Experimental

Preparation of (2,2-Dicarbethoxypropyl)ethoxydimethylsilane (II).—Sodium, 7.3 g. (0.318 g.-atom), was treated with 100 ml. of absolute ethanol. To the cooled mixture was added 152.9 g. (0.954 mole) of diethyl malonate (200% excess). The mixture was then heated at reflux temperature as 25 g. (0.159 mole) of bis(chloromethyl)dimethylsilane[8] in 40 ml. of absolute ethanol was added slowly. Subsequent to refluxing for 24 hr., 100 ml. of ethanol was removed by distillation and replaced with 200 ml. of water. The mixture was extracted several times with ether and dried over sodium sulfate. Following the removal of solvent and excess diethyl malonate by distillation, there was obtained 28.5 g. (92.5%, based on the g.-atom of sodium employed) of product, b.p. 79–81° (0.25 mm.), $n^{20}_{\rm D}$ 1.4345, d^{20}_{20} 1.0101 [lit.[1] b.p. 141–143° (15 mm.), $n^{25}_{\rm D}$ 1.4318, d^{25}_{4} 0.997].

Anal. Calcd. for $C_{13}H_{26}O_5Si$: C, 53.80; H, 8.96; M_D, 76.19. Found: C, 53.90, 54.09; H, 8.93, 8.72; M_D, 74.96.

The infrared spectrum of II as a capillary cell contained the pertinent absorption bands shown in Table I.

TABLE I

THE INFRARED SPECTRUM OF II

Band position, μ	Intensity[a]	Characteristic[b,c]
3.35, 3.44	m, w	Aliphatic C–H
5.78	s	CO_2R
7.8	m	
8.0	m	$Si–CH_3$
8.2	s	CO_2R
8.50, 8.62	m, m	Possibly Si–alkyl
9.12, 9.27, 10.58	s, m, m	$Si–O–C_2H_5$
11.94, 12.67	s, m	$Si–CH_3$

[a] Letters indicate the relative intensities of absorption bands: s, strong; m, medium; w, weak. [b] L. J. Bellamy "The Infrared Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1954. [c] A. L. Smith, *Spectrochim. Acta*, **16**, 87 (1960).

The reaction residue consisted of 3.5 g. of red oil. Distillation of this residue under reduced pressure gave small amounts of materials which were not investigated completely.[9]

Hydrolysis of II.—A mixture of 4.0 g. (0.1 mole) of sodium hydroxide, 5.0 g. (0.0172 mole) of II, and 50 ml. of ethanol was refluxed for 5 hr. The precipitated potassium salt was removed by filtration and the filtrate discarded. The crude potassium salt was dissolved in 10 ml. of warm water and made just acidic with concentrated hydrochloric acid. The acidified solution was extracted with four 30-ml. portions of ether and dried over sodium sulfate. Evaporation of the solvent gave a white solid which was taken up in ethyl acetate. Addition of petroleum ether (b.p. 60–70°) gave 1.76 g. (62%) of *sym*-bis(2,2-dicarboxypropyl)tetramethyldisiloxane (III), m.p. 133–135° dec. (lit.[2] m.p. 131–133° dec.).

The infrared spectrum of III as a potassium bromide pellet contained the pertinent absorption bands shown in Table II.

TABLE II

THE INFRARED SPECTRUM OF III

Band position, μ	Intensity[a]	Characteristic[b]
2.75 to 4.15	broad	CO_2H
5.76	s, s	CO_2H
7.8	m	
8.0	m	$Si–CH_3$
8.40	m	Possibly Si–alkyl
9.65	s	Si–O–Si
11.91, 12.35, 12.55	s, s, m	$Si–CH_3$

[a] See footnote *a* in Table I. [b] See footnotes *b* and *c* in Table I.

Acknowledgment.—This research was supported by the United States Air Force under Contract AF 33(616)-6463 monitored by the Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio. The authors are grateful to Dr. R. King for determination of the n.m.r. spectrum and to Dr. G. Morris for aid in its interpretation.

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[8] We wish to express our thanks to Dr. R. N. Meals for providing us with this material.

