liquor was evaporated to yield a residue which was then washed with dilute sodium hydroxide and recrystallized from 95% ethanol to give 0.17 g. (25%) of the pyrimidone derivative **13b**: m.p. 258–259°; λ_{max}^{KBr} 6.06 μ; $\lambda_{max}^{95\%\ C_2H_5OH}$ 265 mμ (ϵ 52,500), 289 (17,100), 300 (16,400), 322 (12,860); n.m.r. τ 6.01 (1 proton) and 8.87 (9 protons).

Anal. Calcd. for $C_{21}H_{20}N_2O$: C, 79.70; H, 6.37; N, 8.86. Found: C, 79.38; H, 6.43; N, 8.70.

Preparation of 1-Cyano-1-tetralylmalononitrile (**14**).—A solution of α-tetrylidenemalononitrile, 6 ml. of *t*-butyl alcohol and 1 g. of sodium cyanide was stirred for 4 hr. The resulting red solution was poured over ice and acidified with dilute sulfuric acid, precipitating 3.57 g. of sticky orange solid melting at 128–130°. Recrystallization from 95% ethanol gave 2.69 g. (81%) of colorless crystals of **14**, m.p. 131–132.5°, λ_{max}^{KBr} 4.5 μ (CN), n.m.r. τ 5.52 (1 proton).

Anal. Calcd. for $C_{14}H_{11}N_2$: C, 76.00; H, 5.01; N, 18.99. Found: C, 76.11; H, 5.22; N, 18.76.

Cyclization of 1-Cyano-1-tetralylmalononitrile (**14**).—A solution of 2 g. of **14** in 20 ml. of concentrated sulfuric acid was allowed to stand at room temperature for 3 hr., poured into 200 ml. of water, and boiled for 10 min. After several days, the dilute acidic solution yielded 1.91 g. (83%) of colorless crystals of the succinimido derivative **15**, m.p. 226–228°. Recrystallization from 95% ethanol gave colorless crystals: m.p. 233–235°; λ_{max}^{KBr} 2.95 (NH), 5.68 and 5.8 (CO–N–CO), 6.05 μ (amide CO).

Anal. Calcd. for $C_{14}H_{14}N_2O_3$: C, 65.10; H, 5.46; N, 10.85. Found: C, 65.37; H, 5.50; N, 11.04.

β-Substituent Stabilization of Carbanion Intermediates

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Nucleophilic attack by an ethoxide ion on 1,2-dichlorocyclobutenes yielded mixtures of products in ratios that substantiates the presence of a "β-effect." The β-substituents were found to stabilize a carbanion intermediate in this order: *gem*-dichloro > *gem*-ethoxychloro > *gem*-fluorochloro > *gem*-diethoxy ≥ *gem*-difluoro.

The question of the β-substituent effect on the stabilization of a carbanion intermediate has been described to be unresolved.[1] Hine[2] and Roberts[3] found that β-fluorine stabilized an intermediate carbanion better than a β-chlorine and a β-methoxy in their benzenoid systems. Their results supported the supposition that carbanions would best be stabilized by induction by the most electronegative substituent in the β-position.

Hine[2] also reported seemingly contradictory results in a base elimination study of pentahaloethanes. He found that CF_2HCCl_3 dehydrohalogenated 55 times as fast as CF_3CCl_2H. As an explanation, it was thought that perhaps this elimination went by a concerted mechanism rather than through the carbanion. Some reconsideration of this statement must now be made in view of Andreades' recent proof[4] of carbanion intermediates in the reaction of monohydrofluorinated compounds with base.

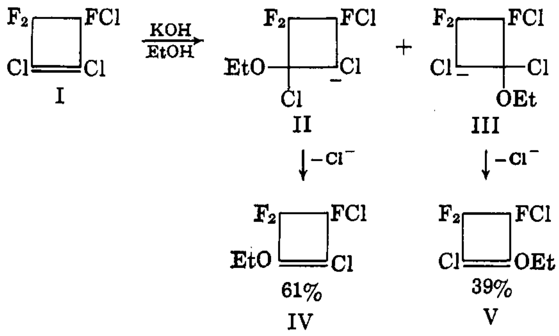
Tiers[5] reported n.m.r. data on linear fluorinated molecules that indicated that electron withdrawal toward the halogen in question increased with bulkier halogens. The ability to disperse or delocalize the negative charge over the larger volume of the atom appeared to overcome the lesser electronegativity. From this data, one could conclude that a carbanion would be stabilized better by bulkier halogens in the β-position.

A study was undertaken to examine the effects of β-substituents as applied to a halogenated cyclobutene system, which has recently been shown[1] to have carbanion intermediate character upon nucleophilic attack by ethoxide ion.

Results and Discussion

A series of 1,2-dichloro-3,3-difluorocyclobutenes was treated with potassium hydroxide dissolved in absolute ethanol at 0°. The resulting ether product distribution showed the relative effect of β-ethoxy and β-chlorine in comparison with β-fluorine in stabilizing the intermediate carbanion. The α-substituent was chlorine for ethoxide attack at either end of the double bond. The product ratios, with the exception of the first case, were determined by calibrated gas–liquid chromatograph integration with an accuracy of ±2%.

1,2,3-Trichloro-3,4,4-trifluorocyclobutene (I) yielded two inseparable isomers detected only by n.m.r. The ethoxy group was in a slightly different environment in each isomer so the methylene quartets and methyl triplets were centered at different τ-values. One isomer was later prepared by an unequivocal synthesis so the proper n.m.r. assignments could be made for each isomer. The ratio of the two products was calculated by measuring the area under each of the expanded methylene quartets by a planometer. This measurement showed 1-ethoxy-2,3-dichloro-3,4,4-trifluorocyclobutene (IV) predominating over 2-ethoxy-1,3-dichloro-3,4,4-trifluorocyclobutene (V) by a 61 to 39 ratio and thereby demonstrated that the carbanion intermediate favored the β-*gem*-fluorochloro group over the β-*gem*-difluoro group.



