resulted in the isolation of a monobromide product, m.p. 117–119° (sealed tube).

Anal. Calcd. for $C_{10}H_{15}Br$: Br, 37.16. Found: Br, 36.85.

Bromination of adamantane on a 1-mole scale, using the proportions described previously and a catalyst ratio of BBr_3–Al_2Br_6 of 10[3], resulted in the isolation of dibromoadamantane in a yield of 74%. The course of the reaction was established as dibromination on the basis of melting point, bromine analysis, and characteristic slight solubility in *n*-hexane at room temperature.

Silver ion-promoted hydrolysis of a portion of this material by Stetter's procedures[3] resulted in the synthesis of 1,3-dihydroxyadamantane, m.p. (sealed tube) 315°, lit.[3] m.p. 315°.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.14; H, 9.28.

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Three-Membered Rings. VI. A Possible Explanation for the "Solvent Effect" Noted in the Partial Asymmetric Synthesis of *trans*-1,2-Cyclopropanedicarboxylic Acid

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Recently, Walborsky and several co-workers[1] reported an apparent "solvent effect" in which the solvent used in a reaction to form the 1,2-cyclopropanedicarboxylate system controlled which enantiomer of the *trans* isomer was observed. Subsequently, in a paper on a related topic, Walborsky and Pitt[2] suggested briefly that the "solvent effect" might arise through the solvent controlling "the cisoidal–transoidal rotamer equilibrium" of the optically active chloro ester starting material.

The statement in ref. 9 of the original communication[1] that only "minor to trace amounts of the *cis* acid" could be isolated suggested two possibilities: (1) the bulky menthyl ester group controlled the stereochemistry of ring closure so that the *trans* isomer was formed independent of any stereoselective solvent effect[3]; (2) the *cis* isomer was present in the crude ester, but was isomerized to the *trans* isomer during the saponification step. If the first possibility were correct, it might offer a means of controlling the stereochemical formation of cyclopropane diesters by varying the size of the ester group. Consequently, the following brief investigation was carried out.

(−)-Menthyl chloroacetate and methyl acrylate were allowed to react with sodium hydride and methyl alcohol at about 25° in benzene diluent. Addition of water and removal of benzene left a mixture of unchanged (−)-menthyl chloroacetate and products. Half of this crude mixture was saponified by potassium hydroxide in boiling ethylene glycol[4] and resulted in the isolation of *trans*-1,2-cyclopropanedicarboxylic acid in 35% over-all yield from the (−)-menthyl chloroacetate; no indication of *cis* isomer was observed The other half of the mixture was reduced with lithium aluminum hydride and the resulting complex was decomposed with acetic anhydride and acetic acid.[5] The mixture of acetates obtained was analyzed by gas phase chromatography with the results shown in Table I. A similar sequence (the saponification step was omitted) run in dimethylformamide followed by reduction, acetylation, and gas phase chromatographic analysis gave the results also shown in Table I.

TABLE I

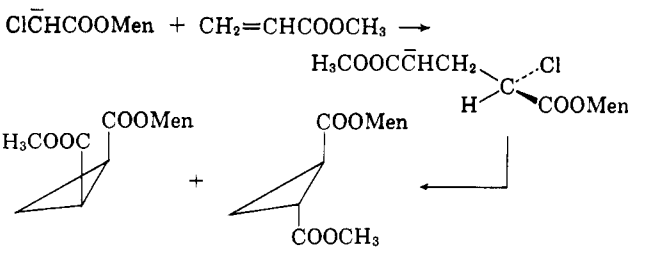
GAS PHASE CHROMATOGRAPHIC ANALYSIS OF THE REDUCTION–ACETYLATION PRODUCTS OBTAINED FROM CRUDE MENTHYL METHYL 1,2-CYCLOPROPANEDICARBOXYLATE

Compound	C_6H_6 solvent	$HCON(CH_3)_2$ solvent
Menthyl acetate	100[a]	92[a]
I[b] + II[b]	18[a]	24[a]
I[b]	18[c]	>92[c,d]
II[b]	82[c]	<8[c,d]

[a] These are over-all yields based on initial (−)-menthyl chloroacetate. [b] I is *trans*-1,2-bis(acetoxymethyl)cyclopropane; II is *cis*-1,2-bis(acetoxymethyl)cyclopropane. [c] These are the relative amounts of the two isomers. [d] The *cis* isomer peak appeared as an incompletely resolved small shoulder on the long retention time side of the *trans* peak.

