

## Bicyclobutyl Derivatives. IV. Bromination of Fluorinated Bicyclobutenyl Derivatives<sup>1-3</sup>

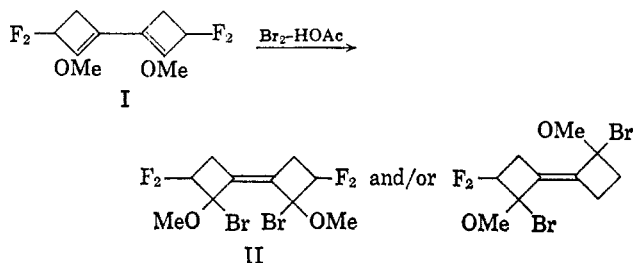
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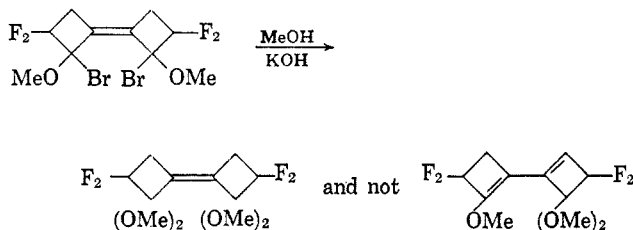
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The addition reactions of bromine to several fluorinated bicyclobutenyl derivatives have been investigated. 2,2'-Dimethoxy-3,3,3',3'-tetrafluorobicyclobutenyl forms a dibromide by 1,4 addition. This adduct on methanolysis and subsequent sulfuric acid treatment forms a novel reactive diketone, 2,2'-diketo-3,3,3',3'-tetrafluorobicyclobutylidene. A tetrabromide obtained from 2,2'-dimethoxy-3,3'-diketobicyclobutenyl, on treatment with triethylamine, underwent dehydrobromination and rearrangement to 2,2'-dimethoxy-3,3'-diketo-4,4'-dibromobicyclobutenyl.

Bicyclobutenyl derivatives were found to readily add 1 mole of bromine. Thus, when 2,2'-dimethoxy-3,3,3',3'-tetrafluorobicyclobutenyl (I) was treated with bromine (1 mole) in methylene chloride or glacial acetic acid, 1,4 addition occurred to give a symmetrical dibromide (II). The structural assignment was based on the microanalysis and the lack of olefinic absorption in the infrared spectrum (as would be expected for a symmetrically tetrasubstituted olefin). It was not possible to deduce whether the product was a *cis* or *trans* isomer with respect to the double bond, however.

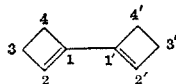


Dibromide II reacted with potassium hydroxide in methanol to give a tetraether, 2,2,2',2'-tetramethoxy-3,3,3',3'-tetrafluorobicyclobutylidene (III), which is a mixture of *cis* and *trans* isomers. It was expected that 1,4 elimination of hydrogen bromide might occur in preference to allylic replacement and thus give a diene. Apparently, the methylene hydrogens are not sufficiently acidic to promote elimination.



The reaction of 2,2',3,3,3',3'-hexafluorobicyclobutenyl (IV) with excess bromine also gave a mixture of

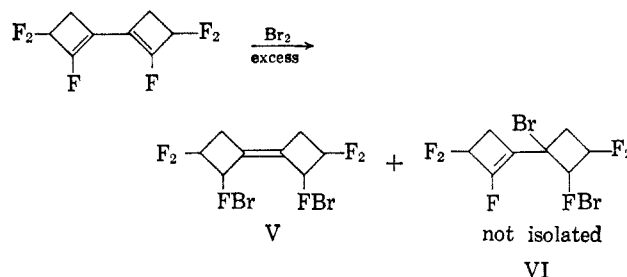
(1) This structure is more properly written bi-1,1'-cyclobut-1-enyl consistent with the *Chemical Abstracts* nomenclature guide. To permit smoother reading, the shortened form will be used throughout the text. The numbering for the bicyclobutenyl structure is as follows.



