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NEGATIVE SUBSTITUENTS IN THE CLAISEN REARRANGEMENT

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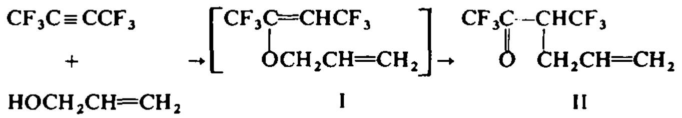
Abstract—Several instances of the Claisen rearrangement are demonstrated with allyl vinyl ethers in which the vinyl segment is heavily substituted with negative groups. With fluoro, fluoroalkyl, chloro and alkoxy as negative substituents, these reactions proceed with unusual ease at 25–100°. A related isomerization of a propargyl vinyl ether to an allenyl ketone is also described.

ALTHOUGH the Claisen rearrangement is usually associated with allyl aryl ethers, allyl vinyl ethers also undergo the rearrangement.[1] This latter aspect of the reaction has in recent years been used to synthesize numerous unsaturated nonaromatic compounds. Such studies have been confined to allyl vinyl ethers bearing hydrogen and alkyl substituents, except for an occasional negative substituent (ester[1,2], acyl[3] and aryl[4]) on the vinyl group. The present work shows that allyl vinyl ethers with multiple negative substituents undergo the Claisen rearrangement with great ease and that such ethers provide a convenient route to some unusual structures.

Base-catalyzed addition of allyl alcohol to hexafluoro-2-butyne was used as a route to allyl 1,2-bis(trifluoromethyl) vinyl ether (I), but the product that distilled at 89° had completely isomerized to 1,1,1-trifluoro-3-trifluoromethylhex-5-en-2-one (II). This rapid and clean isomerization at temperatures below 90° can be compared to the slow isomerization observed for allyl vinyl ether (36% after 72 hr at 100°),[5] the more rapid isomerization of allyl isopropenyl ether,[6] and the still more rapid isomerization of allyl 1-cyclohexenyl ether (ca. 55% after 2 hr at temps presumably between 50° and 100° followed by distillation at 75–78° (16 mm).[7]


$$\begin{array}{l} CF_3C\equiv CCF_3 \\ \quad + \\ HOCH_2CH{=}CH_2 \end{array} \rightarrow \left[\begin{array}{l} CF_3C{=}CHCF_3 \\ \quad\ | \\ \quad\ OCH_2CH{=}CH_2 \end{array}\right] \rightarrow \begin{array}{l} CF_3C{-}CHCF_3 \\ \quad\ \| \quad\ | \\ \quad\ O \quad CH_2CH{=}CH_2 \end{array}$$

I

II

An even more highly fluorinated group is available by displacement of fluoride from a fluoroolefin by an alkoxy group. As reported by Koshar, *et al.*,[8] octafluoroisobutylene reacts with alcohols even without base present to form a mixture of

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[1] L. Claisen, *Chem. Ber.* **45**, 3157 (1912).

[2] J. W. Ralls, R. E. Lundin and G. F. Bailey, *J. Org. Chem.* **28**, 3521 (1963).

[3] M. Bertrand and J. LeGras, *C.R. Acad. Sci., Paris*, **260**, 6926 (1965).

[4] D. S. Tarbell, *Chem. Rev.* **27**, 495 (1940).

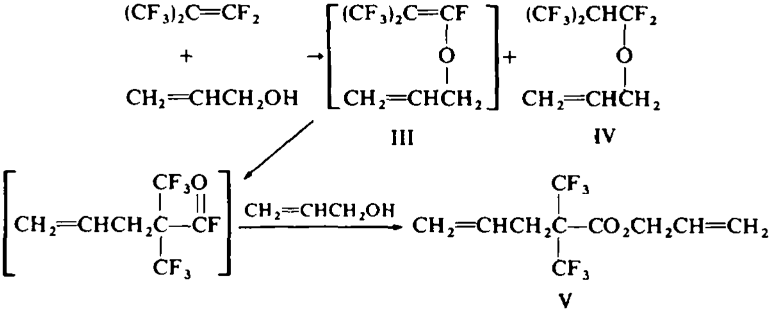
[5] R. Paul, G. Roy, M. Fluchaire and G. Collardeau, *Bull. Soc. Chim. Fr.* 121 (1950).

