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Photolysis of Tetramethyl-1,3-cyclobutanedione

Sir:

Potentially, the photolytic decarbonylation of tetrasubstituted 1,3-cyclobutanediones in solution or in the gas phase is an attractive and simple route to substituted cyclopropanones, either as stable species or as intermediates. Photodecarbonylation reactions are well known in the gas phase,[1] but they usually occur with very low efficiencies in solution.[2] However, irradiation of a benzene solution of tetramethyl-1,3-cyclobutanedione (I) through Pyrex leads to the rapid evolution of carbon monoxide and the formation of tetramethylethylene in 80% net yield. The quantum yield for disappearance of I under these conditions is 0.4 at 3660 Å. Apparently, a small amount of dimethyl ketene is also produced since the photolyzed solution quickly develops a yellow color and a strong band in the infrared[3] at 4.7 μ. Addition of a few drops of isopropyl alcohol to the irradiated solution results in disappearance of both the yellow color and the 4.7 μ band.
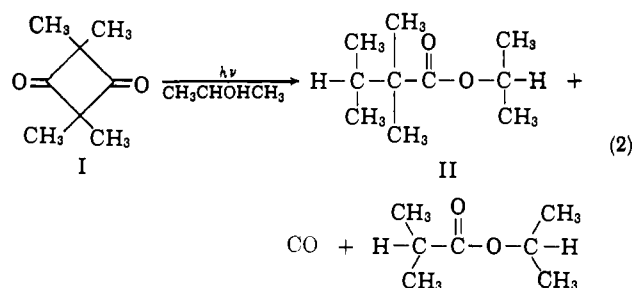

$$\text{(1)}$$
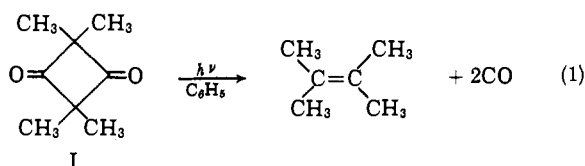
Irradiation of I in isopropyl alcohol leads to rather different results, as no tetramethylethylene is produced (although carbon monoxide is still formed), and several products appear in the vapor chromatogram of the irradiated solution. The quantum yield for the disappearance of I in this case is 0.5. The two major products of the photolysis, both formed in about 30% net yield, are isopropyl isobutyrate (presumably formed by addition of isopropyl alcohol to dimethyl ketene) and compound II. The latter was obtained pure by preparative v.p.c. and possesses an n.m.r. spectrum[4] consisting of two septets centered at 4.8 (one proton) and 1.65 p.p.m. (one proton), two doublets centered at 1.10 (six protons) and 0.70 p.p.m. (six protons), and a singlet at 0.90 p.p.m. (six protons). This spectrum, as well as the infrared spectrum of the compound, is completely consistent with II being the ester isopropyl 2,2,3-trimethylbutyrate. *Anal.* Calcd. for $C_{10}H_{20}O_2$: C, 69.6; H, 11.7. Found: C, 69.2; H, 11.8. In methanol, competing reactions similar to both eq. 1 and 2 take place, with formation of both tetramethylethylene in about 5% net yield and, as the major

product, the methyl ester III (methyl 2,2,3-trimethylbutyrate), the quantum yield for disappearance of I being 0.5. III possesses an n.m.r. spectrum consisting of a sharp singlet at 3.40 p.p.m. (3 protons), a septet centered at 1.6 p.p.m. (one proton), a sharp singlet at 0.82 p.p.m. (6 protons), and a doublet centered at 0.60 p.p.m. (6 protons). *Anal.* Calcd. for $C_8H_{16}O_2$: C, 66.6; H, 11.2. Found: C, 66.7; H, 11.2. Methyl isobutyrate is also formed as a major product upon irradiation of I in methanol.