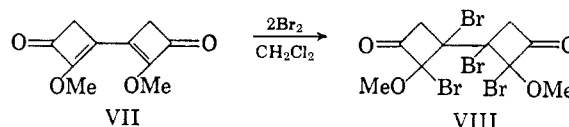
(2) This paper represents part of a Ph.D. thesis submitted to the Graduate School, University of Colorado, 1965.

(3) Previous papers in this series: J. D. Park and W. C. Frank, *J. Org. Chem.*, **29**, 1445 (1964); **32**, 1333, 1336 (1967).

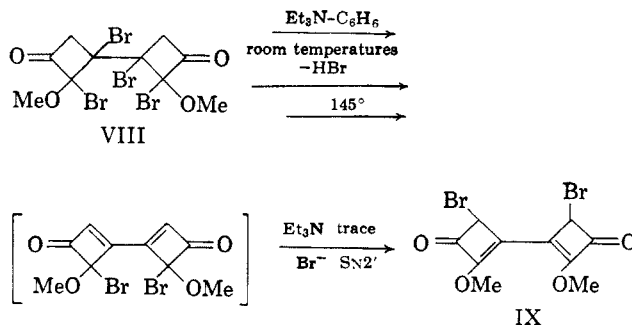
bromides—mainly dibromides. Only the symmetrical dibromide, 2,2'-dibromo-2,2',3,3,3',3'-hexafluorobicyclobutylidene (V) was isolated from the mixture.



The addition of 2 moles of bromine to 2,2'-dimethoxy-3,3'-diketobicyclobutenyl (VII) in methylene chloride, surprisingly enough, proceeded very easily to give a readily isolable tetrabromide, 1,1',2,2'-tetrabromo-2,2'-dimethoxy-3,3'-diketobicyclobutenyl (VIII) as the only product.



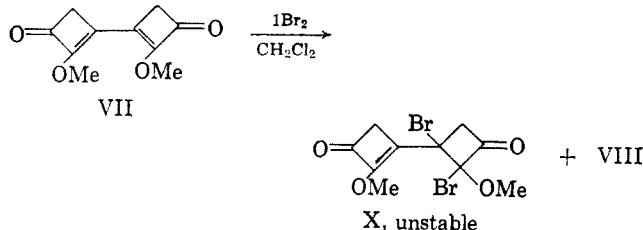
Tetrabromide VIII lost bromine and hydrogen bromide on heating to 145° to form a mixture of diene-diketones. It spontaneously lost hydrogen bromide at room temperature on standing. The dehydrobromination seemed to be autocatalytic since samples left in open air failed to decompose, but bottled samples quickly lost hydrogen bromide. The final product is 2,2'-dimethoxy-3,3'-diketo-4,4'-dibromobicyclobut-1-enyl (IX) which was best prepared by the reaction of tetrabromide VIII with triethylamine in benzene.



The structure of IX is based largely on the infrared spectrum which is almost identical with that of dione VII. The transformation occurs *via* a simple dehydrobromination followed by two simultaneous Sn2' rear-

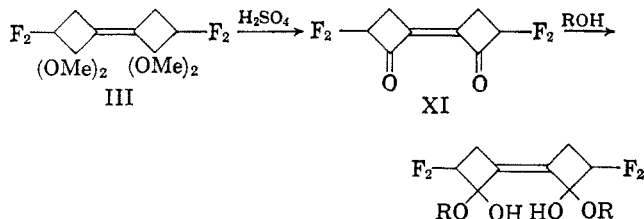
rangements. Rearrangements of this type are expected with *gem*-disubstituted cyclobutenones and have been observed by Roberts and co-workers.<sup>4</sup>

The addition of 1 mole of bromine to VII in methylene chloride gave a mixture of compounds including starting material, tetrabromide VIII, and a very unstable, unisolable dibromide to which structure X has been assigned on the basis of the infrared spectrum of the crude product mixture.



It was not possible to form more highly brominated derivatives of VII. The reaction of VII with a large excess of bromine in tetrachloroethane at 145° gave the addition-dehydrobromination product (IX) as the main product.

