In another experiment *trans*-1-phenylpropene (0.163 g, 0.0014 mole), paraformaldehyde (0.378 g, 0.0126 mole, as formaldehyde), 3 ml of dioxane, and concentrated sulfuric acid (0.125 g) were mixed and stirred, protected from light, at room temperature for 4 days. The reaction mixture was then worked up in the usual manner and analyzed by glpc. The yield of 5-methyl-4-phenyl-1,3-dioxanes was 45.3 mg (19%). *trans*-1-Phenylpropene (2.4 mg) was also found in the crude product. Nmr analysis showed that the product dioxanes were in the ratio, *cis/trans*, of 0.89.

B. In Water.—In one experiment the published procedure[25] was followed, using *trans*-1-phenylpropene (6.36 g, 0.054 mole), 37% formalin (11.2 g, 0.14 mole), and 1.0 g of concentrated sulfuric acid. The mixture was refluxed in the dark for 7 hr. Work-up gave 4.13 g of a mixture of *cis*- and *trans*-5-methyl-4-phenyl-1,3-dioxanes, bp 97–100° (2.5 mm), which was 1/1 *cis/trans* (determined by nmr). The yield was 43%. In another experiment the same relative amounts of reactants were used, but the reaction was carried out at 80–90° for 1.5 hr. A 1:1 mixture of the *cis*- and *trans*-dioxanes was obtained in 28% yield. Recovered *trans*-1-phenylpropene showed no isomerization.

In another experiment using the same relative amounts of reactants, the reaction was carried out at 70–75° for 22 hr. The reaction mixture was worked up and analyzed as before and gave 5-methyl-4-phenyl-1,3-dioxane in 46% yield. The ratio of *cis/trans* was 1.71. A duplicate reaction gave a 51% yield of the dioxanes with a *cis/trans* ratio of 1.62. Analysis of the recovered *trans*-1-phenylpropene showed no isomerization had occurred.

C. In Acetic Acid.—*trans*-1-Phenylpropene (0.163 g, 0.0014 mole), paraformaldehyde (0.378 g, 0.0126 mole, as formaldehyde), concentrated sulfuric acid (0.125 g), and 3 ml of glacial acetic acid were mixed and stirred in the dark for 4 days at room temperature. The reaction mixture was poured into an excess of 5% sodium carbonate solution and extracted with ether. The ether was dried and evaporated to yield 226.8 mg of oily product. The product was analyzed in the usual manner. 5-Methyl-4-phenyl-1,3-dioxane was found (59 mg, 24%). The ratio of the *cis/trans* isomers was 0.60. Glpc analysis of the recovered *trans*-1-phenylpropene showed less than 10% isomerization.

Prins Reaction of *cis*-1-Phenylpropene in Dioxane.—The same procedure was followed for this reaction as in the *trans*-1-phenylpropene case. The reaction yielded a mixture of the *cis*- and *trans*-5-methyl-4-phenyl-1,3-dioxanes (1:1) in 74% yield. Recovered *cis*-1-phenylpropene showed no isomerization.

In another experiment, *cis*-1-phenylpropene (0.163 g, 0.0014 mole) was added to paraformaldehyde (0.378 g, 0.0126 mole, as formaldehyde), 3 ml of dioxane, and concentrated sulfuric acid (0.125 g). The reaction mixture was stirred in the dark 4 days at room temperature and then worked up as before. The 5-methyl-4-phenyl-1,3-dioxanes were obtained in 48% yield. The ratio *cis-/trans*-5-methyl-4-phenyl-1,3-dioxane was 0.87. Analysis of recovered 1-phenylpropene showed that less than 5% isomerization had occurred.

Stability of 5-Methyl-4-phenyl-1,3-dioxanes. A. Dioxane Conditions.—*cis*-5-Methyl-4-phenyl-1,3-dioxane (0.110 g, 0.0006 mole) was added to paraformaldehyde (0.061 g, 0.0007 mole), 0.142 g of concentrated sulfuric acid, and 3 ml of dioxane. The mixture was stirred 3 days at room temperature and protected from light. At the end of that time the mixture was poured into an excess of 5% potassium carbonate solution and extracted with ether. The ether yielded 0.107 g of *cis*-5-methyl-4-phenyl-1,3-dioxane. Nmr showed that no detectable isomerization had occurred. The *trans* isomer was also found to be stable under these conditions.

B. Water Conditions.—*cis*-5-Methyl-4-phenyl-1,3-dioxane (0.135 g, 0.008 mole) was added to 0.06 g of concentrated sulfuric acid and 0.324 g of 37% formalin. Two drops of water were added. The mixture was heated at 80–90°, protected from light, for 3 hr after which the mixture was poured into an excess of 5% potassium carbonate solution and extracted with ether. The recovered dioxane (0.050 g) had isomerized about 15%. Pure *trans*-5-methyl-4-phenyl-1,3-dioxane was treated in exactly the same way. No isomerization was observed.

C. Acetic Acid Conditions.—A mixture of 5-methyl-4-phenyl-1,3-dioxanes (49% *cis*) (0.3041 g, 0.0017 mole) was added to paraformaldehyde (0.3058 g, 0.01 mole, as formaldehyde), concentrated sulfuric acid (0.125 g), and 3 ml of glacial acetic acid. The mixture was stirred in the dark at room temperature for 4 days and then worked up as in the Prins reaction. The recovered 5-methyl-4-phenyl-1,3-dioxane was analyzed by nmr and was now 45% *cis* and 55% *trans*.

Qualitative Equilibration Studies. A. 5-Methyl-4-phenyl-1,3-dioxane.—A 1:1 mixture of *cis*- and *trans*-5-methyl-4-phenyl-1,3-dioxanes (0.30 g, 0.0017 mole) was added to 5 ml of dioxane and concentrated sulfuric acid (0.40 g). This mixture was heated at 110° for 15 hr in the dark. At the end of this time the reaction mixture was worked up in the usual way and 0.26 g (87%) of the starting dioxanes was recovered. Nmr showed the composition was now 80% *trans*- and 20% *cis*-5-methyl-4-phenyl-1,3-dioxane.

