

as a mixture of  $C_2H_5OCF_2CH=CH_2$  and  $C_2H_5OCH_2CH_2CF_3$ ,<sup>16</sup> and the second fraction as  $C_2H_5OCF_2CHClCH_3$ .<sup>17</sup>

$CF_3CH_2ONa$  and methyl iodide gave a compound b. p. 26–27°,  $n_D^{25}$  1.3515 which separated into two layers at –78° and was probably a mixture of ether and iodine, in addition to 55% of recovered alcohol. This reaction was repeated with methyl bromide instead of iodide, a modification which permitted the isolation by distillation of the ether,  $CF_3CH_2OCH_3$ , in 43% conversion or 61% net yield. This is the same ether which the action of diazomethane on trifluoroethanol had given in impure form only.

$CF_3CH_2ONa$  and ethyl chloride gave small amounts of crude ether, b. p. 45.2–47.2°,  $n_D^{20}$  1.308. Using ethyl bromide instead of chloride gave 60% of good ether,  $CF_3CH_2OC_2H_5$ , purifiable by distillation.

$CF_3CH_2CH_2ONa$  and methyl bromide gave 43% of good ether,  $CF_3CH_2CH_2OCH_3$ ; with ethyl bromide a 30% yield of the corresponding ethyl ether was obtained.

The reaction between  $CF_3CH_2ONa$  and  $BrCH_2CF_2H$  gave an unstable product, b. p. about 70°, which decomposed steadily to give  $CF_3CH_2OH$ .

**Perchlorination of  $CF_3CH_2OCF_2CF_2H$ .**—This chlorination was performed to obtain a perchlorinated ether at a time when perfluorinated ethers were not yet available; tests were made on both types of materials, and they gave similar results. Chlorination of  $CF_3CH_2OCF_2CF_2H$  was done by means of a stream of chlorine through the liquid held in a quartz flask illuminated by an ultraviolet lamp. The escaping gases (mostly hydrogen chloride) were passed through a Dry-Ice trap, the contents of which were periodically returned to the reaction flask. As soon as chlorination had proceeded far enough to raise the boiling point of the sample, heat was applied to maintain reflux. The chlorination was pursued for a whole week, as it had

(16) This mixture was similar to that obtained in the base catalyzed addition of ethanol to  $CF_3CH=CH_2$ , discussed in a paper now in preparation.

(17) This would be the result of a reaction similar to the formation of  $C_4H_9OCF_2CHClCF_3$  from  $CF_3CHClCF_3$  and sodium phenate, McBee and Bolt, *Ind. Eng. Chem.*, **39**, 412 (1947).

become exceedingly sluggish after the fourth day. The best sample so obtained was still contaminated with some hydrogen containing compound as shown by a chlorine analysis of 33.2% instead of 35.1% for  $C_4OCl_3F_7$  and 26.5% for  $C_4HOCl_2F_7$ .

**Examination of  $C_3OCl_3F_7$ .**—This compound was soluble in ether and in 95% ethanol, insoluble in phosphoric or sulfuric acids; it did not dissolve ferric chloride; it did not hydrolyze in sulfuric acid at 90° in fifteen minutes, as shown by negative tests for the chlorine and fluorine ions; it remained colorless after 48 hours of reflux from fuming nitric acid; after completing this test, the refractive index of the organic layer had dropped to only 1.3294, and the acid layer gave negative tests for the chlorine and fluorine ions; a repetition of the nitric acid test, in sealed tube at 150° gave the same negative results; after 24 hours of heating with 48% hydriodic acid in sealed tube at 150°, the compound showed no change in refractive index.

**Examination of  $C_3F_3O$ .**—After redistillation, a sample of  $C_3F_3OC_2F_5$ , gift of the Minnesota Mining and Manufacturing Co., showed the physical properties listed in the table. It was insoluble in water and in 95% alcohol, and only partly soluble in ether; it did not dissolve ferric chloride, nor react upon addition of calcium hydride; it did not dissolve in phosphoric acid; it was unaffected by a 48-hour period of refluxing from fuming nitric acid, as shown by the absence of fluorine ions; the hydriodic test at 150° for 24 hours caused no change in refractive index, and did not generate fluorine ions.

