was analyzed qualitatively by infrared spectroscopy. In each case partial rearrangement to III was found to have occurred as evidenced by the presence of absorption bands at 1585 cm.$^{-1}$ and 1375 cm.$^{-1}$.

No rearrangement took place upon similar treatment with *p*-nitrobenzoic acid or with *p*-toluenesulfonic acid.

Rearrangement of 3,3-Dimethyl-2-phenyl-3*H*-indole (II) with Boron Trifluoride.—The addition of 1 g. of II to 10 ml. of boron trifluoride in ethyl ether caused the precipitation of the Lewis salt which was collected by filtration and added to 5 ml. of tetralin. This mixture was placed in a hot air bath and heated at 150° for 2 hr. The reaction was worked up as the other Lewis acid rearrangements to give 0.75 g. (75%) of an oil which by infrared spectroscopy was shown to consist of a mixture of II and III. No attempt was made to analyze quantitatively or separate the mixture.

Rearrangement of 1,3,3-Trimethyl-2-phenyl-indoleninium Iodide (IIM).—A solution of 0.5 g. of IIM was dissolved in 6 ml. of methanol and heated in a sealed tube at 150° for 3 hr. in the manner described by Nakazaki and co-workers.[6] The tube was cooled and opened and the solvent was removed from the red-brown solution. Ether was added causing the precipitation of 0.4 g. of a violet solid, which was recrystallized from ethanol–ether to give a light brown solid, m.p. 216–218° dec. The infrared and ultraviolet absorption spectra showed this compound to be 1,2,3-trimethyl-3-phenylindoleninium iodide (IIIM). No trace of IIM was detected.

The Rearrangement of 3,3-Dimethyl-2-phenyl-3*H*-indole (II) with Hydrobromic Acid.—A solution of 1 g. of II in 15 ml. of 48% hydrobromic acid was heated under reflux for 2 hr. After cooling, the solution was neutralized with solid potassium carbonate, and the oil which separated was taken up in ether. The ether solution was washed with water and dried over anhydrous potassium carbonate. Removal of the ether gave 0.67 g. (67%) of an oil which was shown to consist of a mixture of II and III by infrared absorption spectroscopy. No resolution of the mixture was attempted.

Reduction of 3,3-Dimethyl-2-phenyl-3*H*-indole (II) with Sodium Borohydride.—A solution of 1.0 g. of II in 10 ml. of methanol was treated with an excess of sodium borohydride. The solution was maintained at room temperature, being cooled only when violent effervescence occurred. After completion of the reaction, the methanol solution was stirred gently for 5 min. and was poured into dilute hydrochloric acid. The acidic solution was neutralized with potassium carbonate, and the indoline separated as a white solid which was separated by filtration. Recrystallization of the solid from an ethanol–water mixture gave 0.95 g. (95%) of the 3,3-dimethyl-2-phenylindoline, m.p. 89–91°, lit.,[8] m.p. 95°, in the form of white needles.

The picrate was prepared in ethanol and melted at 200° dec. The picrate prepared from 0.1 *N* hydrochloric acid solution melted at 121–123°, lit.,[8] m.p. 123–124°.

Reduction of 2,3-Dimethyl-3-phenyl-3*H*-indole (III) with Sodium Borohydride.—A solution of 2 g. of III in methanol was treated with an excess of sodium borohydride in the manner described above to give 1.6 g. of an oil. The infrared spectrum of this oil was consistent with the structure 2,3-dimethyl-3-phenylindoline. The picrate was prepared in 0.1 *N* hydrochloric acid to give a derivative, m.p. 169–171° dec.

Anal. Calcd. for $C_{22}H_{20}N_4O_7$: C, 58.41; H, 4.45. Found: C, 58.72; H, 4.14.

Acknowledgment.—The authors express appreciation to the National Heart Institute of the National Institutes of Health for partial support of this research under grant H-1713 and continuation grants and for the PHS Predoctoral Fellowship to one of us (F.J.E.). This work was further assisted by a generous supply of polyphosphoric acid from Victor Chemical Corporation and the proton magnetic resonance spectra determined by Professor H. G. Kuivila for which we are grateful.

Diels-Alder Reactions of 3,3,4,4-Tetrafluorocyclobutene. Syntheses of Some Fluorinated Benzocyclobutenes

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3,3,4,4-Tetrafluorocyclobutene is an active dienophile. The adducts with butadienes are catalytically converted to 7,7,8,8-tetrafluorobenzocyclobutenes, while basic treatment of the dibromide from the butadiene adduct leads to 7,7,8-trifluorobenzocyclobutene. The adduct with cyclopentadiene consists of the *endo* and *exo* isomers. Adducts with furans and certain of their reactions are described.

