

in the ultraviolet region. We have observed similar melting-point behavior in the 1,2- and 2,3-bis-(*p*-methoxyphenyl)-cyclohexenes⁴ and nearly identical absorption spectra for the 1,3- and 2,4-isomers.⁵

Although 3-(*p*-methoxyphenyl)-cyclopentene-2-one is only slightly soluble in ether, several attempts were made to induce reaction between it and *p*-methoxyphenylmagnesium bromide. The unsaturated ketone and dianisyl were the only products isolated from these reactions.

The alkaline demethylation procedure was applied to III in the hope that the phenolic isomers could be separated. However, the only product was a light-red crystalline material, m.p. 157–159°. This was an indicator, red in acid and blue in alkali, which could be hydrogenated to a colorless compound, m.p. 32–34°, but was not further characterized. However, III was hydrogenated easily to give 1,3-bis-(*p*-methoxyphenyl)-cyclopentane which was demethylated in the usual manner to 1,3-bis-(*p*-hydroxyphenyl)-cyclopentane. The yield of this product was 44% from 3-(*p*-methoxyphenyl)-cyclopentanone.

Experimental⁶

3-(*p*-Methoxyphenyl)-cyclopenten-2-one.—The procedure of Wilds and Johnson² was used, except that the crude product was not recrystallized directly from ethanol. This procedure always gave brown, poorly crystalline products. However, sublimation at 120° and 0.5–1.0 mm. in a convenient tubular apparatus⁷ yielded material which crystallized well from ethanol as colorless needles (69% yield), m.p. 140–141°.

3-(*p*-Methoxyphenyl)-cyclopentanone.—When 3.76 g. of the unsaturated ketone was hydrogenated over 0.2 g. of palladium oxide at 40 p.s.i. in 150 ml. of ethanol, made just basic to litmus with potassium hydroxide, the reaction stopped completely after one equivalent of hydrogen had been absorbed. After neutralization of the filtrate, the product was isolated and recrystallized from petroleum ether. The yields from several preparations ranged between 86 and 94% of colorless prisms, m.p. 47–49°, as previously described.

1,3-Bis-(*p*-methoxyphenyl)-cyclopentene.—To the Grignard reagent prepared under nitrogen from 3.00 g. (0.125 mole) of magnesium turnings and 23.3 g. (0.125 mole) of *p*-bromoanisole in 400 ml. of dry ether was added 21.5 g. (0.113 mole) of 3-(*p*-methoxyphenyl)-cyclopentanone dissolved in 300 ml. of dry ether. The addition was made slowly to maintain refluxing and the mixture allowed to stand overnight. Hydrolysis was accomplished at 5° with a concentrated ammonium chloride solution and the ethereal solution washed, dried and concentrated under reduced pressure. Distillation of the residue gave a fraction, b.p. 161–163° (0.025 mm.), which was recrystallized twice from methanol, yielding colorless needles, m.p. 90.0–92.5°; $\lambda_{\text{max}}^{95\% \text{ alc.}}$ 264 m μ (ϵ 23,130).

Anal. Calcd. for C₁₉H₂₀O₂: C, 81.40; H, 7.12. Found: C, 81.49; H, 7.12.

Attempts to isolate two isomers by chromatography of the crude distillate on alumina led to the isolation of many fractions from the petroleum ether–benzene eluates. After recrystallization all of these melted in the range 87 to 93° and were indistinguishable from each other on the basis of melting point, crystalline form, or ultraviolet absorption. Fractional crystallization led to similar results.

1,3-Bis-(*p*-methoxyphenyl)-cyclopentane.—Hydrogenation of 2.80 g. of the cyclopentene in 150 ml. of 95% ethanol

over 0.50 g. of 10% palladium-on-carbon catalyst at 40 p.s.i. was complete in seven minutes. After filtration and concentration to 50 ml., the solution was allowed to stand. The crystalline product was collected and recrystallized from methanol to yield 2.3 g. (82%) of colorless needles. The analytical sample, m.p. 48.0–49.5°, was obtained after two more recrystallizations, $\lambda_{\text{max}}^{95\% \text{ alc.}}$ 228 m μ (ϵ 23,830), 278 m μ (ϵ 3,750).

Anal. Calcd. for C₁₈H₂₂O₂: C, 80.81; H, 7.86. Found: C, 80.84; H, 7.72.

