via the *in situ* formation of diphenylphosphine oxide (eq 7) rather than involving direct addition of diphenylchlorophosphine to the carbonyl group.

$$Ph_2PCl + H_2O \longrightarrow Ph_2P(O)H + HCl \xrightarrow{RCHO} Ph_2P(O)CH(OH)R \quad (7)$$

Aliphatic aldehydes (*e.g.*, butyraldehyde) slowly decomposed and benzophenone was unreactive under the reaction conditions employed.

Experimental Section

Hydroxymethyldiphenylphosphine Oxide.—A 1-l. flask, previously flushed with nitrogen and filled with 19.5 g (0.113 mol) of diphenylchlorophosphine, 200 ml of concentrated hydrochloric acid and 200 ml of 37% aqueous formaldehyde solution (2.47 mol, a 22-fold excess) was heated on a steam bath overnight. Evaporation of the reaction mixture at reduced pressure left an oil which was neutralized with aqueous sodium bicarbonate and extracted with chloroform. The dried chloroform extracts were evaporated and the resulting residue was crystallized from benzene–heptane to give 16.6 g (63%) of product, mp 134°. Another recrystallization from benzene gave material with mp 136.0–136.5° (lit.[3] mp 137–139°). A mixture melting point with authentic material[3] was not depressed.

α-Hydroxy-β,β,β-trichloroethyldiphenylphosphine Oxide.—To a stirred solution of 3.64 g (22 mmol) of chloral hydrate in 44 ml of concentrated hydrochloric acid in an ice bath under nitrogen was added 4.88 g (22 mmol) of diphenylchlorophosphine. The flask was sealed and stirred at room temperature for 17 hr; then 150 cc of ice water was added. The aqueous acid solution was decanted from the solids. The solids were washed with water, then recrystallized from methanol–water to give 2.21 g of product. A second crop weighed 0.29 g (total yield 32.5%). Recrystallization gave an analytical sample, mp 169.5–170.5° (lit.[10] mp 171.5–172.5°). *Anal.* Calcd for $C_{14}H_{12}O_2Cl_3P$: C, 48.10; H, 3.46; Cl, 30.43. Found: C, 48.36; H, 3.47; Cl, 30.50.

Substituted α-Hydroxybenzyldiphenylphosphine Oxides. Procedure A.—The identical procedure was used as above, substituting 22 mmol of the respective aldehyde for the chloral hydrate.

Procedure B was similar to procedure A, but the reactants were combined at room temperature and placed on the steam bath without stirring overnight. The following products were obtained: **α-hydroxybenzyldiphenylphosphine oxide** [mp 177–178° (lit.[6] mp 178–179.5°); 85% (A), 75% (B) yields]; **α-hydroxy-p-chlorobenzyldiphenylphosphine oxide** [mp 181.5–183.0°, recrystallized to constant melting point (lit. mp 188°,[2] 168–170°;[4] 64% (A), 60% (B) yields) (*Anal.* Calcd for $C_{19}H_{16}ClO_2P$: C, 66.58; H, 4.71; Cl, 10.34. Found: C, 66.74; H, 4.83; Cl, 10.64)]; **α-hydroxy-p-methylbenzyldiphenylphosphine oxide** [mp 152.5–155.0°; 86% (A), 61% (B) yields (*Anal.* Calcd for $C_{20}H_{19}O_2P$: C, 74.52; H, 5.94. Found: C, 74.28; H, 5.83)]; **α-chloro-p-methoxybenzyldiphenylphosphine oxide** [mp 181–182°; 30% crude (A), 65% (B) yields (*Anal.* Calcd for $C_{20}H_{18}ClO_2P$: C, 67.33; H, 5.08; Cl, 9.94. Found: C, 67.39; H, 5.16; Cl, 9.89)]; **α-hydroxy-p-nitrobenzyldiphenylphosphine oxide** [mp 191.5–193.0°; 62% (A), 73% (B) yields (*Anal.* Calcd for $C_{19}H_{16}NO_4P$: C, 64.59; H, 4.57. Found: C, 64.70; H, 4.65)].

α-Hydroxy-*p*-methoxybenzyldiphenylphosphine Oxide.—To a stirred mixture of 20 ml of water, 10 ml of dioxane and 14 ml of concentrated sulfuric acid in an ice bath under nitrogen was added 2.72 g (20 mmol) of *p*-anisaldehyde followed by 4.04 g (20 mmol) of diphenylphosphine oxide. The mixture was stirred for 5 min until homogeneous, then the ice bath was removed and stirring continued for 22 hr at room temperature. Water (60 ml) was added and the precipitate was filtered off and washed with water, then recrystallized from methanol, yielding in three crops, 5.65 g (84% yield). Recrystallization gave an analytical sample, mp 160–162°. *Anal.* Calcd for $C_{20}H_{19}O_3P$: C, 71.00; H, 5.66. Found: C, 70.84; H, 5.66.

