Chemistry of Methylenecyclopropane

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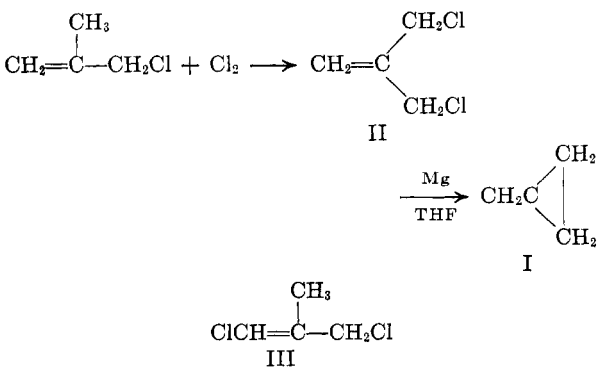
The known preparation of methylenecyclopropane has been repeated and some reactions studied. Highly reactive, the olefin adds such reagents as hydrogen bromide, bromine, hypobromous acid, methanethiol, heptafluoropropyl iodide, and tetrafluoroethylene to the double bond to form stable products containing cyclopropane rings. Spectra of the products confirm the presence of the cyclopropane ring and allow determination of the direction of addition of unsymmetrical addends.

Although there has been considerable interest in some substituted methylenecyclopropanes,[1] knowledge of the chemical reactivity of the simple C_4 hydrocarbon is lacking. It was of interest to us to determine whether methylenecyclopropane (I) would participate in cycloaddition reactions as does allene.[2] Although a cyclo-addition reaction was observed in only one case, several addition reactions which demonstrate unexpected stability for the 1-methylcyclopropyl carbonium ion have been found.

Synthesis of Methylenecyclopropane.—The elegant synthesis described by Gragson, Greenlee, Derfer, and Boord[3] has been used to obtain the methylenecyclopropane used in these studies. In contrast to previous results, we have found methylenecyclopropane to be stable for long periods to storage in stainless steel cylinders at room temperature with no tendency to polymerize or decompose.

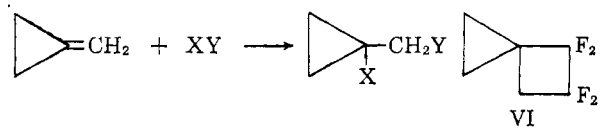
In the synthesis, chlorination of methallyl chloride formed a mixture, the largest portion of which was composed of nearly equal parts of 3-chloro-2-chloromethyl-1-propene (II),[4] b.p. 58° (50 mm.), $n^{25}D$ 1.4748, and 1,3-dichloro-2-methyl-1-propene (III), b.p. 54° (50 mm.), $n^{25}D$ 1.4699. Very careful distillation through an efficient column was necessary to separate these isomeric compounds. The course of the distillation and degree of separation were followed readily by gas chromatography.



When pure dichloride II (99% according to gas chromatography) was treated with magnesium in carefully dried tetrahydrofuran according to the procedure of ref. 3, methylenecyclopropane was obtained in about 30% yield. The gaseous product was 98% pure according to gas chromatographic analysis; an impurity amounting to about 2% and having the same retention time as isobutylene (see ref. 3) was the only other product. The identity of the product with that of Gragson, Greenlee, Derfer, and Boord was shown by comparison of infrared spectra. NMR spectra and mass spectrographic analysis further confirmed the structure. Methylenecyclopropane, b.p. 11–12°, was distilled through a helices-packed column. It was routinely stored in stainless steel cylinders at room temperature and periodic gas chromatographic analysis indicated that no decomposition occurred over a period of months at room temperature.

We are at a loss to explain the previously reported instability of compound I. The pure dichloride III, when treated with magnesium in tetrahydrofuran, gave no volatile products in our work, so the presence of III in starting II probably is not responsible for the differences in products.

Reactions of Methylenecyclopropane.—In general, the reactions of methylenecyclopropane are those of a reactive olefin. In the reactions studied, major products resulted from addition without opening of the ring.