In recent years there has been considerable interest shown in the benzocyclobutenes.[1] We wish to report studies of some Diels-Alder reactions of 3,3,4,4-tetrafluorocyclobutene (TFCB)[2] and conversion of certain of the adducts to fluorinated benzocyclobutenes.

Adducts with Butadienes.—Reaction of TFCB with butadiene at 100–150° gives the Diels-Alder adduct (Ia) in 75% yield.[3] When this adduct is refluxed with palladium-on-carbon catalyst, disproportionation occurs to give a mixture of the aromatic compound (IIa) and the reduced compound (IIIa). Separation was achieved by gas chromatog-

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[1] See (a) M. P. Cava, R. L. Little, and D. R. Napier, *J. Am. Chem. Soc.*, **80**, 2255 (1958); (b) H. Hart and R. W. Fish, *ibid.*, **82**, 749 (1960); (c) M. P. Cava, A. A. Deana, and K. Muth, *ibid.*, **82**, 2524 (1960); and (d) W. Baker, J. F. W. McOmie, and D. R. Preston, *J. Chem. Soc.*, 2971 (1961).

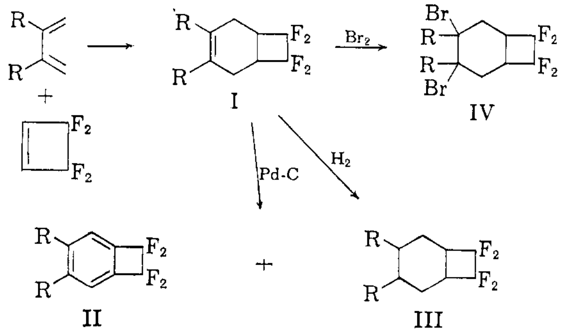
[2] J. L. Anderson, R. E. Putnam, and W. H. Sharkey, *J. Am. Chem. Soc.*, **83**, 382 (1961).

[3] An isomer of this compound was prepared by the cycloaddition reaction of tetrafluoroethylene and 1,3-cyclohexadiene. D. D. Coffman, P. L. Barrick, R. C. Cramer, and M. S. Raasch, *ibid.*, **71**, 490 (1949).

raphy. Small amounts of IIa are also obtained by dehydrogenation of Ia over platinum-on-silica catalyst at 350°.

Spectroscopic data assisted in establishing the structure of IIa. The F^{19} NMR spectrum has a single peak characteristic of the fluorine atoms of the four-membered ring, and the proton NMR spectrum has a single peak for aromatic hydrogen.[4]

The product (IIIa) obtained by disproportionation is identical to that prepared by catalytic hydrogenation of Ia.

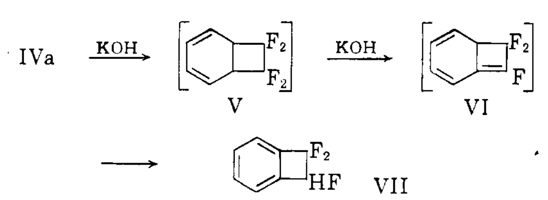


a. R = H; b. R = CH_3

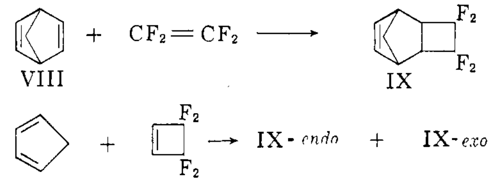
Tetrafluorocyclobutene reacts with 2,3-dimethylbutadiene at 100° to give the adduct (Ib). Treatment of this adduct with palladium-on-carbon catalyst leads to a mixture from which the aromatic compound (IIb) is easily separated by crystallization. The remainder of the product is a complex mixture. Its F^{19} NMR spectrum indicates that one of the components is the cyclohexane derivative (IIIb) which was prepared in the pure state by the catalytic hydrogenation of Ib.

The bromide (IVa) obtained from Ia is converted to the aromatic trifluoro derivative (VII) upon treatment with methanolic potassium hydroxide. The proton NMR spectrum of VII has a peak for aromatic hydrogen and a doublet for the CHF group. The doublet arises by interactions within the CHF group. Each branch of the doublet is further split into doublets because of interactions with the CF_2 group. The F^{19} NMR spectrum has two principal peaks. One, due to the CF_2 group, is split into a weak-strong-strong-weak pattern by the fluorine atoms of the group. Further splitting of each peak into doublets is caused by the CHF group. The fluorine peak arising from the CHF group is split into a doublet by the proton and each branch of this doublet is split by the CF_2 group to give the appearance of a triplet.