A new and interesting diketone, 2,2'-diketo-3,3',3',3'-tetrafluorobicyclobutylidene (XI), was prepared by the reaction of tetraether III with concentrated sulfuric acid. It appears to form highly soluble hydrates in aqueous solvents and hemiketals when dissolved in alcohols.



The diketone (XI) was found to be very reactive to bases. In methylene chloride it reacted vigorously with triethylamine or with pyridine to give an intense purplish red solution. On working this up, a black, polymeric solid, very soluble in acetone, was obtained which was not further characterized.

### Experimental Section

**Preparation of 2,2'-Dimethoxy-3,3',3',3'-tetrafluorobicyclobutenyl (I).**—This compound was prepared according to the method previously shown by Park and Frank.<sup>3</sup>

**2,2'-Dibromo-2,2'-dimethoxy-3,3',3',3'-tetrafluorobicyclobutylidene (II).**—A solution of bromine (26.4 g, 0.165 mole) in 50 ml of glacial acetic acid was added in portions with stirring to a solution of diether I (36.5 g, 0.155 mole) in 100 ml of glacial acetic acid. The mixture was stirred for 10 min and then poured over 500 ml of ice in a large flask with vigorous shaking. A yellowish solid quickly separated. Sodium bisulfite solution was added to remove the bromine color. The solid compound (II, now white), was then filtered off, washed, and pumped dry (63 g, 100% of theory). The crude product, recrystallized from hot Skellysolve C, melted at 106–107°. The infrared spectrum contained strong characteristic peaks at 720, 812, 881, and 989 cm<sup>-1</sup>, and lacked peaks in the olefinic region as would be expected for a symmetrically tetrasubstituted olefin.

*Anal.* Calcd for C<sub>10</sub>H<sub>10</sub>Br<sub>2</sub>F<sub>4</sub>O<sub>2</sub>: C, 30.3; H, 2.53; Br, 40.0; F, 19.4. Found: C, 30.50; H, 3.06; Br, 39.70; F, 20.62.

**2,2',2',2'-Tetramethoxy-3,3',3',3'-tetrafluorobicyclobutylidene (III).**—Dibromide II (as prepared above, 63 g, (0.155 mole)

was dissolved in 150 ml of absolute methanol. To this was added, slowly, with stirring and cooling, a solution of 17 g (0.30 mole) of potassium hydroxide in 50 ml of absolute methanol. After the addition, stirring was continued for 10 min and the mixture was poured over ice. The creamy white, fluffy precipitate which formed was filtered and washed with water. After pumping dry for 30 min, 37 g of crude tetraether III (ca. 80%) was obtained. Further recrystallization from hot Skellysolve C yielded 30 g of colorless plates, mp 122°. The crude product was of sufficient purity to be used for the preparation of the diketone (XI). The infrared spectrum had strong characteristic peaks at 716, 749, 878, 1007, and 1310 cm<sup>-1</sup>. The proton nmr spectrum showed a strong singlet for OCH<sub>3</sub> and two separate close triplets for CH<sub>2</sub>CF<sub>2</sub> in *cis* and *trans* configurations.

*Anal.* Calcd for C<sub>12</sub>H<sub>16</sub>F<sub>4</sub>O<sub>4</sub>: C, 48.0; H, 5.33; F, 25.3. Found: C, 47.78; H, 5.71; F, 26.39.

**Bromination of 2,2',3,3',3',3'-Hexafluorobicyclobutenyl (IV).**—Bromine (39 g, 0.244 mole) and 21.4 g (0.1 mole) of diene IV were dissolved in 100 ml of methylene chloride and left in a stoppered flask for 8 days. The solvent was stripped off in a Roto-Vac to yield about 40 g of a pale yellowish, viscous liquid. The infrared spectrum of the crude mixture showed an absorption band at 1720 cm<sup>-1</sup> (vinylic fluorine). On standing for several weeks, colorless crystals had separated. These were filtered off and washed with cold Skellysolve F. The 2,2'-dibromo-2,2',3,3',3',3'-hexafluorobicyclobutylidene (V) thus obtained amounted to 10 g and melted at 97–98°. The infrared spectrum was quite similar to that of the crude material but lacked absorption in the olefinic region. Major, significant peaks were at 1390, 1290, 1220, 900, and 717 cm<sup>-1</sup>. The filtrate is considered to be a mixture of the two isomeric dibromides (1,2-dibromo and 2,2'-dibromo).