IV. X = Br; Y = H
VII. X = H; Y = CH_3S—
VIII. X = H; Y = C_2H_5S—
IX. X = I; Y = n-C_3F_7—
X. X = Br; Y = Br
XIV. X = Br; Y = OH

Methylenecyclopropane added hydrogen bromide in ether solution to form 1-bromo-1-methylcyclopropane (IV). The structure of the product was confirmed by NMR peaks at −95 c.p.s. (methyl)

(1) M. G. Ettlinger, *J. Am. Chem. Soc.*, **74**, 5805 (1952).
(2) H. N. Cripps, J. K. Williams, and W. H. Sharkey, *J. Am. Chem. Soc.*, **81**, 2723 (1959).
(3) J. T. Gragson, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Am. Chem. Soc.*, **75**, 3344 (1953).
(4) A. Mooradian and J. B. Cloke, *J. Am. Chem. Soc.*, **67**, 942 (1945); A. S. Matlack and D. S. Breslow, *J. Org. Chem.*, **22**, 1723 (1957).

and −39 and −60 c.p.s. (doublet; ring hydrogens).[4a]

Compound I and 2,4-dinitrobenzenesulfenyl chloride reacted in methylene chloride to form 1-chloro-1-(2,4-dinitrophenylthiomethyl)-cyclopropane (V), m.p. 139–140.5°. The direction of addition could not be shown spectroscopically but is assigned by analogy.

Tetrafluoroethylene reacted[5] with I at 175° in a sealed tube to form 1,1,2,2-tetrafluorospirohexane (VI), b.p. 98°. Infrared bands (9.7 μ and 3.28 μ) and NMR peaks (doublet −64, −45 c.p.s.) indicate that the cyclopropane ring is intact in the product. A triplet in the NMR at −157, −144, and −131 c.p.s. indicates a methylene next to a difluoromethylene group. We were not able to isolate cyclo-adducts from maleic anhydride or acrylonitrile.

Methanethiol added to compound I in ether to form 63% of methyl cyclopropylmethyl sulfide (VII). The direction of addition[6] is shown by a methylene doublet, −138, −132 c.p.s., a methyl singlet, −118 c.p.s., a doublet for ring methylenes, −32, −11 c.p.s. (complex splitting), and a small peak for the tertiary ring hydrogen, −52 c.p.s. (complex splitting).

Ethanethiol added to methylenecyclopropane in a similar way to form ethyl cyclopropylmethyl sulfide (VIII) in 44% yield. The NMR spectrum of this compound confirmed the structure assigned, but was more complex than that of VII because of the ethyl resonance. In addition, the tertiary hydrogen atom was not as well separated from the ring methylene doublet.

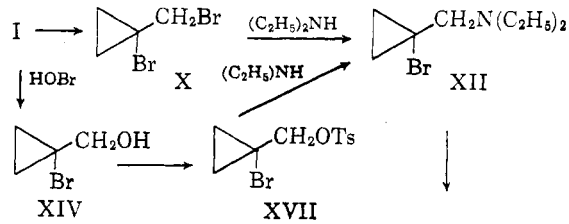
The azonitrile-catalyzed addition of heptafluoropropyl iodide to methylenecyclopropane forms 96% 1-iodo-1-(2,2,3,3,4,4,4-heptafluorobutyl)cyclopropane (IX).[7] The NMR spectrum clearly shows the direction of the addition, since the methylene group is split into a triplet (−122, −141, −160 c.p.s.) by the fluorine atoms on the adjacent carbon atom. If the iodine atom were bonded to the methylene group, no such splitting would occur.

Bromine in carbon tetrachloride added to methylenecyclopropane in tetrahydrofuran to form 1-bromo-1-bromomethylcyclopropane (X) in 60% yield. The NMR spectrum again shows a single methylene resonance, −211, c.p.s., and a doublet for ring methylenes, −77, −65 c.p.s. No other products were isolated.

The dibromide X reacted with excess dimethylamine in tetrahydrofuran at 100° to form 80% of 1-bromo-1-dimethylaminomethyl-cyclopropane (XI). The structure XI is assigned rather than that of the isomeric 1-bromomethyl-1-dimethylaminocyclopropane on the basis of chemical shift of the methylene protons (−137 *vs.* −211 in X). The NMR spectrum of XI shows methylene (−137 c.p.s.), methyl (−127 c.p.s.) and ring methylene (−46, −48 c.p.s.). resonances.