Conversion of α-Hydroxy-*p*-methoxybenzyldiphenylphosphine Oxide into α-Chloro-*p*-methoxybenzyldiphenylphosphine Oxide.—In a flask was placed 1.69 g of the hydroxy compound and 20 ml of concentrated hydrochloric acid. The flask was sealed with a balloon and heated on the steam bath for 15 hr. The mixture was cooled and diluted with an equal volume of water, refrigerated 30 min, then the acid solution was decanted off. The residue was rinsed with water, then recrystallized from 20 ml of methanol, affording 0.97 g of the chloro compound, mp 181–182°; the mixture melting point was undepressed. The infrared spectra of these products were in agreement with the structures given.

Registry No.—Hydroxymethyldiphenylphosphine oxide, 884-74-2; $C_{19}H_{16}ClO_2P$, 18872-82-7; $C_{20}H_{19}O_2P$, 18872-83-8; $C_{20}H_{18}ClO_2P$, 18872-84-9; $C_{19}H_{16}NO_4P$, 18872-85-0; $C_{20}H_{19}O_3P$, 18872-86-1.

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[10] L. D. Quin and R. E. Montgomery, *J. Org. Chem.*, **28**, 3315 (1963).

Electron-Transfer Polymers. XXXVI. Acetylated Trimethylhydroquinone Derivatives

NOBUO NAKABAYASHI, GERHARD WEGNER,
AND HAROLD G. CASSIDY[1]

*Sterling Chemistry Laboratory, Yale University,
New Haven, Connecticut 06520*

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Among the many redox polymers that may be conceived[2] those from hydroquinone tetrasubstituted with alkyl groups have seemed particularly interesting because of the chemical stability and low potential expected of them. Because a low-potential polymer is difficult to maintain unprotected in the reduced form we designed, prepared, and reported a durobenzoquinonyl glycol,[3a] the monomer of which is related to tocopherol. In the subsequent investigations of this synthesis it has turned out that in preparing 3-acetoxy-6-hydroxy-2,4,5-trimethylbenzyl chloride (XIV) according to the method of Smith and Carlin,[3b] another compound could be isolated, namely, 2-acetoxy-5-hydroxy-3,4,6-trimethylbenzylchloride (XV). Compound XV is less soluble in ether than XIV and may be separated in this way.[4] The mixture melting point of XIV (149–151°) and XV (149–150°) was 147–150°; the nmr of XIV showed three peaks and that of XV four peaks around τ 7.6–8.0. The determination of structure, carried out by comparing nmr spectra of these and reference compounds, is discussed below (see Chart I).

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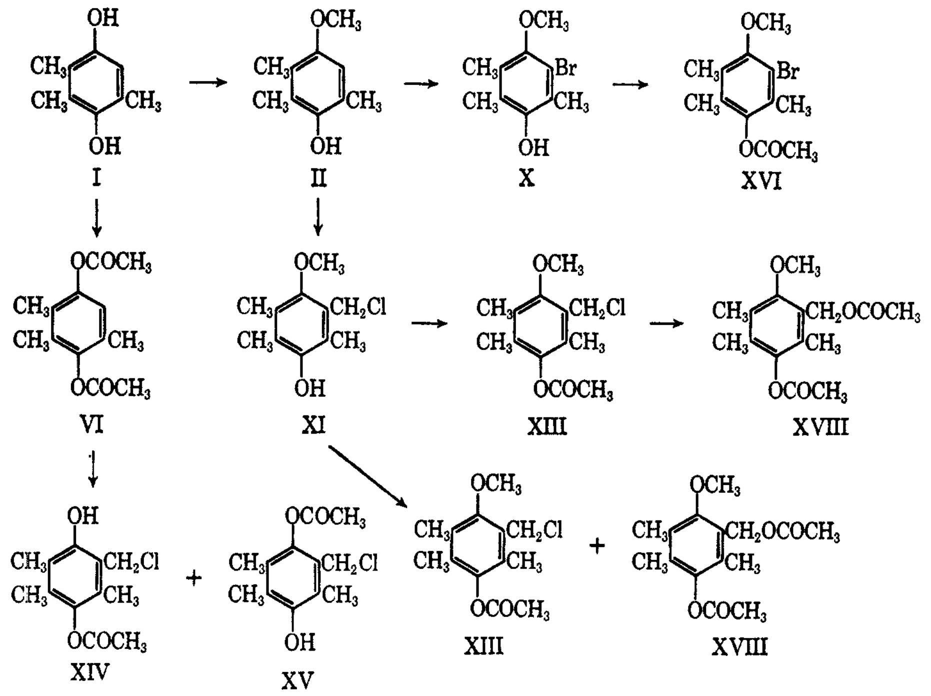
(1) To whom inquiries should be addressed.

