dified with concentrated HCl to precipitate 1.1 g (5%) of **3b**, mp 133–135° (reported[3] mp 134°).

B. From Base Rearrangement of 1b. A mixture of 1.0 g (0.005 mol) of **1b** and 100 ml of 1 *N* NaOH was warmed on the steam bath for 5 min or until complete solution took place. The cooled solution was acidified with concentrated HCl to precipitate **3b:** 0.80 g (86%); mp 133–135°; ir (Nujol) 1730 (acetyl C=O), 1615 cm^{-1} (2-pyrone C=O); uv max (95% EtOH) 212 nm (ϵ 23,000), 300 (14,000), 320 sh (9600); mass spectrum *m/e* (rel intensity) 204 (60), 189 (40), 162 (20), 121 (60), 120 (60), 105 (10), 93 (15), 92 (50), 77 (25), 43 (100).

4-Hydroxy-3-(1-oxopropyl)-*2H*-1-benzopyran-2-one (3c). A mixture of 5.5 g (0.028 mol) of methyl salicyloylacetate, 150 ml of xylene, 19.5 g (0.15 mol) of propionic anhydride, and 30 g of powdered potassium carbonate was heated with stirring at 135° for 0.5 hr. Ether (300 ml) was added to the cooled mixture and the solids were filtered and washed with ether. The filter cake was stirred with 500 ml of water, the insoluble portion was filtered, and the filtrate was acidified with concentrated HCl to precipiate 4.8 g (78%) of **3c:** mp 122–124° (reported[3] mp 123°); ir (Nujol) 1720 (acyl C=O), 1610 cm^{-1} (2-pyrone C=O); uv max (95% EtOH) 226 nm sh (ϵ 15,200), 301 (13,300); mass spectrum *m/e* (rel intensity) 218 (50), 200 (15), 189 (100), 162 (17), 121 (50), 120 (25), 105 (12), 93 (12), 92 (25), 77 (25), 43 (5).

In this reaction the 3-carbomethoxy-2-ethylchromone **1c** could not be isolated from work-up of the above xylene–ether reaction filtrate as was the case in the preparation of **1b.**

4-Oxo-*4H*-1-benzopyran-3-carboxylic Acid (5a). A solution of 1.09 g (0.005 mol) of **1a**[1] and 100 ml of concentrated HCl was heated at 100° for 1 hr. Ice water (100 ml) was added and the mixture was filtered to give **5a**, 0.90 g (95%), mp 198–200°. Recrystallization was effected by dissolution in 100 ml of ethyl acetate and concentration to 25-ml volume to give pure crystals of **5a:** mp 199–201° (reported[1] mp 199–201°); ir (Nujol) 1740 (carboxylic C=O), 1620 cm^{-1} (pyrone C=O); uv max (95% EtOH) 213 nm (ϵ 18,000), 238 sh (11,000), 300 (5600); mass spectrum *m/e* (rel intensity) 190 (10), 173 (5), 146 (100), 120 (20), 104 (30), 92 (15), 63 (15), 53 (20).

2-Methyl-4-oxo-*4H*-1-benzopyran-3-carboxylic Acid (5b). A solution of 10.0 g (0.046 mol) of **1b** in 100 ml of concentrated HCl was heated at 80–90° for 20 min. Ice (400 g) was added to precipitate a tacky solid. The crude product was dissolved in 300 ml of 5% NaHCO$_3$ and the insoluble portion was extracted away with ether. The aqueous phase was acidified with concentrated HCl to give 6.4 g (68%) of **5b**, mp 120–135°. Recrystallization from 2-propanol gave pure **5b:** mp 145–147°; ir (Nujol) 1725 (carboxylic C=O), 1618 cm^{-1} (pyrone C=O); uv max (95% EtOH) 232 nm (ϵ 21,300), 298 (5660); mass spectrum *m/e* (rel intensity) 204 (57), 186 (22), 160 (100), 131 (5), 120 (98), 92 (32); nmr (CDCl$_3$) δ 14.33 (broad, 1, COOH), 8.35 (q, 1, H-5), 7.3–8.0 (m, 3, H-6, -7, -8), 3.04 (s, 3, CH$_3$).

Anal. Calcd for $C_{11}H_8O_4$: C, 64.70; H, 3.95. Found: C, 64.79; H, 4.11.