### Summary

Ethers with polyfluorinated groups on one or on both sides of their oxygen atom have been synthesized. The stability of the halogens, the strength of the oxygen bridge and the loss of basic character of the ether function have been examined and related to the position of the fluorinated groups.

COLUMBUS, OHIO

RECEIVED JANUARY 19, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

## The Preparation and Some Reactions of 1,1,1-Trifluoro-2-alkenes<sup>1</sup>

BY KENNETH N. CAMPBELL, JAMES O. KNOBLOCH<sup>2</sup> AND BARBARA K. CAMPBELL

The addition reactions of olefins containing a trifluoromethyl group adjacent to the double bond should be of considerable interest. This group would be expected to exert a strong electron-attracting inductive effect and, as it contains no double bonds, there is no possibility of addition to a conjugated system to complicate the results. Some work has been done on the closely related trichloro methyl ethylenes<sup>3,4</sup> but in this case an allylic shift of one of the chlorine atoms is apt to occur.<sup>3,4,5</sup> The fluorine atoms of the trifluoromethyl group are held so tightly to the carbon atom<sup>6</sup> that a similar allylic re-

arrangement appears unlikely. Practically no work seems to have been reported on the addition reactions of trifluoromethyl ethylenes. We have therefore, undertaken a study of the addition re-

actions of olefins containing the group  $F_3C-C=C<$ , and in the present paper are reporting methods of preparation and preliminary results on some addition reactions.

Very few trifluoromethyl ethylenes have been reported. Henne and Hinkamp<sup>7</sup> have prepared 1,1,1-trifluoro-2-butene by the dehydrohalogenation of 1,1,1-trifluoro-3-chlorobutane, and 1,1,1-trifluoro-2-propene has been prepared in a similar manner.<sup>8,9</sup> This procedure is not practical for the preparation of higher homologs, however, as the intermediate chloro compounds are not readily available.

Swarts<sup>10</sup> synthesized 1,1,1-trifluoro-2-methyl-2-

(1) From the Ph.D. dissertation of James O. Knobloch, University of Notre Dame, June, 1949. Presented at the Organic Division, Atlantic City meeting of the American Chemical Society, September 1949.

(2) Standard Oil of Indiana Fellow, University of Notre Dame, 1947–1949.

(3) Price and Marshall, *J. Org. Chem.*, **8**, 532 (1943).

(4) Kharasch, Rossin and Fields, *This Journal*, **63**, 2558 (1941).

(5) Jacob, *Bull. soc. chim.*, [5] **7**, 581 (1940).

(6) Gilman, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 2nd ed., 1943, Vol. 1, 956.

(7) Henne and Hinkamp, *This Journal*, **67**, 1194 (1945).

(8) Sherer, I. G. Farbenindustrie A.-G. Report, Frankfurt (Main), April 3, 1941.

(9) Henne and Waalkes, *This Journal*, **68**, 497 (1946).

(10) Swarts, *Bull. soc. chim. Belg.*, **36**, 199 (1927).



The trifluoromethyl group adjacent to the double bond has a marked influence on the addition reactions of 1,1,1-trifluoro-2-octene. This olefin, like trichloroisobutene,<sup>3</sup> is not soluble in concentrated sulfuric acid and like trifluoroisobutene<sup>10</sup> reacts but slowly with bromine; after 17 days in the light only 23% of the calculated amount of bromine in chloroform was used up. Addition was somewhat more rapid when aqueous bromine-potassium bromide was used; 17% of the theoretical amount of halogen was consumed in forty hours. On the other hand, trifluoroöctene was readily oxidized by potassium permanganate in the cold to caproic acid, and when hydrogenated over Raney nickel at room temperature and atmospheric pressure one mole of hydrogen was taken up and absorption then ceased.