In a similar way the dibromide X reacted with diethylamine to form 1-bromo-1-diethylaminomethylcyclopropane (XII), identified as its crystalline picrate salt (XIII), m.p. 136–137°.

The addition of hypobromous acid to I in water[8] formed 47% of 1-bromo-1-hydroxymethylcyclopropane (XIV). The alcohol XIV formed a crystalline phenylurethan (XV), m.p. 71.2–72.0°, and a crystalline 3,5-dinitrobenzoate ester (XVI), m.p. 106.5–107.2°. The gross structure of the alcohol XIV is confirmed by NMR peaks at −252 c.p.s. (alcoholic proton), −208 c.p.s. (methylene resonance) and −60 c.p.s. (cyclopropane ring methylenes). The compound was shown to be the primary alcohol by conversion to the *p*-toluenesulfonate ester (XVII), m.p. 57–58°, which reacted with diethylamine to form the bromoamine XII. The identity of XII prepared from X with that prepared from XVII was shown by melting point and mixed melting point of the picrates, and examination of the infrared spectra, which were identical.



1-Bromo-1-diethylaminomethylcyclopropane picrate (XIII), m.p. 137-138°

Spectral Data.—The NMR data and the infrared spectral data for the compounds described above were useful in confirming the presence of the cyclopropane ring in the products and, in some cases, in determining the direction of addition of reagents to the double bond of methylenecyclopropane. The proton NMR data and the infrared bands assigned to the cyclopropane ring and ring hydrogens are summarized in Table I.

The NMR spectrum of methylenecyclopropane shows that there is interaction between the vinyl and ring protons. The vinyl proton resonance at −303 c.p.s. is split into 5 lines and the ring proton resonance at −56 c.p.s. is split into 3 lines. Both resonances are symmetrical and the splitting does not change over a wide range of temperature.

(4)(a) NMR spectra were determined at 56.4 Mc. and calibrated in c.p.s. from tetramethylsilane as an internal standard.

(5) D. D. Coffman, P. L. Barrick, R. D. Cramer, and M. S. Raasch, *J. Am. Chem. Soc.*, **71**, 490 (1959).

(6) The addition of thiol may occur by a radical mechanism, the catalyst being peroxides or oxygen. S. O. Jones and E. E. Reid, *J. Am. Chem. Soc.*, **60**, 2452 (1938).

(7) See A. M. Lovelace, D. A. Rausch, and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Corp., New York, 1958, p. 37 ff, for a discussion of this reaction. The author is indebted to Dr. N. O. Brace for suggesting the reaction and reaction conditions used.

(8) C. O. Guss and R. Rosenthal, *J. Am. Chem. Soc.*, **77**, 2549 (1955). J. G. Traynham and O. S. Pascual, *Tetrahedron*, **7**, 165 (1959).

TABLE I

SPECTRAL DATA OF 1,1-DISUBSTITUTED CYCLOPROPANES

Compound	NMR spectra: Line(s) for cyclopropane ring protons	NMR spectra: Line(s) for Protons on carbon adjacent to ring	NMR spectra: Line(s) for other protons	Infrared spectral bands: Band for ring	Infrared spectral bands: Band for ring hydrogens
Methylenecyclopropane (I)	−56 (3 lines)	−303 (5 lines)		9.65 μ (broad)	3.25 μ
1-Bromo-1-methylcyclopropane (IV)	−39, −60 doublet (fine structure)	−95		9.84 μ	3.23 μ
1-Bromo-1-bromomethylcyclopropane (X)	−65, −77 (fine structure)	−211		9.77 μ	3.24 μ
1-Bromo-1-dimethylaminomethylcyclopropane (XI)	−46, −58 (fine structure)	−137	−127 *N*-methyls	9.6 μ	3.25 μ
Methyl cyclopropylmethyl sulfide (VII)	−11, −32 doublet \ −52 —C—H complex / splitting	−132, −138	−118	9.85 μ	3.25 μ
1-Bromo-1-hydroxymethylcyclopropane (XIV)	−60 splitting visible only at high resolution	−208	−253	9.79 μ	3.3 μ
1,1,2,2-Tetrafluorospirohexane (VI)	−45, −64 (fine structure)	−131, −144, −157 triplet		9.7 μ	3.28 μ
1-Iodo-1-(2,2,3,3,4,4,4-heptafluorobutyl)cyclopropane (IX)	−56, −66 (fine structure)	−122, −141, −160 triplet		9.70 μ	3.27 μ
1,1-Dimethylcyclopropane	−12	−60			