1-Bromo-2-chloro-3,3,4,4-tetrafluorocyclobutene (VI) has been found[6] to give both the bromo ether (VII) and chloro ether (VIII) in a 75 to 25 ratio, respectively,

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[1] J. R. Dick, J. R. Lacher, and J. D. Park, *J. Org. Chem.*, in press.

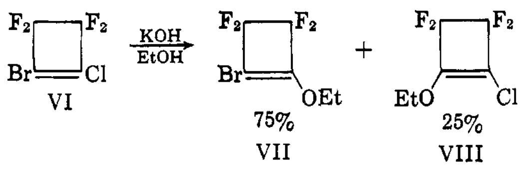
[2] J. Hine and P. B. Langford, *ibid.*, **27**, 4149 (1962).

[3] G. E. Hall, R. Piccolini, and J. D. Roberts, *J. Am. Chem. Soc.*, **77**, 4540 (1955).

[4] S. Andreades, *ibid.*, **86**, 2003 (1964).

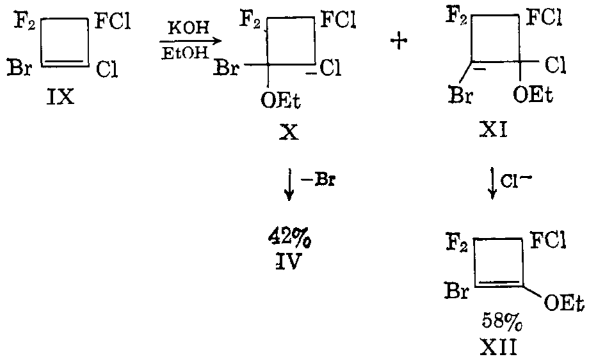
[5] G. V. D. Tiers, *ibid.*, **78**, 2914 (1956).

[6] R. Sullivan, Ph.D. Thesis, University of Colorado, 1964.

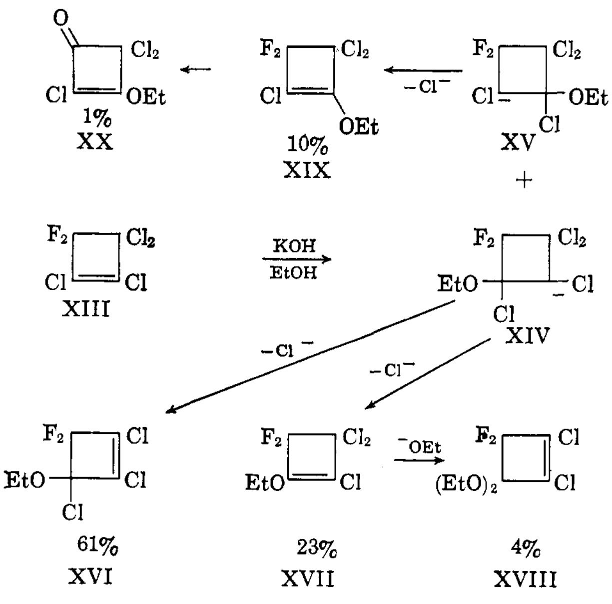


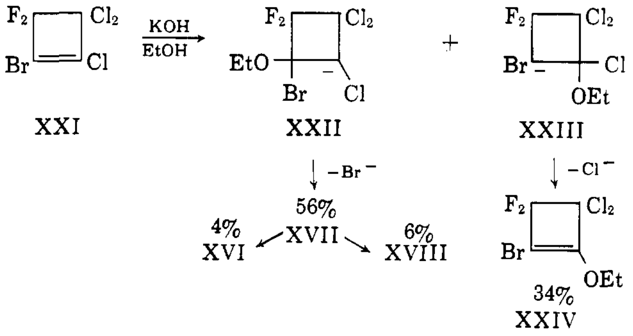
showing the greater carbanion stabilizing ability of α-bromine over that of an α-chlorine.

Upon adding the effects of the α- and β-substituents on the carbanion for the previous two reactions, one would then expect 1-bromo-2,3-dichloro-3,4,4-trifluorocyclobutene (IX) to give 1-bromo-2-ethoxy-3-chloro-3,4,4-trifluorocyclobutene (XII) and IV in a ratio of 57 to 43. Indeed, IX gave XII and IV in a 58 to 42 ratio showing that this system appears to give a straight additivity of the α- and β-substituent effects on the intermediate carbanion. Even though the thought that the product distribution control was due to steric rather than electric effects was ignored because of the extremely fast reaction at 0°, the above ratio was reassuring in that it showed that the major product occurred as the result of the carbanion intermediate with the greater possible steric repulsions.

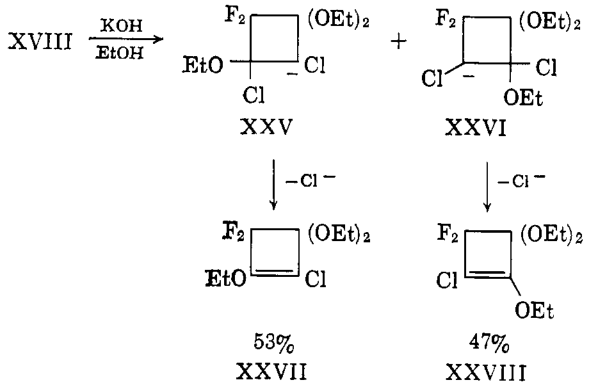


1,2,3,3-Tetrachloro-4,4-difluorocyclobutene (XIII) gave five products, the origin of which will be discussed later, going through two carbanion intermediates. The product distribution showed that the carbanion intermediate favored the β-*gem*-dichloro over the β-gem-difluoro group by an 89 to 11 ratio. The reaction with 1-bromo-2,3,3-trichloro-4,4-difluorocyclobutene (XXI) yielded four products from the two intermediate carbanions that were found to be in a 66 to 34 ratio in favor of the β-*gem*-dichloro-stabilized intermediate (XXII). The calculated ratio (from adding the α- and β-substituent effects) predicted a 57 to 43 ratio. Apparently, the β-substituent effect was greater than the α-substituent effect in stabilizing the carbanion.

