heptanone, 18341-63-4; 3-acetoxymethylcyclohexanone, 20500-51-0; 4-methyl-4-cycloheptenone, 13015-11-7; 4-methyl-3-cycloheptenone, 20500-53-2; **1**, $n = 2$, R = H, 5771-58-4; **1**, $n = 2$, R = $CH_3$, 14845-41-1; **1**, $n = 1$, R = H, 4160-49-0; **1**, $n = 1$, R = $CH_3$, 14845-46-6.

# Anomalous Low Solvolytic Reactivity of 2,2-Dichlorocyclopropylcarbinyl Chlorides

G. C. Robinson

*Ethyl Corporation, Baton Rouge, Louisiana 70821*

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The solvolyses (50 vol % aqueous ethanol, 100°) of 2,2-dichlorocyclopropylcarbinyl chloride, 1-methyl-2,2-dichlorocyclopropylcarbinyl chloride, and *trans*-3-methyl-2,2-dichlorocyclopropylcarbinyl chloride have been studied as to rate and products. The absence of rearranged solvolysis products suggests that the cyclopropyl group is not interacting with the carbinyl carbon during solvolysis. In agreement with the product picture the solvolysis rates are substantially normal for a primary alkyl chloride and are at least $10^3$ slower than is suggested by a $\sigma^+$ correlation of literature data on methyl- and ethoxy-substituted cyclopropylcarbinyl systems. The solvolysis rate of cyclopropylcarbinyl chlorides is, therefore, unexpectedly sensitive to electron-withdrawing substituents on the cyclopropane ring.

The most striking special features of cyclopropylcarbinyl systems in solvolysis are greatly enhanced solvolysis rates and formation of rearranged products having allylcarbinyl and cyclobutyl structures. The effect of methyl, phenyl, and ethoxy substituents on solvolysis rates have been studied.[1] However, no systematic study has been made of the effect of deactivating substituents such as chlorine on solvolysis in cyclopropylcarbinyl systems.

We have been interested[2] in the reactions of the *gem*-dichlorocyclopropyl functional group and have now studied its behavior as part of a cyclopropylcarbinyl solvolytic system. We report in this paper solvolysis rates (50% aqueous ethanol, 100°) and products for 2,2-dichloro-1-chloromethylcyclopropane, 2,2-dichloro-1-methyl-1-chloromethylcyclopropane, and *trans*-2,2-dichloro-3-methyl-1-chloromethylcyclopropane. The results are surprising in that participation of the cyclopropane ring appears to be completely suppressed.

## Experimental Section

**General.**—The nmr data were obtained on a Varian A-60; chemical shifts and $J$ values are reported in cycles per second (cps) relative to tetramethylsilane. The glpc unit was fitted unless otherwise stated with a 2-ft Carbowax 20M column. Distillations were normally through an 18-in. spinning-band column. The chemicals were obtained from laboratory supply houses except for acrolein dimethyl acetal which was furnished by Shell Chemical Co.

**Kinetic Runs.**—Solutions were prepared by dilution of a weighed sample of dichlorocyclopropylcarbinyl chloride to volume with 50% (v/v) aqueous ethanol. The initial run was made using a standard sealed ampoule technique titrating 5-ml aliquot portions with standard base (phenolphthalein indicator, calculated infinity). Subsequent runs were carried out using duplicate glpc analyses of 10-μl portions (2-ft Carbowax 20M, programmed from 50° at 11°/min) of 30-μl aliquots sealed in Kimax capillaries. First-order rate constants were calculated using the area of the dichlorocyclopropylcarbinyl chloride peak *vs.* an internal standard (2,5-dimethoxytoluene or *o*-diethoxybenzene). Material balances were run on the high-conversion points. Identity of the products was verified by comparison with authentic samples on the Carbowax 20M column and on an SE 30 column. The constant-temperature bath was a steam chamber.

**1,1-Dichloro-2-chloromethylcyclopropane.**—Into a 200-ml three-necked creased flask fitted with a Stir-O-Vac[3] high shear stirrer and an ice condenser was put allyl chloride (20.3 ml, 0.25 mol), chloroform (20 ml, 0.25 mol), sodium hydroxide pellets (40 g, 1.00 mol), and tetraglyme (25 ml). The mixture was stirred and the temperature was increased first to 80° during 1.5 hr and then to 98° for 2 hr more. Work-up by water dilution, ether extraction, and distillation of the dried ether extract gave 1,1-dichloro-2-chloromethylcyclopropane [9.1 g, 23%, bp 72–74° (46 mm), lit.[4] 56° (17 mm)]: infrared 3096 (cyclopropyl $CH_2$), 1372 ($CH_2Cl$), 1029 (cyclopropane ring), and 755 and 709 $cm^{-1}$ ($CCl_2$ group in cyclopropane ring).

