material could not be crystallized and was probably a mixture of Ia and IIa.

The Reaction of Cyclohexylidene Diphenylmethane (IIa) with Peracetic Acid.—To 2.5 g. (0.01 mole) of cyclohexylidene diphenylmethane (IIa) in 20 ml. of glacial acetic acid was added 0.3 g. of anhydrous sodium acetate in 2.5 g. of 45% peracetic acid. The mixture was stirred for two hours at which time all of the solid starting material was in solution. The reaction mixture was poured into 10 ml. of a saturated salt solution in water and the solid which precipitated was filtered by suction. The yield of cyclohexylidene diphenylmethane oxide was 2.5 g. (95%) and, on recrystallization from ethanol, melted 120.5–121°.[5] This material was identical with that obtained from the peracid oxidation of the retropinacolone rearrangement product.

2,2-Diphenylcyclohexanol (Ib).—A suspension of 0.8 g. (0.021 mole) of lithium aluminum hydride in 40 ml. of dry ether was prepared in a 200-ml. three-necked flask equipped for anhydrous conditions. To this mixture was added a solution of 5 g. (0.02 mole) of 2,2-diphenylcyclohexanone[6] in 15 ml. of ether. Very little heat was generated by the reaction. The mixture was stirred for one hour and water was added dropwise until no further reaction occurred. The mixture was then acidified with dilute sulfuric acid and the ether layer removed. The aqueous layer was extracted with an additional 25 ml. of ether and the organic layers combined and dried over sodium sulfate. On evaporation of the ether 4.6 g. (92%) of solid remained which, after recrystallization from ethanol, melted 82.5–83°. Because of the similarity in melting point with that of the starting material a mixture melting point was determined giving a value of 60–67°.

Anal. Calcd. for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.15; H, 7.91.

Dehydration of 2,2-Diphenylcyclohexanol (Ib). a. With Phosphorus Tribromide.—On treatment of 5.3 g. (0.021 mole) of molten 2,2-diphenylcyclohexanol (Ib) with 4.1 g. (0.015 mole) of phosphorus tribromide as described in (b) above, 3.8 g. (75%) of oil, b.p. 175–180° at 8 mm., was obtained. A portion of this oil was crystallized from petroleum ether using a Dry Ice-acetone bath. Recrystallization produced a white solid, m.p. 60.8–61.2°. These physical constants agree with those reported[7] for cyclopentylidene diphenylmethane (IIb), lit. b.p. 180–181° at 6–7 mm., m.p. 62–62.5°.

b. Attempted Dehydration on Distillation at Atmospheric Pressure.—After three consecutive distillations at atmospheric pressure 5 g. of Ib gave 4.68 g. of oil from which 3.71 g. (74%) of 2,2-diphenylcyclohexanol (Ib) was recovered.

The ultraviolet spectra of IIa and IIb were determined using a Beckmann Model DU quartz spectrophotometer. The concentrations of the solutions of IIa and IIb were 1.73 × 10^{-5} and 2.22 × 10^{-5} *M*, respectively, in 95% ethanol.

Acknowledgment.—The authors wish to express appreciation to Buffalo Electro-chemical Company, Inc., for generous supplies of peracetic acid used in this research.

(7) G. Egloff, "Physical Constants of Hydrocarbons," Vol. III, Reinhold Publ. Corp., New York, N. Y., 1946, p. 456.

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The Reaction of Sodium with Ethyl Trifluoroacetate

