These two melting points are in fair agreement with the melting points given in the literature.[17]

Summary

1. The preparation of 9,10-dihydroanthracene and 1,2,3,4-tetrahydroanthracene by high-pressure hydrogenation of anthracene is described.

2. The Friedel–Crafts reaction of tetrahydroanthracene with acetyl chloride yields two methyl ketones. To the solid ketone of m. p. 101–102° the structure of a 6-acetyl derivative is assigned. For the oily ketone the structure of a 5-acetyl derivative is tentatively assumed.

3. Three amino alcohols of the type —CHOHCH$_2$NR$_2$ were prepared from 6-acetyl-1,2,3,4-tetrahydroanthracene.

BETHESDA, MARYLAND RECEIVED AUGUST 20, 1945

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[17] (a) Börnstein, *Ber.*, **16**, 2609 (1883); (b) Limpricht, *Ann.*, **309**, 96 (1899); (c) Weigert and Kummerer, *Ber.*, **47**, 898 (1914); (d) Lauer, *ibid.*, **70**, 1288 (1937).

[CONTRIBUTION FROM THE CENTRAL RESEARCH DIVISION OF THE MONSANTO CHEMICAL COMPANY]

Isomerization of Alkyl Phosphites. IV. The Synthesis of Some Alkaryl Phosphonic Acids and Esters

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The difficulties encountered in the synthesis of aromatic phosphonic acids present a rather effective barrier against a thorough study of the chemistry of these substances. The specific difficulties which occur in the classical Friedel–Crafts type synthesis are usually very poor yields and conversions and a degree of uncertainty as to the site of substitution (except in the relatively few cases of primarily simple hydrocarbons). The synthesis through the aryl mercurials is not a satisfactory one chiefly because of the tendency for by-product formation and because of the hazards connected with the toxicity of the intermediates.

A certain progress may be reported now in an indirect solution of the above difficulties, a solution based on the view that the greater part of the chemical characteristics of the true aromatic phosphonic acids are carried over into the class of alkaryl phosphonic acids, *i. e.*, aromatically chain-substituted alkanephosphonic acids. The method previously reported for the synthesis of aliphatic phosphonic acids[1] was successfully applied to the synthesis of compounds of this type in satisfactory yields in standard laboratory apparatus. The present paper deals with the synthesis of a number of the simpler members of the series, covering most of the principal aromatic nuclei and is limited to the compounds in which the bridge between the phosphono group and the aromatic nucleus is the shortest possible, *i. e.*, one methylene group.

The compounds of this type may be readily prepared by chloromethylation of the desired hydrocarbon, reaction of the chloromethyl derivative with an alkyl phosphite (either a trialkyl phosphite or a sodium dialkyl phosphite may be used) to form the corresponding dialkyl phosphonate and hydrolysis of the ester to the free phosphonic acid. Although bromo- and iodomethyl derivatives may be used in this scheme, the obvious economy of the chloromethyl compounds and the relative ease of their preparation need not be stressed. The choice of tri-alkyl or di-alkyl phosphites is resolved in favor of the latter by the reason of their considerably lower cost; the reactivity of the chloromethyl aromatics is generally sufficiently high to enable them to react with tri-alkyl phosphites satisfactorily, in contrast with the alkyl halides.[1] In the present paper the sodium dibutyl phosphite was again selected as the phosphonating agent for reasons which were cited earlier,[1] with one example of the use of a tri-alkyl phosphite being cited. Examples of the extension of this reaction to the preparation of di-phosphonic acids of this type are also presented for hydrocarbons which readily yield bis-chloromethyl derivatives. The general reaction scheme may be represented as

$$\mathrm{RH} \longrightarrow \mathrm{RCH_2Cl} \longrightarrow \mathrm{RCH_2P(O)(OR')_2} \longrightarrow \mathrm{RCH_2P(O)(OH)_2}.$$

Experimental

The preparation of sodium dibutyl phosphite and the procedure of its use were described previously.[1]

Phenylmethanephosphonic Acid (Benzylphosphonic Acid).—Benzyl chloride (63.3 g., 0.5 mole) was treated with sodium dibutyl phosphite prepared from 97 g. (0.5 mole) of dibutyl phosphite, the reaction being run in 300 cc. of xylene. After three hours of refluxing, the mixture was cooled, washed thoroughly with water to remove sodium chloride and distilled under reduced pressure to yield 121 g. (85%) of dibutyl benzylphosphonate as a colorless liquid, b. p. 140–143° (4 mm.); n^{25}_{D} 1.4820; calcd. P, 10.9; found: P, 10.8.

When the above ester was refluxed overnight with 250 cc. of concentrated hydrochloric acid, it was essentially quantitatively hydrolyzed to benzylphosphonic acid, which was recovered by the distillation of the hydrolyzate to approximately a half of its original volume, followed by the evaporation of the residue under an infra-red ray lamp to dryness. The acid, which readily crystallized on cooling, was recrystallized from water and had the melting point of 166°, in accord with the literature data.

***p*-Methylphenylmethanephosphonic Acid.**—*p*-Methylbenzyl chloride (30 g., 0.213 mole) was treated as above with 0.213 mole of sodium dibutyl phosphite in 200 cc. of toluene. There was obtained 54 g. (85%) of dibutyl *p*-

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[1] G. M. Kosolapoff, THIS JOURNAL, **67**, 1180 (1945).

methylphenylmethanephosphonate as a colorless oil, b. p, 213–215° at 20 mm., n^{25}D 1.4852; calcd. P, 10.4, found P, 10.4.

Hydrolysis with concentrated hydrochloric acid, as above, gave quantitatively the *p*-methylphenylmethanephosphonic acid as small colorless plates (from water), m. p. 185°; equiv. wt., calcd. 93, found 92.6.