**1,1-Dichloro-2-dimethoxymethylcyclopropane.**—Into the usual apparatus was put acrolein dimethyl acetal (30 ml, 0.25 mol), chloroform (20 ml, 0.25 mol), sodium hydroxide pellets (60 g, 1.5 mol), and tetraglyme (25 ml). The mixture was stirred vigorously 3 hr at 25–40° and the evolved gas (1.6 l., 0.064 mol as carbon monoxide) was measured. The reaction mixture was diluted with water, the organic products were ether extracted, and the ether extracts were dried and fractionally distilled yielding 1,1-dicloro-2-dimethoxymethylcyclopropane [12.2 g, 26%, bp 92–93° (35 mm)]: nmr 198 and 203 (methoxy groups, three protons each, peak separation was temperature independent to 140°, split by adjacent asymmetric center), 72–132 (cyclopropyl H, complex, three protons), and 254 cps (tertiary acetal H, one-proton doublet, $J = 6$). A mixture of 1,1-dichloro-2-dimethoxymethylcyclopropane (10 g, 54 mmol), *p* toluenesulfonylhydrazine (10.1 g, 54 mmol), and hydrochloric acid (1 ml of concentrated acid in 40 ml of 50% aqueous ethanol) was heated on a steam bath 1.5 hr yielding crude *p*-toluenesulfonylhydrazone (17.1 g). A 2 g sample was recrystallized (50 ml of 50% aqueous ethanol) giving pure *p*-toluenesulfonylhydrazone derivative (1.5 g, indicated yield 77%, mp 134–137° dec).

**2,2-Dichlorocyclopropylcarboxaldehyde.**—A mixture of the 1,1-dichloro-2-dimethoxymethylcyclopropane (44.3 g, 0.24 mol), water (200 ml), concentrated sulfuric acid (5 ml), and tetraglyme (10 ml) was stirred at 25–30° for 30 hr. Examination (glpc) of the mixture indicated about 80% conversion to aldehyde. The crude product was extracted with ether and the extract was washed (water), dried (sodium sulfate), and distilled giving 2,2-dichlorocyclopropylcarboxaldehyde [8.3 g, 30%, bp 70–71° (25 mm)]: nmr 100–170 (three-proton multiplet, cyclopropyl H) and 559 cps (one-proton doublet, aldehyde, $J = 4$); 2,4-dinitro-

(1) For a recent review, *cf.* M. Hanack and H. J. Schneider, *Angew. Chem. Intern. Ed. Engl.*, **6**, 666 (1967).

(2) (a) G. C. Robinson, *J. Org. Chem.*, **32**, 3218 (1967); (b) *ibid.*, **33**, 607 (1968).

(3) Cole-Parmer Instrument and Equipment Co., Chicago, Ill. 60626.

(4) W. M. Wagner, H. Kloosterziel, and S. van der Ven, *Rec. Trav. Chim. Pays-Bas*, **80**, 740 (1961).

phenylhydrazone, mp 145.5–147° (ethanol); hydantoin[5] (analytical sample, mp 215–216.5°, aqueous ethanol).

*Anal.* Calcd for $C_6H_6Cl_2N_2O_2$: C, 34.47; H, 2.89. Found: C, 34.11, 34.20; H, 3.05, 3.06.

**1,1-Dichloro-6-hydroxymethylcyclopropane.**—A mixture of methyl orthoformate (8.9 g, 0.083 mol), allyl alcohol (20 g, 0.345 mol), and ammonium nitrate (0.30 g) was stirred and heated under a distilling column until the distillate temperature reached 80°. The residual material was distilled under reduced pressure yielding triallyl orthoformate [8.88 g, 57%, bp 101–110° (34 mm), lit.[6] bp 196–205°]. The triallyl orthoformate (0.048 mol) was allowed to react with chloroform (20 ml, 0.25 mol) and sodium hydroxide pellets (40 g, 1.00 mol) in tetraglyme (25 ml) in an ice bath with vigorous stirring (Stir-O-Vac high shear stirrer) during 1.5 hr. The mixture stood at 25° for 16 hr and was then diluted with water and extracted with ether. The ether extract was shaken twice with 20% aqueous hydrochloric acid. Examination of the ether phase (glpc) showed two products (area ratio 1:2). Removal of solvent gave 6.50 g of crude product having a carbonyl band in the infrared (formate ester). Column chromatography on alumina decomposed the formate ester giving pure 1,1-dichloro-2-hydroxymethylcyclopropane (5.42 g, 27% on triallyl orthoformate): infrared 3.0 (bonded OH), 3.33, 3.42, 3.48, 6.85, 7.00, 7.20, 8.08, 8.22, 9.00, 9.60, 10.32, 10.70, 11.30, 12.40, and 13.40 $\mu$; nmr 245 (OH), 218–230 (pair of doublets, $-CH_2O-$), 65–135 ppm (complex cyclopropyl H) and integrates for 3.1 protons $-CH_2OH$ and 3.0 protons on cyclopropane ring (calcd three protons and three protons).