(2) H. G. Cassidy and K. A. Kun, "Oxidation-Reduction Polymers (Redox Polymers)," Interscience Publishers, Inc., New York, N. Y., 1965.

(3) (a) N. Nakabayashi, G. Wegner, and H. Cassidy, *J. Org. Chem.*, **33**, 2539 (1968); (b) L. I. Smith and R. B. Carlin, *J. Am. Chem. Soc.*, **64**, 524 (1942).

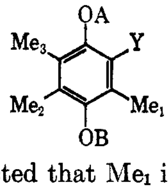
(4) We imagine that this compound was missed by these careful workers[3b] only because the ether solution containing it was treated with Norit. Charcoal is an excellent adsorbent, particularly from ether, *cf.* H. G. Cassidy in "Technique of Organic Chemistry," Vol. X, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1957, p 253 ff., and would be especially effective when, as in this case, the missed compound is less soluble than that isolated.

CHART I



In the acetylation of 3-hydroxy-6-methoxy-2,4,5-trimethylbenzyl chloride (XI)[5] with acetic anhydride with the expectation of obtaining the acetate, 3-acetoxy-6-methoxy-2,4,5-trimethylbenzyl chloride (XIII), 3-acetoxy-6-methoxy-2,4,5-trimethylbenzyl acetate (XVIII) was isolated. Compound XVIII was also prepared from XIII by the action of acetic anhydride. In this reaction acetyl chloride was also produced. Normally, substitution of halide on an alkyl carbon by acetoxy is carried out by means of an inorganic, usually silver, salt of the acid. This seems to be the first report of acetate formation from alkyl halide by acetic anhydride and concentrated sulfuric acid. The unusual reactivity of the benzyl group to form by loss of chloride a cation which reacts with acetate anion suggests itself as the mechanism. This suggestion is supported by the isolation of acetyl chloride from the products of the reaction. The possibility that this mechanism accounts for phosphoryl transfer in quinone systems[6] is being investigated.

To decide the structure of XIV and XV, a study was made of the assignment of chemical shift to the methyl group (Table I). All the acetates, compounds VI, VII, XIII–XVIII, showed signals at τ 7.65–7.68 and 7.93–7.98, which could belong to the methyl of acetyl and to the ring methyl *ortho* to the acetoxy group. On the evidence of durohydroquinone diacetate (VII) the lower value, τ 7.67, corresponds to acetyl methyl, and the higher, τ 7.96, corresponds to the ring methyl.



It would be expected that Me_1 is affected chiefly by the groups Y and OB, and Me_2 and Me_3 mainly by OB and OA in a relationship such that, for example, $Me_{2(XIV)}$ could correspond to $Me_{3(XV)}$, and *vice versa*. It is concluded that 7.84 (XIV) and 7.85 (XV) are *ortho* to hydroxy and are assigned to $Me_{3(XIV)}$ and $Me_{2(XV)}$. The signal at 7.95 in XIV is given by two methyls *ortho* to acetoxyl, and in XV the signal at 7.95 is given by the methyl *ortho* to acetoxyl. The signal at 7.90 in XV corresponds to Me_1, a methyl between chloromethyl and hydroxy. In the case of XIV this assignment supports the structure given by Smith and Carlin.[3]

