lent being known from the amount of sodium triphenylmethide used in the titration. Each tube gave one point on the rate curve.

The occasional appearance of a precipitate did not affect the rate. The precipitate dissolved in the acetic acid added to stop the reaction, and was presumably sodium alkoxide.

To the acidified reaction mixture was added an excess of 10% aqueous copper acetate, and the resulting copper chelate of the β-diketone extracted with ethyl ether. The ether was removed by distillation, and the residue taken up in chloroform. The solution was diluted to 100 ml. with more chloroform in a volumetric flask. The optical density of the chloroform solution then was determined in a Cenco photelometer, using a red filter. The concentration of copper chelate, and thus of the diketone, was determined by comparison of the photelometer reading with that of a series of known concentrations of the copper chelates.

The identity over the entire visible spectrum of the absorption of an authentic sample of the copper chelate of *n*-butyrylisovalerylmethane with that obtained from the reaction of methyl isobutyl ketone and ethyl butyrate under the conditions of the rate measurements showed that no interfering colored substances were present. All the copper chelates of β-diketones were found to follow the Lambert–Beer law. Although the presence of a large amount of acid interfered with the determination, presumably by preventing complete extraction of the copper chelate, it was shown experimentally that if the excess did not exceed 0.5 ml. of 1 *M* acetic acid, the colorimetric method was reproducible to within 2%.

The rate constants given in Tables I and II were calculated from the integrated equation, using the colorimetric diketone concentration obtained as just described, and the initial ester and sodio ketone concentrations. They are average constants obtained from three to six different reaction tubes kept in the thermostat for different lengths of time.

Reaction of Sodio Methyl Isobutyl Ketone with Isovalerylacetone.—An ether solution of 1.60 g. (0.016 mole) of methyl isobutyl ketone was converted to its anion with an equivalent of sodium triphenylmethide, and 2.58 g. (0.0182 mole) of isovalerylacetone added. The reaction mixture was thoroughly shaken and immediately poured onto an excess of powdered Dry Ice, the elapsed time being less than five seconds.

When carbon dioxide ceased to be evolved, water and ether were added and, after shaking, the layers were separated. The aqueous layer was extracted three times with ether and the extracts combined with the ether layer. Careful acidification of the aqueous layer (below 15°) failed to give either an oil or a precipitate, and the acidified solution gave negative tests with ferric chloride and with 2,4-dinitrophenylhydrazine. The combined ether solution was extracted several times with 10% sodium hydroxide until the ether layer failed to give a positive ferric chloride test. The sodium hydroxide solution was then acidified and extracted with ether. After distilling the ether, the residue was dissolved in methanol and the solution added to copper acetate solution. Upon filtering and air drying, a yield of 2.3 g. of copper compound was obtained, corresponding to 73% of the original isovalerylacetone.

The ether remaining after the sodium hydroxide extraction was washed with water, dried and distilled. The residue was transferred to a Büchner funnel and washed with methanol. The methanol washings were treated with 2,4-dinitrophenylhydrazine to give, after recrystallization from ethanol, 4 g. of the bright yellow 2,4-dinitrophenylhydrazone of methyl isobutyl ketone, corresponding to 89% of the original ketone. The compound melted at 93°, reported[19] m.p. 95°.

In a blank experiment, an ether solution of the sodio methyl isobutyl ketone was carbonated with Dry Ice. The mixture was extracted with water and, after extracting with ether to remove any unreacted ketone, the aqueous solution was acidified. The liberated ketone carboxylic acid was taken up in ether and, after drying, the solvent was removed. Decarboxylation was effected on the steam-bath (0.5 hr.), and the residual ketone converted to its 2,4-dinitrohydrazone. There was obtained a 70% yield of this derivative, m.p. 95°.[19]

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[19] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 262.

DURHAM, N. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Synthesis and Polymerization of Tetrafluoroallene[1,2]

BY THOMAS L. JACOBS AND RONALD S. BAUER[3,4]

RECEIVED AUGUST 28, 1958

Tetrafluoroallene was synthesized by dehydrobromination of 3-bromo-1,1,3,3-tetrafluoropropene or 1,3-dibromo-1,1,3,3-tetrafluoropropane and less satisfactorily by zinc debromination of 2,3-dibromo-1,1,3,3-tetrafluoropropene. Small amounts were also obtained by pyrolysis of 3-bromo-1,1,3,3-tetrafluoropropene. Tetrafluoroallene polymerizes at room temperature under autogenous pressure to an insoluble, sharp-melting, highly crystalline powder shown by X-ray and infrared data to be a linear polymeric fluorocarbon with the group $=CF_2$ on alternate carbons along the chain. When this polymerization was inhibited, mild heating converted the monomer to perfluoro-1,2-dimethylenecyclobutane.

