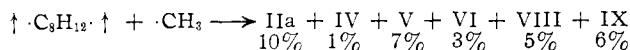
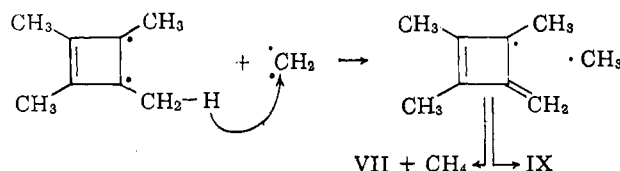


On the other hand generation of a fivefold excess of methyl radicals (from methyl bromide) in the reaction zone with tetramethylcyclobutadiene gave no detectable VII. Instead the usual mixture was formed along with two new products, hexamethylcyclobutene (VIII)<sup>16</sup> and 1-methylene-2,2,3,4-tetramethylcyclobutene (IX).<sup>16</sup>



Tetramethylcyclobutadiene has a marked preference for loss of two hydrogen atoms in reaction with triplet methylene, a behavior not shown in reactions with methyl radicals despite the fact that triplet methylene and methyl radicals show similar selectivities in hydrogen abstractions from alkanes.<sup>14</sup> The very high yield of VII can be easily explained with a transition state involving simultaneous transfer of the two hydrogen atoms from tetramethylcyclobutadiene to methylene.

An alternative hypothesis, stepwise transfer of hydrogen to the methylene, should give VII and IX, but since IX was not detected as a product, this is excluded as a significant reaction.



These experiments support the hypothesis that free tetramethylcyclobutadiene has been synthesized, and also indicate a triplet ground state, a result which is in accord with the prediction from theory.<sup>17</sup>

(16) Compounds VIII and IX were identified by their infrared spectra (Prof. Criegee, private communication) and their n.m.r. spectra (T. J. Katz and E. H. Gold, *J. Am. Chem. Soc.*, **86**, 1600 (1964)).

(17) J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *ibid.*, **74**, 4579 (1952).

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### Tunneling in a Proton Transfer. A Large Isotope Effect

Sir:

The rate-determining step in iodination of 2-nitropropane or 2-nitropropane-2*d* catalyzed by pyridine bases is the proton (or deuterium) transfer from the nitro compound to the base.<sup>1</sup> It is slowed by steric hindrance when 2- and 2,6-substituents are used on the pyridine. When a solvent is used that is made by diluting six volumes of *t*-butyl alcohol to ten with water and is free from the excess iodide used in the previous work to simplify the conversion of absorbance to concentration, the isotope effects at 24.88° are large, as shown in Table I. We have searched for sources of

(1) E. S. Lewis and J. D. Allen, *J. Am. Chem. Soc.*, **86**, 2022 (1964); see also R. G. Pearson and F. V. Williams, *ibid.*, **75**, 3073 (1953).

gross error in these isotope effects, including those arising from effects of impurities (including acetone) in the nitro compounds, the pyridine bases, and the solvent and from nonreproducibility in solvent composition, uncertainties in temperature, extinction coefficients, and time errors, and we have not found any.

TABLE I

ISOTOPE EFFECTS IN THE PYRIDINE BASE-CATALYZED IODINATION OF 2-NITROPROPANE IN AQUEOUS *t*-BUTYL ALCOHOL AT 24.88°

Base	Isotope effect, $k_H/k_D$
Pyridine	9.84
2-Picoline	10.6
2,6-Lutidine	24.1
2,4,6-Collidine	24.2 <sup>a</sup>

<sup>a</sup> Without a correction for 1.3% ordinary nitropropane in the deuterio compound (determined by n.m.r.) this value is over 18. The correction is applied in all cases.

The last two entries in Table I are larger than any previously reported isotope effects.<sup>2,3</sup> They are also larger than those calculated as the upper limit on the basis of ordinary absolute reaction rate theory. Thus, Melander<sup>4</sup> calculated for a breakage of a normal C-H bond a maximum  $k_H/k_D = 17$  at room temperature, and various other estimates are about the same or lower and the transition states required to give these results are highly unrealistic for a proton transfer.

