

large reduction in energy. This is equivalent to saying that the barrier is high and thin, and this is an ideal situation for tunneling. It seems reasonable that slow sterically hindered hydrogen transfer reactions in other cases will also show extremely large isotope effects, and that tunneling will prove to be more common than was believed.

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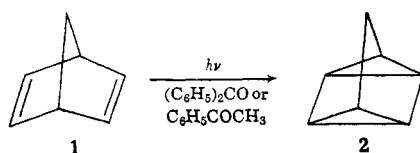
RECEIVED MAY 13, 1964

Photosensitized Isomerization Involving Saturated Centers¹

Sir:

At an earlier date we reported evidence that *cis*-stilbene can accept triplet excitation from low-energy photosensitizers by a process called nonvertical excitation.³ We now wish to describe two examples of photosensitized isomerization reactions which apparently involve energy transfer with consequent breaking of single bonds in the acceptors.

We have reported that photoisomerization of [2.2.1]-bicycloheptadiene (**1**) to [2.2.1.0.^{2,6}0^{3,5}]quadricycloheptane (**2**) can be accomplished through the agency of sensitizers such as benzophenone or acetophenone.⁴ This transformation was considered as unexceptional since interaction between the double bonds in **1** may give rise to "spectroscopic" triplet states lying lower than those of the sensitizers.



The subsequent observation that the reverse transformation **2** → **1** could be effected in the presence of certain sensitizers was, however, not comprehensible on the basis of similar postulates. Table I shows typical results.

The occurrence of side reactions makes precise measurement of stationary states difficult and the above data only serve to demonstrate that **1** is formed from **2** in the presence of all sensitizers except acetophenone. Since the side reactions may produce new sensitizers, changes in the relative rates of the **1** → **2** and **2** → **1** processes may occur during the course of the reactions. The reaction was studied in more detail using fluorenone ($E_T = 54$ kcal.) as the sensitizer. Early points indicated that a mixture containing about 70% **1** was approached from both sides; however, after 2-hr. irradiation time the proportion of **2** gradually increased in all samples and at the end of 63 hr. only about 25% of the original C₇ hydrocarbons remained as such in the reaction mixtures. Preliminary measurements of the quantum yields at low conversion indicate that, in the absence of side reactions, the stationary states should actually

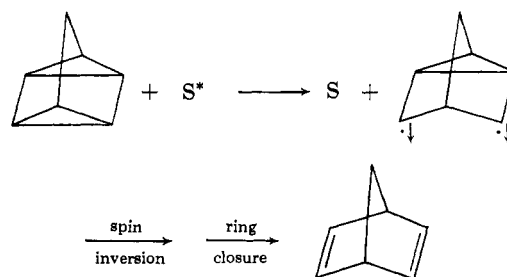
TABLE I
PHOTOSENSITIZED INTERCONVERSION OF
BICYCLOHEPTADIENE (**1**) AND QUADRICYCLOHEPTANE (**2**)^a

Sensitizer	E_T^b	Starting material	Per cent 2	
			after irradiation ^c 1 hr.	6 hr.
Acetophenone	73.6	1	100	100
Acetophenone	73.6	2	100	100
Benzophenone	68.5	1	84	86
Benzophenone	68.5	2	87	84
2-Naphthaldehyde	59.5	1	28	53
2-Naphthaldehyde	59.5	2	95	90
Benzil	53.9	1	14	50
Benzil	53.9	2	84	98

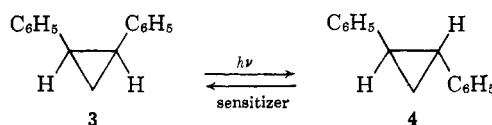
^a Irradiated with a medium-pressure mercury arc in ether solution; initial concentrations of the substrates were 1% and those of the sensitizers were 2% by weight; 2% *n*-hexane was included as an internal standard for v.p.c. analysis. Values are obtained from phosphorescence spectra reported in the literature or measured (or remeasured) in this laboratory. ^b Triplet excitation energies of sensitizers in kcal./mole. ^c Substantial amounts of the starting material were consumed in side reactions in all cases.

contain more than 70% of **1**. This, the initial rate of **1** → **2** was not large enough to measure whereas the quantum yield for **2** → **1** was initially 0.08 and subsequently decreased regularly. Mixtures initially containing 70 and 80% **1** were irradiated in the presence of fluorenone. In each case the relative amount of **1** increased during the early stages of irradiation, confirming the view that the stationary states, in the absence of extraneous materials, would be very rich in **1**.

