excess allylamine with the anhydride IX, 5 g. (0.02 mole), and cyclization at 180° for 1 hr. It melted at 101–102° on recrystallization from acetone–water.

Anal. Calcd. for $C_{17}H_{25}NO_2$: C, 74.14; H, 9.15; N, 5.09. Found: C, 74.18; H, 9.14; N, 5.29.

2-Allyl-2-azadispiro[4.2.5.2]pentadecane (XI, R = Allyl).—Reduction of the preceding imide, 5.5 g., dissolved in benzene, with lithium aluminum hydride in ether, gave 4 g., 84%, of the title base, b.p. 90–95° (0.08 mm.).

Anal. Calcd. for $C_{17}H_{29}N$: C, 82.52; H, 11.81; N, 5.66. Found: C, 82.82; H, 11.87; N, 5.73.

The **hydrochloride**, prepared in the usual way, melted at 203–204° on recrystallization from acetone–ether.

Anal. Calcd. for $C_{17}H_{30}ClN$: Cl, 12.49. Found: Cl, 12.21.

The **methiodide**, prepared in the usual way, melted at 169–170° on recrystallization from acetone–ether.

Anal. Calcd. for $C_{18}H_{32}IN$: I, 32.60. Found: I, 32.83.

2-Methyl-2-azadispiro[4.2.5.2]pentadecane-1,3-dione (X, R = Methyl).—The methyl imide, obtained quantitatively by reaction of the anhydride IX, 5 g. (0.02 mole), with excess aqueous methylamine and cyclization at 180° for 1 hr., melted at 108–109° on recrystallization from acetone–water.

Anal. Calcd. for $C_{15}H_{23}NO_2$: C, 72.25; H, 9.30; N, 5.62. Found: C, 72.49; H, 9.62; N, 5.88.

2-Methyl-2-azadispiro[4.2.5.2]pentadecane (XI, R = Methyl).—Reduction of the preceding imide, 5 g., in benzene with an ether solution of lithium aluminum hydride gave the title base, 3.8 g., 86%, b.p. 85–90° (0.12 mm.).

Anal. Calcd. for $C_{15}H_{27}N$: C, 81.38; H, 12.29; N, 6.33. Found: C, 81.11; H, 12.59; N, 6.03.

The **hydrochloride**, prepared from HCl and the base in ether, melted at 256–257°.

Anal. Calcd. for $C_{15}H_{28}ClN$: Cl, 13.75. Found: Cl, 13.63.

The **methiodide**, prepared in ethyl acetate, melted at 294–295°.

Anal. Calcd. for $C_{16}H_{30}IN$: I, 34.93. Found: I, 34.98.

Preparation of Acetoxybenzyl Bromides

D. L. FIELDS, J. B. MILLER, AND D. D. REYNOLDS

Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

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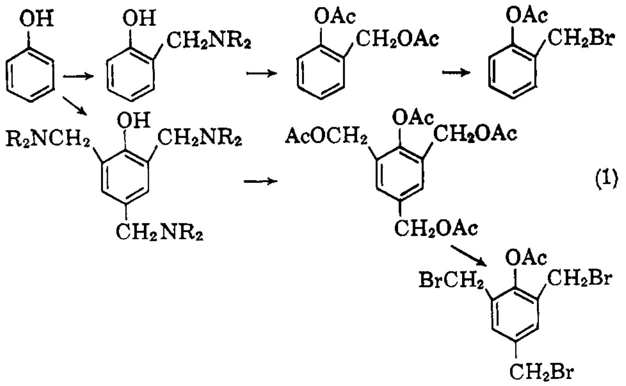
A three-step synthesis of acetoxybenzyl bromides from the corresponding phenols is described. The procedure gives high yields and can be used for large-scale preparations. All of the mono-, di-, tri-, and tetrabromomethylhydroquinone diacetates are described, together with some similar derivatives of catechols and phenols.

