2-*O*-*p*-tolylsulfonyl-D-threitol, R_f 0.41; and an unidentified component, R_f 0.95.

Basic Hydrolysis of the Presumed 2-*O*-*p*-Tolylsulfonyl-D-threitol.—Chromatography and electrophoresis of 2-*O*-*p*-tolylsulfonyl-D-threitol, performed in the same manner as for 2-*O*-*p*-tolylsulfonyl-L-erythritol, showed that basic hydrolysis of 2-*O*-*p*-tolylsulfonyl-D-threitol gave only erythritol.

1,4-Di-*O*-benzoyl-1,2,4-butanetriol.—A well stirred solution of 15 g. of 1,2,4-butanetriol[16] in 100 ml. of dry pyridine was cooled to −10° in a Dry-Ice bath, and 31.5 ml. of benzoyl chloride in 50 ml. of dry pyridine was added so as to maintain the temperature of the reaction mixture below 15°. When the addition was complete the reaction mixture was left at room temperature for 4 hr. and then concentrated to a sirup. The sirup was dissolved in methylene chloride and this solution washed in the usual fashion. After removal of the solvent, a sirup (45 g.) was obtained which crystallized spontaneously. After four recrystallizations from isopropyl ether the material (42 g.) melted at 70–71°.

Anal. Calcd. for $C_{18}H_{18}O_5$ (314.3): C, 68.78; H, 5.77. Found: C, 68.93; H, 5.82.

1,4-Di-*O*-benzoyl-2-*O*-*p*-tolylsulfonyl-1,2,4-butanetriol.—To a solution of 1,4-di-*O*-benzoylbutanetriol (42 g.) in 100 ml. of dry pyridine was added a solution of 30 g. of *p*-toluenesulfonyl chloride in 100 ml. of dry pyridine. The reaction was worked up after 8 hr. at room temperature to give 55 g. of a sirup which deposited 46.5 g. (73%) of crystals, m.p. 106–109°, from solution in 1.5 l. of ethanol. Three recrystallizations from ethanol raised the m.p. to 118–119.5°.

Anal. Calcd. for $C_{25}H_{24}O_7S$ (468.5): C, 64.09; H, 5.16. Found: C, 64.17; H, 5.26.

Basic Hydrolysis of 1,4-Di-*O*-benzoyl-2-*O*-*p*-tolylsulfonyl-1,2,4-butanetriol.—A solution of 10 g. of 1,4-di-*O*-benzoyl-2-*O*-*p*-tolylsulfonylbutanetriol in 100 ml. of 1 *N* sodium hydroxide was refluxed for 12 hr. concentrated to 50 ml., and passed through columns containing 100 ml. of IR 120 (H^+) and 200 ml. of IR 45(OH^-). The eluent was concentrated to give 2.27 g. (97.5%) of 1,2,4-butanetriol. A sample of this material was converted to the tri-*p*-nitrobenzoate in 84% yield.

1,2-Epoxy-4-butanol.—To an ice-cold solution of 10 g. of 1,4-di-*O*-benzoyl-2-*O*-*p*-tolylsulfonylbutanetriol in 75 ml. of dry chloroform was added 50 ml. of dry methanol and 10 ml. of freshly prepared 3.5 *N* sodium methoxide. After remaining 8 hr. at 10° the reaction mixture was neutralized by the addition of Dry Ice and concentrated to dryness at 25°. The residue was taken up in 100 ml. of chloroform, and the solution was filtered to remove the sodium *p*-toluenesulfonate (4.4 g.). The filtrate was concentrated, and the residue was taken up in 30 ml. of cyclohexane and applied to a Florisil[17] column prepared by packing a 55 × 4 cm. tube with a slurry of 70 g. of Florisil (100/200 mesh) in cyclohexane. Elution with 1 l. of cyclohexane gave 5.4 g. (93%) of methyl benzoate; elution with 500 ml. of benzene gave 0.3 g. of an unidentified compound; elution with 1 l. of ether gave 1.4 g. (74%) of 1,2-epoxy-4-butanol.

Anal. Calcd. for $C_4H_8O_2$ (88.0): C, 54.54; H, 9.09; epoxy (C_2H_4O), 50.00. Found: C, 54.52; H, 8.98; epoxy (C_2H_4O), 50.00.

The Action of Alkali on 1,2-Epoxy-4-butanol.—A solution of 1 g. of 1,2-epoxy-4-butanol in 20 ml. of 1 *N* sodium hydroxide was heated for 30 min. at 60° and passed through a column containing 30 ml. of IR 120(H^+).[12] The eluent was concentrated to give 1.18 g. (98%) of 1,2,4-butanetriol, which was converted to the tri-*p*-nitrobenzoate in 80% yield.

1,2,4-Tri-*O*-*p*-nitrobenzoylbutanetriol.—Prepared in the usual fashion (in 82% yield) from 1,2,4-butanetriol, was crystallized from acetone–ethanol (1:1) and melted at 101–102°.

Anal. Calcd. for $C_{25}H_{19}N_3O_{12}$ (553.4): C, 54.25; H, 3.46. Found: C, 54.10; H, 3.58.

---

[16] General Aniline and Film Corporation, New York 14, N. Y.