Base Degradation of 5b to Salicylic Acid (6). A solution of 2.5 g (0.012 mol) of **5b** in 100 ml of 1 *N* NaOH was heated at 100° for 1 min. The cooled solution was acidified with concentrated HCl to precipitate **6**, 1.5 g (88%), mp 157–159° [reported (Lange Handbook) mp 158.3°].

4-Hydroxy-3-(iminomethyl)-*2H*-1-benzopyran-2-one (4). A mixture of 2.0 g (0.009 mol) of **1a** was heated with 5 ml of concentrated NH$_4$OH on the steam bath. The ester soon dissolved and after 5 min crude **4** separated, 1.5 g (81%), mp 223–225°. Recrystallization from ethanol gave pure **4**, mp 236–238° (reported[6] mp 240–242°).

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Registry No.—**1a,** 51085-94-0; **1b,** 51751-33-8; **3a,** 51751-34-9; **3a** sodium salt, 51751-35-0; **3b,** 2555-37-5; **3c,** 4139-73-5; **4,** 51751-36-1; **5a,** 39079-62-4; **5b,** 51751-37-2; **6,** 69-72-7; methyl salicyloylacetate, 20349-86-4.

References and Notes

(1) S. Klutchko, M. P. Cohen, J. Shavel, Jr., and M. von Strandtmann, *J. Heterocycl. Chem.*, **11**, 183 (1974).

(2) E. Ziegler and H. Maier, *Monatsh. Chem.*, **89**, 787 (1958).

(3) T. Ukita, S. Nojima, and M. Matsumoto, *J. Amer. Chem. Soc.*, **72**, 5143 (1950).

(4) (a) F. Korte and K. H. Buchel, "Newer Methods of Preparative Organic Chemistry," Vol. III, Academic Press, New York, N. Y., 1964, p 199; (b) H. Wamhoff, G. Schorn, and F. Korte, *Chem. Ber.*, **100**, 1296 (1967).

(5) G. Casini, F. Gualtieri, and M. L. Stein, *J. Heterocycl. Chem.*, **6**, 279 (1969).

(6) S. Checchi, *Gazz. Chim. Ital.*, **90**, 440 (1960).

(7) Melting points were determined with the Thomas-Hoover capillary melting point apparatus, which was calibrated against known standards. Infrared spectra were determined with a Baird Model 455 double-beam instrument. Nmr spectra were measured with a Varian A-60 spectrophotometer.

Selective Demethylation of 2,5-Dimethoxybenzaldehyde to 5-Hydroxy-2-methoxybenzaldehyde

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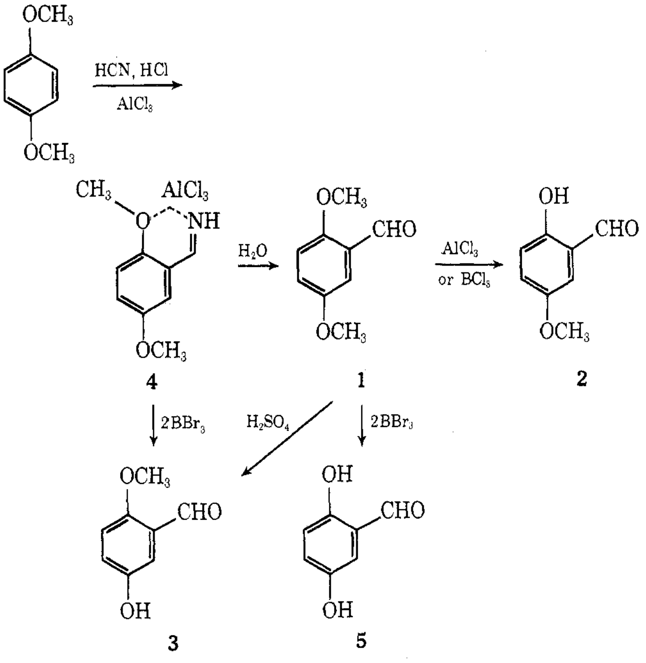
The selective demethylation of 2,5-dimethoxybenzaldehyde (**1**) with boron trichloride to give 2-hydroxy-5-methoxybenzaldehyde (**2**) is well known.[1] This reaction proceeds by a cyclic process involving the boron trichloride complex of 2,5-dimethoxybenzaldehyde. However, 5-hydroxy-2-methoxybenzaldehyde (**3**), the isomer of **2**, has not been synthesized previously.

