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1,1,4,4-Tetrafluoro-1,2,3-butatriene

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1,1,4,4-Tetrafluoro-1,2,3-butatriene has been prepared by the dehydrobromination of 1,4-dibromo-1,1,4,4-tetrafluoro-2-butene. This butatriene is a colorless liquid boiling at about −5°. It reacts with two moles of bromine to give 1,2,3,4-tetrabromo-1,1,4,4-tetrafluoro-2-butene and with three moles of chlorine to give 1,2,2,3,3,4-hexachloro-1,1,4,4-tetrafluorobutane. In the liquid state, 1,1,4,4-tetrafluoro-1,2,3-butatriene detonates violently at temperatures near 0°.

During the course of studies on the chemistry and stability of compounds having fluorine on unsaturated carbon, we have prepared 1,1,4,4-tetrafluoro-1,2,3-butatriene, $CF_2{=}C{=}C{=}CF_2$. This compound together with the recently reported[1] tetrafluoroallene comprise the first examples of a new class of perfluoroderivatives, *i.e.*, the perfluorocumulenes. The triene was obtained in approximately 50% yields by dehydrobromination of 1,4-dibromo-1,1,4,4-tetrafluoro-2-butene over molten potassium hydroxide. It was identified by mass spectrographic analysis that indicated a molecular formula of C_4F_4; by infrared spectrographic analysis that indicated the presence of a fluorinated carbon–carbon double bond (Fig. 1); and by fluorine nuclear magnetic resonance (n.m.r.) that indicated only one type of fluorine atom. Resonance was observed at +885 c.p.s., which is in the region expected for fluorine on unsaturated carbon.

The structure of 1,1,4,4-tetrafluoro-1,2,3-butatriene was substantiated by conversion of the triene to derivatives that were identified unequivocally. These derivatives were bromodifluoroacetic acid and 1,2,2,3,3,4-hexachloro-1,1,4,4-tetrafluorobutane. Their preparation and identification is illustrated in Fig. 2.

Reaction of the triene with two moles of bromine gave 1,2,3,4-tetrabromo-1,1,4,4-tetrafluoro-2-butene. This compound upon oxidation with permanganate was converted to bromodifluoroacetic acid.[2] The acid was identified as its *p*-chlorophenylammonium salt, which is an easily crystallizable compound melting at 112–113°.

Inasmuch as bromodifluoroacetic acid has not been well characterized in the literature, it appeared advisable to prepare it from 1,1,4,4-tetrafluoro-1,3-butadiene, the structure of which has been established. Bromination of the tetrafluorobutadiene gave 1,4-dibromo-1,1,4,4-tetrafluoro-2-butene. Oxidation of this dibromide with permanganate led to bromodifluoroacetic acid identical to that from tetrafluorobutatriene as indicated by boiling point, infrared absorption and melting point of its *p*-chlorophenylammonium salt. When the dibromide was oxidized with a limited quantity of permanganate, a second compound, 1,4-dibromo-1,1,4,4-tetrafluoro-2,3-butanediol, was formed in addition to bromodifluoroacetic acid. Further oxidation of the glycol with permanganate converted it to bromodifluoroacetic acid.

Upon chlorination, 1,1,4,4-tetrafluoro-1,2,3-butatriene added three moles of chlorine to form 1,2,2,3,-3,4 - hexachloro - 1,1,4,4 - tetrafluorobutane.[3] This hexachloro compound was also formed from 1,1,4,4-tetrafluoro-1,3-butadiene by a series of chlorination and dehydrochlorination reactions. These are illustrated in Fig. 2. The infrared spectra of the two samples of hexachlorotetrafluorobutane were identical with the published infrared spectrum[4] for 1,2,2,3,3,4-hexachloro-1,1,4,4-tetrafluorobutane prepared by an alternate method.

1,1,4,4-Tetrafluoro-1,2,3-butatriene is a colorless gas at room temperature. It condenses to a colorless, mobile liquid that boils at about −5°. An accurate boiling point was not obtained because of the explosive nature of the triene. Liquid samples of the 1,1,4,4-tetrafluoro-1,2,3-butatriene, either at atmospheric pressure or in sealed glass tubes, detonate with considerable force at about −5°. Small samples of the liquid tetrafluorobutatriene on storage in sealed, evacuated tubes at −80° for 8–12 days appeared to change to a colorless, transparent solid. However, on warming to about −5°, all tubes detonated violently. Tetrafluorobutatriene also reacts with oxygen. When a receiver containing a small amount of the triene was exposed to air for a few seconds, a violent decomposition accompanied by a brilliant flash of light occurred.