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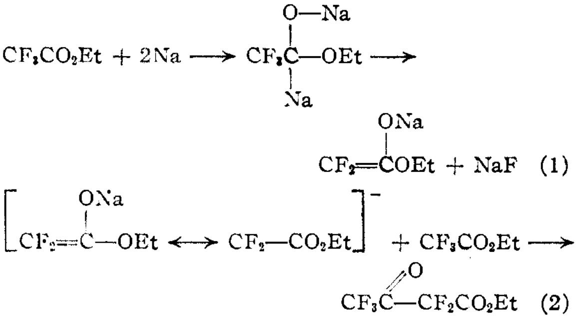
In an attempt to prepare a fluorine-containing acyloin, it was found that sodium reacted with ethyl trifluoroacetate in anhydrous ether yielding, on hydrolysis of the reaction mixture, ethyl γ,γ,γ-trifluoroacetoacetate in yields of 25–30%. A similar observation was made by Haszeldine[2] but no experimental details of explanations were offered. None of the expected acyloin was obtained and the only other products observed were unidentifiable high boiling materials, thought to be polymeric forms of 1,1,1,4,4,4-hexafluoroacetoin.

In an effort to delineate the reaction mechanism, ethyl pentafluoroacetoacetate[3] was treated with sodium under similar conditions and found to yield ethyl γ,γ,γ-trifluoroacetoacetate. This would indicate a possible reaction sequence which involves the formation of an intermediate acetoacetic ester. The latter compound could be obtained in the following manner



$$CF_3CO_2Et + 2Na \longrightarrow CF_3\overset{\overset{\displaystyle O-Na}{|}}{\underset{\underset{\displaystyle Na}{|}}{C}}-OEt \longrightarrow CF_2{=}\overset{\overset{\displaystyle ONa}{|}}{C}OEt + NaF \quad (1)$$

$$\left[CF_2{=}\overset{\overset{\displaystyle ONa}{|}}{C}-OEt \longleftrightarrow CF_2-CO_2Et\right]^- + CF_3CO_2Et \longrightarrow CF_3\overset{\overset{\displaystyle O}{\|}}{C}-CF_2CO_2Et \quad (2)$$

Corroborating evidence may be found in the fact that sodium fluoride was isolated from the reaction mixture in appreciable quantities and that only two moles of sodium per mole of ester was readily consumed.

Experimental

Ethyl Trifluoroacetate and Sodium in Anhydrous Ether.—A 500-ml., 3 necked flask was equipped with a sealed stirrer, a reflux condenser and an addition funnel with a side-arm pressure equalizer tube. The apparatus was flame-dried in a stream of dry nitrogen and one mole of sodium sand and 200 ml. of anhydrous ether were placed in the flask. One-half mole of ethyl trifluoroacetate (b.p. 60.5°, $n^{20}D$ 1.3073) was added dropwise to the stirred mixture of ether and sodium sand. After the first few ml. of ester had been added, the ether solution became dark red and the ether began to reflux vigorously. The remaining portion of the ester was added at such a rate that a steady reflux was maintained. After all the ester had been added, the mixture was stirred for an additional 2 hours. The ether solution was then poured over a mixture of 200 g. of crushed ice and 60 g. of concd. sulfuric acid. The ether layer was separated and the aqueous solution was extracted with ether. The ether solution was dried with anhydrous sodium sulfate and Drierite. After distillation of the ether, 20 g. of ethyl trifluoroacetate was recovered and 14 g. of ethyl γ,γ,γ-trifluoroacetoacetate was obtained boiling at 131–132°. A copper chelate was prepared, m.p. 188–189°.[4] The γ,γ,γ-trifluoroacetoacetic ester yielded 1,1,1-trifluoroacetone (b.p. 22°) upon hydrolysis with 30% sulfuric acid. A 2,4-dinitrophenylhydrazone was prepared, m.p. 139°.[4]

Anal. Calcd. for $C_9H_7F_3N_4O_4$: C, 37.0; H, 2.39. Found: C, 37.09; H, 2.52.

Sodium and Ethyl Pentafluoroacetoacetate in Anhydrous Ether.—A mixture of 70 ml. of anhydrous ether and 4.6 g. of sodium sand was placed in a 200-ml., 3-necked flask. A solution of 23 g. of ethyl pentafluoroacetoacetate and 50 ml. of anhydrous ether was added dropwise to the ether-sodium mixture. The ether solution was stirred for 6 hours and then poured over a mixture of 100 g. of crushed ice and 20 g. of concd. sulfuric acid. The ether layer was separated and the aqueous solution was extracted with ether.