Tetrafluoroallene is of special interest as a monomer which might yield useful polymers. When we began attempts to prepare this compound it had not been mentioned in the literature. In 1954, a brief report of its synthesis by the reaction of 2-chloro-3-iodo-1,1,3,3-tetrafluoropropene with zinc in dioxane appeared.[5] However, in a definitive paper published in 1957, Fainberg and Miller reported that this reaction gave an excellent yield of the coupling product, decafluoro-1,5-hexadiene,[6] and no mention was made of tetrafluoroallene or of any other low boiling products.

Dehydrohalogenation has occasionally been used to prepare allenes, but the method is usually unsatisfactory because the isomeric acetylenes accompany the desired products. There is no report in the literature of the preparation of a haloallene by this reaction. However, the hydrogen atoms

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[1] This report is taken from a dissertation submitted by Ronald S. Bauer to the graduate school of the University of California, Los Angeles, in partial fulfillment of the requirements for the Ph.D. degree, June, 1958. The material was presented at the San Francisco Meeting of the American Chemical Society, April, 1958 (Abstracts of that Meeting, p. 51-N). This research was sponsored by the Office of Ordnance Research, U. S. Army.

[2] A preliminary report of this work has appeared, T. L. Jacobs and R. S. Bauer, THIS JOURNAL, **78**, 4815 (1956).

[3] Dow Chemical Co. Fellow, 1957–1958.

[4] We wish to thank Dr. Arnold H. Fainberg for advice during earlier stages of the work.

[5] W. T. Miller, Jr., U. S. Patent 2,668,182, Feb. 2, 1954; *C. A.*, **49**, 2478 (1954).

[6] A. H. Fainberg and W. T. Miller, Jr., THIS JOURNAL, **79**, 4170 (1957).

on the central carbon atom of a system such as $CF_3CH_2CHX_2$ (X = Cl or Br), I, are relatively acidic as a result of the inductive effect of the adjacent trifluoromethyl group and are easily removed as protons to form HX. Haszeldine[7] obtained 3,3,3-trifluoropropyne in fair yield from I with dry powdered potassium hydroxide, and $CF_3CH{=}CHX$ (X = Cl or Br) gave the propyne similarly in good yield. It therefore appeared probable that strong alkali would dehydrohalogenate $CF_2XCH_2CF_2X$ or $CF_2{=}CHCF_2X$ to tetrafluoroallene, and this was found to be the case. 1,3 - Dibromo - 1,1,3,3 - tetrafluoropropane, (II), readily available from the reaction of 1,1-difluoroethylene with dibromodifluoromethane,[8] was converted by distillation from pellets of potassium hydroxide to a mixture of 3-bromo-1,1,3,3-tetrafluoropropene (III) and tetrafluoroallene (IV) which was separated to give pure III in 51% yield and IV in 5% yield; III was converted similarly to IV in 24% yield. Compound III was also

$$\underset{\text{II}}{CF_2BrCH_2CF_2Br} \longrightarrow \underset{\text{III}}{CF_2{=}CHCF_2Br} \longrightarrow \underset{\text{IV}}{CF_2{=}C{=}CF_2}$$

prepared from II with aqueous sodium hydroxide as reported by Tarrant[8] and in earlier work[2] the dehydrobromination of III was accomplished with powdered potassium hydroxide, but this was less satisfactory. Various other conditions and basic reagents were tried as described in the Experimental Part with varying success, but the method using pellet potassium hydroxide is the best yet found. When a mixture of potassium hydroxide and barium hydroxide was used, so much heat was generated that the reaction mixture burst into flame.

The possibility of dehydrohalogenating 1,3-dichloro-1,1,3,3-tetrafluoropropane or 3-chloro-1,1,-3,3-tetrafluoropropene was also attractive, but this route was abandoned after a single attempt to prepare the starting propane by free radical addition of dichlorodifluoromethane to 1,1-difluoroethylene under the conditions used for the dibromopropane had failed; the product was polymeric and may have been simply the homopolymer of 1,1-difluoroethylene.