***p*-Ethylphenylmethanephosphonic Acid.**—*p*-Ethylbenzyl chloride (77.25 g., 0.5 mole) was treated with 0.5 mole of sodium dibutyl phosphite in 350 cc. of xylene. After refluxing the mixture for three hours, there was obtained 88% (137 g.) of dibutyl *p*-ethylphenylmethanephosphonate as colorless liquid, b. p. 147–150° at 3 mm.; n^{25}D 1.4845; calcd. P, 9.9; found P, 9.86.

Heating of equimolar amounts of the above chloride with triethyl phosphite to 150° for four hours yielded 78% of diethyl *p*-ethylphenylmethanephosphonate as a colorless liquid, b. p. 176–178° at 14 mm.

Hydrolysis of either ester by boiling concentrated hydrochloric acid gave the *p*-ethylphenylmethanephosphonic acid as large flat colorless needles (from water), m. p. 178–178.5°; equiv. wt., calcd. 100, found 99.8.

***p*-Butylphenylmethanephosphonic Acid.**—*p*-Butylbenzyl chloride (41 g.) reacted with sodium dibutyl phosphite from 44 g. of dibutyl phosphite in 500 cc. of hexane. After refluxing for six hours, there was obtained 70% of dibutyl *p*-butylphenylmethanephosphonate, as a colorless oil, b. p. 175–178° at 2 mm.; calcd. P, 9.1; found P, 9.2.

Hydrolysis by boiling concentrated hydrochloric acid followed by crystallization from hexane gave 80% of *p*-butylphenylmethanephosphonic acid, as small flat needles, m. p. 162–163°; equiv. wt., calcd. 114, found 113.5.

1-Naphthylmethanephosphonic Acid.—1-Chloromethylnaphthalene (43 g.) was heated with 41 g. of triethyl phosphite at 150–160° for four hours to yield 58 g. (87%) of diethyl 1-naphthylmethanephosphonate as a colorless oil, b. p. 205–206° at 5 mm., n^{25}D 1.5610; calcd. P, 11.1; found P, 11.1.

Hydrolysis by boiling concentrated hydrochloric acid and crystallization from hot water gave 90% of 1-naphthylmethanephosphonic acid as small lustrous plates, m. p. 212–212.5°; equiv. wt., calcd. 111, found 110.5.

***p*-Biphenylmethanephosphonic Acid.**—*p*-Chloromethylbiphenyl (1 g., 0.005 mole) was treated with 0.005 mole of sodium dibutyl phosphite in 50 cc. of toluene. After refluxing for two hours, cooling and washing with water, the solvent was removed under reduced pressure to yield crude dibutyl *p*-biphenylmethanephosphonate as a yellowish viscid oil. This was refluxed overnight with 50 cc. of concentrated hydrochloric acid to yield the *p*-biphenylmethanephosphonic acid, which was purified by solution in dilute sodium hydroxide, precipitation by hydrochloric acid and crystallization from hot water; 0.6 g., m. p. about 250°, with decomposition; equiv. wt., calcd. 124, found 125.

9-Phenanthrylmethanephosphonic Acid.—9-Chloromethylphenanthrene (2 g., 0.009 mole) was treated with 0.009 mole of sodium dibutyl phosphite in 50 cc. of toluene. The mixture was treated analogously to the biphenyl compound above to yield, after separation from gummy byproducts and crystallization from a mixture of ethanol, benzene and hexane, 1.1 g. of 9-phenanthrylmethanephosphonic acid, as slightly yellowish fine plates, which darken and decompose at 212°, equiv. wt., calcd. 136, found 137. (*Note:* Since the complex polycyclic systems afford a certain possibility of migration of the substituent group during the reaction sequence, the above structure is given provisionally. The writer is not aware of migrations involving the phosphono group in aromatic compounds, but in view of the lack of other synthetic methods, the above synthesis is felt to be of some weight in assigning the given structure.)

1,3,5-Trimethylbenzene-2,4-bis-(methanephosphonic Acid).—Bis-chloromethylmesitylene (4.3 g., 0.02 mole) was treated with 0.04 mole of sodium dibutyl phosphite in 200 cc. benzene–hexane mixture. After the vigorous reaction subsided, the mixture was refluxed for three hours, cooled, washed with water and the organic layer separated. Volatiles were removed by heating to 265° at 1 mm. and the residual mass was refluxed for two days with 100 cc. of concentrated hydrochloric acid. The precipitated solid was separated, dried, dissolved in dilute sodium hydroxide, the solution acidified with hydrochloric acid and the product separated and washed with cold water. Three grams of 1,3,5-trimethylbenzene-2,4-bis-(methanephosphonic acid) were thus obtained as a colorless powder, which does not melt at 300°. Titration of the material was impossible due to extremely vague endpoints. *Anal.* Calcd.: P, 20.1. Found: P, 19.8.

Anthracyl-9,10-bis-(methanephosphonic Acid.)—9,10-Bis-chloromethylanthracene (3 g., 0.011 mole) was treated with 0.022 mole of sodium dibutyl phosphite in 200 cc. xylene and refluxed for six hours. After washing with water and removal of volatiles by heating *in vacuo*, the residual mass was hydrolyzed by boiling hydrochloric acid for twenty-four hours. The solid residuum was dissolved in dilute sodium hydroxide and precipitated by hydrochloric acid, to give 75% anthracyl-9,10-bis-(methanephosphonic acid) as minute pale yellow needles, which decompose at 215°. The acid could not be titrated. *Anal.* Calcd. P, 16.9. Found: P, 17.0.

Summary

A satisfactory synthetic procedure was developed for preparation of alkaryl phosphonic acids and their esters. Eight new alkarylphosphonic acids and esters were prepared.

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RECEIVED OCTOBER 11, 1945