B. 5-Chloro-4-phenyl-1,3-dioxane.—*cis*-5-Chloro-4-phenyl-1,3-dioxane (100 mg, 0.5 mmole) was added to paraformaldehyde (100 mg, 3.3 mmoles as formaldehyde), concentrated sulfuric acid (180 mg), and 1 ml of glacial acetic acid. This mixture was heated at 85° for 8 hr. The reaction mixture was then worked up in the usual way and 75 mg (75%) of starting dioxanes was recovered. Glpc showed that the mixture was 66% *trans*-5-chloro-4-phenyl-1,3-dioxane. *trans*-5-Chloro-4-phenyl-1,3-dioxane was treated in exactly the same way and yielded a mixture of the dioxanes which contained 75% *trans* isomer.

Nucleophilic Substitution in Halogenated Cyclobutenes[1]

J. D. PARK,[2] J. R. LACHER, AND J. R. DICK

Department of Chemistry, University of Colorado, Boulder, Colorado

Received October 15, 1965

The reaction of 1,4,4-trichloro-3,3-difluorocyclobutene with ethoxide ion has been found to give the rearranged monoether, 1,2-dichloro-3-ethoxy-4,4-difluorocyclobutene, which undergoes further nucleophilic attack to yield 1-chloro-2,3-diethoxy-4,4-difluorocyclobutene. The results are interpreted on the basis of relative carbanion stabilities. A set of rules which predict the course of nucleophilic displacements in highly halogenated systems is presented.

The extensive studies during the past 20 years of the reactions of nucleophilic agents with fluoro olefins have given rise to numerous mechanistic interpretations. In 1948, Miller, Fager, and Griswold[3] explained the sodium-catalyzed addition of methanol to chlorofluoro olefins on the basis of rate-determining carbanion formation, followed by proton abstraction from solvent, and suggested that the fluorine atoms predisposed the system to polar activation by a resonance effect.

A paper[4] from our laboratory the following year suggested that the reaction of perfluorocyclobutene

---

(1) This paper represents part of a thesis submitted by J. R. Dick to the Graduate School, University of Colorado, in partial fulfillment of the requirements for the Ph.D. degree, June 1964.

(2) To whom inquiry may be addressed.

(3) W. T. Miller, Jr., E. W. Fager, and P. H. Griswold, *J. Am. Chem. Soc.*, **70**, 431 (1948).

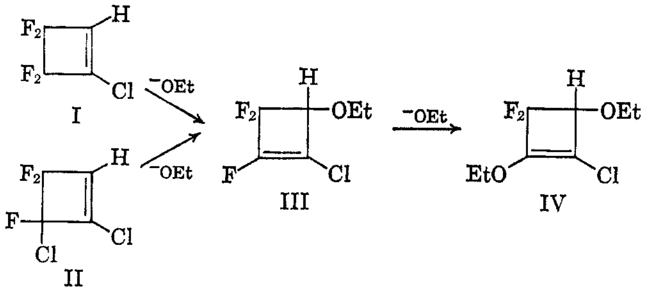
(4) J. D. Park, M. L. Sharrah, and J. R. Lacher, *ibid.*, **71**, 2337 (1949).

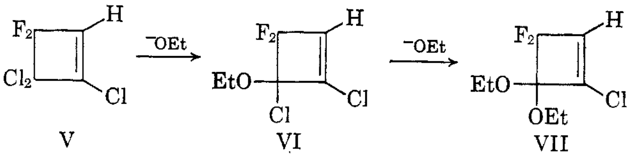
with methanolic potassium hydroxide to give 1,2-dimethoxy-3,3,4,4-tetrafluorocyclobutene might be similar to the formation of an anisole from a phenyl halide. Later papers[5,6] explained displacements of vinylic halogens by alkoxides in both cyclic and acyclic systems in terms of carbanion intermediates. This interpretation was disputed by Rapp, *et al.*,[7,8] who proposed instead an addition–elimination mechanism.

In the latter fifties, Miller's group[9-12] studied the reactions of various nucleophiles with acyclic fluoro olefins, and concluded that, depending upon the structure of the olefin, such reactions could result in addition to form saturated products, direct substitution of vinylic halogen, or displacement of allylic halogen accompanied by rearrangement. The last type was said to proceed through a "lower energy SN2′ transition state,"[13] although the possibility of a carbanion intermediate was acknowledged. The concerted mechanism was favored, however, because the saturated products which would have resulted from proton abstraction from the solvent by a carbanion were not found in reactions involving allylic rearrangement.

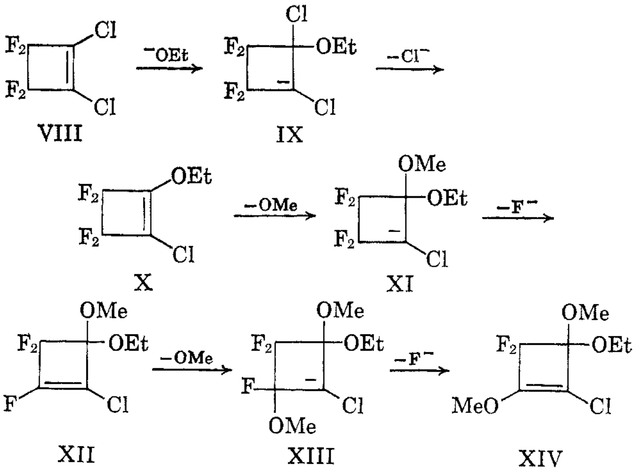
Roberts' group[14-17] has studied the reactions of various cyclobutenes with nucleophiles; the results have been interpreted in terms of *concerted* SN2 and SN2′ processes.