NMR spectra were determined at 56.4-Mc. oscillator frequency. Calibrations are in c.p.s. from tetramethylsilane.

All the 1,1-disubstituted cyclopropanes in which the substituents are different show splitting of the ring protons into a doublet, which at very high resolution shows further splitting into complex patterns. The similarity of these splittings and the high field strengths at which they occur (−77 to −11 c.p.s.) leave little doubt that the cyclopropane ring is intact. 1,1-Dimethylcyclopropane does not show this splitting of the ring hydrogen peak at −12 c.p.s. Infrared absorption at 9.6–9.85 μ (ring) and 3.2–3.3 μ (ring hydrogen) in all of these compounds is further confirmation of structure.

The mass spectrum of methylenecyclopropane is shown in Table II. It is interesting that the most abundant ion found has mass number 39, corresponding to $C_3H_3^+$. This may be the cyclopropenyl cation, recently postulated to have aromatic character.[9]

TABLE II

MASS SPECTRUM OF METHYLENECYCLOPROPANE

(Included are ions of 2% relative abundance or greater)

Mass	Rel. abundance (%)	Mass	Rel. abundance (%)
12	3.5	37	11.7
13	3.7	38	14.9
14	6.9	39	100.0
15	3.6	40	3.6
25	4.4	49	8.8
25.5	2.8	50	26.4
26	27.5	51	24.6
27	65.0	52	8.6
28	40.9	53	47.9
36	2.5	54	92.0
		55	4.1

(9) R. Breslow and H. Hover, *J. Am. Chem. Soc.*, **82**, 2644 (1960).

Experimental

3-Chloro-2-chloromethyl-1-propene.—A large sample of methallyl chloride was treated with chlorine until the refractive index (25°) was 1.4760. The reaction mixture was washed with cold water, dried, and distilled through a short-path still. Distillate, b.p. 40–80° (50 mm.), was redistilled through a very efficient Podbielniak still. Fractions of 1,3-dichloro-2-methyl-1-propene, b.p. 54° (50 mm.), $n^{25}D$ 1.4699, and 3-chloro-2-chloromethyl-1-propene, b.p. 58° (50 mm.), $n^{25}D$ 1.4748, were obtained. Fractions of intermediate composition were redistilled. The purity of the fractions was checked by gas chromatography on columns packed with 3-methyl-3-nitro-1,5-dicyanopentane on firebrick, and only fractions of 97% or better purity were used.

Methylenecyclopropane.—The procedure of ref. 1 was followed exactly. Samples of 25–40 g. of methylenecyclopropane were obtained. The material was highly pure as shown by gas chromatographic analysis on columns known to separate all the potential 3- and 4-carbon compounds. Infrared, NMR, and mass spectrometric analyses were consistent with the structure and all indicated high purity. A sample distilled through a helices-packed still had b.p. 11–12°.

1,1,2,2-Tetrafluorospirohexane.—A Carius tube was charged with about 9 g. of methylenecyclopropane, 0.2 g. of phenothiazine, and 20 g. of tetrafluoroethylene. The tube was sealed and heated at 175° for 12 hr. The products from two such runs were distilled, and there was obtained 28.7 g. (0.186 mole or 56%) of 1,1,2,2-tetrafluorospirohexane, b.p. 93–98°, $n^{25}D$ 1.3507–1.3500. A heart cut, $n^{25}D$ 1.3502, was analyzed.

Anal. Calcd. for $C_6H_8F_4$: C, 46.76; H, 3.93; F, 49.31. Found[10]: C, 47.18; H, 4.18; F, 49.31, 49.36.