Although liquid samples are treacherously explosive, gaseous 1,1,4,4-tetrafluoro-1,2,3-butatriene appears to be safe to handle. However, gas samples stored at atmospheric pressure and room temperature in glass containers polymerize with the formation of a pale yellow film on the walls of the container. Dilution with a large amount of oxygen-free nitrogen did not inhibit polymerization.

Experimental[5]

1,1,4,4-Tetrafluoro-1,2,3-butatriene.[6]—A mixture of 75 g. of 85% potassium hydroxide and 7.5 ml. of water in a 300-ml. round-bottom flask fitted with a thermometer, dropping funnel, gas inlet tube and condenser connected to a receiver cooled in solid carbon dioxide–acetone mixture was melted under an atmosphere of deoxygenated nitrogen. The mixture was stirred by means of a Teflon tetrafluoroethylene-coated magnetic stirring bar. The temperature was adjusted to 140° and 10 g. of 1,4-dibromo-1,1,4,4-tetrafluoro-2-butene[6] was added dropwise during the course of 30 minutes. The reaction was exothermic and the temperature was maintained at 110–150° by controlling the rate of addi-

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[1] T. L. Jacobs and R. S. Bauer, THIS JOURNAL, **81**, 606 (1959).

[2] F. Swartz, *Bull. acad. roy. Belg.*, 597 (1903); *Chem. Zentr.*, **74**, II, 709 (1903).

[3] W. T. Miller, U. S. Patents 2,668,182, issued February 2, 1954, and 2,716,141, issued August 23, 1955.

[4] American Petroleum Institute Research Project 44, Serial No. 1390.

[5] Melting and boiling points are not corrected.

[6] E. L. Martin and R. E. Putnam, U. S. Patent 2,888,447 issued May 26, 1959.

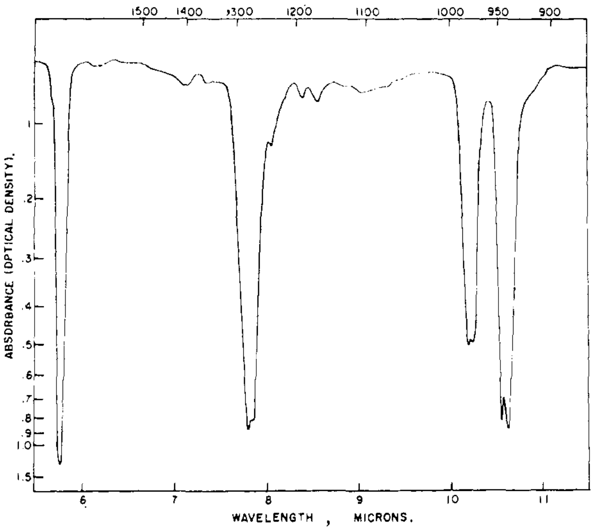

Fig. 1.—Infrared spectrum of 1,1,4,4-tetrafluoro-1,2,3-butatriene.

tion of the dibromide. A continuous stream of deoxygenated nitrogen was passed over the molten potassium hydroxide, and the tetrafluorobutatriene was collected in the receiver. In most runs, approximately 2 ml. of a colorless liquid was collected. This liquid was essentially pure tetrafluorobutatriene as determined by mass spectrographic analysis. The reaction product was transferred by distillation under reduced pressure to small glass tubes. The fluorine nuclear magnetic resonance spectrum of a sample of the liquid at about −50°[7] had a single resonance at +885 c.p.s. indicating only one type of fluorine. The infrared spectrum obtained on gas samples, showed absorption at 5.77 μ indicating the presence of a fluorinated carbon–carbon double bond (Fig. 1) and at 7.8 μ for carbon–fluorine bonds. Mass spectrographic analysis of a mixture of the tetrafluorobutatriene and deoxygenated nitrogen indicated that the material had a mass of 124 which corresponds to C_4F_4.

