Tris(trimethylsiloxy)isopropoxytitanium. Trimethylacetoxysilane (26.4 g., 0.20 mole) was treated with 19.0 g. (0.067 mole) of tetraisopropoxytitanium as described previously. Isopropyl acetate was removed. Fractionation of the residual material yielded 16.3 g. (65.3% yield) of product boiling at 107°/8 mm., n_D^{25} 1.4321.

Anal. Calcd. for $C_{12}H_{34}O_4Si_3Ti$: C, 38.49; H, 9.15. Found: C, 38.48; H, 9.08.

Tetrakis(trimethylsiloxy)titanium. This compound was prepared by the addition of 26.4 g. (0.20 mole) of trimethylacetoxysilane to 14.3 g. (0.05 mole) of tetraisopropoxytitanium. After isopropyl acetate was removed, fractionation of the reaction mixture gave 16.6 g. 82.5% yield of product distilling at 125°/8 mm., n_D^{25} 1.4283.

Anal. Calcd. for $C_{12}H_{36}O_4Si_4Ti$: C, 35.62; H, 8.98. Found: C, 35.42, H, 8.73.

Reaction of tetrakis(trimethylsiloxy)titanium with acetic anhydride. Acetic anhydride (5.1 g., 0.05 mole) was added over a period of 10 min. to 10.1 g., (0.025 mole) of tetrakis-(trimethylsiloxy)titanium. The temperature of the reaction mixture rose from 28° to 51° during the addition, and a low boiling material was observed refluxing on the wall of the flask. The contents of the flask became increasingly cloudy and a viscous, opaque gel appeared after 15 min. After 30 min. the gel turned into a white solid. The reaction mixture was heated for 30 min. At this time the mixture consisted of two phases, a clear fluid and a white solid. Distillation of the volatile material yielded 9.4 g. of the product boiling at 102°, n_D^{25} 1.3810. The infrared spectrum taken on the volatile product was similar to that of trimethylacetoxysilane. The white solid pot residue weighed 4.5 g. (Si, 10.7%; Ti, 13.8%).

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The Preparation of *i*-Propyl Cyanomethyl Fumarate

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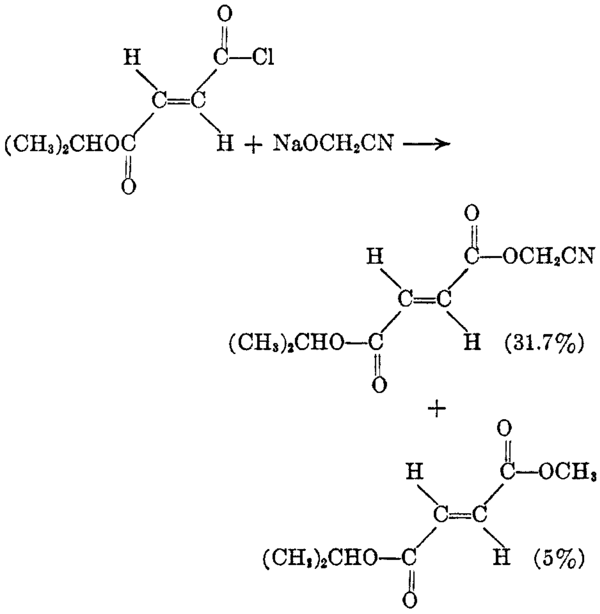
Received May 2, 1960

In the course of the preparation of new vinyl monomers, a convenient synthesis for alkyl fumaryl chlorides was developed. These acid chlorides served as intermediates for the preparation of various thiolfumarate esters and alkyl aryl fumarates *via* the Schotten-Baumann reaction.[1] As there are numerous examples of the synthesis and polymerization of cyanomethyl esters of α,β-unsaturated acids reported in the literature,[2] it was thought that alkyl cyanomethyl fumarates might also have useful properties.