In 1961 it was found in this laboratory[18] that both 1-chloro-3,3,4,4-tetrafluorocyclobutene, I, and 1,4-dichloro-3,3,4-trifluorocyclobutene, II, react with ethanolic potassium hydroxide to give the same rearranged monoether, III. Treatment with a second equivalent of ethoxide resulted in the displacement of the vinylic fluorine and the formation of a diether, IV. When the same reaction was carried out with 1,4,4-trichloro-3,3-difluorocyclobutene, V, there was obtained a monoether thought on the basis of its infrared spectrum to have the unrearranged structure, VI. Further treatment with ethoxide gave a supposedly *gem*-diether, VII, identified by oxidation with permanganate to a succinic acid, and conversion by phosphorus pentachloride to a ketone. These results were explained on the basis of barriers to transition states leading to carbanions or direct SN2 displacements. The direct displacement of the allylic chlorines in the trichlorocyclobutene was attributed to a lowering of the activation energy for SN2 displacement.





It was recently shown[19] that the reaction of 1-ethoxy-2-chloro-3,3,4,4-tetrafluorocyclobutene, X, with methoxide ion involves a rearrangement, rather than a direct SN2 displacement of the allylic fluorines. One explanation of the results is an SN2′ *concerted* step, of the type proposed by Hughes[20] and Young.[13,21] While this explains the rearrangement, it sheds no light on the preceding and following displacements of vinylic halogens. An alternative way[22] to consider the entire displacement sequence is to assume the formation of discrete carbanions, which form and then lose halide ions according to principles to be discussed.



It has been shown by Hine,[23,24] and Slaugh and Bergman[25] that, on the basis of exchange reactions of various "haloforms," the stabilization of carbanions by α substituents is in the order: I ~ Br > Cl > F > OEt. Nmr studies by Tiers[26] have established the following order of "apparent electron-withdrawing power" for α substituents: I > Br > Cl > F >> CF_2Br > CF_2Cl > CF_3. Considerable evidence has accumulated indicating that third row and higher elements can stabilize carbanions by 2p–3d overlap.[27-30]

---

[5] J. D. Park, C. M. Snow, and J. R. Lacher, *J. Am. Chem. Soc.*, **73**, 2342 (1951).

[6] J. D. Park, E. Halpern, and J. R. Lacher, *ibid.*, **74**, 4104 (1952).

[7] K. E. Rapp, R. L. Pruett, J. T. Barr, C. T. Bahner, J. D. Gibson, and R. H. Lafferty, Jr., *ibid.*, **72**, 3642 (1950).

[8] J. T. Barr, K. E. Rapp, R. I. Pruett, C. T. Bahner, J. D. Gibson, and R. H. Lafferty, Jr., *ibid.*, **72**, 4480 (1950).

[9] W. T. Miller, Jr., and Arnold H. Fainberg, *ibid.*, **79**, 4164 (1957).

[10] A. H. Fainberg and W. T. Miller, Jr., *ibid.*, **79**, 4170 (1957).

[11] J. H. Fried and W. T. Miller, Jr., *ibid.*, **81**, 2078 (1959).

[12] W. T. Miller, Jr., J. H. Fried, and H. Goldwhite, *ibid.*, **82**, 3091 (1960).

[13] For a review of the SN2′ reaction, see R. H. DeWolfe and W. G. Young, *Chem. Rev.*, **56**, 769 (1956), and references contained therein.

[14] J. D. Roberts, G. B. Kline, and H. E. Simmons, Jr., *J. Am. Chem. Soc.*, **75**, 4765 (1953).

[15] Y. Kitahara, M. C. Caserio, F. Scardigla, and J. D. Roberts, *ibid.*, **82**, 3106 (1960).

[16] C. M. Sharts and J. D. Roberts, *ibid.*, **83**, 871 (1961).

[17] M. C. Caserio, H. E. Simmons, Jr., A. E. Johnson, and J. D. Roberts, *ibid.*, **82**, 3102 (1960).

[18] J. D. Park, L. H. Wilson, and J. R. Lacher, *J. Org. Chem.*, **28**, 1008 (1963).

[19] J. D. Park, J. R. Dick, and J. R. Lacher, *ibid.*, **28**, 1154 (1963).

[20] E. D. Hughes, *Trans. Faraday Soc.*, **34**, 185 (1938).

[21] W. G. Young, I. D. Webb, and J. L. Goering, *J. Am. Chem. Soc.*, **73**, 1076 (1951).

[22] Our choice of the terms SN2 and SN2′ in the original communication was unfortunate, as others have interpreted this as meaning concerted processes.

[23] J. Hine, N. W. Burske, M. Hine, and P. B. Langford, *J. Am. Chem. Soc.*, **79**, 1406 (1957).

[24] J. Hine, R. Wiesboeck, and R. G. Ghirardelli, *ibid.*, **83**, 1219 (1962).

[25] L. H. Slaugh and E. Bergman, *J. Org. Chem.*, **26**, 3158 (1961).

[26] G. V. D. Tiers, *J. Am. Chem. Soc.*, **78**, 2914 (1956).

[27] W. von E. Doering and L. K. Levy, *ibid.*, **77**, 509 (1955).

[28] H. E. Zimmerman and B. S. Thyagarajan, *ibid.*, **82**, 2505 (1960).

[29] S. Oae, W. Tagaki, and A. Ohno, *ibid.*, **83**, 5036 (1961).

[30] D. J. Cram and A. S. Wingrove, *ibid.*, **85**, 1100 (1963).

This type of stabilization is unlikely with α-fluorine, owing to the high energy required to expand the octet of second row elements. The configuration of the carbanion, *i.e.*, whether it is tetrahedral with sp bonding or planar with sp bonding to the stabilizing group, does not appear to be of great importance.