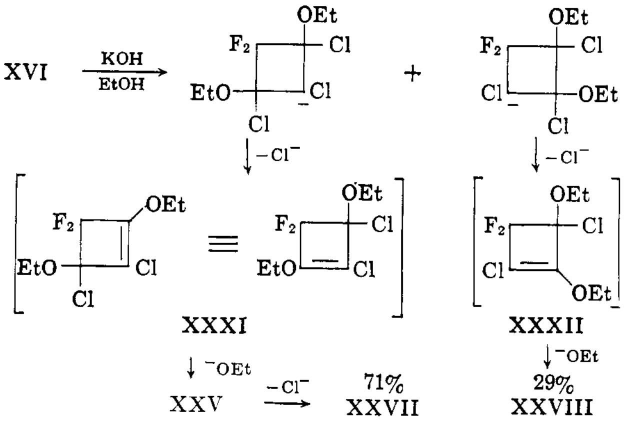




The question of the β-ethoxy *vs.* the β-fluoro stabilization was resolved by reacting XVIII with ethoxide to yield an almost equal molar mixture of two products. The distribution showed that the β-*gem*-diethoxy stabilized the intermediate carbanion slightly better than the β-*gem*-difluoro group.



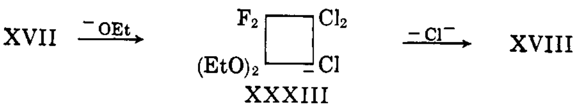
The reaction of XVI with ethoxide yielded two isomeric triethers (XXVII and XXVIII) in a ratio of 71 to 29 showing a preference for the carbanion to be stabilized by the *gem*-ethoxychloro over the *gem*-difluoro group. This ratio is exactly the average of the *gem*-dichloro and *gem*-diethoxy cases, demonstrating again the additivity of carbanion stabilization effects in this system.



Rearrangement of the Chloro Ether Cyclobutenes.—The reactions of ethoxide ion with XIII and XXI yielded several products due to further reactions under the reaction conditions and during the work-up as well as nucleophilic attack at both ends of the double bond.

XVII was never obtained in better than 93% purity because of spontaneous thermal isomerization to XVI in the preparative scale gas-liquid chromatograph column. This observation accounted for the isolation of XVI in the reaction of XXI with ethoxide.

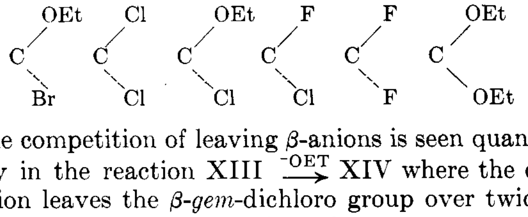
In a control reaction of both XIII and XXI during the progress of which aliquots were analyzed by g.l.c., the concentration of XVIII in the product mixture was found to increase along with a corresponding decrease in XVII with increasing ethoxide concentration. The following rearrangement apparently took place.



The ketone XX was not isolated as its g.l.c. retention time was identical with XVIII. It was discovered by the appearance of a carbonyl absorption (1775 cm.$^{-1}$) and a 1-chloro-2-ethoxycyclobutene absorption (1685 cm.$^{-1}$) in the infrared and a methylene quartet in the n.m.r. in a region characteristic of a vinylic ethoxy group. Finally, an analytical g.l.c. column of Carbowax 20M substrate resolved the mixture so that the relative amounts of the compounds occurring in the reaction could be determined. XX undoubtedly occurred as a result of some hydrolysis of XIX during the water-wash step of the work-up or during the distillation since XIX is a vinylog of an α,α-difluoro ether which is known to hydrolyze readily.[1]

The isolation of the triether XXVIII in the ethoxide reaction of XVI was due to a direct S$_N$2 displacement on the α-chloro ether intermediate XXXII by ethoxide ion. Roberts encountered the same result in one of his reactions.[7] An attempt to isolate XXXII was unsuccessful. Interestingly enough no trace of XVIII was detected in this reaction which one might expect if this reaction of the allylic *gem*-chloro ether goes so readily to the *gem*-diether in all instances.

Leaving Group Correlation.—Once the carbanion is formed by the nucleophilic attack of an ethoxide ion, the product formation is determined by the relative leaving ability of the β-substituents. In the first reference,[1] it was mentioned that "the less basic a β-substituent is, the better it is as a leaving group." In view of this work, the list given there can be expanded and substantiated. In the list below (in order of leaving ability) the dotted line indicates the leaving halogen group. The *gem*-diethoxy group has never been observed to leave.



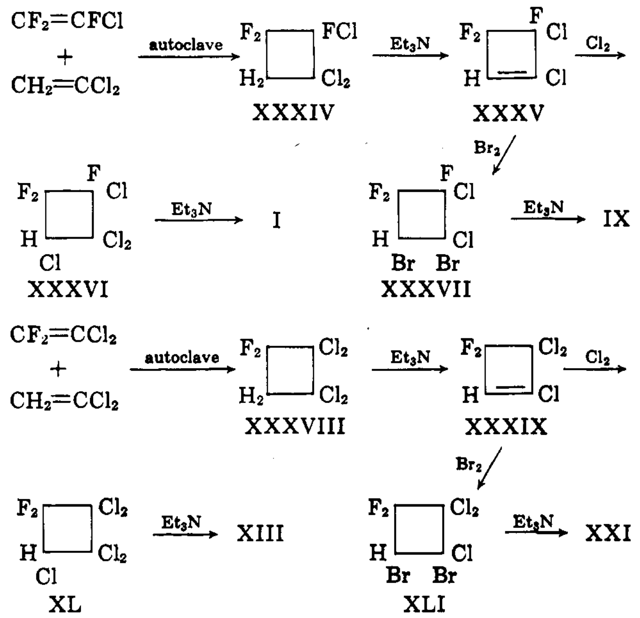
The competition of leaving β-anions is seen quantitatively in the reaction XIII $\xrightarrow{^-OET}$ XIV where the chloride ion leaves the β-*gem*-dichloro group over twice as readily as from the β-*gem*-chloroethoxy group.