1,2,3,4-Tetrabromo-1,1,4,4-tetrafluoro-2-butene.—The tetrafluorobutatriene obtained by adding 28.6 g. of 1,4-dibromo-1,1,4,4-tetrafluoro-2-butene to a mixture of 100 g. of 85% potassium hydroxide and 8.5 ml. of water at 160–180°, as described previously, was passed into a solution of 40 g. of bromine in 50 ml. of carbon tetrachloride at −10°. After standing at room temperature for two days in a closed container, the reaction mixture was fractionated. The fraction boiling at 102–104° (28 mm.) weighed 20 g.

Anal. Calcd. for $C_4Br_4F_4$: Br, 72.05. Found: Br, 72.10.

Bromodifluoroacetic Acid. (a) From 1,4-Dibromo-1,1,4,4-tetrafluoro-2-butene.—To a vigorously stirred mixture of 28.6 g. of 1,4-dibromo-1,1,4,4-tetrafluoro-2-butene and 30 ml. of water at 20° was added slowly a solution of 33 g. of potassium permanganate and 3 g. of potassium carbonate in 250 ml. of water. As soon as the addition of the permanganate was complete, the temperature was increased to 30° and the manganese dioxide was reduced by means of sulfur dioxide. The solution was made strongly acid with sulfuric acid and extracted continuously with ether for 24 hours. The ethereal extract was dried with magnesium sulfate, concentrated, and the residue distilled. The fraction boiling at 87° (82 mm.) solidified on standing at room temperature and had a neutral equivalent of 177 (theory 175).

The addition of one equivalent of *p*-chloroaniline in a small volume of benzene to one equivalent of bromodifluoroacetic acid in a small volume of benzene gave a crystalline salt. Crystallization of the salt from benzene gave colorless plates melting at 112–113°.

Anal. Calcd. for $C_8H_7O_2NBrClF_2$: N, 4.63; neut. equiv., 302.4. Found: N, 4.48; neut. equiv., 302.4.

(b) From 1,2,3,4-Tetrabromo-1,1,4,4-tetrafluoro-2-butene.—To a vigorously stirred mixture of 30 g. of 1,2,3,4-tetrabromo-1,1,4,4-tetrafluoro-2-butene and 50 ml. of water was added slowly a solution of 14 g. of potassium permanganate and 16 g. of sodium bicarbonate in 100 ml. of water at 30°. After the addition of the permanganate was complete, the solution was decolorized with sulfur dioxide, was made strongly acid by the addition of concentrated hydrochloric acid, and was extracted continuously with ether for 26 hours. The ethereal solution was dried with magnesium sulfate, was concentrated and the residue was distilled. There was obtained 20 g. of bromodifluoroacetic acid boiling at 87° (82 mm.) and solidifying on standing at room temperature. The infrared spectrum of this sample of bromodifluoroacetic acid was identical with that of the bromodifluoroacetic acid prepared as described above. The *p*-chloroaniline salt of this sample of bromodifluoroacetic acid melted at 112–113° either alone or in admixture with the salt described above.

1,4-Dibromo-1,1,4,4-tetrafluoro-2,3-butanediol.—To a vigorously stirred mixture of 37.2 g. of 1,4-dibromo-1,1,4,4-tetrafluoro-2-butene and 50 ml. of water was added slowly a solution of 30 g. of potassium permanganate and 5 g. of sodium carbonate in 300 ml. of water at 5–10°. The

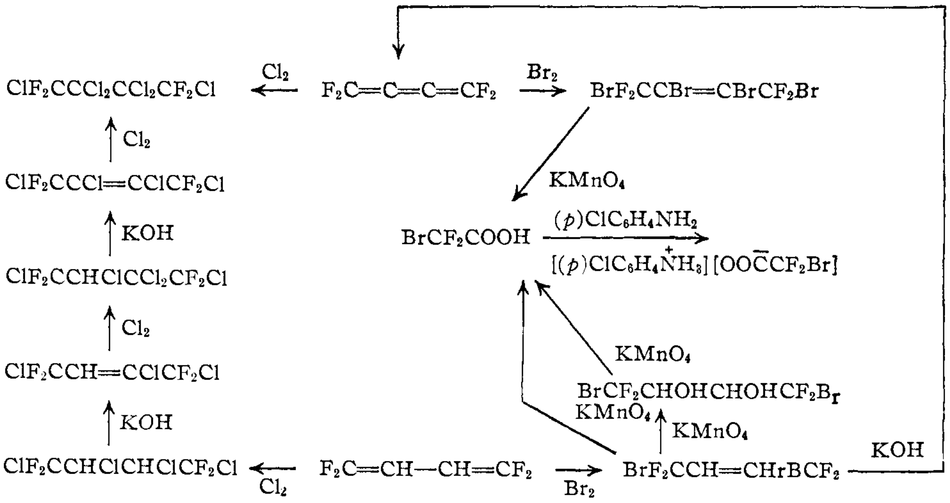

Fig. 2.—Bromo- and chloro- derivatives of 1,1,4,4-tetrafluoro-1,2,3-butatriene.