[17] Floridin Co., Tallahassee, Fla.

Nucleophilic Displacement Reactions of Halogenated Cyclobutenes[1]

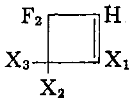
J. D. PARK, L. H. WILSON, AND J. R. LACHER

University of Colorado, Boulder, Colorado

Received April 6, 1962

The nucleophilic displacement reactions of 3,3,4,4-tetrafluorocyclobutene (I), 1-chloro-3,3,4,4-tetrafluorocyclobutene (II), 1,4-dichloro-3,3,4-trifluorocyclobutene (III), and 1,4,4-trichloro-3,3-difluorocyclobutene (IVa) were carried out with ethanolic potassium hydroxide. I yielded 3-ethoxy-3,4,4-trifluorocyclobutene and 3,3-diethoxy-4,4-difluorocyclobutene (allylic substitution without rearrangement). II and III both gave identical rearranged products, 1-fluoro-2-chloro-3-ethoxy-4,4-difluorocyclobutene, and IVa yielded 1-chloro-3,3-difluoro-4,4-diethoxycyclobutene (allylic substitution).

Recent investigations concerning nucleophilic displacement reactions of halogenated cyclobutenes have shown that these cyclobutenes readily undergo reaction with nucleophilic reagents with and without rearrangement. In most studies,[2–6] the cyclobutenes possessed highly activated double bonds or groups attached thereon capable of stabilizing a charge. For this work, a series of halogenated cyclobutenes, namely 3,3,4,4-tetrafluoro-, 1-chloro-3,3,4,4-tetrafluoro-, 1,4-dichloro-3,3,4-trifluoro-, and 1,4,4-trichloro-3,3-difluorocyclobutene (I–IVa, respectively), were selected that contained neither highly activated double bonds nor charge stabilizing groups in a vinylic position.



I. $X_1 = H, X_2 = X_3 = F$
II. $X_1 = Cl, X_2 = X_3 = F$
III. $X_1 = X_2 = Cl, X_3 = F$
IVa. $X_1 = X_2 = X_3 = Cl$

These compounds were found to undergo interesting nucleophilic displacement reactions which include allylic rearrangement. The present paper describes this work, and specifically, the displacement reactions of I–IVa with ethanolic potassium hydroxide.

Discussion

The reactivity of the allylic halogens in the cyclobutenes I through IVa is demonstrated in their respective reactions with potassium hydroxide in ethanol. An exothermic reaction took place between I and one equivalent of the basic reagent with the immediate precipitation of potassium fluoride. The organic product isolated was a colorless liquid to which is assigned the structure 3-ethoxy-3,4,4-trifluorocyclobutene (V), resulting from direct displacement of

---

[1] This paper represents part of a thesis submitted by L. H. Wilson to the Graduate School, University of Colorado, in partial fulfillment of the requirements for the Ph.D. degree, June, 1961.

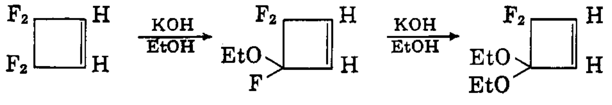
[2] J. D. Park, C. Snow, and J. R. Lacher, *J. Am. Chem. Soc.*, **73**, 2342 (1951).

[3] F. J. Lorenzi, Ph.D. thesis, University of Colorado, 1948.

[4] S. Cohen, Ph.D. thesis, University of Colorado, 1959.

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

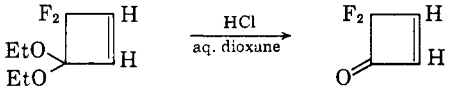
[6] E. F. Jenny and J. Drury, *ibid.*, **82**, 3111 (1960).



I V VI

allylic fluorine. This structure is indicated from the infrared spectrum of V, which shows a carbon–carbon double bond absorption maximum at 5.99 μ, as compared to the starting cyclobutene at 5.91 μ. The alternative product resulting from vinylic attack with subsequent rearrangement would have the —CF═CH— moiety, which has been shown by Burdon and Whiffen[7] to absorb at 5.86 μ. The proposed structure was conclusively demonstrated by oxidation of the monoether (V) to ethoxytrifluorosuccinic acid. The reason for the lack of attack at a vinylic position and possible rearrangement may perhaps be attributed to the unreactive carbon–carbon double bond. Tatlow and co-workers[8] have demonstrated the relative unreactivity of this —CH═CH— moiety with nucleophilic reaction.

Treatment of the monoether V with a second equivalent of ethoxide resulted in the elimination of fluoride ion and a nearly quantitative yield of 3,3-diethoxy-4,4-difluorocyclobutene (VI). Here, as in the preparation of V, the rearranged product resulting from an S_N2' reaction path was ruled out by spectral data and oxidation to a specific succinic acid. The infrared spectrogram of VI showed no shift of the double bond stretching frequency to higher energy wave lengths as might be expected if rearrangement had occurred to give a —C(OEt)═CH— or —CF═CH— moiety. To determine conclusively that displacement of fluoride by ethoxide ion had occurred at the same carbon atom as in the first step, hydrolysis to the ketone, 2,2-difluorocyclobutenone (VII) was accomplished. That the ketal VI was obtained from the monoether (V) by the action of ethoxide ion was not surprising. Alpha-halo ethers have been shown by several workers[9–11] to be highly reactive to nucleophilic reagents.