Although chloromethylation[1] of mildly activated aromatic compounds is a valuable synthetic tool, it has had very limited application in the alkylation of phenols and phenolic acetates. In general, phenols are so highly activated that the reaction cannot be controlled and diarylmethanes as well as polymers result. Bromomethylation has been effected under the same general conditions as chloromethylation but in even poorer yields.[2]

We describe here a three-step synthesis applicable to phenols which affords bromomethyl derivatives, usually in good yields. The three steps, as typified in eq. 1, are the Mannich-type condensation, acetolysis of the Mannich base, and treatment of the resulting acetoxymethyl acetate with hydrogen bromide in acetic acid. The bromomethylphenol product is acetylated, which is often advantageous since esters of halomethylphenols are much less prone to polymerize than the parent phenol.

In the present study, we have been primarily concerned with derivatives of hydroquinone and catechol, although two examples using phenol (eq. 1) are included to illustrate better the scope of the reaction.



(1)

Mannich Condensation.—The characterizations and structures of the Mannich bases derived from hydroquinone and catechol are summarized in Tables I and II, respectively. Aminomethylhydroquinones, Ia, Ic, Ie, and If (Table I), were prepared by varying the stoichiometry and reaction conditions in direct condensations of hydroquinone with formaldehyde and morpholine.

Morpholinomethylhydroquinone (Ia) was isolated in 65% yield by allowing equimolar amounts of starting materials to react at 25° for 8 hr.

At reaction temperatures below 80°, 2,5-bis(morpholinomethyl)hydroquinone (Ic) was obtained in greater than 70% yield even when greater than the stoichiometric quantity of 2 molar equiv. of amine and formaldehyde per molar equivalent of hydroquinone was used.

A higher reaction temperature and a longer reaction time (*e.g.*, 140°, 20 hr.) were necessary for the production of tris- and tetrakis(morpholinomethyl)hydroquinone, Ie and If, respectively.[3] Purification of Ie (m.p. 168–169°) by fractional crystallization from trace amounts of Ic and If was difficult, but material of sufficient purity (m.p. 150–160°) for subsequent reactions was readily obtained by this method.

2,6-Bis(morpholinomethyl)hydroquinone (Id) was prepared by the procedure of Burke, *et al.*,[4] from 4-benzyloxyphenol. Conversion of Id to Ie by their method did not seem to offer any particular advantage over the more direct route described here, nor was the purity of their product (m.p. 159–160°) significantly better.

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[1] R. C. Fuson and C. H. McKeever, *Org. Reactions*, **1**, 63 (1942).

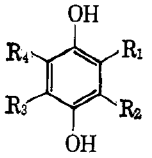
[2] G. Darzens, *Compt. rend.*, **208**, 818 (1939).

[3] Previously prepared by W. J. Burke, J. L. Bishop, and J. A. Warburton, *J. Org. Chem.*, **27**, 4003 (1962).

[4] W. J. Burke, J. A. Warburton, J. L. Bishop, and J. L. Bills, *ibid.*, **26**, 4669 (1961).

Table I

Aminomethylhydroquinones

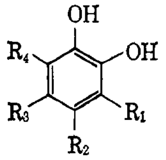


No.	R_1	R_2	R_3	R_4	M.p., °C.	Yield, %[a]	Calcd., % C	H	N	Found, % C	H	N
Ia	$C_5H_{10}NO$[b]	H	H	H	148–149	66	63.2	7.2	6.7	63.4	7.3	6.5
Ic	$C_5H_{10}NO$	H	$C_5H_{10}NO$	H	203–205 205[c]	75						
Id	$C_5H_{10}NO$	H	H	$C_5H_{10}NO$	182–183[d]							
Ie	$C_5H_{10}NO$	$C_5H_{10}NO$	$C_5H_{10}NO$	H	168–169 159–160[d]	33	51.9	8.1	10.3	62.1	8.3	10.1
If	$C_5H_{10}NO$	$C_5H_{10}NO$	$C_5H_{10}NO$	$C_5H_{10}NO$	256–257 250[e]	55	61.6	8.3	11.1	61.7	8.4	11.2

[a] Yields of products obtained by the direct condensation of hydroquinone, formaldehyde, and morpholine. [b] $C_5H_{10}NO$ = morpholinomethyl. [c] H. A. Bruson, U. S. Patent 2,040,040 (1935). [d] Ret. 4. [e] Ref. 3.

