Bicyclobutyl Derivatives. I. Synthesis of Conjugated Diolefins and Diolefin Diketones

J. D. Park and William C. Frank[1]

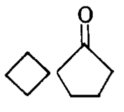
Department of Chemistry, University of Colorado, Boulder, Colorado

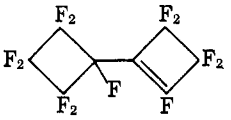
Received December 13, 1963

2,2'-Dichloro-2,2',3,3,3'3'-hexafluorobicyclobutyl- and 1-(2',3',3'-trifluoro-1-cyclobutenyl)-2,3,3-trifluoro-2-chlorocyclobutane were synthesized by cycloaddition reactions and their elimination and replacement reactions were studied. 2,2'3,3',3'-Hexafluorobicyclobutenyl, 2,2'-dialkoxy-3,3,3',3'-tetrafluorobicyclobutenyl, and 2,2'-dialkoxy-3,3'-diketobicyclobutenyl were also synthesized. Several substituted 1-vinyl-1-cyclobutenes were prepared as intermediates in the preparation of the "dibox"[2] compounds.

Work done in the past on the synthesis and reactions of bicyclobutyl derivatives has been meager and quite limited.

Vogel[3] obtained a pinacol of cyclobutanone. This rearranged in acid to a spirooctanone (I). Miller[4] treated perfluorocyclobutene with fluorine at −78° to synthesize a cyclobutylcyclobutene (II). 2,2,2',2',3,3,-3',3'-Octafluorobicyclobutyl (III) was prepared by Du Pont workers[5] in low yield (10–15%) by successive cycloadditions of tetrafluoroethylene with butadiene. 1-(2',2',3',3'-Tetrafluorocyclobutyl)-2,2,3,3-tetrafluorocyclobutene (IV) was prepared also by the above workers[5] by the cycloaddition of vinylacetylene with tetrafluoroethylene.


I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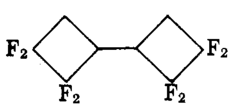
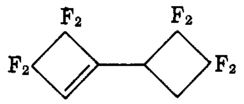
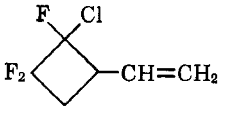

III

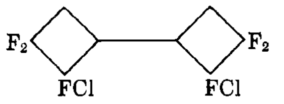

IV

The relative inaccessibility of these "dibox" compounds and their intermediates has probably prevented active interest in their chemistry. This paper reports the results of a study leading to routes to several reactive "dibox" compounds.

Discussion

The thermal cycloaddition of butadiene with trifluorochloroethylene has been reported and 1:1 adduct characterized.[6] In repeating this work it was found that, in addition to the 1:1 cycloadduct V, a considerable amount (5–10%) of a 1:2 (diene-CF_2=CFCl) adduct VI was also formed. By using 2 moles of trifluorochloroethylene per mole of butadiene, the proportion of 1:2 adduct (VI) was increased, but only to 15–20%, the main products being the 1:1 adduct (V) and the cyclic dimer of trifluorochloroethylene.


V

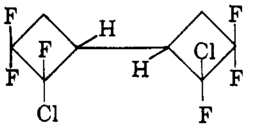

VI

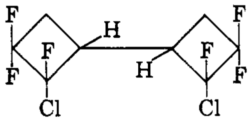
Addition of a second mole of trifluorochloroethylene to the pure 1:1 adduct V proceeded with low conversion (10–15%) to VI and offered no advantage over direct combination of trifluorochloroethylene to butadiene.

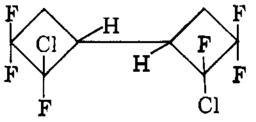
VI was especially difficult to purify. Vapor phase chromatography on a strongly polar absorbent showed the presence of three stereoisomers.

The structure predicted on the basis of the most stable diradical intermediate is the symmetrical head-to-head adduct.

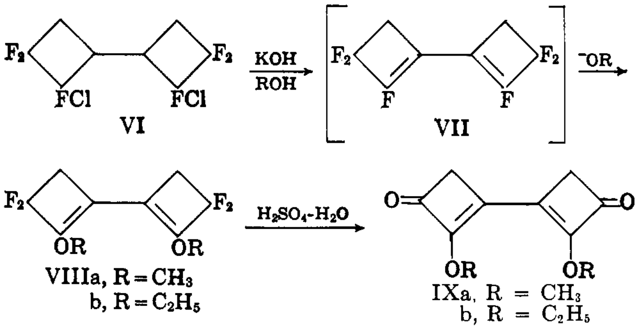
Compound VI would have two *dl* pairs and one *meso* form in agreement with the three v.p.c. peaks found.


dl pair
cis–cis
(F with resp. to H)


meso pair
cis–trans


dl pair
trans–trans

The formal structure proof for this compound (VI) is based on microanalyses, infrared, ultraviolet, and n.m.r. spectra of the derivatives prepared as follows.