1,3-Bis-(*p*-hydroxyphenyl)-cyclopentane.—Dimethylation of 2.25 g. of 1,3-bis-(*p*-methoxyphenyl)-cyclopentane in 45 ml. of 95% ethanol with 6.25 g. of potassium hydroxide by heating at 200 to 212° for 24 hours⁸ yielded, after extraction with ether, acidification and extraction of the product with ether, a material which was most conveniently recrystallized from 33% water in methanol. In this way 1.84 g. (81%) of the diphenol, m.p. 153–160°, was obtained as tiny, slightly pink rosettes. The analytical sample obtained after two more recrystallizations, m.p. 158–160°, was colorless and gave a negative phenol reaction with ferric chloride solution.

Anal. Calcd. for C₁₇H₁₈O₂: C, 80.28; H, 7.13. Found: C, 80.21; H, 6.94.

1,3-Bis-(*p*-acetoxyphenyl)-cyclopentane was prepared by acetylating the diphenol with acetic anhydride in the presence of anhydrous sodium acetate. This compound crystallized from methanol as colorless platelets, m.p. 67–68°.

Anal. Calcd. for C₂₁H₂₂O₄: C, 74.53; H, 6.85. Found: C, 74.43; H, 6.78.

(8) E. C. Dodds, L. Golberg, W. Lawson and R. Robinson, *Nature*, **141**, 247 (1938).

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Some Observations Concerning the Acidic Salts of Phosphonic Acids

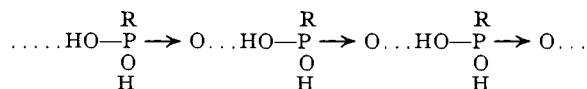
BY GENNADY M. KOSOLAPOFF

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Several notes about the existence of relatively insoluble acid salts of phosphonic acids are found in the literature, beginning with the work of Michaelis.¹ No specific inquiry into the possible structure of these salts has been made although they have been used for a convenient isolation of phosphonic acids from aqueous solutions by Doak and Freedman.²

The probably similar relatively insoluble partial salts of mono-esters of phosphoric acid have been investigated quite recently and hydrogen-bonded cyclic formulations for them have been proposed.³

It was shown recently⁴ that phosphonic acids tend to associate very extensively with the very probable formation of long-chain linear aggregates which can be formulated as



The very considerable water solubility of these acids, coupled with the generally low order of solu-

(1) A. Michaelis and C. Panek, *Ber.*, **13**, 653 (1880); *Ann.*, **212**, 203 (1882).

(2) G. O. Doak and L. D. Freedman, *This Journal*, **73**, 5658 (1951).

(3) T. Wagner-Jauregg, *et al.*, *Ber.*, **74**, 1513 (1941); **75**, 178 (1942); I. R. Hunter, R. L. Roberts and E. B. Kester, *This Journal*, **70**, 3244 (1948); especially, O. M. Friedman and A. M. Seligman, *ibid.*, **73**, 5292 (1951).

(4) G. M. Kosolapoff and J. S. Powell, *J. Chem. Soc.*, 3535 (1950).

(4) G. P. Mueller and R. May, *This Journal*, **71**, 3313 (1949).

(5) G. P. Mueller and C. B. Honaker, *ibid.*, **73**, 2377 (1951).

(6) All melting points were observed at fifty magnifications on the Kofler apparatus and are corrected.

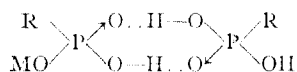
(7) A. F. Helin and C. A. VanderWerf, *Anal. Chem.*, **21**, 1284 (1949).

bility in hydrocarbon solvents, also appears to support such a formulation.

When a phosphonic acid is gradually neutralized by addition of a base, the above formulation would indicate the possibility of initial neutralization of the "free" chain ends and a preservation, in whole or in part, of the essential structure of the chain.

In experiments with *n*-butanephosphonic acid, which is a readily available experimental material, the acid was neutralized in aqueous solution with sodium hydroxide added in small steps. Specimens of solutions so obtained ranging up to the point of exact half-neutralization in 5% steps were carefully evaporated to dryness. The products obtained by neutralization up to one-quarter of all available hydrogen ions, *i.e.*, up to empirical formulation of $RPO_3H_2 : RPO_3HNa$, were waxy substances which melted well below the melting point of the free acid (m.p. 106°); generally the softening began at $60-70^\circ$ and extended to approximately 110° , with formation of a very viscous transparent liquid. At the point of "25%" neutralization the nature of the products underwent a decided change. The substance obtained at this juncture was a freely mobile powder which showed the first sign of partial liquefaction only at 143° and the translucent jelly-like consistency was maintained even at well above 200° . Extraction of these lower products with hot benzene resulted in slow removal of the free acid from specimens containing less than 25% neutralized material; the residual matter was identical with the "quarter" salt described above. Since the free acid is rapidly soluble in hot benzene on heating, the relative slowness of the extraction of the partial salts (0.5-1.0 hour) may serve as an indication of the time requirement for the separation of the chain fragments of the residual phosphonic acid chain from the neutralized portion, possibly through cleavage of monomer units which then associate.