The formation of VII may be rationalized in the following way. If it is assumed that IVa is formed by the *trans*-addition of bromine, treatment of the resulting *trans*-dibromide with base would be expected to eliminate two moles of hydrogen bromide to form the cyclohexadiene V.[5] Removal of a bridgehead proton and an adjacent fluorine atom would result in the formation of VI which could easily isomerize to the more stable VII.[6] An alternate mechanism in which hydrogen fluoride is eliminated prior to elimination of one or both moles of hydrogen bromide cannot be rejected with the present data. The intermediate V[7] was not detected in an experiment in which only two equivalents of base were added. Instead, VII and unchanged IVa were isolated.



Adducts with Cyclopentadiene.—The reaction of cyclopentadiene with TFCB affords a nearly equimolar mixture of two adducts that were separated by gas chromatography. One adduct is identical to the product prepared[8] by the cycloaddition of 2,5-bicycloheptadiene (VIII) and tetrafluoroethylene and shown to have structure IX. Because of similarities in the infrared and NMR spectra of the adducts from TFCB, we conclude that the new compound is the *endo* or *exo* isomer of IX.[9]



Adducts with Furans.—Furan reacts with TFCB at 100° to give a mixture of 1:1 and 2:1 adducts X and XI. The crude 1:1 adduct appears to be a single isomer from its F^{19} NMR spectrum but contains impurities which are not easily removed by crystallization. Treatment with methanolic hy-

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[4] For general references to the interpretation of NMR spectra, see (a) J. D. Roberts, "Nuclear Magnetic Resonance," McGraw-Hill, New York, 1959; (b) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, 1959.

[5] M. Mousseron and F. Winternitz, *Bull. soc. chim. France*, 232 (1946). The reaction of 1,2-dibromo-4-methylcyclohexane and sodium ethoxide leads to 5-methyl-1,3-cyclohexadiene.

[6] The facile isomerization of 5-methylene-1,3-cyclohexadiene to toluene was observed by W. J. Bailey and R. A. Baylouney, Abstracts of Papers, 138th Meeting, American Chemical Society, September, 1960, p. 73P.

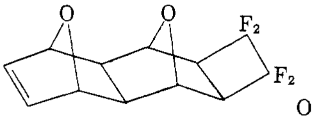
[7] For discussions pertinent to the valence tautomerism of the bicyclo[4.2.0]octa-2,4-diene/1,3,5-cyclooctatriene system, see (a) E. Vogel, O. Roos, and K. H. Disch, *Angew. Chem.*, **73**, 342 (1961); (b) A. C. Cope, A. C. Haven, Jr., F. L. Ramp, and E. R. Trumbull, *J. Am. Chem. Soc.*, **74**, 4867 (1952).

[8] W. R. Brasen, U. S. Patent 2,928,865 (1960).

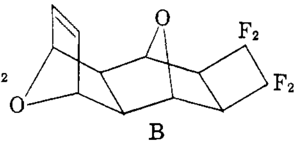
[9] The product from VIII and tetrafluoroethylene probably has the *exo* configuration by virtue of the preferred orientation of addition to bicyclo[2.2.1]heptenes, the high temperature used in its formation, and its lower melting point; see, for example: R. B. Woodward and H. Baer, *J. Am. Chem. Soc.*, **70**, 1161 (1948). The co-product from cyclopentadiene and TFCB should then have the *endo* configuration.

drogen chloride affords pure X after an additional crystallization.[10]

The 2:1 product fraction is a mixture of isomeric compounds. Two constant melting fractions have nearly identical infrared absorption spectra. No evidence of polymorphism was observed. When pure X is reacted with furan, a mixture of the same 2:1 adducts (XI) is formed,[11] while reaction with dimethylbutadiene gives a Diels-Alder adduct (XII).



A



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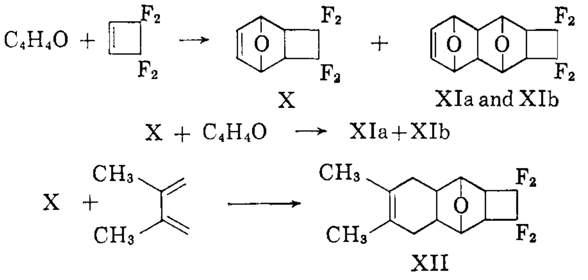
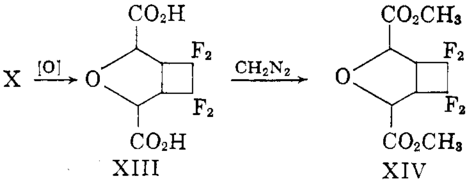
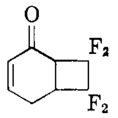


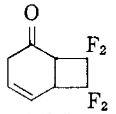
Oxidation of X with potassium permanganate gives the dibasic acid XIII which was converted to its dimethyl ester XIV.



