tion state acquires its stabilization from resonance between structures each of which has two unpaired electrons: (1) a free-radical and Cr^{V}, and (2) a carbonium ion and Cr^{IV}.

Acknowledgment.—The authors gratefully acknowledge the support of this research by the Petroleum Research Fund of the American Chemical Society.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY, NEW YORK 27, N. Y.]

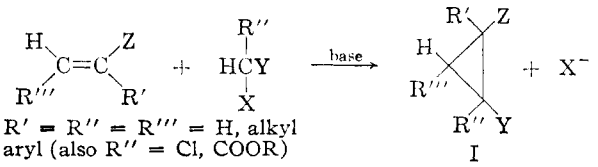
Three-membered Rings. IV. Solvent Control for the Stereoselective Formation of Cyclopropanes Substituted at Two of the Ring Carbons

BY LAYTON L. MCCOY

RECEIVED DECEMBER 4, 1961

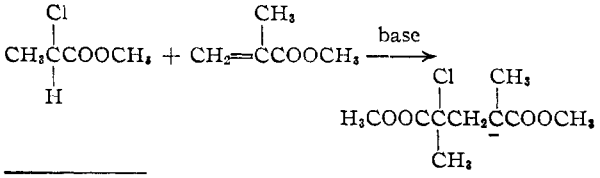
The interaction of α-substituted acrylic esters or acrylonitriles with α-halo-esters in the presence of base may be controlled by the solvent so as to allow the stereoselective formation of either *cis*- or *trans*-cyclopropane compounds. Reaction with no solvent or with hydrocarbon or ether solvents gives predominantly or exclusively the *cis* isomer; reaction in hexamethyl phosphoramide–benzene mixtures or in dimethylformamide gives predominantly the more stable isomer, usually the *trans* isomer. Ring closure of suitably substituted glutarate esters (and probably a number of related types of compounds) also is controlled by solvent in the same way.

The formation of polysubstituted cyclopropanes from α,β-unsaturated systems and α-halo-compounds in the presence of base is now well established.[1] It is also clear that under the experimental conditions normally



used, when R‴ = H the *cis* isomer (I, Y and Z *cis*) is the predominant or exclusive product.[1,b,e,g,h,j] This preference for *cis* isomer formation is to a large extent independent of the functional groups (Y,Z), substituents (R′,R″) and the tempeature of the reaction.

This preference for *cis* isomers was quite surprising when first noted. Most other procedures leading to cyclopropanes from non-stereoisomeric starting materials usually produce the more stable *trans* isomers. To explain this *cis* selectivity a simple assumption was made that some sort of attractive interaction between the two functional groups is occurring at an intermediate step of the reaction. On the basis of the previous suggestion as to the general reaction path,[1a] the intermediate involved would be the anion produced by a Michael addition. Thus, as a specific example



Models of the anion suggest that in certain conformations the C–C–O of the anion can "wrap" around the carbon of the second carboxyl group. This would allow the charge of the anion to be distributed over the carbonyl of the second carboxyl group. Such charge distribution probably contributes very appreciably to stabilization of the intermediate anion in solvents of low dielectric constant, benzene, toluene, ethers and esters. Models also suggest that only slight, essentially unhindered rotation of the anionic group is necessary to result in displacement of the halogen and formation of the *cis*-cyclopropane isomer. Much greater, appreciably hindered rotation is required for a conformation leading to the *trans* isomer. Although this proposal is rather simple and presents some difficulties of interpretation, it does offer a working hypothesis: if the proposed interaction could be minimized, it should be possible to form *trans* isomers. To accomplish this, it seemed reasonable that in a medium of high dielectric constant and good solvating properties, external solvation of the anion would take place in preference to the proposed "internal solvation." With the attractive interaction removed, the transition states leading to the two possible isomers probably would have much of the character, the steric and electronic interactions, present in the products. Thus, the isomer ratios observed in the polar solvents should approach those expected on the basis of the relative stabilities of the stereoisomers. To test these ideas, a number of reactions were run in several solvents.[2] The results are summarized in Tables I and II.

