

Notes

A department for short papers of immediate interest.

Decarbethoxylation of Perfluoroacid Esters

ELLIOT BERGMAN¹

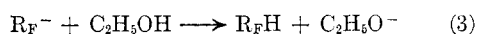
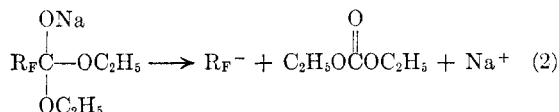
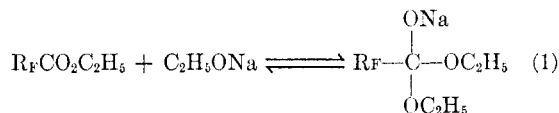
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The cleavage of negatively substituted esters with alkoxide is a well known reaction. Diethyl nitromalonate is cleaved by sodium ethoxide in ethanol to ethyl carbonate and ethyl nitroacetate.² Ethyl trichloroacetate reacts smoothly with ethoxide at room temperature to yield diethylcarbonate.³ We wish to report an extension of this reaction to the esters of perfluoroacids.

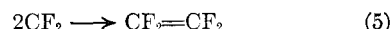
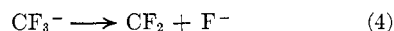
Nes and Burger⁴ reported the ethoxide-catalyzed condensation of ethyl trifluoroacetate with benzyl cyanide in refluxing ethanol to yield α -cyanobenzyl trifluoromethyl ketone in 87% yield. Our attempts to extend this reaction using ethyl heptafluoro-*n*-butyrate proved less successful; the best yield obtained was 24% of the corresponding α -cyanoketone. In addition, 1,1,2,2,3,3,3-heptafluoropropane was formed. The cleavage of the ethyl esters of perfluoroacetic, perfluoropropionic, perfluoro-*n*-butyric, and perfluoro-*n*-octanoic acids with sodium ethoxide was, therefore, investigated in order to design procedures for the utilization of higher perfluoroacid esters in condensation reactions. The esters were refluxed with approximately 2 molar sodium ethoxide in absolute ethanol and the rates of evolution of the gaseous monohydrogen compounds were observed (except for 1-*H*-perfluoroheptane, which is a liquid at room temperature). At the same concentration the perfluorobutyrate and perfluoropropionate esters reacted at about 16 times the rate of ethyl perfluoroacetate. By this procedure the monohydrogen perfluoroalkanes could be produced in high yield under relatively mild conditions. This method thus affords a convenient way of decarboxylating perfluoroacids which ordinarily require much more drastic decarboxylating conditions.^{5,6}

The general reaction is illustrated in Equations 1-3. Only in the case of the decarbethoxylation of ethyl trifluoroacetate was decomposition to fluoride

noted with the consequent decrease in the yield of monohydrogen compound.



Decomposition of ethyl trifluoroacetate to give fluoride probably proceeds *via* a difluorocarbene intermediate. The tendency of trifluoromethyl anion to decompose into difluorocarbene and fluoride ion is implied by the fact that McBee *et al.*⁷ produced perfluoro-*n*-propyllithium by an exchange reaction between methyl lithium and perfluoro-*n*-propyl iodide but obtained only tetrafluoroethylene in the same exchange when trifluoromethyl iodide was employed.



Experiments are now being conducted, using the technique of Doering and Hoffman,⁸ to determine whether or not difluorocarbene is an intermediate in the degradation of trifluoromethyl derivatives to fluoride ion.

EXPERIMENTAL

*Ethyl trifluoroacetate, ethyl pentafluoropropionate, and ethyl heptafluoro-*n*-butyrate* were prepared as follows: A flask containing 434 g. (3.80 moles) of trifluoroacetic acid was cooled in an ice bath while 212 g. (4.60 moles) of ethyl alcohol was added. After heat ceased evolving 445 ml. (8.0 mles) of concentrated sulfuric acid was added with cooling. The product was refluxed for 0.5 hr. and then distilled from the concentrated sulfuric acid through a long Vigreux column. Fractions boiling 62-64° at 755 mm. were collected. A total of 509 g., 94%, having n_D^{20-5} of 1.3069 to 1.3072 was obtained.

Similarly, ethyl pentafluoropropionate, b.p. 75.0-75.5° at 750 mm., n_D^{25} 1.2988, was prepared in 93% yield. Likewise, ethyl heptafluoro-*n*-butyrate, b.p. 94.5-96.0°, n_D^{25} 1.3001-1.3003 was prepared in 90% yield.

*Preparation of ethyl perfluoro-*n*-octanoate.* To a solution of 166 g. (2.30 moles) of silver perfluoro-*n*-octanoate in 200 ml. of reagent acetone was added with swirling, 78 g. (0.50 mole) of pure ethyl iodide in 100 ml. of acetone such that the mixture refluxed gently. After standing overnight 74 g. (98%) of silver iodide was filtered from the acetone solution

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and the latter distilled to yield 2 fractions, the first, 69 g. (49%) of ethyl perfluoro-*n*-octanoate, b.p. 74–76° at 18 mm., n_D^{20} 1.3119 and the second, 37% of perfluoro-*n*-octanoic acid.

Anal. Calcd. for $C_{10}H_5F_{15}O_2$: C, 27.17; H, 1.14. Found: C, 26.59; H, 1.49.