When vapors of X are passed over a boron phosphate catalyst,[12] a small amount of material melting at 149° may be isolated. This product is isomeric with X, but its infrared spectrum has peaks for carbonyl absorption at 5.80 and 5.97 μ. The position of the ultraviolet absorption maximum at 230 mμ is typical of an α,β-unsaturated ketone, but the extinction coefficient (5180) is only half as great as would be expected for such a structure.[13] The NMR spectrum is complex and confirms the presence of a mixture. The data are consistent with that expected from a mixture of the isomeric α,β- and β,γ- unsaturated ketones (XV and XVI).



XV



XVI

Condensation of 2,5-dimethylfuran with TFCB gives a 1:1 adduct analogous to X as the only detectable product.

Experimental[14]

7,7,8,8-Tetrafluorobicyclo[4.2.0]oct-3-ene (Ia).—Four 100-ml. Carius tubes, each charged with 20 g. (0.16 mole) of TFCB, 0.1 g. of hydroquinone, and about 16 g. (0.3 mole) of butadiene were heated for 40 hr. at 140°. The combined product was distilled to give 2.8 g. of TFCB; 22.3 g. of butadiene dimer fraction, b.p. 51.5–82.6°/102 mm.; and 84.3 g. (74.5%) of Ia, b.p. 84–86°/102 mm., $n^{25}D$ 1.4043. Similar yields were obtained in runs carried out at 100°. Infrared: 3.29, 3.43, 3.51, 6.02, 6.94, 7.25, 8.20, 9.20, and 13.85 μ.

7,7,8,8-Tetrafluorobicyclo[4.2.0]octane (IIIa).—Nine grams of Ia was hydrogenated in a Parr apparatus in 25 ml. of ethanol containing 0.1 g. of platinum oxide. One mole of hydrogen was adsorbed. Distillation gave 5.25 g. of liquid product, b.p. 82°/100 mm., $n^{25}D$ 1.3920. Infrared: 3.37, 3.46, 6.88, 6.92, 7.20, 7.39, 7.52, 7.69, 8.0–9.9, 10.22, 10.89, 11.27, 11.78, 12.08, 12.80, 13.58, and 14.07 μ. F—NMR: 2483, 2696, 3114, 3327 cps. (w,s,s,w).

Anal. Calcd. for $C_8H_{10}F_4$: C, 52.74; H, 5.54; F, 41.72. Found: C, 52.64; H, 5.57; F, 41.75.

7,7,8,8-Tetrafluorobenzocyclobutene (IIa).—A stirred mixture of 20 g. of Ia and 3 g. of 10% palladium-on-carbon was refluxed for 20 hr. The mixture was diluted with ether, filtered, and distilled to give a series of fractions totaling 14.5 g., b.p. 77–81.5°/110 mm. Fluorine resonance spectra indicated a composition of 27% IIa and 73% IIIa. Separation was achieved by vapor phase chromatography on a 12 ft. by ¾ in. column packed with 30% perfluoroalkylpyromellitate on "Chromasorb" at 125° with a helium sweep of 810 ml./min. The aromatic compound (IIa) was obtained as the fraction which eluted at 26.5 min.; b.p. 154–155°, $n^{25}D$ 1.4310. Infrared: 3.22, 6.16, 6.75, 7.33, 7.69, 7.95, 8.97, 10.35, 11.28, 11.88, 13.22, 13.69 μ. F—NMR: single unsplit peak at 2155 c.p.s.

Anal. Calcd. for $C_8H_4F_4$: C, 54.56; H, 2.29; F, 43.15. Found: C, 54.57; H, 2.06; F, 41.58.

Passage of Ia through a "Vycor" tube packed with 0.6% Pt on silica catalyst at 350° gave a 5–10% conversion to IIa.

3,4 - Dibromo - 7,7,8,8 - tetrafluorobicyclo[4.2.0]octane (IVa).—A solution of 23 g. of bromine in 10 ml. of methylene chloride was added dropwise to a stirred solution of 25 g. of Ia in 25 ml. of methylene chloride. Evaporation of the solvent gave 44.3 g. (94%) of crude dibromide, m.p. 40.5–42°. Crystallization from pentane at −80° gave white plates, m.p. 41–42°.