A substantial tunnel correction is necessary to reconcile these results with absolute reaction rate theory, and we believe that this is clearly demonstrated here. Tunneling was also postulated in this same reaction in aqueous ethanol<sup>1</sup> on the basis that the apparent pre-exponential factor of the Arrhenius equation for the protium compound was substantially less than that for the deuterium compound. This criterion for tunneling was proposed and originally found by Bell.<sup>5</sup> In the present work the temperature dependence of the isotope effect for the reaction with 2,4,6-collidine fits eq. 1, and again the small pre-exponential factor ratio indicates tunneling, as does the 3

$$k_H/k_D = 0.146e^{3030/RT} \quad (1)$$

kcal. difference in activation energy, which is inconceivably large for any difference in loss of zero-point energy. The presence of a large tunnel correction is therefore further demonstrated.

The connection between the steric hindrance and the tunneling, suspected but not demonstrated before,<sup>1</sup> is now clear, and we may wonder why this is the case. A plausible explanation is that an ordinary potential barrier results from stretching or bending bonds, and the potential energy is not very strongly dependent on distance. In a sterically hindered transition state much of the energy is compressional, and this is known to depend on a high power of the distance. Thus a slight change in either direction along the reaction coordinate away from the maximum will correspond to a

(2) To our knowledge the largest deuterium isotope effect at about room temperature is  $k_H/k_D = 16$ , reported by R. Stewart and R. van der Linden, *Discussions Faraday Soc.*, **29**, 211 (1960); R. P. Bell, *ibid.*, **29**, 253 (1960), suggests that tunneling is important here, on the basis of the size of the isotope effect and its temperature dependence.

(3) Preliminary results indicate that even larger isotope effects can be observed in the same reaction merely by changing the water content of the solvent.

(4) L. Melander, "Isotope Effects on Reaction Rates," Ronald Press, New York, N. Y., 1960, p. 42.

(5) R. P. Bell, T. A. Fendley, and J. R. Hulett, *Proc. Roy. Soc. (London)*, **A235**, 453 (1956).

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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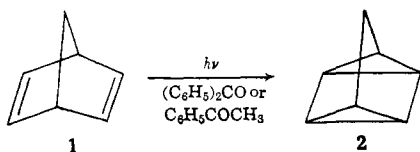
RECEIVED MAY 13, 1964

### Photosensitized Isomerization Involving Saturated Centers<sup>1</sup>

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.<sup>3</sup> 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]quadricycloheptane (**2**) can be accomplished through the agency of sensitizers such as benzophenone or acetophenone.<sup>4</sup> 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 C<sub>7</sub> 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

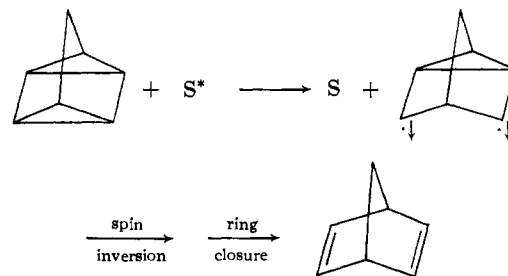
TABLE I  
PHOTOSENSITIZED INTERCONVERSION OF  
BICYCLOHEPTADIENE (**1**) AND QUADRICYCLOHEPTANE (**2**)<sup>a</sup>

Sensitizer	$E_T^b$	Starting material	Per cent <b>2</b>	
			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

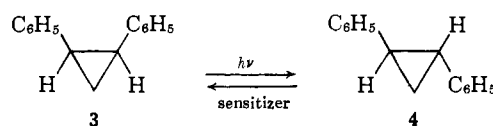
<sup>a</sup> Irradiated with a medium-pressure mercury arc in ether solution; initial concentrations of the substrates were 1% and those of the sensitizers were 2% by weight; 2% *n*-hexane was included as an internal standard for v.p.c. analysis. Values are obtained from phosphorescence spectra reported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