ing with decomposition at 260° were obtained. The yield (based on amine) was 39%.

Anal. Calcd. for $C_8H_{14}N_4 \cdot 2HCl$: C, 40.3; H, 6.7; N, 23.5; Cl, 29.8. Found: C, 40.5; H, 7.2; N, 23.7; Cl, 29.8.

Crystals of *the free base* could be kept for a short time at room temperature in a tightly stoppered bottle. Exposed to air they turned brown in a few hours. They melted between 65–75°, were very soluble in water, ethanol, acetone, carbon tetrachloride, and ether, but insoluble in petroleum ether.

N-diallylcyanoformamidine. A solution of 20 g. of diallyl amine in 40 ml. of anhydrous ethyl acetate was cooled to 40° and treated with cyanogen until the mixture turned yellow. After standing in the ice chest for 2 days, it was heated to 75° in a water bath under the hood to remove any unreacted cyanogen. Ethyl acetate was distilled off at atmospheric pressure and the remaining mixture was fractionated at 16 mm. pressure. Unreacted diallylamine weighing 9.8 g. was recovered. The yield of diallylcyanoformamidine boiling at 102–104°/16 mm. was 9.5 g. which on the basis of the diallylamine which reacted was 66.9%. The liquid was colorless and had a refractive index, n_D^{20}, of 1.4903.

The *hydrochloride* was prepared by saturating an ether solution of diallylcyanoformamidine with dry hydrogen chloride. The white solid was filtered, washed with cold ether, and dried in a vacuum desiccator over concentrated sulfuric acid. The crystals melted at 136–138° with decomposition.

Anal. Calcd. for $C_8H_{11}N_3 \cdot HCl$: C, 51.8; H, 6.52; N, 22.6; equiv. wt., 185.5. Found: C, 52.0; H, 6.95; N, 22.2; equiv. wt. (by NaOH titration), 186.4.

It was also possible to prepare the hydrochloride by cyanogenating diallylamine in petroleum ether. The cyanoformamidine, which settled out as an insoluble layer, was separated, washed with petroleum ether, dissolved in diethyl ether, and saturated with dry hydrogen chloride. This procedure eliminated the time-consuming distillation of the cyanoformamidine involved in the other procedure.

sym-Bis(2,3-dibromopropyl)oxamidine dihydrochloride. To 1 g. of *sym*-diallyloxamidine dihydrochloride dissolved in water was added bromine water until a yellow color persisted. Sufficient normal NaOH solution was added to remove excess bromine and to liberate the free base of the brominated product. The solution was extracted with ether, the extract dried, and saturated with gaseous hydrogen chloride. The crystalline product was recrystallized from ethanol. It melted at 212°.

The same product was obtained by adding a carbon tetrachloride solution of bromine to a carbon tetrachloride solution of *sym*-diallyloxamidine. The gummy precipitate was dissolved in ethanol and saturated with hydrogen chloride. Cooling in a dry ice chest caused the separation of crystals which melted at 212°.

Anal. Calcd. for $C_8H_{14}N_4Br_4 \cdot 2HCl$: C, 17.2; H, 2.9; N, 10.0; Br, 57.2; Cl, 12.7. Found: C, 17.5; H, 3.2; N, 10.3; Br, 57.0; Cl, 13.0.

The hydrochloride neutralized with dilute sodium hydroxide gave a solid presumed to be the *free base* which melted at about 112°.

Bromination of N-diallylcyanoformamidine. (a) Attempts to isolate the product of the bromination of *N*-diallylcyanoformamidine in carbon tetrachloride, ether, or ethanol solution produced only a gummy material. This, dissolved in ethanol and saturated with hydrogen chloride likewise failed to produce crystals. (b) *N*-diallylcyanoformamidine hydrochloride, dissolved in water, decolorized bromine water readily but gave a gummy product on which no analysis was attempted. (c) Two samples of *N*-diallylcyanoformamidine, quantitatively brominated with KBr-$KBrO_3$-HCl mixture, consumed respectively 3.90 and 3.89 equivalents of bromine per mole.

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DEPARTMENT OF CHEMISTRY
UNIVERSITY OF BUFFALO
BUFFALO, N. Y.