Applying the above rule along with the carbanion stabilization criteria, the products of a nucleophilic attack on a halogenated cyclobutene may be predicted with confidence.

Syntheses of the Cyclobutenes.—There were two general synthetic pathways involved to make the cyclobutenes that were reacted with ethoxide ion. The first, after a two-step synthesis to the known[8] 2,3-dichloro-3,4,4-trifluorocyclobutene (XXXV), involved a low-temperature chlorination in the dark under slight pressure to convert XXXV to the chlorinated product XXXVI in 97% yield isolated as a 50:50 mixture of two geometric isomers. XXXVI was then dehydrochlorinated to I. All of the dehydrohalogenations were carried out with triethylamine at 0° to effect a 90% or better yield.

Bromine was also added to XXXV in methylene chloride at reflux temperature to give the cyclobutane XXXVII present as two geometric isomers in a 78 to 22 ratio. XXXVII was dehydrobrominated to IX.

The second pathway was carried out in identical fashion as the first as seen in the scheme below.



Experimental

Boiling points were taken by the Siwoloboff method.[9] Infrared spectra were taken by a Perkin-Elmer Infracord. N.m.r. spectra were taken using a Varian A-60 analytical spectrometer with pure liquid samples except where otherwise indicated with tetramethylsilane as reference. Microanalysis was performed by the Galbraith Laboratories. The product ratios were determined on a F and M Model 300 programmed temperature gas chromatograph with a Texas Instruments, Inc., Servariter Model recorder with Disc integrator. The thermal conductivities of the compounds in question were shown to be identical ±1%.

Preparation of 1,1,2-Trichloro-2,3,3-trifluorocyclobutane (XXXIV).—A procedure according to that reported by Raasch[8] was used to affect a 47% yield of the codimer, b.p. 115° at 630 mm., n^{25}D 1.4138 (lit.[8] b.p. 120–121°, n^{25}D 1.4139).

The n.m.r. spectrum (carbon tetrachloride solution) contained a complex multiplet centered at τ 6.64.

Preparation of 2,3-Dichloro-3,3,4-trifluorocyclobutene (XXXV).—A solution of 160.5 g. (0.774 mole) of 1,1,2-trichloro-2,3,3-trifluorocyclobutene and 50 ml. of ethyl ether was added dropwise

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[7] M. C. Caserio, F. Scardiglia, and J. D. Roberts, *J. Am. Chem. Soc.*, **82**, 3106 (1960).

[8] M. S. Raasch, R. E. Miegel, and J. E. Castle, *ibid.*, **81**, 2678 (1959).

[9] A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1948, p. 86.

at ice-bath temperature to a stirred solution of 150 ml. (1.07 moles) of triethylamine and 50 ml. of ethyl ether in a 500-ml., three-neck flask fitted with reflux condenser, stirrer, and dropping funnel. The addition was complete after 3 hr. After stirring for an additional 3 hr., 24 ml. of concentrated hydrochloric acid in 100 ml. of water was added. The organic layer was separated and washed with water. The aqueous layer was extracted four times with ether. The extracts and product layer were dried over anhydrous magnesium sulfate for 18 hr. and fractionally distilled to yield 129.2 g. (95% of theory) of 2,3-dichloro-3,4,4-trifluorocyclobutene, b.p. 86° at 629 mm., n^{25}_{D} 1.3942 (lit.[8] b.p. 91–92°, n^{25}_{D} 1.3942).

The infrared spectrum contained a strong absorption at 1590 cm.$^{-1}$. The n.m.r. spectrum contained two equal intensity quartets centered at τ 3.40 and 3.44 with $J_{\mathrm{HF}^1} = 5.5$, $J_{\mathrm{HF}^2} = 0.9$, $J_{\mathrm{HF}^{1'}} = 6.2$, and $J_{\mathrm{HF}^{2'}} = 1.6$ c.p.s. when run neat. There was a large chemical shift when run in different solvents and the coupling constants for the first quartet varied with solvent.

Preparation of 1,2,2,3-Tetrachloro-3,4,4-trifluorocyclobutane (XXXVI).—Chlorine gas was bubbled through 29.3 g. (0.165 mole) of 2,3-dichloro-3,4,4-trifluorocyclobutene at room temperature, in the dark, under 1000 mm. of Hg for 25 hr. The reaction vessel was then heated and nitrogen gas was bubbled through to dispel excess chlorine gas. The reaction mixture was washed with a cold, aqueous solution of sodium carbonate, followed by a water wash, and dried over magnesium sulfate. Vacuum distillation yielded 0.5 g. of starting material and 39.6 g. (97% of theory) of 1,2,2,3-tetrachloro-3,4,4-trifluorocyclobutane, b.p. 136° at 625 mm., n^{25}_{D} 1.4326, d^{25}_{4} 1.682.

Anal. Calcd. for $C_4HCl_4F_3$: C, 19.38; H, 0.41; Cl, 57.21; F, 22.99; MR, 38.72. Found: C, 19.59; H, 0.50; Cl, 57.06; F, 23.15; MR, 38.28.

Analysis by gas–liquid chromatography showed the product to have two equal peaks due to geometric isomers. The isomers were separated by preparative-scale g.l.c. The isomer with the shorter retention time was found to have a boiling point of 133.0° at 631 mm. and n^{25}_{D} 1.4310. The n.m.r. spectrum contained an equal intensity octet centered at τ 5.07 with $J_{\mathrm{HF}^1} = 9.9$, $J_{\mathrm{HF}^2} = 9.5$, and $J_{\mathrm{HF}^3} = 6.6$ c.p.s. The other isomer had b.p. 137.5° at 631 mm. and n^{25}_{D} 1.4341. Its n.m.r. spectrum contained an octet centered at τ 5.24 with $J_{\mathrm{HF}^1} = 9.7$, $J_{\mathrm{HF}^2} = 8.15$, and $J_{\mathrm{HF}^3} = 2.7$ c.p.s.