Reaction of ethyl trifluoroacetate with sodium ethoxide. A cold solution of freshly prepared sodium ethoxide [6.9 g. (0.30 g.-atom) of sodium in 100 ml. of absolute ethanol] was mixed with a solution of 43 g. (0.30 mole) of ethyl trifluoroacetate in 15 ml. of ethanol. The cool reaction mixture was attached to a reflux condenser in series with a sulfuric acid bubbler, a Dry Ice trap, and a liquid nitrogen trap. The whole system was blanketed under dry nitrogen and the mixture was warmed to reflux whence gas began evolving at a measurable rate. After approximately 4 hr. the gas evolution ceased. A total of 9.0 g. (43%) of fluoroform identified by its infrared spectrum and its molecular weight (found 70.5, 70.5; calcd. 70.0) collected in the liquid nitrogen trap. The reaction mixture gave a strong test for fluoride. No diethyl carbonate was obtained on distillation of the reaction mixture. Presumably, this compound was decomposed by long exposure to ethoxide.

Reaction of ethyl pentafluoropropionate with sodium ethoxide. When ethyl pentafluoropropionate was subjected to the above reaction conditions, a 72% yield of pentafluoroethane, was evolved during a 20-min. period. Distillation of the fluoride free reaction mixture yielded 1 g. of diethyl carbonate, b.p. 126°, n_D^{25} 1.3821.

*Reaction of ethyl heptafluoro-*n*-butyrate with sodium ethoxide.* When a solution of 0.10 mole of ethyl heptafluoro-*n*-butyrate in 50 ml. absolute ethanol was added all at once to a solution of 2*N* sodium ethoxide in ethanol and the resulting solution was refluxed, a 71% yield of heptafluoropropane, free of perfluoropropene, evolved over a 15-min. period. Distillation of the fluoride free reaction mixture yielded 30% of diethyl carbonate, b.p. 126°, n_D^{25} 1.3827.

*Reaction of ethyl perfluoro-*n*-octanoate with sodium ethoxide.* A solution of 0.14 g.-atom of sodium in 40 ml. of absolute ethanol was mixed with a solution of 55 g. (0.124) mole of ethyl perfluoro-*n*-octanoate in 20 ml. of ethanol and refluxed for one hour. Distillation of the fluoride free reaction mixture yielded 44.5 g., b.p. 69–70°, of an ethanol azeotrope with 1-*H*-pentadecafluoroheptane. In addition, 10.5 g., b.p. 124–125°, n_D^{25} 1.3845–1.3855 was obtained, corresponding to a 72% yield of diethyl carbonate. The azeotrope was washed with saturated calcium chloride and redistilled from phosphorous pentoxide to give 33.5 g. (73%) yield of pentadecafluoroheptane, b.p. 94.0° at 762 mm.

Anal. Calcd. for C_7HF_{15} : C, 22.71; H, 0.27. Found: C, 22.53; H, 0.93.

DEPARTMENT OF CHEMISTRY AND
CHEMICAL ENGINEERING
UNIVERSITY OF CALIFORNIA
BERKELEY 4, CALIF.

A New Synthesis for Triphenylene¹

CORWIN HANSCH AND C. FRED GEIGER²

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Although several different methods for the synthesis of triphenylene and its derivatives have

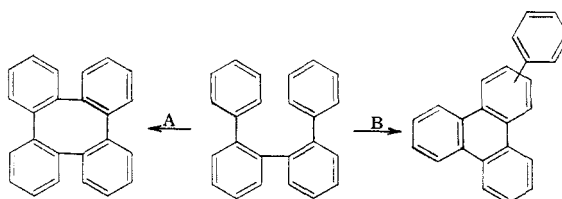
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(2) Department of Chemistry, Chaffey College, Ontario, Calif.

been devised,^{3–9} none offers a convenient route with good yield.

We have discovered that triphenylene can be made in approximately 10% yield in the one step dehydrocyclization of 1,2-diphenylbenzene. 1,2-Diphenylbenzene is a commercial product. The material used in this work is called Santowax and was supplied by the Monsanto Chemical Company. We have found that the dehydrogenation of the crude Santowax gives as good yields as the dehydrogenation of pure 1,2-diphenylbenzene.

This synthesis of triphenylene was suggested by the results we obtained in an attempted synthesis of 1,2,3,4,5,6,7,8-tetrabenzocyclooctatetraene. The dehydrocyclization of 2,2'-diphenylbiphenyl did not give the cyclooctatetraene as was hoped, but instead the reaction seems to have gone by path B to give either 1-, or 2-phenyltriphenylene.



The compound we obtained from the above dehydrogenation did not form a picrate and melted at 183–184°. Rapson¹⁰ reports a melting point of 233° for the tetrabenzocyclooctatetraene. Although 1-phenyltriphenylene is what would be expected to form it is very likely that this would rearrange to the 2-isomer which would be more stable because of less steric strain. It has been shown, for example, that 1-phenylnaphthalene rearranges at 350° over silica gel to 2-phenylnaphthalene.¹¹

EXPERIMENTAL¹²

Phenyltriphenylene. 2,2'-Diphenylbiphenyl (8 g. in liquid form) was processed over 10 ml. of 8% chromia on alumina catalyst¹³ at 615° during a period of 27 min. The 5.8 g. of condensate obtained was chromatographed over 180 g. of alumina. First the alumina column was eluted with six 100-ml. portions of petroleum ether. Evaporation of the solvent from these fractions gave 0.2 g. of starting material. Then the column was eluted with eleven 100-ml. portions of 10% benzene-10% petroleum ether. Evaporation of the solvents

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