VI
VII
VIIIa, R = CH_3
b, R = C_2H_5
IXa, R = CH_3
b, R = C_2H_5

Refluxing VI with potassium hydroxide in methanol resulted in the elimination of 2 moles of hydrochloric acid followed rapidly by the replacement of both vinylic

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(1) This paper represents part of a Ph.D. thesis submitted to the Graduate School, University of Colorado.

(2) "Dibox" is a trivial name used to designate bicyclobutyl and its derivatives.

(3) E. Vogel, *Chem. Ber.*, **85**, 25 (1952).

(4) W. T. Miller, U. S. Patent 2,716,141 (1951); *Chem. Abstr.*, **50**, P7852a (1950).

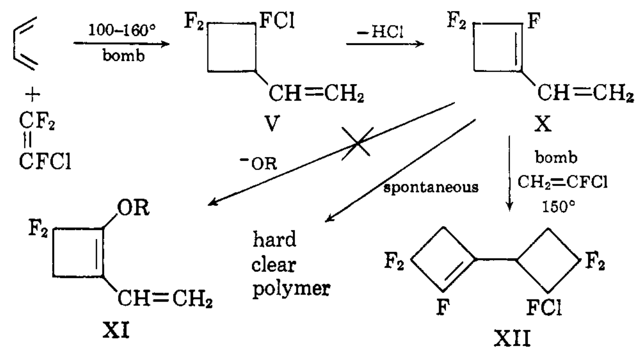
(5) D. D. Coffman, P. L. Barrick, R. D. Cramer, and M. S. Raasch, *J. Am. Chem. Soc.*, **71**, 490 (1949).

(6) J. D. Park, H. V. Holler, and J. R. Lacher, *J. Org. Chem.*, **25**, 990 (1960).

fluorines to give a conjugated diene diether (VIIIa where R = CH_3). Potassium hydroxide in ethanol gave similarly VIIIb (R = C_2H_5). Numerous unsuccessful attempts were made to perform the elimination reaction to yield VII without the accompanying replacement reaction. Two moles of potassium hydroxide in methanol were treated with VI slightly below room temperature in hopes of eliminating hydrochloric acid twice. Instead of obtaining VII, *ca.* 0.5 mole each of diether VIIIa and the starting material (VI) was recovered. The relative proportions of the stereoisomers of VI in the latter were compared with that of the fresh starting material VI and found to be virtually identical. Thus, there was no stereospecificity in this elimination reaction. This does not imply a carbanion mechanism for the elimination; but it does, however, cast much doubt for a concerted mechanism since the latter would be expected to exhibit some degree of stereospecificity.

The diene diethers (VIII) were hydrolyzed to corresponding diketones (IX) very easily with sulfuric acid containing water. This was affected by simply dissolving the diethers in sulfuric acid and slowly dropping in water. The yellow diketones (IX) were quickly precipitated on pouring the acid solutions into cold water. Similar hydrolyses have been reported with fluorinated phenyl- and cyclohexenylcyclobutene ethers.[7,8]

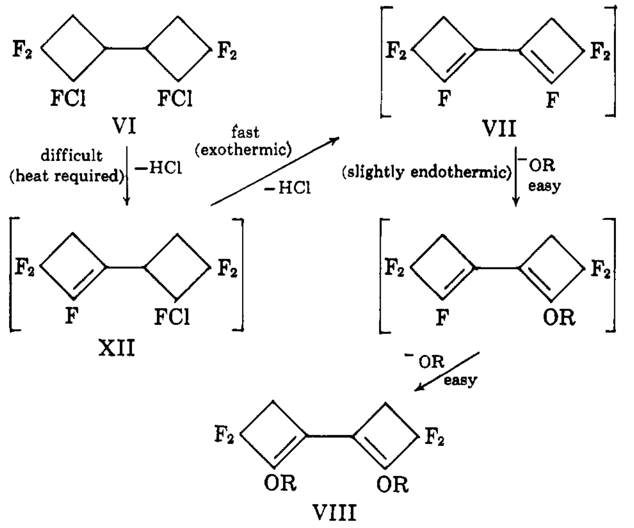
Since conjugated diolefins undergo cycloaddition reactions much more easily than monoolefins, owing to greater stabilization of the free-radical intermediates, the best cycloaddition route to "dibox" compounds would be the addition to one molecule of trifluorochloroethylene, then an elimination reaction to regenerate the diene system, followed by a second cycloaddition of trifluorochloroethylene.



The dehydrochlorination V to X with potassium hydroxide in alcohol was expected to be accompanied by replacement of vinylic fluorine. To avoid this, a suspension of potassium hydroxide in mineral oil was tried first to affect the elimination. This method gave 1-vinyl-2,3,3-trifluoro-1-cyclobutene (X) but in low yield and conversion. Triethylamine in ether with V gave the same product but with even lower conversion. Potassium hydroxide in ethanol was then tried. Vapor phase chromatography showed a high conversion and the infrared spectrum showed that the product was not the expected vinyl ether XI but was X, identical with that prepared by the two previous methods. In fact, replacement of the vinylic fluorine of X with ethoxide was found to be very difficult even on refluxing overnight. X was found to be a very reactive monomer. A freshly distilled sample polymerized spontaneously overnight to a hard, clear, glassy solid.

