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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(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

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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).

tive of acetoacetic ester with β-carbalkoxypropionyl chloride with subsequent removal of the acetyl group by ammonolysis;[4] (b) Acylation of the magnesium enolate of malonic ester with the same acid chloride, followed by decarbalkoxylation by thermal decomposition in the presence of β-naphthalenesulfonic acid;[5,6] and (c) Saponification and decarboxylation or cleavage of the acylated intermediate (prepared by any method above) to the β-ketoadipic acid, followed by esterification.[3]

While the magnesium enolate method (b) appears to be the most facile, this laboratory has never been able to realize the yields reported, nor were the results consistent. Successful decomposition of the tricarboxylic ester intermediate presented the most difficulty and in many cases only tar resulted.

It has been found that the desired compound can be readily prepared in quantity by employing the procedure for the synthesis of ethyl diacetylacetate.[7] In this particular case, the magnesium enolate of methyl acetoacetate and β-carbomethoxypropionyl chloride were used. The resulting intermediate was treated with gaseous ammonia as in method (a). In spite of the relatively low yield (38% over-all) the procedure has certain merits. No isolation of intermediate is required, and except for the final distillation, the preparation can easily be completed in one day. The method is quite satisfactory for the methyl ester; in one experiment using the corresponding ethyl esters only a 25% over-all yield of diethyl β-ketoadipate was obtained. This was not investigated further.

EXPERIMENTAL[8]

Dimethyl β-ketoadipate. To 30 g. (1.23 moles) of magnesium metal turnings and 287 g. (2.47 moles) of methyl acetoacetate in 800 ml. of dry benzene was added all at once 565.8 g. (3.76 moles) of β-carbomethoxypropionyl chloride[9] and the mixture refluxed for 3.5 hr. on the steam bath. Provision was made for the removal of hydrogen chloride, which was evolved. During this time additions of fresh magnesium metal were made as follows: 7.5 g. after 1.5 hr. and 15 g. after 2.5 hr. After cooling, as much of the benzene solution as possible was decanted, and the residue treated with water and ether. The solutions were combined after filtering from unused magnesium. The separated organic layer was washed with water, 5% sodium bicarbonate solution, and finally with water, and dried over anhydrous sodium sulfate. The filtered solution was cooled to 0° and dry ammonia passed in for 40 min. After standing at room temperature for 30 min., the reaction mixture was washed with water until neutral and dried over anhydrous sodium sulfate. Removal of the solvent and distillation through a 30-cm. Vigreux column gave 174.5 g. (37.8%) of product boiling at 114–126°/0.8 mm. with most of the material distilling at 119–120° (reported 122° at 0.5 mm.[1]); n_D^{25} 1.4414. It gave a reddish-brown color with ferric chloride solution.

Anal. Calcd. for $C_8H_{12}O_5$: C, 51.06; H, 6.43. Found: C, 51.03; H, 6.45.

The *1-phenyl-3-(β-carbomethoxyethyl)-pyrazolone* was obtained in 70% yield upon heating an equimolar mixture of the adipic ester and phenylhydrazine on the steam bath for 2 hr. After recrystallization from a mixture of ethyl acetate and petroleum ether, it melted at 79–80°.

Anal. Calcd. for $C_{13}H_{14}N_2O_3$: C, 63.40; H, 5.73; N, 11.38. Found: C, 63.50; H, 5.79; N, 11.60.

Saponification and decarboxylation of a sample, and treatment of the resulting oil with semicarbazide hydrochloride, gave the semicarbazone of levulinic acid, m.p. 183–184.5° (reported 184–185°[1]).

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(4) *Cf.* ref. 1,3: P. Ruggli and A. Maeder, *Helv. Chim. Acta*, **25**, 936 (1942); J. R. Stevens and R. H. Beutel, *J. Am. Chem. Soc.*, **65**, 449 (1943); R. Robinson and J. S. Watt, *J. Chem. Soc.*, 1536 (1934).

(5) B. Riegel and W. M. Lilienfeld, *J. Am. Chem. Soc.* **67**, 1273 (1945).

(6) Presumably acylation of *t*-butyl malonate and thermal decomposition in the presence of *p*-toluenesulfonic acid according to the method of D. S. Breslow, E. Baumgarten, and C. R. Hauser, *J. Am. Chem. Soc.*, **66**, 1286 (1944) would be a source of product.

(7) A. Spassow, *Org. Syntheses*, **Coll. Vol. III**, 390 (1955).

(8) Melting points are uncorrected.

(9) J. Cason, *Org. Syntheses*, **Coll. Vol. III**, 169 (1955).

N-Vinyl-2-oxazolidone

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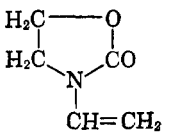
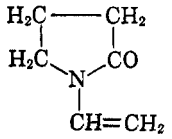
Widespread attention has been focused upon the rapid growth of the synthetic water-soluble polymer field.[1] In this connection, polyvinylpyrrolidone (PVP) has been given special recognition because of its original use as a blood plasma extender and because of its versatility in many industrial applications. Structurally related compounds are thus of considerable interest.

A recent German patent application[2] describes a process for the preparation of *N*-vinyl-2-oxazolidone and prompts a preliminary disclosure of our own research with this material. The structural similarity between this compound and *N*-vinyl-2-pyrrolidone is shown below:



N-vinyl-2-oxazolidone
(cyclic carbamate)



N-vinyl-2-pyrrolidone
(cyclic amide)

In spite of the structural similarity, these compounds and their polymers belong to different chemical families. The substitution of an oxygen atom for a methylene group within the heterocyclic ring (see formulas above) contributes an additional

(1) Symposia on Water-Soluble Polymers, Polymer and Cellulose Divisions, American Chemical Society, Dallas Meeting, April 8–13, 1956.

(2) W. Arend and H-G. Trieschmann, German Patent application Klasse 12p Gruppe 3, B340321Vb/12p; Filed 1/8/55, Published 3/29/56.