The "quarter-neutralized" product was not soluble in hot benzene and its solubility in water at 25° was appreciably lower than that of the free acid: approximately 17 weight per cent. against 31 weight per cent. This suggests that the essentially chain-linked free acid has been transformed at this juncture into a ring-linked structure, similar to that found in phosphonous acids,⁴ *i.e.*



The analogy is obviously incomplete, since the phosphonous acids appear to form a trimeric ring, lacking free hydroxyl groups.

Products obtained by further neutralization of the acid are freely flowing powders of microcrystalline appearance; they shrink and sinter at temperatures that rise from 143° shown by the "quarter" salt to 245° shown by the "half" salt, *i.e.*, product corresponding to RPO_3HNa . The latter is less soluble than the "quarter" salt, dissolving only to the extent of 13 weight per cent. in water at 25° . The behavior of this salt suggests the structure similar to that of the "quarter" salt with the hydroxyl being replaced by ONa group, thus affording a very symmetrical aggregate. Heated to red heat the

substance decomposes with evolution of an organic phosphine, a behavior that is not observed with the free acid and thus suggesting a different aggregation of the constituents. Such a reaction is rather typical of phosphonous acids on pyrolysis and underlines the apparent similarity of the overall structures of these two classes of substances. The amounts of the generated phosphine were too small for positive identification but absorption in strong nitric acid resulted in formation of an acid that appears to be butanephosphonic acid.

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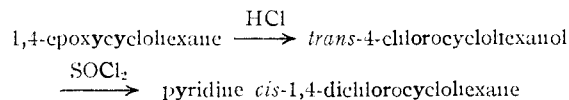
cis-1,4-Dichlorocyclohexane^{1,2}

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Of the seven possible dichlorocyclohexanes, the *trans*-1,2- is well known and the 1,1- and *cis*-1,2- have recently been reported.³ In regard to other isomers, Rothstein⁴ obtained a mixture of 1,4-dichlorocyclohexanes from which a solid melting at 102° , considered to be the *trans* isomer, was separated. The *cis*-1,4- was apparently not completely separated from the *trans* isomer as it remained liquid on cooling to -15° .

It was thought that the *cis*-1,4-dichlorocyclohexane might be obtained in satisfactory purity by means of the reactions



These reactions did furnish a dichloro derivative which, on the basis of its history and the mechanisms generally accepted for the reactions by which it was made, is assumed to be the *cis*-1,4-dichlorocyclohexane. Since the preparation of *trans*-4-chlorocyclohexanol from 1,4-epoxycyclohexane has recently been described,⁵ only the conversion of the chlorohydrin to the dichloride is reported here.

Reaction of thionyl chloride on 4-chlorocyclohexanol in the absence of pyridine produced no dichloride.

Experimental

A mixture of 48.6 g. (0.36 mole) of *trans*-4-chlorocyclohexanol, 100 ml. of chloroform and 34.4 g. (0.43 mole) of pyridine (freshly distilled) was stirred until the chlorohydrin dissolved, then 51.5 g. (0.43 mole, 20% excess) of thionyl chloride was added dropwise. The temperature was allowed to rise until reflux started and refluxing was continued for one hour after all the thionyl chloride was added. After cooling, the mixture was washed twice with water, the water extracted with ether and the ether combined with the chloroform solution. After drying, the solvents were

(1) This paper represents part of a thesis submitted by T. W. Lunney to the University of South Carolina in partial fulfillment of the requirements for the degree of Master of Science.

(2) Part of a paper presented before the Southwide Chemical Conference, Wilsont Dam, Ala., October, 1951.

(3) (a) B. Carroll, D. G. Kubler, H. W. Davis and A. M. Whaley, *This Journal*, **73**, 5382 (1951); (b) H. C. Stevens and O. Gronvittl, International Congress of Pure and Applied Chemistry, Sept. 10-13, 1951, New York, N. Y.

(4) B. Rothstein, *Ann. chim.*, **14**, 461 (1930).

(5) E. A. Feluel, S. Goodyear and J. Berkowitz, *This Journal*, **71**, 4978 (1951).