It is quite obvious that solvents do have a marked effect on the isomer ratios, but usually an insignificant effect on the yields. The choice of polar solvents, dimethylformamide and hexamethylphosphoramide, was suggested by the work of Zaugg and co-workers[3]; also many of the commonly used polar solvents such as alcohols were not compatible with the reaction conditions. In the polar reaction

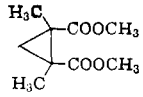
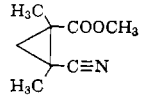
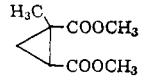
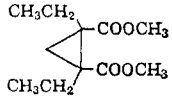
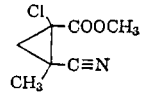
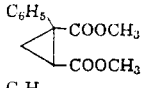
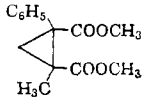
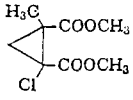
(1) (a) L. L. McCoy, *J. Am. Chem. Soc.*, **80**, 6568 (1958); (b) L. L. McCoy, *J. Org. Chem.*, **25**, 2078 (1960); (c) L. L. McCoy, *J. Am. Chem. Soc.*, **82**, 6416 (1960); (d) R. Fraisse and R. Jacquier, *Bull. soc. chim. France*, 986 (1957); (e) M. Mousseron and R. Fraisse, *Compt. rend.*, **248**, 887 (1959); (f) M. Mousseron, R. Fraisse, R. Jacquier and G. Bonavent, *ibid.*, **248**, 1465 (1959); (g) M. Mousseron, R. Fraisse, R. Jacquier and G. Bonavent, *ibid.*, **248**, 2840 (1959); (h) R. Fraisse, *Bull. soc. chim. France*, 1102 (1959); (i) R. Fraisse and M. Guitard, *ibid.*, 418 (1960); (j) R. Fraisse and M. Guitard, *ibid.*, 788 (1960); (k) R. Fraisse and M. Guitard, *ibid.*, 200 (1961); (l) D. T. Warner and C. E. Morreal, *J. Am. Chem. Soc.*, **82**, 439 (1960); (m) O. Widman, *Ber.*, **51**, 533, 907 (1918).

(2) A preliminary report of this work has been published, ref. 1c.

(3) (a) H. E. Zaugg, B. W. Horrom and S. Borgwardt, *J. Am. Chem. Soc.*, **82**, 2895 (1960); (b) H. E. Zaugg, *ibid.*, **82**, 2903 (1960); (c) H. E. Zaugg, D. A. Dunningan, R. J. Michaels, L. R. Swett, T. S. Wang, A. H. Sommers and R. W. de Net, *J. Org. Chem.*, **26**, 644 (1961).

TABLE I

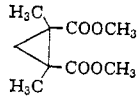
THE VARIATION OF YIELD AND ISOMER RATIO FOR SEVERAL DIFUNCTIONAL CYCLOPROPANES PREPARED IN VARIOUS SOLVENTS

Compound	C_6H_6 or C_7H_8[a]	Dimethylformamide[a]	50% C_6H_6–50% hexamethylphosphoramide[a]
Part A			
	71(7)[b]	62(66)	60(64)[e]
	59(25)[b]	55(66)	
	70[c](17)		70(90)
	55(0)		67(75)
	64(20)[b]	13(45)	65(38)
Part B			
	43[d](0,100)		65(56,21)
	38[d](0,100)[b]		46(43,25)
	74(0,100)[b]	50(36,62)	

[a] The first number is the yield of mixed isomeric esters. In part A the number in parentheses is the percentage of *trans* isomer in the ester mixture, the remainder being the *cis* isomer; these results were obtained by gas phase chromatography, ref. 1b. In part B the esters were saponified to the acids and these were separated: the first number in parentheses is the percentage of *trans* isomer isolated from the total acid mixture (90–100% recovery in the saponification) and the second number is the amount of *cis* isomer isolated. [b] Ref. 1b. [c] Ref. 1a. [d] These yields are for the acid mixtures obtained by saponification of the crude esters. [e] This result is obtained by interpolation from Table II.