Utilization of the complexing ability of the aldehydic group with the o-methoxy group could be used to advantage to block the approach of the demethylating agent, providing that the complexing agent does not cleave the neighboring ether group as observed with boron trichloride or aluminum trichloride. In the Gattermann reaction of 1,4-dimethoxybenzene with hydrogen cyanide in the presence of aluminum chloride, an iminium complex **4** is produced in which the aluminum chloride in fact could coordinate with the neighboring methoxy group. A cyclic ether cleavage process analogous to the boron trichloride demethylation is not operative, as evidenced by the fact that **2** was not isolated on hydrolysis of **4**. The approach of a



sterically bulky ether cleavage reagent, such as boron tribromide, to the *o*-methoxy group ought to be prevented in **4**.

In order to test this hypothesis 1,4-dimethoxybenzene was treated with hydrogen cyanide, aluminum chloride, and hydrogen chloride in methylene chloride to produce a soluble iminium complex **4**. Treatment of this complex with 2 equiv of boron tribromide gave exclusively 5-hydroxy-2-methoxybenzaldehyde (**3**), mp 114–116°. Hydrolysis of **4** gave **1**, which on treatment with 2 equiv of boron tribromide afforded 2,5-dihydroxybenzaldehyde (**5**) in excellent yield.

Since the 5-methoxy group in **1** is more nucleophilic than the 2-methoxy group, a certain degree of selectivity should also be achieved on treatment of **1** with concentrated sulfuric acid. Thus, heating of **1** with concentrated sulfuric acid at 50–54° for 46 hr indeed gave a 42% yield of **3**; the only other product isolated was **1** (20%).[2]

Experimental Section

5-Hydroxy-2-methoxybenzaldehyde (3). A. From the Iminium Complex 4 and Boron Tribromide. To 27.6 g (0.2 mol) of 2,5-dimethoxybenzene in 200 ml of methylene chloride with ice cooling and stirring, 28.4 g (0.22 mol) of aluminum chloride and 8.1 g (0.3 mol) of hydrogen cyanide were added. The cooling bath was removed and 21 g of hydrogen chloride was added slowly at room temperature over a period of 4 hr. After stirring for 40 hr one-quarter of the reaction mixture (85 ml) was stirred with 25 g (0.1 mol) of boron tribromide for an additional 20 hr. After hydrolysis with dilute hydrochloric acid (100 ml), 6.65 g of a mixture of hydroquinone and **3**, mp 145–155°, precipitated. Extraction of this solid with two 200-ml portions of methylene chloride and evaporation of the combined methylene chloride portions gave 4.55 g (60%) of **3**, mp 112–115°. Hydrolysis of the remaining reaction mixture (255 ml) with dilute hydrochloric acid, extraction of the methylene chloride layer with 5% sodium hydroxide, drying with magnesium sulfate, evaporation, and vacuum distillation of the residue gave a first fraction of 2,5-dimethoxybenzene and 20.2 g (91.5%) of **1**, bp 98° (0.1 mm), mp 49–52°.

B. From 2,5-Dimethoxybenzaldehyde (1) and Concentrated Sulfuric Acid. To 20.75 g (0.125 mol) of **1** with ice cooling, 112.5 ml of concentrated sulfuric acid was added and the mixture was heated at 50–54° for 46 hr. The reaction mixture was poured onto ice and the precipitated oil was extracted with diethyl ether. Extraction of the solvent with 200 ml of 5% sodium hydroxide, acidification, extraction with diethyl ether, drying over anhydrous $MgSO_4$, and evaporation of the solvent gave 8.15 g (42.3%) of **3**: mp 114–116° after recrystallization from aqueous alcohol; ir ($CHCl_3$) 1672 cm^{-1} (C=O); nmr (acetone-d_6) δ 3.88 (s, 3, OCH_3), 3.0–4.0 (s, 1, OH), 6.9–7.3 (m, 3, aromatic), 10.38 (s, 1, CHO).

Anal. Calcd for $C_8H_8O_3$: C, 63.15; H, 5.30. Found: C, 62.93; H, 5.31.

From the neutral diethyl ether layer 4.3 g (20.7%) of **1** was recovered.