It has been reported in another connection[7] that when Y is vinyl the signal for Me_1 appears at lower magnetic field. The observations on VIII, IX, XII, and XVII are in agreement with this. When a group of compounds such as II, X, XI, XVI, and XVIII show the same values of the methoxy methyl signal, namely, 6.25, 6.28, 6.26, 6.24, 6.29, respectively, then the Me_3 signals are likely to be the same, for in all of them Me_2 is present. The values found, respectively, for Me_3 are 7.79, 7.78, 7.77, 7.76, and 7.78. This reasoning can be extended by analogy to the cases of Me_3 in V, VIII, XII, and XVII, and Me_2 in III. The environments of Me_2 of I and Me_3 of I are nearly the same, as also of Me_2 of II. Me_3 of III, 7.81, is not expected to be much affected by methylation at B of II (Me_3 of II is 7.79) and should thus have the same value, and Me_1 of III can be expected at 7.96 since its environment, hydrogen and methoxy (6.48), is the same as that of Me_3 of IX (7.90) (A of IX is 6.47). Me_2 of X (7.89) was assigned by reference to Me_2 of XI (7.86). Because of the presence of vinyl, as noted above, Me_1 of XII is lower than the other ring methyls of this molecule. Me_3 of XII is assigned 7.88, the higher of the remaining signals, by analogy to the cases of VIII and XVII. Y of XVIII (7.93) was assigned from the data of the tetraacetates of hydroquinone diols.[8] Here the single signal at 7.63–7.68 must correspond to the methyl of phenyl-

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(5) W. John and F. H. Rathmann, *Ber.*, **74**, 890 (1941).

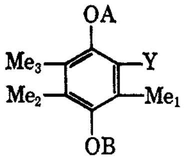
(6) V. M. Clark and D. W. Hutchinson, *Progr. Org. Chem.*, **7**, 75 (1968).

(7) K. Uno, M. Ohara, and H. G. Cassidy, *J. Polym. Sci., Part A-1*, **6**, 2729 (1968).

(8) G. Wegner, N. Nakabayashi, and H. G. Cassidy, *J. Org. Chem.*, **32**, 3155 (1967).

TABLE I

CHEMICAL SHIFTS OF THE METHYL GROUPS[k]



Compd	Y (τ)	A (τ)	B (τ)	Me1	Me2	Me3
I	H	H	H	7.98	7.83	7.83
II[a]	H (3.50)	CH_3 (6.25)	H	7.84	7.84	7.79
III[b]	H (3.65)	CH_3 (6.33)	CH_3 (6.48)	7.95	7.88	7.81
IV[c]	H	CH_3 (6.31)	CH_3 (6.31)	7.88		7.88
V[d]	CH_3 (7.89)	CH_3 (6.46)	CH_3 (6.46)	7.89	7.89	7.89
VI[e]	H	$COCH_3$ (7.68)	$COCH_3$ (7.65)	7.88	7.93	7.93
VII[f]	CH_3 (7.96)	$COCH_3$ (7.67)	$COCH_3$ (7.67)	7.96	7.96	7.96
VIII[g]	$CH{=}CH_2$	CH_3 (6.45)	CH_3 (6.50)	7.84	7.90	7.90
IX[c g]	$CH{=}CH_2$	CH_3 (6.47)	CH_3 (6.34)	7.81		7.90
X	Br	CH_3 (6.28)	H	7.68	7.89	7.78
XI[h]	CH_2Cl (5.31)	CH_3 (6.26)	H	7.86	7.86	7.77
XII[i]	$CH{=}CH_2$	CH_3 (6.41)	H	7.82	7.82	7.88
XIII	CH_2Cl (5.27)	CH_3 (6.20)	$COCH_3$ (7.68)	7.82	7.95	7.82
XIV[j]	CH_2Cl (5.30)	H	$COCH_3$ (7.66)	7.95	7.95	7.84
XV	CH_2Cl (5.29)	$COCH_3$ (7.67)	H	7.90	7.85	7.95
XVI	Br	CH_3 (6.24)	$COCH_3$ (7.66)	7.76	7.98	7.76
XVII[i]	$CH{=}CH_2$	CH_3 (6.39)	$COCH_3$ (7.69)	7.81	7.96	7.89
XVIII	CH_2OCOCH_3 (4.77) (7.93)	CH_3 (6.29)	$COCH_3$ (7.66)	7.89	7.93	7.78

[a] Reference 10. [b] L. I. Smith, *J. Am. Chem. Soc.*, **56**, 472 (1934). [c] L. I. Smith and J. W. Opie, *J. Org. Chem.*, **6**, 427 (1941). [d] L. I. Smith and H. C. Miller, *J. Am. Chem. Soc.*, **64**, 440 (1942). [e] R. Nietzki and J. Schneider, *Ber.*, **27**, 1426 (1894). [f] L. Rügheimer and M. Hankel, *ibid.*, **29**, 2171 (1896). [g] K. A. Kun and H. G. Cassidy, *J. Polym. Sci.*, **56**, 83 (1962) [h] Reference 5. [i] N. Nakabayashi, G. Wegner, and H. G. Cassidy, *J. Polym. Sci., A-1*, **6**, 869 (1968). [j] Reference 3. [k] All data taken in $CDCl_3$ on a Varian Associates Model A-60 spectrometer.

acetate, and 7.92–7.95 to the methyl of the acetates on the side chains.