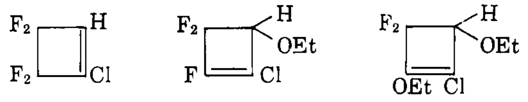


VI VII

The *gem*-diethoxycyclobutene (VI) showed no change when reacted further with ethoxide ion.

The reaction of 1-chloro-3,3,4,4-tetrafluorocyclobutene (II) with ethanolic potassium hydroxide could be arrested at the point of displacement of only one fluorine by the controlled addition of exactly one equivalent of ethoxide to the cyclobutene in ethanol. Roberts[5] has shown that in analogous systems where phenyl, rather than chlorine, is the vinyl substituent, exclusive rearrangement is found. The rearrangement found in this case may be considered as evidence for similar double bond activation, or carbanion stabilization, by chlorine. Comparison of compound II with 4,4-dichloro-3,3-difluoro-1-phenylcyclobutene, which Roberts showed proceeded by rearrangement upon reaction with ethoxide ion, indicated that II might undergo rearrangement in the course of reaction.

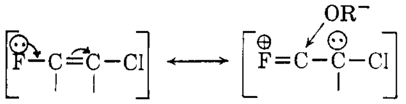
Upon reaction of II with ethoxide ion, fluorine was displaced to yield a colorless oil which was assigned the structure 1-chloro-4-ethoxy-2,3,3-trifluorocyclobutene (major product) along with a small amount of an, as yet, unidentified monoether different from VIII. Preliminary investigations indicated that the reaction had proceeded by a rearrangement reaction path. The monoether VIII showed a carbon-carbon double bond absorption peak at 5.85 μ as compared to II at 6.30 μ. If rearrangement had not taken place, the shift in the double bond absorption frequency would have been small, since only substituents directly attached to vinylic carbons affect the frequency to any great extent.[12] Park and co-workers[2] have shown that the —CF═CCl— grouping absorbs in the region 5.85 μ. Further, permanganate oxidation of the cyclobutene ether VIII yielded 3-ethoxy-2,2-difluorobutanedioic acid, showing conclusively that (a) rearrangement had taken place, and (b) the direction of the rearrangement.



II VIII IX

When VIII was subjected to the action of an equivalent of ethoxide, fluoride ion was eliminated. A diethyl ether (IX) was formed, the infrared spectrum of which had an intense band at 5.96 μ indicative of the presence of the —CCl═C(OEt)— moiety.[3,4] It is apparent that the formation of this diether (IX) must involve displacement of vinylic fluorine. This is not too remarkable as several instances of vinylic fluorine substitutions are known.[13] Further, the vinylic carbon containing the fluorine atom is the logical site for attack by a nucleophilic reagent. It has been demonstrated[3] that a double bond containing a fluorine and a chlorine atom shows preferential attack at the carbon atom having fluorine attached.

This preferential replacement of the vinylic fluorine over that of the allylic fluorines may be said to be due to the activation of the double bond by the mesomeric assistance of the vinylic fluorine, thus making it more susceptible to nucleophilic attack.



Confirmation of the assigned structure was accomplished by oxidation of IX to 3-ethoxy-2,2-difluorobutanedioic acid.

The diether IX gave no further reaction when treated with additional alcoholic potassium hydroxide.

---

(7) J. Burdon and D. N. Whiffen, *Spectrochim. Acta*, **12**, 139 (1958).

(8) E. Nield, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 3800 (1960).

(9) J. Young and P. Tarrant, *J. Am. Chem. Soc.*, **72**, 1860(1950).

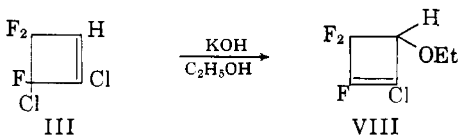
(10) C. T. Mason, C. W. R. Wade, and H. W. Pouncy, Jr., *ibid.*, **76**, 2255 (1954).

(11) P. Ballinger, P. B. D. de la Mare, G. Kohnstann, and B. M. Prestt, *J. Chem. Soc.*, 3641, (1955).

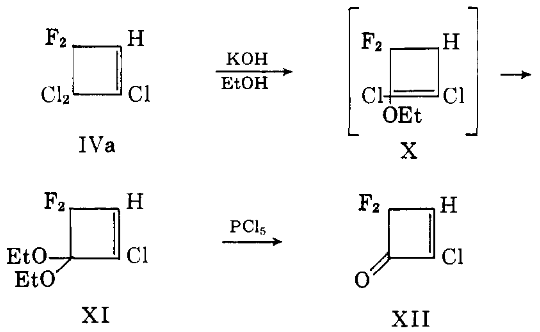
(12) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N.Y., 1956.

(13) (a) J. D. Park, M. L. Sharrah, and J. R. Lacher, *J. Am. Chem. Soc.*, **71**, 2337 (1949); (b) E. F. Silversmith and J. D. Roberts, *ibid.*, **80**, 4083 (1958); (c) A. T. Blomquist and E. A. LaLancette, 135th National Meeting of American Chemical Society, Boston, Mass., April, 1959, p. 54–O.