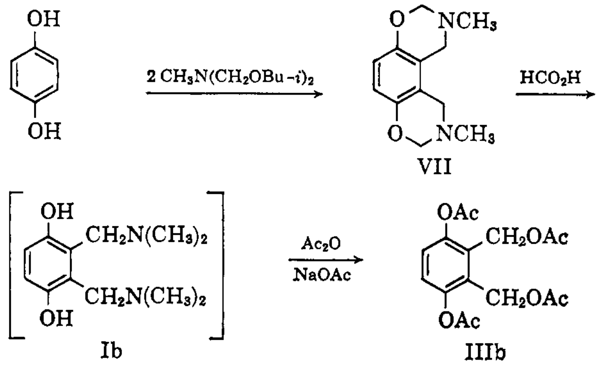
Table II

Aminomethylcatechols



No.	R_1	R_2	R_4	R_3	M.p., °C	Yield, %	Calcd., % C	H	N	Found, % C	H	N
IIa	$C_5H_{10}NO$[a]	H	H	H	127–128	45	63.2	7.2	6.7	63.2	7.3	6.8
IIb	$C_5H_{10}NO$	H	H	$C_5H_{10}NO$	173–174 173–174[b]	74						
IIc	$C_5H_{10}NO$	$C_5H_{10}NO$	H	$C_5H_{10}NO$	142–143	65	61.9	8.1	10.3	62.0	8.1	10.0
IId	$C_5H_{10}NO$	H	C_6H_5	H	172	90	71.5	6.6	4.9	71.3	6.5	5.0
IIe	$C_5H_{10}NO$	H	C_6H_5	$C_5H_{10}NO$	216–217	82	68.7	7.3	7.3	68.4	7.4	7.0

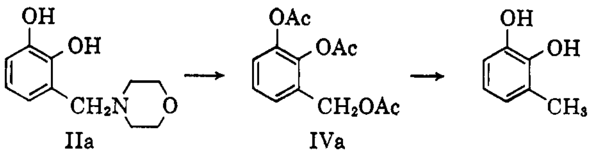
[a] $C_5H_{10}NO$ = morpholinomethyl. [b] Ref. 6.



(2)

Using a modification of a recently described procedure,[5] 2,3-bis(dimethylaminomethyl)hydroquinone (Ib) derived from VII (eq. 2) was converted without isolation into IIIb.

The preparations of the aminomethyl derivatives of catechol and 4-phenylcatechol (IIa–IIc and IId–IIe, Table II, respectively) were analogous to those for the hydroquinone derivatives. The most successful synthesis of 3-morpholinomethylcatechol (IIa) entailed conducting the condensation below 10° to minimize disubstitution. The position of substitution was determined unambiguously by the acetolysis of IIa to IVa which, in turn, gave the known 3-methylcatechol upon hydrogenolysis over palladium on charcoal and methanolysis of the resulting 3-methylcatechol diacetate (eq. 3).



(3)

A bis(morpholinomethyl)catechol (IIb) was readily obtained from the condensation product of catechol with 2 molar equiv. of morpholine and formaldehyde following the procedure of Caldwell and Thompson.[6] Identification of this product as 3,6-bis(morpholinomethyl)catechol, however, is at variance with the structural assignment of these authors. Their structural assignment as a 3,5-disubstituted catechol was based upon its hydrogenolysis over copper chromite to 3,5-dimethylcatechol (m.p. 73–74°). In our hands, hydrogenolysis of this product over palladium on charcoal gave the known 3,6-dimethylcatechol (m.p. 98.5–99.5°). A second independent proof of structure was provided through the sequence of reactions of Chart I. Bisoxazine VIII, which must necessarily be substituted in the 3,6-positions, was the precursor of the same tetraacetate (IVb) obtained by the acetolysis of IIb.