[9] Earlier workers (see ref. 2) have reported the isolation of a material believed to be *sym*-tetramethyldi(2,2-dicarbethoxy)propyldisiloxane, b.p. 155–161° (0.05 mm.), $n^{24}_{\rm D}$ 1.4468. We isolated a small amount (*ca.* 0.5 g.) of material which on the basis of its physical constants [b.p. 140–142° (0.005 mm.), $n^{20}_{\rm D}$ 1.4500] and infrared spectrum (band at 9.55 μ indicative of the Si–O–Si linkage) may be this symmetrical siloxane.

Dibromination of Adamantane[1]

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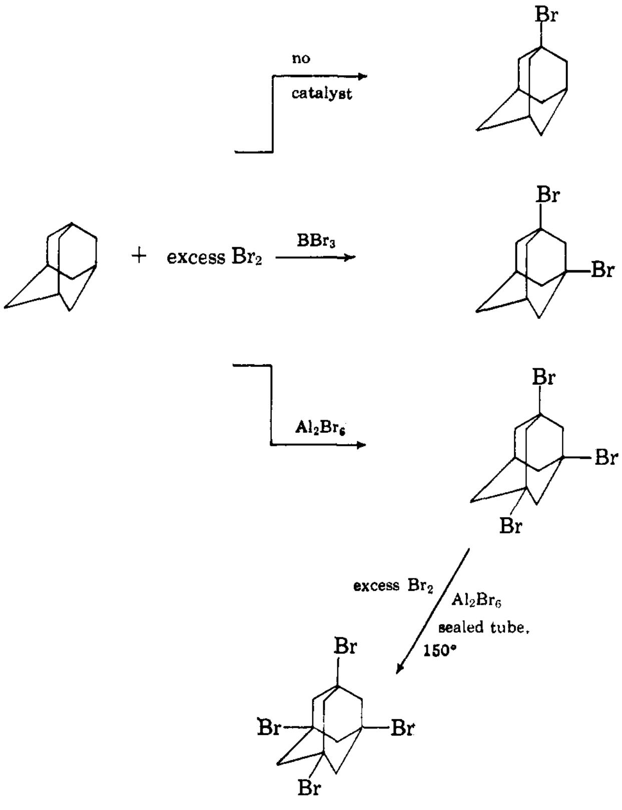
It has been reported that highly selective substitution on the adamantane ring system can be effected by bromination.[2,3] Thus, by the use of proper catalysts and conditions, one, two, three, or four bromine atoms can be inserted on the bridgehead sites.



Attempts in this laboratory to prepare the dibromosubstituted adamantane derivative using boron bromide as catalyst resulted in every case in the isolation of monobrominated adamantane in yields of 60 to 80%.

It was postulated that trace amounts of aluminum bromide may be necessary as cocatalyst since boron bromide can be made easily by a metathetical reaction

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[1] The semitrivial name "adamantane" has been used to designate the tricyclo[3.3.1.1^{3,7}]decane ring system.

[2] H. Stetter, M. Schwarz, and A. Hirschhorn, *Ber.*, **92**, 1629 (1959).

[3] H. Stetter and C. Wulff, *ibid.*, **93**, 1366 (1960).

of boron fluoride with aluminum bromide.[4,5] To investigate this hypothesis, a qualitative experiment was performed in which a trace of aluminum bromide was added to the boron bromide–bromine reaction mixture. The isolated product was identified as dibromoadamantane by melting point, depression of mixture melting point with authentic monobromoadamantane, and bromine analysis. Significant differences in retention times in vapor phase chromatograms, and in the chemical shifts and their relative intensities observed in proton magnetic resonance spectra for authentic monobromoadamantane and the product from the previous experiment also indicated nonidentity.

Repetition of this experiment resulted in a mixture of products with slightly high bromine content for disubstitution. This suggested, as might be predicted from earlier work,[3] that the degree of substitution might be quite sensitive to aluminum bromide concentration. Experiments with various boron bromide–aluminum bromide ratios indicated that at a molar ratio of BBr_3–Al_2Br_6 of 1000:1, dibromoadamantane was the major reaction product. At a ratio of 9:1, tribromination was the predominant course of reaction; while at a catalyst ratio significantly less than 1000:1, monobromide was the only product isolated. Aluminum bromide at this critical concentration (10^{-4} moles of Al_2Br_6 per mole of adamantane) in the absence of boron bromide did not effect dibromination.