Fluoro olefins such as 1,1-difluoro-2,2-dichloroethylene react readily with nucleophilic reagents<sup>17</sup> and it was expected that 1,1,1-trifluoro-2-octene would be attacked by these reagents also. Preliminary attempts however, to add sodium methoxide, sodiomalonic ester, diethylamine and tert-butylmagnesium chloride failed but further work on the addition reactions of trifluoromethyl ethylenes is in progress.

### Experimental<sup>18,19</sup>

**Esters of Trifluoroacetic Acid.**—The ethyl ester was prepared by the method of Gilman and Jones.<sup>20</sup> Fractionation of the crude product from phosphorus pentoxide through a helix-packed column gave material of b. p. 60–62°,  $n_{D}^{20}$  1.3076, in 88% yield. The *n*-butyl ester was prepared similarly, except that the refluxing period was extended to twenty-four hours. The yield was 84% of product having b. p. 102.7–102.8°,  $n_{D}^{20}$  1.3391,  $d_{4}^{20}$  1.016, *A* *R* 1.30.

*Anal.* Calcd. for  $C_8H_9F_3O_2$ : C, 42.36; H, 5.33. Found: C, 42.47; H, 5.29.

**Trifluoroethanol.**—It was found more convenient to reduce butyl trifluoroacetate than trifluoroacetyl chloride because of the low boiling point of the latter (–27°). Butyl trifluoroacetate (116 g., 0.68 mole) was added with stirring, during the course of two hours, to a solution of 17.8 g. (0.46 mole) of lithium aluminum hydride in 500 ml. of dry ether. The heat of reaction caused the mixture to reflux, and refluxing was continued for fifteen minutes after addition was complete. Excess lithium aluminum hydride was destroyed by the cautious addition of water, the mixture was poured onto ice and dilute sulfuric acid and the aqueous layer was extracted with two 100-ml. portions of ether. The trifluoroethanol obtained by distillation of the dried (magnesium sulfate) extracts still contained water, and was converted to the anhydrous material by distillation over phosphorus pentoxide. The yield was 76%, b. p. 73.9–74.1° (750 mm.),  $d_{4}^{20}$  1.3842. The 3,5-dinitrobenzoate had m. p. 62–63°.

*Anal.* Calcd. for  $C_8H_9F_3N_2O_5$ : C, 36.75; H, 1.71. Found: C, 36.85; H, 1.42.

(17) Miller, Fager and Griswold, *THIS JOURNAL*, **70**, 431 (1948); Brown and Tarrant, paper presented at Atlantic City A. C. S. meeting, September, 1949.

(18) Some of the analyses were carried out by the Clark Micro-analytical Laboratory, Urbana, Illinois, and the rest by Microtech Laboratory, Skokie, Illinois.

(19) We wish to thank the Hooker Electrochemical Company for furnishing the sodium trifluoroacetate used in this work.

(20) Gilman and Jones, *THIS JOURNAL*, **65**, 1458 (1943).

Attempts to prepare trifluoroethyl bromide by the action of phosphorus pentabromide on the alcohol failed.

**Attempted Preparation of 1,1,1-Trifluoro-3-octen-2-one.**—Trifluoroacetyl chloride<sup>21</sup> was treated with 1-hexene in carbon disulfide using aluminum chloride and aluminum bromide as catalysts, by the general procedure of Simons and Ramler,<sup>12</sup> but only small amounts of impure products were obtained.