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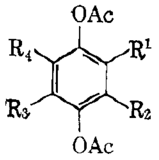
[5] D. L. Fields, J. B. Miller, and D. D. Reynolds, *J. Org. Chem.*, **27**, 2749 (1962).

[6] W. T. Caldwell and T. R. Thompson, *J. Am. Chem. Soc.*, **61**, 2354 (1939).

TABLE III

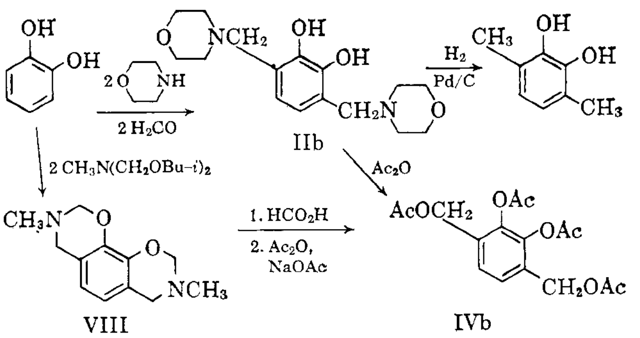
ACETOXYMETHYLHYDROQUINONE DIACETATES



No.	R_1	R_2	R_3	R_4	M.p., °C.	Yield, %	Calcd., % C	Calcd., % H	Found, % C	Found, % H
IIIa	$AcOCH_2$	H	H	H	(b.p. 147° at 0.08 mm.) (b.p. 120–125° at 0.001 mm.)[a]	84	58.6	5.3	58.2	5.0
IIIb	$AcOCH_2$	$AcOCH_2$	H	H	106–108, 106–108[b]	50[c]				
IIIc	$AcOCH_2$	H	$AcOCH_2$	H	117–119, 119[d]	97				
IIId	$AcOCH_2$	H	H	$AcOCH_2$	76–77	84	56.8	5.4	56.7	5.2
IIIe	$AcOCH_2$	$AcOCH_2$	$AcOCH_2$	H	Sirup	34				
IIIf	$AcOCH_2$	$AcOCH_2$	$AcOCH_2$	$AcOCH_2$	157–159 156–156.5[e]	34				

[a] A. Brock, *Helv. Chim. Acta*, **30**, 1 (1947); *Chem. Abstr.*, **41**, 4128*g* (1947). [b] Ref. 5. [c] Over-all yield from VII. [d] Ref. 8. [e] H. v. Euler, E. Alder, H. Hasselquist, and M. Lundin, *Arkiv Kemi, Mineral. Geol.*, **18A**, No. 7 (1944); *Chem. Abstr.*, **39**, 3786 (1945).