Tetrafluoroallene was also produced in low yield by passing the vapors of III through a platinum tube at 740° and approximately 25 mm. The volatile products of this reaction always contained large amounts of carbonyl fluoride which may have been formed by high temperature oxidation of tetrafluoroallene. Further work will be done on this pyrolysis which may prove to be the best method for preparing tetrafluoroallene in view of results obtained by other workers on related compounds.[9-11]

The classical synthesis of allenes involves dehalogenation of a compound containing the grouping $>C{=}CX{-}\overset{|}{\underset{|}{C}}X$, usually with zinc, as the final step. This method was the one reported in the patent literature[5] for tetrafluoroallene from 2-chloro-3-iodo-1,1,3,3-tetrafluoropropene with zinc in dioxane as the reagent. We were unable to obtain any tetrafluoroallene in this way. Attempts were also made to dehalogenate 1,2,2,3-tetrachloro-1,1,3,3-tetrafluoropropane or 2,3-dichloro-1,1,3,3-tetrafluoropropene with zinc in such solvents as alcohol, dioxane and acetic acid, or with sodium shot in xylene, but none of the desired compound was obtained; 2,5-dichloroperfluoro-1,5-hexadiene was the main product in these reactions. Removal of phenoxyl and chlorine from 2-chloro-3-phenoxy-1,1,3,3-tetrafluoropropene (V) was also attempted, but without success.

$$\underset{\text{V}}{CF_2{=}CClCF_2OC_6H_5} \xrightarrow{\text{Metal}} \underset{\text{IV}}{F_2C{=}C{=}CF_2} + MCl + MOC_6H_5$$

A successful synthesis of tetrafluoroallene by the dehalogenation method was realized when the halogen on the central carbon atom was bromine instead of chlorine. Bromine was added to III and the resulting tribromo compound VI was dehydrobrominated to 2,3-dibromo-1,1,3,3-tetra-fluoropropene (VII) with aqueous potassium hydroxide; VII was debrominated to IV by zinc in alcohol, but the yield was only 14%. This synthetic method is more tedious and less satisfactory than the dehydrobromination procedure.

$$\underset{\text{III}}{CF_2{=}CHCF_2Br} \longrightarrow \underset{\text{VI}}{CF_2BrCHBrCF_2Br} \longrightarrow \underset{\text{VII}}{CF_2{=}CBrCF_2Br} \longrightarrow \underset{\text{IV}}{F_2C{=}C{=}CF_2}$$

One other synthetic method for tetrafluoroallene was tried. The high yields of perhalo-olefins obtained by pyrolysis of the sodium salts of perhalocarboxylic acids made the disodium salt of perfluoroglutaric acid appear to be an attractive starting material. When this salt was pyrolyzed at 230-260°, volatile products were obtained, but on the bases of their infrared spectra these seemed to be mainly perfluoroglutaric anhydride and perfluorobutyrolactone; no tetrafluoroallene could be detected.

Sodium 3-chloro-2,2,4,4-tetrafluoro-3-butenoate is even more attractive as a starting material for this pyrolytic method. The acid is not reported in the literature but it should be obtainable from the corresponding nitrile which has been prepared from 2,3-dichloro-1,1,4,4-tetrafluoropropene and sodium cyanide.[12] However, attempts to synthesize the nitrile by this method resulted in black residues from which no organic material could be extracted. The method was, therefore, abandoned.

Tetrafluoroallene is a colorless gas, b.p. −38 ± 0.5°. Its structure was established by analysis, molecular weight determination and addition of

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(7) R. N. Haszeldine, *J. Chem. Soc.*, 2495 (1951).

(8) P. Tarrant, A. M. Lovelace and M. R. Lilyquist, THIS JOURNAL, **77**, 2783 (1955).

(9) J. D. Park, A. F. Benning, F. B. Downing, J. F. Laucius and R. C. McHarness, *Ind. Eng. Chem.*, **39**, 354 (1947).

(10) F. B. Downing, A. F. Benning and R. C. McHarness, U. S. Patent 2,480,560 (Aug. 30, 1949); *C. A.*, **44**, 4922 (1950); U. S. Patent 2,551,573 (May 8, 1951); *C. A.*, **45**, 9072 (1951).

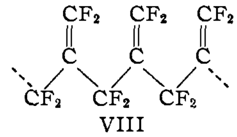
(11) J. L. Anderson, U. S. Patent 2,733,278 (Jan. 31, 1956); *C. A.*, **50**, 15575 (1956).

(12) W. T. Miller, Jr., U. S. Patent 2,671,799 (March 9, 1954); *C. A.*, **49**, 4007 (1954).