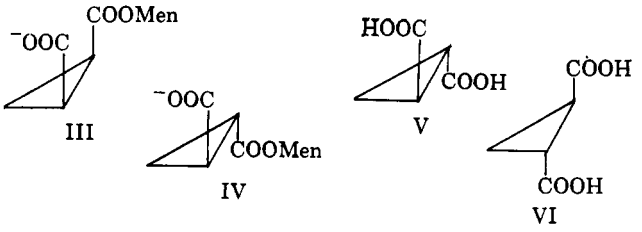
The results clearly show that the crude 1,2-cyclopropanedicarboxylate esters have a "normal" isomer composition expected under solvent control of their formation.[3] The absence of *cis* isomer in the saponification product shows that the second possibility, isomerization from *cis* to *trans* during saponification, must occur.

This *cis* to *trans* isomerization permits a relatively simple interpretation of the previously observed "solvent effect" in partial asymmetric synthesis.[1] The initial addition of menthyl chloroacetate anion to methyl acrylate will establish an asymmetric center of the same enantiomeric form in all solvents, but the solvent will control the *cis* to *trans* ratio in the subsequent ring closure. Note that because the two ester groups are unlike, both the *trans* and *cis* isomers will be partially asymmetric and to the same extent because of their common origin. Saponification would be expected



to proceed stepwise, and for the *cis* isomer the initial product would be III. This methyl ester saponification should compete favorably with isomerization since it is known that saponification of methyl ethyl esters of these diacids produced in much the same way as described in this work does result in an excess of *cis*

(1) Y. Inouye, S. Inamasu, M. Ohno, T. Sugita, and H. M. Walborsky, *J. Am. Chem. Soc.*, **83**, 2962 (1961).
(2) H. M. Walborsky and C. G. Pitt, *ibid.*, **84**, 4831 (1962).
(3) L. L. McCoy, *ibid.*, **84**, 2246 (1962).
(4) F. J. Impastato, L. Barash, H. M. Walborsky, *ibid.*, **81**, 1514 (1959).
(5) A. T. Blomquist and D. T. Longone, *ibid.*, **81**, 2012 (1959).



over *trans* diacid.[6] The menthyl group should hinder saponification of that ester, while the carboxylate anion should stabilize the adjacent position towards isomerization, at least relative to the ease of isomerization of the ester position. These two factors should lead to isomerization at the next step to produce IV. When the menthyl group eventually is saponified, the resulting *trans* diacid V will be the enantiomer of *trans* diacid VI, obtained directly by saponification of the *trans* diester.

Some isomerization of the *cis* diester undoubtedly will occur, but this should lead to *racemic* diacid. The rotations of the *trans* diacids obtained should be roughly proportional to the excess of one isomer over the other. For the present system, it is probably true that the *cis* to *trans* ratio in benzene will always be less than the *trans* to *cis* ratio in dimethylformamide. These two factors, isomerization of the diester and difference in the relative isomer ratios, should both operate so as to make the optical yield in benzene smaller than that in dimethylformamide. This is consistent with observation.[7]

In summary, it is suggested that partial asymmetric synthesis of the 1,2-cyclopropanedicarboxylate system is independent of the solvent, but that the solvent does control the *cis* to *trans* isomer ratio; and that the observed formation of enantiomeric *trans*-1,2-cyclopropanedicarboxylic acids can be accounted for by an asymmetric *cis* to *trans* isomerization during saponification.[7]

Experimental[8]

(−)-Menthyl chloroacetate was prepared in 87% yield, b.p. 125–126° (10 mm.).[9,10] *cis*-1,2-Bis(acetoxymethyl)cyclopropane, b.p. 115–120° (13–14 mm.), 46% yield, and *trans*-1,2-bis(acetoxymethyl)cyclopropane, b.p. 125–128° (17–18 mm.), m.p. 43–45° (petroleum ether, b.p. 30–60°), 67% yield, were prepared from the pure *cis* and *trans* dimethyl cyclopropanedicarboxylates essentially as described by Blomquist and Longone[5] for the *trans* isomer. Gas phase chromatographic analyses were made with a Beckman GC-2A chromatograph operating at 190° with a Beckman Column No. 70026.