CHART I

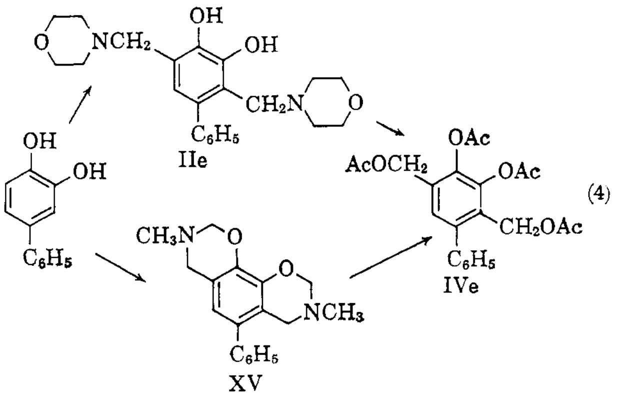


Further support for the 3,6-disubstituted structure was provided by the infrared spectrum which showed broad absorption between 3600 and 2250 cm.$^{-1}$, characteristic of strong intramolecular hydrogen bonding. We found that this broad absorption was typical of all those phenols with *ortho*-morpholinomethyl groups reported here. However, in those compounds having a phenolic group not thus located (Ia, Id, IIa, IId), we found relatively sharp —OH absorption at 3300 cm.$^{-1}$, in addition to the broad absorption already cited. The absence of sharp —OH absorption in the spectrum of IIb is thus consistent with the assigned 3,6-structure but not with a 3,5-structure.

Tris(morpholinomethyl)catechol (IIc) was isolated in 65% yield on reaction of catechol with an excess of morpholine and formaldehyde at 85° for 24 hr.

A mono-Mannich base was obtained in 90% yield from 4-phenylcatechol, formaldehyde, and morpholine. The proof of structure of this product as 3-morpholinomethyl-5-phenylcatechol (IId) is outlined in Chart II. The same triacetate (IVd) was obtained from 4-phenylcatechol, starting with either IId or IX. This established that the nuclear alkylation employing either a primary or a secondary amine was the same and that it must occur in either the 3- or 6-position. Catalytic reduction of IId yielded the new 3-methyl-5-phenylcatechol (X) which was prepared by independent synthesis from 4-phenylphenol. A more direct route to this compound *via* the available 1-chloro-4-phenylphenol was not successful since hydrogenolysis of the precursor Mannich base (XIV) also removed the chloro group.[7]

As with catechol, the bismorpholinomethyl product from 4-phenylcatechol proved to be a 3,6-derivative. This was proved (eq. 4) by its conversion to the same tetraacetate (IVe) obtained from the corresponding bisoxazine (XV).



Acetolysis and Bromide Substitution.—The acetolysis[8] of the aminomethyl derivatives, Tables I and II, was effected by refluxing the base in acetic anhydride for 18–48 hr. The characterizations of the resulting acetoxymethyl acetates are summarized in Tables III and IV.

Early in the study of the conversion of an acetoxymethyl compound into the corresponding bromomethyl derivative, the product was obtained in 70–80% yield by reaction with 30% hydrogen bromide in acetic acid overnight at room temperature. In the case of 3,6-bis(acetoxymethyl)catechol diacetate (IVb), a second product, identified as 3,6-bis(bromomethyl)catechol monoacetate[9] (XVI), was isolated in 26% yield in addition to a 71% yield of the expected 3,6-bis(bromomethyl)catechol diacetate (VIb). This suggested that