Anal. Calcd. for $C_8H_8Br_2F_4$: Br, 47.01; F, 22.35. Found: Br, 46.81; F, 22.34.

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[10] This adduct would have the *exo* configuration if stabilities in this series parallel those of the maleic anhydride adducts of furan; see Woodward and Baer (ref. 9) and H. Stockmann, *J. Org. Chem.*, **26**, 2025 (1961).

[11] Structures A and B are favored for these products on the following grounds: Of the eight possible isomers, the four with an *endo*-cyclobutane ring are considered unlikely for the reason expressed in footnote 10. Models of the remaining isomers suggest that A and B should be the most stable. This is further supported by the observations of Stockmann (footnote 10) who found that these same configurations of the oxygen-bridged rings are found exclusively in the product from two moles of furan and acetylenedicarboxylic acid.

[12] The boron phosphate catalyst is prepared by heating a mixture of orthoboric acid and phosphoric acid on a steam bath. See C. Ellis, "The Chemistry of Petroleum Derivatives," Vol. II, Reinhold, New York, 1937, p. 115.

[13] E. A. Gillam and E. S. Stern, "An Introduction to Electron Absorption Spectroscopy in Organic Chemistry," Edward Arnold, Ltd., London, 1954, p. 90.

[14] Melting points are corrected. The fluorine NMR spectra were determined on a Varian Associates nuclear magnetic spectrometer at 56.4 Mc./sec. using Freon 112 as an external reference. The proton resonance spectra were determined on the same instrument at 60 Mc./sec. using tetramethylsilane as an external reference. Positive values are assigned to frequencies at a higher field with regard to the reference.

7,7,8-Trifluorobenzocyclobutene (VII).—A solution of 51 g. of IV in 50 ml. of methanol was mixed with a stirred solution of 30 g. of 85% potassium hydroxide in 100 ml. of methanol. After the original exothermic reaction subsided, refluxing was maintained by external heating for 1 hr. The cooled mixture was diluted with 600 ml. of water and the product was separated. The aqueous phase was extracted five times with 50-ml. portions of ether. The product and ether extracts were combined, washed with water, dried over magnesium sulfate, and distilled to remove the ether. The residue was distilled rapidly through a short column at 5 mm. Another distillation gave 15.4 g. (65%) of VII, b.p. 74.5°/38 mm., $n^{25}\mathrm{D}$ 1.4609. Infrared: 3.22, 3.35, 6.28, 6.76, 7.38–10.20, 11.34, 11.67, 13.09, 13.30, 13.48, 13.85, 14.80 μ. F—NMR: 1610, 1810, 2300, 2500 c.p.s. (w,s,s,w, doublets, CF_2); 6070, 6130 c.p.s. (each split into triplets; CHF). Proton—NMR: −409 c.p.s. (ArH); −354, −295 (split into doublets; CHF).

Anal. Calcd. for $C_8H_5F_3$: C, 60.78; H, 3.19; F, 36.06. Found: C, 60.73; H, 3.33; F, 36.14.

3,4-Dimethyl-7,7,8,8-tetrafluorobicyclo[4.2.0]oct-3-ene (Ib).—A solution of 65 g. (0.52 mole) of TFCB and 85 g. (1.04 moles) of dimethylbutadiene was distributed among five 100-ml. Carius tubes which were heated on a steam bath for 17 hr. The combined product was distilled to give 30.5 g. of TFCB; 42.3 g. of dimethylbutadiene; and 54.5 g. (95.5%) of Ib, b.p. 86–87.5°/39 mm., $n^{25}\mathrm{D}$ 1.4203. Infrared: 6.91, 7.25, 7.49, 7.73, 7.99, 8.31, 8.66, 8.92, 9.19, 9.51, and 10.21 μ. F—NMR: 2470, 2670, 3270, 3490 c.p.s. (w,s,s,w).

Anal. Calcd. for $C_{10}H_{12}F_4$: C, 57.70; H, 5.79; F, 36.51. Found: C, 57.28; H, 5.88; F, 35.61.

3,4 - Dimethyl - 7,7,8,8 - tetrafluorobicyclo[4.2.0]octane (IIIb).—After hydrogenation of 9.4 g. of Ib in 10 ml. of ethanol in a Parr apparatus using 0.1 g. of Pt oxide catalyst, distillation gave 5.05 g. of colorless liquid, b.p. 85.8–87.2°/40 mm., $n^{25}\mathrm{D}$ 1.4064. Infrared: 3.38, 3.46, 6.80, 6.87, 6.95, 7.2–9.5, 9.95, 10.25, 10.38, 10.82, 11.62, 13.29, 13.60 μ. F—NMR: 2485, 2700, 3060, 3275 c.p.s. (w,s,s,w).