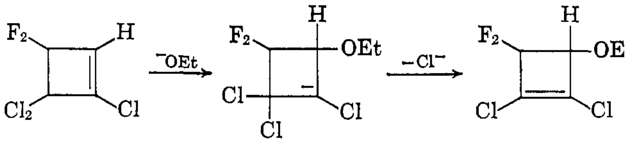
The relative effects of various β substituents on the stability of carbanions is not clear. The possibility of stabilization of β-fluorine by no-bond resonance has been proposed,[24,31-33] and it appears that β-fluorine stabilizes a carbanion more than α-fluorine.[34] The exchange reactions of *m*-dihalobenzenes[35] indicate that β-fluorine may be more effective than β-chlorine, but other evidence points to the same order as for α substituents.[24,26]

We have found the following set of rules, which were derived from what is known about carbanion stabilities, to be quite useful, both in explaining the direction of known nucleophilic substitutions, and in predicting the course of untried reactions. (1) Nucleophilic displacement reactions of olefins highly substituted with electron-withdrawing substituents may best be considered as proceeding through a carbanion intermediate. (2) Usually, a nucleophile will attack the carbon atom leading to the carbanion best stabilized by α substituents. (3) If either position of nucleophilic attack leads to carbanions with equivalent stabilization by α substituents, the effects of β substituents and steric interactions, if significantly different, will prevail. (4) In keeping with Hine's "saturation effect,"[23] the relative importance of β effects diminishes with increasing stabilization by either α or β effects. (5) Carbanions which are adequately stabilized are discrete intermediates, with no knowledge of their origin. Thus, loss of a substituent may occur from either β-carbon atom, irrespective of whether it was vinylic or allylic in the reacting olefin. Complete realization of this principle occurs when a substituent may leave with equal ease either *cis* or *trans* to the attacking nucleophile. This will happen if the carbanion either inverts, or attains a planar configuration, sufficiently faster than it loses a β substituent. (6) The less basic a β substituent is, the better it is as a leaving group. Hence, the order of leaving groups for carbanions is I > Br > Cl > F > OR > H. (7) Fluorine will not be lost from a *gem*-difluoro group if there is another β-halogen which can leave. (8) If a choice must be made between two equivalent leaving moieties, loss will occur so as to give the more stable olefin.

It can be seen that the terms SN2 and SN2′ are not adequate for describing the alternative mechanistic possibilities in these systems in view of the fact that SN2′ has become synonymous with a *concerted* displacement with allylic rearrangement. The term *addition–elimination* is likewise unsuitable in view of the earlier controversy over the formation of saturated products, followed by a normal elimination, *vs.* the formation of a carbanion, followed by the loss of a β substituent.

As an illustration of the carbanion hypothesis, consider the previously described reaction of VIII with ethoxide ion. Only one carbanion, IX, is possible; this loses the β-chlorine in accordance with rules 5-7 to give X. Nucleophilic attack of the monoether by methoxide ion could lead to either of two carbanions, but rule 2 predicts that XI will be more stable, and rule 6 predicts the loss of fluorine. The next attack by methoxide would give the carbanion, XIII, which would lose another β-fluorine to give the product isolated,[19] XIV.

The reactions of I, II, and III with ethoxide ion are perfectly compatible with the carbanion hypothesis; in each case, the most stable carbanion is formed, and the least basic β substituent is lost. Consideration of a similar reaction, that of V with ethoxide, reveals an apparent contradiction. The carbanion hypothesis predicts the formation of an intermediate carbanion, XV, which would then lose a β-chlorine to give the rearranged ether, XVI. As this reaction had been reported to give the unrearranged ether, VI, a further study of the reaction was undertaken. The supposed direct SN2 displacement of an allylic chlorine had been attributed to a lowering of the activation energy leading to an SN2 transition state, but this seemed questionable in view of the known retardation effects of α- and β-halo substituents on SN2 reactions,[36-38] and the known accelerating effects of the same substituents on SN2′ reactions.[39-42]



V XV XVI

Results

When the cyclobutene, V, was treated with 1 equiv of ethoxide, a monoether was obtained which had a strong absorption in the infrared at 1630 cm^{-1}, characteristic of a 1,2-dichlorocyclobutene. Cyclobutenes with one vinylic hydrogen and one vinylic chlorine have been found in this laboratory to absorb at 1590 cm^{-1}. The nmr spectrum contained an equal-intensity quartet centered at τ 5.38, in agreement with structure XVI, which has an allylic ring hydrogen. If the monoether were VI, as previously reported, the resonance of the vinylic ring hydrogen would be considerably downfield, as in the case of the starting cyclobutene, V, which has a triplet centered at τ 3.8. It is difficult to visualize a path by which the monoether, XVI, could be converted to the reported *gem*-diether, VII. A more likely course would be the formation of the carbanion, XVII, followed by loss of a chloride ion. The nmr spectrum of the diether obtained by us had a doublet centered at τ 5.47, and 1:3:3:1 quartets centered at τ 5.65 and 6.35, with an intensity ratio of 1:2:2. This is in complete agree-

---

(31) J. D. Roberts, R. L. Webb, and E. A. McElhill, *J. Am. Chem. Soc.*, **72**, 408 (1950).

(32) S. Andreades, *J. Org. Chem.*, **27**, 4163 (1962).

(33) W. A. Sheppard, *J. Am. Chem. Soc.*, **85**, 1314 (1963).

(34) S. Andreades, *ibid.*, **86**, 2003 (1964).

(35) J. Hine and P. B. Langford, *J. Org. Chem.*, **27**, 4149 (1962).

(36) J. Hine, C. H. Thomas, and S. J. Ehrenson, *J. Am. Chem. Soc.*, **77**, 3886 (1955).

(37) J. Hine, S. J. Ehrenson, and W. H. Bradler, Jr., *ibid.*, **78**, 2282 (1956).

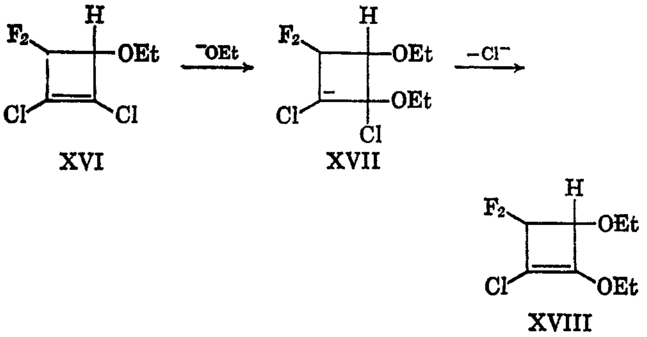
(38) J. Hine and W. H. Bradler, Jr., *ibid.*, **75**, 3964 (1953).

