20% ethanol–water mixture at the same temperature.

TABLE II

Temp., °C.	Solvent % by volume	k in liters/mole-hr.
62.36	60% dioxane–water	1.64
62.36	60% dioxane–water	1.75
54.09	60% dioxane–water	0.69
53.90	60% dioxane–water	.58
46.4	60% dioxane–water	.31
62.36	40% dioxane–water	.24
62.36	20% dioxane–water	.03

The Neutral Hydrolysis.—Table III shows that the Hinshelwood, Laidler and Timm theory, as applied in a previous paper,[2] again is applicable. It should be especially noted in this table that the qualitative trends in the activation energy can be successfully correlated with the inductive effect of the group attached to the carbon undergoing substitution, but the rate constant itself cannot. This shows that the entropy of activation is the factor which does not vary in a systematic manner and also shows the inadequacy of the statement by Hughes and Ingold[8] that "rate constant itself is more truly related to the chemical conditions than is the measured temperature coefficient."

TABLE III

Alkyl halide	k in days^{-1} at 60.0° in pure water	E (kcal.)
CH_2OHCH_2I[2]	0.0330	28.9
$CH_3OCH_2CH_2I$	.0094 (extrap.)	27.4
CH_3I[9]	.00720	25.8
CH_3CH_2I[10]	1.46	21.2

The variation of the rate constant with different ethanol–water mixtures, summarized in Table IV, shows that the neutral hydrolysis of 2-methoxyethyl iodide falls into the S_N2 type of reaction by the empirical method given in a previous paper.[2]

TABLE IV

Wt. % C_2H_5OH	$D - 1/2D + 1$[11]	$k \times 10^{-2}$ at 91.06° in hr.$^{-1}$
0	0.4870	2.98
20.8	.4845	1.91
44.1	.4795	1.23

The Alkaline Hydrolysis.—In a previous paper[3] the kinetics of the reaction between ethylene iodohydrin and hydroxyl ion in dioxane–water and ethanol–water mixtures was studied. It was shown that the mechanism involves the loss of a hydrogen ion from the iodohydrin, followed by an S_N2 intramolecular displacement of I^- by the O^- to form ethylene oxide. One would predict that on going to the reaction of OH^- and 2-methoxyethyl iodide, the above mechanism would not be able to be operative in view of the stability of the C–O bond to ionization. The ordinary S_N2 reaction of the OH^- on C–I would be expected to take place. This is borne out by the product analysis showing the formation of methyl cellosolve.

Table II shows that the velocity constant increases with increasing dioxane concentration in the solvent. The enormous increase in velocity of reaction of the alkaline over the neutral hydrolysis shows that the alkaline reaction is an S_N2 reaction by the Hughes–Ingold criterion.[12] They further predict[13] for this type of reaction that the rate will be higher in media of lower dielectric constant. This is indeed the case.

PITTSBURGH 13, PENNA.

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[8] E. D. Hughes and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 672 (1941).

[9] E. A. Moelwyn-Hughes, *Proc. Roy. Soc.* (*London*), **A164**, 295 (1938).

[10] E. A. Moelwyn-Hughes, *J. Chem. Soc.*, 1577 (1933).

[11] G. Åkerlöf, THIS JOURNAL, **54**, 4125 (1932).

[12] E. D. Hughes, *Trans. Faraday Soc.*, **37**, 611 (1941).

[13] E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 252 (1935).

1,3-Bis-(*p*-hydroxyphenyl)-cyclopentane[1]