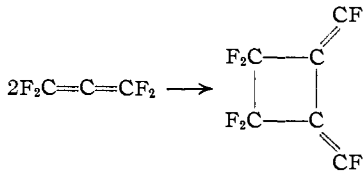
chlorine to give 1,2,2,3-tetrachloro-1,1,3,3-tetrafluoropropane. At low pressures tetrafluoroallene has three strong absorption bands in the infrared at 2065, 1243 and 1037 cm.$^{-1}$. The very intense band at 2065 cm.$^{-1}$ is believed to arise from the carbon–carbon stretching of the allene system. Although allene exhibits this absorption at 1950 cm.$^{-1}$, replacement of the hydrogens by fluorines would be expected to shift the absorption to higher frequencies[13] as in the case of 1,1-difluoroallene which absorbs at 2020 cm.$^{-1}$.[14]

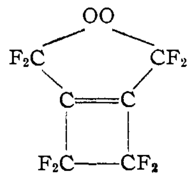
The mass spectrum of the allene shows large peaks at mass-to-charge ratios of 112(C_3F_4), 93(C_3F_3), 74(C_3F_2), 69(CF_3), 62(C_2F_2) and 31(CF).[15] Compounds such as perfluoroethylene and perfluorocyclobutane show CF_3 peaks,[16] but tetrafluoroallene gives an unusually high value at 69.

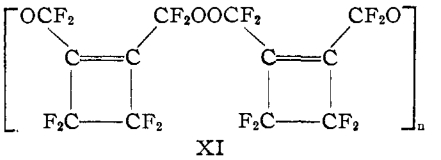
Tetrafluoroallene polymerizes at room temperature under autogenous pressure to a waxy powder which is white or faintly yellowish in color. This polymer has a relatively sharp melting range of 1 or 2 degrees, but values varied between 103 and 126° for samples prepared in different runs. The polymer was found to be insoluble in all solvents examined. It is highly crystalline and was assigned structure VIII on the basis of X-ray and infrared data.[17] The spiro structure suggested by Lebedev[18] for polymers of certain allenic hydrocarbons is excluded by the X-ray results. It was found that an ether suspension of the polymer reacts exothermally with both primary and secondary amines to give dark colored amorphous products. Such reactivity would be expected of a polymer containing $CF_2{=}C<$ groups.[19] A preliminary attempt to depolymerize the polymer under reduced pressure failed to yield the monomer at temperatures up to 700°; a mixture of products, mainly polymeric, was obtained. This pyrolysis will be investigated further.


VIII

The polymerization of tetrafluoroallene was inhibited by small amounts of Terpene B.[20] When the inhibited monomer was heated at 40° for several days, a liquid dimer was obtained. This dimer would be expected to be perfluoro-1,2-dimethylenecyclobutane (IX) by analogy with the structures established for the dimers of allenic hydrocarbons.[18] Oxidation of the dimer with permanganate gave perfluorosuccinic acid as expected, but ozonization gave a white waxy material which had the composition C_3F_4O. The infrared spectrum indicated that the structure has no double bonds with fluorines attached directly to doubly-bonded carbons, but a weak band at 1630 cm.$^{-1}$ could possibly arise from the carbon–carbon stretching of a double bond in a cyclobutene ring.[21] Structures such as X and XI appear possible for the ozonization product.


IX


X


XI

Structure IX for the dimer was confirmed by the infrared and nuclear magnetic resonance spectra. The infrared spectrum shows a strong double peak at 1730 and 1780 cm.$^{-1}$ which not only indicates the presence of an $F_2C{=}C<$group, but also suggests that there could be a conjugated system.[13] In IX the four fluorine atoms on the cyclobutane ring are equivalent and should give rise to a single n.m.r. peak. The fluorines on the methylene carbons are of two kinds if the system is essentially planar and should produce two smaller peaks of equal area. The n.m.r. spectrum is that expected.

Experimental Part[22]

3-Bromo-1,1,3,3-tetrafluoropropene (III) and Tetrafluoroallene (IV).—1,3-Dibromo-1,1,3,3-tetrafluoropropane (II) was prepared from 1,1-difluoroethylene and dibromodifluoromethane[23] as described by Tarrant, *et al.*[8] Compound II was dehydrohalogenated in a 1 l. 3-necked flask fitted with an addition funnel, glass stopper and a Claisen-type distillation head. The receiver was immersed in ice-water and in turn was vented through a Dry Ice trap. Enough potassium hydroxide pellets were placed in the flask to fill it about a quarter full. The flask was then warmed on a steam-bath and II added at such a rate that the temperature of the material distilling was between 40–50°. When the potas-

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[13] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954.