Preparation of 1,2,3-Trichloro-3,4,4-trifluorocyclobutene (I).—1,2,2,3-Tetrachoro-3,4,4-trifluorocyclobutane (56.7 g., 0.229 mole) was treated according to the previously described procedure for dehydrohalogenation to yield 44.8 g. (93% of theory) of 1,2,3-trichloro-3,4,4-trifluorocyclobutene, b.p. 95.0° at 625 mm., n^{25}_{D} 1.4153, d^{25}_{4} 1.590.

Anal. Calcd. for $C_4Cl_3F_3$: C, 22.72; Cl, 50.32; F, 26.96; MR, 33.39. Found: C, 22.91; Cl, 50.52; F, 26.78; MR, 33.32.

Analysis by gas–liquid chromatography showed this material to be 100% pure. The infrared spectrum contained a sharp, weak absorption at 1630 cm.$^{-1}$.

Reaction of 1,2,3-Trichloro-3,4,4-trifluorocyclobutene with Ethoxide Ion.—In a 250-ml., three-neck flask, equipped with stirrer, condenser, and addition funnel was placed 35.6 g. (0.168 mole) of 1,2,3-trichloro-3,4,4-trifluorocyclobutene. The flask was cooled in an ice–water bath, and 11.2 g. (0.17 mole) of potassium hydroxide dissolved in 70 ml. of absolute ethanol was added dropwise with rapid stirring for 1 hr.

The reaction mixture was then stirred for an additional 5 hr., then poured through a filter into a separatory funnel half filled with cold water. The flask and filter were washed with methylene chloride which was added to the funnel. The organic layer was drawn off and washed twice with water. The washings and aqueous layer were extracted four times with 10-ml. portions of methylene chloride. The methylene chloride and product mixture were dried over magnesium sulfate and fractionally distilled under vacuum to yield 6 g. of starting material and 28.0 g. (75% of theory) of 1-ethoxy-2,3-dichloro-3,4,4-trifluorocyclobutene (IV) and 1,3-dichloro-2-ethoxy-3,4,4-trifluorocyclobutene (V), n^{25}_{D} 1.4187 (1-ethoxy-2,3-dichloro-3,4,4-trifluorocyclobutene, n^{25}_{D} 1.4215). Analysis by gas–liquid chromatography on three different columns showed only one peak for the product which had a retention time identical with an authentic sample of IV.

The infrared spectrum on a Perkin-Elmer 21 spectrometer was similar to that of IV with the exception of three new peaks at 775, 960, and 1370 cm.$^{-1}$.

The n.m.r. spectrum contained two 1:3:3:1 quartets centered at τ 5.58 and 5.50 and two 1:2:1 triplets at 8.60 and 8.57. More of the known 1-ethoxy-2,3-dichloro-3,4,4-trifluorocyclobutene was added to the sample and the quartet at τ 5.58 and the triplet at 8.60 increased in relative intensity. The spectrum of the methylene quartets of the original product mixture was expanded to the 50-c.p.s. scale. The area under the peaks of each isomer was measured by a planometer, and the ratio of products was thus determined to be 61 parts of the known isomer IV to 39 parts of V.

Preparation of 1,2-Dibromo-2,3-dichloro-3,4,4-trifluorocyclobutane[10] (XXXVII).—A solution of 69.2 g. (0.39 mole) of 2,3-dichloro-3,4,4-trifluorocyclobutene, 45 ml. of methylene chloride, and 0.53 mole of molecular bromine was stirred in a 250-ml., three-neck flask fitted with reflux condenser and stirrer. The mixture was heated to a gentle reflux for 60 hr. by a 75-w. light bulb and aluminum foil reflector. The reaction mixture was then cooled in an ice bath and an aqueous solution of sodium bisulfite added to remove excess bromine. The reaction mixture was then poured into a separatory funnel and the organic layer was drawn off, washed with water, dried over magnesium sulfate, and vacuum distilled to yield 113.2 g. (86% of theory) of 1,2-dibromo-2,3-dichloro-3,4,4-trifluorocyclobutane, b.p. 172° at 623 mm. (lit.[10] 50° at 3 mm.). The infrared spectrum was identical with that of the literature value.[10] Analysis by g.l.c. showed a slight trace of starting material and a shoulder on the product peak which is presumed to be due to conformational isomers in an approximate distribution of 78:22.

The n.m.r. spectrum contained two octets. The octet of the lower boiling, predominant conformer was centered at τ 4.82 with $J_{\mathrm{HF}^1} = 11.0$, $J_{\mathrm{HF}^2} = 9.5$, and $J_{\mathrm{HF}^3} = 6.0$ c.p.s. The octet of the lesser conformer was centered at τ 5.21 with a $J_{\mathrm{HF}^1} = 11.0$, $J_{\mathrm{HF}^2} = 8.5$, and $J_{\mathrm{HF}^3} = 2.7$ c.p.s.

Preparation of 1-Bromo-2,3-dichloro-3,4,4-trifluorocyclobutene[10] (IX).—1,2-Dibromo-2,3-dichloro-3,4,4-trifluorocyclobutene (112.0 g., 0.332 mole) was treated according to the previously described procedure for dehydrohalogenation to yield 8.1 g. of starting material and 63.3 g. (75% of theory) of 1-bromo-2,3-dichloro-3,4,4-trifluorocyclobutene, b.p. 114° at 626 mm. (lit.[10] 114.5° at 627 mm.). The infrared spectrum was identical with the literature value containing a sharp, medium absorption at 1610 cm.$^{-1}$. Analysis by g.l.c. showed this material to be 98.2% pure.

The reaction of 1-bromo-2,3-dichloro-3,4,4-trifluorocyclobutene with ethoxide ion was carried out according to the previously described procedure. G.l.c. analysis of the reaction mixture showed 80% conversion to two products in a ratio of 42 to 58. The products were separated by preparative-scale g.l.c. The lesser of the two products was identified as 1-ethoxy-2,3-dichloro-3,4,4-trifluorocyclobutene (IV), b.p. 157° at 627 mm., n^{25}_{D} 1.4215, d^{25}_{4} 1.420.