Methylenecyclopropane. 2,4-Dinitrobenzenesulfenyl Chloride Adduct.—A solution of 0.20 g. of 2,4-dinitrobenzenesulfenyl chloride in 3 ml. of methylene chloride was mixed

(10) Considerable difficulty was encountered in obtaining satisfactory analyses for five compounds in this series. Because all the elements present were determined and the total exceeds 100%, we believe the analyses are satisfactory. NMR spectra showing no impurities were obtained, and the three samples that were gas chromatographed appeared pure.

with excess methylenecyclopropane at 0°, then stored at room temperature in a stoppered flask. After 16 hr., the solvent was allowed to evaporate and the crude product was recrystallized from hexane–ethyl acetate. There was obtained 0.23 g. of crystalline adduct, which after a second recrystallization had m.p. 139–140.5°.

Anal. Calcd. for $C_{10}H_9N_2O_4ClS$: C, 41.60; H, 3.14; Cl, 12.28. Found: C, 41.72; H, 3.23; Cl, 12.21.

In a repetition of this experiment on a larger scale, 16.5 g. (0.070 mole) of 2,4-dinitrobenzenesulfenyl chloride was converted to 17.8 g. (0.062 mole or 88%) of the crystalline adduct.

1-Bromo-1-methylcyclopropane.—A solution of about 8 g. of methylenecyclopropane in 25 ml. of ether was cooled to −80° and 10 ml. of liquid hydrogen bromide at −80° was added. The mixture was warmed slowly to room temperature. After the mixture had stood for 1 hr., it was poured into excess sodium bicarbonate solution. The product was extracted with ether, the extracts were combined and dried, and the mixture was distilled in a semimicro column. There was obtained 7.91 g. of impure 1-bromo-1-methylcyclopropane, b.p. 72–85°, $n^{25}D$ 1.4382–1.4458. A small sample purified by gas chromatography (13 ft. × 3/4 in. column packed with silicone oil on firebrick and heated to 100°, helium back pressure, 1 atm.) had $n^{25}D$ 1.4467. The NMR spectrum was consistent with the structure and indicated the sample was pure.

Anal. Calcd. for C_4H_7Br: C, 35.58; H, 5.23; Br, 59.20. Found[10]: C, 36.56; H, 5.51; Br, 59.44.

1-Bromo-1-bromomethylcyclopropane.—A solution of methylenecyclopropane (about 10 g., 0.185 mole) in tetrahydrofuran was cooled to 0° and a solution of bromine in carbon tetrachloride was added until the color of the bromine persisted (about 25 g. of bromine was used). The solvents were distilled, and the residue was distilled under reduced pressure in a semimicro column. There was obtained 23.8 g. (0.111 mole or 60%) of 1-bromo-1-bromomethylcyclopropane, b.p. 54–62° (12 mm.), $n^{25}D$ 1.5323–1.5338. A heart cut, b.p. 60° (12 mm.), $n^{25}D$ 1.5338, was pure.

Anal. Calcd. for $C_4H_6Br_2$: C, 22.46; H, 28.3; Br, 74.73. Found[10]: C, 22.95; H, 3.06; Br, 74.65.

1-Bromo-1-dimethylaminomethylcyclopropane.—A Carius tube was charged with 50 ml. of tetrahydrofuran, 13 g. of dimethylamine, and 15.3 g. (0.0715 mole) of 1-bromo-1-bromomethylcyclopropane. The tube was cooled to −80°, sealed, and warmed cautiously to 25°. After standing at 25° for 16 hr., the reaction mixture was heated at 50° for 2 hr., then at 100° for 2 hr. The tube was opened and the reaction mixture was poured into aqueous potassium hydroxide. The aqueous solution was extracted with three 250-ml. portions of ether. The extracts were combined and dried and the solvents were distilled. The residue was distilled in a semimicro column to give 10.1 g. (0.057 mole or 79%) of 1-bromo-1-dimethylaminomethylcyclopropane, b.p. 59–62° (25 mm.), $n^{25}D$ 1.4658–1.4719. A heart cut, b.p. 61–61.5° (25 mm.), $n^{25}D$ 1.4719, was pure.