Anal. Calcd. for $C_{10}H_{14}F_4$: C, 57.14; H, 6.71; F, 36.16. Found: C, 57.49; H, 7.08; F, 36.25.

3,4-Dimethyl-7,7,8,8-tetrafluorobenzocyclobutene (IIb).—A stirred mixture of 30 g. of Ib and 5 g. of 10% palladium-on-carbon was refluxed, with stirring, for 16 hr. The mixture was cooled, diluted with hexane, and filtered. A total of 10.5 g. (35%) of IIb was isolated by repeatedly cooling the solution to −80° and filtering through a cold funnel. Crystallization from hexane gave short colorless needles, m.p. 74–75°. Infrared: 6.18, 6.81, 6.87, 7.19–9.18, 10.18, 11.43, 12.04, 13.39, and 13.65 μ. F—NMR: Single unsplit peak at 2060 c.p.s. ($CDCl_3$).

Anal. Calcd. for $C_{10}H_8F_4$: C, 58.83; H, 3.95; F, 37.22. Found: C, 59.00; H, 4.20; F, 36.92.

The hexane filtrate was distilled to give a series of fractions totaling 13.5 g., b.p. 76–84.5°, $n^{25}\mathrm{D}$ 1.4022–1.4088. Infrared and fluorine resonance spectra indicated the presence of IIb, IIIb, and unidentified products.

3,3,4,4-Tetrafluorotricyclo[4.2.1.0^{2,5}]non-7-ene (IXa and IXb).—A mixture of 6.3 g. (0.05 mole) of TFCB and 13.2 g. (0.2 mole) of freshly distilled cyclopentadiene was charged into a Carius tube which was then sealed and heated at 90° for 24 hr. Distillation afforded a mixture of product and dicyclopentadiene, b.p. 67–74°/45 mm. Analytical gas chromatography on a column of "Silicone 200" oil on firebrick showed the product to be two materials in a ratio of 53:47. Preparative scale gas chromatography on a similar column confirmed this ratio and showed the total product to be present in 60% yield. The isomer (a) present in larger amount boiled at 67°/45 mm., $n^{25}\mathrm{D}$ 1.4179, and was identical to that previously prepared by reaction of tetrafluoroethylene with bicycloheptadiene (lit.,[8] b.p. 67°/45 mm.). The second isomer (b) melted at 25° and boiled at 70°/45 mm., $n^{25}\mathrm{D}$ 1.4216. The infrared and NMR spectra were similar. Infrared: Isomer (a)—7.39, 7.99, 8.54, 8.99, 9.29, 9.92, 12.68, 13.05, 13.15, and 14.25 μ. Isomer (b)—7.85, 7.67, 7.78, 7.94, 8.02, 8.09, 8.56, 8.88, 8.95, 9.07, 9.46, 9.92, 11.66, 11.75, 11.86, 12.94, 13.04, and 13.86 μ. F—NMR: Isomer (a)—2480, 2700, 2930, 3175 c.p.s. (w,s,s,w); isomer (b)—2235, 2450, 2960, 3175 c.p.s. (w,s,s,w).

3,3,4,4-Tetrafluoro-9-oxatricyclo[4.2.1.0^{2,5}]non-7-ene (X) and 1,1,2,2-tetrafluoro-1,2,2a,3,3a,4,7,7a,8,8a-decahydro-3,-8,4,7 - diepoxycyclobuta[*b*]naphthalene (XIa and XIb).—A mixture of 49 g. (0.72 mole) of furan and 49 g. (0.39 mole) of TFCB was distributed among three 100-ml. Carius tubes and heated on a steam bath for 40 hr. The combined product was separated by ether extraction. The ether-soluble material consisted of 50.2 g. of white powder, m.p. 75–84°. The white ether-insoluble solid, m.p. 165–200°, weighed 28 g.

Ether-Soluble Fraction.—Crystallization from methanol did not affect purification. A solution of 9.9 g. of the crude adduct in 30 ml. of methanol and 6 g. of anhydrous hydrogen chloride was sealed in a Carius tube and heated on a steam bath for 5 hr.; a 77% yield of pure X was isolated after crystallization from methanol, m.p. 99.5–100°. Infrared: 7.38, 7.61, 8.09, 8.14, 8.48, 8.56, 8.85, 8.96, 9.04, 9.15, 9.52, 9.82, 11.04, 12.92, 14.05, and 14.14 μ. F—NMR: 2620, 2835, 3325, 3545 c.p.s. (w,s,s,w; $CDCl_3$).