**Reaction of Dihexylcadmium with Trifluoroacetyl Chloride.** (a) **In Benzene Solution.**—Di-*n*-hexylcadmium was prepared from 1.15 moles of *n*-hexyl bromide by the general procedure of Cason<sup>22</sup>; 430 ml. of ether was removed by distillation and 750 ml. of dry benzene was added. The apparatus was equipped with a Dry Ice-isopropyl alcohol condenser, the reaction flask was immersed in an ice-bath and the trifluoroacetyl chloride generated from 30 g. (0.264 mole) of trifluoroacetic acid and excess benzoyl chloride<sup>21</sup> was passed into the well-stirred suspension of dihexylcadmium in the course of two and one-half hours. The mixture was refluxed for one hour, cooled and poured onto ice and dilute sulfuric acid. The aqueous layer was extracted with two 125-ml. portions of benzene; and the combined extracts were washed with water, dilute carbonate and brine solutions and dried over sodium sulfate. Distillation through a helix-packed column gave 11 g. of material of b. p. 135–144°,  $n_{D}^{20}$  1.3773–1.3788, which was redistilled from phosphorus pentoxide to yield 7.3 g. of anhydrous trifluoromethyl hexyl ketone, b. p. 70–72° (187 mm.),  $n_{D}^{20}$  1.3727,  $d_{4}^{20}$  1.0498.

The *p*-nitrophenylhydrazone melted at 89–90° after two recrystallizations from aqueous pyridine.

*Anal.* Calcd. for  $C_{14}H_{18}F_3N_2O_2$ : C, 52.99; H, 5.72. Found: C, 52.97; H, 5.74.

The 2,4-dinitrophenylhydrazone originally precipitated as an oil which gradually solidified. After two recrystallizations from ethanol it had m. p. 45–46°.

*Anal.* Calcd. for  $C_{14}H_{17}F_3N_4O_4$ : C, 46.41; H, 4.73; N, 15.47. Found: C, 46.50; H, 4.68; N, 15.15.

(b) **In Ether Solution.**—When the ether was not replaced by benzene before addition of the acid chloride no ketone was obtained, but a 13% yield of trifluoromethyl-dihexylcarbinol was isolated; b. p. 97.5–100° (1.3 mm.),  $n_{D}^{20}$  1.4180;  $d_{4}^{20}$  0.9891, *A* *R* 1.10. Attempts to prepare a crystalline derivative were unsuccessful.

*Anal.* Calcd. for  $C_{14}H_{27}F_3O$ : C, 62.65; H, 10.14. Found: C, 62.78; H, 10.40.

**Reaction of Grignard Reagents with Esters of Trifluoroacetic Acid.** (a) ***n*-Propylmagnesium Bromide.**—A solution of 25.0 g. (0.176 mole) of ethyl trifluoroacetate in 40 ml. of dry ether was added dropwise to the Grignard reagent prepared from 72.3 g. (0.587 mole) of *n*-propyl bromide and 14.3 g. (0.587 g. atom) of magnesium in 150 ml. of dry ether. The reaction mixture was cooled in an ice-bath during the addition, which required thirty minutes. It was then stirred at room temperature for three hours, refluxed for one and a quarter hours and allowed to stand overnight. The mixture was poured onto ice and ammonium chloride, the aqueous layer extracted with two 100-ml. portions of ether, the ether extracts dried over calcium chloride and distilled through a helix-packed column. There was obtained 18.6 g. (74.4%) of 1,1,1-trifluoro-2-pentanol, b. p. 109.2–111.5° (745 mm.),  $n_{D}^{20}$  1.3533,  $d_{4}^{20}$  1.136, *A* *R* 1.21.

*Anal.* Calcd. for  $C_5H_9F_3O$ : C, 42.25; H, 6.38. Found: C, 42.66; H, 6.68.

(b) ***n*-Hexylmagnesium Bromide.**—This reaction was carried out as described above, using 122 g. (0.86 mole) of ethyl trifluoroacetate and the Grignard reagent obtained from 3 moles of *n*-hexyl bromide and 3 g. atoms of magnesium. The main fraction (b. p. 142–181.5°) obtained on distillation of the hydrolysis product was redistilled through a helix-packed column to give 122 g. (77.8%) of

(21) Brown, *ibid.*, **60**, 1325 (1938); Tinker, U. S. 2,257,868 (1941); *G. A.*, **36**, 495 (1942).