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] Obtained by gas phase chromatography; see ref. 1b.

media the *cis* isomer preference is no longer present except in the chlorine substituted compounds, and even in these exceptional cases the *cis*:*trans* ratio is reduced. Although the relative stability of such halogen substituted cyclopropanedicarboxylic acids has not been studied, it would not be very surprising if the *cis* and *trans* isomers were more nearly equal in stability compared to related alkyl and aryl substituted compounds, or even if the *cis* isomer were the more stable. Thus, the results of Table I are consistent with a pattern: In poor solvating, low dielectric media the *cis* isomer (I, Y and Z *cis*, R''' = H) predominates, while in strongly solvating, high dielectric media the more stable isomer, usually *trans* (I, Y and Z *trans*, R''' = H) predominates. *This means that in most cases a stereoselective synthesis of either stereoisomer of I, R''' = H, is possible.*

Another possible explanation, or an important factor, for *cis* isomer formation might be that the sodium cation is complexing with both carboxyl functions in the anion and thereby maintaining a conformation leading to *cis* closure. Zaugg[3a,b] suggested that dimethylformamide and hexamethyl phosphoramide affect anionic reactions by specific solvation of the cation (sodium ion). Zook and Russo[4] have suggested that the enhanced reactivity of some carbanions in mono- or diglyme is a result of solvation of the cation.[5] In the present work with monoglyme as a solvent, dimethyl 1,2-dimethyl-1,2-cyclopropanedicarboxylate, 65% yield, showed the same isomer ratio, 92% *cis*:8% *trans*, as when prepared in toluene. This result in monoglyme solvent indicates that solvation of the cation is not the controlling factor for the stereoselective reaction.[6]

Since the stereochemistry of the products arises from the intermediate anion, the origin of the anion should not influence the stereochemical results. Thus, the anion might be formed from a suitably substituted three-carbon chain, *e.g.*, a glutaric ester. Dimethyl α-chloro-α'-methylglutarate[7] on treatment with sodium hydride in benzene solvent gave a 40% yield of dimethyl 1-methyl-1,2-cyclopropanedicarboxylate, 54% *cis*:46% *trans*, while in 50% benzene–50% hexamethylphosphoramide it gave a 46% yield of cyclopropane diester, 5% *cis*: 95% *trans*. This suggests that most anionic ring closures to cyclopropanes in which functional groups are situated at the ends of a three-carbon chain and the center carbon is unsubstituted can be stereoselective by suitable choice of the reaction medium.

The more complex cases in which all three ring carbons are substituted will be reported separately.[8]

Acknowledgment.—This work was supported in part by a grant from the Research Corporation. Eastman Chemical Products, Inc., Kingsport, Tenn., furnished a generous sample of hexamethylphosphoramide.

Experimental[9]

General Procedure.—The preparation of the cyclopropane esters and nitriles is based on the procedure using sodium

(4) H. D. Zook and T. J. Russo, *J. Am. Chem. Soc.*, **82**, 1258 (1960).

(5) However, Zaugg[3a] found monoglyme to be only slightly effective.

(6) An alternative, but unlikely explanation might be that the monoglyme cannot compete with the two carboxyl functions in complexing the cation, but that dimethylformamide and hexamethylphosphoramide can.

(7) C. K. Ingold, *J. Chem. Soc.*, **127**, 393 (1925); F. R. Goss and C. K. Ingold, *ibid.*, **127**, 2779 (1925).

(8) Our results in this area so far suggest that solvent effects do occur, but in most cases are dominated by additional steric effects not present in the compounds discussed in this paper.

