would have much of the character, repulsions and steric interactions present in the products. On this assumption, the isomer ratios observed in the polar solvents should approach the isomer ratios expected on the basis of the relative stabilities of the stereoisomers. The results are not inconsistent with this idea. *This means that in most cases a stereoselective synthesis of either isomer of IV,* $R' = H$, *is possible;* in poor solvating and low dielectric media the *cis* isomer IV, $R' = H$, Y and Z *cis*, predominates, while in strongly solvating and high dielectric media the more stable isomer, usually *trans*, predominates.

Nothing reported in the present work concerns the origin of anion III. By implication, the anion could be formed from suitably substituted three carbon chains, *e.g.*, glutaric esters, and the same solvent effects should apply to these cases also. This possibility is being examined as well as the extension of these solvent effects to our current research on cyclopropanes substituted at all three ring carbons.

Acknowledgment.—This work was supported in part by a grant from the Research Corporation. Tennessee Eastman Company furnished a sample of hexamethylphosphoramide.

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RECEIVED OCTOBER 29, 1960

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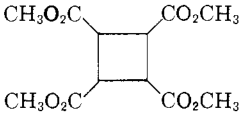
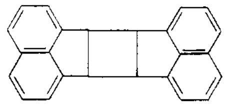
cis,cis,cis-1,2,3,4-TETRACARBOMETHOXYCYCLOBUTANE; STRUCTURE OF β-HEPTACYCLENE

Sir:

In connection with stereochemical studies on photodimers of fumaric and maleic acid derivatives,[1] we have synthesized *cis,cis,cis*-1,2,3,4-tetracarbomethoxycyclobutane (I) by ozonolysis of β-heptacyclene (II), the low melting dimer of acenaphthylene. This isomer is the last of the four possible tetracarbomethoxycyclobutanes which remained to be synthesized.



I, *cis,cis,cis*
IV, *cis,trans,cis*
V, *trans,trans,trans*



II, *cis*, β
III, *trans*, α

The high melting isomer of heptacyclene, the so-called α-form (III), was shown unequivocally by X-ray diffraction studies[2] to possess a cyclobutane ring and a *trans*-orientation of the peri-naphthalene groups. The low melting β-form generally has been assumed to have the *cis*-configuration.[3,4] The results of ozonolysis prove this conclusively.

β-Heptacyclene[5] was ozonized at 25° for seventeen hours in 90% aqueous acetic acid.[6] Subsequent oxidative decomposition of the reaction mixture with 30% hydrogen peroxide at room temperature (3 days) and removal of solvents afforded a white solid. Esterification of this residue with diazomethane in benzene and recrystallization from xylene gave I in 5.6% yield, m.p. 203–205°. *Anal.* Calcd. for $C_{12}H_{16}O_8$: C, 50.00; H, 5.60; mol. wt., 288. Found: C, 50.19; H, 5.77; mol. wt. (Rast), 287.

The assignment of *cis*-stereochemistry and the cyclobutane character to both β-heptacyclene and its ozonolysis product I is based upon these data:

(a) Degradation of α-heptacyclene (III) under identical conditions affords the expected and thermodynamically unstable *cis,trans,cis*-1,2,3,4-tetracarbomethoxycyclobutane (IV) of independently proved configuration.[1] Since no rearrangement occurs in this case, it appears doubtful whether any occurs during ozonolysis of the β isomer, II.

(b) Both I and IV are isomerized to the well characterized and thermodynamically more stable "all-*trans*"-tetraester V by heating at 300° in a sealed tube for twenty hours.[1]

(c) The physical properties of I differ from those of the remaining stereoisomers of tetracarbomethoxycyclobutane. The other three isomers were prepared independently by Criegee from cinnamic acid dimers of known stereochemistry and in our laboratories from dimers of fumaric and maleic acid derivatives.[1,7]

(d) The infrared spectrum of a totally esterified but not otherwise characterized product obtained in very small yield by Criegee from the irradiation of maleic anhydride in solution (cyclohexane) is identical with the spectrum of I. Although the major product obtained by irradiation in solution is the known *trans*-cyclobutane-bis-anhydride,[7,8] a small amount of another anhydride is formed and most likely possesses *cis*-stereochemistry since only two unrearranged cyclobutane isomers are possible from maleic anhydride.[7,8]

(e) The infrared spectrum of I is reminiscent of those of the other tetracarbomethoxycyclobutanes. Absorption bands (KBr) are found at these wave lengths (μ): 3.34, 3.38 (w), 5.72 (s) (C=O), 6.95 (m), 8.34, 8.47 (s), 9.31 (m), 10.45 (m), 12.00 (m), 12.84 (m).

Our work dealing with the chemistry of I and other symmetrically tetra-substituted cyclobutane derivatives will be reported at a later date.

We gratefully acknowledge support of this work by the National Science Foundation and the Research Corporation.

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RECEIVED NOVEMBER 19, 1960

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[1] G. W. Griffin, J. E. Basinski and A. F. Vellturo, *Tetrahedron Letters*, **3**, 13 (1960).

[2] J. D. Dunitz and L. Weissman, *Acta Cryst.*, **2**, 62 (1949).

[3] Unpublished n.m.r. data obtained by Dr. Harold Shechter are consistent with the *cis*-cyclobutane structure.

[4] A. Mustafa, *Chem. Revs.*, **51**, 1 (1952).

[5] K. Dziewonski and C. Paschalski, *Ber.*, **46**, 1986 (1913).

[6] A Welsbach Model T-23 laboratory ozonator was employed with a flow rate of 3.66 g. of ozone per hour.

[7] R. Criegee and H. Höver, private communication.

[8] G. Griffin and A. Vellturo, unpublished results. When the irradiation of maleic anhydride is carried out in the solid state, the only product detected is the *trans*-cyclobutane-bis-anhydride. Similarly, acenaphthylene affords only the *trans*-dimer in the solid state in sharp contrast to irradiation in solution.

[9] Undergraduate National Science Foundation Summer Fellowship Recipient, 1960.