The phenylurethan was an oil. The $\alpha$-naphthylurethane was a solid (mp 100–102°): nmr 70–135 (cyclopropyl H), 235–285 ($-CH_2O-$), 420–430 (broad, NH), and 430–480 ppm (aromatic), integrated area aromatic plus NH to $-CH_2O-$ is 7.9/2 (calcd 8/2) and of $-CH_2O-$ to cyclopropyl H is 2/3 (calcd 2/3).

*Anal.* Calcd for $C_{15}H_{13}Cl_2NO_2$: C, 58.06; H, 4.22; Cl, 22.86. Found: C, 58.14, 58.38; H, 4.36, 4.37; Cl, 22.5.

**1,1-Dichloro-2-ethoxymethylcyclopropane.**—Allyl ethyl ether (21.5 g, 0.25 mol), chloroform (20 ml, 0.25 mol), sodium hydroxide pellets (40 g, 1.00 mol), and tetraglyme (25 ml) were allowed to react with high-shear stirring at 98° for 3 hr yielding crude 1,1-dichloro-2-ethoxymethylcyclopropane[7] [21 g, 50%, bp 82–90° (40 mm)] containing a minor impurity. The major component was isolated by careful distillation, bp 90–90.5° (43 mm).

*Anal.* Calcd for $C_6H_{10}Cl_2$: C, 42.63; H, 5.96. Found: C, 42.9, 42.8; H, 5.92, 6.11.

**1,1-Dichloro-2-methyl-2-chloromethylcyclopropane.**—A mixture of methallyl chloride (26.5 g, 0.292 mol), chloroform (40 ml, 0.50 mol), sodium hydroxide pellets (80 g, 2.0 mol), and 100 ml of tetraglyme was stirred vigorously at 30° for 2 hr. Steam distillation followed by fractional distillation of the organic distillate gave 1,1-dichloro-2-methyl-2-chloromethylcyclopropane [24.6 g, 49%, bp 86° (30 mm), $n^{25}D$ 1.4855, lit.[8] bp 89° (50 mm), $n^{25}D$ 1.4858]: nmr 87.2 and 91.7 (cyclopropyl H *cis* and *trans* to methyl group, $J$ = 13), 92.8 (methyl group), and 223.1 and 232.8 cps (chloromethyl protons adjacent to asymmetric center, $J$ = 16); integral 2.0 (chloromethyl, calcd 2.0) and 4.8 (cyclopropyl H plus methyl, calcd 5.0).

*Anal.* Calcd for $C_5H_7Cl_3$: C, 34.62; H, 4.07; Cl, 61.32. Found: C, 34.61, 34.42; H, 4.19, 4.17; Cl, 60.7.

**1,1-Dichloro-2-methyl-2-hydroxymethylcyclopropane.**—A mixture of methallyl alcohol (18.0 g, 0.25 mol), chloroform (20 ml, 0.25 mol), sodium hydroxide pellets (40 g, 1.00 mol), and tetraglyme (25 ml) was stirred for 1 hr. The usual work-up followed by distillation gave crude material, bp 103° (30 mm), contaminated with 25% impurity. The phenylurethan formed readily (mp 78.5–79.5°): nmr ($DCCl_3$) 77.6 and 89.2 (cyclopropyl H *trans* and *cis* to methyl, $J$ = 7.4), 86.3 (methyl), 246.7 and 269.3 ($-OCH_2-$ adjacent to asymmetric center, $J$ = 11.4), and 430–500 cps (aromatic and NH protons), integral five cyclopropyl plus methyl protons and two methylene protons.

*Anal.* Calcd for $C_{12}H_{13}Cl_2NO_2$: C, 52.57; H, 4.78. Found: C, 52.21, 52.36; H, 4.73, 4.96.

**1,1-Dichloro-2-methyl-2-ethoxymethylcyclopropane.**—To a solution of sodium ethoxide in ethanol (0.25 mol of sodium to 125 ml of absolute ethanol) was added methallyl chloride (22.64 g, 0.25 mol) and the mixture was allowed to stir at 25° for 4 days. After dilution with water an ether extract was distilled giving ethyl methallyl ether, 14.60 g, 58%, bp 86–88° (lit.[9] bp 84.6–86.8°). The ethyl methallyl ether (0.15 mol), chloroform (16 ml, 0.20 mol), sodium hydroxide pellets (40 g, 1.0 mol), and tetraglyme (25 ml) were stirred at 0° for 2.5 hr. Dilution with water and ether extraction followed by distillation of the ether extract gave 1,1-dichloro-2-methyl-2-ethoxymethylcyclopropane, 21.9 g, 80%, bp 83–85° (34 mm).