Application of this information to a larger scale experiment (one mole of adamantane) resulted in the synthesis of dibromoadamantane in a 74% yield. Hydrolysis to give the diol added confirmatory evidence.

Although the mechanism for cocatalysis by aluminum bromide is not in hand, it would appear that both boron bromide and aluminum bromide are necessary, and that there exists a critical concentration of aluminum bromide required to selectively effect dibromination.

Experimental

Monobromination.—Procedures as described by Stetter[3] in all cases resulted in monobromination. Bromine content of the products in some cases was low even for monobromide, suggesting contamination with unreacted adamantane.

When bromine was dried with concentrated sulfuric acid and the boron bromide freshly distilled, crude monobromoadamantane was isolated in an 80% yield. An aliquot for analysis was purified by recrystallization from *n*-hexane at −78°, m.p. (sealed tube) 117°, lit.[2] m.p. 118° for 1-bromoadamantane.

Anal. Calcd. for $C_{10}H_{15}Br$: Br, 37.16. Found: Br, 37.34.

With bromine distilled from phosphorus pentoxide and boron bromide distilled from mercury, monobromoadamantane was isolated in a 65% yield after recrystallization from *n*-hexane at −78°, m.p. (sealed tube) 118°.

Anal. Calcd. for $C_{10}H_{15}Br$: Br, 37.16. Found: Br, 37.73.

Dibromination.—To a stirred mixture of 50 ml. (1 mole) of bromine and 2.5 ml. (0.025 mole) boron bromide there was added a few milligrams of aluminum bromide. The only precautions to operate under anhydrous conditions was to maintain a blanket of nitrogen over the reaction mixture during addition of reactants to a four-necked flask fitted with stirrer, reflux condenser, and gas inlet. Adamantane,[7] 13.6 g. (0.1 mole), was added portionwise from a small flask attached to the fourth neck by means of Gooch crucible tubing. After refluxing for 90 min., hydrogen bromide evolution was no longer evident. Excess bromine was decomposed and product isolation accomplished as described previously. The residue, after removal of carbon tetrachloride, was recrystallized from methanol and from *n*-hexane at room temperature, m.p. (sealed tube) 112–113°, lit.[3] m.p. 112° for 1,3-dibromoadamantane. A mixture of this material with authentic 1-bromoadamantane melted 88–100°.

Anal. Calcd. for $C_{10}H_{14}Br_2$: Br, 54.36. Found: Br, 54.65.

Vapor phase chromatographic analysis on a 1-m. column of 20% Dow Corning high vacuum grease on 40–60 Chromosorb W at 178°, preheater at 287°, and carrier gas flow of 60 cc. per min. gave a single peak with retention time of 6.7 min.[8] A proton magnetic resonance spectrum of three bands at 7.17, 7.70, and 8.28 τ with relative intensities of 1:5:1, respectively, was recorded in carbon tetrachloride with tetramethylsilane as internal standard.[9]

Additional dibromoadamantane, isolated from the hexane and methanol mother liquors, was found to be of 98–99% purity by v.p.c. The combined weights of all fractions was 17.9 g., a 61% yield of dibromoadamantane.

Repetition of the preceding experiment, using three times the quantities in the same proportions resulted in the isolation of two fractions: m.p. 113°, 54.98% Br; m.p. 96–105°, 55.41% Br. V.p.c. indicated the lower melting fraction to be a mixture of several components, some with retention times greater than that for dibromoadamantane.