(22) Cason, *THIS JOURNAL*, **68**, 2078 (1946).

material of b. p. 163.5–166° (751 mm.),  $n_D^{20}$  1.3886–1.3870. Analysis indicated that the trifluoro-2-octanol was contaminated with about 5% of dodecane which could not be removed by distillation. Analytically pure 1,1,1-trifluoro-2-octanol was obtained by dissolving the material in concentrated sulfuric acid and recovering the carbinol by dilution with water. The purified carbinol had the following physical constants: b. p. 165.7–166.2° (751 mm.),  $n_D^{20}$  1.3834,  $d_4^{20}$  1.056,  $ARF$  1.12.

*Anal.* Calcd. for  $C_8H_{15}F_3O$ : C, 52.16; H, 8.21. Found: C, 51.97; H, 8.51.

(c) **Ethylmagnesium Bromide.**—When the Grignard reagent from 0.88 mole of ethyl bromide reacted with 0.26 mole of ethyl trifluoroacetate two main fractions were obtained: (1) the first fraction boiled from 80 to 116° and appeared to be an inseparable mixture of ethanol and 1,1,1-trifluoro-2-butanol; (2) the second fraction had b. p. 117.1–117.2° (750 mm.),  $n_D^{20}$  1.3723,  $d_4^{20}$  1.145,  $ARF$  0.97, and represented a 39% yield of the tertiary alcohol, trifluoromethyldiethylcarbinol.

*Anal.* Calcd. for  $C_8H_{11}F_3O$ : C, 46.15; H, 7.10. Found: C, 46.28; H, 6.82.

When butyl trifluoroacetate was used instead of the ethyl ester, it was possible to isolate pure secondary alcohol. The 1,1,1-trifluoro-2-butanol, obtained in 31% yield, had b. p. 90.8–91.8° (752 mm.),  $n_D^{20}$  1.3403,  $d_4^{20}$  1.166,  $ARF$  1.38.

*Anal.* Calcd. for  $C_4H_7F_3O$ : C, 37.50; H, 5.51. Found: C, 37.53; H, 5.77.

In this case the tertiary alcohol could not be isolated pure, as it formed an azeotrope, b. p. 115–118°, with the *n*-butyl alcohol present.

(d) **Reverse Addition of *n*-Hexylmagnesium Bromide to Ethyl Trifluoroacetate.**—*n*-Hexylmagnesium bromide (from 0.18 mole of hexyl bromide) in 35 ml. of dry ether was added during two and one-half hours to a solution of 0.18 mole of ethyl trifluoroacetate in 35 ml. of ether, cooled in an ice-bath. The mixture was then stirred at room temperature for two hours, refluxed for two hours and hydrolyzed with ice and dilute sulfuric acid. The aqueous layer was saturated with salt and extracted with two 40 ml. portions of ether. On redistillation of the main fraction (b. p. 79–177°) most of the material boiled between 150 and 170°,  $n_D^{20}$  1.3733–1.3880. From the boiling point and index of refraction data this appeared to be a mixture of 1,1,1-trifluoro-2-octanone and its reduction product, 1,1,1-trifluoro-2-octanol. The presence of the ketone was demonstrated by the formation of a 2,4-dinitrophenylhydrazone, m. p. 43.5–44.5°, which did not depress the m. p. of the derivative prepared from the dihexylcadmium reaction.

**Reaction of 1,1,1-Trifluoro-2-octanone with Propylmagnesium Bromide.**—A solution of 5.3 g. (0.03 mole) of the ketone in 25 ml. of dry ether was added, with cooling, to propylmagnesium bromide prepared from 1.8 g. of *n*-propyl bromide. The addition required fifteen minutes and the mixture was then refluxed for one hour and hydrolyzed. Distillation gave 3.2 g. of 1,1,1-trifluoro-2-octanol, b. p. 165–167.5°,  $n_D^{20}$  1.3842,  $d_4^{20}$  1.049.