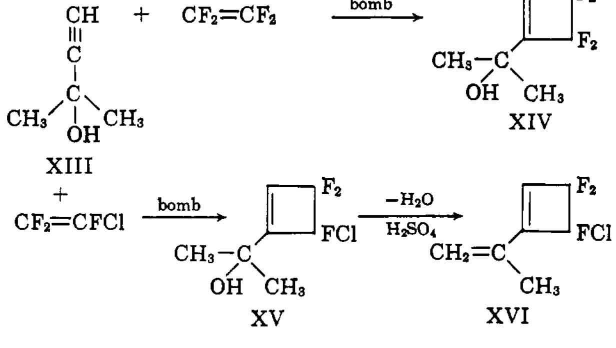
The cycloaddition of trifluorochloroethylene with the vinylcyclobutene (X) preceeded rather easily to give the unsaturated "dibox" compound XII in good yield, which was readily purified by distillation.

The reaction of XII with potassium hydroxide in alcohols was very exothermic yielding VIII identical with that prepared from the saturated "dibox" compound VI by refluxing with alcoholic potassium hydroxide. However, by adding 2 moles of base per mole of XII and holding the temperature below 25°, elimination occurred without replacement of the vinylic fluorine to yield 2,2′,3,3,3′,3′-hexafluorobicyclobutenyl (VII) which had been sought earlier from VI but without success. The inability to isolate VII as an intermediate on treating VI with an alkoxide can thus be explained by the instability of the intermediates in the conditions required for the first elimination step.



The *ability* to isolate VII from XII can be rationalized by the relative ease of the elimination reaction compared with that of the replacement reaction. The conversion of XII to VII proceeded best using triethylamine in anhydrous ether; however, high concentration of triethylamine caused the formation of a black tarry material.

The cycloadditions of tetrafluoroethylene and of trifluorochloroethylene with 3-methyl-1-butyn-3-ol (XIII) were successfully performed to obtain intermediates for other "dibox" compounds. The products were the expected cyclobutenylisopropyl alcohols (XIV and XV). These can be dehydrated with sulfuric acid to the corresponding conjugated dienes , *e.g.*, XVI.



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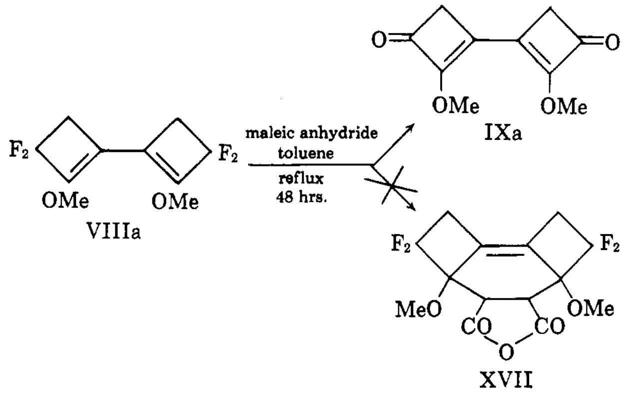
[7] E. F. Silversmith and J. D. Roberts, *J. Am. Chem. Soc.*, **80**, 4083 (1958).

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

Cycloaddition reactions were also attempted with 2,3-dichlorobutadiene and with 1,3-cyclooctadiene using trifluorochloroethylene as coreactant. In the case of 2,3-dichloro-1,3-butadiene, heating at 130° for 7 hr. caused formation of a rubber-like polymer. No codimerization was observed with 1,3-cyclooctadiene and trifluorochloroethylene at 160° for 15 hr. Apparently the cyclooctane structure causes steric inhibition for the interaction between the two double bonds of the diene in addition to making approach by the fluoro olefin difficult. Thiophene also failed to react with $CF_2{=}CFCl$, but here the failure to react is probably due to inhibition of radical formation by the sulfur atom.

Diels–Alder reactions were attempted using tetracyanoethylene as dienophile and compounds VIIIa, X, and XVI as dienes. In each case, there was no colored π-complex observed and no adducts were isolated. X polymerized on refluxing with maleic anhydride in toluene, and VIIIa was converted to diketone IXa.



