

PHOTODIMERIZATION OF MALEIC AND FUMARIC ACID DERIVATIVES

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DURING the course of studies directed toward the synthesis of the elusive 1, 2, 3, 4-cyclobutanetetracarboxylic acids^{1, 2, 3, 4, 5} and the unknown tetramethylenecyclobutane,⁶ we have irradiated several derivatives of maleic and fumaric acid in the solid state with formation of the corresponding cyclobutane derivatives. We wish to report our preliminary results with dimethyl fumarate, fumaronitrile, and maleic anhydride.

The olefins were deposited on the inner surface of a glass tube in a thin layer by evaporation of solvent (ether and/or chloroform). An ultraviolet lamp⁷ was then placed in the tube and irradiation was continued for a period of 7-10 days. Cold water passed over the surface of the tube served to dissipate the heat generated in the region of the filaments.

¹ Y. Shibata, Ber. 43, 2619 (1910).

² J. Owen and J.L. Simonsen, J. Chem. Soc. 1424 (1932); 1225 (1933).

³ S. K. Ranganathan, J. Ind. Chem. Soc. 13, 419 (1936).

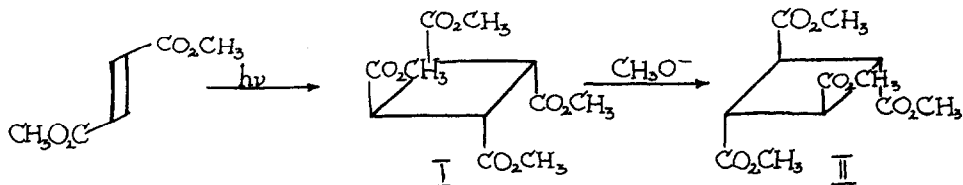
⁴ E. B. Reid and M. Sack, J. Amer. Chem. Soc. 73, 1985 (1951).

⁵ E. B. Reid, Chem. and Ind. 846 (1953).

⁶ J. D. Roberts, A. Streitwieser and C. M. Regan, J. Amer. Chem. Soc. 74, 4579 (1952).

⁷ Westinghouse 15T8 Germicidal Sterilamp; 95% of the UV radiation in the 253.7 m μ region.

Dimethyl fumarate (10 g), upon irradiation for a period of 10 days, afforded 1,2,3,4-tetracarboxymethoxycyclobutane (2 g), m.p. $144-5^{\circ}$.⁸ (Found: C, 50.28; H, 5.55; M. W., 263, Rast. $C_{12}H_{16}O_8$ requires: C, 50.00; H, 5.60, M. W., 288). IR, 5.74 (S), 5.80 (M) (C=O),⁹ 7.72 (S), 8.33 (M), 9.79 (W), 10.55 (W), 11.85 (W), 12.21 (W). Fortunately, Professor R. Criegee and coworkers have recently synthesized three of the four isomeric 1,2,3,4-cyclobutanetetracarboxylic acids in small quantities by ozonolysis of cinnamic acid dimers of known stereochemistry. Through the kindness of Professor Criegee, mixture melting point determination and comparison of IR spectra show that our ester is identical to his tetramethyl ester of structure I.



Treatment of I with sodium methoxide in methanol effects stereochemical equilibration and leads to an ester, the melting point of which (127°) is identical to that of the all-trans product II, obtained by Professor Criegee.

The NMR data¹⁰ also are in agreement with the assignment of

⁸ The infrared spectra were all determined in KBr and the results are reported in microns. We wish to thank R. Hager for assistance in obtaining NMR spectra.

⁹ Only one peak was present in the carbonyl region when the IR spectrum was determined in chloroform.

¹⁰ G. V. D. Tiers, *J. Phys. Chem.* **62**, 1151 (1958); L. M. Jackman, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, p. 50, Pergamon Press, London (1959).

structure I. The spectrum determined in deuteriochloroform shows only two types of protons in the expected ratio of 1:3 with the less intense peak at $\tau = 6.15$ and the other at $\tau = 6.20$. The position of the latter peak is consistent with that of the $-\text{OCH}_3$ protons of methyl acetate ($\tau = 6.35$). The lack of absorption in the region $\tau = 3-4$ attests to the absence of vinyl protons.

Irradiation of fumaronitrile, under similar conditions (7 days), and recrystallization of the ether-insoluble material from acetonitrile provided a product, m.p. $237-9^\circ$ (dec), whose elementary analysis, molecular weight and IR spectrum are consistent with those to be expected for 1,2,3,4-tetracyanocyclobutane. (Found: C, 61.31, 61.45; H, 2.71, 2.79; N, 35.91, 35.86. M. W., 152 (ebullioscopic). $\text{C}_8\text{H}_4\text{N}_4$ requires: C, 61.53; H, 2.58; N, 35.88, M. W., 156). IR, 4.43 (S) ($\text{C}\equiv\text{N}$), 3.35 (S), 7.98 (S), 8.25 (S), 8.72 (S), 9.72 (M), 9.54 (W), 9.64 (W), 10.47 (M), 12.22 (S). The stereochemistry is shown to be the same as that of the dimer of dimethyl fumarate (I) by hydrolysis with hydrogen chloride in acetic acid and esterification with diazomethane to yield I.

Maleic anhydride, upon irradiation, yields a high melting product ($>200^\circ$) which can be isolated by sublimation at 0.005 mm -- first at 93° to remove unreacted maleic anhydride, then at 200° . Its IR spectrum shows the characteristic unconjugated anhydride doublet at 5.40 and 5.62 μ , indicating that it is one of the bis-anhydrides of 1,2,3,4-cyclobutanetetracarboxylic acid (anhydride doublet of cis, cis-3-methylcyclobutane-1,2-dicarboxylic acid at 5.41 and 5.63 μ).¹¹ We are

¹¹ H. N. Cripps, J. K. Williams, V. Tullio and W. H. Sharkey, J. Amer. Chem. Soc. **81**, 4904 (1959).

currently in the process of further characterizing this material.

Although we are primarily interested in the use of these products as starting materials for the preparation of novel small ring systems, we plan to study the scope and mechanism of the dimerization by investigating other selected pure, as well as mixed, substrates. Additional data, which should allow us to determine whether or not the stereochemistry of the dimer is inevitably dictated by the crystal structure of the monomer, as is apparently the case with dimethyl fumarate,¹² will be reported at a later date.

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¹² I. Ellie Knaggs and K. Lonsdale, J. Chem. Soc. 417 (1942).