[6] L. Stein and G. W. Murphy, *J. Am. Chem. Soc.* **74**, 1041 (1952).

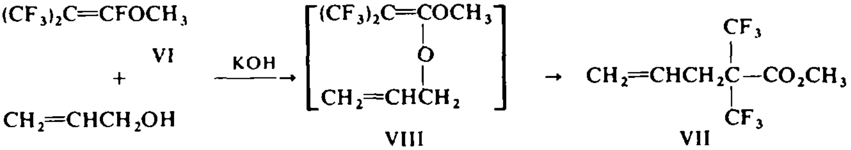
[7] N. B. Lorette and W. L. Howard, *J. Org. Chem.* **26**, 3112 (1961).

[8] R. J. Koshar, T. C. Simmons and F. W. Hoffmann, *J. Am. Chem. Soc.* **79**, 1741 (1957).

saturated and unsaturated ethers. With allyl alcohol, no unsaturated vinyl ether III was obtained along with saturated ether IV; instead a product V was obtained in which were incorporated two allyloxy residues. Rather than the postulated[8] ketene acetal, V is an allyl ester formed by a facile Claisen rearrangement. Although V is probably obtained *via* an isomerization of III at 50° or less, the ketene acetal is not completely eliminated as an intermediate.



No spontaneous reaction was evident on mixing methyl 1-fluoro-2,2-bis(trifluoromethyl)vinyl ether (VI) and allyl alcohol, but reaction proceeded at 0° in the presence of base to lead cleanly to the ester VII, b.p. 51–52° (30 mm). Formation of the allyl methyl ketal VIII is presumed to have occurred, and its rearrangement must have then proceeded readily at temperatures below 50°.



An analogous reaction of the unfluorinated compound, diallyl ketene acetal, has been reported[9] to go in 5 hr at 80° in t-butanol. These low temperatures can probably be related to the formation of a stable ester group as the driving force. Formation of a conjugated diene system is similarly felt to be responsible for the rearrangement of the vinyl ether of divinylcarbinol to 4,6-heptadienal at only 25° in 10 days.[10]

Reaction of allyloxy anion with an internal fluoroolefin allows the use of a completely fluorinated olefin to give a reaction uncomplicated by ester formation. Octafluorocyclopentene gave only one neutral product, b.p. 105–106°, which was shown to be the ketone IX expected from complete isomerization of the first-formed allyl ether.

An allyl ether formed from a halogenated cyclobutene would have a relatively

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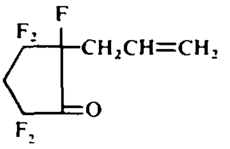
[9] S. M. McElvain, H. I. Anthes and S. H. Shapiro, *J. Am. Chem. Soc.* **64**, 2525 (1942).

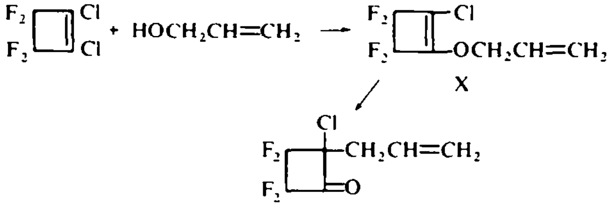
[10] S. F. Reed, *J. Org. Chem.* **30**, 1663 (1965) cites this rearrangement as the first of a vinyl allyl ether to occur at room temp.

large $C{=}C{-}O$ angle and might therefore encounter some steric difficulty in undergoing a concerted rearrangement.[1, 11, 12] In addition, the formation of a carbonyl group would be less effective as a driving force in this case, since a double bond



IX

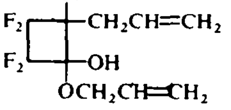
exo to a small ring is of relatively high energy. Fluorinated cyclobutanones, in particular, have an extremely reactive carbonyl group.[13] The isomerization of allyl 1-(2-chlorotetrafluorocyclobutenyl) ether (X) was therefore attempted and found to proceed, but less readily than the other cases.