(9) Boiling points and melting points are uncorrected. Analyses are by Micro-Tech Laboratories.

hydride previously described.[1a,b] A. Benzene or Toluene Solvent: Reactions in these solvents use olefinic compound (1 mole), halogen compound (1 mole), sodium hydride (1 mole) and solvent (100–300 ml.). The reactions are exothermic, but seldom warm appreciably because of the slow rate of reaction. Cooling is applied as necessary to maintain the reaction temperature at about 20–30°, the minimum temperature at which hydrogen is evolved at a slow, but steady rate. The work-up procedure is as previously described.[1a] B. Benzene–Hexamethylphosphoramide Solvent: The same reactant ratios as in A are used, but the total solvent volume is larger (1000 ml.). The reactions are invariably faster than in pure hydrocarbon solvent. Heating is more marked, and cooling is required to maintain the reaction temperature at or below about 50–60°. In the work-up at least 5 ml. of water per ml. of hexamethylphosphoramide is used in each of two washes to ensure complete removal of the phosphorus compound; in some of the mixtures containing a high concentration of hexamethylphosphoramide, additional benzene is added before the aqueous washing. Subsequent treatment of the benzene solution is the same as when benzene alone is used as a solvent. C. Dimethylformamide and Monoglyme Solvent: The reactant and solvent ratios are the same as in B. Reactions in dimethylformamide show characteristics similar to those in benzene–hexamethylphosphoramide, while reaction in monoglyme is similar to that in benzene. With both solvents reaction mixtures are filtered to remove sodium chloride and the filtrates are distilled; filtration (suction) is usually very slow unless some form of filter aid is used.

Reactions with methyl dichloroacetate as the halogen compound are markedly more exothermic than when other halogen compounds are used. Cooling is always necessary, and in dimethylformamide or benzene–hexamethylphosphoramide ice-bath temperatures are usually essential for satisfactory yields.

In the present work all reactions were continued until gas evolution ceased.

With the exception of three examples (see below), the distilled products were analyzed for isomer ratios by gas phase chromatography.[1b] Known products were identified by their infrared spectra and retention times in the chromatographic analysis; new compounds were saponified and the resultant diacids were analyzed and characterized.

The results of the various reactions are summarized in Tables I and II. Only those reactions involving new compounds or procedures different from those previously reported[1a,b] are given here.

Dimethyl 1,2 - Diethyl - 1,2 - cyclopropanedicarboxylate. A.—Methyl α-chlorobutyrate (4.1 g., 0.03 mole) and methyl α-ethylacrylate[10] (3.4 g., 0.03 mole) were added dropwise with stirring to sodium hydride (0.72 g., 0.03 mole) in toluene (10 ml.). Processing the reaction mixture gave 3.5 g. (55%) of dimethyl 1,2-diethyl-1,2-cyclopropanedicarboxylate, b.p. 109–112° (10 mm.). Saponification of the ester produced the *cis*-diacid. The diacid is rather soluble in water, but is best recrystallized from this solvent; partial conversion to the anhydride occurs on recrystallization from nitromethane. The anhydride was not obtained in crystalline form. An analytical sample of the diacid was recrystallized from water; m.p. 128.0–128.6°.

Anal. Calcd. for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C, 57.82; H, 7.76.

B.—Methyl α-chlorobutyrate (5.5 g., 0.04 mole) and methyl α-ethylacrylate (4.5 g., 0.04 mole) in benzene (20 ml.) were added dropwise with stirring to sodium hydride (0.96 g., 0.04 mole) suspended in hexamethylphosphoramide (20 ml.). Work-up of the reaction mixture gave 5.7 g. (67%) of dimethyl 1,2-diethyl-1,2-cyclopropanedicarboxylate, b.p. 100–105° (10 mm.). Saponification of the ester gave a mixture of the two stereoisomeric acids. The *trans* isomer was separated readily by recrystallization of the mixture from acetonitrile. An analytical sample was recrystallized from acetonitrile and then sublimed, m.p. 207–208°.

Anal. Calcd. for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C, 58.17; H, 7.53.