Experimental

Cycloaddition of Butadiene with Trifluorochloroethylene (1 Mole).[4]—A 2-l. steel bomb containing 5 ml. of limonene as inhibitor was cooled in a Dry Ice–acetone bath for several hours and then charged with 350 g. (2.9 moles) of trifluorochloroethylene and 150 g. (2.78 moles) of butadiene. This was heated under autogenous pressure in a shaker at 105° for 24 hr., 125° for 24 hr., 150° for 15 hr., and 175° for 24 hr. On cooling, bleeding off excess gases, and opening, 412 g. of liquid product was obtained, plus a considerable amount of solid material. On distillation, 350 g. (75%) of the 1-vinyl-2,3,3-trifluoro-2-chlorocyclobutane (V)[4] was obtained, boiling at 108.5–109.0° (630 mm.). The distillation residue was placed in a refrigerator at −20° for 2 weeks, at which time 15 g. of colorless crystalline material was filtered off *in the cold* (−15°). The crystals melted at 49–60° and were identified as 2,2′-dichloro-2,2′-3,3,3′,3′-hexafluorobicyclobutyl (VI). The product was dissolved in hot ethanol (50 ml.) and decolorized twice with charcoal; water was added to the boiling solution. The clear solution on cooling yielded colorless needles, m.p. range 57–67°.

Cycloaddition of Butadiene with Trifluorochloroethylene (2 Moles).—A 0.5-l. stainless steel bomb containing 2 ml. of "Terpene B" inhibitor was chilled in a Dry Ice–acetone bath and then charged with 270 g. (2.28 mmoles) of trifluorochloroethylene and 60 g. (1.1 moles) of butadiene. The bomb was then heated under autogenous pressure at 100° for 4 hr., 140° for 28 hr., and 170° for 28 hr. On cooling the bomb, bleeding off gases, and opening, 330 g. of crude liquid product was obtained. Distillation yielded 162.5 g. of 1,2,3,3,4,4-hexafluoro-1,2-dichlorocyclobutane, b.p. 54–55° (630 mm.); 36.0 of 1-vinyl-2-chloro-2,3,3-trifluorocyclobutane (V), b.p. 107–109° (630 mm.); and about 75 g. of distillation residue. The residue was diluted with 20 ml. of ethanol, cooled to −20° for 2 days, and filtered *in the cold* (−15°). About 60 g. of 2,2′-dichloro-2,2′,3,3,3′,3′-hexafluorobicyclobutyl (VI) was thus obtained (17–20% yield). This was recrystallized from ethanol–water mixture, m.p. 65–67°. An analytical sample was prepared by two recrystallizations from ethanol–water solution.

Anal. Calcd. for $C_8H_6Cl_2F_6$: C, 33.5; H, 2.09; Cl, 24.7; F, 39.7. Found: C, 33.09; H, 2.06; Cl, 22.88; F, 38.38.

Vapor phase chromatography of compound VI on a highly polar absorbent (Fluorocarbon FS on Firebrick R) gave three peaks in the ratios 1.0:1.3:1.0. These peaks correspond to the three types of stereoisomers, the *cis–cis* isomers (F with respect to adjacent H), the *trans–cis* isomer, and the *trans–trans* isomers. The compound gave distinctive infrared peaks at 2930 and 1420 cm.$^{-1}$. Nuclear magnetic resonance showed a very complex splitting pattern.

Cycloaddition of 1-Vinyl-2-chloro-2,3,3-trifluorocyclobutane (V) with Trifluorochloroethylene.—A 0.5-l. stainless steel bomb containing 175 g. (1.02 moles) of V and 1 ml. of "Terpene B" was cooled and charged with 135 g. (1.16 moles) of trifluorochloroethylene. It was then heated at 160° for 25 hr. On cooling the bomb, bleeding off the gases, and opening, 267 g. of liquid product was obtained. The product was not worked up in the usual manner (see previous experimental procedure), but rather was analyzed by vapor phase chromatography, which showed 16 parts of trifluorochloroethylene dimer (50% of orig. $CF_2{=}CFCl$), thirty-six parts of V (86% recovery), seven parts of VI (10% yield), and five parts of an unidentified higher boiling product.

2,2′-Dimethoxy-3,3,3′,3′-tetrafluorobicyclobutenyl (VIIIa).—About 2.78 g. (0.0097 moles) of 2,2′-dichloro-2,2′,3,3,3′,3′-hexafluorobicyclobutyl (VI) was dissolved in 20 ml. of methanol and to this solution was added a solution of 3.0 g. (0.053 moles) of potassium hydroxide in 15 ml. of methanol. This was then heated over a steam bath to slow reflux for 15 min. The yellow-orange fluid was filtered hot and the crystals formed in the funnel were washed through with hot methanol. The methanolic solution was concentrated *in vacuo* and allowed to cool and crystallize. A 1.10-g. sample of pale yellow needles of VIIIa (m.p. 98–99°) was obtained. A second crop gave 0.2 g. more of VIIIa, making a yield of 56%. VIIIa was further purified by treatment with activated charcoal and recrystallization from an alcohol–water solution to give colorless needles, m.p. 101°; ultraviolet spectrum: λ_{max} 2700 Å. (ϵ 18,000); infrared spectrum: bands at 1440, 1620, and 2990 cm.$^{-1}$; n.m.r. spectrum showed a —CH_2— split by an adjacent —CF_2—.

