

diene. No marked polymerization took place within 1 hr. The remainder of the blue-black mixture was carbonated. The carboxylic acid therefrom distilled at 69–86°/1 mm. The neutralization equivalent was 76 and the refractive index was 1.4362. The yield was 1.3 g.

Metalation in the absence of alkoxide. A suspension (250 ml.) of amylsodium was prepared in the usual way¹⁰ from 0.5 g.-atoms of sodium sand and 0.25 mole of amyl chloride, and, next, was saturated with cyclopropane and allowed to stand. The disappearance of amylsodium was followed by infrared measurements^{11,12} of a Nujol mull. After one week the bands at 919 and 755 cm^{-1} characteristic for the amyl anion had become very much weaker. Meanwhile strong absorption bands had appeared at 1155, 1055, 1030, 860, and 810 cm^{-1} ; a moderate one at 1570 cm^{-1} and a weak band at 745 cm^{-1} . These bands are not far from some of those for cyclopropane itself which were very strong at 1434, 1024, and 866, moderate at 1510 and 1188, and very weak at 745 cm^{-1} . The bands are different from those for the allyl ion¹² which are very strong at 1525, 1247, and 600 cm^{-1} .

From this reaction mixture a 25-ml. aliquot was evaporated to dryness under reduced pressure. Then the dried residue was heated to 100° for 1 hr. The condensate caught in a nitrogen cooled trap showed an absorption curve identical with that for cyclopropane itself except for contamination from the pyrolysis of some amylsodium which was still present.

The remainder of the reaction mixture was carbonated and the recovered acids fractionated. The fraction of impure acid (4.4 g.), collected at 90°/30 mm., had n_D^{25} 1.4355. The recorded¹³ refractive index for cyclopropanecarboxylic acid is n_D^{25} 1.4359, and boiling point is 105°/48 mm. The amide from the acid chloride and ammonia melted at 124–127° (recorded¹⁴ 124.5–126°).

DEPARTMENT OF CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE 39, MASS.

(11) E. J. Lanpher, *J. Org. Chem.*, **21**, 830 (1956); *J. Am. Chem. Soc.*, **79**, 5578 (1957).

(12) E. J. Lanpher, *J. Am. Chem. Soc.*, **79**, 5578 (1957).

(13) J. D. Roberts, *J. Am. Chem. Soc.*, **73**, 5030 (1951).

(14) N. J. Demjanow and M. Dojasenko, *Ber.*, **56**, 2200 (1923).

A Synthesis of Fluorene-3-carboxylic Acid¹

D. C. MORRISON

Received December 17, 1957

Alder² and coworkers have shown that the sulfuric acid cyclization of phenyl terephthalic acid (diphenyl 2-5-dicarboxylic acid) gives fluorenone-3-carboxylic acid. Their synthesis of the diphenyl dicarboxylic acid, however, presents several difficulties and it was thought that if this acid were more readily available, a convenient route to 3-substituted fluorenes would be at hand. In the present work, the ester of phenyl terephthalic acid was prepared by a one-step process from diethyl terephthalate, though in mediocre yield.

(1) The work described in this paper was carried out under a research grant (No. C-327) to Prof. D. M. Greenberg, from the National Cancer Institute, U. S. Public Health Service.

(2) K. Alder, K. Heimbach, and K. Neufang, *Ann.*, **586**, 138 (1954); *Chem. Abstr.*, **49**, 5396 (1955).

Hey³ has demonstrated that the free radical decomposition of dibenzoyl peroxide in ethyl benzoate yields a mixture of esters of phenyl benzoic acids. In a similar reaction with diethyl terephthalate, only one isomer is possible due to the symmetry of para di-substituted benzenes. This operation has now been carried out yielding the ester of the desired phenyl terephthalic acid in about 12% yield. The poor yields (expected in this type of reaction) are compensated for by the economy of starting materials. The ester was hydrolyzed under alkaline conditions to the phenyl terephthalic acid which was cyclized by sulfuric acid to the fluorenone-3-carboxylic acid.² The latter was purified through its methyl ester as was done by Campbell and Stafford.⁴ Reaction of the methyl ester with red phosphorus and hydriodic acid in glacial acetic acid caused reduction and hydrolysis to give fluorene-3-carboxylic acid. This acid was further characterized by its methyl ester.