Dimethyl 1-Methyl-2-phenyl-1,2-cyclopropanedicarboxylate.—Methyl α-chloropenylacetate (9.2 g., 0.05 mole) and methyl methacrylate (5.0 g., 0.05 mole) in benzene (25 ml.) were added in the usual way to sodium hydride (1.2 g., 0.05 mole) in hexamethylphosphoramide (25 ml.). The product, dimethyl 1-methyl-2-phenyl-1,2-cyclopropanedicarboxylate, amounted to 5.7 g. (46%) with b.p. 165–167° (19 mm.). Saponification of the diester gave a mixture of the stereoisomeric diacids. These were separated by treatment with a slight excess of acetyl chloride in the cold[11]; filtration gave the *trans* isomer, m.p. 198–203°, while evaporation of the filtrate and sublimation of the residue gave the anhydride, m.p. 87–92° (lit.[1b] m.p. 92–93°). A small additional amount of *trans*-diacid remained in the residue. Total yield of 1-methyl-2-phenyl-*trans*-1,2-cyclopropanedicarboxylic acid was 43% and of the *cis*-anhydride was 25%. An analytical sample of the *trans*-diacid was recrystallized from acetonitrile and then sublimed, m.p. 203–204°.

Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.44; H, 5.49. Found: C, 65.54; H, 5.72.

Dimethyl 1-Phenyl-1,2-cyclopropanedicarboxylate. A.—Methyl α-chlorophenylacetate (9.2 g., 0.05 mole) and methyl acrylate (4.3 g., 0.05 mole) in benzene (25 ml.) were added to sodium hydride (1.2 g., 0.05 mole) suspended in hexamethylphosphoramide (25 ml.). The product, dimethyl 1-phenyl-1,2-cyclopropanedicarboxylate, distilled at 170–177° (20 mm.) and weighed 7.7 g. (65%). After standing for about 3 days the distillate suddenly partially crystallized to a very thick mush. The crystalline material was separated, recrystallized twice from cyclohexane, and identified as dimethyl 1-phenyl-*trans*-1,2-cyclopropanedicarboxylate, m.p. 96–97° (lit.[1h] m.p. 94°). Saponification of a sample of the liquid distillate before partial crystallization occurred and separation of the isomers by a procedure similar to that described in the previous section gave 56% *trans* and 21% *cis*. A sample of the *trans*-diacid recrystallized from water had m.p. 198.5–199° (lit.[1h] m.p. 190–191°); the *cis*-diacid purified in the same way had m.p. 152.5–153° (lit.[1h] m.p. 148°); the anhydride was not obtained in crystalline form.[12]

B.—Methyl α-chlorophenylacetate (36.9 g., 0.2 mole) and methyl acrylate (17.2 g., 0.2 mole) were added to sodium hydride (4.8 g., 0.2 mole) in toluene (50 ml.). A sample of the crude ester product obtained by the usual work-up procedure and removal of low boiling components was saponified and the acid isolated had m.p. 145–147°. The crude acid was recrystallized from water, m.p. 148.5–150°, and represented a 43% over-all yield from methyl acrylate. Some *trans*-acid may have been lost in the recrystallization, but since the m.p. was not very depressed, the percentage of *trans* isomer was undoubtedly quite small.

Dimethyl 1-Chloro-2-methyl-1,2-cyclopropanedicarboxylate.—Methyl dichloroacetate (14.3 g., 0.1 mole) and methyl methacrylate (12.5 g., 0.125 mole) in dimethylformamide (50 ml.) were added to sodium hydride (2.4 g., 0.1 mole) suspended in dimethylformamide (50 ml.). Work-up of the reaction mixture gave dimethyl 1-chloro-2-methyl-1,2-cyclopropanedicarboxylate, b.p. 115–121° (24 mm.), 10.3 g. (50%). Saponification of a sample of the ester gave a mixture which was analyzed as described in previous sections; the *trans*-diacid, m.p. 239–241 (lit.[1b] m.p. 246–247°) was obtained in 36% yield and the *cis*-anhydride, m.p. 45–55° (lit.[1b] m.p. 55–56.5°), was obtained in 62% yield.