[14] A. T. Blomquist and D. T. Longone, THIS JOURNAL, **79**, 4981 (1957).

[15] A modified Westinghouse model LV mass spectrometer was used. We wish to thank Dr. Robert D. Vanselow for this spectrogram.

[16] "Catalog of Mass Spectral Data," National Bureau of Standards, American Petroleum Institute Research Project 44, spectra 361 and 362.

[17] J. D. McCullough, R. S. Bauer and T. L. Jacobs, *Chemistry & Industry*, 706 (1957).

[18] S. V. Lebedev and B. K. Merezhkovskii, *J. Russ. Phys.-Chem. Soc.*, **45**, 1249 (1913); *C. A.*, **8**, 320 (1914).

[19] R. L. Pruett, J. T. Barr, K. E. Rapp, C. T. Bahner, J. D. Gibson and R. H. Lafferty, Jr., THIS JOURNAL, **72**, 3646 (1950).

[20] Terpene B is mainly *p*-menthadiene with some *p*-cymene and *p*-menthane. We wish to thank Dr. Herman Enos of the Hercules Powder Co. for a generous sample of this inhibitor.

[21] D. E. Applequist and J. D. Roberts, THIS JOURNAL, **78**, 4012 (1956).

[22] All boiling points are uncorrected. Melting points were taken with total immersion Anschütz thermometers but were otherwise uncorrected. Infrared spectra were determined on a Perkin–Elmer double beam spectrophotometer, model 21. Analyses were carried out by Miss Heather King unless otherwise indicated.

[23] We wish to thank the Dow Chemical Co. for the gift of a generous supply of this compound.

sium hydroxide became quite discolored, the flask was cooled in ice-water and more potassium hydroxide pellets were added. After all of the starting material had been added, the flask was heated until no more product distilled.

The material in the receiver was dried with anhydr. magnesium sulfate and distilled to give 3-bromo-1,1,3,3-tetrafluoropropane. The low boiling product in the Dry Ice trap was tetrafluoroallene; it was separated by a vaporization distillation and then purified by distillation through a single center rod column.

In a typical run 200 g. of II gave 72 g. (51% yield) of 3-bromo-1,1,3,3-tetrafluoropropene, b.p. 34°, n^{25}_{D} 1.3460, and 4.4 g. (5.4% yield) of tetrafluoroallene, b.p. −38°; literature values[8] for the propene, b.p. 35°, n^{25}_{D} 1.3463.

Anal.[24] Calcd. for C_3F_4: C, 32.1; mol. wt., 112. Found: C, 31.8; mol. wt. (vapor density), 114.

Compound III was dehydrobrominated in 60-g. portions in a 500-ml. 3-necked flask equipped as for II and about a third full of potassium hydroxide pellets. About one-sixth of the III was added to the warm potassium hydroxide and as soon as the reaction started as indicated by refluxing of the liquid in the flask, III was added dropwise. More potassium hydroxide was added when the alkali became dark and sticky as in the dehydrobromination of II. The low boiling material was purified as described above. In a series of four runs, 240 g. (1.23 moles) of III gave 33.0 g. (24% yield) of IV.

The reaction of III with powdered 85% potassium hydroxide was erratic; yields varied from 0 to 15% and the reaction mixture became dark and sticky more rapidly than with pellet potassium hydroxide. Suspensions of powdered potassium hydroxide in diethyl ethers, di-*n* butyl ether or mineral oil gave only low yields. Mixing the alkali with Celite or asbestos did not prevent the caking and did not improve yields.

Other dehydrohalogenating reagents were also tried, such as 95% potassium hydroxide, sodium hydroxide, sodium carbonate, lithium hydroxide, and calcium hydroxide, but these reagents either did not react or they produced lower yields than ordinary potassium hydroxide.

It was found that both II and III could be dehydrobrominated in the vapor phase. Preliminary experiments with sodium hydroxide on asbestos (Ascarite) at room temperature were not satisfactory and less than 2% of III was converted to the allene. It seems probable, however, that the procedure could be improved to make it a practical preparative method if the proper base and conditions were employed.