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(7) N.m.r. spectra were obtained by means of a high resolution nuclear magnetic resonance spectrometer and associated electromagnet, both manufactured by Varian Associates, Palo Alto, Calif., operating at 40 Mc. and approximately 10,000 gauss. Spectra were calibrated in terms of displacements in cycles per second (c.p.s.) from the fluorine resonance of trifluoroacetic acid. Positive frequency displacements indicate resonances occurring at lower field relative to the reference.

reaction mixture was decolorized with sulfur dioxide, the aqueous solution was made strongly acid with concentrated hydrochloric acid and was extracted continuously with ether for 24 hours. The ethereal extract was dried with magnesium sulfate, was concentrated and the residue was distilled. After a small amount of bromodifluoroacetic acid had distilled, 42 g. of 1,4-dibromo-1,1,4,4-tetrafluoro-2,3-butanediol boiling at 80–82° (1 mm.) and solidifying immediately was obtained. Sublimation at 0.25 mm. from an oil-bath at 70° gave colorless crystals melting at 74–75°.

Anal. Calcd. for $C_4H_4O_2Br_2F_4$: C, 15.00; H, 1.26; Br, 49.95. Found: C, 15.05; H, 1.57; Br, 50.01.

Smaller quantities of this same compound were isolated in oxidations of the dibromotetrafluoro-2-butene at 20° as described previously. Infrared analysis showed absorption in the 3.0 μ region consistent with the diol structure The fluorine n.m.r. spectrum[8] at a temperature above the melting point showed a doublet centered at +752 c.p.s. relative to trifluoroacetic acid at zero and was consistent with the proposed structure. Alkaline permanganate oxidation of the 1,4-dibromo-1,1,4,4-tetrafluoro-2,3-butanediol in aqueous solution gave bromodifluoroacetic acid, identified as the *p*-chlorophenylammonium salt, m.p. 112–113°, alone or in admixture with a known sample of the salt.

1,2,3,4-Tetrachloro-1,1,4,4-tetrafluorobutane.[6]—To a solution of 93.5 g. of 1,1,4,4-tetrafluoro-1,3-butadiene[9] in 25 ml. of methylene chloride was added slowly by distillation 106 g. of chlorine. The reaction flask was cooled in ice and a condenser cooled with solid carbon dioxide–acetone was used to condense the low-boiling reactants. After the addition of the chlorine was complete, the temperature was increased gradually to 85° during the course of two hours. The fraction boiling at 72–74° (60 mm.) weighed 184 g.

Anal. Calcd. for $C_4H_2Cl_4F_4$: C, 17.95; H, 0.75; Cl, 52.93; F, 28.37; mol. wt., 268. Found: C, 17.94; H, 1.16; Cl, 52.81; F, 28.30; mol. wt., 270.

1,2,4-Trichloro-1,1,4,4-tetrafluoro-2-butene.—A mixture of 1,2,3,4-tetrachloro-1,1,4,4-tetrafluorobutane, 120 g. of 85% potassium hydroxide and 400 ml. of water was gradually brought to reflux and heated under reflux gently for 8 hours. The reaction mixture was steam distilled, and the organic layer was separated and dried. The yield of halogenated butene boiling at 100–102° was 64 g. Infrared absorption was observed at 3.2 (=CH), at 6.0 (C=C), and at 8–9 μ (strong absorption characteristic of C–F). The fluorine nuclear magnetic resonance spectrum was consistent with the 2-butene structure.

1,2,2,3,4-Pentachloro-1,1,4,4-tetrafluorobutane.–A mixture of 66 g. of 1,2,4-trichloro-1,1,4,4-tetrafluoro-2-butene and 21 g. of chlorine was gradually heated to 60° during the course of 6 hours. A solid carbon dioxide–acetone cooled condenser was used to condense the chlorine. Fractionation of the reaction product gave 92 g. of 1,2,2,3,4-pentachloro-1,1,4,4-tetrafluorobutane boiling at 90° (49 mm.).

