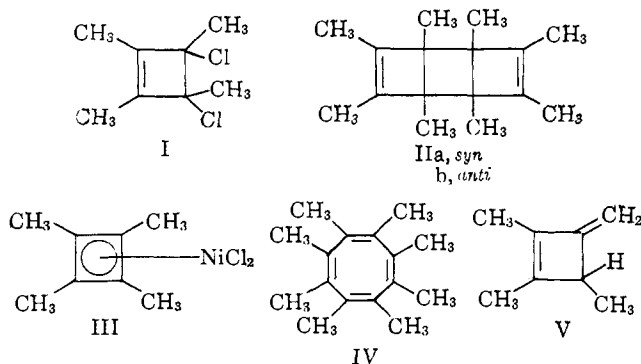


Tetramethylcyclobutadiene<sup>1</sup>

Sir:

Criegee's pioneering investigations on tetramethylcyclobutadiene showed that different methods of preparing transient tetramethylcyclobutadiene led to diverse products. We thought that preparation of this species in the gas phase would remove the complications engendered by weak bondings to the reaction media.

We became interested in tetramethylcyclobutadiene for a number of reasons. It has defied attempts at isolation. Its related chemistry was exceptionally well worked out by Criegee and his co-workers. Yet, so many anomalies appeared in this system that one cannot be sure what products are derived from tetramethylcyclobutadiene and what products arise from a complex intermediate similar to it. To illustrate: dehalogenation of I with lithium amalgam leads to the *syn* dimer IIa,<sup>10</sup> whereas decomposition of the nickel complex III in hot aqueous solution<sup>11</sup> or pyrolysis of the phenanthroline adduct of III<sup>3a</sup> under vacuum leads to IIb containing no IIa whatsoever. Pyrolysis of III under vacuum leads to IV as one of the products; however, no trace of IIa



or IIb could be found.<sup>11</sup> Vacuum thermolysis of the phenanthroline adduct of III leads to V as a by-product.<sup>3a</sup> Reaction of I with zinc in 2-butyne leads to hexamethylbenzene, presumably through a Dewar benzene intermediate; dehalogenation of I with lithium amalgam under similar conditions leads only to IIa as previously found.<sup>3b</sup> The highly specific courses of these reactions outlined here indicate that tetramethylcyclobutadiene must be reacting in most, or even all, of the experiments reported as a complex with zinc, mercury, silver, lithium, nickel, or solvent.<sup>3a</sup>

(1) (a) This work was supported by the National Science Foundation. For previous work on cyclobutadiene derivatives, see ref. 1b-9. (b) W. C. Lothrop, *J. Am. Chem. Soc.*, **63**, 1187 (1941).

(2) M. Avram, I. G. Dinulescu, E. Marica, G. Mateescu, E. Sliam, and C. D. Nenitzescu, *Chem. Ber.*, **97**, 382 (1964), and previous references.

(3) (a) R. Criegee, *Angew. Chem. Intern. Ed. Engl.*, **1**, 519 (1962), and previous references; (b) C. E. Berkoff, R. C. Cookson, J. Hudec, and R. O. Williams, *Proc. Chem. Soc.*, 312 (1961).

(4) E. H. White and H. C. Dunathan, *J. Am. Chem. Soc.*, **86**, 453 (1964).

(5) K. Nagarajan, M. C. Caserio, and J. D. Roberts, *ibid.*, **86**, 449 (1964).

(6) (a) I. H. Freedman and R. S. Gohlke, *Proc. Chem. Soc.*, 249 (1963), and previous references; (b) R. C. Cookson and D. W. Jones, *ibid.*, 115 (1963); (c) A. T. Blomquist and P. M. Maitlis, *J. Am. Chem. Soc.*, **84**, 2329 (1962).

(7) (a) M. Avram, I. G. Dinulescu, D. Dinu, G. Mateescu, and C. D. Nenitzescu, *Tetrahedron*, **19**, 309 (1963), and previous references; (b) M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **80**, 2255 (1958), and previous references.

(8) C. D. Nenitzescu, M. Avram, I. G. Dinulescu, and G. Mateescu, *Ann.*, **663**, 79 (1962).

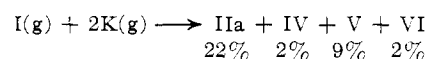
(9) M. P. Cava, B. Hwang, and J. P. Van Meter, *J. Am. Chem. Soc.*, **85**, 4032 (1963).

(10) R. Criegee and G. Louis, *Chem. Ber.*, **90**, 417 (1957).

(11) R. Criegee and G. Schroder, *Ann.*, **623**, 1 (1959).