1,2,3-Tribromo-1,1,3,3-tetrafluoropropane (VI).—To 130 g. (0.674 mole) of refluxing 3-bromo-1,1,3,3-tetrafluoropropene (III) was added dropwise 100 g. of bromine. The reaction flask was illuminated with a "Mineralight" (mercury vapor bulb (G. E., H-100, FL-4) having a filter with maximum transmission at 365 mμ). Uptake of bromine was rapid at first, but decreased as the reaction proceeded. After two days the reaction appeared to be complete as evidenced by the excess bromine. The reaction mixture was washed with 35 ml. of 5% sodium sulfite solution. There was obtained 230 g. of a milky-white organic layer, which when dried with magnesium sulfate was found to be almost pure tribromide, b.p. 59.2–59.3° (32 mm.), n^{25}_{D} 1.4489, yield 96%; Infrared spectrum (neat), 2920(w), 1308(s), 1090–1210(vs), 1010–1030(s), 945(s), 920(s), 848(m), 812 (s), 785(s), 768(m), 758(m), 720(s), 700(s) cm.$^{-1}$.

Anal. Calcd. for $C_3Br_3F_4H$: C, 10.21; H, 0.29. Found: C, 10.38; H, 0.52.

2,3-Dibromo-1,1,3,3-tetrafluoropropene (VII).—The dehydrohalogenation of the 1,2,3-tribromo-1,1,3,3-tetrafluoropropane was carried out in such a way that the product was removed from the reaction mixture as soon as it was formed. This was done in a 500-ml. 3-necked flask fitted with a Hershberg stirrer, addition funnel and wide-bore take-off tube leading into a 100-ml. receiver cooled in Dry Ice. A water-pump, bleeder valve for control of pressure, and open arm manometer were connected to the receiver.

The reaction flask was immersed in a water-bath, the pressure was reduced to between 80–90 mm. and a 15 *N* potassium hydroxide solution was slowly added to the starting material while the mixture was stirred vigorously.

From two runs using a total of 339 g. of VI there was obtained about 230 g. of crude VII (88% yield). On the basis of its infrared spectrum this product appeared to contain 90–95% of the unsaturated compound. It was used without further purification for the preparation of the allene.

Tetrafluoroallene from 2,3-Dibromo-1,1,3,3-tetrafluoropropene.—In a 250-ml. flask equipped with an addition funnel, magnetic stirrer and reflux condenser vented through a Dry Ice trap were placed 20 g. of zinc dust and 40 ml. of absolute alcohol. The dehalogenation mixture was heated to reflux and 26 g. (0.095 mole) of VII was added dropwise over a period of 3 hours. After 3 hours about 1.5 g. (yield 14%) of volatile material had collected; it was shown to be tetrafluoroallene by its infrared spectrum.

Addition of Chlorine to Tetrafluoroallene.—About 1.0 g. of the allene was condensed in a small flask cooled in liquid nitrogen. A small Dry Ice condenser was fitted to the flask and chlorine gas was then admitted through the side arm on the condenser. As soon as the liquid chlorine dropped onto the allene sample the reaction started as evidenced by rapid refluxing and the disappearance of the ice coating on the flask. The mixture was refluxed for 1.5 hours and then dried with magnesium sulfate. After distillation there was obtained 1.7 g. (74% yield) of a colorless liquid, b.p. 111.8° (micro-determination corrected), n^{25}_{D} 1.3930; reported[25] for 1,2,2,3-tetrachloro-1,1,3,3-tetrafluoropropane, b.p. 112.4°, n^{20}_{D} 1.3954. An authentic sample was prepared by fluorination of $CCl_3CCl_2CClF_2$[26] and found to have b.p. 112.0° (760 mm.), n^{25}_{D} 1.3940. The infrared spectra of the two samples were identical.

2-Chloro-3-phenoxy-1,1,3,3-tetrafluoropropene (V) was prepared in low yield from 2,3-dichloro-1,1,3,3-tetrafluoropropene. A solution of 15 g. (0.16 mole) of phenol in 50 ml. of acetone was added slowly with stirring to 30 g. of the propene (0.33 mole) in 100 ml. of acetone containing 35 g. of potassium carbonate in an ice-bath under a Dry Ice condenser. The mixture was stirred for 7 hours, then poured into water. The organic layer was separated, washed with 10% potassium hydroxide solution, dried over anhyd. magnesium sulfate, filtered and distilled to 54° to remove solvent and unreacted starting material. The residue was distilled through a double center rod column at reduced pressure, b.p. 61.8° (9 mm.), n^{25}_{D} 1.4438.