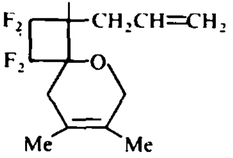
XI

The reaction of 1,2-dichlorotetrafluorocyclobutene with allyl alcohol and base was conducted in the cold as described in the literature.[14] The allyl ether X, isolated by distillation at 82–85° (100 mm), contained a small amount of ketone XI, showing that isomerization proceeds at an appreciable rate at 85°. When ether X was refluxed for eight hours, the pot temperature fell from 132° to 118°, and ketone XI was obtained in good yield. The product described by Ruh as the ether seems instead to be the already rearranged product, ketone XI.

The high reactivity of the carbonyl group in XI was demonstrated by its exothermic addition of allyl alcohol to form a distillable hemiketal, XII. This ketal was obtained directly from a reaction in which excess allyl alcohol was removed by distillation at



XII



XIII

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[11] R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.* **87**, 2511 (1965) predict by analysis of orbital symmetry relationships that the Claisen rearrangement is favored to go thermally in a concerted manner.

[12] S. J. Rhoads, *Molecular Rearrangements* (Edited by P. de Mayo) Part I; pp. 655–706. Interscience, New York, N.Y (1963), reviews the experimental evidence for a cyclic transition state in the Claisen rearrangement. .

[13] D. C. England, *J. Am. Chem. Soc.* **83**, 2205 (1961).

[14] R. P. Ruh, U.S. Patent 2,613,228 (1952).

ca. 100°, rather than by washing with water. A slow Diels-Alder reaction of XI with 2,3-dimethylbutadiene occurred at 25° to give adduct XIII.

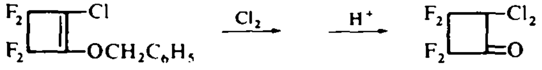
A more strained cyclic transition state would be expected for the reaction in which 1-(2-chlorotetrafluorocyclobutenyl) propargyl ether (XIV) is the starting material and 2-allenyl-2-chlorotetrafluorocyclobutanone (XV) the Claisen product, since the propargyl and allenyl groups are both normally linear.

XIV XV

Propargyl ether XIV, isolated by distillation at 75–76° (100 mm), contained no impurities detectable by infrared. At 132–146°, isomerization of XIV went with inversion to give allenic ketone XV. Not only does this rearrangement proceed as readily as the usual Claisen, but it also provides a rare example of one involving a propargyl group.[15–18]

Earlier studies on the rearrangement of allyl aryl ethers showed that only slight rate changes occurred with introduction of aryl substituents, and that the electron-withdrawing substituents slightly retarded the reaction.[19,20] However, the ease with which the rearrangements of the present partially halogenated ethers occur suggests that, in these nonaromatic cases, the transition state may develop varying degrees of polar character.[21,22]

One attempt to involve an aromatic ring in a rearrangement with a fluorinated vinyl group failed. Benzyl 1-(2-chlorotetrafluorocyclobutenyl) ether (XVI) underwent acid-catalyzed decomposition at reflux, and attempts at photochemical, radical and anionic catalysis of the rearrangement met with no success. The benzyl ether was, however, easily converted to the very reactive perhalocyclobutanone XVII by chlorination and hydrolysis with sulfuric acid. This route to α-halopolyfluoroketones may be generally useful.



XVI XVII

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[15] B. G. Thyagarajan, K. K. Balasubramanian and R. Bhima Rao, *Tetrahedron Letters* No. 21, 1393 (1963) report what may be the first Claisen reaction involving an acetylenic bond, the product of which is saturated rather than allenic because of presumed secondary cyclization reactions. Simple phenyl propargyl ethers give no rearranged product when refluxed.

[16] P. Cresson, *C.R. Acad. Sci., Paris*, **261**, 1707 (1965) describes the rearrangement at 200° of some propargyl vinyl ethers to mixtures of allenic and dienic aldehydes.