(39) P. B. D. de la Mare and C. A. Vernon, *J. Chem. Soc.*, 3325 (1952).

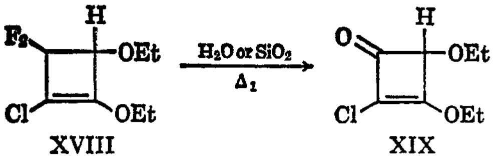
(40) P. B. D. de la Mare and C. A. Vernon, *ibid.*, 3331 (1952).

(41) P. B. D. de la Mare and C. A. Vernon, *ibid.*, 3628 (1952).

(42) P. B. D. de la Mare and C. A. Vernon, *ibid.*, 3555 (1953).

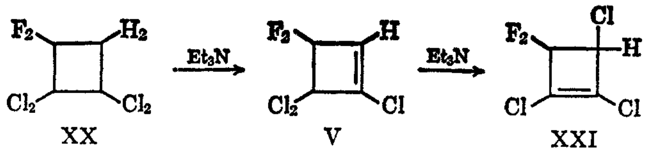


ment with structure XVIII and incompatible with structure VII. Furthermore, distillation of the diether after drying over magnesium sulfate gave a diethoxy ketone, XIX. This is not surprising, as XVIII is a



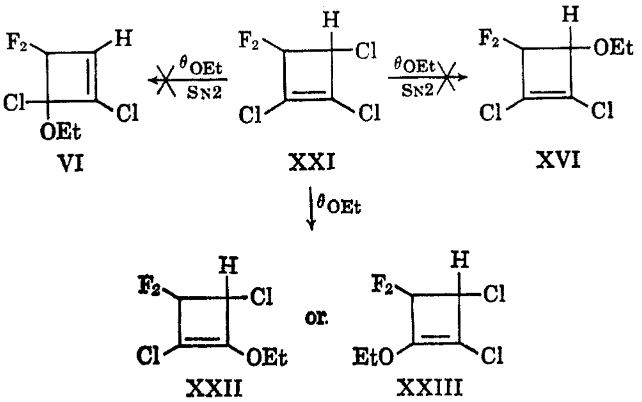
vinylog of an α,α-difluoro ether, a structure known to be particularly susceptible to acid hydrolysis.[43-48] The previously reported[18] oxidation of the diether to diethoxydifluorosuccinic acid appears to be in error.

The starting material for this investigation, V, was prepared by the dehydrohalogenation of 2,2,3,3-tetrachloro-4,4-difluorocyclobutane (XX) with triethylamine. By a fortunate accident, a large-scale



preparation of V escaped control and became exothermic, resulting in the formation of XXI by rearrangement of V.[49] The absorption of XXI in the infrared at 1630 cm^{-1} suggested that it was an isomer of V. The structure was confirmed by the nmr spectrum, which contained an equal-intensity quartet centered at τ 4.83. The preparation of XXI permitted the discounting of the suggestion[52] that the monoether, VI, could have arisen by an SN2′ reaction of XXI, mistakenly identified as V. More important, it permitted a demonstration that the actual monoether, XVI, did *not* result from an SN2 reaction of XXI.

Treatment of the isomeric cyclobutene, XXI, with 1 equiv of ethoxide gave a new monoether, XXII or XXIII. The infrared spectrum had an absorption at 1675 cm^{-1}, characteristic of a 1-chloro-2-ethoxycyclobutene. The nmr spectrum contained a doublet centered at 5.05, consistent with an allylic ring hydrogen. Furthermore, there was a 1:3:3:1 quartet centered τ 5.45, typical of the methylene protons in a vinylic ethoxy group. A differentiation between the two possible structures is now in progress.



Discussion

While these results have by no means ruled out competitive SN2 and SN2′ processes for these systems, we prefer the carbanion hypothesis because of its consistency and simplicity.

The theory proposed here is applicable to olefins having charge-dispersing groups other than halogen. The benzene ring should be especially effective as an α substituent, owing to the large volume over which it can disperse a negative charge. The 1-phenyl-4,4-dichloro-3,3-difluorocyclobutene system of Roberts[15] is analogous to our compound V. Whereas Roberts interpreted his results in terms of combinations of SN2 and SN2′ displacements and considered the displacement of a vinylic chlorine to be "remarkable,"[53] the present carbanion theory easily accounts for all of his results.

Miller[9-12] has argued against carbanion processes on the basis of the saturated products of proton abstraction by carbanions not having been isolated. It seems reasonable that the more stable a carbanion is, the less likely it is to abstract a proton from the solvent. Furthermore, if a proton is abstracted by a relatively stable carbanion, it is just that more easily lost again. Therefore, one should not assume that a reaction must be concerted simply because the saturated products which should not have been expected were not found.

It seems superfluous to propose the addition of alcohol to give a saturated product, followed by a concerted elimination to form an olefin, when the product can be explained without recourse to the two extra steps. The findings of Barr,[8] wherein more alcohol reacted with perfluorocyclobutene than could be accounted for on the basis of potassium hydroxide used, are easily explainable in view of Edelson's[54] potassium fluoride catalyzed addition of alcohols to fluoro olefins.

While the work of Stork and White[55,56] is often cited as proof of the necessity of a *cis* relationship between entering and leaving groups in SN2′ processes, the stereochemistry of their cyclohexene system was such

---

(43) J. D. Park, S. Cohen, and J. R. Lacher, *J. Am. Chem. Soc.*, **84**, 2919 (1962).

(44) J. A. Young and P. Tarrant, *ibid.*, **71**, 2432 (1949).

(45) J. A. Young and P. Tarrant, *ibid.*, **72**, 1860 (1950).

