansion Route to the [3.3]Paracyclophane System

*Sir:*

One of the more interesting questions which arose during our investigation of the bridge chemistry of paracyclophanes was the fate of the carbonium ion derived from solvolysis of the tosylate IV. In particular, rarely observed fragmentation[1] generating the stabilized benzylcarbonium ion I might occur because of the high strain energy[2a,b] (31.3 kcal $mole^{-1}$) of the [2.2]paracyclophane ring. Alternatively, the role of the distorted phenyl ring[2c–e] as a neighboring group[3] is of interest. Furthermore, the rate of ionization of tosylate IV might be predicted to be sterically accelerated[4] to the extent that strain relaxation occurs in the transition state.

The 1-carbomethoxy[2.2]paracyclophane was prepared by chloroformylation of [2.2]paracyclophane with oxalyl chloride in the presence of benzoyl peroxide and subsequent methanolysis of the crude acid chloride (see Chart I).[5] Reduction of the ester and tosylation of the resulting alcohol gave the tosylate IV in high yield.[6] When the tosylate IV was solvolyzed in refluxing acetic acid for 19 hr, a single acetate was obtained in 97% yield which, on the basis of the nmr, has structure Va. Less than 1% of unrearranged acetate or olefin was obtained on the basis of vpc analysis.

Chemical proof of structure was obtained by oxidation of the alcohol Vb derived from the corresponding acetate to give the ketone VI in 80–90% yield. The simplicity of the nmr spectrum for VI which displayed resonances at 6.86–6.33 (multiplet, aromatic), 3.70 (singlet, $CH_2$–CO), and 2.97 ppm (singlet, –$CH_2CH_2$–) (relative to tetramethylsilane in chloroform-*d*) in an area ratio of 2:1:1 rules out the alternate structure for the acetate which would result from benzyl migration and carbonium ion II. Conversion of ketone VI by Wolff–Kishner reduction to [2.3]paracyclophane (VII) which was identical in all respects with authentic material[7] offers chemical proof for the hydrocarbon skeleton.

Kinetic analysis of the solvolysis in acetic acid by the method of Winstein and Schreiber[3a] generated the rate constants for rearrangement of IV to tosylate Vc ($k_r$), solvolysis of IV to acetate Va ($k_p$), and solvolysis of rearranged tosylate Vc to acetate Va ($k_s$). These data

---

(1) (a) J. Meinwald, P. G. Gassmann, and J. J. Hurst, *J. Am. Chem. Soc.*, **84**, 3722 (1962); (b) V. J. Shiner, Jr., and G. F. Meir, *J. Org. Chem.*, **31**, 137 (1966).

(2) (a) R. H. Boyd, *Tetrahedron*, **22**, 119 (1966); (b) P. K. Gantzel and K. N. Trueblood, private communication; (c) C. J. Brown, *J. Chem. Soc.*, 3265 (1953); (d) K. Lonsdale, H. J. Milledge, and K. V. K. Rao, *Proc. Roy. Soc.* (London), **A255**, 82 (1960); (e) D. A. Bekoe and K. N. Trueblood, Meeting of American Crystallographic Association, Bozeman, Mont., 1964.

(3) (a) S. Winstein and K. C. Schreiber, *J. Am. Chem. Soc.*, **74**, 2165 (1952); (b) R. Huisgen, G. Seidl, and S. Wimmer, *Tetrahedron*, **20**, 623 (1964); (c) R. Huisgen and G. Seidl, *Chem. Ber.*, **96**, 2740 (1963); (d) D. J. Cram and L. S. Singer, *J. Am. Chem. Soc.*, **85**, 1084 (1963).

(4) H. C. Brown, Special Publication No. 16, The Chemical Society, London, 1963.

(5) (a) M. S. Kharasch and H. C. Brown, *J. Am. Chem. Soc.*, **64**, 329 (1942); (b) M. S. Kharasch, S. S. Kane, and H. C. Brown, *ibid.*, **64**, 1621 (1942); (c) E. Hedaya and L. M. Kyle, in preparation.

(6) All new compounds had correct elemental analyses along with consistent infrared, ultraviolet, and nmr spectra.

(7) We wish to thank Professor D. J. Cram for sending us an authentic sample.