Trifluoroacetates of Ethylene Glycol

SIDNEY D. ROSS AND MANUEL FINKELSTEIN

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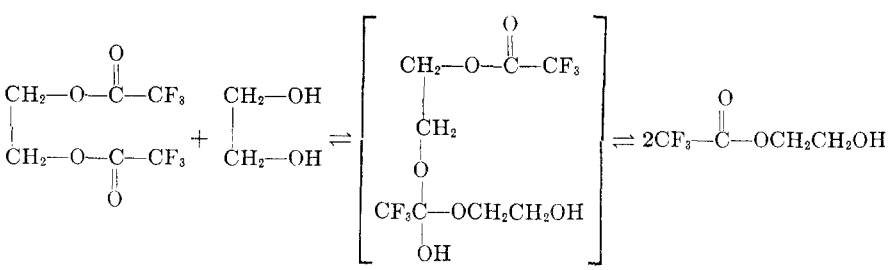
When an excess of ethylene glycol is reacted with either trifluoroacetic acid or trifluoroacetic anhydride and the reaction mixture is distilled at atmospheric pressure, an apparently homogeneous product is obtained. This product has a constant boiling point of 151–152°; n_D^{25} 1.3450. If this product is arbitrarily divided during distillation into successive fractions, all of the fractions have the same index of refraction and the same infrared spectrum.

Nevertheless, this product gives a saponification equivalent of 144, a value intermediate between those calculated for 2-trifluoroacetoxyethanol (158) and 1,2-bis(trifluoroacetoxy)ethane (127). It may be shown that this product is, in fact, a mixture by subjecting it to vapor phase chromatography at 145°, whereby it is separated into its two components, initially present in a ratio of 1.33 to 1 and having retention times of 10.5 min. and 7.6 min. respectively. This product is a mixture of 2-trifluoroacetoxyethanol and 1,2-bis(trifluoroacetoxy) ethane and results from an equilibration, at the temperature of distillation, according to the following equation:



By selecting appropriate reaction conditions it is possible to prepare both the pure ditrifluoroacetate and the pure monotrifluoroacetate. The former is readily obtained by treating ethylene glycol, in the cold, with a large excess of trifluoroacetic anhydride; the latter may be obtained by adding trifluoroacetic anhydride in benzene in the presence of *N,N*-dimethylaniline to an excess of glycol and carrying out the distillation of the product at reduced pressure. Pure 1,2-bis(trifluoroacetoxy)ethane is stable to distillation at atmospheric pressure, but when it is heated with glycol at 65°, a mixture of the two trifluoroacetates is obtained. Alternatively, if the pure monotrifluoroacetate is heated at 150° for 2 hr. in a sealed tube, a mixture of glycol, the monotrifluoroacetate and the ditrifluoroacetate is obtained. The reactions involved here are ester interchange reactions.[1] The ditrifluoroacetate requires glycol for equilibration, but the monotrifluoroacetate has both the ester and alcohol function and can react with itself. The reaction is probably particularly facile in this case because of the strong electron withdrawal from the carbonyl carbon atom by the trifluoromethyl group.

EXPERIMENTAL

Reaction of ethylene glycol with trifluoroacetic anhydride. Ethylene glycol (25.6 g.; 0.41 mole) was added, in several portions with shaking, to a cooled solution of trifluoroacetic anhydride (43 g.; 0.20 mole) in dry benzene (100 ml.). After standing overnight the reaction mixture was distilled at atmospheric pressure through a Vigreux column; yield, 52 g.; b.p., 150–155°; n_D^{25}, 1.3487. After redistillation this product had b.p., 151–152°; n_D^{25}, 1.3450; saponification equivalent found, 144, 145. The same procedure with just one equivalent of the glycol gave 41 g. of product; b.p., 151–152°; n_D^{25}, 1.3330; saponification equivalent, 135.

1,2-Bis(trifluoroacetoxy)ethanol. A large excess of trifluoroacetic anhydride (90 g.; 0.43 mole) was added slowly to ethylene glycol (5.5 g.; 0.08 mole) cooled in an ice bath. After standing overnight the mixture was distilled at atmospheric pressure; yield, 16.1 g. (79%); b.p., 152–154°; n_D^{25}, 1.3293. This product was dissolved in ether, washed with sodium bicarbonate solution, dried, and redistilled; b.p., 151–153°; n_D^{25}, 1.3286. Vapor phase chromatography indicated that this product contained at least 95% of one component, which had a retention time of 8.15 min.