(46) P. Tarrant and H. C. Brown, *ibid.*, **73**, 1781 (1951).

(47) P. Tarrant and H. C. Brown, *ibid.*, **73**, 5831 (1951).

(48) E. R. Larsen, *J. Org. Chem.*, **28**, 1133 (1963).

(49) The rearrangement of V to XXI has been studied in detail[50] and will be described in a later paper. Analogous rearrangements have previously been reported.[14,16,51]

(50) Unpublished work of J. D. Park, J. R. Dick, and G. Moore.

(51) E. F. Jenny and J. Druey, *J. Am. Chem. Soc.*, **82**, 3111 (1960).

(52) Suggested by a referee of ref 27.

(53) The displacement of a vinylic chlorine does not seem at all "remarkable" in view of previously published work.[4,5]

(54) N. A. Edelson, Ph.D. Thesis, Cornell University, 1962; *Dissertation Abstr.*, **23**, 1923 (1962).

(55) G. Stork and W. N. White, *J. Am. Chem. Soc.*, **75**, 4119 (1953).

(56) G. Stork and W. N. White, *ibid.*, **78**, 4609 (1956).

as to make a *trans* displacement quite unlikely because of steric repulsions.

It must be pointed out that the reason for the directive effects of α and β substituents is not known. Although the discussion thus far has been in terms of electronic effects, it may well be that the carbanions under consideration are so well stabilized by electronic effects, that the directive influence of the substituents is due to steric repulsion. Thus, our observation[57] that β-chlorine is more effective than β-fluorine in stabilizing a carbanion, may merely be a reflection of the chlorine sterically hindering the attack of a nucleophile at the α-carbon. The fact that perfluorocyclobutene produces 1,2-diethoxy-3,3,4,4-tetrafluorocyclobutene upon treatment with ethanolic potassium hydroxide,[4] whereas 1-chloro-2,3,3,4,4-pentafluorocyclobutene and 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene give the same triether,[5] may be a manifestation of steric repulsion by the α substituent. Experiments to settle this question are now underway.

It must also be pointed out that the arguments put forth here would also apply to transition states with a large amount of carbanion character. An unequivocal differentiation requires the trapping of the carbanion, and experiments along these lines are also in progress.

Experimental Section

Melting and boiling points are uncorrected. Infrared spectra were obtained using a Perkin-Elmer Infracord. Nmr spectra were taken using a Varian A-60 analytical spectrometer and pure liquid samples with tetramethylsilane as an internal reference except where otherwise indicated.

1,1,2,2-Tetrachloro-3,3-difluorocyclobutane (XX).—Modified procedures of Coffman[58] and Henne[59] were employed, the desired codimer being obtained in 48% yield: bp 150–151° (630 mm), mp 52.5°. (Previously reported values are mp 41°, bp 143°. As the product was shown by glpc to contain no impurity, the values now reported are considered to be correct.)

The nmr spectrum (carbon tetrachloride solution) contained a triplet centered at τ 6.52 with a J_{HF} of 9.8 cps.

Dehydrochlorination of 1,1,2,2-Tetrachloro-3,3-difluorocyclobutane (V and XXI).—In a 5-l. three-neck flask, equipped with stirrer, reflux condenser, and addition funnel, was placed 950 g (9.40 moles) of triethylamine. A solution of 1800 g (7.83 moles) of 1,1,2,2-tetrachloro-3,3-difluorocyclobutane in 250 ml of ethyl ether was added in a steady stream with rapid stirring. The temperature rose to *ca.* 50°, and the reaction mixture became yellow; after 2 hr, it had solidified. After standing for 2 days, the black reaction mixture was diluted with 100 ml of ether, and the excess triethylamine was neutralized with 130 ml (1.56 moles) of concentrated hydrochloric acid in 1500 ml of water. The heavier organic layer was separated, washed with water until neutral, and dried twice over magnesium sulfate. Rectification through a 20-in. Fenske column gave two major fractions. The first, bp 116–117° (627 mm), 1003 g, was shown by glpc to consist of 69.5% of the expected 1,4,4-trichloro-3,3-difluorocyclobutene (V) and 30.5% of the rearranged olefin, 1,2,3-trichloro-4,4-difluorocyclobutene (XXI), while the second fraction, bp 113–120° (627 mm), 33.5 g, contained 94.3% rearranged product and 5.7% unrearranged olefin. The first fraction was strongly acidic. The total yield of olefins was 1036 g (5.36 moles, 68.3%).

A 675-g portion of the first fraction was rectified through a 48 in. × 25 mm Podbielniak "Hyper-cal," "Heligrid"-packed column. Fractions of varying composition were obtained. After rectification, the total product was 59% unrearranged, 41% rearranged; hence, 11% more rearranged during rectification. The best fraction of unrearranged olefin, V, was obtained in 97.9% purity by glpc: bp 117.0° (624 mm); $n^{25}{}_D$ 1.4418; $d^{25}{}_4$ 1.5459 [lit. bp 118° (631 mm), $n^{25}{}_D$ 1.4344, $d^{25}{}_{25}$ 1.5820]; molecular refraction, calcd 33.27, found 33.07.

The infrared spectrum contained a strong absorption at 1590 cm^{-1}. The nmr spectrum contained a triplet centered at τ 3.81, with a J_{HF} of 1.9 cps.

The best fraction of the rearranged cyclobutene, XXI, was obtained in 98.5% purity by glpc: bp 119.5° (624 mm); $n^{25}{}_D$ 1.4468; $d^{25}{}_4$ 1.5366; molar refractivity, calcd 33.27, found 33.62.

Anal. Calcd for $C_4HCl_3F_2$: C, 24.78; H, 0.52; Cl, 54.95; F, 19.63. Found: C, 24.92; H, 0.64; Cl, 55.06; F, 19.78.

The infrared spectrum contained a strong absorption at 1625 cm^{-1}. The nmr spectrum contained an equal intensity quartet centered at τ 4.83, with $J^1{}_{HF}$ of 2.6 cps, and $J^2{}_{HF}$ of 0.4 cps.