*Anal.* Calcd for $C_7H_{12}Cl_2O$: Cl, 38.73. Found: Cl, 38.8, 38.4.

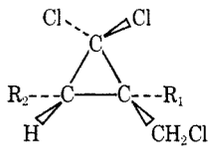
**1,1-Dichloro-2-methyl-3-chloromethylcyclopropane.**—Crotyl chloride (0.25 mol, contains about 25% *cis*-crotyl chloride), chloroform (20 ml, 0.25 mol), sodium hydroxide pellets (40 g, 1.00 mol), and tetraglyme (50 ml) was stirred at 37° for 2.5 hr. Steam distillation followed by careful fractional distillation gave 1,1-dichloro-2-methyl-3-chloromethylcyclopropane [19.8 g, 46%, bp 85° (30 mm), $n^{25}D$ 1.4813] contaminated with a small amount of a second material (shoulder on glpc trace) which could not be removed by extraction of a dilute petroleum ether solution with concentrated sulfuric acid: nmr 1.36 (methyl group doublet, $J$ = 2.5), 1.2–1.8 (cyclopropyl H multiplet), and 3.75 ppm (chloromethyl doublet, $J$ = 7.5); integral 2.0 chloromethyl protons and 5.2 methyl plus cyclopropyl protons (calcd 5.0).

*Anal.* Calcd for $C_5H_7Cl_3$: Cl, 61.32. Found: Cl, 61.0.

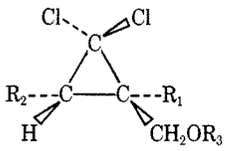
**1,1-Dichloro-2-methyl-3-hydroxymethylcyclopropane.**—A mixture of crotyl alcohol (18.0 g, 0.25 mol), chloroform (20 ml, 0.25 mol), sodium hydroxide pellets (40 g, 1.00 mol), and tetraglyme (25 ml) was allowed to react in the usual way and crude product was distilled giving a low yield (3 g) of product containing 80% of the major component. Column chromatography on alumina yielded this major component in about 95% purity. The presumed 1,1-dichloro-2-methyl-3-hydroxymethylcyclopropane did not yield a crystalline phenylurethane. An $\alpha$-naphthylurethane solidified but melted over a wide range. A variety of methods of purification failed to yield a tractable product. The material is probably a mixture of *cis–trans* isomers.

## Results

Solvolysis of 1,1-dichloro-2-chloromethylcyclopropane in 50% (v/v) aqueous ethanol was found to give two product peaks on glpc. Comparison on SE-30 and Carbowax 20M glpc columns with authentic samples identified the products as 1,1-dichlorocyclopropyl-2-ethoxymethylcyclopropane (IIb) and 1,1-dichlorocyclopropyl-2-hydroxymethylcyclopropane (IIa). No



Ia, $R_1 = R_2 = H$
b, $R_1 = CH_3$; $R_2 = H$
c, $R_1 = H$; $R_2 = CH_3$



IIa, $R_1 = R_2 = R_3 = H$
b, $R_1 = R_2 = H$; $R_3 = C_2H_5$
c, $R_1 = CH_3$; $R_2 = R_3 = H$
d, $R_1 = CH_3$; $R_2 = H$; $R_3 = C_2H_5$
e, $R_1 = R_3 = H$; $R_2 = CH_3$
f, $R_1 = H$; $R_2 = CH_3$; $R_3 = C_2H_5$

other products were detected and 87% of reacted starting material could be accounted for.

The alcohol IIa had not previously been reported and its synthesis was approached by two routes. One proposed route involved dichlorocyclopropanation of

(5) The hydantoin was prepared by the procedure of H. R. Henze and R. J. Speer [*J. Amer. Chem. Soc.*, **64**, 522 (1942)], but formation of a coproduct (mp 80°) presumed (from its infrared and nmr spectra) to be aldehyde trimer complicated the work-up. Facile trimerization was a continual complication with this aldehyde.

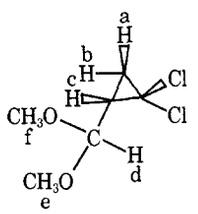
(6) F. Beilstein, *et al.*, *Ber.*, **18**, 482 (1885).

(7) D. Seyferth, *et al.*, *J. Amer. Chem. Soc.*, **87**, 4259 (1965).

(8) H. A. Bruson and H. L. Plant, U. S. Patent 3,376,348 (April 2, 1968).