In order to study the effect $-CX_2-CF_2-$ moiety on the double bond of cyclobutenes in nucleophilic displacement reactions, the preparation of 1,4-dichloro-3,3,4-trifluorocyclobutene (III)[14] was accomplished. On reaction of III with one equivalent of ethoxide, an organic product (VIII) was isolated that was identical with that formed from II and ethoxide. Chloride ion was eliminated exclusively, giving a nearly quantitative yield of VIII. The only significant difference between the reaction of II and III with ethoxide ion was the exclusion of side reactions.



When 1,4,4-trichloro-3,3-difluorocyclobutene IVa[15] was treated with an excess of basic reagent, a diethyl ether (XI) was isolated from the reaction mixture.



The ketal structure XI was assigned on the basis of its infrared spectrum, hydrolysis, and oxidation products. The infrared spectrum of XI showed only a small shift in the double bond absorption frequency and a ketal structure was strongly hinted by a broad band in the region 9–10 μ due to $-\underset{|}{C}(-OEt)_2$. The absence of rearrangement when IVa reacted with ethanolic potassium hydroxide was shown by oxidation of XI to a diethoxydifluorosuccinic acid and the ready hydrolysis of XI to the ketone, 1-chloro-3,3-difluorocyclobuten-2-one (XII). The absence of rearrangement in this system is surprising. The similarity between this system (IVa) and 4,4-dichloro-3,3-difluoro-1-phenylcyclobutene reported by Roberts[5] was even more striking than II, since both are α-dichlorides and differing only in the effect a chloro- *vs.* phenyl-group has on the double bond. Rearrangement was expected in this system since the susceptibility of α-dihalides to displacement with rearrangement (S_N2') had been demonstrated,[16] and rearrangement had been observed in the cases of II and III.

By careful addition of exactly one equivalent of ethoxide to IVa, the α-chloro ether intermediate X was isolated. The formation then of the *gem*-diether (XI) is perfectly in keeping with the expected mode of reaction of α-halo ethers with nucleophilic reagents. Roberts and co-workers[5] were unable to isolate the α-chloro ether intermediate in the reaction of 2,4-dichloro-3,3-difluoro-1-phenylcyclobutene with ethoxide ion. Thus, the highly reactive α-chloro ether X, once it formed, would not likely proceed by an S_N2' reaction path, but rather would undergo direct displacement to give the ketal.

Experimental

Preparation of Cyclobutanes.—Thermal cyclo-dimerization reactions of the appropriate halogenated ethylenes were run in a 500-ml. stainless steel autoclave following the general procedure outlined by Coffman, *et al.*[17]

3,3,4,4-Tetrafluorocyclobutene (I).—Exactly 340 g. (2.1 moles) of 3-chloro-1,1,2,2-tetrafluorocyclobutene was added dropwise to a slurry of 235 g. (4.2 moles) of powdered potassium hydroxide suspended in 300 ml. of heavy mineral oil under constant agitation. The reaction mixture was slowly heated to 70° and maintained at this temperature throughout the course of the addition. After the addition was complete, the reaction mixture was stirred for 3 hr. at 80°. The crude products were then removed from the reaction mixture under reduced pressure and distilled. This yielded 100.2 g. (40.7%) of 3,3,4,4-tetrafluorocyclobutene,[18] b.p. 50.0–50.5°/629 mm.; $n^{20}D$ 1.3114; d_4^{20} 1.358.

3-Ethoxy-3,4,4-trifluorocyclobutene (V).—A solution of 14.6 g. (0.26 mole) of potassium hydroxide in 25 ml. of 95% ethanol was added slowly to a vigorously agitated solution of 40 g. (0.26 mole) of 3,3,4,4-tetrafluorocyclobutene (I) in 100 ml. of 95% ethanol. An exothermic reaction took place and a white precipitate of potassium fluoride formed immediately on the addition of the first portion of ethanolic potassium hydroxide solution. The temperature reached 70° and it was necessary to cool the reaction in an ice bath. The reaction mixture was poured into cold water. The crude product was washed several times with cold water until neutral to litmus and dried over anhydrous magnesium sulfate. Distillation yielded 29.3 g. (74.5%) of V, b.p. 95.8–96.0° /630 mm.; $n^{25}D$ 1.3608; $d^{25}{}_{25}$ 1.1628.

Anal. Calcd. for $C_6H_7F_3O$: C, 47.30; H, 4.62; F, 37.41. Found: C, 46.99; H, 4.80; F, 37.22.

Ozonolysis of 3-Ethoxy-3,4,4-trifluorocyclobutene.—A mixture of ozone and oxygen from a type MLP Montgomery Brothers ozone generator was slowly passed through a fritted glass bubbler into a solution of 5.0 g. (0.03 mole) of 3-ethoxy-3,4,4-trifluorocyclobutene in 50 ml. of methylene dichloride at 0°. Ozone uptake was quantitative for the first 8 hr. of treatment. A light blue solution resulted. The solution was swept free of excess ozone by bubbling nitrogen through the cold solution. The colorless solution resulting was allowed to warm up to room temperature.