Another dehydrochlorination of the codimer on a smaller scale (0.67 mole) gave 95% unrearranged olefin, and only 5% of the rearranged cyclobutene.

1,2-Dichloro-3-ethoxy-4,4-difluorocyclobutene (XVI).—In a 1-l. three-neck flask, equipped with stirrer, reflux condenser, and addition funnel, was placed 80.0 g (0.414 mole) of 1,4,4-trichloro-3,3-difluorocyclobutene (V, 94.2%) in 200 ml of 95% ethanol. The solution was cooled in an ice–water bath, and a solution of 27.3 g (0.414 mole) of potassium hydroxide in 200 ml of ethanol was added dropwise with rapid stirring over a 2-hr period. The reaction mixture was diluted with 1500 ml of water and extracted with methylene chloride, and the extracts were washed with water until neutral and dried over magnesium sulfate. Two rectifications through a 315-mm Fenske column yielded 33.8 g of material 100% pure by glpc: bp 75.5–76.3° (50 mm); $n^{25}{}_D$ 1.4256; $d^{25}{}_4$ 1.3107 [the compound previously reported as 1,4-dichloro-4-ethoxy-3,3-difluorocyclobutene had bp 141° (628 mm), $n^{25}{}_D$ 1.4265, $d^{25}{}_{25}$ 1.3122]; molar refractivity, calcd 39.31, found 39.66.

Anal. Calcd for $C_6H_6Cl_2F_2O$: C, 35.50; H, 2.98; Cl, 34.94; F, 18.73. Found: C, 35.70; H, 3.23; Cl, 34.90; F, 18.51.

The infrared spectrum contained an absorption at 1625 cm^{-1}. The nmr spectrum contained an equal-intensity quartet centered at τ 5.38 with $J^1{}_{HF}$ of 1.9 cps and $J^2{}_{HF}$ of 0.4 cps. There was also a 1:3:3:1 quartet centered at τ 6.28. The total yield of monoether was 38.3 g (0.189 mole, 48%).

Reaction of 1,2-Dichloro-3-ethoxy-4,4-difluorocyclobutene (XVI) with Ethoxide Ion.—In a 1-l. three-neck flask, equipped with stirrer, reflux condenser, and addition funnel, was placed 25.0 g (0.123 mole) of 1,2-dichloro-3-ethoxy-4,4-difluorocyclobutene (XVI) in 75 ml of 95% ethanol. A solution of 8.13 g (0.123 mole) of potassium hydroxide in 75 ml of ethanol was added dropwise with rapid stirring over a period of 1.5 hr, the flask being cooled in an ice–water bath. Only a slight turbidity resulted. Separation without further treatment on an Aerograph Autoprep Model A-700, using a $^3/_8$ in. × 20 ft column packed with 30% Silicone SE-30 on Chromosorb P, gave, in addition to ethanol and monoether, diether in *ca.* 80% yield.

Anal. Calcd for $C_8H_{11}ClF_2O_2$: C, 45.19; H, 5.21; Cl, 16.68; F, 17.87. Found: C, 45.33; H, 5.11; Cl, 16.54; F, 17.69.

The infrared spectrum contained a strong absorption at 1680 cm^{-1}. The nmr spectrum contained a doublet centered at τ 5.47 with a J_{HF} of 1.4 cps, 1:3:3:1 quartets centered at τ 5.65 and 6.35; and 1:2:1 triplets centered at τ 8.65 and 8.8.

In another run, after standing for another 15 hr at room temperature, the reaction mixture was cooled in an ice–water bath, diluted with *ca.* 1 l. of water, and extracted with methylene chloride. The combined extracts were washed with water until neutral and dried over magnesium sulfate. After 4 days, the solution was deep amber and fumed upon exposure to air. The flask was etched, indicating the presence of hydrofluoric acid. After a second drying over magnesium sulfate, the product was rectified through a 315-mm Fenske column to give 9.5 g of material shown to be 98% pure: bp 89° (1 mm); $n^{25}{}_D$ 1.4857; $d^{25}{}_4$ 1.1644; molar refractivity, calcd for $C_8H_{11}ClO_3$ 45.13, found 46.85.

Anal. Calcd for $C_8H_{11}ClO_3$: C, 50.40; H, 5.82; Cl, 18.60. Found: C, 50.70; H, 5.60; Cl, 18.25.

The infrared spectrum contained a strong absorption at 1775 cm^{-1}, and medium-strong absorptions at 1610 and 1570 cm^{-1}.

The nmr spectrum contained a singlet at τ 5.02, 1:3:3:1 quartets centered at τ 5.37 and 6.33, and 1:2:1 triplets centered at τ 8.53 and 8.82.

---

[57] J. H. Adams, J. R. Dick, and J. D. Park, *J. Org. Chem.*, **30**, 400 (1965).

[58] D. D. Coffman, P. L. Barrick, R. D. Cramer, and M. S. Raasch, *J. Am. Chem. Soc.*, **71**, 490 (1949).

[59] A. L. Henne and R. P. Ruh, *ibid.*, **69**, 279 (1947).

Reaction of 1,2,3-Trichloro-4,4-difluorocyclobutene (XXI) with Ethoxide Ion.—In a 1-l. three-neck flask, equipped with stirrer, reflux condenser, and addition funnel, was placed 80.0 g (0.414 mole) of a mixture of 94.7% 1,2,3-trichloro-4,4-difluorocyclobutene (XXI, 0.392 mole) and 5.3% 1,4,4-trichloro-3,3-difluorocyclobutene (V, 0.022 mole) in 200 ml of 95% ethanol. The solution was cooled in an ice–water bath, and a solution of 27.3 g (0.414 mole) of potassium hydroxide in 200 ml of ethanol was added dropwise with rapid stirring over a 2-hr period. The reaction mixture was diluted with water and extracted with methylene chloride, and the extracts were washed with water until neutral and dried twice over magnesium sulfate. Rectification through a 315-mm Fenske column gave 43.0 g of product 100% pure by glpc: bp 100° (50 mm); $n^{25}\text{D}$ 1.4438; $d^{25}{}_4$ 1.3531; molar refractivity, calcd 39.31, found, 39.80.