Experimental Section[9]

3-Bromo-4-methoxy-2,5,6-trimethylphenol (X).—To a solution of 33.2 g (0.20 mol) of 4-methoxy-2,3,6-trimethylphenol[10] (II) in 400 ml of carbon disulfide was added 32.0 g (0.20 mol) of bromine gradually with stirring. After a 1-hr reaction at room temperature, the solvent was taken off and the residue was recrystallized from *n*-heptane to give 36.6 g (74.8%) of X, mp 119.5–120°. *Anal.* Calcd for $C_{10}H_{13}BrO_2$: C, 49.00; H, 5.34. Found: C, 48.97; H, 5.39.

3-Acetoxy-6-hydroxy-2,4,5-trimethylbenzyl Chloride (XIV) and 2-Acetoxy-5-hydroxy-3,4,6-trimethylbenzyl Chloride (XV).—The preparation of XIV had been reported.[3] By following those directions, omitting the Norit treatment, 9.7 g of XIV (mp 149–151°, recrystallized from ether–*n*-hexane) and 5.0 g of XV (mp 149–150° from ether) were obtained. The latter was less soluble in ether than the former. The mixture melting point of XIV and XV was 147–150°.

3-Acetoxy-6-methoxy-2,4,5-trimethylbenzyl Chloride (XIII).—To a stirred and cooled solution of 4.3 g (0.02 mol) of XI and 2.4 g (0.03 mol) of acetyl chloride in 30 ml of THF and 30 ml of ether was added 3.0 g (0.03 mol) of triethylamine in 10 ml of ether over a period of 10 min. Two hours later triethylamine hydrogen chloride was filtered off, the organic solvents were evaporated to dryness, and the residue was recrystallized from *n*-hexane. The yield of XIII was 4.6 g (90.1%), mp 99–100°. *Anal.* Calcd for $C_{13}H_{17}ClO_3$: C, 60.83; H, 6.67. Found: C, 60.86; H, 6.48.

3-Acetoxy-6-methoxy-2,4,5-trimethylbromobenzene (XVI).—The compound was prepared quantitatively from X, acetyl chloride, and triethylamine. The purification was carried out from *n*-hexane; mp 97–98°. *Anal.* Calcd for $C_{12}H_{15}BrO_3$: C, 50.19; H, 5.26. Found: C, 50.20; H, 5.31.

3-Acetoxy-6-methoxy-2,4,5-trimethylbenzyl Acetate (XVIII).—A mixture of 4.3 g (0.02 mol) of XI and 30 ml of acetic anhydride was refluxed in the presence of one drop of concentrated sulfuric acid for 1 hr. The anhydride was evaporated and the brown viscous residue was recrystallized from *n*-hexane to give 2.9 g of small white needles, mp 62–65°. This is a 50% mixture of XIII and XVIII, on the basis of the nmr spectra (compared at τ 4.80, 5.28 and 6.19, 6.28, respectively). Fractional crystallization, twice, from a rather large amount of *n*-hexane gave pure XVIII, mp 88–89°. The mixture mp of XIII and XVIII was 62–65°. Compound XVIII could be purified by sublimation. The ir spectrum of XVIII showed two carbonyl bands at 1754 and 1731 cm^{-1}. *Anal.* Calcd for $C_{15}H_{20}O_5$ (XVIII): C, 64.27; H, 7.19. Found: C, 64.11; H, 7.12.

Compound XVIII was also prepared from XIII by refluxing 1 hr with acetic anhydride and 1 drop of concentrated sulfuric acid; yield 55%.

Registry No.—I, 700-13-0; X, 18910-32-2; XIII, 18910-33-3; XIV, 18910-34-4; XV, 18910-35-5; XVI, 18910-36-6; XVIII, 18910-37-7.

Acknowledgment.—We are glad to acknowledge that this work was supported by PHS Research Grant GM 10864, Research Grants Branch, National Institute of General Medical Sciences, Public Health Service.

Formation of Benzyne by the Reaction of *o*-Phenylene Carbonate with Neutral Trivalent Phosphorus Nucleophiles

C. E. GRIFFIN AND D. C. WYSOCKI

Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15213

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Keough and Grayson have shown that the reaction of ethylene carbonate (**1**) with triphenylphosphine (**2**) at

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[9] Methods for new compounds only are given; see Table I. Melting points are all corrected.

[10] W. John and F. H. Rathmann, *Ber.*, **73**, 995 (1940).