Effects of Catalyst Ratio.—In a nitrogen atmosphere, 5.3 g. (0.01 mole as Al_2Br_6) of aluminum bromide was dissolved in bromine in a 10-ml. volumetric flask, resulting in a solution approximately 1 *M* in Al_2Br_6. Aliquots were diluted stepwise with bromine, giving aluminum bromide solutions of decreasing concentrations. A series of experiments was performed in which 6.8 g. (0.05 mole) adamantane was added portionwise in 30 min. to 25 ml. (0.5 mole) of bromine and a combination of boron bromide and of aluminum bromide–bromine solution. Boron bromide, 1.1 ml. (0.0113 mole), and 1.3 ml. of 1 *M* Al_2Br_6 in Br_2 was used in the first experiment, resulting in a molar ratio of BBr_3–Al_2Br_6 of approximately 9:1. For catalyst ratios of BBr_3–Al_2Br_6 of 10^3 and 10^5, 1.2 ml. (0.013 mole) of boron bromide and 1.3 ml. of 10^{-2} *M* and 10^{-4} *M* Al_2Br_6–Br_2 solutions, respectively, were used. The mixtures were refluxed for 90 min., allowed to cool to room temperature in 30 min., and poured into ice. Carbon tetrachloride, 75 ml., was added, excess bromine decomposed with sodium bisulfite, and the aqueous layer extracted twice with 25-ml. portions of carbon tetrachloride. The combined carbon tetrachloride layers were washed with 40 ml. of water, 40 ml. of 5% aqueous sodium carbonate, and dried over anhydrous calcium sulfate. The desiccant was removed by filtration and the solvent distilled at reduced pressure. The product from the experiment with a catalyst ratio of 9:1 was purified by sublimation at 5–7 mm., 110–125° bath temperature. Successive recrystallizations from methanol and *n*-hexane were used for the other two experiments (see Table I).

TABLE I

BROMINATED ADAMANTANE AS A FUNCTION OF CATALYST RATIO

BBr_3–Al_2Br_6	M.p. (sealed tube), °C.	% Br[a]
9:1	74–109[b]	62.83
10	114–116	54.50
10^5	119–120	38.11

[a] Calcd. for $C_{10}H_{15}Br$: Br, 37.16. Calcd. for $C_{10}H_{14}Br_2$: Br, 54.36. Calcd. for $C_{10}H_{13}Br_3$: Br, 64.29. [b] Vapor phase chromatographic analysis indicated a mixture of components, 80% of which had retention times greater than dibromoadamantane.

Repetition of the second experiment, using 1.3 ml. of 10^{-2} *M* Al_2Br_6–Br_2 solution but omitting the boron bromide completely,

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[4] E. L. Gamble, "Inorganic Syntheses," Vol. III, L. F. Audrieth, Ed., McGraw-Hill Book Co. Inc., New York, N. Y., 1950, p. 27.

[5] Although there is a considerable difference in normal boiling points for BBr_3 and Al_2Br_6, 91.7° *vs.* 256.3°, aluminum bromide has a finite vapor pressure even as a solid (1 mm. at 81.3°[6]). It does not seem unlikely that some samples of boron bromide could be contaminated with traces of aluminum bromide by codistillation.

[6] D. R. Stull, *Ind. Eng. Chem.*, **39**, 540 (1947).

[7] Prepared by aluminum chloride isomerization of tetrahydrodicyclopentadiene; *cf.* P. von R. Schleyer and M. M. Donaldson, *J. Am. Chem. Soc.*, **82**, 4645 (1960).

[8] Adamantane and monobromoadamantane were eluted under the same conditions at 1.0 and 2.7 min., respectively.

[9] 1-Bromoadamantane shows three bands at 7.66, 8.05 and 8.24 τ with relative intensities of 3:1:3, respectively [H. F. Reinhardt, this laboratory, private communication].

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

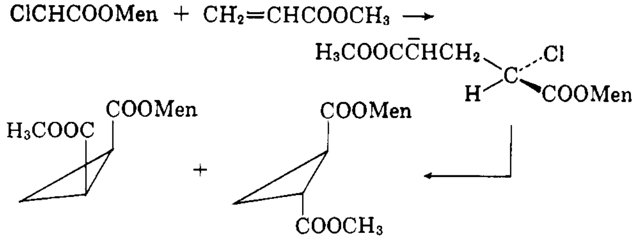
GAS PHASE CHROMATOGRAPHIC ANALYSIS OF THE REDUCTION–ACETYLATION PRODUCTS OBTAINED FROM CRUDE MENTHYL METHYL 1,2-CYCLOPROPANEDICARBOXYLATE

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*



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[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).