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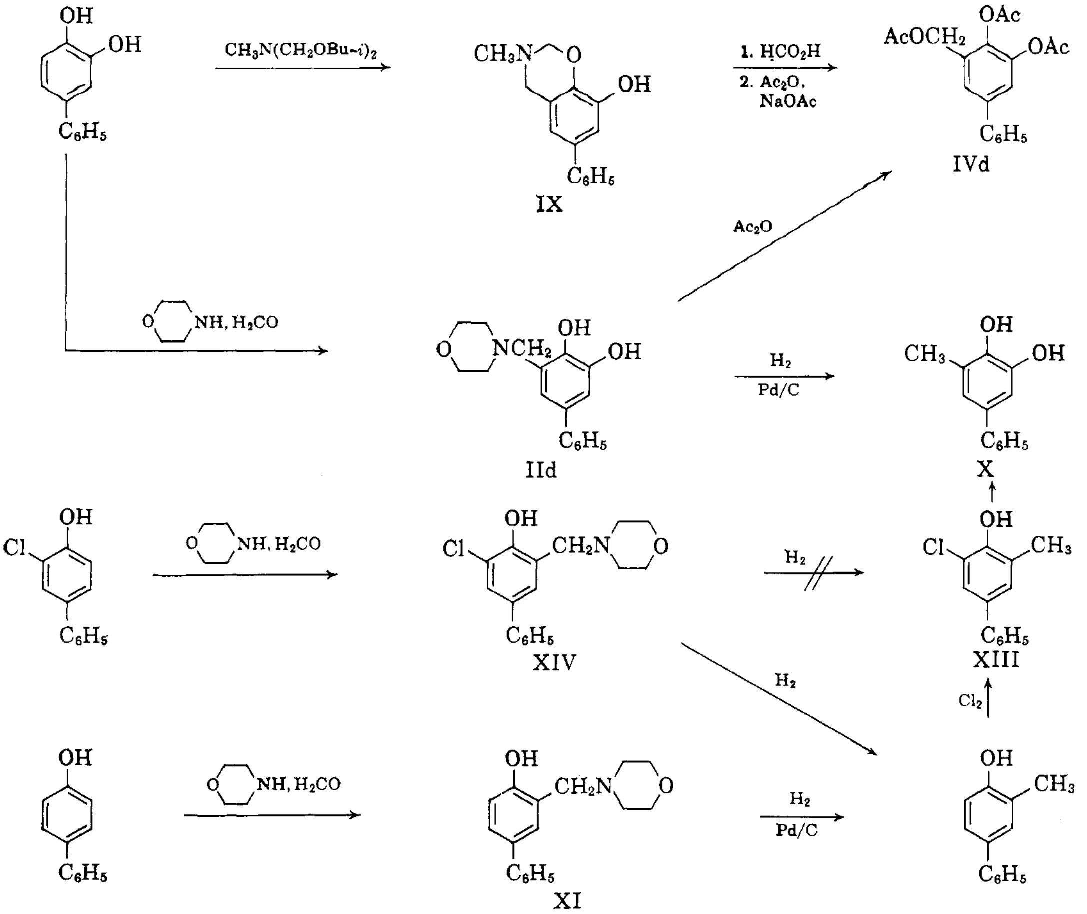
[7] W. E. Solodar and M. Green, *J. Org. Chem.*, **27**, 1077 (1962).

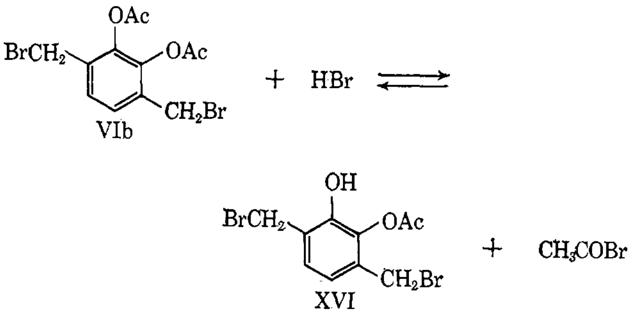
[8] H. A. Bruson, U. S. Patent 2,265,141 (1941); H. A. Bruson and C. W. MacMullen, *J. Am. Chem. Soc.*, **63**, 270 (1941).

[9] The structure of XVI was assigned based on its elemental analysis, infrared spectrum ($C{=}O$ at 1770, strong —OH at 3440 cm.$^{-1}$), and by its quantitative acetylation with acetic anhydride-sulfuric acid to Vb ($C{=}O$ at 1790 cm.$^{-1}$, no —OH absorption).

Chart II



the reversible reaction shown below was occurring and both products, being relatively insoluble in acetic acid, crystallized from the reaction mixture. Since VIb was the initial product, it was obtained in the greater amount.



By utilizing a more differential solvent, the ratio of the products could presumably be varied in a predictable fashion. Thus, for example, the use of methylene chloride in which VIb is quite soluble and XVI only sparingly so gives rise to a 59:37% mixture of XVI–VIb Similarly, starting with VIb in a methylene chloride–benzene mixture, one obtains a 72:24% mixture of XVI–VIb.