Anal. Calcd. for $C_6H_5Cl_2F_3O$: C, 32.56; H, 2.28; Cl, 32.10; F, 25.80; MR, 39.40. Found: C, 32.53; H, 2.41; Cl, 32.36; F, 26.06; MR, 39.51.

The infrared spectrum contained a strong, sharp absorption at 1680 cm.$^{-1}$. The n.m.r. spectrum contained a 1:3:3:1 quartet centered at τ 5.58 and a 1:2:1 triplet at 8.60.

The predominant product was identified as 1-bromo-2-ethoxy-3-chloro-3,4,4-trifluorocyclobutene (XII), b.p. 175° at 627 mm., n^{25}_{D} 1.4423, d^{25}_{4} 1.635.

Anal. Calcd. for $C_6H_5BrClF_3O$: C, 27.14; H, 1.90; F, 21.47; MR, 42.30. Found: C, 27.48; H, 2.11; F, 21.46; MR, 42.99.

The infrared spectrum contained a strong, sharp absorption at 1670 cm.$^{-1}$. The n.m.r. spectrum (carbon tetrachloride solution) contained a 1:3:3:1 quartet centered at τ 5.45 and 1:2:1 triplet at 8.53.

The preparation of 1,1,2,2-tetrachloro-3,3-difluorocyclobutene (XXXVIII) and 2,3,3-trichloro-4,4-difluorocyclobutene (XXXIX) was carried out according to the procedures outlined by Park and Dick.[1]

Preparation of 1,2,2,3,3-Pentachloro-4,4-difluorocyclobutane (XL).—In a 340 × 45 mm. Pyrex chlorination vessel, fitted with a fritted gas inlet and a reflux condenser connected to a trap immersed in Dry Ice–acetone, was placed 287 g. (1.48 moles) of a mixture containing 69.5% 1,4,4-trichloro-3,3-difluorocyclobutene and 30.5% 1,2,3-trichloro-4,4-difluorocyclobutene. The reaction mixture was kept at *ca.* −10° and protected from light by a black cloth, while chlorine was recycled through the system for 28 days. G.l.c. analysis at the end of this time showed 72.5% conversion. (No reaction was observable at 0°.)

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[10] D. C. Gini, Ph.D. Thesis, University of Colorado, 1961.

Rectification of the 362 g. of crude product through a 315-mm. Fenske column yielded 250.7 g. of material analyzing 100% pure by g.l.c., b.p. 174–175.5° at 626 mm., m.p. 29.7–31.0°.

Anal. Calcd. for $C_4HCl_5F_2$: C, 18.18; H, 0.38; Cl, 67.10; F, 14.37. Found: C, 17.96; H, 0.36; Cl, 66.93; F, 14.16.

The infrared spectrum showed no absorption in the double bond region. The n.m.r. spectrum contained an equal intensity quartet centered at τ 4.98, with J_{HF}^1 of 10.8 and J_{HF}^2 of 7.0 c.p.s.

Also recovered was 83.6 g. (0.43 mole) of the mixed olefins, greatly enriched in rearranged material. The conversion was thus 71%.

Preparation of 1,2,3,3-Tetrafluoro-4,4-difluorocyclobutene (XIII).—1,2,2,3,3-Pentachloro-4,4-difluorocyclobutane (200 g., 0.757 mole) was treated according to the previously described procedure for dehydrohalogenation to yield 153 g. (89% of theory) of 1,2,3,3-tetrachloro-4,4-difluorocyclobutene, b.p. 127.5–128.0° at 627 mm., $n^{25}_{\rm D}$ 1.4600, d^{25}_4 1.6136.

Anal. Calcd. for $C_4Cl_4F_2$: C, 21.08; Cl, 62.25; F, 16.68; MR, 38.17. Found: C, 20.91; Cl, 61.96; F, 16.97; MR, 38.68.

The infrared spectrum contained a moderately strong, sharp absorption at 1625 cm.$^{-1}$.

The reaction of 1,2,3,3-tetrachloro-4,4-difluorocyclobutene with ethoxide ion was carried out according to the previously described procedure to effect an 80% conversion to several products isolated in an over-all yield of 67%. The product mixture was separated by preparative-scale g.l.c. on a 15-ft. Ucon LB 550X column which resolved three peaks.

The first peak was due to 1,2,3-trichloro-3-ethoxy-4,4-difluorocyclobutene (XVI); refractive index, infrared spectrum, n.m.r. spectrum, and g.l.c. retention time all were identical with an authentic sample.[11] Analysis by g.l.c. showed this material to be greater than 99% pure.

The second peak contained mostly 1,2-dichloro-3,3-diethoxy-4,4-difluorocyclobutene (XVIII), $n^{25}_{\rm D}$ 1.4308 (lit.[11] $n^{25}_{\rm D}$ 1.4289). The infrared spectrum was identical with the authentic sample[11] except for a large absorption in the carbonyl region (1775 cm.$^{-1}$) and another sharp absorption in the olefin region at 1685 cm.$^{-1}$ (characteristic of a 1-chloro-2-ethoxycyclobutene). The n.m.r. spectrum contained a quartet at τ 6.21 and a triplet at 8.78 attributed to the *gem*-diether, and a smaller quartet and triplet at τ 5.66 and 8.67, respectively, evidence for a vinyl ethoxy group and believed due to 1,3,3-trichloro-2-ethoxy-4-ketocyclobutene (XX). G.l.c. analysis on a Carbowax 20M analytical column resolved the mixture and showed the mixture to be 73% XVIII and 27% the presumed ketone XX.

The third peak contained an inseparable mixture of the isomers 1,4,4-trichloro-2-ethoxy-3,3-difluorocyclobutene (XVII) and 1,3,3-trichloro-2-ethoxy-4,4-difluorocyclobutene (XIX), $n^{25}_{\rm D}$ 1.4556 (authentic[11] XVII, $n^{25}_{\rm D}$ 1.4550).