Anal. Calcd. for $C_{10}H_{10}F_4O_2$: C, 50.4; H, 4.20; F, 31.9. Found: C, 50.20; H, 4.44; F, 31.62.

1,2′-Dimethoxy-3,3′-diketobicyclobutenyl (IXa).—Approximately 2.0 g. (0.0075 mole) of the diene diether (VIIIa) as prepared above was added with stirring to 10 ml. of concentrated sulfuric acid. When the solid had dissolved, 5 ml. of cold water was slowly added dropwise with stirring, care being taken to avoid severe overheating. The resulting brownish solution was poured into 100 ml. of cold water. A yellow solid immediately precipitated. After the addition, the yellow solid was filtered off and washed with water. Typical yields of IXa were 1.2–1.5 g. (85–100% yield). The diketone was conveniently recrystallized from hot toluene or hot aqueous ethanol (the former was a better solvent). Yellow needles were thus obtained, m.p. 203°; ultraviolet spectrum: λ_{max} 3650 Å. (ϵ 13,000); infrared spectrum: bands at 1277, 1580, and 1730 cm.$^{-1}$; the n.m.r. spectrum showed two single peaks for —OCH_3 and for —CH_2—CO—.

Anal. Calcd. for $C_{10}H_{10}O_4$: C, 61.9; H, 5.16. Found: C, 61.91; H, 5.40.

2,2′-Diethoxy-3,3,3′,3′-tetrafluorobicyclobutenyl (VIIIb).—A 2.78-g. sample (0.0097 mole) of VI was dissolved in 25 ml. of absolute ethanol and to this was added a solution of 3.0 g. (0.053 mole) of potassium hydroxide in 20 ml. of ethanol. It was heated to reflux for 10 min. The orange fluid was filtered to remove the salts. The filtrate was concentrated to half its original volume by heating under vacuum. The concentrated solution was poured into cold water (100 ml.) and then extracted with one 25-ml. portion of chloroform followed by extraction with a 10-ml. portion of the same solvent. The chloroform extracts were dried over anhydrous potassium carbonate and then evaporated *in vacuo*. A red liquid (about 1.2 g., 50% yield) was thus obtained. This crystallized readily upon refrigeration and melted readily on warming. The material was heated in alcohol with activated charcoal, allowed to recrystallize at −20°, and filtered off *in the cold*. After two such recrystallizations, white crystals were obtained melting at 32.3°. The crude liquid product is of sufficient purity for subsequent steps; infrared spectrum: bands at 1440, 1620, and 2960 cm.$^{-1}$. No microanalysis was submitted since the product darkened rapidly on standing.

2,2'-Diethoxy-3,3'-diketobicyclobutenyl (IXb).—The diethoxy diketone (IXb) was prepared by the same procedure as the corresponding dimethoxy compound (IXa) from XI. Recrystallization from hot alcohol-water yielded bright yellow needles, m.p. 118–119°; typical yields were 80%; ultraviolet spectrum: $\lambda_{\max}$ 3650 Å. (ϵ 12,670); infrared spectrum: peaks at 1260, 1580, and 1730 cm.$^{-1}$; the n.m.r. spectrum showed an unsplit methylene for —CH$_2$—CO and the expected series of peaks for —O—CH$_2$—CH$_3$.

Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.9; H, 6.3. Found: C, 65.23; H, 6.64.

1-Vinyl-2,3,3-trifluoro-1-cyclobutene (X).—About 34.0 g. (0.20 mole) of 1-vinyl-2,2,3-trifluoro-2-chlorocyclobutane (V) was dissolved in 50 ml. of absolute methanol. A solution of 13.0 g. of potassium hydroxide (0.23 mole) in 50 ml. of methanol was added dropwise with stirring and cooling. The temperature was maintained at 10–20° throughout the addition. After the addition, the temperature was allowed to rise to 25–30° for 0.5 hr. and then the mixture was heated to reflux for 10 min. It was then poured into 500 ml. of cold water in a separatory funnel. After shaking, the product which separated to the bottom was removed. After drying over anhydrous calcium chloride, 20–25 g. (80–90% yield) of crude straw-colored liquid (XV) was obtained. (Additional portions were obtained by extracting the aqueous phase with chloroform.) Fractional distillation under reduced pressure yielded 1-vinyl-2,3,3-trifluoro-1-cyclobutene (X), b.p. 44.0° (174 mm.), n^{25}D 1.3971. Freshly distilled samples were found to polymerize very readily to a hard, clear and colorless solid. It can be stored for short periods of time (1–2 days) at −20° in the presence of inhibitors (*e.g.*, hydroquinone or *t*-butylcatechol); infrared spectrum: bands at 1370, 1460, and 1720 cm.$^{-1}$.

Anal. Calcd. for $C_6H_5F_3$: C, 53.5; H, 3.73; F, 42.5. Found: C, 53.2; H, 4.06; F, 42.1.