(9) M. Tamele, C. J. Ott, K. E. Marple, and G. Hearne, *Ind. Eng. Chem.*, **33**, 115 (1941).

acrolein dimethyl acetal, hydrolysis to the aldehyde, and reduction with sodium borohydride to IIa. The dichlorocyclopropanation proceeded in reasonable (26%) yield giving 1,1-dichloro-2-dimethoxymethylcyclopropane. This substance, interestingly, showed two methoxyl peaks in its nmr spectrum and the appearance of the doublet was unchanged up to 140°. The methoxyl doublet is attributed to the adjacent asymmetric center[10] and not to restricted rotation. A detailed analysis of this unusual spectrum has been carried out.[11]

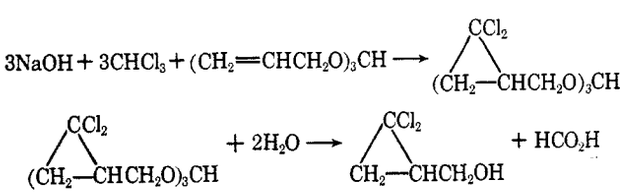



| | | | | | | |
|---|---|---|---|---|---|---|
| Chemical shift cps | $H_a$ 83.6 | $H_b$ 105.9 | $H_c$ 103.3 | $H_d$ 253 | $H_e$ 199 | $H_f$ 203 |

| | | | | |
|---|---|---|---|---|
| Coupling constants cps | $J_{ab}$ 6.5 | $J_{ac}$ 9.1 | $J_{bc}$ 5.1 | $J_{cd}$ 6.0 |

Difficulties were met during hydrolysis of the acetal to 2,2-dichlorocyclopropylcarboxaldehyde. The yield of aldehyde was rather poor and the aldehyde was difficult to handle, appearing to trimerize very readily to the rather unreactive substituted trioxane. This approach was abandoned when an alternate synthesis of the desired alcohol proved simpler.

The successful synthesis used dichlorocyclopropanation of triallyl orthoformate with subsequent hydrolysis directly to IIa. This synthesis proceeded smoothly except that the product alcohol was contaminated initially with some formate ester owing to incomplete hydrolysis. This was converted into alcohol by chromatography on alumina. The nmr spectrum of the alcohol was in accord with the postulated structure and the α-naphthylurethan derivative gave the expected nmr pattern and the correct analysis.




Preparation of 1,1-dichloro-2-methyl-2-chloromethylcyclopropane (Ib) according to our standard procedure went in good (49%) yield. The protons of the chloromethyl group were nonequivalent in the nmr, presumably again owing to the adjacent asymmetric center. Solvolysis in aqueous ethanol gave two products, 1,1-dichloro-2-methyl-2-hydroxymethylcyclopropane (IIc) and the corresponding ethyl ether (IId), which were identified by glpc comparison with authentic materials. Material balances were initially about 80% declining to 60% at 604 hr. The initial solvolysis products rapidly reacted further with solvent at 120°. The alcohol (IIc) was prepared in low yield directly by dichlorocyclopropanation of methallyl alcohol and readily formed a phenylurethane which gave the correct elemental analysis and had an nmr spectrum similar to that of parent Ib. The ethyl ether (IId) was prepared in the standard way from methallyl ethyl ether in excellent (80%) yield.

Preparation of 1,1-dichloro-2-methyl-3-chloromethylcyclopropane utilized dichlorocyclopropanation of crotyl chloride containing 25% *cis* crotyl chloride. The product, isolated by careful distillation in fair (46%) yield, revealed a small shoulder on glpc which was not removed by extraction of a dilute pentane solution of the product with sulfuric acid. The impurity cannot, therefore, be an olefinic product from dichloromethylene insertion at a carbon–hydrogen bond and is presumably an isomeric *gem*-dichlorocyclopropane. The nmr spectrum was consistent with the expected structure as was the elemental analysis.

Solvolysis of the 1,1-dichloro-2-methyl-3-chloromethylcyclopropane yielded two products, one of which was shown by glpc to be 1,1-dichloro-2-methyl-3-hydroxymethylcyclopropane and the second was presumed from its retention time to be the corresponding ethyl ether. Material balances were 95% based on areas. Authentic 1,1-dichloro-2-methyl-3-hydroxymethylcyclopropane was prepared by dichlorocyclopropanation of crotyl alcohol. Conversion to an α-naphthylurethan gave a solid derivative which melted over a wide range in spite of repeated attempts at purification. It seems likely that *cis* isomer is present and is difficulty separable.

Rate data were obtained at 100° (steam chamber) in 1:1 (v/v) aqueous ethanol. Most of the rates were obtained using glpc analysis with an internal standard. This procedure permits continual scrutiny of the solvolysis products. An initial study of 1,1-dichlorocyclopropyl-2-chloromethylcyclopropane solvolysis used a conventional sealed ampoule titrimetric procedure. A summary of the rate data together with some comparative literature data are given in Table I. Representative kinetic runs are detailed in Tables II and III.