Anal. Calcd. for $C_6H_5Cl_3F_2O$: C, 30.35; H, 2.12; Cl, 44.80; F, 16.00. Found: C, 30.51; H, 2.40; Cl, 44.88; F, 16.30.

Analysis by g.l.c. on three different substrates showed 98% purity for only one peak for the product which had a retention time identical with an authentic sample of XVII.[11] The infrared spectrum was identical with that of the authentic XVII with the exception of five new peaks due to the other isomer. The n.m.r. spectrum contained a quartet at τ 5.61 and a triplet at 8.61 due to XI and a quartet at 5.45 and triplet at 8.55 due to the new isomer XIX since the ethoxy groups were situated in slightly different environments. The spectrum of the methylene quartets was expanded on the 50-c.p.s. scale. The area under the peaks of each isomer was measured by planometer. The ratio of isomers was thus determined to be 70 to 30 XVII and XIX.

The reaction was repeated twice with small amounts of materials to check the ratio of products. By combining g.l.c. analysis and n.m.r. data, the product ratio was determined after 90% conversion to be 61% XVI, 4% XVIII, 1% XX, 23% XVII, and 10% XIX.

Preparation of 1,2-Dibromo-2,3,3-trichloro-4,4-difluorocyclobutane[10] (XLI).—1,4,4-Trichloro-3,3-difluorocyclobutene (140 g., 0.734 mole) was treated according to the previously described procedure for bromination. G.l.c. analysis of product layer and methylene chloride showed no trace of starting material.

Preparation of 1-Bromo-2,3,3-trichloro-4,4-difluorocyclobutene[10] (XXI).—The above solution of methylene chloride and 1,2-dibromo-2,3,3-trichloro-4,4-difluorocyclobutane was treated according to the previously described procedure for dehydrohalogenation to yield 3.3 g. and 10.6 g. of two unknown compounds (probably due to rearrangement) and 142.6 g. (71% over-all yield) of 1-bromo-2,3,3-trichloro-4,4-difluorocyclobutene, b.p. 148° at 625 mm., $n^{25}_{\rm D}$ 1.4850 (lit.[10] 1.4847), d^{25}_4 1.893, MR 41.23 (calcd. 41.05). The infrared spectrum was identical with the literature value.[10] Analysis by g.l.c. showed this material to be 100% pure.

The reaction of 1-bromo-2,3,3-trichloro-4,4-difluorocyclobutene with ethoxide ion was carried out according to the previously described procedure. As 60% conversion was noted by g.l.c., an excess of potassium hydroxide in ethanol was added to drive it closer to completion. Vacuum distillation and preparative-scale g.l.c. yielded four products in 71% yield.

The first product was 1.75 g. (3.9% of theory) of 1,2,3-trichloro-3-ethoxy-4,4-difluorocyclobutene (XVI), b.p. 157.2° at 622 mm., $n^{25}_{\rm D}$ 1.4446, d^{25}_4 1.404.

Anal. Calcd. for $C_6H_5Cl_3F_2O$: C, 30.35; H, 2.12; Cl, 44.80; F, 16.00; MR, 44.16. Found: C, 30.18; H, 2.35; Cl, 44.63; F, 16.25; MR, 44.98.

Analysis by g.l.c. showed this material to be greater than 99% pure. The infrared spectrum contained a sharp, weak absorption at 1630 cm.$^{-1}$. The n.m.r. spectrum contained a quartet at τ 6.05 and a triplet at 8.71.

The second product was 11.3 g. (25% of theory) of 1,2-dichloro-3,3-diethoxy-4,4-difluorocyclobutene (XVIII), b.p. 176.5° at 621 mm., $n^{25}_{\rm D}$ 1.4289, d^{25}_4 1.265.

Anal. Calcd. for $C_8H_{10}Cl_2F_2O_2$: C, 38.89; H, 4.08; Cl, 28.70; F, 15.38; MR, 50.17. Found: C, 39.09; H, 4.20; Cl, 28.90; F, 15.65; MR, 50.34.

Analysis by g.l.c. showed this material to be greater than 99% pure. The infrared spectrum contained a sharp, weak absorption at 1630 cm.$^{-1}$. The n.m.r. spectrum contained a quartet centered at τ 6.22 and a triplet at 8.78.

The third product was 11.8 g. (26.4% of theory) of 1,4,4-trichloro-2-ethoxy-3,3-difluorocyclobutene (XVII), b.p. 184° at 622 mm., $n^{25}_{\rm D}$ 1.4550, d^{25}_4 1.427, MR 45.15 (calcd. 44.16). Analysis by g.l.c. showed this material to be 93% pure. The impurity was XVI. The infrared spectrum contained a strong, sharp absorption at 1685 cm.$^{-1}$. The n.m.r. spectrum contained a quartet centered at τ 5.62 and a triplet at 8.61.

The fourth product was 7.8 g. (15% of theory) of 1-bromo-2-ethoxy-3,3-dichloro-4,4-difluorocyclobutene (XXIV), b.p. 200° at 618 mm., $n^{25}_{\rm D}$ 1.4788, d^{25}_4 1.673.

Anal. Calcd. for $C_6H_5BrCl_2F_2O$: C, 25.56; H, 1.79; Br, 28.35; Cl, 25.15; F, 13.48; MR, 47.06. Found: C, 25.67; H, 1.93; Br, 28.38; Cl, 25.02; F, 13.46; MR, 47.77.

Analysis by g.l.c. showed this material to be 100% pure. The infrared spectrum contained a strong, sharp absorption at 1670 cm.$^{-1}$. The n.m.r. spectrum contained a quartet centered at τ 5.46 and a triplet at 8.55.

The reaction was repeated twice with small amounts of material in order to determine accurately the ratio of products by g.l.c. For a 93% conversion, the product distribution was determined to be 4% XVI, 6% XVIII, 56% XVII, and 34% XXIV.