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[1] Abstracted, in part, from the doctoral theses of H. W. Kilbourne and J. A. Barone, Purdue University.

[2] R. N. Haszeldine, *Nature*, **168**, 1028 (1951).

[3] E. T. McBee, O. R. Pierce, H. W. Kilbourne and E. R. Wilson, THIS JOURNAL, **75**, 3152 (1953).

[4] A. L. Henne, L. L. Quill, M. S. Newman and R. A. Staniforth, *ibid.*, **69**, 1819 (1947).

The ether solutions were combined and dried with Drierite and then distilled. Twelve grams of a mixture of pentafluoro- and trifluoroacetoacetic esters was obtained boiling at 130–133°. The presence of the trifluoroacetoacetic ester was shown by the formation of a copper chelate, m.p. 188–189°[4] and by hydrolysis to trifluoroacetone which gave a 2,4-dinitrophenylhydrazone, m.p. 139°.[4]

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1,3,3,3-Tetrafluoropropylene Oxide

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It was of interest to prepare an epoxide containing a fluorine atom substituted on a bridge carbon atom for a study of the orientation effect of fluorine in epoxide ring opening. Only two fluorine-containing propylene oxides have been previously reported[2] and no compound having fluorine substituted directly on the epoxide ring has been described.

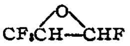
The synthesis of the desired epoxide was based on bromotetrafluoroacetone. It was found that this material could be obtained directly in excellent yield by treating ethyl α,γ,γ,γ-tetrafluoroacetoacetate[3] with a mixture of sulfuric acid and bromine at moderate temperatures. The bromotetrafluoroacetone obtained was reduced with lithium aluminum hydride at 0° in an excess of the ketone to produce 3-bromo-1,1,1,3-tetrafluoro-2-propanol in 80% yield. Dehydrobromination of the alcohol was accomplished by reaction with hot 50% sodium hydroxide and 1,3,3,3-tetrafluoropropylene oxide was obtained in 96% yield.

It was first thought that bromination probably occurred during the decarboxylation reaction in accordance with the postulates of other researchers.[4] However, it was found that use of excess bromine produced 3,3-dibromo-1,1,1,3-tetrafluoroacetone in high yield. This would indicate that the introduction of the first bromine atom took place before decarboxylation since any further bromination of the ketone formed would be extremely difficult under these conditions.[5] In support of this postulate, ethyl α-bromo-α,γ,γ,γ-tetrafluoroacetoacetate was prepared and found to undergo ready hydrolysis and decarboxylation yielding the monobromoketone. If this reaction was conducted in the presence of bromine, the principal product was the dibromoketone.

The properties of the compounds prepared are given in Table I.

TABLE I

NEW COMPOUNDS

Formula	B.p., °C.	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
$CF_3COCHFBr$	65	17.20	17.01	0.48	0.60
$CF_3COCFBr_2$	81	12.50	12.81	0.00	0.10
$CF_3CHOHCHFBr$	124	17.10	17.12	1.43	1.54
 $CF_3\overset{O}{CH—CHF}$	37	27.70	27.78	1.53	1.89
$CF_3COCFBrCO_2C_2H_5$	51 at 15 mm.	25.60	25.90	1.78	1.81

Experimental

3-Bromo-1,1,1,3-tetrafluoroacetone.—A solution of 40% sulfuric acid (200 ml.) was prepared in a 500-ml., round bottomed flask which was equipped with a reflux condenser, a sealed stirrer and an addition funnel. Ethyl α,γ,γ,γ-tetrafluoroacetoacetate (86 g.) was added to the aqueous acid and the mixture was heated to 80–90°. While the mixture was being stirred vigorously, bromine (75 g.) was added dropwise and at such a rate that only a light red color was maintained in the solution. After all the bromine had been added, the mixture was heated and stirred for an additional two hours. The cooled mixture was diluted with 100 ml. of water and extracted with ether. The ether solution was dried with Drierite and then distilled. When the pot temperature reached 50°, the distillation was stopped and the residue was cooled in an ice bath. An equal volume of concd. sulfuric acid was added to the flask and the contents were mixed. Distillation was then continued and 87 g. (95%) of ketone was obtained. The material had an unpleasant odor similar to that of 3-bromo-1,1,1-trifluoroacetone.[2b]