Anal. Calcd. for $C_6H_{12}NBr$: C, 40.45; H, 6.79; N, 7.87; Br, 44.84. Found[10]: C, 41.36; H, 6.95; N, 7.91; Br, 44.54.

Cyclopropylmethyl Methyl Sulfide.—A Carius tube was charged at −78° with 25 ml. of anhydrous ether, 6.7 g. (0.124 mole) of distilled methylenecyclopropane, and 6 g. of methanethiol. The tube was sealed, kept at room temperature for 20 hr., and finally warmed in a steam bath for 1.5 hr. The tube was opened and the product was distilled through a 368 × 6 mm. column with a platinum spinning band. There was obtained 7.90 g. (0.9775 mole or 63%) of methyl cyclopropylmethyl sulfide, a particularly bad-smelling compound. A heart cut, b.p. 48° (28 mm.), $n^{25}D$ 1.4759, was pure.

Anal. Calcd. for $C_5H_{10}S$: C, 58.76; H, 9.86; S, 31.38. Found: C, 58.48; H, 9.72; S, 30.72.

(Methylenecyclopropane and methanethiol reacted spontaneously and vigorously at room temperature in a steel cylinder and should be regarded as potentially dangerous.)

Cyclopropylmethyl Ethyl Sulfide.—A Carius tube was charged at −80° with 5.4 g. (0.10 mole) of methylenecyclopropane, 6.2 g. (0.10 mole) of ethanethiol, 20 ml. of ether, and 0.2 g. of benzoyl peroxide. The tube was warmed to room temperature and allowed to stand 3 days, then heated at 100° for 24 hr. The tube was cooled and opened and the mixture was distilled. There was obtained 5.1 g. (0.044 mole or 44%) of cyclopropylmethyl ethyl sulfide, b.p. 59–62° (35 mm.), $n^{25}D$ 1.4719–1.4738. A heart cut, b.p. 61–61.5° (35 mm.), $n^{25}D$ 1.4738 was pure.

Anal. Calcd. for $C_6H_{12}S$: C, 62.00; H, 10.41; S, 27.60. Found:[10] C, 61.98; H, 10.71; S, 28.59, 28.87.

1-Iodo-1-(2,2,3,3,4,4,4-heptafluorobutyl)cyclopropane.—A Carius tube was charged with 5.4 g. (0.10 mole) of methylenecyclopropane, 30 g. of heptafluoropropyl iodide, and 0.2 g. of α,α'-azodiisobutyronitrile and sealed at −80°. It was warmed to room temperature, then heated at 50° for 3 hr. After it had stood overnight at room temperature the mixture was heated at 80° for 4 hr. and 100° for 1 hr. The tube was opened and the product was distilled in a semimicro still. There was obtained 33.5 g. (0.096 mole or 96%) of 1-iodo-1-(2,2,3,3,4,4,4-heptafluorobutyl)cyclopropane, b.p. 50–55° (17 mm.), $n^{25}D$ 1.4002–1.4010. A heart cut, b.p. 52–53° (17 mm.), $n^{15}D$ 1.4010, was pure.

Anal. Calcd. for $C_7H_6F_7I$: C, 24.02; H, 1.73; F, 38.00; I, 36.26. Found: C, 24.20; H, 1.95; F, 37.50; I, 36.01.

The structure of the compound was based on spectral data. The infrared spectrum showed bands attributed to C—F absorption and the cyclopropane ring but showed no olefinic or other functional absorption.

1-Bromo-1-hydroxymethylcyclopropane.—In a 250-ml., three-necked flask fitted with a True-Bore stirrer, a gas inlet tube, and a reflux condenser connected to a trap cool d with solid carbon dioxide were placed 44.5 g. (0.25 mole) of *N*-bromosuccinimide and 100 ml. of water. About 13.7 g. (0.25 mole) of methylenecyclopropane was distilled in slowly during 1 hr. A slightly exothermic reaction occurred and the amount of *N*-bromosuccinimide in suspension gradually diminished. The reaction mixture was held at 0° for 16 hr., when it was filtered to remove 7 g. of unchanged *N*-bromosuccinimide. The water was extracted with three 75-ml. portions of ether and the ether extracts were combined and dried. Distillation through a semimicro column afforded 17.9 g. (0.118 mole) of 47% of 1-bromo-1-hydroxymethylcyclopropane, b.p. 51–57° (12 mm.), $n^{25}D$ 1.5056–1.5018. Redistillation through a 12 in. × 8 mm. semimicro column with a spinning band afforded 14.0 g. of XIV, b.p. 68° (12 mm.), $n^{25}D$ 1.5016.