The reaction of 1,2-dichloro-3,3-diethoxy-4,4-difluorocyclobutene (XVIII) with ethoxide ion was carried out according to the previously described procedure, except the temperature had to be raised to 25° to yield 2.2 g. (86% of theory) of a mixture of two triether isomers, b.p. 58–60° at 0.7 mm. The mixture was separated by preparative-scale g.l.c. to yield 0.90 g. of pure 1,3,3-triethoxy-2-chloro-4,4-difluorocyclobutene (XXVII), m.p. −19.5 $n^{25}_{\rm D}$ 1.4290, d^{25}_4 1.180 (lit.[12] $n^{25}_{\rm D}$ 1.4282, d^{25}_4 1.173). G.l.c. retention time and infrared spectrum were identical with that of an authentic sample. The n.m.r. spectrum contained two triplets centered at τ 8.80 and 8.65, the triplet at 8.80 being twice as large as the other, and two quartets centered at 6.24 and 5.70, the quartet at 6.24 being twice as intense as the other.

The other product separated was 0.78 g. of pure 1-chloro-2,3,3-triethoxy-4,4-difluorocyclobutene (XXVIII), m.p. 22.0°, $n^{25}_{\rm D}$ 1.4291, d^{25}_4 1.180.

Anal. Calcd. for $C_{10}H_{15}ClF_2O_3$: C, 46.79; H, 5.89; Cl, 13.81; F, 14.80; MR, 56.19. Found: C, 47.01; H, 5.78; Cl, 14.01; F, 15.00; MR, 56.14.

The infrared spectrum was identical with that of XXVII in the 1400–4000-cm.$^{-1}$ region. The n.m.r. spectrum contained two triplets centered at τ 8.80 and 8.63, the triplet at 8.80 being twice

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(11) See reaction of XXI with ethoxide.

(12) S. D. Cohen, Ph.D. Thesis, University of Colorado, 1959.

as intense as the other, and two quartets centered at 6.28 and 5.59, the quartet at 6.28 being twice as intense as the other.

The Reaction of 1,2,3-trichloro-3-ethoxy-4,4-difluorocyclobutene (XVI) with ethoxide ion was carried out according to the previously described procedure to yield 2.0 g. (49% of theory) of pure XXVII, $n^{25}\mathrm{D}$ 1.4289, whose infrared spectrum and g.l.c. retention time were identical with an authentic sample, and 0.8 g. (20% of theory) of pure XXVIII, m.p. 22.0°, $n^{25}\mathrm{D}$ 1.4295, and infrared spectrum and g.l.c. retention time identical with an authentic sample.

The reaction was repeated at −10° and was worked up after a 1-hr. reaction time in an attempt to isolate the proposed intermediate XXXII. G.l.c. analysis showed 60% starting material, trace of a new peak, 28% XXVII, and 12% XXVIII. The infrared spectrum of each compound indicated no impurities.

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Rates of Solvolysis of *meta*-Substituted Benzyldimethylcarbinyl Chlorides[1]

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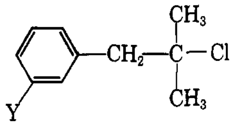
The rates of solvolysis in 80% ethanol of benzyldimethylcarbinyl chloride and the *meta*-methyl-, -ethyl-, -isopropyl-, -fluoro-, -chloro-, and -bromo-substituted carbinyl chlorides have been measured at 40.5, 50.0, and 61.1°. The unusual relative rate sequence was explained by means of solvent and dipole–dipole interactions on the transition state.

This work was undertaken in an attempt to evaluate the effect of inductance on the stability of tertiary carbonium ions in a system where resonance and steric effects are negligible.

The model compounds selected for the study were the heretofore unknown *meta*-substituted benzyldimethylcarbinyl chlorides, where Y = Me, Et, *i*-Pr, F, Cl, and Br.



With the substituent being in the *meta* position to minimize resonance effects and the methylene group serving as an insulator to block the transmission of any resonance effect, the *meta* substituent should influence the chlorine-bearing carbon only by an inductive mechanism.

The reaction chosen for study was solvolysis in 80% aqueous ethanol. It has been well established that tertiary halides hydrolyze in this solvent by the SN1 mechanism.[3,4] The transition state is probably not a free carbonium ion, but it is thought to approach this condition.[5] Since the rate of the reaction is a measure of the formation of a carbonium ion, the effects of substituents upon the stability of the transition state and upon the stability of the carbonium ion can be considered as essentially identical.

Studies on the hydrolysis of the homologous alkylphenyldimethylcarbinyl chlorides,[6] and the halophenyldimethylcarbinyl chlorides[7] have been reported by Bown and co-workers. The analogous *para*-substituted benzyldimethylcarbinyl chlorides have been shown to be stabilized in a hyperconjugative order by alkyl groups and destabilized through the inductive effect by the halogen groups, although there was also evidence for the operation of a resonance effect with the halogens.[8] The elimination reactions of the unsubstituted benzyldimethylcarbinyl chloride have also been investigated.[9]

Results

The series of *meta*-substituted benzyldimethyl carbinols was synthesized by the reaction of the appropriate *meta*-substituted benzylmagnesium halide with acetone. These compounds are oily liquids which are stable at room temperature. With the exception of the unsubstituted carbinol,[8-10] the compounds are new. Their physical properties and analyses are reported in Table I.

The *meta*-substituted benzyldimethylcarbinyl chlorides were synthesized by mixing the pure carbinols with concentrated hydrochloric acid and simultaneously bubbling through hydrogen chloride gas. The resulting tertiary chlorides were contaminated with trace amounts of olefin and unreacted carbinol. These impurities were removed by washing the chloride with cold concentrated sulfuric acid, immediate separation of the layers by means of centrifugation, treatment of the organic layer with a mixture of calcium chloride and calcium carbonate, and distillation of the chloride under reduced pressure. The resulting purified chloride was, in each case, a colorless oil which decomposed upon standing for several weeks. With the exception of the unsubstituted carbinyl chloride,[8,9] all of the compounds

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