[17] D. K. Black and S. R. Landor, *J. Chem. Soc.* 6784 (1965) also report the rearrangement of propargyl vinyl ethers to allenic aldehydes.

[18] R. Gardi, R. Vitali and P. P. Castelli, *Tetrahedron Letters* No. 27, 3203 (1966) describe the first successful isomerizations to allenic ketones. These workers used propargyl enol ethers of ketosteroids.

[19] H. L. Goering and R. R. Jacobson, *J. Am. Chem. Soc.* **80**, 3277 (1958).

[20] W. N. White, D. Gwynn, R. Schlitt, C. Girard and W. K. Fife, *J. Am. Chem. Soc.* **80**, 3271 (1958).

[21] See D. N. Matthews and E. I. Becker, *J. Org. Chem.* **31**, 1135 (1966) for a recent example of similar considerations with respect to the Diels-Alder reaction.

[22] C. A. Vander Werf and V. L. Heasley, *J. Org. Chem.* **31**, 3534 (1966) discuss polar effects in rearrangements of allyl azides.

EXPERIMENTAL

1,1,1-Trifluoro-3-trifluoromethylhex-5-en-2-one (II). Hexafluorobut-2-yne (23 g, 0·14 mole) was admitted about as rapidly as it reacted to a flask containing 1 g NaOH dissolved in 50 ml allyl alcohol and topped by a −80° condenser. The mixture was stirred and warmed at 50° until the slight reflux stopped, then shaken with 500 ml water. The lower layer was washed with 100 ml water, dried and distilled. The product was 22·7 g (74%) of II; b.p. 88·5–89°, n_D^{25} 1·3228. IR bands were found at 3·21 and 3·31 μ (unsaturated CH), 3·38 and 3·46 μ (saturated CH), 5·61 μ (C=O), 6·03 μ (C=C), and in the 8–9 μ region (C—F). (Found: C, 38·42; H, 2·84; F, 51·73. Calc. for $C_7H_6F_6O$: C, 38·19; H, 2·75; F, 51·79%.)

Allyl 2,2-bis(trifluoromethyl)pent-4-enoate (V). A scrubbing tower with a fritted glass inlet was filled with 250 ml allyl alcohol and cooled at 0° while 58 g of an 80/20 mixture[23] of octafluoroisobutylene (*toxic*!) and octafluorocyclobutane (46·4 g or 0·23 mole of octafluoroisobutylene) was bubbled in over a period of 1·5 hr. The resulting mixture was warmed to 50° for 1 hr, cooled, and shaken with 2 l. cold water. The lower layer was washed with two 1-l. portions water, dried and distilled to give 2 products. The first was 34·9 g (59%) of IV; b.p. 55–59° (150 mm), n_D^{25} 1·3129.[24] IR absorption at 3·24 μ (unsaturated CH), 3·38 and 3·46 μ (saturated C—H), 6·05 μ (C=C), in the 8–9 μ region (C—F and C—O), and in the 10 and 11 μ regions ($CH=CH_2$) is compatible with the postulated adduct.

The second product, after an intercut of only 1·7 g, was 9·4 g (15%) of V; b.p. 66–68° (20 mm), n_D^{25} 1·3721.[25] IR absorption bands were at 3·24 and 3·31 μ (unsaturated CH), 3·35, 3·39 and 3·48 μ (saturated CH), 5·67 μ (ester C=O), 6·06 μ (C=C), in the 8–9 μ region (CF and C—O), and in the 10 and 11 μ regions ($CH=CH_2$).

Methyl 2,2-bis(trifluoromethyl)pent-4-enoate (VII). A mixture of 42·4 g (0·20 mole) of VI and 40 ml allyl alcohol was stirred and cooled at 0° while a soln of 14 g (0·2–0·21 mole) KOH pellets in 80 ml allyl alcohol was added over a 10-min period. The mixture was stirred 1 hr at 25° and then shaken with 1 l. cold water. The lower layer was washed with 500 ml water, dried and distilled to give 19·3 g (39%) of VII; b.p. 51–52° (30 mm), n_D^{24} 1·3541. The IR spectrum contained bands at 3·24 μ (unsaturated CH), 3·37 and 3·50 μ (saturated CH), 5·67 μ (ester C=O), 6·09 μ (C=C), in the 8–9 μ region (C—F and C—O), and in the 10 and 11 μ regions ($CH=CH_2$). (Found: C, 38·84; H, 3·50; F, 45·29. Calc. for $C_8H_8F_6O_2$: C, 38·41; H, 3·22; F, 45·57%.)