Generally, the cyanomethyl esters of α,β-unsaturated acids have been prepared by alcoholysis of methyl or ethyl acrylates,[2d] the esterification reaction between an acyl halide and glycolonitrile,[2a,b,c,f] dehydrochlorination of the appropriate ester with quinoline,[2c] and the reaction of an acyl halide, formaldehyde, and an alkali metal cyanide.[2a,c] While Mowry was able to prepare a series of cyanomethyl esters by essentially a Schotten-Baumann reaction involving sodium cyanide and an appropriate acyl halide, these derivatives of dibasic acid halides, including fumaryl chloride, were formed in insignificant yield by this method. Instead biscyanomethyl fumarate was prepared from fumaryl chloride and glycolonitrile in the presence of a tertiary amine. However, as previously mentioned, the Schotten-Baumann reaction had been used successfully with various alkyl fumaryl chlorides, and the reaction between *i*-propyl fumaryl chloride, formaldehyde, and sodium cyanide was undertaken. The yield of *i*-propyl cyanomethyl fumarate obtained was 31.7%. However, material of the empirical formula $C_8H_{12}O_4$ was also formed. This was shown to be methyl *i*-propyl fumarate by comparison with an authentic sample prepared from *i*-propyl fumaryl chloride and methanol in the presence of pyridine. The probable explanation for the presence of this by-product is the formation of methanol by the Cannizzaro reaction involving formaldehyde in the alkaline sodium cyanide solution. The methanol could then compete for the available acyl halide.



EXPERIMENTAL

Boiling points are uncorrected. Unless otherwise indicated, distillations were carried out through an 80-cm. Podbielniak-type column.

i-Propyl fumaryl chloride. A sample of crude *i*-propyl hydrogen maleate was prepared by warming a mixture of 0.5 mole each of maleic anhydride and *i*-propyl alcohol on the steam bath until a sirupy liquid resulted. To this

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(1) P. G. Campbell, G. Sumrell, and C. H. Schramm, to be published.

(2a) D. T. Mowry, *J. Am. Chem. Soc.*, **66**, 371 (1944); (b) J. Harmon and C. J. Mighton, U. S. Patent **2,379,297** [*Chem. Abstr.*, **39**, 5128 (1945)]; (c) D. T. Mowry, U. S. Patents **2,380,061** and **2,380,062** [*Chem. Abstr.*, **40**, 91 (1946)]; (d) C. E. Rehberg, M. B. Dixon, and W. A. Faucette, *J. Am. Chem. Soc.*, **72**, 5199 (1950); (e) G. F. D'Alelio, U. S. Patent **2,583,062** [*Chem. Abstr.*, **48**, 11806 (1954)]; (f) C. S. Marvel, *et al.*, *Ind. Eng. Chem.*, **47**, 344 (1955).

mixture was added dropwise and with stirring, 0.6 mole of thionyl chloride. After the addition was complete, the mixture was gradually heated to 100°, in *ca.* 2 hr., and maintained at this temperature for an additional 4 hr. The amber colored mixture was fractionally distilled, yielding 41.2 g. (46.8%) of product at 87–89° (12 mm.), n_D^{25} 1.4539.

Anal. Calcd. for $C_7H_9ClO_3$: C, 47.60; H, 5.14; Cl, 20.08. Found: C, 47.69; H, 5.30; Cl, 20.23.

i-Propyl cyanomethyl fumarate. This compound was prepared by essentially the method of Mowry.[2a] A mixture of 13.9 g. (0.17 mole as a 37% aqueous solution) of formaldehyde, 8.4 g. (0.17 mole) of sodium cyanide, and 100 ml. of water was cooled to 5–10°. *i*-Propyl fumaryl chloride, 26.5 g. (0.15 mole) was added dropwise and the mixture was allowed to stir overnight. The solution was extracted with ether and the combined ether extracts were washed with dilute sodium carbonate, dilute hydrochloric acid, and finally with water. After drying over Drierite, the material was distilled through a 15-cm. Vigreux column. The bulk of the distillate, 9.4 g., b.p. 112–113° (1.1 mm.), n_D^{25} 1.4534, represented a 31.7% yield of the desired product.

Anal. Calcd. for $C_9H_{11}NO_4$: C, 54.82; H, 5.62; N, 7.10. Found: C, 54.80; H, 5.75; N, 6.82.

However, in the forerun, there was obtained 1.3 g. of material of b.p. 40° (0.2 mm.), n_D^{25} 1.4364.

Anal. Calcd. for $C_8H_{12}O_4$: C, 55.80; H, 7.03. Found: C, 55.65; H, 7.15; N, 0.26.

Methyl i-propyl fumarate. A mixture of 6 g. (0.18 mole) of methanol and 50 ml. of pyridine was cooled to 0°, 12.4 g. (0.07 mole) of *i*-propyl fumaryl chloride was added dropwise and the mixture was allowed to stir overnight. The solution was poured into ice water with stirring. The aqueous solution was extracted with ether and the combined ether extracts were washed with dilute hydrochloric acid and water. The material was fractionally distilled and 7.0 g. (63.4%) of product at 98° (10 mm.), n_D^{25} 1.4354 was obtained.