The route to fluorenone-3-carboxylic acid by oxidation of 3-methyl fluorene by permanganate⁵ or by chromic acid⁶ gave poor yields of material which was difficult to purify due to its contamination with acids probably produced by further oxidation of the desired acid (with cleavage of the fluorene ring).

EXPERIMENTAL

Melting points are uncorrected.

The better known dimethyl terephthalate was not employed in the reaction as it is a solid at steam bath temperatures. The diethyl terephthalate was made by two days refluxing of the acid with sulfuric acid and ethanol, followed by conventional purification.

Diethyl phenylterephthalate. Diethyl terephthalate (260 g.) was melted and kept at 60–70° while 50 g. of dibenzoyl peroxide were added in portions. The solution was immersed in a bath of boiling water for 4 hr. and then excess diethyl terephthalate was distilled under vacuum directly from the flask. If the temperature during the first hour of the reaction should rise above 100°, the decomposition may become violent. The distillation was carried out at 5 mm. and a forerun of diphenyl was discarded. This was followed by a large amount of recovered terephthalate which could be used again in another run. A similar reaction was done using 357 g. of diethyl terephthalate and 60 g. of dibenzoyl peroxide, and the distillation residues combined with those from the first run. These were now dissolved in ether and the solution extracted with aqueous sodium carbonate and then washed with sodium chloride solution (if water is used, a stable emulsion results). The ether was distilled and the product taken at 140–195°/3 mm. It was redistilled at about 160°/3 mm. The yield was 31.76 g. of a light yellow viscous oil. This is 11.73% based on the peroxide. The yield may perhaps be improved by reaction at higher dilution or by better temperature control. A resinous residue is left in the distillation flask.

Phenyl terephthalic acid. The 31.76 g. of ester was refluxed for 32 hr. with 40 g. of potassium hydroxide in 50% ethanol and the acid isolated as usual, by acidification with hydro-

(3) D. H. Hey, *J. Chem. Soc.*, 1966 (1934).

(4) N. Campbell and W. H. Stafford, *J. Chem. Soc.*, 299 (1952).

(5) D. Vorlander and A. Pritsche, *Ber.*, **46**, 1793 (1913).

(6) O. Kruber, *Ber.*, **65**, 1395 (1932).

chloric acid after removing ethanol. The yield of precipitated acid was 24.29 g. or 94.2%. It was very sparingly soluble in water. After one recrystallization from ether, the acid sintered above 200° and melted at 268–275° and after an additional recrystallization it melted at 277–280° (lit.² 277–278°).

Fluorenone-3-carboxylic acid. Alder *et al.*² give few details so these were worked out again. The cyclization in sulfuric acid gives yields of 79–87%. It was found to be temperature sensitive and should not be heated over 45° or further reaction occurs. Twenty g. of finely powdered phenyl terephthalic acid was stirred with 180 ml. of concentrated sulfuric acid at 25–30° until all was dissolved. The resulting dark solution was then kept at 40° (internal temp.) for 20–30 min. It was poured into ice water, and the precipitated acid filtered, washed, and dried. A yield of 15.17 g. or 81.9% of acid was obtained which sintered at 265° with melting 270–300°. Hydrolysis of the purified methyl ester and recrystallization from aqueous acetone gave a product of m.p. 299–304° with previous sintering (lit.⁴ 304°).

Methyl fluorenone-3-carboxylate. The acid was esterified by refluxing for 1 day a mixture of 8.0 g. acid with 5 ml. concentrated sulfuric acid and 750 ml. of methanol. After the usual isolation, a yield of 7.66 g. or 90% was obtained. Four recrystallizations from aqueous acetone gave a product sintering at 133° and melting at 146–147° (lit.⁴ 145°). Recrystallization eliminates any phenyl terephthalate or other impurities. The ester is decomposed by hot concentrated potassium hydroxide solution, giving a dark brown solution, and for hydrolysis, short contact with warm alkali is necessary.

Fluorene-3-carboxylic acid. A solution of 8.24 g. of methyl fluorenone-3-carboxylate in 300 ml. of acetic acid was mixed with 9 g. of red phosphorus and 10 ml. of 47–50% hydriodic acid and the liquid refluxed 45 hr. Most of the solvent was distilled and the residue diluted with 450 ml. of water and ice cooled several hours. The solids were filtered and then extracted with an excess of dilute potassium carbonate solution. The carbonate extract was filtered and acidified and the precipitated acid filtered off, washed, and dried. It weighed 7.18 g. or 98.7%. This preparation melted at 220–230° with previous sintering. Three recrystallizations from acetone-water with a minimum of heating gave a product of m.p. 229.5–231.5° with sintering at 222° (lit.⁴ 230 and 231°).