2-Allylheptafluorocyclopentanone (IX). A mixture of 42·4 g (0·20 mole) octafluorocyclopentene and 50 ml allyl alcohol was stirred and cooled at 0 while a soln of 14 g (0·2 mole) KOH pellets in 80 ml allyl alcohol was added in a 30-min period. The mixture was stirred another 30 min at 0° and 2 hr at 25°. Then it was poured into 1 l. water, and the lower layer was separated, washed with a 500-ml portion of water, dried and distilled. There was thus isolated 17·3 g (35%) of IX; b.p. 105–106°, n_D^{25} 1·3392. IR absorption bands occurred at 3·22 and 3·28 μ (unsaturated CH); 3·33 and 3·40 μ (saturated CH); 5·52 μ (C=O); 6·05 μ (C=C), and in the 8–9 μ region (CF). (Found: C, 38·54; H, 2·25; F, 54·04, 52·26. Calc. for $C_8H_5F_7O$: C, 38·41; H, 2·02; F, 53·17%.)

Allyl 1-(2-Chlorotetrafluorocyclobutenyl) ether (X). A mixture of 156 g (0·80 mole) 1,2-dichlorotetrafluorocyclobutene, 150 ml allyl alcohol and 10 drops phenolphthalein soln was cooled at 0° and stirred while a soln of 56 g (0·8–0·85 mole) KOH pellets in 300 ml allyl alcohol was added rapidly enough to maintain slight basicity. The mixture was stirred 1 hr at 0° and 2 hr at 25°. The reaction mixture was shaken with 2·5 l. water, and then the lower layer was washed with two 500-ml portions water, dried and distilled. There was thus obtained 134 g (77%) of X, b.p. 74–85° (100 mm), containing ketone XI as an impurity. Much of the ketone was concentrated in 14·5 g of a fraction with b.p. 74–82° (100 mm). However, the major cut, 119·5 g with b.p. 82–85° (100 mm), n_D^{24} 1·3949, exhibited in the IR a weak C=O absorption at 5·45 μ in addition to the very strong vinyl ether C=C absorption at 5·94 μ. Gas chromatography confirmed the presence of a more volatile impurity in small amount.

2-Allyl-2-chlorotetrafluorocyclobutanone (XI). Isomerization of X occurred at a decreasing rate when refluxed for 8 hr. The pot temp dropped from 132 to 118, and g.c. analysis showed starting material to be nearly gone. During the latter stages of the isomerization, g.c. analysis indicated ether X to have a half life of less than 3 hr at 120°. Distillation afforded 119 g (69%) of XI, b.p. 113–115° A sample, b.p. 115°

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[23] Obtained by pyrolysis of octafluorocyclobutane as described by W. H. Pearlson and L. J. Hals, U.S. Patent 2,617,836 (1952).

[24] Ref. 8 reports a similar yield of IV; b.p. 100°, n_D^{25} 1·3135.

[25] Ref. 8 reports b.p. 79° (49 mm) and n_D^{25} 1·3727 for this compound, which they mistakenly identify as a bis-ether.

and n_D^{25} 1·3823, was analyzed.[26] (Found: C, 39·25; H, 2·47; Cl, 16·39; F, 34·88. Calc. for $C_7H_5ClF_4O$: C, 38·82; H, 2·33; Cl, 16·37; F, 35·09%.) IR absorption occurred at 3·24 and 3·30 μ (unsaturated C—H), 3·35 and 3·43 μ (saturated C—H), 5·45 μ (C═O), 6·06 μ (C═C), and in the 8–9 μ region (C—F). Absence of vinyl ether was indicated by lack of a band at 5·94 μ, and of carbonyl addition products by lack of OH absorption.