These results show that at least two paths for reaction are possible during the photolysis of I: (a) a bis-fragmentation without decarbonylation to yield dimethyl ketene[5]; and, more importantly (b) decarbonylation to yield products which are consistent with the intermediacy of either tetramethylcyclopropanone (IV), or the diradical resonance hybrid (V), or a combination of both. The intermediate decarbonylates in
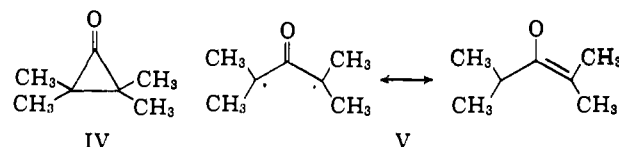
inert solvents[6] to give good yields of tetramethylethylene, while in nucleophilic solvents, such as alcohols, addition to form the respective 2,2,3-trimethylbutyrate esters competes with decarbonylation. It is not clear at this time why isopropyl alcohol should be more efficient in this capacity than methanol.

Piperylene (0.3 *M*), a quencher of triplet states of energy greater than 55 kcal.,[7] has virtually no effect on the photolysis of the diketone in both benzene and alcohol solvents, and benzophenone was ineffective at sensitizing the photoreaction. Although we have not yet obtained a low temperature emission spectrum of the compound, these results (while not rigorously excluding the triplet) are consistent with the assumption that the above reactions occur only from the singlet state.

Preliminary experiments on the photolysis of I in the vapor phase reveal that tetramethylethylene, a lower boiling material, and carbon monoxide are the only isolable products. Further investigation of this and related systems as well as complete characterization of all products in the various solvents is in progress.

(1) W. A. Noyes, Jr., G. Porter, and E. J. Jolley, *Chem. Rev.*, **56**, 49 (1956); J. N. Pitts, *J. Chem. Educ.*, **34**, 112 (1957).

(2) Numerous reports concerning photodecarbonylations in solution have appeared recently: R. H. Eastman, J. E. Starr, R. St. Martin, and M. K. Sakata, *J. Org. Chem.*, **28**, 2162 (1963); O. L. Chapman, D. J. Pasto, G. W. Borden, and A. A. Griswold, *J. Am. Chem. Soc.*, **84**, 1220 (1962); D. C. England, *ibid.*, **84**, 2205 (1962); G. Quinkert, K. Opitz, and J. Weinlich, *Angew. Chem.*, **74**, 507 (1962); C. D. Gutsche and C. W. Armbruster, *Tetrahedron Letters*, **No. 26**, 1297 (1962); K. Mislow and A. J. Gordon, *J. Am. Chem. Soc.*, **85**, 3521 (1963); G. Quinkert, K. Opitz, and V. Weinlich, *Tetrahedron Letters*, 1863 (1963); P. A. Leermakers, P. C. Warren, and G. F. Vesley, *J. Am. Chem. Soc.*, in press.

(3) Dimethyl ketene possesses a strong infrared absorption at 4.7 μ. [R. A. Holroyd and F. E. Blacet, *ibid.*, **79**, 4830 (1957)].

(4) N.m.r. spectra were taken at 60 Mc. in carbon tetrachloride, employing tetramethylsilane as an external standard.

(5) It must be pointed out that while the yields of ketene adducts in alcohol solvents (the isobutyrate esters) account for 30–40% of the products, only 15–20% of the reaction proceeds by this path since *two* molecules of dimethyl ketene will be formed from one molecule of I. Several reports concerning photochemical elimination of ketene have appeared recently: J. C. Anderson and C. B. Reese, *Tetrahedron Letters*, 1 (1962); W. H. Urry, D. J. Trecker, and D. A. Winey, *ibid.*, 609 (1962); D. L. Schuster, M. Axelrod, and J. Auerbach, *ibid.*, 1911 (1963); G. O. Schenck and R. Steinmetz, *Chem. Ber.*, **96**, 520 (1963).

(6) The mechanism of the second decarbonylation is not known, but may be either a thermal reaction or secondary photolysis. Cyclopropanone itself appears to be stable in solution [A. Kende, Ph.D. Thesis, Harvard University, 1956], but a possible example of spontaneous decarbonylation has been reported [A. Kende, *Chem. Ind.* (London), 1053 (1956)]. We wish to thank a referee for pointing out the latter reference to us.