A similar reaction was carried out with *n*-hexylmagnesium bromide, but although the product had the very characteristic odor of trifluoro-2-octanol, the carbinol was contaminated with dodecane from which it could not be separated by distillation.

**1,1,1-Trifluoro-2-octanone by Oxidation of 1,1,1-Trifluoro-2-octanol.**—A 30-g. portion of 1,1,1-trifluoro-2-octanol was oxidized with sodium dichromate in sulfuric acid, using the general procedure of Conant and Quayle.<sup>23</sup> Distillation of the product through a Podbielniak column gave a 49% yield of ketone. The best fraction had b. p. 135.9° (737 mm.),  $n_D^{20}$  1.3650,  $d_4^{20}$  1.053.

*Anal.* Calcd. for  $C_8H_{13}F_3O$ : C, 52.74; H, 7.19. Found: C, 52.87; H, 6.89.

The derivatives prepared from this ketone agreed with

those of 1,1,1-trifluoro-2-octanone obtained from ethyl trifluoroacetate and dihexylcadmium.

**Methyl Xanthate of 1,1,1-Trifluoro-2-octanol.**—Powdered potassium hydroxide (85%, 7.3 g., 0.11 mole) was dissolved in 20 g. (0.11 mole) of trifluoro-2-octanol by heating. A solution of 16 g. (0.22 mole) of carbon disulfide in 100 ml. of decalin was added with stirring to the cold solution, followed by 22 g. (0.156 mole) of methyl iodide. The reaction mixture was kept at 70° for two and one-half hours and then allowed to stand overnight. It was distilled at atmospheric pressure until the distillation temperature reached 185°. Since the distillate did not appear to contain any olefin, the residue was washed with water, dried over potassium carbonate and distilled *in vacuo*. The main fraction came over at 125.5–127.5° (15 mm.),  $n_D^{20}$  1.4694,  $d_4^{20}$  1.1342. It boiled at 241–243° at atmospheric pressure with but little decomposition. Analyses indicated that the methyl xanthate contained about 3% of decalin.

*Anal.* Calcd. for  $C_{10}H_{17}F_3OS_2$ : C, 43.77; H, 6.25. Calcd. for 97%  $CF_3CH(OCS_2CH_3)C_6H_{13}$  + 3% decalin (the expected impurity) C, 45.02; H, 6.45. Found: C, 44.97; H, 6.50.

**1,1,1-Trifluoro-2-acetoxyoctane.**—Acetyl chloride (109 ml., 1.53 mole) was added to 121.4 g. (0.659 mole) of trifluoro-2-octanol, and after one hour at room temperature the mixture was refluxed for five hours and allowed to stand overnight. The ester, isolated by pouring the reaction mixture into water, weighed 139 g. (93%) and had  $n_D^{20}$  1.3818. It was pure enough for conversion to the olefin. Distillation of a portion of the ester through a Podbielniak column gave a main fraction, b. p. 177.2–177.5° (736 mm.),  $n_D^{20}$  1.3800,  $d_4^{20}$  1.041.

*Anal.* Calcd. for  $C_{10}H_{17}F_3O_2$ : C, 53.10; H, 7.58. Found: C, 53.7; H, 7.82.

Use of acetic anhydride gave lower yields (55–57%) of the ester.

**1,1,1-Trifluoro-2-acetoxypentane.**—This was obtained in 85% yields by the procedure described above. It had b. p. 119–124° (744 mm.),  $n_D^{20}$  1.3587.

**1,1,1-Trifluoro-2-octene.**—1,1,1-Trifluoro-2-acetoxyoctane (containing a few drops of glacial acetic acid<sup>24</sup>) was pyrolyzed over Pyrex glass wool at 500 ± 10°, using an apparatus similar to that described by Wibaut and van Pelt.<sup>14</sup> The reaction product, which was caught by a Dry Ice trap, was brought to room temperature and diluted with water to obtain two liquid phases. The organic layer, freed of acetic acid by carbonate and dried over magnesium sulfate, was distilled through a Podbielniak column. Of 76 g. of trifluoroacetoxyoctane used, 16.7 g. was recovered unchanged, and 25.6 g. of trifluoro-2-octene was obtained. This is a 59% yield based on ester consumed. In other runs the yield was raised to 65%.