Dimethyl 1-Methyl-1,2-cyclopropanedicarboxylate. A. Dimethyl α-methyl-α′-chloroglutarate[7] (6.2 g., 0.03 mole)

(10) The acid was prepared by the method described for α-*n*-propylacrylic acid (M. F. Hawthorne, *J. Am. Chem. Soc.*, **82**, 1886 (1960)), and then esterified by the procedure described for 2-methyl-3-butenoic acid (R. B. Wagner, *ibid.*, **71**, 3214 (1949)).

(11) This method of separation and analysis has been reported previously (ref. 1 e, g), but few experimental details were given. Although about 95% recovery of the separated isomeric diacids was reported, in the three small-scale examples described in the present paper, the recovery has been less satisfactory (70–95%). In all cases, the bulk of the *trans* isomer was isolated readily by filtration, but invariably a small amount remained dissolved in the anhydride, acetic acid, acetyl chloride mixture, and it appears that the major losses are involved in this part of the separation. It is expected that considerably better total recovery of pure isomeric acids would be observed in large-scale runs.

(12) S. Ruhemann, *J. Chem. Soc.*, **81**, 1212 (1902), reported the preparation of a crystalline anhydride, m.p. 99°, rather poorly identified as that from 1-phenyl-1,2-cyclopropanedicarboxylic acid. The preparation of this anhydride starting with ethyl chlorofumarate, ethyl phenylmalonate and sodium ethoxide was repeated, and the final product, m.p. 96.6–97.8°, was shown to be methyl phenyl maleic anhydride by comparison of m.p., mixed m.p. and infrared spectra with an authentic sample (J. Schreiber, *Compt. rend.*, **217**, 353 (1943); **220**, 200 (1945)).

was added to sodium hydride (0.72 g., 0.03 mole) in benzene (10 ml.). Dimethyl 1-methyl-1,2-cyclopropanedicarboxylate, b.p. 88–91° (10 mm.), 2.1 g. (40%), was obtained.

B.—Repetition of the experiment, but using benzene (15 ml.) and hexamethylphosphoramide (15 ml.) mixture, gave 2.4 g. (46%) of the cyclopropane diester, b.p. 90° (10 mm.).

[CONTRIBUTION FROM KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY, EAST LANSING, MICH.]

Proton Magnetic Resonance Spectra of Cyclopropane Derivatives[1]

BY JOHN D. GRAHAM[2] AND MAX T. ROGERS

RECEIVED NOVEMBER 20, 1961

The proton magnetic resonance absorption of several cyclopropane derivatives has been studied at 60.000 mc. The observed chemical shifts and nuclear spin–spin coupling constants have been interpreted in terms of substituent effects and the structures of the molecules. Although the structure of the cyclopropane ring is often thought to be somewhat unusual, the observed proton–proton coupling constants for ring protons in the cyclopropane derivatives are not anomalous. The magnitude of, and variations in, the observed proton–proton coupling constants can be satisfactorily explained on the basis of the geometry of the molecules. Substituent effects have not been found to be important in the consideration of the proton–proton coupling constants, but the chemical shifts of the ring protons have been found to be strongly influenced by the nature of the substituents on the ring.

Introduction

Recently, the proton magnetic resonance spectra of some substituted cyclopropane derivatives have been reported. According to Jackman[3] the *cis* and *trans* coupling constants in *trans*-dibromocyclopropane are equal. However, Gutowsky[4] has shown that in A_2X_2 spin systems the invoking of accidentally equal J_{AX} coupling constants is not always correct. Also, Roberts[5] has suggested that the spectrum of *trans*-dibromocyclopropane is consistent with coupling constants of 8 and 2 c.p.s. for the *cis* and *trans* coupling constants. Closs[6] has assumed that the *trans* coupling constants are larger than the *cis* coupling constants in several substituted cyclopropanes. The vicinal coupling constants in 1-nitro-1,2-dicarboxylic anhydride have been reported[7] as 9.0 and 6.0 c.p.s., but the authors made no statement concerning which was *cis* and which *trans*. Muller and Pritchard[8] have reported that the C^{13} satellite lines in cyclopropane consist of a "normal" quintet, the coupling constant being equal to 7.5 c.p.s.