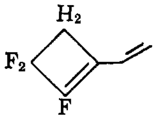
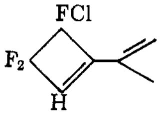
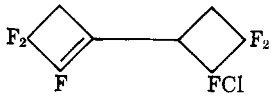
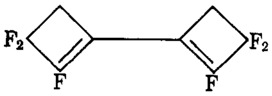
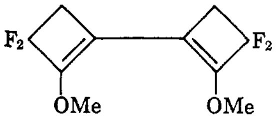
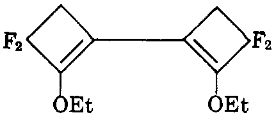
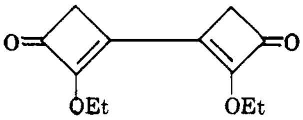
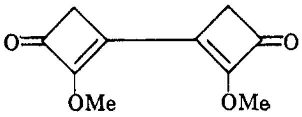
1-(2,3,3-Trifluoro-1-cyclobutyl)-2,3,3-trifluoro-2-chlorocyclobutene (XII).—About 186 g. (1.37 moles) of 1-vinyl-2,3,3-trifluoro-1-cyclobutene (X, freshly prepared by the previous method, dried over magnesium sulfate, but not distilled) was placed in a 0.5-l. stainless steel bomb along with 1 g. of hydroquinone and about 2 ml. of "Terpene B" inhibitor. The bomb was sealed, checked for leaks, chilled in Dry Ice, and evacuated; then 190 g. (1.63 moles) of trifluorochloroethylene was bled in. It was then heated in a heater-shaker at 150° for 5.5 hr. On cooling and opening the bomb, 316 g. of an orange liquid was obtained. Vapor phase chromatography showed the absence of starting diolefin, the presence of a small amount of trifluorochloroethylene and its dimer, and a high proportion of the desired product (XII). Distillation at atmospheric pressure gave 255 g. (75%) of a colorless liquid boiling at 160° (630 mm.); n^{25}D 1.4676, n^{25}D 1.3910; infrared spectrum: bands at 1440, 1650 (w), and 1720 cm.$^{-1}$.

Anal. Calcd. for $C_8H_5ClF_6$: C, 38.3; H, 2.00; F, 45.5. Found: C, 38.52; H, 1.83; F, 45.70.

2,2'-Dimethoxy-3,3,3',3'-tetrafluorobicyclobutyl (VIIIa). Method B.—About 3.16 g. (0.0126 mole) of XII was dissolved in 10 ml. of methanol and to this was added dropwise 20 ml. of a 10% solution of potassium hydroxide in methanol. The reaction was quite exothermic and salts precipitated immediately. After the initial reaction, the mixture was warmed slightly for 5 min. and then poured into 100 ml. of cold water. The white solid was filtered off, washed with water, and air-dried, yielding 2.80 g. of VIIIa, m.p. 101–102°. The infrared spectrum was identical with that of VIIIa prepared from VI. Hydrolysis with sulfuric acid–water yielded a diketone identical with XIVa described earlier.

2,2'-Diethoxyl-3,3,3',3'-tetrafluorobicyclobutyl (VIIIb). Method B.—To a solution of 3.16 g. of XII (0.0126 mole) in 10 ml. of ethanol was added dropwise 20 ml. of a 10% solution of potassium hydroxide in ethanol. The reaction was vigorous. After the initial reaction, the mixture was warmed slightly for 5 min. The solution was filtered and the filtrate was concentrated to half its original volume. The concentrated solution was poured into water and extracted with two 15-ml. portions of dichloromethane. The extracts were dried over magnesium sulfate, and the solvent then was stripped *in vacuo* to yield 2.70 g. of straw-colored liquid (80% yield). The infrared spectrum was identical with that of VIIIb prepared directly from VI.

Table I

		Infrared, cm.$^{-1}$	Ultraviolet, $\lambda_{\max}$ Å. (ϵ)
X		1370, 1460, *1720*	
XVI		1588, *1635*	
XII		1440 (1650), *1720*	
VII		1340, *1655*	2375 (8330)
VIIIa		1440, *1620*, 2990	2700 (18,000)
VIIIb		1440, *1620*, 2960	
IXb		1260, *1580*, 1730	3650 (12,670)
IXa		1277, *1580*, 1730	3650 (13,000)

2,2',3,3,3',3'-Hexafluorobicyclobutenyl (VII). A.—About 25 g. (0.10 mole) of XII was dissolved in 100 ml. of absolute ethanol, and the solution was cooled in an ice-water bath. A 56-ml. quantity of a 10 g./100 ml. solution of potassium hydroxide in absolute ethanol was added slowly with stirring and cooling. Precipitation occurred immediately. After the addition, the solution was allowed to warm to 25°, and then poured into a separatory funnel with 500 ml. of water. On separation of the organic layer, much of the material solidified, requiring use of a heat lamp to remove it. This yielded 7.8 g. of VII. The product melted at 50–55°. The filtrate was also found to be very rich in product, along with some of the diether VIIIb.