Anal. Calcd. for $C_9H_5OClF_4$: C, 44.93; H, 2.09. Found: C, 44.81; H, 1.97.

Five grams of V was added slowly to a magnetically-stirred suspension of 3 g. of sodium in 50 ml. of xylene at 130°. Reaction occurred rapidly to yield a black residue, but no volatile products were obtained. Compound V (5 g.) was added similarly to 2 g. of magnesium powder in 50 ml. of bis-2-ethoxyethyl ether (Diethylcarbitol) under nitrogen at 130° but no reaction occurred; addition of several crystals of iodine did not catalyze the reaction. Similar treatment of V with lithium at 187° also failed to give a reaction.

Pyrolysis of Sodium Perfluoroglutarate.—Perfluoroglutaric acid (Columbia Organic Chemicals Co.) was converted to its sodium salt which was dried over phosphorus pentoxide at 100° under reduced pressure. A 200-ml. r.b. flask connected to a receiver cooled in liquid nitrogen was charged with 34 g. of the salt, evacuated to the full capacity of a water aspirator and heated with a Glas-Col mantle. The salt decomposed in the range 230–260° to give a slightly colored liquid in the trap and a dark flask residue. The trap liquid was distilled through a short column (glass spiral as packing) to yield two fractions, b.p. 22–29° and 29–50°. The infrared spectrum of the lower boiling fraction indicated that it was mainly perfluorobutyrolactone (b.p. 18°, strong absorption at 1875 cm.$^{-1}$)[27] and of the higher boiling fraction that it was mainly perfluoroglutaric anhydride (b.p. 72°, strong absorption at 1852 and 1790 cm.$^{-1}$).[28]

Polymerization of Tetrafluoroallene.—A heavy-walled, glass tube was charged with 8.7 g. of uninhibited tetrafluoro-

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[24] The combustion analysis was carried out by Dr. Adalbert Elek, Elek Microanalytical Laboratories, Los Angeles, Calif.

[25] W. T. Miller, Jr., and A. H. Fainberg, THIS JOURNAL, **79**, 4164 (1957).

[26] A. H. Fainberg, private communication; the method is mentioned on page 4169, ref. 25, and will be published by W. T. Miller, Jr., and A. H. Fainberg.

[27] M. Hauptschein, C. S. Stokes and A. V. Grosse, THIS JOURNAL, **74**, 1974 (1952).

[28] M. Hauptschein, C. S. Stokes and E. A. Nodiff, *ibid.*, **74**, 4005 (1952).

allene, sealed, and rocked for 3 days at room temp. in a hydrogenation bomb. At the end of this period the bomb was cooled in Dry Ice, opened, the glass tube cooled further in liquid nitrogen and opened. The low boiling material, mainly unreacted monomer, was distilled out at room temp. leaving 4.9 g. of a white waxy solid which melted sharply at 118°. Other runs produced polymer having the same infrared spectrum but with melting points of 100–103° and 125–126°.

The polymer was insoluble in all of the common organic solvents and also in such fluorocarbons as perfluoroheptane. It did not dissolve in dimethylformamide, but when a suspension in this solvent was allowed to stand overnight the precipitate was dark red and the solvent a clear orange. The infrared spectrum of the polymer was determined in a potassium bromide disk; strong bands were observed at 1715, 1343, 1196, 1072 and 1020 cm.$^{-1}$.

Dimerization of Tetrafluoroallene.—Tetrafluoroallene (6.7 g., 0.06 mole) to which had been added less than 1% Terpene B[20] as an inhibitor was sealed in a heavy-walled glass tube. The tube was placed in a small hydrogenation bomb and heated for 20 hours at 40°.

At the end of this period the tube was cooled in liquid nitrogen, opened, and the volatile components distilled out by allowing them to vaporize at room temperature. The higher boiling components of the reaction mixture consisted of 0.225 g. of a solid polymer and 5.3 g. (yield 83%) of a liquid, b.p. 64.0°, which was found to have a molecular weight (by vapor density) of 225; calcd. for $(C_3F_4)_2$, 224.