An attractive formulation of the mechanism involves direct excitation of **2** to a triplet having approximately the same nuclear configuration as would be formed by excitation of **1** in accordance with the Franck-Condon principle. Since **2** is a high-energy isomer of **1**, the **2** → **1*** process would have a lower energy requirement than would the **1** → **1*** excitation, thereby accounting for the relatively high reactivity of low-energy sensitizers toward **2**. An alternate formulation of the nonvertical excitation process would involve breaking of single bonds to form a biradical in the first step.



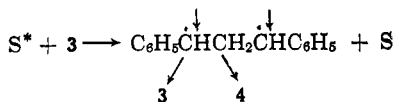
An especially interesting isomerization reaction is the photosensitized interconversion of *cis*- and *trans*-1,2-diphenylcyclopropane, **3** and **4**.



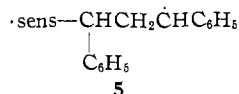
Conversion in either direction is observed when solutions of **3** or **4** in benzene and various sensitizers are irradiated with light absorbed only by the latter. Effective sensitizers include benzophenone, fluorenone, 9,10-dibromoanthracene, and 2-acetonaphthone.

(1) Mechanisms of Photochemical Reactions in Solution. XXIII.²
 (2) Part XXII: G. S. Hammond, *et al.*, *J. Am. Chem. Soc.*, in press.
 (3) G. S. Hammond and J. Saltiel, *ibid.*, **85**, 2515 (1963).
 (4) G. S. Hammond, N. J. Turro, and A. Fischer, *ibid.*, **83**, 4674 (1961).

An obvious mechanism for the reaction involves energy transfer with breaking of the weak carbon-carbon bond connecting the two ring members which bear the phenyl substituents.



Mechanisms in which the sensitizers become permanently bonded to the substrates seem highly unlikely since biradicals such as **5** would be expected to cyclize rather than re-form the three-membered ring by elimination reactions.



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(5) This report is abstracted in part from the freshman honors report of this author.

(6) National Science Foundation Predoctoral Fellow, 1962–present.

(7) National Science Foundation Predoctoral Fellow, 1959–1963.

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Synthesis of *Lycopodium* Alkaloids. I. A Synthetic Proof for the Structure of Lyconotine

Sir:

Recently, structure I was proposed¹ for lyconotine, an alkaloid from *Lycopodium annotinum* L. We describe here a synthesis of the lyconotine transformation products VI and VII, which firmly establishes the lyconotine structure and provides an interesting route for the synthetic elaboration of other *Lycopodium* alkaloids.

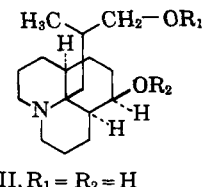
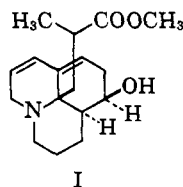
Compounds VI and VII were obtained from lyconotine in the following way. The alkaloid, m.p. 123°, was reduced with lithium aluminum hydride in ether and the resulting diol was hydrogenated with platinum in ethanol to give the diol II, m.p. 188–189°, infrared maxima (CHCl₃) 3600 and 3450 cm.⁻¹. *Anal.* Found: C, 72.27; H, 10.68; N, 5.27; O, 11.56. Its acetylation in acetic anhydride-pyridine yielded the diacetate III, infrared maximum (CCl₄) 1735 cm.⁻¹, n.m.r.² peaks at τ 5.0 (1H; broad singlet), 6.0 (2H's; octet, $J_{AB} = 10.5$ c.p.s., $J_{AX} = 5.2$ c.p.s., $J_{BX} = 8.4$ c.p.s.), and 7.96 (two acetate methyls, singlet), which on selective hydrolysis with potassium carbonate in aqueous methanol gave the monoacetate IV, infrared maxima (CCl₄) 3600 and 1735 cm.⁻¹, n.m.r. peaks at τ 5.07 (1H, broad singlet) and 7.95 (one acetate methyl, singlet). Treatment of the hydrochloride of IV with phosphorus tribromide in benzene, followed by a reduction of the resulting salt with zinc dust in acetic acid, gave the