B.—About 25 g. (0.10 mole) of XII was dissolved in 70 ml. of absolute ether, and 12 g. (0.12 mole) of triethylamine in 10 ml. of absolute ether was added at once. The mixture was left in a stoppered flask for 2 days after which time it was poured into 300 ml. of lukewarm water, care being taken to keep the ether from boiling over. It was then left for 1 day at which time the product crystallized. The product was filtered off and washed with water. A 17-g. sample (80%) of XII, m.p. 57°, was obtained. An analytical sample was prepared by sublimation; ultraviolet spectrum: $\lambda_{\max}$ 2375 Å. (ϵ 8330); infrared spectrum: bands at 1340 and 1655 cm.$^{-1}$; n.m.r. spectrum: CH$_2$ split by cross-ring vinylic F, and resplit by adjacent —CH$_2$—.

Anal. Calcd. for $C_8H_4F_6$: C, 44.9; H, 1.87; F, 53.3. Found: C, 44.51; H, 1.89; F, 53.02.

2-(3,3,4,4-Tetrafluoro-1-cyclobutenyl)isopropyl Alcohol (XIV).—A 0.5-l. stainless steel bomb containing 42 g. (0.50 mole) of 3-methyl-1-butyn-3-ol (XIII) and 1 ml. of "Terpene B" inhibitor was cooled in Dry Ice–acetone and charged with 65 g. (0.65 mole) of tetrafluoroethylene. It was then heated for 24 hr. at 140°. At the end of the heating period, it was cooled and the excess gaseous material was bled off. On opening the bomb, 75 g. of liquid was obtained. This was extracted with three 15-ml. portions of water to remove the unchanged methylbutynol. On distillation at 100-mm. pressure, the material decomposed considerably, but 20 g. of product (XIX) boiling at 101° (100 mm.) was obtained (19.9% yield); infrared spectrum: bands at 1610, 1650, 2960, and 3350 cm.$^{-1}$; n.m.r. spectrum showed a single peak for a hydroxyl H, a single peak for 2(—CH_3), and a series of peaks corresponding to a vinylic hydrogen split by a cross-ring —CH_2— and resplit by an adjacent —CH_2—.

Anal. Calcd. for $C_7H_8F_4O$: C, 45.6; H, 4.35; F, 41.3. Found: C, 45.85; H, 4.38; F, 40.95.

2-(3,3,4-Trifluoro-4-chloro-1-cyclobutenyl)isopropyl Alcohol (XV).—A 2-l. steel bomb containing 600 g. (7.15 moles) of 3-methyl-1-butyn-3-ol (XIII) and 5 ml. of "Terpene B" inhibitor was chilled in a Dry Ice bath and then evacuated. A 610-g. sample (5.25 moles) of trifluorochloroethylene was bled in, and the bomb was heated at 160° for 24 hr. On cooling, bleeding off gases, and opening, 1110 g. of brown liquid was obtained. This was steam distilled to yield 676.3 g. (after drying over magnesium sulfate) of steam volatile material. Vapor phase chromatography showed this to be 70% pure adduct XV. The yield was thus 45%. The product had the following properties: b.p. 97–98° (38 mm.); $d^{25}{}_{25}$ 1.468; $n^{26}{}_D$ 1.4198; infrared spectrum: bands at 1610, 2960, and 3350 cm.$^{-1}$; n.m.r. spectrum showed single peaks for a hydroxyl H and a methyl H, and a series of peaks corresponding to a vinylic hydrogen split once by a cross-ring —CFCl— and split again by an adjacent —CF_2—.

Anal. Calcd. for $C_7H_8ClF_3O$: C, 42.0; H, 4.00; Cl, 17.7; F, 28.5. Found: C, 41.83; H, 3.77; Cl, 18.99; F, 28.93.

1-Isopropenyl-3,4,4-trifluoro-3-chloro-1-cyclobutene (XVI).—About 50 g. (0.25 mole) of the above 2-(3,3,4-trifluoro-4-chloro-1-cyclobutenyl)isopropyl alcohol was added dropwise with stirring into 130 ml. of concentrated sulfuric acid previously cooled to 5° in an ice bath. The temperature was maintained at 5–15° throughout the addition. Afterwards the temperature was allowed to rise to 20° for 2.5 hr., at which time it was poured into 500 g. of ice with stirring. A black tar resulted which was extracted several times with dichloromethane (a process which proved very messy and tedious). The extracts were dried over anhydrous magnesium sulfate and then stripped to a volume of about 75 ml. The product was distilled at 38-mm. pressure. A 12-g. sample of XXI (27% yield) was obtained, boiling at 61–65° (38 mm.), $n^{26}{}_D$ 1.4304; infrared spectrum: bands at 1588 and 1635 cm.$^{-1}$. Sharts and Roberts[8] reported this compound earlier and listed properties as follows: infrared bands at 1588 and 1635 cm.$^{-1}$, b.p. 60–65° (32–37 mm.), $n^{25}{}_D$ 1.4288–1.4295.