## Conclusions

The solvolysis products show a simple pattern and no rearranged cyclobutyl or homoallylic chlorides, alcohols, or ethyl ethers were detected. The material balances are adequate to exclude any substantial formation of these products.

The rather unexpected product data are supported by the kinetic data. The rate of solvolysis of Ia is anomalously slow. From the solvolytic rate data of Schleyer and Van Dyne[12] (on polymethyl- and ethoxycyclopropylcarbinyl 3,5-dinitrobenzoates which are well correlated by a $\sigma^+$ plot[13]) one can estimate that the solvolysis rate of 2,2-dichlorocyclopropylcarbinyl 3,5-dinitrobenzoate should be 0.16 times that of cyclopropylcarbinyl 3,5-dinitrobenzoate.

This value can be transferred to a chloride leaving group by assuming that the relative rates of substituted cyclopropylcarbinyl systems are substantially

(10) H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2196 (1962).

(11) The HaHbHc portion of the spectrum was calculated as an ABX pattern. $J_{ax}$ and $J_{bx}$ were of unlike sign.

(12) P. von R. Schleyer and G. W. Van Dyne, *J. Amer. Chem. Soc.*, **88**, 2321 (1966).

(13) H. C. Brown, personal communication.

TABLE I

SOLVOLYSIS RATES OF SUBSTITUTED CYCLOPROPYLCARBINYL CHLORIDES (50% AQUEOUS ETHANOL, 100°)

| $RCH_2Cl$, R | $k_1 \times 10^6$, $sec^{-1}$ | Relative rate |
|---|---|---|
| Cyclopropyl | $\gg 1.3 \times 10^2$ [a] | $\gg 67$ |
| $C_2H_5$ | 9.7[b] | 5.0 |
| 2,2-Dichlorocyclopropyl | $1.8 \pm 0.1$[c] | 1 |
| 2,2-Dichlorocyclopropyl | $1.92 \pm 0.06$ | |
| 2,2-Dichlorocyclopropyl | $1.97 \pm 0.13$ | |
| 1-Methyl-2,2-dichlorocyclopropyl | $1.32 \pm 0.04$ | 0.68 |
| 2,2-Dichloro-3-methylcyclopropyl | $4.0 \pm 0.2$ | 2.05 |

[a] 50° rate is $1.3 \times 10^{-4}$ $sec^{-1}$; J. D. Roberts and R. H. Mazur, *J. Amer. Chem. Soc.*, **73**, 2509 (1951). [b] 101.6°, C. A. Vernon, *J. Chem. Soc.*, 423 (1954). [c] Titrimetric rate, calculated infinity.

TABLE II

TITRIMETRIC DATA.
1,1-DICHLORO-2-CHLOROMETHYLCYCLOPROPANE SOLVOLYSIS[a]

| Time, hr | Titer, (ml of 0.0957 *M* NaOH) | $k_1 \times 10^6$, $sec^{-1}$ |
|---|---|---|
| 0 | | |
| 21 | 0.40 | 1.9 |
| 45 | 0.75 | 1.9 |
| 117 | 1.36 | 1.7 |
| 285 | 2.00 | 1.7 |
| | | Av $1.8 \pm 0.1$ |

[a] 1:1 v/v aqueous ethanol, 100°, calcd $\infty$ 2.68 ml.

TABLE III

REPRESENTATIVE DATA.
1,1-DICHLORO-2-CHLOROMETHYLCYCLOPROPANE SOLVOLYSIS[a]

| Time, hr | RCl/ internal standard (relative area) | $10^6 k_1$, $sec^{-1}$ |
|---|---|---|
| 0 | 0.678 | |
| 24 | 0.588 | 1.67 |
| 48 | 0.481 | 1.99 |
| 74 | 0.386 | 2.12 |
| 98.2 | 0.336 | 1.99 |
| 141.2 | 0.217 | 2.24 |
| 194.2 | 0.188 | 1.84 |
| 263 | 0.108 | 1.94 |
| | | Av $1.97 \pm 0.13$ |

[a] 1:1 v/v aqueous ethanol, 100°, glpc internal standard.

unaffected by changes in the leaving group and solvent. In support of this assumption Roberts[14] showed that in solvolysis of 1-methylcyclopropylcarbinyl tosylate changing solvent from methanol to ethanol to acetic acid gave a substantially constant rate relative to cyclopropylcarbinyl tosylate of 4–5. Schleyer and Van Dyne found the same rate ratio for a 3,5-dinitrobenzoate leaving group in aqueous acetone.