Anal. Calcd. for $C_8H_6F_4O$: C, 49.49; H, 3.12; F, 39.15. Found: C, 49.35; H, 3.54; F, 39.10.

Isomerization.—Twelve grams of X was slowly dropped through a column packed with granular boron phosphate catalyst heated to 270–290°. Nitrogen was used as a carrier gas. The product was condensed in a trap cooled in liquid nitrogen. A 30% recovery of X was obtained along with an oil which yielded 1.3 g. of white solid, m.p. 147.5–149.5° (from ethanol). Infrared: 5.79, 5.97, 7.28, 7.36, 7.58, 8.06, 8.20, 8.31, 8.68, 8.90, 9.20, 9.34, 12.51, 13.06, and 13.53 μ. Ultraviolet spectrum: $\lambda_{\max}$ 230 mμ, ϵ 5180; $\lambda_{\max}$ 305 mμ, ϵ 19 (ethanol)

Anal. Calcd. for $C_8H_6F_4O$: C, 49.49; H, 3.12; F, 39.15. Found: C, 49.53; H, 3.55; F, 38.50.

Ether-Insoluble Fraction.—Fractional crystallization from methanol afforded separation into two components. Eight grams of crude product yielded 1.0 g. of white needles, m.p. 229–230°, and 4.2 g. of white needles, m.p. 262–265°. The infrared spectra of the two forms and the original mixture were virtually identical. Infrared: 3.32, 7.32, 7.87, 7.92, 8.46, 8.87, 8.93, 9.18, 9.60, 9.80, 11.12, 11.97, and 14.90 μ.

Anal. Calcd. for $C_{12}H_{10}F_4O_2$: C, 54.97; H, 3.85; F, 28.99. Found (230° isomer): C, 55.01; H, 4.33; F, 28.73. (265° isomer): C, 54.90; H, 4.40; F, 28.74.

A 2.90-g. sample of pure X and 4.7 g. of furan in a Carius tube was heated on a steam bath for 22 hr. Unchanged furan was allowed to evaporate. Extraction of the remaining white solid gave 1.82 g. of X, m.p. 83–87°, and 1.27 g. of ether-insoluble material, m.p. 177–192°. Fractional crystallization of the insoluble fraction showed it consisted of XIa and XIb.

1,1,2,2-Tetrafluoro-1,2,2a,3,3a,4,7,7a,8,8a-decahydro-6,7-dimethyl-3,8-epoxycyclobuta[*b*]naphthalene (XII).—A mixture of 5 g. (0.025 mole) of X and 10 g. (0.13 mole) of 2,3-dimethylbutadiene in a Carius tube was heated on a steam bath for 22 hr. The volatile material was evaporated, leaving 6.5 g. (93%) of white powder; m.p. 153–154.5°, after crystallization from methanol. Infrared: 3.32, 3.36, 3.40, 3.49, 7.33, 7.96, 8.12, 8.45, 8.83, 8.93, 9.53, 9.91, and 10.92 μ.

Anal. Calcd. for $C_{14}H_{16}F_4O$: C, 60.88; H, 5.84; F, 27.50. Found: C, 61.21; H, 5.77; F, 27.16.

6,6,7,7-Tetrafluoro-3-oxabicyclo[3.2.0]heptane-2,4-dicarboxylic Acid (XIII).—A solution of 10 g. of X in 15 ml. of acetone was added all at once to a vigorously stirred mixture of 32.6 g. of potassium permanganate in 300 ml. of water. The temperature rose to 64° and was maintained at 60–65° for 30 min. The mixture was filtered through a "Solka Floc" mat. The filtrate was acidified with hydrochloric acid, and the product was isolated by continuous extraction with ether. There was obtained 9.95 g. (75%) of a light tan solid, m.p. 165–176°. Crystallization from hexane gave XIII as a white solid, m.p. 178–179°.

Anal. Neut. equiv.: Calcd., 129; Found, 134, 136. F—NMR: 2515, 2735, 2975, 3190 c.p.s. (w,s,s,w; H_2O).

2,4-Bis(methoxycarbonyl)-6,6,7,7-tetrafluoro-3-oxabicyclo-[3.2.0]heptane (XIV).—A solution of 6.4 g. of XIII in 50 ml. of ether was treated with an ether solution of diazomethane. Evaporation left 6.90 g. (97%) of a white solid. Two crystallizations from methanol yielded white needles, m.p. 122–124°. Infrared: 3.31, 3.36, 5.73, 7.30, 7.47, 7.78, 7.92, 7.99, 8.34, 8.76, 8.85, 9.06, 9.17, 9.48, 9.54, 10.0, 10.40, 11.33, 12.19, and 13.48 μ.