BY GEORGE P. MUELLER AND JOSEPH A. MEREDITH

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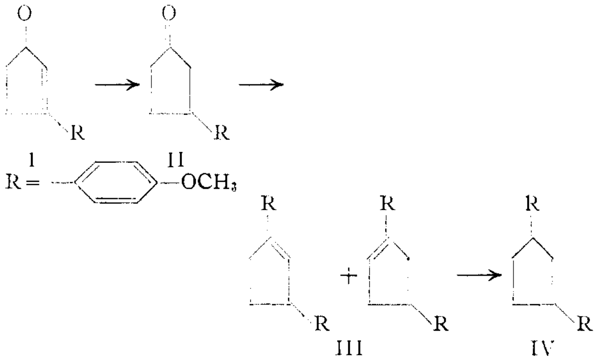
In preparing this member of the diarylcycloalkane group by the series of reactions outlined in our previous papers we were fortunate in having available the excellent directions of Wilds and Johnson[2] for the preparation of 3-(*p*-methoxyphenyl)-cyclopenten-2-one. These authors also described



the hydrogenation of I to 3-(*p*-methoxyphenyl)-cyclopentanone over a palladium–charcoal catalyst in dioxane in fair yield, with the comment that further hydrogenation seemed to occur. Although we were able to isolate the saturated ketone from this reaction, the yields were unsatisfactorily low, the main product being an oily mixture. Apparently, the hydrogenation does not proceed with initial attack at the double bond but under these conditions gives rise to a mixture of products by the scheme described by Weidlich[3] for hydrogenation of α,β-unsaturated ketones in neutral or acid media. We found that application of Weidlich's alkaline conditions with the palladium oxide catalyst gave II in excellent yields.

p-Methoxyphenylmagnesium bromide reacted readily with the ketone, II, to yield a mixture of 1,3- and 1,4-bis-(*p*-methoxyphenyl)-cyclopentenes (III). In accord with previous experience none of the carbinol intermediate could be isolated, even under mild conditions. On the other hand both unsaturated isomers were expected, and although a definite separation on an alumina column was indicated, the products in the various fractions were indistinguishable either by their melting points or absorption

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[1] Abstracted from a thesis presented by Joseph A. Meredith in partial fulfillment of requirements for the M.Sc. Degree.

[2] A. L. Wilds and T. L. Johnson, THIS JOURNAL, **67**, 286 (1945).

[3] H. Weidlich, *Die Chemie*, **58**, 30 (1945).

in the ultraviolet region. We have observed similar melting-point behavior in the 1,2- and 2,3-bis-(*p*-methoxyphenyl)-cyclohexenes[4] 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 bianisyl 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.

Experimental[6]

3-(*p*-Methoxyphenyl)-cyclopenten-2-one.—The procedure of Wilds and Johnson[2] 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 apparatus[7] 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°; $\lambda_{\max}^{95\%\text{ alc.}}$ 264 mμ (ε 23,130).

Anal. Calcd. for $C_{19}H_{20}O_2$: 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, $\lambda_{\max}^{95\%\text{ alc.}}$ 228 mμ (ε 23,830), 278 mμ (ε 3,750).

Anal. Calcd. for $C_{19}H_{22}O_2$: 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 hours[8] 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 $C_{17}H_{18}O_2$: 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 $C_{21}H_{22}O_4$: C, 74.53; H, 6.85. Found: C, 74.43; H, 6.78.

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[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).

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

Department of Chemistry
University of Tennessee
Knoxville, Tennessee

Some Observations Concerning the Acidic Salts of Phosphonic Acids

By Gennady M. Kosolapoff

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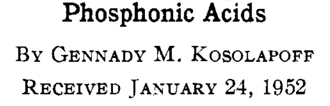
Several notes about the existence of relatively insoluble acid salts of phosphonic acids are found in the literature, beginning with the work of Michaelis.[1] No specific inquiry into the possible structure of these salts has been made although they have been used for a convenient isolation of phosphonic 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 recently[4] that phosphonic acids tend to associate very extensively with the very probable formation of long-chain linear aggregates which can be formulated as



$$\ldots\ldots\text{HO}-\underset{\underset{\text{H}}{\text{O}}}{\overset{\text{R}}{\text{P}}}\rightarrow\text{O}\ldots\text{HO}-\underset{\underset{\text{H}}{\text{O}}}{\overset{\text{R}}{\text{P}}}\rightarrow\text{O}\ldots\text{HO}-\underset{\underset{\text{H}}{\text{O}}}{\overset{\text{R}}{\text{P}}}\rightarrow\text{O}\ldots$$

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

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[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).