Thus one predicts a solvolysis rate for Ia (50°, 50% aqueous ethanol) of $2.7 \times 10^{-5}$ $sec^{-1}$. Activation energy data are not available for the extrapolation from 50 to 100° but a factor of 100 is assumed as a lower limit giving an estimated rate as $>2.7 \times 10^{-3}$. This is a factor of $>1.4 \times 10^3$ higher than the observed rate.

(14) D. D. Roberts, *J. Org. Chem.*, **31**, 2000 (1966).

Alternatively one can assume that the solvolysis mechanism is similar to that of *n*-propyl chloride. From the $pK_a$ of 2,2-dichlorocyclopropane carboxylic acid[15] one calculates $\sigma^*$ of the 2,2-dichlorocyclopropyl group as +0.72. Although $\rho^*$ for primary alkyl chloride solvolysis in 50% aqueous ethanol at 100° is not available, it should be near the value (−0.74) for primary alkyl brosylate solvolysis in ethanol at 100°.[16] To a first approximation using $\rho^*$ as −0.74 one calculates the solvolysis rate of *gem*-dichlorocyclopropylcarbinyl chloride as 0.246 times that of *n*-propyl chloride or $2.4 \times 10^{-6}$ $sec^{-1}$ in good agreement with the observed $1.8 \times 10^{-6}$ $sec^{-1}$ solvolysis rate.

Clearly the solvolysis of *gem*-dichlorocyclopropylcarbinyl chloride gives a product pattern and kinetic behavior characteristic of primary alkyl chloride solvolysis without involvement of the cyclopropane ring. This conclusion is strengthened by the effects of methyl substitution on reaction products and rates. The products are completely analogous to those from the parent compound. The solvolysis rate is depressed by a factor of 0.68 on 1-methyl substitution whereas in the simple cyclopropylcarbinyl system solvolysis rate is increased by a factor of 5 on 1-methyl substitution. Rate is increased by a factor of 2.05 by 3-methyl substitution, much less than the factor of 8–11 noted in cyclopropylcarbinyl systems. This pattern of rate effects on methyl substitution strongly suggests a simple solvolytic substitution at the carbinyl carbon not involving charge delocalization into the cyclopropane ring.

No convincing reason for the noninvolvement of the ring in *gem*-dihalocyclopropylcarbinyl chloride solvolysis can as yet be given. Steric explanations seem unpromising since models reveal no obvious steric problems and solvolytic studies on polymethylcyclopropylcarbinyl *p*-nitrobenzoates indicate normal participation by the cyclopropane ring although chlorine and methyl are substantially identical sterically[17] (Pauling and van der Waals radii 1.8 and 2.0, respectively). It appears that participation in cyclopropylcarbinyl chloride solvolysis must be abnormally sensitive to electron-withdrawing substituents, even more sensitive than can be accounted for by a $\sigma^+$ correlation. Even a mildly electronegative group like chlorine is sufficient to nullify participation. The way in which this unusual deactivation is implemented remains to be elucidated.

**Registry No.** —1,1-Dichloro-2-chloromethylcyclopropane, 3722-05-2; 1,1-dichloro-2-dimethoxymethylcyclopropane, 20414-44-2; 1,1-dichloro-2-dimethoxymethylcyclopropane-*p*-toluenesulfonylhydrazone derivative, 20414-45-3; 2,2-dichlorocyclopropylcarboxaldehyde, 20414-46-4; 2,2-dichlorocyclopropylcarboxaldehyde-(2,4-dinitrophenylhydrazone), 20414-47-5; 2,2-dichlorocyclopropylcarboxaldehyde (hydantoin derivative), 20414-48-6; 1,1-dichloro-2-hydroxymethylcyclopropane, 5365-23-1; 1,1-dichloro-2-hydroxymethylcyclopropane (α-naphthylurethan), 20414-49-7; 1,1-dichloro-2-ethoxymethylcyclopropane, 932-59-2; 1,1-dichloro-2-methyl-2-chloromethylcyclopropane, 15997-19-0; 1,1-dichloro-2-methyl-2-chloromethylcyclopro-

(15) R. C. Woodworth and P. S. Skell, *J. Amer. Chem. Soc.*, **79**, 2542 (1957).

(16) A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., 1962, p 126.

(17) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945.

pane (phenylurethan), 20439-52-5; 1,1-dichloro-2-methyl-2-ethoxymethylcyclopropane, 20439-53-6; 1,1-dichloro-2-methyl-3-chloromethylcyclopropane, 20439-54-7.

**Acknowledgment.**—Spectral data were obtained and largely interpreted by Dr. F. J. Impastato and Dr. D. W. Imhoff. Elemental analyses were conducted by Mr. W. J. Easley.