(1) F. A. L. Anet, M. Z. Haq, N. H. Khan, W. A. Ayer, R. Hayatsu, S. Valverde-Lopez, P. Deslongchamps, W. Riess, M. Ternbah, Z. Valenta, and K. Wiesner, *Tetrahedron Letters*, 751 (1964).

(2) All n.m.r. data were obtained at 60 Mc. with tetramethylsilane as internal standard.

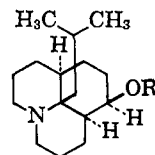
monoacetate V, infrared maximum (CCl₄) 1735 cm.⁻¹. Hydrolysis of V with potassium hydroxide yielded the alcohol VI, m.p. 157–158°, infrared maximum (CCl₄) 3640 cm.⁻¹, n.m.r. peaks at τ 6.2 (1H, broad singlet) and 8.95 (two methyl groups; doublet, $J = 5.6$ c.p.s.), mass spectrum peaks at $m/e = 251$ (molecular ion), 194 (very strong), 192, and 176 (strong), which in the form of its hydrochloride was oxidized with chromium trioxide in 90% acetic acid to give the ketone VII, infrared maximum (CCl₄) 1710 cm.⁻¹.

The stereochemistry of compounds I–VII follows from the lactonization of lyconotine¹ and the fact that all the compounds show Bohlmann bands^{3,4} in their infrared spectra.

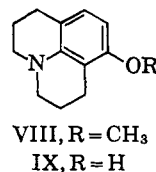
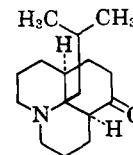


III, R₁ = R₂ = CH₃CO

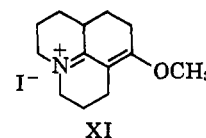
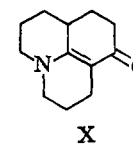
IV, R₁ = H, R₂ = CH₃CO



VI, R = H



IX, R = H



Compounds VI and VII were synthesized in the following way. Prolonged treatment of *m*-anisidine with boiling 1-bromo-3-chloropropane⁵ gave a mixture of the methoxyjulolidine VIII and the hydroxyjulolidine IX, m.p. 135°, ultraviolet maxima 218 (4.35), 256 (3.74), and 299 m μ (3.43). *Anal.* Found: C, 75.02; H, 7.95; N, 7.51; O, 8.83. Phenol IX, isolated in a 30% yield, was reduced with Raney nickel at 140° and 55 atm. pressure to give a 40% yield of X, b.p. 156° at 0.5 mm., ultraviolet maximum 315 m μ (3.91), infrared maxima (CCl₄) 1625 and 1555 cm.⁻¹, analyzed as the picrate, m.p. 165–166°. *Anal.* Found: C, 51.42; H, 4.73; N, 12.92; O, 31.10. Treatment of X with boiling methyl iodide gave an 80% yield of the salt XI,⁶ m.p.

(3) F. Bohlmann and C. Arndt, *Ber.*, **91**, 2167 (1958).

(4) Treatment of ketone VII with sodium methoxide gave a mixture of about equal amounts of VII and an epimer. This new ketone must be the *trans-cis* isomer, since it moves faster on alumina and its infrared spectrum shows no Bohlmann bands.

(5) For the synthesis of unsubstituted julolidine, see G. Pinkus, *Ber.*, **25**, 2798 (1892).

(6) For a comparable O-alkylation, see N. J. Leonard and J. A. Adamcik, *J. Am. Chem. Soc.*, **81**, 595 (1959).