Hemiketal of 2-allyl-2-chlorotetrafluorocyclobutanone with allyl alcohol (XII). A soln of sodium allylate was prepared by the reaction of 5·8 g (0·25 mole) Na pieces with 100 ml allyl alcohol cooled at 0°. To this cooled soln was added 39·0 g (0·20 mole) 1,2-dichlorotetrafluorocyclobutene over a 20-min period. The mixture was stirred 1 hr at 0° and 3 hr at 25°. Salt was removed by filtration, and the filtrate was distilled to give 26 g of the main product at 75–80° (50 mm). Redistillation afforded 20·1 g (37%) of XII, b.p. 74–75° (50 mm); n_D^{25} 1·4252. IR absorption bands occurred at 2·85 μ (OH), 3·24 and 3·31 μ (unsaturated CH), 3·36, 3·41 and 3·47 μ (saturated CH), 6·06 μ (C═C), and in the 8–9 μ region (C—F/C—O). (Found: C, 43·55; H, 4·18; Cl, 12·93; F, 27·66. Calc. for $C_{10}H_{11}ClF_4O_2$: C, 43·73; H, 4·04; Cl, 12·91; F, 27·67%.)

Hemiketal XII was also prepared by mixing 2·9 g (0·05 mole) allyl alcohol and 11·0 g (0·05 mole) 2-allyl-2-chlorotetrafluorocyclobutanone. The resulting exothermic reaction resulted in an 81% yield (11·3 g) of distilled product, identified by its IR spectrum.

Diels-Alder adduct XIII *of 2,3-dimethylbutadiene with 2-allyl-2-chlorotetrafluorocyclobutanone.* No reaction occurred on mixing 21·7 g (0·10 mole) of XI and 8·2 g (0·10 mole) dimethylbutadiene. After 4 hr, a small amount of high-boiling product was detected by g.c. The refractive index of the mixture, n_D^{25} 1·3972, slowly increased as reaction proceeded. After 13 days, g.c. indicated ca. 10% of starting materials left and only one product being formed. After having stood 20 days at 25°, the reaction mixture was distilled to give 18·6 g (62%) of XIII; b.p. 52–53° (0·2 mm), n_D^{24} 1·4513. IR supported the assigned structure with bands at 3·24 μ (unsaturated CH), 3·34, 3·43 and 3·49 μ (saturated CH), 6·06 μ (C═C), in the 8–10 μ region (C—F and C—O), and at 10·06 and 10·85 μ (CH═CH$_2$).

Propargyl 1-(2-chlorotetrafluorocyclobutenyl) ether (XIV). A mixture of 156 g (0·80 mole) 1,2-dichlorotetrafluorocyclobutene and 150 ml propargyl alcohol was stirred and cooled at 0° while a soln of 56 g (0·80–0·85 mole) KOH in 300 ml propargyl alcohol was added over a 45-min period. The reaction mixture was stirred an additional hr at 25° and then shaken with 2 l. cold water. The lower layer was washed with 1 l. water, dried and distilled. There was obtained 93·3 g (54%) of XIV; b.p. 75–76° (100 mm), n_D^{24} 1·4011. The IR spectrum contained bands at 3·04 μ (acetylenic C—H), 3·39 and 3·47 μ (saturated CH), 4·70 μ (C≡C), 5·92 μ (C═C), and in the 8–10 μ region (C—F and C—O). No carbonyl absorption was detected. (Found: C, 39·26; H, 1·56; Cl, 16·46; F, 35·14. Calc. for $C_7H_3ClF_4O$: C, 39·18; H, 1·41; Cl, 16·53; F, 35·42%.)