Anal. Calcd. for C_4H_7BrO: C, 31.81; H, 4.67. Found: C, 31.89; H, 4.88.

1-Bromocyclopropylmethyl-*N*-phenylurethan.—A mixture of 0.68 g. (0.0045 mole) of 1-bromo-1-hydroxymethylcyclopropane and 1 ml. of phenyl isocyanate was heated on a steam cone for a few minutes and then cooled in an ice bath. The crystalline product was recrystallized from a mixture of pentane and carbon tetrachloride and there was obtained 0.45 g. (0.0020 mole or 22%) of 1-bromocyclopropylmethyl-*N*-phenylurethan. After a second recrystallization, the compound had m.p. 71.2–72.0°.

Anal. Calcd. for $C_{11}H_{12}BrNO$: C, 48.91; H, 4.48; N, 5.19. Found: C, 49.52; H, 4.84; N, 5.15.

1-Bromo-1-hydroxymethylcyclopropane 3,5-Dinitrobenzoate.—To a solution of 1.43 g. (0.0095 mole) of 1-bromo-1-hydroxymethylcyclopropane in 25 ml. of pyridine was added a total of 2.30 g. (0.0109 mole) of 3,5-dinitrobenzoyl chloride in small portions. When the reaction mixture had cooled, it was warmed for 5 min. on a steam bath and poured onto ice. The product which crystallized was filtered and recrystallized from carbon tetrachloride. There was obtained 2.55 g. (0.0074 mole or 78%) of 1-bromo-1-hydroxymethylcyclopropane 3,5-dinitrobenzoate, m.p. 106.5–108°.

After two more recrystallizations the compound, m.p. 106.5–107.2°, was pure.

Anal. Calcd. for $C_{11}H_9BrN_2O_6$: C, 38.28; H, 2.63; N, 8.12. Found: C, 38.16; H, 2.82; N, 8.00.

1-Bromo-1-hydroxymethylcyclopropane *p*-Toluenesulfonate.—A solution of 9.5 g. (0.05 mole) of *p*-toluenesulfonyl chloride in 25 ml. of dry pyridine was cooled to 0° and added to a cooled solution of 6.60 g. (0.0437 mole) of 1-bromo-1-hydroxymethylcyclopropane in 25 ml. of dry pyridine. The reaction mixture was stirred 2 hr. and poured into ice water. The crystalline product was recrystallized from carbon tetrachloride and there was obtained 6.70 g. (0.0219 mole or 50%) of 1-bromo-1-hydroxymethylcyclopropane *p*-toluenesulfonate, m.p. 57–58°. A small sample recrystallized from hexane had m.p. 57.0–58.0°.

Anal. Calcd. for $C_{11}H_{13}BrSO_3$: C, 43.28; H, 4.30; Br, 26.18. Found: C, 44.89; H, 4.45; Br, 26.91.

1-Bromo-1-diethylaminomethylcyclopropane.—A solution of 6.30 g. (0.0206 mole) of 1-bromo-1-hydroxymethylcyclopropane *p*-toluenesulfonate and 6.1 g. (0.083 mole) of diethylamine in 25 ml. of tetrahydrofuran was heated under reflux for 17 hr. The reaction mixture was cooled and poured into 100 ml. of 10% potassium hydroxide solution. The solution was extracted with three 150-ml. portions of ether and the extracts were combined, dried over magnesium sulfate, filtered, and dried over potassium hydroxide. Distillation through a semimicro column yielded 2.84 g. (0.0139 mole or 67%) of 1-bromo-1-diethylaminomethylcyclopropane, b.p. 61–73° (11 mm.), $n^{25}D$ 1.4709. Redistillation afforded a heart cut, b.p. 60° (7 mm.), $n^{25}D$ 1.4700, which was pure.

