into the benzene ring. The stereochemical fate of such an intermediate would depend entirely on the symmetry properties of its environment, and would be expected to vary as the character of the solvent and of the basic catalyst were changed.

In the third type of system, exemplified by the nitrile, ester and amide of Table I, a flat carbanion is also envisioned as intermediate.[3] These intermediate anions are ambident, and probably protonate largely on the more electronegative element (oxygen or nitrogen) and produce symmetrical tautomers which in a second stage go to the more stable nitrile, ester or amide forms of the molecule. Such a sequence would invariably involve substitution with racemization as the steric course. The effects of other carbanion-stabilizing groups on the stereochemistry of hydrogen-deuterium reactions, as well as the detailed kinetics of these reactions, are under active investigation.

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[3] S. K. Hsu, C. K. Ingold and C. L. Wilson [*J. Chem. Soc.*, 78 (1938)] observed that the rates of hydrogen–deuterium exchanged and of racemization of 1-phenyl-2-methyl-1-butanone in dioxane–deuterium oxide were equal to one another.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA AT LOS ANGELES
LOS ANGELES 24, CALIFORNIA
DONALD J. CRAM
W. DAVID NIELSEN
BRUCE RICKBORN

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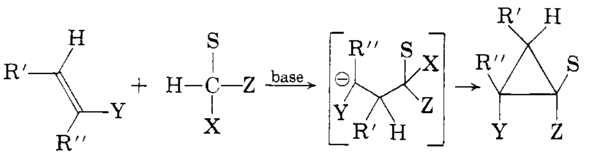
THREE MEMBERED RINGS. II. THE STEREOSELECTIVE FORMATION OF DIFUNCTIONAL CYCLOPROPANES

Sir:

A general method for the preparation of polyfunctional cyclopropanes recently has been described.[1] It generally has been observed that when only two carbons of the cyclopropane ring are substituted (IV, R′ = H), then Y and Z are oriented *cis* in the predominant or exclusive product.[1a,1c,1d,2,3,4] To explain the preference for *cis* isomer formation, the assumption has been made that there is some attractive interaction between Y and Z in an intermediate anion, III. Examination of models based on this assumption has led to the following suggestion: The presence in the reaction medium of a material which can strongly solvate III and/or the cation associated with it, and also can raise the dielectric constant of the medium, should reduce or eliminate the attractive interaction.



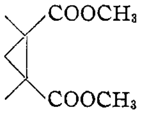
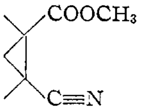
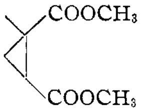
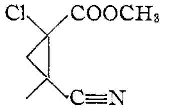
I II III IV

R′, R″ = H, alkyl, aryl; R′ may also be –COOR
S = H, alkyl, aryl, COOR, Cl
Y, Z = –COOR, –C≡N, $-\underset{\overset{\Vert}{O}}{C}C_6H_5$
X = Cl, Br

The suggestion has been tested by running the reaction in dimethylformamide and various mixtures of benzene and hexamethylphosphoramide.[5] The experimental conditions are those using sodium hydride described previously[1a,2] with only minor modifications. In both systems 100 ml. of solvent were used with 0.1 mole of chloride, II; the dimethylformamide reaction mixtures were filtered to remove sodium chloride and then distilled; the hexamethylphosphoramide mixtures required thorough washing to remove the amide completely from the benzene solution. Some results are summarized in Tables I and II; the results of some previously reported runs are included for comparison.

TABLE I

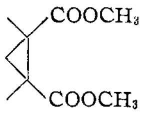
THE VARIATION OF YIELDS AND ISOMER RATIOS[a] FOR SEVERAL DIFUNCTIONAL CYCLOPROPANES PREPARED IN VARIOUS SOLVENTS

Compound	C_6H_6 or C_7H_8[b]	Dimethylformamide[b]	50% C_6H_6:hexamethylphosphoramide[b]
	71 (7)[c]	62 (66)	60 (64)[d]
	59 (25)[c]	55 (66)	
	70[e] (17)		70 (90)
	64 (20)[c]	13 (45)	65 (38)

[a] Isomer ratios were determined by gas phase chromatography; see ref. 1a. [b] The first number is the yield of mixed isomers; the number in parentheses is the percentage of *trans* isomer in the isomer mixture. [c] Ref. 1a. [d] By interpolation from results of Table II. [e] Ref. 2.

TABLE II

VARIATION OF ISOMER RATIO[a] WITH SOLVENT COMPOSITION

FOR 

C_6H_6:hexamethylphosphoramide	9:1	8:2	6:4	4:6
trans:*cis*	37:63	50:50	64:36	64:36

[a] See (a), Table I.

It is quite obvious that solvent has a marked effect on the isomer ratio; the results are consistent with the proposed suggestion. It also seems reasonable to assume that with the attractive interaction of Y and Z of anion III reduced or eliminated the transition states leading to the two possible isomers

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[1] (a) L. L. McCoy, *J. Org. Chem.*, in press; (b) M. Mousseron, R. Fraisse, R. Jacquier and G. Bonavent, *Compt. rend.*, **248**, 1465 (1959); (c) R. Fraisse, *Bull. soc. chim. France*, 1102 (1959); (d) R. Fraisse and M. Guitard, *Bull. soc. chim. France*, 788 (1960); (e) D. T. Warner, *J. Org. Chem.*, **24**, 1536 (1959).

[2] L. L. McCoy, THIS JOURNAL, **80**, 6568 (1958).

[3] M. Mousseron, R. Fraisse, R. Jacquier and G. Bonavent, *Compt. rend.*, **248**, 2840 (1959).

[4] M. Mousseron, R. Fraisse, *ibid.*, **248**, 887 (1959). It is shown here that isomerization is possible under basic conditions if R″ = H in IV.

[5] (a) H. E. Zaugg, B. W. Horrom and S. Borgwardt, THIS JOURNAL, **82**, 2895 (1960); (b) H. E. Zaugg, *ibid.*, **82**, 2903 (1960).

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.

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DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY LAYTON L. MCCOY
NEW YORK 27, NEW YORK

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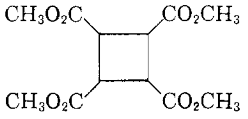
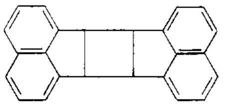
cis,cis,cis-1,2,3,4-TETRACARBOMETHOXYCYCLOBUTANE; STRUCTURE OF β-HEPTACYCLENE

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.

DEPARTMENT OF CHEMISTRY
YALE UNIVERSITY GARY W. GRIFFIN
NEW HAVEN, CONNECTICUT DANIEL F. VEBER[9]

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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.