Anal. Calcd. for $C_8H_{12}O_4$: C, 55.80; H, 7.03. Found: C, 55.91; H, 7.12.

The infrared spectra of this material and the above-mentioned forerun were identical.

Acknowledgment. The authors wish to thank Alfred Foulds for the microanalyses, N. Kerschner for the infrared spectra, and C. F. Hartman for technical assistance in this work.

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New Synthesis of Dibenzo[a,i]pyrene[1]

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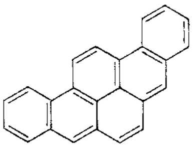
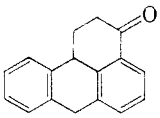
Received May 5, 1960

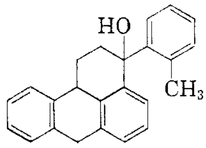
Recently Buu-Hoï and Lavit reported a five-step synthesis of dibenzo[a,i]pyrene (I) from benzo[a]pyrene in approximately 1% over-all yield.[2] Previously, the synthesis of I has been reported by several workers by the reduction of dibenzo[a,i]pyrene-5,8-quinone.[3–5]

A new synthesis of I has been accomplished in 7% over-all yield in this laboratory *via* 3-keto-1,2,3,11b-tetrahydro-7H-*meso*-benzanthracene (II), an intermediate readily available from previously reported research.[6,7] The ketone II was treated with *o*-tolylmagnesium bromide and the resulting carbinol, III, was dehydrated with Lucas reagent and chromatographed on alumina. The red, oily 3-(*o*-tolyl)-1,11b-dihydro-7H-*meso*-benzanthracene (IV) (or isomers thereof) thus obtained was cyclodehydrogenated with palladium on charcoal to dibenzo[a,i]pyrene (I).

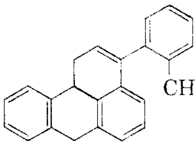

I



II



III



IV

EXPERIMENTAL

3-Hydroxy-3-(o-tolyl)-1,2,3,11b-tetrahydro-7H-meso-benzanthracene (III). A solution of 4.68 g. (0.02 mole) of 3-keto-1,2,3,11b-tetrahydro-7H-*meso*-benzanthracene (II) in 75 ml. of dry benzene was added dropwise over a period of 30 min. to a stirred ether solution of *o*-tolylmagnesium bromide prepared from 4.28 g. (0.025 mole) of *o*-bromotoluene. After refluxing for 1 hr. the reaction mixture was hydrolyzed with 50 ml. of 10% hydrochloric acid. The organic layer was washed with water and dried over anhydrous sodium sulfate. Removal of the solvent left 3-hydroxy-3-(*o*-tolyl)-1,2,3,11b-tetrahydro-7H-*meso*-benzanthracene (III) as a viscous brown oil which failed to crystallize.

3-(o-Tolyl)-1,11b-dihydro-7H-meso-benzanthracene (IV). The crude carbinol, III, was dissolved in anhydrous benzene and refluxed for 90 min. with 30 ml. of Lucas reagent. The organic layer was washed with water and saturated sodium carbonate solution, dried over anhydrous sodium sulfate, and chromatographed on alumina. Removal of the solvent yielded 5.2 g. of the hydrocarbon IV as a light red oil.

Dibenzo[a,i]pyrene (I). The hydrocarbon IV was cyclodehydrogenated by heating with 0.78 g. of 10% palladium on charcoal at 320–400° for 30 min. The crude hydrocarbon was sublimed from the reaction mixture at 275° and 0.05 mm. A toluene solution of the sublimate was chromatographed on alumina and concentration of the eluants yielded 0.42 g. (7% over-all yield from II) of dibenzo[a,i]pyrene (I) as small yellow plates, m.p. 281.5–282.5° uncorr.

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(1) This investigation was supported in part by a research grant (C-1595) from the National Cancer Institute of the National Institutes of Health, U. S. Public Health Service.

(2) N. P. Buu-Hoï and D. Lavit, *Tetrahedron*, **8**, 1 (1960).

(3) R. Scholl and H. Neumann, *Ber.*, **55**, 118 (1922).

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(7) J. L. Adelfang and G. H. Daub, *J. Am. Chem. Soc.*, **77**, 3297 (1955).