3,3-Dibromo-1,1,1,3-tetrafluoroacetone.—A solution of 40% sulfuric acid (100 ml.) was prepared in the reaction flask. Ethyl α,γ,γ,γ-tetrafluoroacetoacetate (20 g.) was added to the flask and the mixture was heated to 90°. Bromine (30 g.) was added to the hydrolysis mixture over a period of 30 minutes. The bromine concentration in the reaction flask was high at all times as shown by the dark red color in the flask. An additional two hours of heating and stirring was required to remove all the bromine color from the solution. The aqueous mixture was cooled and extracted with ether. The ether solution was dried with Drierite and then distilled until the pot temperature reached 50°. The residue was mixed with an equal volume of concd. sulfuric acid and distillation was continued. The monobromo compound (4 g.) was obtained boiling at 65–67°, the temperature then rose to 81° and 23 g. (80%) of the dibromoketone was obtained.

3-Bromo-1,1,1,3-tetrafluoroisopropyl Alcohol.—Anhydrous ether (500 ml.) and lithium aluminum hydride (3.8 g.) were mixed in a 1000-ml., 3-necked flask which was equipped with a reflux condenser, a sealed stirrer, and an addition funnel. The flask was immersed in an ice-bath and a solution of 3-bromo-1,1,1,3-tetrafluoroacetone (41 g.) in anhydrous ether (80 ml.) was added dropwise over a period of 8 hours. The reaction was stirred at 0° for an additional 6 hours and then permitted to stand at room temperature for 8 hours. Absolute ethanol (3 ml.) was added to decompose any unreacted lithium aluminum hydride and the mixture was then poured over a mixture of concd. sulfuric acid (50 g.) and crushed ice (500 g.). The ether solution was separated and the aqueous solution was extracted with ether. The ether solution was dried with Drierite and then distilled. Phosphorus pentoxide (2 g.) was added to the mixture and distillation was continued. The bromoketone (4 g.) was recovered boiling at 60–70° and 33.5 g. (91%) of 3-bromo-1,1,1,3-tetrafluoroisopropyl alcohol was obtained.

1,3,3,3-Tetrafluoropropylene Oxide.—A solution of water (50 g.) and sodium hydroxide (50 g.) was prepared in a 300-ml., 3 necked flask. The reaction flask was equipped with a sealed stirrer, an addition funnel and a side arm distilling head. The side arm of the distilling head was connected to an ice-cooled trap followed by a Dry Ice-cooled trap. A thermometer was inserted through the distilling head into the aqueous sodium hydroxide so that the temperature of the reaction mixture could be checked at all times.

The reaction mixture was heated to 95–100° and 3-bromo-1,1,1,3-tetrafluoroisopropyl alcohol (21 g.) was added dropwise over a period of 3 hours. The bromohydrin was added

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[1] Abstracted, in part, from the doctoral thesis of H. W. Kilbourne, Purdue University.

[2] (a) E. Gryskiewicsz-Trochimowski, A. Sporzynski and J. Wnuk, *Rec. trav. chim.*, **66**, 413 (1947); (b) E. T. McBee and T. M. Burton, THIS JOURNAL, **74**, 3022 (1952).

[3] E. T. McBee, O. R. Pierce, H. W. Kilbourne and E. R. Wilson, *ibid.*, **75**, 3152 (1953).

[4] L. P. Hammett, "Physical Organic Chemistry," First Ed., McGraw-Hill Book Co., Inc., New York, N. Y., p. 362.

[5] E. T. McBee and T. M. Burton, THIS JOURNAL, **74**, 3902 (1952).