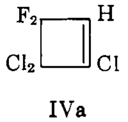
The ozonide solution in methylene dichloride was then added dropwise to a stirred solution of 7.5 g. (1.06 moles, assuming minimum 29% hydrogen peroxide assay) of commercial 30% hydrogen peroxide, 0.30 ml. of conc. sulfuric acid, and 15 ml. of water. On the scale this reaction was carried out, the reaction was not exothermic enough to warrant cooling, but caution should be observed on a larger scale reaction. After the addition of the ozonide solution was complete, the methylene dichloride was removed by reduced pressure. The reaction mixture was stirred overnight at 50°.

The reaction mixture was homogeneous after the above treatment. It was then continuously extracted with ether for 48 hr. The ether solution was then washed three times with 0.1 *N* potassium hydroxide. This salt solution was neutralized to pH 7 and the water removed. The white potassium salt was recrystallized

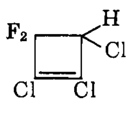
---

(14) M. S. Raasch, R. E. Miegel, and J. E. Castle, *J. Am. Chem. Soc.*, **81**, 2678 (1959).

(15) The n.m.r. spectrum of the pure liquid product confirms that it has structure IVa and not the rearranged structure IVb. The spectrum consists of a symmetrical triplet at 3.87 τ with a J_{HF} of 1.9 c.p.s. The low-field position of the resonance is inconsistent with that due to a proton attached to a saturated carbon atom[5,6] and thus rules out structure IVb. Further, if this product were IVb, two different HF splitting constants would be observed (M. W. Hanna and J. D. Park, to be published) and the spectrum would be an equal intensity quartet.



IVa



IVb

(16) R. H. DeWolfe and W. G. Young, *Chem. Rev.*, **56**, 753 (1956).

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

(18) H. V. Holler, Ph.D. thesis, University of Colorado, 1957.

from 75% ethyl alcohol to yield 6.1 g. of the potassium salt of 2-ethoxy-2,3,3-trifluorobutanedioic acid.

Anal. Calcd. for $C_6H_5F_3O_5K_2$: C, 24.65; H, 1.72; F, 19.52; K, 26.71. Found: C, 24.49; H, 1.57; F, 19.83; K, 26.98.

3,3-Diethoxy-4,4-difluorocyclobutene (VI).—A solution of 5.6 g. (0.1 mole) of potassium hydroxide in 40 ml. of 95% ethanol was added slowly to a stirred solution of 15.2 g. (0.1 mole) of V in 50 ml. of 95% ethanol. After completion of the reaction, the product was retrieved as described above for V. Distillation yielded 14.7 g. (82.5% conversion) of VIa, b.p. 73–75°/1 mm. (micro-boiling point 165°/624 mm.); n^{25}_{D} 1.4070; d^{25}_{25} 1.0898.

Anal. Calcd. for $C_8H_{12}F_2O_2$: C, 53.80; H, 6.79; F, 21.33. Found: C, 53.71; H, 6.63; F, 21.15.

Ozonolysis of 3,3-Diethoxy-4,4-difluorocyclobutene.—A mixture of ozone and oxygen was slowly passed through a fritted glass bubbler into a solution of 17.8 g. (0.1 mole) of 3,3-diethoxy-4,4-difluorocyclobutene in 100 ml. of methylene dichloride at 0°. After ozone uptake ceased to be quantitative, the ozonide solution was worked up in the usual manner. The resulting succinic acid was isolated as the potassium salt of 2,2-diethoxy-3,3-difluorobutanedioic acid; m.p. 260° accompanied by decomposition.

Anal. Calcd. for $C_8H_{12}F_2O_6K_2$: C, 30.30; H, 3.17; F, 11.93; K, 25.01. Found: C, 30.05; H, 3.05; F, 12.11; K, 25.19.

2,2-Difluorocyclobutenone (VII).—A mixture of 35.5 g. (0.2 mole) of VI, 80 ml. of water, 300 ml. of dioxane, and 15 ml. of concentrated hydrochloric acid were gently refluxed for 6 hr. in a 1-l. two-neck flask fitted with stirrer and reflux condenser. The reaction mixture was poured into cold water and the crude product separated, dried, and distilled. Distillation yielded 16.7 g. (80%) of VII, b.p. 62°/0.20 mm.; n^{25}_{D} 1.4531; d^{25}_{25} 1.3942.

Anal. Calcd. for $C_4H_2F_2O$: C, 46.18; H, 1.92; F, 36.62. Found: C, 45.96; H, 1.95; F, 36.57.

1-Chloro-3,3,4,4-tetrafluorocyclobutene (II).—To a slurry of 156 g. (2.8 moles) of potassium hydroxide in 300 ml. of heavy mineral oil, 226 g. (1.15 moles) of 3,3-dichloro-1,1,2,2-tetrafluorocyclobutene (prepared according to the method of Coffman, *et al.*[17]) was added in a dropwise manner. Throughout the addition the reaction mixture was heated on a steam bath. After the addition was complete, the reaction mixture was stirred for 4 hr. The product was obtained in a manner described above for I. Distillation gave 135.1 g. (73%) of II; b.p. 53.8–54°/625 mm.; n^{25}_{D} 1.3452; d^{25}_{25} 1.4547.