Anal. Calcd. for $C_6H_4O_4F_6$: Sapon. equiv., 127. Found: Sapon. equiv., 124.

2-Trifluoroacetoxyethanol. Ethylene glycol (38 g.; 0.61 mole) was added with shaking to a cooled mixture of trifluoroacetic anhydride (43 g.; 0.20 mole) and *N,N*-dimethylaniline (18 g.; 0.15 mole) dissolved in dry benzene (100 ml.). Distillation at 10 mm. yielded 34.2 g. of crude product, b.p., 51–61°. This crude product was twice redistilled through a Vigreux column to yield finally 18.3 g. (58%) of 2-trifluoroacetoxyethanol; b.p., 48° at 8 mm.; n_D^{25}, 1.3520.

Anal. Calcd. for $C_4H_5O_3F_3$: Sapon. equiv., 158. Found: Sapon. equiv., 160.

Equilibration experiments. (1) 1,2-Bis(trifluoroacetoxy)-ethane (5 g.) was mixed with ethylene glycol (3.6 g.) and kept in an oil bath at 65° for 20 hr. The mixture was distilled directly, yielding 4 g. of product; b.p., 151–160°; n_D^{25}, 1.3548. This product was dissolved in ether. The ether solution was washed 3 times with water, dried over magnesium sulfate, and the ether was removed. Redistillation gave 3 g.; b.p. 149–151°; n_D^{25}, 1.3445.

In a typical experiment starting with 2-trifluoroacetoxyethanol, 10 ml. of the monoester was treated as indicated below and then divided by distillation into 3 arbitrary fractions of approximately 3 ml. each and a residue. During the distillation the bath temperature was not permitted to exceed 75°. In a control experiment, in which the monoester received no prior treatment, the successive fractions obtained had the following indices at 25°: 1, 1.3510; 2, 1.3535; 3, 1.3534; 4, 1.3545.

(2) The monoester was heated in a sealed tube at 150° for 2 hr. Distillation, as above, gave fractions having the following indices at 25°: 1, 1.3382; 2, 1.3390; 3, 1.3485; 4, 1.3650.

(3) Distillation of the monoester at atmospheric pressure without prior treatment, gave fractions having the following indices at 25°: 1, 1.3468; 2, 1.3488; 3, 1.3508; 4, 1.4150.

(4) Treatment of the monoester with a trace of sodium for 20 hr. at room temperature resulted in the following fractions: 1, 1.3495; 2, 1.3500; 3, 1.3512; 4, 1.3528. In this case the fourth fraction was obtained by distilling to dryness since the sodium salt was insoluble.

Treatment of the monoester with a trace of *p*-toluenesulfonic acid for 20 hr. at room temperature gave fractions having the following indices of refraction at 25°: 1, 1.3490; 2, 1.3498; 3, 1.3512; 4, 1.3668.

In the vapor phase chromatography experiments, a Perkin-Elmer Model 154 instrument (column "A", 20 p.s.i. He) was used.

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RESEARCH LABORATORIES
SPRAGUE ELECTRIC COMPANY
NORTH ADAMS, MASS.

(1) M. Harfenist and R. Baltzly, *J. Am. Chem. Soc.*, **69**, 362 (1947); L. Farkas, O. Schächter, and B. H. Vromen, *J. Am. Chem. Soc.*, **71**, 1991 (1949).

Preparation of Dimethyl β-Ketoadipate

JEROME KORMAN

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Although its use has been generally restricted to the preparation of substituted phenanthrene derivatives,[1,2] β-ketoadipic ester can be an important intermediate for the synthesis of many interesting compounds.

Numerous procedures for the preparation of the methyl and ethyl esters have appeared in the literature, but none is completely satisfactory.[3] In addition to poor yields all suffer the disadvantage of being quite lengthy, and require the preparation and purification of intermediates. The ester has been prepared by: (a) Acylation of the sodio deriva-

(1) J. C. Bardhan, *J. Chem. Soc.*, 1848 (1936).

(2) W. E. Bachmann and R. E. Holmen, *J. Am. Chem. Soc.*, **73**, 3660 (1951).

(3) An excellent critique and complete experimental data have been assembled by R. E. Holmen, Dissertation, The University of Michigan, 1948 (University Microfilm Publication No. 1173).