Pure 1,1,1-trifluoro-2-octene has b. p. 123.4–123.6° (749 mm.),  $n_D^{20}$  1.3682,  $d_4^{20}$  0.962,  $ARF$  1.18.

*Anal.* Calcd. for  $C_8H_{13}F_3$ : C, 57.82; H, 7.88. Found: C, 58.04; H, 8.03.

When the furnace was kept at 450°, practically no pyrolysis occurred, and most of the ester was recovered unchanged. At 550° extensive decomposition took place and very little of the desired olefin was obtained.

**1,1,1-Trifluoro-2-pentene.**—This was prepared by pyrolysis of the carbinol acetate. The yield of olefin was 95% based on ester not recovered. 1,1,1-Trifluoro-2-pentene has b. p. 48.2–49.2 (750 mm.),  $n_D^{20}$  1.3254,  $d_4^{20}$  0.9971,  $ARF$  1.18.

*Anal.* Calcd. for  $C_5H_7F_3$ : C, 48.38; H, 5.69. Found: C, 48.87; H, 5.72.

**Reactions of 1,1,1-Trifluoro-2-octene.** (a) **Permanganate Oxidation.**—The olefin (4.4 g.) was oxidized with 18.2 g. of potassium permanganate in 300 ml. of water containing 2.1 g. of potassium hydroxide. The precipitated manganese dioxide was washed with three 100-ml.

(23) "Organic Syntheses," Coll. Vol. I, 2nd ed., p. 211.

(24) Houtman, van Steenis and Heertjes, *Rec. trav. chim.*, **65**, 781 (1946).

portions of boiling water, and the original filtrate and wash waters evaporated to 100 ml. This solution was acidified (pH 3) with hydrochloric acid and the organic acids extracted with tributyl phosphate (three 20-ml. portions). The acids were recovered from the phosphate solution by extraction with dilute potassium hydroxide, which was then evaporated to dryness. The residue was taken up in a little water, acidified with hydrochloric acid (total volume 10 ml.) and extracted with ether. Evaporation of the ether under reduced pressure also removed the trifluoroacetic acid (b. p. 72.4°). The residual crude caproic acid was converted to the potassium salt (0.9 g.) and then to the anilide, m. p. 93.5–94.5°, which did not depress the m. p. of known caproic anilide.

(b) **Hydrogenation.**—An 0.542 g. sample of the olefin in alcohol over Raney nickel absorbed the calculated amount of hydrogen at room temperature and atmospheric pressure, in sixty minutes, and absorption then ceased.

(c) **Bromination.**—To a standardized solution of bromine in chloroform (0.00217 mole of bromine) there was added 0.5298 g. (0.00319 mole) of olefin, and the solution was allowed to stand on the desk in a glass stoppered flask. A similar sample of the bromine–chloroform solution (without olefin) was also allowed to stand. At the end of eleven days both solutions were titrated with 0.1055 *N* thiosulfate solution. The blank required 24.98 ml., the solution containing olefin required 10.90 ml. From this it can be determined that the olefin used up 23.3% of the amount of bromine required to saturate the double bond.

The olefin (0.547 g., 0.00329 mole) and 25.0 ml. of an aqueous bromine–potassium bromide solution (0.4012 *N*) were allowed to stand in a glass-stoppered flask in the dark for forty hours. The remaining bromine required 84.5 ml. of 0.1055 *N* thiosulfate, indicating that the olefin consumed 17% of the calculated amount of bromine.