Anal. Calcd. for C_4HClF_4: C, 29.91; H, 0.62; F, 47.35; Cl, 21.90. Found: C, 29.98; H, 0.65; F, 47.17; Cl, 21.90.

1-Chloro-2,3,3-trifluoro-4-ethoxycyclobutene (VIII).—A solution of 28 g. (0.5 mole) of potassium hydroxide in 75 ml. of 95% ethanol was added dropwise to a stirred solution of 80 g. (0.5 mole) of II in 100 ml. of ethanol cooled in an ice bath. After all the base had been added, the reaction was stirred for 3 hr. The reaction mixture was worked up in a manner described above for V. Distillation yielded 72 g. (77%) of VIII, b.p. 108.5°/626 mm.; n^{25}_{D} 1.3838; d^{25}_{25} 1.2735, and less than 5% of an, as yet, unidentified monoether different from VIII.

Anal. Calcd. for $C_6H_6ClF_3O$: C, 38.60; H, 3.21; F, 30.56; Cl, 19.03. Found: C, 38.47; H, 3.11; F, 30.50; Cl, 18.85.

Permanganate Oxidation of 1-Chloro-4-ethoxy-2,3,3-trifluorocyclobutene.—To a stirred solution of 27 g. (0.17 mole) of potassium permanganate and 19.6 g. (0.35 mole) of potassium hydroxide in 300 ml. of water, 31.6 g. (0.17 mole) of the monoether was added. The reaction mixture was refluxed until the organic layer disappeared, then cooled, and a theoretical amount of dilute sulfuric acid needed for neutralization was added. The brown manganese dioxide was reduced to the divalent state by sulfur dioxide. The free acid was then isolated by constant ether extraction, yielding a viscous oil which failed to crystallize after 2 weeks. The potassium salt was prepared, which was recrystallized from 50% ethanol to yield 21 g. of the potassium salt of 3-ethoxy-2,2-difluorobutanedioic acid; m.p. 275° with decomposition.

Anal. Calcd. for $C_6H_6F_2O_5K_2$: C, 26.28; H, 2.27; F, 13.88; K, 28.45. Found: C, 26.04; H, 2.13; F, 14.07; K, 28.71.

1-Chloro-2,4-diethoxy-3,3-difluorocyclobutene (IX).—To a stirred solution of 38 g. (0.20 mole) of VIII in 50 ml. of 95% ethanol, was added slowly 12 g. (0.20 mole) of potassium hydroxide in 75 ml. of 95% ethanol. The reaction mixture was cooled in an ice bath throughout the addition. The product was obtained from the reaction mixture in a manner described above for V. Upon distillation, 34.9 g. (82% conversion) of IX was obtained, b.p. 178°/629 mm.; n^{25}_{D} 1.4234; d^{25}_{25} 1.1923.

Anal. Calcd. for $C_8H_{11}ClF_2O_2$: C, 45.19; H, 5.21; Cl, 16.68; F, 17.87. Found: C, 45.24; H, 5.43; Cl, 16.86; F, 17.70.

1,1,2,2-Tetrachloro-3,3-difluorocyclobutane.—A 0.5 l. stainless steel Parr bomb was charged with 260 g. (2.61 moles) of vinylidene chloride, 266 g. (2.0 moles) of 1,1-dichloro-2,2-difluoroethylene, and 0.5 g. of hydroquinone inhibitor. The bomb was shaken and heated at 175° for 12 hr. After cooling to room temperature, the volatile products were bled from the bomb. The products boiling above room temperature were distilled to yield 300 g. (64%) of 1,1,2,2-tetrachloro-3,3-difluorocyclobutane; m.p. 41°; b.p. 143° at 626 mm.

Anal. Calcd. for $C_4H_2Cl_4F_2$: C, 20.86; H, 0.87; Cl, 61.75; F, 16.51. Found: C, 20.94; H, 1.03; Cl, 61.50; F, 16.43.

1,4,4-Trichloro-3,3-difluorocyclobutene.—A solution of 126 g. (0.55 mole) of 1,1,2,2-tetrachloro-3,3-difluorocyclobutane in 400 ml. of diethyl ether was added dropwise to a stirred solution of 110 g. (1.1 moles) of triethylamine in 100 ml. ether in a 1-l., three-neck flask fitted with a reflux condenser. After the addition was complete, the reaction was stirred for 6 hr. at room temperature and 15 ml. of concentrated hydrochloric acid in 200 ml. of water was added to remove excess triethylamine. The ether layer was separated, dried, and distilled to yield 87 g. (82%) of IVa, b.p. 118°/631 mm.; n^{25}_{D} 1.4344; d^{25}_{25} 1.5820.

Anal. Calcd. for $C_4HCl_3F_2$: C, 24.84; H, 0.52; Cl, 54.99; F, 19.64. Found: C, 24.68; H, 0.46; Cl, 54.95; F, 19.36.

1,4-Dichloro-4-ethoxy-3,3-difluorocyclobutene (X).—A solution of 19.25 g. (0.344 mole) of potassium hydroxide in 60 ml. of 95% ethanol was added slowly to a stirred solution of 67.0 g. (0.344 mole) of IVa in 150 ml. of 95% ethanol and maintained at 0°. The product was retrieved in the manner described above for the preparation of V. Distillation gave 61.5 g. (87% conversion) of X, b.p. 141°/628 mm.; n^{25}_{D} 1.4265; d^{25}_{25} 1.3122.