We believe we have generated free tetramethylcyclobutadiene in the gas phase by the reaction of I with alkali metal vapor, a system wherein complex formation is unlikely. Although we have been unsuccessful in attempts to isolate the hydrocarbon, it could be studied *in situ*, where it reacts with triplet methylene to transfer two hydrogen atoms in a single elementary act. We interpret this as strong evidence for the presence of triplet state tetramethylcyclobutadiene.

Experiments were conducted at 245-255° in a helium atmosphere (200 mm.) saturated with sodium-potassium vapor in a sodium flame apparatus similar to that introduced by Hartel and Polanyi,<sup>12</sup> but modified for preparative purposes. Residence times in the reaction zone were approximately 2 sec. The dehalogenation of I gave a 35% yield of a hydrocarbon mixture consisting of IIa, IV, 1-methylene-2,3,4-trimethylcyclobutene (V), and *cis*-1,2,3,4-tetramethylcyclobutene (VI). Compound VI was identified by comparison with the known material from reduction of I with lithium aluminum hydride.<sup>13</sup>



Under our conditions the gas most prevalent in the reaction zone, besides helium, is monatomic potassium vapor. Tetramethylcyclobutadiene would, therefore, suffer frequent collisions with doublet state potassium atoms before further bimolecular reaction, so that relaxation to ground state (singlet or triplet) multiplicity would occur:  $\uparrow \cdot \text{C}_8\text{H}_{12} + \text{K} \cdot \downarrow \rightleftharpoons \text{C}_8\text{H}_{12} + \uparrow \downarrow + \text{K} \cdot \uparrow$ . We believe the observed products are derived from reactions of a triplet species for the reasons given below.

The concentration of the dichloro compound in the gas phase was varied over a 30-fold range; yet the ratio of IIa to V remained essentially constant. Since IIa must be formed by a bimolecular process, the formation of V must also be bimolecular. Although a rapid, bimolecular disproportionation between two singlet cyclobutadienes is an unlikely process, without precedent in other systems, the observed products are readily explained if a triplet cyclobutadiene is postulated as the intermediate. The analogous monoradical reactions of coupling and disproportionation are well-established rapid processes. The disproportionation reaction applied to the interaction of two triplets,  $\uparrow \cdot \text{C}_8\text{H}_{12} + \downarrow \cdot \text{C}_8\text{H}_{12} \rightarrow \downarrow \downarrow$ , leads to two molecules of V, while coupling leads to IIa.

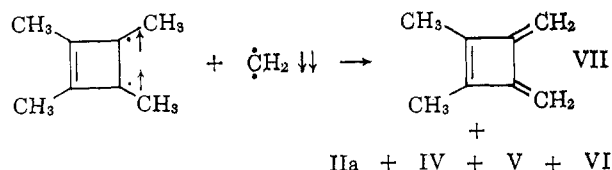
The reaction of dibromomethane with potassium vapor under similar conditions has been shown to give triplet methylene.<sup>14</sup> Successful interaction of tetramethylcyclobutadiene with methylene was accomplished by using a threefold excess of dibromomethane in the gaseous reactant mixture. The coupling and disproportionation products were reduced drastically, IIa, IV, V, and VI amounting to only 10%. The major product (34%) was identified as C<sub>8</sub>H<sub>10</sub>, 1,2-dimethylene-3,4-dimethylcyclobutene (VII),<sup>15</sup> a compound not observed if CH<sub>2</sub>Br<sub>2</sub> is not a reactant.

(12) H. von Hartel and M. Polanyi, *Z. physik. Chem.*, **B11**, 97 (1930).

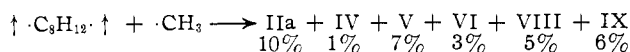
(13) R. Criegee and K. Noll, *Ann.*, **627**, 1 (1959).

(14) P. S. Skell and G. L. Tingey, unpublished work.

(15) This product was identical with (a) a sample prepared by quinoline dehydrohalogenation of I according to the procedure of R. Criegee, J. Dekker, W. Engel, P. Ludwig, and K. Noll, *Chem. Ber.*, **96**, 2362 (1963), and (b) an authentic sample supplied by Prof. Criegee.

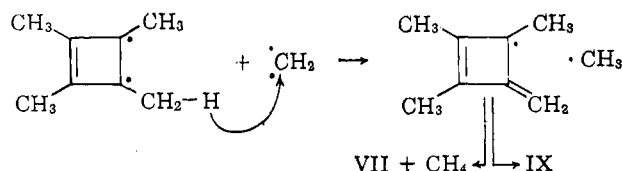


On the other hand generation of a fivefold excess of methyl radicals (from methyl bromide) in the reaction zone with tetramethylcyclobutadiene gave no detectable VII. Instead the usual mixture was formed along with two new products, hexamethylcyclobutene (VIII)<sup>16</sup> and 1-methylene-2,2,3,4-tetramethylcyclobutene (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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RECEIVED MARCH 16, 1964

### 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 deuteron) 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).