Attempted Diels–Alder Reactions of 2,2′-Dimethoxy-3,3,3′,3′-tetrafluorobicyclobutenyl (VIIIa). A. With Maleic Anhydride.—A 2.38-g. sample (0.01 mole) of the above "dibox" compound (VIIIa) and 1.5 g. (0.015 mole) of maleic anhydride were refluxed with 50 ml. of toluene for 55 hr. At the end of the reflux period, a small amount of black solid was filtered off. The filtrate, on cooling, yielded 0.45 g. of bright yellow needles. Infrared spectra (see Table I) showed this to be identical with 2,2′-diethoxy-3,3′-diketobicyclobutenyl (IXa) prepared by sulfuric acid hydrolysis of the same starting material.

B. With Tetracyanoethylene.—A 2.38-g. sample (0.01 mole) of XIIIa and 1.30 g. of tetracyanoethylene (0.01 mole) were dissolved separately in 10 ml. portions of tetrahydrofuran and the two solutions were then mixed. No colored π-complex was observed. A day later the solvent was stripped *in vacuo*. The residual solid was found to be a mixture of the two starting materials. There was no indication of any reaction having occurred.

Acknowledgment.—The authors wish to express their appreciation to the Minnesota Mining and Manufacturing Company, St. Paul, Minnesota, and the U. S. Army Quartermaster Research and Engineering Command, Natick, Massachusetts, under Scientific Project Officer, Dr. Malcolm C. Henry, for their partial support of this work.

The Synthesis and Properties of 1,1-Dimethylindolium Perchlorate, an N-Quaternized Indole

R. L. HINMAN AND J. LANG

The Union Carbide Research Institute, Union Carbide Corporation, Tarrytown, New York

Received December 26, 1963

1,1-Dimethylindolium perchlorate (IVb), the first example of an N-quaternized indole, has been prepared *via* the sequence: isatin, 3-hydroxyindoline (I), 1,1-dimethyl-3-hydroxyindolinium chloride (II), 3-chloro-1,1-dimethylindolinium chloride (III), and dehydrochlorination of the last compound to the indolium salt. The ultraviolet spectrum of IVb bears a striking resemblance to those of indene and styrene. The indolium salts are powerful methylating agents, attacking even chloride ion at room temperature. Dehydrochlorination of III can also be effected by chloride ion. Both reactions are favored by nonpolar media.

In the course of our investigations of the protonation of indoles[1a,b] and pyrroles,[1c,d] it became desirable to know the general characteristics of the ultraviolet spectra of N-protonated indoles. Although N-protonated salts have been isolated,[1a,b] the principal conjugate acid of an indole in solution in strong acids is the 3-protonated isomer.[1b] A model for the N-protonated species was prepared, therefore, in the form of 1,1-dimethylindolium perchlorate (IVb), the first example of an N-quaternized salt of an indole. This report describes the synthesis of the indolium salt and some of its rather remarkable properties as a methylating agent.[2]

Since indoles undergo alkylation—like protonation—on carbon,[3] the double bond of the indolium salt was formed after quaternization of the ring nitrogen. This was accomplished *via* the reaction sequence shown in the accompanying chart. 3-Hydroxyindoline had been prepared previously[4] by reduction of isatin with lithium aluminum hydride. Since the yields were consistently low (12–14% as compared to a reported[4] yield of 21%), other methods of synthesis of this key compound were examined. Indoxyl is an obvious choice as a precursor, but attempts to reduce it selectively have been largely unsuccessful.[4] Our attempts to reduce indoxyl O-acetate with lithium aluminum hydride, sodium borohydride, sodium dithionite, or by catalytic hydrogenation at 3 atm. over

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(1) (a) R. L. Hinman and J. Lang, *Tetrahedron Letters*, **21**, 12 (1960); (b) R. L. Hinman and E. B. Whipple, *J. Am. Chem. Soc.*, **84**, 2534 (1963); (c) E. B. Whipple, Y. Chiang, and R. L. Hinman, *ibid.*, **85**, 26 (1963); (d) Y. Chiang and E. B. Whipple, *ibid.*, **85**, 2763 (1963).

(2) Two examples of pyrrolium salts have been reported [(a) R. Lukeš and J. Trojánek, *Collection Czech. Chem. Commun.*, **18**, 454 (1953); and (b) O. Achmatowicz, S. Achmatowicz, and W. J. Rodwald, *Rocznicki Chem.*, **35**, 497 (1961)], but demethylation was observed only incidentally and under relatively severe conditions.

(3) See, for example, W. C. Sumpter and F. M. Miller, "The Chemistry of Heterocyclic Compounds with Indole and Carbazole Systems," Interscience Publishers, Inc., New York, N. Y., 1954, p. 32.

(4) E. Giovannini and T. Lorenz, *Helv. Chim. Acta*, **40**, 1553 (1957).