Reaction in Benzene Diluent.—Methyl acrylate (10.4 g., 0.24 mole) and (−)-menthyl chloroacetate (28.0 g., 0.12 mole) were added to sodium hydride (2.88 g., 0.12 mole) in benzene (10 ml.). Methanol then was added dropwise very slowly until a convenient, steady rate of gas evolution was obtained. The reaction was maintained between 24–26° by a water bath. Gas evolution stopped after about 4 hr. and after an additional half hour of stirring, water was added, and the organic phase isolated and dried. Removal of the benzene at aspirator pressure left 39.1 g. of crude ester.

A.—Half of the crude ester was saponified with potassium hydroxide (13.4 g., 0.24 mole) in refluxing ethylene glycol (940 ml.).[4] After 72 hr., about 80% of the ethylene glycol was removed by distillation and water was added to the residue which was extracted continuously with ether until no more neutral material was removed. The aqueous solution then was acidified and extracted continuously with ether for 24 hr. Evaporation of the acidic ether extract left a mush which was diluted with a small amount of chloroform and filtered. The solid, 2.7 g., was identified as essentially pure *trans*-1,2-cyclopropanedicarboxylic acid, m.p. 174–176°, by its infrared spectrum; the yield was 35%. No indication for the presence of *cis* isomer was observed.

B.—The second half was reduced and acetylated essentially by the procedure of Blomquist and Longone,[5] but a slight modification of the work-up was used. After filtration of the metal acetate salts, the filtrate was washed with water, and the washes were extracted with ether. The combined ether extracts and organic filtrate were dried and distilled. The product fraction was taken over the range 105–135° (27 mm.) and amounted to 14.2 g.; there was negligible pot residue. This distillate was analyzed by gas phase chromatography; the chromatogram peaks were identified by comparison of retention times with those of known compounds. The analytical results are shown in Table I.

Reaction in Dimethylformamide.—Using dimethylformamide (50 ml.) in place of benzene, the reaction sequence was repeated. The crude ester amounted to 36.2 g. Reduction–acetylation of half of this gave 13.6 g. of product acetates which were analyzed by gas phase chromatography; the results are shown in Table I.

(6) L. L. McCoy, *J. Am. Chem. Soc.*, **80**, 6568 (1958).

(7) The most obvious way of refuting or establishing a direct "solvent effect" in partial asymmetric synthesis would be to isolate the *trans* diacetate (I) from the reduction–acetylation sequence for each solvent and compare their rotations. The small yield of the *trans* isomer in the benzene solvent and the close boiling points of the *cis* and *trans* isomers almost demands that separation be accomplished by preparative scale gas chromatographic equipment; unfortunately, the author does not have the necessary equipment.

(8) Melting points were taken on a Fisher-Johns hot stage and are corrected; boiling points are uncorrected.

(9) K. Sisido, O. Nakanisi, and H. Nozake, *J. Org. Chem.*, **26**, 4878 (1961).

(10) C. R. Hauser, B. E. Hudson, B. Abramovitch, and J. C. Shivers, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N.Y., 1955, p. 142.

Improved Procedures for Converting Higher α-Olefins to Methyl Ketones with Palladium Chloride

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An attractive approach to the synthesis of methyl ketones from normal α-olefins has been described by J. Smidt, *et al.*[3] Their procedure employs an aqueous solution of palladium chloride to oxidize the olefin and utilizes the presence of cupric chloride and oxygen to maintain the palladium in a +2 state. The resulting reactions may be represented by the following equations.

$$PdCl_2 + R{-}CH{=}CH_2 + H_2O \longrightarrow R{-}\overset{\overset{O}{\|}}{C}{-}CH_3 + Pd + 2HCl \quad (1)$$

$$Pd + 2CuCl_2 \longrightarrow PdCl_2 + 2CuCl \quad (2)$$

$$2CuCl + 1/2O_2 + 2HCl \longrightarrow 2CuCl_2 + H_2O \quad (3)$$

Other investigators have utilized such reagents as *p*-benzoquinone or hydrogen peroxide to reoxidize the palladium.[4] The mechanism of the olefin oxidation step has been discussed in several publications.[5,6]

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(2) To whom inquiries should be sent.

(3) J. Smidt, *et al.*, *Angew. Chem.*, **71**, 176 (1959).

(4) I. I. Moiseev, M. N. Vargaftik, and Ya. K. Syrkin, *Dokl. Akad. Nauk. SSSR*, **130**, 820 (1960).

(5) M. N. Vargaftik, I. I. Moiseev, and Ya. K. Syrkin, *ibid.*, **139**, 1396 (1961).

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