The purpose of the work reported herein was to determine the magnitudes of the coupling constants in several cyclopropane derivatives and to ascertain the effect of substituents and geometry upon the coupling constants in these molecules.

Experimental

The 60.000 mc. high-resolution proton magnetic resonance spectra were obtained with a Varian 4300–2 spectrometer and the usual side-band technique was used for calibration purposes. Spectra of the following pure liquids were obtained: 1,1-dichloro-2-methyl-2-phenylcyclopropane, *cis*-1,1-dichloro-2-methyl-3-phenylcyclopropane, 1,1-dichloro-2-methoxycyclopropane and 1,1-dichloro-2-ethoxycyclopropane. The spectrum of *trans*-1,2,3-tribenzoylcyclopropane[9] was obtained using a solution of this compound in CF_3COOH, and the spectra of cyclopropane-1,1,2-tricarboxylic acid and *trans*-3-methylenecyclopropane-1,2-dicarboxylic acid (Feist's acid) were obtained using solutions of these compounds in dilute NaOH.[10]

The 40.000 mc. spectrum of *trans*-1,2,3-tribenzoylcyclopropane has been reported by Shoolery[11] and the *trans* coupling constant in this molecule has been reported as 6.0 c.p.s. by Closs.[6]

The dichlorocyclopropanes were synthesized from the corresponding olefin by the dichlorocarbene reaction following the procedure of Doering.[12] The synthesis of 1,1-dichloro-2-ethoxycyclopropane has been reported by Doering and Henderson,[12] while the syntheses of the remaining three dichlorocyclopropanes have not been previously reported.

1,1-Dichloro-2-methoxycyclopropane was prepared by the addition of dichlorocarbene to vinyl methyl ether (Matheson Co., Inc.); b.p. 51°(mm.), $n^{20}D$ 1.4490.

Anal. Calcd. for $C_4H_6OCl_2$: C, 34.07; H, 4.26; Cl, 50.22. Found: C, 33.95; H, 4.37; Cl, 50.20.

The reaction of α-methylstyrene (Eastman Kodak Co., white label) with dichlorocarbene afforded 1,1-dichloro-2-methyl-2-phenylcyclopropane, b.p. 55–56° (0.3 mm.), $n^{20}D$ 1.5480.

Anal. Calcd. for $C_{10}H_{10}Cl_2$: C, 59.70; H, 4.98; Cl, 35.32. Found: C, 59.77; H, 5.03; Cl, 35.19.

β-Methylstyrene was obtained from Columbia Organic Chemicals Co. and a purity of greater than 99% was indicated by the results of the gas chromatographic separation. The refractive index of this material, $n^{20}D$ 1.5430, agrees with the literature value[13] for the *cis* isomer. The product of the reaction of this olefin with dichlorocarbene was *cis*-1,1-dichloro-2-phenyl-3-methylcyclopropane, b.p. 54–56° (0.2 mm.), $n^{20}D$ 1.5440.

Anal. Calcd. for $C_{10}H_{10}Cl_2$: C, 59.70; H, 4.98; Cl, 35.32. Found: C, 59.78; H, 5.06; Cl, 35.18.

Vinyl ethyl ether, purchased from Matheson Co., Inc., added dichlorocarbene to give 1,1-dichloro-2-ethoxycyclopropane,[12] b.p. 53–54° (28 mm.), $n^{20}D$ 1.4440.

Results and Discussion

The methods used to analyze the spectra of the cyclopropane derivatives have been discussed

(1) Work supported by a grant from the Atomic Energy Commission.

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(9) We are indebted to Prof. W. G. Brown of the University of Chicago for the gift of a sample of this compound.

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