Anal. Calcd. for $C_6H_6Cl_2F_2O$: C, 35.50; H, 2.98; Cl, 34.93; F, 18.72. Found: C, 35.77; H, 3.16; Cl, 35.20; F, 18.49.

1-Chloro-4,4-diethoxy-3,3-difluorocyclobutene (XI).—A solution of 10.2 g. (0.175 mole) of potassium hydroxide in 50 ml. of 95% ethanol was added dropwise to a solution of 32.8 g. (0.175 mole) of X in 50 ml. ethanol kept at 0°. The product was obtained by the procedure described above for V. Distillation gave 35.0 g. (94% conversion) of XI, b.p. 82–85°/1 mm. (microboiling point 192.5° with decomposition); n^{25}_{D} 1.4267; d^{25}_{25} 1.2051.

Anal. Calcd. for $C_8H_{11}ClF_2O_2$: C, 45.19; H, 5.21; Cl, 16.68; F, 17.87. Found: C, 45.35; H, 5.07; Cl, 16.69; F, 17.79.

Permanganate Oxidation of 1-Chloro-4,4-diethoxy-3,3-difluorocyclobutene.—Into a 1-l. three-neck flask fitted with stirrer, reflux condenser, and a dropping funnel were placed 22.2 g. (0.14 mole) of potassium permanganate, 15.7 g. (0.28 mole) of potassium hydroxide, and 500 ml. of water. The permanganate was warmed to 80° and 30 g. (0.14 mole) of 1-chloro-4,4-diethoxy-3,3-difluorocyclobutene added dropwise. After the addition was complete, the mixture was refluxed for 20 hr. The mixture was then cooled and the brown manganese dioxide removed by bubbling in sulfur dioxide. The succinic acid was isolated by continuous ether extraction. The viscous oil was converted to the potassium salt and purified by recrystallization from 50% ethanol to give 14.2 g. of a white powder; m.p. 260–265° accompanied by decomposition.

Anal. Calcd. for $C_8H_{12}F_1O_6K_2$: C, 30.20; H, 3.17; F, 11.93; K, 25.01. Found: C, 29.96; H, 2.87; F, 12.05; K, 25.36.

1-Chloro-3,3-difluorocyclobuten-2-one (XII).—In a 250-ml flask were placed 26.22 g. (0.123 mole) of XI and 25.60 g. (0.123 mole) of phosphorus pentachloride. The flask was fitted with a thermometer and a water-cooled condenser to which a cold trap in Dry Ice was connected. After a few minutes, an exothermic reaction took place with much frothing. At the end of the initial exothermic reaction, the mixture was heated to 50° for 3 hr. in an oil bath. Ethyl chloride was collected in the cold trap.

The contents of the flask were poured into ice to hydrolyze the phosphorus oxychloride. The organic layer was washed with cold water, dried, and distilled to give 10.2 g. of XII; b.p. 68°/0.15 mm. (microboiling point 208°/631 mm.); n^{25}_{D} 1.4846; d^{25}_{25} 1.3572.

Anal. Calcd. for C_4HClF_2O: C, 34.65; H, 0.72; Cl, 24.64; F, 27.44. Found: C, 34.60; H, 0.92; Cl, 24.75; F, 27.31.

1-Chloro-4-ethoxy-3,3,4-trifluorocyclobutene.—1,1,2-Trichloro-2,3,3-trifluorocyclobutane and 1,4-dichloro-3,3,4-trifluorocyclobutene were prepared according to the method of Raasch, *et al.*[14]

A solution of 26 g. (0.46 mole) of potassium hydroxide in 100 ml. of ethanol was added dropwise to 80 g. (0.45 mole) of 1,4-dichloro-3,3,4-trifluorocyclobutene in 100 ml. of ethanol in a 500-ml. three-neck flask fitted with a reflux condenser, stirrer, and dropping funnel. During the addition, the reaction flask was cooled to 0° in an ice bath. A white precipitate of potassium chloride formed throughout the course of the addition. After the addition was complete, the reaction was stirred for 3 hr. The ethanol solution was washed several times with cold water. The crude product was dried over anhydrous magnesium sulfate and distilled to yield 78.5 g. (92% conversion) of 1-chloro-4-ethoxy-3,3,4-trifluorocyclobutene; b.p. 108.5°/628 mm.; $n^{25}D$ 1.3838.

Acknowledgment.—The authors wish to express their appreciation to the Minnesota Mining and Manufacturing Company, St. Paul, Minn., and the U. S. Army Quartermaster Research and Engineering Command, Natick, Mass., under scientific project officer, Dr. Juan Montermoso, for their partial support of this work.