Anal. Calcd for $C_6H_6Cl_2F_2O$: C, 35.50; H, 2.98; Cl, 34.94; F, 18.73. Found: C, 35.49; H, 3.11; Cl, 35.06; F, 18.54.

The infrared spectrum contained a strong absorption at 1675 cm^{-1}. The nmr spectrum contained a doublet centered at τ 5.05 with a J_{HF} of 0.9 cps, evidence for an allylic proton split by a fluorine nucleus, and a 1:3:3:1 quartet centered at τ 5.45, indicative of a methylene proton on a vinylic ethoxy group. Integration showed the areas of the doublet and the quartet to be in the ratio 1:2.

The total yield of vinyl ether was 59.3 g (0.292 mole, 75%).

Also obtained was 5.5 g (0.027 mole, 12%) of 1,2-dichloro-3-ethoxy-4,4-difluorocyclobutene, identified by its infrared spectrum and glpc retention time.

Acknowledgment.—The authors wish to express their appreciation to Professor Melvin Hanna of this Chemistry Department for assistance in the interpretation of the nmr spectra, and to the Minnesota Mining and Manufacturing Company, St. Paul, Minnesota, for their support of this work.

Catalytic Actions of Aluminum Chloride on the Isoprene–Methyl Acrylate Diels–Alder Reaction

TAKASHI INUKAI AND TAKESHI KOJIMA

The Central Research Laboratories, Chisso Corporation, Kamariya, Kanazawa-ku, Yokohama, Japan

Received August 24, 1965

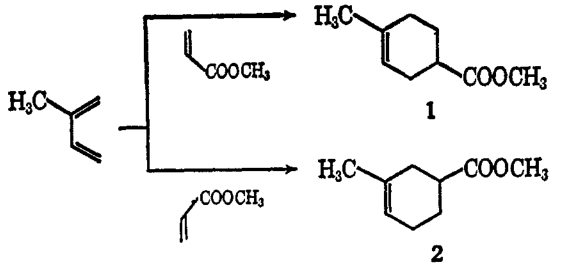
The ratio of methyl 4- and 3-methyl-3-cyclohexene-1-carboxylates (**1** and **2**) formed by the aluminum chloride catalyzed reaction[1] (at 7–12°) of isoprene with methyl acrylate was found to be 95:5. The corresponding ratio for the uncatalyzed reaction (Diels–Alder reaction) was found to be 70:30 (at room temperatures and at 120°) in agreement with the literature.[2] The measurements of the relative rate of butadiene, isoprene, and 2,3-dimethylbutadiene toward methyl acrylate were made to get the partial rate factors (see Figure 1). The aluminum chloride catalyzed reaction is shown to be free from steric complications by inspection of the partial rate factors obtained. A heterolytic two-step mechanism involving rate-determining electrophilic attack of the β-carbon atom of the complexed methyl acrylate on dienes is suggested by the comparison of partial rate factors and an enormous accelerating effect of aluminum chloride.

It recently has been shown that methyl acrylate reacts with 1,3-dienes very rapidly in the presence of anhydrous aluminum chloride to give Diels–Alder condensation products in high yields.[1] The complex formation between aluminum chloride and the acrylate, presumably at the carbonyl oxygen, may polarize the α,β double bond more both to activate the dienophile toward a diene and to make the isomer ratio of the adducts, with an unsymmetrical diene, different from that in the uncatalyzed reaction. Such an effect on orientation has actually been reported by Lutz and Bailey[3] on the reaction of isoprene with methyl vinyl ketone or acrolein under the catalysis of stannic chloride pentahydrate. These workers explained the increased preponderance of the 1,4 isomer in the products by assuming the increased steric retardation against the 1,3-isomer formation where the pendant methyl group of isoprene must come close to the complexed carbonyl group of larger steric requirement.

In the present paper we report the isomer distribution **1**:**2** and the relative rate, *k*(isoprene):*k*(butadiene), for the aluminum chloride catalyzed reaction as well as those for the uncatalyzed reaction, as reference of comparison, and present a probable mechanism of the catalyzed reaction.

Results and Discussion

Two groups of workers have reported on the isomer distribution **1**:**2** for the uncatalyzed condensation with some contradictions. Thus Nazarov, *et al.*,[4] reported a ratio of 5.4:1 (16% of **2**) for the room temperature and 3.8:1 (21% of **2**) for the 120° reaction. On the other hand Hennis[2] recently has reported a ratio of 70:30 which was independent of the reaction temperature. This situation induced us to reexamine the ratio.[5]



The analytical procedures adopted here were to dehydrogenate the reaction products and determine the resulting *p*- and *m*-toluates by the infrared absorbance measurements. The dehydrogenation with palladium on carbon in the liquid phase or in solution,

---

(1) T. Inukai and M. Kasai, *J. Org. Chem.*, **30**, 3567 (1965).

(2) H. E. Hennis, *ibid.*, **28**, 2570 (1963).

(3) E. F. Lutz and G. H. Bailey, *J. Am. Chem. Soc.*, **86**, 3899 (1964).

(4) I. N. Nazarov, Yu. A. Titov, and A. I. Kuznetsova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1412 (1959); *Chem. Abstr.*, **54**, 1409 (1960).

(5) Hennis[2] used the key bands of 12.5 (for **1**) and 12.7 μ (for **2**) for determination of the isomer ratio. We found that the product of the uncatalyzed reaction did not give rise to 12.7-μ absorption, even a shoulder, which according to the literature[2] would show surprising absence of **2**. Since isomer **2** does not seem to have been isolated pure and identified by this author, we could not have full assurance of this assignment of the 12.7-μ band to **2**. The glpc analysis was not convincing for the same reason.