Oxidation of the Dimer from Tetrafluoroallene.—About 2.0 g. (0.009 mole) of the dimer was sealed in a heavy-walled glass tube at Dry Ice temperature with a solution containing 2.76 g. (0.018 mole) of potassium permanganate and 1.95 g. (0.035 mole) of potassium hydroxide. The tube was allowed to warm to room temperature, placed in a shaker, and vigorously agitated. After three days the tube was opened and the theoretical amount of sulfuric acid needed to neutralize the reaction mixture was added. The manganese oxide was reduced with sulfur dioxide and the organic material was isolated by continuous ether extraction. The ether extract was dried with magnesium sulfate and evaporated to give 0.91 g. of an oil which after chromatographing on a 1:1 mixture of Celite and Baker Analyzed silicic acid ($SiO_2.n.H_2O$) gave 0.39 g. (yield 23%) of a solid white acid believed to be the monohydrate of perfluorosuccinic acid. The infrared spectrum of this acid in acetonitrile was found to be identical with that of an authentic sample[29] in the same solvent with strong absorption bands at 3440, 1765, 1230 and 1150 cm.$^{-1}$. Also a 1:1 mixture of equal molar solutions in water of this acid and of the authentic sample gave a nuclear magnetic resonance spectrum with a single peak which was of the same area as that found for the authentic perfluorosuccinic acid.

Anal. Calcd. for $C_4H_4O_5F_4$ [$HO_2CCF_2CF_2CO_2H \cdot H_2O$]: C, 23.13; H, 1.93; equiv. wt., 104.0. Found: C, 23.18; H, 2.09; equiv. wt., 105.5.

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(29) We wish to thank Dr. Tom Brice of the Minnesota Mining and Manufacturing Co. for sending us a sample of this compound.

LOS ANGELES, CALIF.

[CONTRIBUTION FROM THE RADIOCARBON LABORATORY, UNIVERSITY OF ILLINOIS]

Reduction of Organic Compounds by Mixed Hydrides. III. 3-Bromopropionic Acid, 3-Bromopropionyl Chloride, Methyl 3-Bromopropionate and Halides

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By application of the lithium aluminum hydride–aluminum chloride reagent improvements have been made in the conversion of 3-bromopropionic acid, 3-bromopropionyl chloride and methyl 3-bromopropionate to 3-bromo-1-propanol. The halogen is reduced slowly or not at all by use of the acidic hydride.

In two previous publications[1,2] the reduction of nitriles, nitro compounds, bromoacid chlorides, ketones and alcohols by the lithium aluminum hydride–aluminum chloride reagent has been described. The purpose of the present work has been to further investigate the behavior of the mixed hydride toward a representative acid, acid chloride and ester of the β-bromoacid series in order to utilize the knowledge gained to simplify future synthetic work.

The mechanism of halide reductions with lithium aluminum hydride has been reported.[3,4] In one publication,[4] a 62% yield of 1-propanol and a 21% yield of 3-chloro-1-propanol was obtained when 3-chloropropionic acid was reduced by lithium aluminum hydride at 35° for one to two hours.

The results achieved with the lithium aluminum hydride–aluminum chloride reagent indicate that this process offers definite advantages in the preparation of bromohydrins when compared to the lithium aluminum hydride method. First, reduction of halogen is retarded or prevented by use of the acidic hydride. Second, the experimental procedures are simpler because the bromohydrin can be obtained without resorting to reverse order of addition techniques or lowered temperatures. Finally, a decided advantage in yield is realized.

Reduction of 3-bromopropionic acid, 3-bromopropionyl chloride and methyl 3-bromopropionate by both lithium aluminum hydride and the lithium aluminum hydride–aluminum chloride reagent was studied by normal and reverse order of addition and at temperatures of 35, −15 and −75°. In all instances a ratio of one mole of organic compound per mole of hydride was employed.

Treatment of 3-bromopropionyl chloride with the mixed hydride furnished 76-90% yields of 3-bromo-1-propanol regardless of mode of addition and temperature as shown in Table I. The corresponding reaction with lithium aluminum hydride proceeded well under all conditions listed except when it was carried out by normal order of addition at 35°. These results can best be explained by assuming that the acidic hydride is formed "*in situ*" during the reduction of the bromoacid chloride by lithium aluminum hydride. Accordingly, one would expect to obtain higher yields of bromohydrin from the hydride reduction of a bromoacid chloride than from the corresponding ester or acid. This is readily apparent by inspection of Tables I, II and III.

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(1) R. F. Nystrom, THIS JOURNAL, **77**, 2544 (1955).

(2) R. F. Nystrom and C. R. A. Berger, *ibid.*, **80**, 2896 (1958).

(3) E. E. Eliel and T. J. Prosser, *ibid.*, **78**, 4045 (1956).

(4) E. E. Eliel and J. T. Traxler, *ibid.*, **78**, 4049 (1956).