Condensed Cyclobutane Aromatic Compounds. XXIV. The Mechanism of Thermal Rearrangement of the Linear Benzocyclobutadiene Dimer: Synthesis of 9,10-Benzocyclobutenoanthracene[1]

M. P. Cava[2] and R. Pohlke

Department of Chemistry, The Ohio State University, Columbus 10, Ohio

Received October 31, 1962

The thermal isomerization of the linear benzocyclobutadiene dimer to 1,2,5,6-dibenzocycloöctatetraene proceeds *via* a two-stage process. The initial *o*-quinodimethane type intermediate has been intercepted in the form of adducts with several dienophiles. The *p*-benzoquinone adduct has been transformed into a hydrocarbon which is identical with the direct adduct of anthracene with benzocyclobutadiene.

It has been reported that the linear benzocyclobutadiene dimer (I)[3] undergoes rearrangement to 1,2,5,6-dibenzocycloöctatetraene (II) on heating for several hours at 150–155°, or even during the slow determination of its melting point (133°).[4,5]

The path originally envisaged[4,5] for this reaction involved the concerted cleavage of the two central benzocyclobutenoid bonds of I to give isomer II directly. An alternative two-step mechanism would consist of cleavage of one of the benzocyclobutene systems of I to give an unstable *o*-quinoid intermediate (III), followed by rearrangement of III to the octatetraene II. Confirmation of this latter mechanism now has been obtained by the trapping of the transient intermediate III by various dienophiles.[6] The trapping of *o*-quinoid intermediates in this manner has ample analogy in a number of other recent investigations.[7]

Three Diels–Alder adducts (IV, V, and VI) were prepared by heating dibenzotricycloöctadiene (I) with solutions of maleic anhydride, N-phenylmaleimide, and *p*-benzoquinone, respectively. It was found that the additions occurred slowly even at temperatures as low as 80–110°. In the reaction with benzoquinone, which was studied the most carefully, it was found that in boiling toluene (110°) and in the presence of about four equivalents of benzoquinone, adduct VI was obtained in 47% yield along with a 37% yield of dibenzocycloöctatetraene (II). Clearly, it appears that the intramolecular rearrangement of III to II occurs so readily that this process competes favorably with the bimolecular reaction of III with the quinone.[8] The Diels–Alder products of III have been assigned tentatively the configurations resulting from maximum overlap of the intermediates in the transition state (Alder rule), as shown in Chart I.

Although the thermal decomposition of benzocyclobutene[9] and the naphthocyclobutenes[10] to *o*-quinoid hydrocarbons, as evidenced by adduct formation, has been observed at high temperatures (200° and above) benzocyclobutene itself is known to be quite stable at 150°.[11] On the other hand, 1,2-diphenylbenzocyclobutene reacts slowly with maleic anhydride even at room temperature[12]; the ease of ring cleavage in this unusual case may most likely be attributed to resonance stabilization of the open quinomethane form by the phenyl groups. Indeed, the recently reported hydrocarbon VII has been isolated as the stable quinoid structure[7c] rather than as a closed benzocyclobutene derivative (VIIa), undoubtedly because *the fusion of an additional small ring to the four-membered ring of benzocyclobutene destabilizes the benzocyclobutenoid form relative to the corresponding open o-quinoid form.* The ready thermolysis of dibenzotricycloöctadiene may be viewed as another example of this principle, since

---

[1] Presented before the Division of Organic Chemistry at the 141st National Meeting of the American Chemical Society, Washington, D. C., March 26, 1962.

[2] Alfred P. Sloan Fellow, 1958–1962.

[3] 3,4,7,8-Dibenzotricyclo[4.2.0.^{2,5}]octadiene-3,7.

[4] M. Avram, D. Dinu, and C. D. Nenitzescu, *Chem. Ind.* (London), 257 (1959).

[5] M. Avram, D. Dinu, G. Mateescu, and C. D. Nenitzescu, *Chem. Ber.*, **93**, 1789 (1960).

[6] Similar results and conclusions have been reached concerning this reaction in another independent study: M. Avram, I. G. Dinulescu, D. Dinu, G. Mateescu, and C. D. Nenitzescu, *Tetrahedron*, in press. We thank Professor Nenitzescu for his friendly communication of these results to us prior to publication.

[7] For example, see: (a) M. P. Cava, A. A. Deana, and K. Muth, *J. Am. Chem. Soc.*, **81**, 6458 (1959); (b) I. G. Dinulescu, M. Avram, and C. D. Nenitzescu, *Chem. Ber.*, **93**, 1795 (1960); (c) K. Alder and M. Fremery, *Tetrahedron*, **14**, 190 (1961).

[8] (a) A related set of competing reactions involving diphenyl-*o*-quinodimethane and 1,4-naphthoquinone has been recorded: M. P. Cava, M. J. Mitchell, and A. A. Deana, *J. Org. Chem.*, **25**, 1481 (1960). (b) The possibility that the octatetraene II is in equilibrium with the closed quinoid form III was discounted by refluxing II overnight in benzene with N-phenylmaleimide, when II was recovered quantitatively. Under these conditions (see Experimental), I gives an adduct.

[9] F. R. Jensen, W. E. Coleman, and A. J. Berlin, *Tetrahedron Letters*, **15** (1962).

[10] M. P. Cava, R. L. Shirley, and B. W. Erickson, *J. Org. Chem.*, **27**, 755 (1962).

[11] M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **80**, 2255 (1958).

[12] F. R. Jensen and W. E. Coleman, *ibid.*, **80**, 6149 (1958).