(7) G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1144 (1962).

(8) National Science Foundation Postdoctoral Fellow, Harvard University, 1963-1964.

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The Structure and Interconversion of Cycloheptatriene

Sir:

Recent interest[1-4] in the structure of cycloheptatriene (Ia) has concerned the contribution of the norcaradiene structure (III) to a resonance hybrid or as a discrete molecule in equilibrium with Ia. We now report that the low temperature proton magnetic resonance spectra show that I is a mixture

Ia, R = H
b, R = D

IIa
b

III
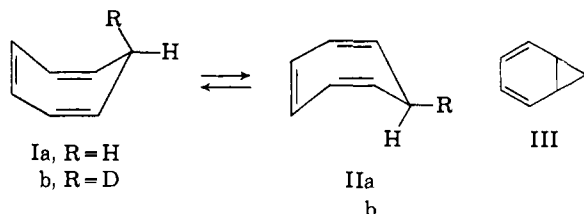
of rapidly equilibrating, nonplanar conformers Ia and IIa, and report the energy barrier for this interconversion. The equilibrium I $\rightleftarrows$ II has been shown previously for 2-t-butyl-3,7,7-trimethylcycloheptatriene[1] and suggested from spectroscopic evidence for 7-deuteriocycloheptatriene (Ib $\rightleftarrows$ IIb).[5] The spectra of Ib and IIb, in addition to supporting a nonplanar conformation, show that the equilibrium constant for the Ib $\rightleftarrows$ IIb interconversion is not one, but the conformer with hydrogen *syn* to the ring (IIb) is present in greater concentration. This difference in stability is attributed to greater eclipsing effects of the *anti*-1-hydrogen with the 2- and 7-hydrogens for protium than for deuterium.

Using new apparatus[6] developed in this laboratory, it was possible to obtain good high resolution n.m.r. spectra at very low temperatures. The spectrum of cycloheptatriene in trifluorobromomethane does not change between room temperature and about $-120°$, but below this temperature, the methylene triplet begins to broaden. Between $-130°$ and $-140°$ there is only a single broad peak in the aliphatic region. At $-141°$, two peaks begin to appear at the sides of the main peak, and as the temperature is lowered, the side peaks grow at the expense of the main peak and move away from it. At $-170°$, the two signals are separated by 86 c.p.s. From the theory of rate processes and assuming an AX spin system,[7] ΔF^* for interchange of the two protons at $^3/_4$ separation is

(1) K. Conrow, M. E. H. Howden, and D. Davis, *J. Am. Chem. Soc.*, **85**, 1929 (1963).
(2) K. Conrow, *ibid.*, **83**, 2958 (1961).
(3) E. J. Corey, H. J. Burke, and W. A. Remers, *ibid.*, **77**, 4941 (1955).
(4) W. von E. Doering, G. Laber, R. Vonderwahl, N. F. Chamberlain, and R. B. Williams, *ibid.*, **78**, 5448 (1956).
(5) C. la Lau and H. de Ruyter, *Spectrochim. Acta*, **19**, 1559 (1963).
(6) The apparatus will be described elsewhere.
(7) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, p. 224.

calculated as 5.7 ± 0.1 kcal./mole ($T_{3/4} = 120.6 \pm 1°$K., $\delta_{max} = 87.5 \pm 3$ c.p.s.).