Anal. Calcd. for $C_8H_{16}BrN$: C, 46.61; H, 7.83. Found: C, 47.01; H, 7.86.

A sample of 1-bromo-1-diethylaminomethylcyclopropane (0.30 g.) added to picric acid in ether gave 1-bromo-1-diethylaminomethylcyclopropane picrate (0.65 g.), which when recrystallized from methyl cyclohexane–ethyl acetate had m.p. 137–138°.

1-Bromo-1-diethylaminomethylcyclopropane Picrate.—In a 50-ml. round-bottomed flask were placed 20 ml. of tetrahydrofuran and 7.4 g. (0.105 mole) of diethylamine. 1-Bromo-1-bromomethylcyclopropane (5.6 g., 0.026 mole) was added cautiously. After about 5 min., diethylamine hydrobromide began to separate. The reaction mixture was allowed to stand 64 hr., and then was poured into aqueous potassium hydroxide. The solution was extracted with ether, the ether extracts were combined and dried, and the product was distilled in a semimicro column. There was obtained 3.07 g. of impure 1-bromo-1-diethylaminomethylcyclopropane, b.p. 46–52° (10 mm.). NMR analysis of the product indicated the presence of the amine. A sample of this material was treated with a solution of picric acid in ether. Recrystallization of the crude product from methylcyclohexane afforded pure 1-bromo-1-diethylaminomethylcyclopropane picrate, m.p. 136–137°.

Anal. Calcd. for $C_{14}H_{19}N_4O_7Br$: C, 38.63; H, 4.40; N, 12.87. Found: C, 38.86; H, 4.36; N, 13.24.

The picrate was identical with the sample prepared from 1-bromo-1-hydroxymethylcyclopropane *p*-toluenesulfonate as shown by mixed melting point (136.5–137.5°) and comparison of the infrared spectra, which were identical.

Characterization of the Products from the Claisen Rearrangement of Allyl 3-Methylphenyl Ether and of Allyl 3-Methyl-4,6-dichlorophenyl Ether[1]

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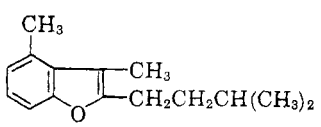
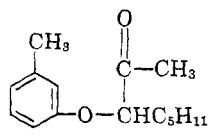
The Claisen rearrangement of allyl 3-methylphenyl ether has been shown by vapor phase chromatography analysis to yield a mixture of about 47% of 3-methyl-6-allylphenol (E) and 53% of 2-allyl-3-methylphenol (D). The structure of the latter has been established by relating it to the product of rearrangement of allyl 3-methyl-4,6-dichlorophenyl ether. The action of hydrazine and palladium on charcoal in Methyl Cellosolve on 2-allyl-3-methyl-4,6-dichlorophenol (G) leads to 2-propyl-3-methylphenol.

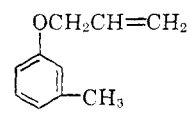
The synthesis of a degradation product from fumagillin,[2] 2-isoamyl-3,4-dimethylbenzofuran (A), required the study of methods for obtaining substitution in the 2-position of 3-methylphenol. This was accomplished satisfactorily by using 3-methyl-4,6-dichlorophenol,[2] with subsequent reductive removal of the halogen atoms. It was observed, however, that cyclization of the unblocked compound B yielded 40% of A, along with 60% of the isomeric 2-isoamyl-3,6-dimethylbenzofuran. In connection with synthetic approaches to compounds in the fumagillin series, it was desirable to examine various procedures for preparing 1,2,3-substituted compounds derived from 3-methylphenol. We have studied the Fries reaction[3] in



A



B



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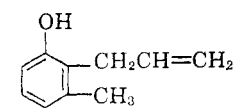
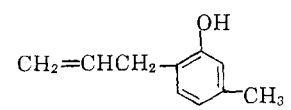


D



E

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(2) D. S. Tarbell, *et al.*, *J. Am. Chem. Soc.*, **83**, 3096 (1961).

(3) S. E. Cremer and D. S. Tarbell, *J. Org. Chem.*, **26**, 3653 (1961).