2,5-Dihydroxybenzaldehyde (5). To 7 g (0.028 mol) of boron tribromide in 40 ml of methylene chloride, 3.32 g (0.02 mol) of 2,5-dimethoxybenzaldehyde was slowly added and the mixture was stirred at room temperature for 20 hr. Addition to ice water (70 ml), separation of the organic layer, and evaporation of the dried methylene chloride layer gave **5**, 0.8 g, mp 100–102° (lit.[3] mp 100–101°). Extraction of the aqueous layer with 100 ml of ethyl acetate produced another 1.8 g of **5**, total yield 2.6 g (92.2%).

Registry No.—**1**, 93-02-7; **3**, 35431-26-6; **4**, 51801-41-3; **5**, 1194-98-5.

References and Notes

(1) F. M. Dean, J. Goodchild, L. E. Houghton, J. A. Martin, R. B. Morton, B. Parton, A. W. Price, and N. Somvichien, *Tetrahedron Lett.*, 4153 (1966).

(2) D. V. Rao and H. Ulrich, U. S. Patent 3,652,675 (1972).

(3) E. C. Armstrong, T. H. James, and A. Weissberger, *J. Amer. Chem. Soc.*, **63**, 182 (1941).

Light-Induced Reaction of 3,3′,5,5′-Tetramethyldiphenoquinone in Benzene

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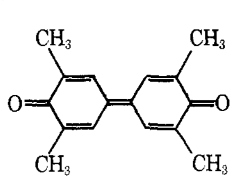
The irradiation of substituted *p*-benzoquinones, as solids or in solution, has been reported to yield photoaddition products as well as various types of dimers. These dimers include cyclobutanes,[2] spirooxetanes,[3] cage-like structures,[4] and unidentified products.[5]

In contrast to the photoinduced reactions of benzoquinone derivatives, no dimer was detected when **1** was irradiated in benzene in a nitrogen atmosphere. The products were 2,2′,6,6′-tetramethyl-*p*,*p*′-biphenol (**2**) and biphenyl (**3**).



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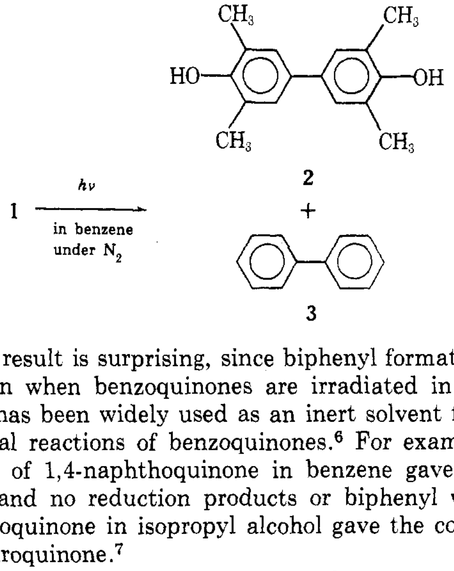

This result is surprising, since biphenyl formation is not common when benzoquinones are irradiated in benzene, which has been widely used as an inert solvent for photochemical reactions of benzoquinones.[6] For example, irradiation of 1,4-naphthoquinone in benzene gave only the dimer and no reduction products or biphenyl while 1,4-naphthoquinone in isopropyl alcohol gave the corresponding hydroquinone.[7]

The photolysis of iodoaromatic or bromoaromatic compounds in benzene solution results in a good yield of biphenyl or the result of the generation of an intermediate phenyl radical by the following photoinduced primary process.[8] The formation of biphenyl in the present work

$$\mathrm{PhX} \xrightarrow{h\nu} \mathrm{Ph}\cdot + \cdot\mathrm{X} \quad \mathrm{X} = \text{halogen atom}$$

indicates that here, too, a phenyl radical is generated as a reactive intermediate and that a benzene molecule may function as a hydrogen donor in the present photoinduced reaction of diphenoquinone.

Hay[9] has found that the thermolysis of molten 3,3′,5,5′-tetraphenyldiphenoquinone gave the corresponding biphenol as one of the products and demonstrated that diphenoquinones such as 3,3′,5,5′-tetraphenyldiphenoquinone were powerful oxidizing agents. Hence it appears reasonable to assume that species such as **4** are participating in the light-induced reaction. One possible route to the two products is the abstraction of a hydrogen atom from solvent benzene by the excited biradical (**4**)[10,11] followed by reaction of the resulting phenyl radical with a benzene molecule as follows, even though the possibility