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The Photochemistry of $C_{10}Cl_8O_2$, m.p. 190°.
A Stereochemical Structure Reassignment

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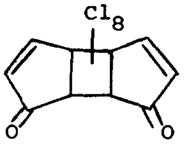
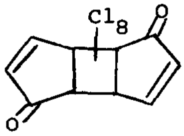
A pair of $C_{10}Cl_8O_2$ diketones [(1) m.p. 190° and (2) m.p. 280°] has been described by P. E. Eaton for which, based on their spectral and chemical behavior, the structural framework of A or B has been tentatively proposed.[1] Subsequently Scribner, who obtained the same diketones by alternate reactions, ascribed, tentatively again, the cis,anti,cis stereochemical structures C and D to (1) and (2), respectively.[2]



A



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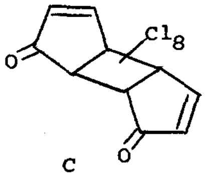
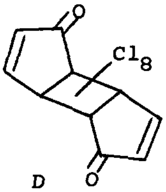
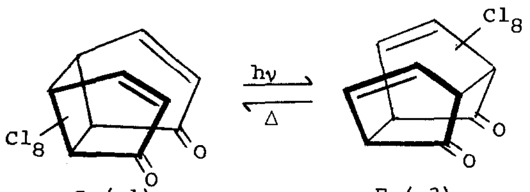


C



D

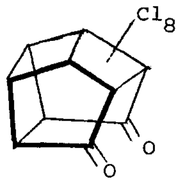
We now wish to report some of our results on the photochemical behavior of (1) which are compatible only with a cis,syn,cis carbon framework for this compound. Irradiation of (1) through a pyrex filter led to a stable photoisomer (3), m.p. 164-165° (dec.) in about 95% yield. Its spectral parameters were: i.r. $\nu(C_2Cl_4)$ an unequal doublet[3] centered at 1820 (C=O) and 1560 cm^{-1} (C=C); u.v. λ(cyclohexane) 217 (ϵ $4x10^4$) and 373 nm (ϵ 25); its mass spectrum displayed a weak parent ion at 432 and a strong C_5Cl_4O peak at 216 m/e; the $C_{10}Cl_8O_2$ composition was also confirmed by combustion analysis (Anal. Calcd: C, 27.56; Cl, 65.09 Found: C, 27.48; Cl, 64.87).



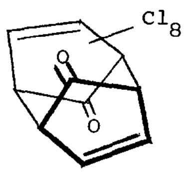
G (=1) E (=3)

Further support for the isomeric structure of (3) was provided by its ready and quantitative reversion to (1) on heating at slightly above its melting point. The facile and nearly quantitative photochemical-thermal cycle indicates that no deep-seated rearrangement took place on irradiation. This fact plus the presence of the high frequency (bridge) carbonyl in the i.r. and the absence of a conjugated unsaturated carbonyl system in the u.v. suggest structure E for the photoketone (3) (the presence of olefinic unsaturation in the i.r. eliminates the cage diketone structure F for (3)).[4]

The most convincing spectral support for the symmetrical structure E of (3) was provided by ^{13}C nmr (c.m.r.) spectroscopy, which revealed the presence of only three kinds of carbon in the molecule: ($\delta CHCl_3$; reference: CS_2) 14.2 (C=O), 55.0 (C=C) and 121.7 p.p.m. (sp^3 C) in the area ratio of 1:2:2.[6] Although two structures, the syn-fused (E) and its anti-fused analog (H), could fit the c.m.r. data, a distinction between these alternatives became possible by dipole moment determination. The high experimental value of 3.4D found for (3) definitely rules out the centrosymmetric structure H and thus establishes, in conjunction with the previous data, structure E for (3) and, consequently, structure G for (1).[8]

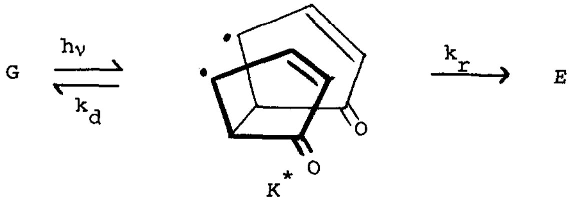


F



H

The reaction of **1** to **3** has a quantum efficiency of 0.033 and is slightly diminished by triplet sensitization ($\Phi = 0.022$ with acetophenone). Photolysis of **1** in the presence of 1,3-cyclohexadiene (1M) reduced the quantum yield to 0.014. The slope of the Stern-Volmer plot obtained equals $k_q\tau$ where k_q is the rate constant for quenching and τ is the triplet lifetime. Assumption of the value of $5 \times 10^9 M^{-1}sec^{-1}$ for k_q[9] allows calculation of $1/\tau$ $(4.2 \times 10^9 sec^{-1})$. The large value of $1/\tau$ is indicative of a very reactive triplet state. A tentative rationalization to account for both the low quantum yield and rapid rate involves a facile deactivation step which could readily occur *via* bond formation as shown below.



Acknowledgement:

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References

1. P. E. Eaton, *Thesis*, Harvard University, 1960.
2. R. M. Scribner, *J. Org. Chem.*, 1965, **30**, 3657.
3. A simple model for E, hexachloro-3-cyclopenten-1-one, also has a split, unsymmetrical C=O centered at 1823 cm^{-1}; the ν (C=C) of this compound is at 1600 cm^{-1}.
4. Under identical, and even more strenuous, photochemical conditions (**2**) did not undergo isomerization as did neither the chlorocarbon $C_{10}C_{12}$ corresponding to syn-B[5] (the carbonyl functions replaced by the CCl_2 groups), the geometry of which precludes a simple (2 + 2) cycloaddition.
5. V. Mark and E. D. Weil, *J. Org. Chem.*, **36**, 676 (1971).

6. Diketone (1), which, depending on the effective planarity of the cyclobutane ring, has a more or less symmetrical structure, displayed five c.m.r. peaks at 10.9(C=O), 55.6 and 34.1 (α and β sp^2 carbons) and 116.9 and 123.3 p.p.m. (sp^3 carbons). Diketone (2) was too insoluble for c.m.r. analysis. The well known, unsymmetrical diketone, octachloroendo-3a-4,7,7a-tetrahydro-4,7-methanoindene-1,8-dione, the presence of which was not detectable by i.r. in the thermolysis and photolysis product, displayed in its c.m.r. spectrum the ten peaks anticipated from its unsymmetrical structure (two C=O at 12.0 and 13.2, the α and β sp^2 carbons at 53.4 and 36.8, the isolated sp^2 carbons at 61.3 (twice the intensity of any of the other peaks) and the four sp^3 carbons at 114.8, 115.6, 117.8, and 119.8 ppm).[7]
7. We are deeply indebted to Professor J. D. Roberts and Dr. R. A. Smith of California Institute of Technology for the c.m.r. determinations of the diketones and of a variety of model compounds. We also acknowledge the participation of Dr. R. Gruber in the early phase of the investigation and Daniel Padowski for the dipole moment measurements.
8. The synthesis of the protio analog of G has recently been reported; P. E. Eaton and S. A. Cerefice, *Chem. Communications*, 1970, 1494.
9. P. J. Wagner and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 1245 (1966).