Methyl fluorene-3-carboxylate. 10 g. of the above acid with 8 ml. of concentrated sulfuric acid and 350 ml. of methanol were refluxed 24 hr. and the ester isolated as usual. The light brownish ester was washed with alkali and dried. It was then distilled from a small short-path still at 1 mm. and the solid distillate recrystallized from acetone-water and dried. The yield of white product was 10.1 g. or 94.7%. After four recrystallizations from aqueous acetone, the ester had m.p. 79–80°.

Anal. Calcd. for C₁₅H₁₂O₂: C, 80.36; H, 5.36. Found: C, 80.13; H, 5.32.

DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY
SCHOOL OF MEDICINE
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIF.

Preparation of Diethyl 4-Phosphonovalero-4-lactone

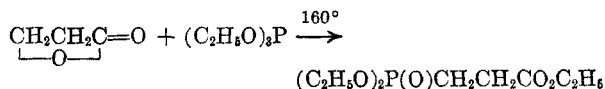
J. A. CADE

Received January 31, 1958

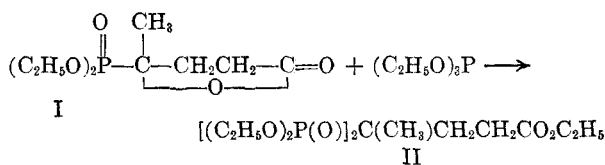
The preparation of esters of 1-hydroxyalkane-phosphonic acids by the base-catalyzed interaction

of carbonyl compounds with dialkyl hydrogen-phosphonates is well known,¹ but the behavior of 1-ketocarboxylic acids in this reaction does not appear to have been examined hitherto. Interest in such a reaction was provoked during a search for new methods of obtaining methanediphosphonates and related derivatives, *i.e.*, compounds containing a P-C-P bridge.²

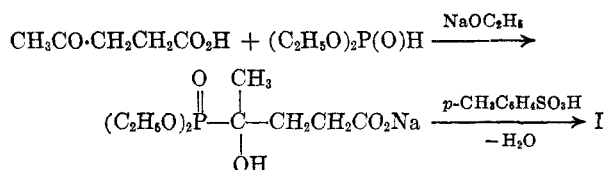
It had been shown,³ that trialkyl phosphite reacts with a lactone to give predominantly the trialkyl ester of a phosphonocarboxylic acid, *e.g.*:



Such a reaction might be expected to produce a *gem*-bis(dialkyl phosphono)carboxylic ester, II, from a dialkyl phosphonolactone in which the phosphorus atom is joined to the same carbon atom as the oxygen bridge; especially since the presence of the dialkyl phosphono group should enhance the electrophilic power of this atom:



This aspect of the investigations had to be suspended before it was brought to satisfactory completion, but an example of the type of lactone required *viz.* diethyl 4-phosphonovalero-4-lactone, I, was made from levulinic acid by the reactions:



Because of competition from the carboxyl group for the base, more than one equivalent of the latter is necessary to effect interaction, whereas with ordinary ketones a trace suffices. The product, I, is very sensitive to water and alcohols, and could not be isolated in a sufficiently pure condition to warrant quoting a value for the molecular refraction, even after repeated redistillation. It is acknowledged that most 1-hydroxyalkanephosphonates are not stable and easily revert to equilibrium with the components from which they are derived,⁴ but one would have expected ring formation in the lactone to prevent this. The triethyl ester obtained by in-

(1) R. L. McConnell and H. W. Coover, Jr., *J. Am. Chem. Soc.*, **78**, 4450 (1956) and references.

(2) Atomic Energy Research Establishment reports C/R 2011; C/R 2012 (1957).

(3) R. L. McConnell and H. W. Coover, Jr., *J. Am. Chem. Soc.*, **78**, 4453 (1956).

(4) V. S. Abramov and N. A. Ilyina, *J. Gen. Chem. (U.S.S.R.)* (Consultants Bureau English Translation), **24**, 121 (1956).