(d) **Nucleophilic Reagents.**—A mixture of 1,1,1-trifluoro-2-octene (7.4 g.) and excess diethylamine (14 ml.) was refluxed for seven days. From the amount of diethylamine (84%) and olefin (93%) recovered little or no addition could have occurred.

Equimolar amounts of trifluoroctene and sodiummalonic ester were refluxed in benzene for twenty-five hours.

Most of the olefin and malonic ester were recovered unchanged, and no addition product could be found.

A mixture of equimolar amounts of trifluoroctene and sodium methoxide in dry methanol was refluxed for two hours. The solvent was removed by distillation and the residue taken up in aqueous hydrochloric acid. The aqueous solution gave a positive test for fluoride ion, but no definite products could be isolated.

1,1,1-Trifluoro-2-octene was refluxed for twenty-four hours with an excess of *t*-butylmagnesium chloride in ether. Most of the olefin (82%) was recovered on working up the reaction mixture in the usual way.

### Summary

1. The reaction of aliphatic Grignard reagents with esters of trifluoroacetic acid has been investigated. With the larger Grignard reagents (*n*-propyl and *n*-hexyl) only the secondary alcohol was obtained; with ethylmagnesium bromide both the secondary and the tertiary alcohol were formed.

2. 1,1,1-Trifluoro-2-octanone was reduced to the secondary alcohol by propylmagnesium bromide and no addition occurred.

3. When trifluoroacetyl chloride was treated with dihexylcadmium in benzene solution a low yield (22%) of the expected ketone was obtained. When the reaction was carried out in ether, the only product isolated was the tertiary alcohol, trifluoromethyldihexylcarbinol.

4. 1,1,1-Trifluoro-2-octene and 1,1,1-trifluoro-2-pentene were prepared by pyrolysis of the corresponding secondary acetates.

5. Some addition reactions of 1,1,1-trifluoro-2-octene have been investigated.

NOTRE DAME, INDIANA

RECEIVED APRIL 27, 1950

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIFORNIA, NO. 1402]

## An Adsorption System for the Fractionation of Nitrocellulose with Respect to Molecular Weight<sup>1,2</sup>

BY MARVIN C. BROOKS<sup>3</sup> AND RICHARD M. BADGER

This paper describes a study of the adsorption of nitrocelluloses on starch from several binary solvent mixtures. The results indicate the feasibility of the molecular weight fractionation of nitrocellulose by elution chromatographic procedures. One chromatographic experiment is described which demonstrates the application.

The fractionation of high polymers by chromatographic methods has been attempted by several workers. The first report to the best of our knowledge, was made in 1936 by Mark and Saito<sup>4</sup>

who demonstrated that cellulose acetate was adsorbed on blood charcoal selectively on a molecular weight basis. Levi and Giera<sup>5</sup> also studied the adsorption of cellulose acetates on charcoal. More recently Landler<sup>6</sup> has reported on the adsorption of GR-S, Perbunan, and Vistanex on charcoal from mixtures of toluene and methanol. Claesson<sup>7</sup> has made a preliminary report on the use of the chromatographic method of frontal analysis. Fractionation of a high polymer by this method does not appear practical, though some information can be obtained regarding molecular weight distribution.

The investigations just mentioned appear to show that charcoal is not likely to be a very useful

(1) This paper is based on work supported by the Bureau of Ordnance and done under contract with the Office of Naval Research, Contract N6-ori-102, Task Order VI.

(2) Presented before the High Polymer Forum at the Atlantic City meeting of the American Chemical Society, September 19, 1949.

(3) General Laboratories, U. S. Rubber Co., Passaic, N. J.

(4) H. Mark and G. Saito, *Mosash.*, **68**, 237 (1936).

(5) G. R. Levi and A. Giera, *Gazz. chim. ital.*, **67**, 719 (1937).

(6) I. Landler, *Compt. rend.*, **225**, 629 (1947).

(7) S. Claesson, *Arkiv Kem. Mineral. Geol.*, **26A**, No. 24 (1949).