*Anal.* Calcd for C<sub>8</sub>H<sub>4</sub>Br<sub>2</sub>F<sub>6</sub>: C, 25.7; H, 1.07; Br, 42.5. Found: C, 26.00; H, 1.00; Br, 41.17.

**1,1',2,2'-Tetrabromo-2,2'-dimethoxy-3,3'-diketobicyclobutyl (VIII).**—In a clean, dry, 500-ml erlenmeyer flask was placed 19.4 g (0.01 mole) of 2,2'-dimethoxy-3,3'-diketobicyclobutenyl (VII) and 150 ml of methylene chloride. The mixture was shaken to dissolve the solid. To this was added, with swirling, 40.0 g (0.25 mole) of bromine diluted in methylene chloride. The mixture was shaken until solution was complete and then exposed to an ultraviolet lamp for 2 hr. After this time colorless crystals of tetrabromide were formed. The solution was concentrated by stripping off most of the solvent. Skellysolve F (300 ml) was added and the white solid was filtered and washed with more Skellysolve F. A white product (VIII, 43 g, mp 145° dec) was obtained (yield, 85%). An analytical sample was prepared by recrystallization from methylene chloride-petroleum ether (bp 30–60°). The infrared spectrum had strong characteristic peaks at 1800, 1270, 1000, and 719 cm<sup>-1</sup>. The material loses hydrogen bromide on standing in a bottle.

*Anal.* Calcd for C<sub>10</sub>H<sub>10</sub>Br<sub>4</sub>O<sub>4</sub>: C, 23.4; H, 1.95; Br, 62.3. Found: C, 23.42; H, 2.02; Br, 62.05.

**2,2'-Dimethoxy-3,3'-diketo-4,4'-dibromobicyclobutenyl (IX).**—In a 250-ml, round-bottomed flask equipped with a mechanical stirrer, reflux condenser, thermometer, and addition funnel, 10.0 g (0.02 mole) of 1,1',2,2'-tetrabromo-2,2'-dimethoxy-3,3'-diketobicyclobutyl (VIII) was dissolved in 200 ml of dry benzene. Triethylamine (4.0 g, 0.04 mole) in 20 ml of benzene, was added dropwise keeping the temperature below 40°. After the addition, the flask was warmed to reflux for 40 min and then filtered hot to give 7.8 g of dull gray salts. The salts were extracted to give 1.1 g of black, water-insoluble solid. The filtrate was concentrated *in vacuo* to about 50 ml. Skellysolve F (150 ml) was then added and the solution was chilled to -15° for several hours. The product (IX) was filtered to yield a yellowish, crystalline solid (6.5 g, 90% yield) melting at 130° dec. The infrared spectrum contained strong characteristic peaks at 1740, 1590, 1280, 993, and 727 cm<sup>-1</sup>. The spectrum was relatively simple and very similar to that of 2,2'-dimethoxy-3,3'-diketobicyclobutenyl (VII).

*Anal.* Calcd for C<sub>8</sub>H<sub>8</sub>Br<sub>2</sub>O<sub>4</sub>: C, 34.2; H, 2.37; Br, 45.4. Found: C, 34.51; H, 2.40; Br, 45.14.

**Addition of Bromine (1 Mole) to 2,2'-Dimethoxy-3,3'-diketobicyclobutenyl (VII).**—Bromine (4.95 g, 0.031 mole) and 6.0 g (0.031 mole) of diketone VII were dissolved together in 100 ml of methylene chloride and allowed to react for 2 hr. The solvent was then stripped off and the solid was washed with Skellysolve F. It was found to be a mixture of starting material and brominated product. The infrared spectrum of the bromide mixture

(4) M. C. Caserio, H. E. Simmons, A. E. Johnson, and J. D. Roberts, *J. Am. Chem. Soc.*, **82**, 3102 (1960).