Since the spectra are broadened by coupling and do not allow more accurate calculations, 7-deuteriocycloheptatriene (Ib) was synthesized by reduction of tropilium bromide with lithium aluminum deuteride (LiAlD$_4$, 95%; 7-deuterium in product was $94 \pm 1\%$ by n.m.r. spectroscopy). The spectra of Ib and IIb in trifluorobromomethane are similar to those of Ia and IIa, and a triplet structure in the methylene peaks can be discerned at $-168°$. However, the chemical shift of the methylene peak above the transition temperature changes with temperature and the areas of the methylene peaks below the transition are not equal (Table I). From a consideration of the dihedral angles between the methylene and vinyl hydrogens ($124 \pm 3°$ and $4 \pm 3°$ from Dreiding models), and the coupling constants calculated from the Karplus curve ($J_{124°} = 3.4$ and $J_{4°} = 8$),[8] the high-field hydrogen is assigned ($J_{H-vinyl} = 4.0 \pm 0.3$) to IIb and the low-field one ($J_{H-vinyl} = 7.2 \pm 0.3$) to Ib. These data allow the calculation of thermodynamic parameters for the equilibrium Ib $\rightleftarrows$ IIb. From the variation of the areas with temperature and the formula $\Delta H \cdot T\Delta S = RT \ln K$ ($K = $ IIb/Ib), $\Delta H = -142 \pm 30$ cal./mole and $\Delta S = -0.7 \pm 0.3$ e.u. Thus, the structure with hydrogen *syn* to the ring is favored.

TABLE I

CHEMICAL SHIFTS OF THE METHYLENE PROTONS OF CYCLOHEPTATRIENE AND 7-DEUTERIOCYCLOHEPTATRIENE AT VARIOUS TEMPERATURES AND THE ENERGY DIFFERENCES FOR THE EQUILIBRIUM OF Ib AND IIb

Cycloheptatriene

Temp., °C.	$\delta_A{}^d$	$\delta_B{}^d$	$\delta_A + \dfrac{\delta_B - \delta_A}{2}$	$K_{areas}{}^a$
+25	$132 + 1^b$			
-86 ± 5	130.8 ± 0.1^b			
-158 ± 1	94.4 ± 0.2	166.8 ± 0.3	130.6 ± 0.3	
-166 ± 1	91.3 ± 1	169.7 ± 0.3	130.5 ± 1	0.97 ± 0.02
-168 ± 1	91.2 ± 0.6	170.4 ± 1	130.8 ± 1	
-170.7 ± 1	86.1 ± 1	172.9 ± 0.6	129.5 ± 1	

7-Deuteriocycloheptatriene

Temp., °C.	$\delta_A{}^d$	$\delta_B{}^d$	$\delta_A + \dfrac{\delta_B - \delta_A}{2}$	K^a	ΔF, cal./mole
+25	$128 \pm 1s$				
-114 ± 1	125.8 ± 0.4^b			1.10^c	-30
-127 ± 1	$125.0 \pm .4^b$			1.14^c	-38
-141 ± 1	$123.2 \pm .3^b$			1.24^c	-56
-158 ± 1	87.3 ± 0.1	168.6 ± 0.3	127.9 ± 0.3	133 ± 0.02	-65
-166 ± 1				1.37 ± 0.02	-67
-168 ± 1	86.2 ± 0.8	169.3 ± 0.1	127 ± 0.3	1.41 ± 02	-72

^{a} II/I. All data taken at 60 Mc.; solvent is CF$_3$Br. ^{b} Spectra show only a single average peak. ^{c} From average chemical shift. ^{d} From TMS internal standard c.p.s. downfield.

Preferential methylene protium– over deuterium–hydrogen bond formation with the 4,5-double bond cannot account for the observed conformational preference, since deuterium hydrogen bonds are stronger than protium hydrogen bonds.[9] Similarly, the effect cannot arise from a steric effect with the opposite double bond, since deuterium is smaller than protium.[10] However, the correct explanation appears to be steric in origin and to arise from eclipsing of the *anti*-1-hydrogen by the 2- and 7-hydrogens. The interactions with eclipsed deuterium are expected to be smaller than with protium leading to a greater stability for structure IIb. From these results, it is estimated that in ethane and derivatives, each deuterium–protium eclipsed pair

(8) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).
(9) C. J. Creswell and A. L. Allred, *J. Am. Chem. Soc.*, **84**, 3966 (1962).
(10) L. S. Bartell, *J. Chem. Phys.*, **32**, 1827 (1960); A. O. McDougall and F. A. Long, *J. Phys. Chem.*, **66**, 429 (1962).