2-Allenyl-2-chlorotetrafluorocyclobutanone (XV). Compound XIV (25 g; 0·12 mole) was refluxed for 5 hr. The pot temp dropped from 146° to 132°; at the end of this time the temp of overhead vapor was 113°. Slow distillation to maintain b.p. 113–118° gave 14·6 g of distillate and a dark viscous residue. Redistillation afforded 13·7 g (55%) of XV; b.p. 60–61° (100 mm), n_D^{25} 1·4070. The IR spectrum had bands at 3·25 and 3·33 μ (unsaturated CH), 5·07 and 5·14 μ (C═C═C), 5·44 μ (C═O), and in the 8–9 μ region (C—F). (Found: C, 39·60; H, 1·88; Cl, 16·94; F, 35·28. Calc. for $C_7H_3ClF_4O$: C, 39·18; H, 1·41; Cl, 16·53; F, 35·42%.)

Benzyl 1-(2-chlorotetrafluorocyclobutenyl) ether (XVI). A mixture of 156 g (0·80 mole) 1,2-dichlorotetrafluorocyclobutene and 92 g (0·85 mole) benzyl alcohol was stirred and cooled at 0° while a soln of 56 g (0·8–0·85 mole) KOH pellets in 60 ml water was added over a 30-min period. The mixture was stirred 1 hr at 0° and another hr at 25°, washed with two 500-ml portions water, dried and distilled. The product was 130 g (61%) of XVI; b.p. 46–48° (0·2 mm), n_D^{23} 1·4712. IR absorption bands appeared at 3·26 and 3·29 μ (unsaturated C—H), 3·38 and 3·46 μ (saturated C—H), 5·94 μ (C═C), 6·24, 6·31 and 6·68 μ (aromatic C═C), in the 8–10 μ region (C—F and C—O), and at 13·50 and 14·38 μ (monosubstituted aromatic). (Found: C, 49·88; H, 2·69; Cl, 13·39; F, 28·80. Calc. for $C_{11}H_7ClF_4O$: C, 49·55; H, 2·65; Cl, 13·30; F, 28·50%.)

Attempted rearrangement of benzyl 1-(2-chlorotetrafluorocyclobutenyl) ether. Ether XVI was heated slowly to reflux (ca. 220°) with no evidence of change. Shortly after reflux started, vigorous reaction

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[26] Ref. 14 reports a similar yield of a compound with b.p. 113° and n_D^{25} 1·3861 from the reaction of allyl alcohol and 1,2-dichlorotetrafluorocyclobutene in the presence of base. Although claimed to be the allyl ether, this product must be the isomeric ketone XI. This reference also reports a b.p. of 116° for methyl 1-(2-chlorotetrafluorocyclobutenyl) ether.

occurred with evolution of acidic gases and formation of a dark tarry product mass. The decomposition is probably acid catalyzed, since an attempt to use the same glass container at lower temp resulted in vigorous decomposition at only 135°.

Irradiation of ether XVI in a quartz tube with a low pressure mercury lamp for 6 hr gave no appreciable change in the IR spectrum. Similarly, attempted radical catalysis with t-butyl hydroperoxide at 70° for 6 hr gave no rearrangement. Attempted catalysis with tetraethylammonium chloride at 70° for 2 hr gave dark condensation products.

2,2-Dichlorotetrafluorocyclobutanone (XVII). A soln of 26·7 g (0·10 mole) of XVI in 50 ml methylene chloride was stirred in a 250-ml round-bottom flask fitted with −80° condenser and gas inlet tube Cl_2 (22·2 g, 0·315 mole, 43·8 ml at −80°) was passed in over a 2-hr period. Rapid decolorization and evolution of HCl occurred until the last 0·1 mole Cl_2 was added. The mixture was allowed to react slowly for an additional 4 hr, after which time the color was nearly gone. Distillation afforded mainly solvent at 40° and a high-boiling residue. This residue was treated cautiously with 55 ml conc H_2SO_4 (evolution of HCl) and heated to drive off volatile liquid. Distillation of this liquid from 10 ml of conc H_2SO_4 gave 11·3 g of crude XVII, b.p. 58–66°. Redistillation from P_2O_5 yielded 6·9 g (33%) of XVII, b.p. 66–68°.[27] Identification was made by comparison of the IR spectrum with that of an authentic sample.

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[27] D. C. England, U.S. Patent 3,129,248 (1964) reports b.p. 67·5° for this ketone.