Anal. Calcd. for C_4HCl_5F: Cl, 58.65. Found: Cl, 58.62, 58.73.

1,2,3,4-Tetrachloro-1,1,4,4-tetrafluoro-2-butene.—A vigorously stirred mixture of 70 g. of 1,2,2,3,4-pentachloro-1,1,4,4-tetrafluorobutane, 60 g. of 85% potassium hydroxide and 200 ml. of water was refluxed gently for five hours. The organic material was recovered by steam distillation and the organic layer was separated, dried, and fractionated. The fraction boiling at 94° (215 mm.) weighed 38 g.

Anal. Calcd. for $C_4Cl_4F_4$: Cl, 53.35. Found: Cl, 53.40, 53.68.

1,2,2,3,3,4-Hexachloro-1,1,4,4-tetrafluorobutane. (a) **From 1,2,3,4-Tetrachloro-1,1,4,4-tetrafluoro-2-butene.**—A mixture of 38 g. of tetrachlorotetrafluoro-2-butene and 12 g. of chlorine was illuminated with a RS sun lamp for 10 hours. During this time, a condenser cooled with solid carbon dioxide–acetone was used to condense the chlorine. Fractionation of the reaction mixture gave 1,2,2,3,3,4-hexachloro-1,1,4,4-tetrafluorobutane, b.p. 102° (28 mm.), $n^{25}\text{D}$ 1.4581; reported[3] b.p. 125–126° (76 mm.), $n^{28}\text{D}$ 1.457.

Anal. Calcd. for $C_4Cl_6F_4$: Cl, 63.17. Found: Cl, 63.14, 63.27.

(b) **From 1,1,4,4-Tetrafluoro-1,2,3-butatriene.**—The tetrafluorobutatriene obtained by adding 28.6 g. of 1,4-dibromo-1,1,4,4-tetrafluoro-2-butene to a mixture of 100 g. of 85% potassium hydroxide and 7 ml. of water at 140–150° as previously described was passed into a solution of 28 g. of chlorine in 100 ml. of carbon tetrachloride at −20°. After addition of the tetrafluorobutatriene was complete, the reaction mixture was allowed to warm to room temperature and illuminated for 30 minutes with a RS sun lamp. Distillation of the reaction mixture gave 20 g. of a fraction boiling at 102° (28 mm.), $n^{25}\text{D}$ 1.4582. The infrared spectra of the two samples of hexachlorotetrafluorobutane were identical. They were also the same as the published infrared spectrum[4] for 1,2,2,3,3,4-hexachloro-1,1,4,4-tetrafluorobutane[3] prepared by an alternate method.

Acknowledgment.—Helpful discussions with Dr. R. E. Putnam of this Laboratory are gratefully acknowledged.

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(8) The authors wish to thank Dr. Harlan Foster for the nuclear magnetic resonance determinations.

(9) J. L. Anderson, U. S. Patent 2,743,303, issued April 24, 1956.

COMMUNICATIONS TO THE EDITOR

TOTAL SYNTHESIS OF A β-AMYRIN DERIVATIVE, OLEAN-11,12;13,18-DIENE (V)

Sir:

The β-amyrin (oleanane) series of pentacyclic triterpenes has not previously been reached by total synthesis despite the possibility of a relatively simple synthetic route involving the coupling of A/B and D/E ring moieties and subsequent closure of ring C. Such a synthesis has now been accomplished via terminal stages which are as follows. Reaction of the Grignard reagent derived from the (+)-bromide I with (±) enol lactone II afforded an oily mixture of epimeric tricyclic diketones (III) ($\nu_{\max}^{CS_2}$ 1706 cm.$^{-1}$) which was converted using potassium *t*-butoxide to a mixture of epimeric conjugated ketones (IV), $\nu_{\max}^{CS_2}$ 1668, 1606 cm.$^{-1}$, $\lambda_{\max}^{EtOH}$ 252 mμ (ϵ 14,600) (C, 84.53; H, 11.52). Treatment of IV with methyllithium produced the expected C_{30} tertiary alcohol mixture which was subjected (without separation) to acid-catalyzed cyclization using hydrogen chloride–acetic acid (saturated) at 25° for 20 hours and 55°