# Bicyclobutyl Derivatives. V. Syntheses of Conjugated Perhalogenated Diolefins[1]

J. D. PARK, SAM KWON CHOI,[2] AND H. ERNEST ROMINE[2]

*Department of Chemistry, University of Colorado, Boulder, Colorado 80302*

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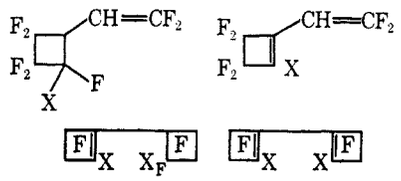
The cycloaddition of 1,1,4,4-tetrafluorobutadiene-1,3 to $CF_2$=CFCl and $CF_2$=$CCl_2$, respectively, led to the formation of the following perhalogenated derivatives which have been examined and characterized.

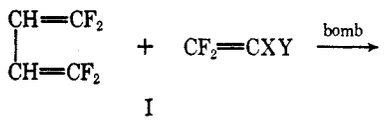


X = Cl or F

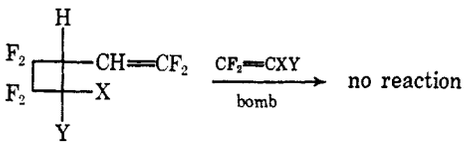
This paper reports the cycloaddition of 1,1,4,4-tetrafluorobutadiene-1,3 to $CF_2$=CFCl and $CF_2$=$CCl_2$ leading to perhalogenated "dibox" compounds.[3]

## Results and Discussion

The thermal cycloaddition of 1,1,4,4-tetrafluorobutadiene-1,3 (I) with excess tetrahaloethylenes has led to the 1:1 adducts, 1-(β,β-difluorovinyl)-2,2-dihalo-3,3,4,4-tetrafluorocyclobutanes (IIa and b, 60–90%). No 1:2 diadducts were detected even in the presence of a large excess of tetrahaloethylene. The vinyl cyclobutane



I

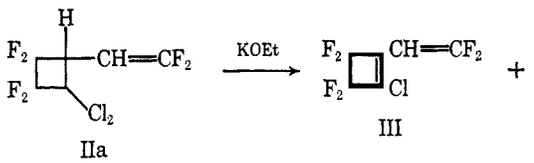


IIa, X = Y = Cl
b, X = F; Y = Cl

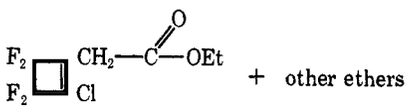
adducts are stable, colorless liquids. They have been characterized by microanalysis, H and $^{19}$F nmr spectra, infrared spectra, and mass spectra.

The observed resistance of IIa and IIb to further cycloaddition reactions implied the requirement of a diene intermediate in these highly halogenated systems. Dehydrohalogenation of IIa or IIb would lead to more reactive vinylcyclobutenes.

Several classical dehydrohalogenation media were tested on this system with limited success. Ethanolic potassium hydroxide reacts exothermically with IIa to

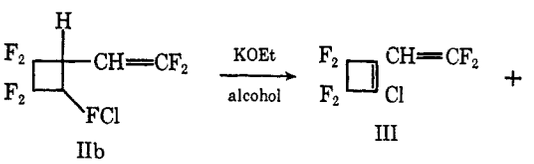


IIa III

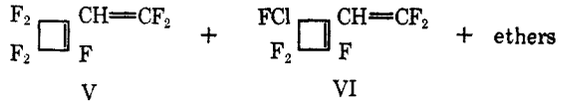


IV

give 1-(β,β-difluorovinyl)-2-chloro-3,3,4,4-tetrafluorocyclobutene (III, 45%) and a complex mixture of ether substitution products. The ester IV (18%) apparently stems from base-catalyzed hydrolysis of one or more product ethers. Potassium ethoxide converts IIb into a mixture of three possible dienes, III, V, and VI, along with a very complex mixture of ethers. The three vinylcyclobutenes were characterized by their infrared and mass spectra and by microanalysis. They are colorless liquids which polymerize to waxy solids within several hours at room temperature. Potassium hydroxide in mineral oil successfully dehydrohalogenates IIa to III (35%) and IIb to III (10%), V (25%), and VI



IIb III



V VI

(1) Previous papers in this series: (a) J. D. Park and W. C. Frank, *J. Org. Chem.*, **29**, 1445 (1964); (b) *ibid.*, **32**, 1333 (1967); (c) *ibid.*, **32**, 1336 (1967); (d) *ibid.*, **32**, 1340 (1967).

(2) This paper represents parts of Ph.D. Theses submitted to the Graduate School, University of Colorado, Boulder, Colo., by S. K. Choi, 1969, and by H. E. Romine, 1968.

(3) "Dibox" is a trivial name used to designate dicyclobutene.