Anal. Calcd. for $C_{10}H_{10}F_4O_5$: C, 41.96; H, 3.53; F, 26.55. Found: C, 42.39; H, 3.91; F, 26.72.

1,6-Dimethyl-3,3,4,4-tetrafluoro-9-oxatricyclo[4.2.1.0^{2,5}]-non-7-ene.—A mixture of 20 g. (0.16 mole) of TFCB and 20 g. (0.21 mole) of 2,5-dimethylfuran was sealed in a Carius tube and heated on a steam bath for 49 hr. After the volatile components evaporated, 16.9 g. (40%) of brown needles remained. Sublimation at 100°/1 mm. and crystallization from methanol gave 9.5 g. of white needles, m.p. 97.5–99°. Infrared: 7.16, 7.60, 7.54, 7.58, 7.96, 8.26, 8.63, 8.69, 9.15, 9.39, 9.62, 10.9, 11.61, 12.75, 12.87, 13.87, 13.95, and 14.08 μ.

Anal. Calcd. for $C_{10}H_{10}F_4O$: C, 54.08; H, 4.54; F, 34.22. Found: C, 54.08; H, 4.73; F, 34.45.

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Condensed Cyclobutane Aromatic Compounds. XIX. The Course of Dimerization of 1,2-Dibromobenzocyclobutadiene[1]

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The generation of 1,2-dibromobenzocyclobutadiene from 1,1,2-tribromobenzocyclobutene or 1,1,2,2-tetra-bromobenzocyclobutene leads to the formation of 5,6-dibromobenzo[*a*]biphenylene. A synthesis of the latter from compounds of known structure is described. The mechanism of the dehydrobromination of $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene is discussed in the light of these observations.

It has been reported[2] that $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene reacts with excess potassium *t*-butoxide to yield a mixture of 5,10-dibromobenzo[*b*]biphenylene (II) and 1,2,5,6-tetrabromo-3,4,7,8-dibenzotricyclo[4.2.0.0^{2,5}]octadiene (III). In attempting to explain this unusual transformation, it was suggested that the initial loss of hydrogen bromide from tetrabromide I would produce first an *o*-quinodimethane intermediate (IV). Intramolecular cyclization of IV, in analogy with a closely related and established reaction,[3] would give 1,1,2-tribromobenzocyclobutene (V). Under the strongly basic reaction conditions, rapid dehydrobromination of V could occur with the generation of 1,2-dibromobenzocyclobutadiene (VI). Linear dimerization of VI would lead directly to the observed product III and, by a more obscure process involving loss of bromine, to product II.

The recent synthesis of tribromide V[4] has now allowed this hypothesis to be tested. The reaction of V with potassium *t*-butoxide gave none of the expected products II and III, but instead an excellent yield of an orange compound, $C_{16}H_8Br_2$, shown to be 5,6-dibromobenzo[*a*]biphenylene (VII). The formation of VII is envisaged as proceeding *via* 1,2-dibromobenzocyclobutadiene (VI) which dimerizes not in a linear manner to give rise to II and III, but rather in the angular fashion observed previously in the dimerization of 1-bromobenzocyclobutadiene[5] and of benzocyclobutadiene itself.[6] The initial dimerization product VIII apparently lost the elements of molecular bromine during the course of the reaction and was aromatized to bromide VII. Although VIII could not be isolated directly by dehydrobromination of tribromide V, a colorless compound of composition VIII was obtained by the direct addition of bromide to the benzobiphenylene derivative VII. Reaction of tetrabromide VIII with potassium *t*-butoxide easily regenerated the orange bromide VII, strengthening the assumption that VIII is indeed an intermediate in the conversion of V into VII. The possibility that VIII in solution is in equilibrium with a small amount of dibromide VII and elemental bromine was discounted by warming a solution of VIII in *t*-butyl alcohol with phenol, a good bromine scavanger, when VIII was recovered unchanged. One must conclude therefore that the conversion of VIII into VII by *t*-butoxide ion involves attack upon one of the tertiary bromines in the molecule with concommitant elimination of the second tertiary bromine as bromide ion.

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(1) For a preliminary communication of this subject, see M. P. Cava and K. Muth, *Tetrahedron Letters*, No. 42, 140 (1961).

(2) F. R. Jensen and W. E. Coleman, *Tetrahedron Letters*, No. 20, 7 (1959).

(3) M. P. Cava, A. A. Deana, and K. Muth, *J. Am. Chem. Soc.*, **81**, 6458 (1959).

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