Although only one other crystalline deacetylation product analogous to XVI has been isolated (from IVc) in the bromide substitution reactions studied, these results suggest that deacetylation might be occurring to the extent of 20–30% in the other cases. This now has experimental foundation as the yields of bromomethyl derivatives of Tables V and VI initially obtained to the extent of 70–80% have been increased to practically quantitative by adding acetic anhydride to the reaction mixture prior to work-up (Tables V and VI).

The synthesis described is now being successfully extended to other related systems, including the naphthols as well as a variety of phenols. The resulting bromomethyl derivatives possess the high reactivity toward nucleophilic substitution reactions expected of benzyl bromides and are thus proving to be of considerable value in the synthesis of phenol derivatives not heretofore available.

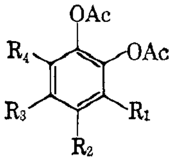
Experimental

Mannich-Type Condensation (Tables I and II). Morpholinomethylhydroquinone (Ia).—A mixture of paraformaldehyde (90 g., 3 moles) and morpholine (262 g., 3 moles) was warmed on a steam bath until it was homogeneous. The solution was cooled to 25° and added to a solution of hydroquinone (330 g., 3 moles) in 2.5 l. of acetone. The mixture was concentrated on a rotary evaporator at 25° under aspirator vacuum. After about 8 hr., a hard, white crystalline product remained. Recrystallization from 2 l. of isopropyl alcohol gave 85 g. of 2,5-bis(morpholinomethyl)hydroquinone (Ic). Evaporation of the mother liquor and trituration with ether yielded crude morpholinomethylhydroquinone (411 g., 65.5%), m.p. 137–140°. This material was used for the preparation of acetoxymethylhydroquinone diacetate (IIIa). An analytical sample was prepared by recrystallization from isopropyl alcohol, m.p. 148–149°.

2,5-Bis(morpholinomethyl)hydroquinone (Ic).—To a homogeneous solution of morpholine (262 g., 3.0 moles) and paraformaldehyde (90 g., 3.0 moles) in 200 ml. of isopropyl alcohol was added a solution of hydroquinone (110 g., 1.0 mole) in 500 ml. of isopropyl alcohol. The solution was refluxed for 1.5 hr., and then concentrated to give a white crystalline product. After

TABLE IV

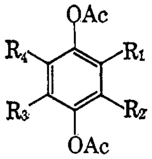
ACETOXYMETHYLCATECHOL DIACETATES



No.	R_1	R_2	R_3	R_4	M.p., °C.	Yield, %	Calcd., %		Found, %	
							C	H	C	H
IVa	$AcOCH_2$	H	H	H	56–57 (b.p. 147° at 0.07 mm.)	80	58.6	5.3	58.4	5.6
IVb	$AcOCH_2$	H	H	$AcOCH_2$	113–114	90	56.8	5.3	57.2	5.4
IVc	$AcOCH_2$	$AcOCH_2$	H	$AcOCH_2$	70–71	74	55.6	5.4	55.5	5.4
IVd	$AcOCH_2$	H	C_6H_5	H	112–113	97	66.7	5.3	67.0	5.5
IVe	$AcOCH_2$	H	C_6H_5	$AcOCH_2$	99–101	89	63.8	5.3	63.4	5.3

TABLE V

BROMOMETHYLHYDROQUINONE DIACETATES

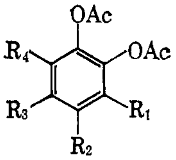


No.	R_1	R_2	R_3	R_4	M.p., °C.	Yield, %	Calcd., %			Found, %		
							C	H	Br	C	H	Br
Va	$BrCH_2$	H	H	H	109 107[a]	95						
Vb	$BrCH_2$	$BrCH_2$	H	H	137–139	99.5	37.9	3.2	42.2	37.7	3.4	41.8
Vc	$BrCH_2$	H	$BrCH_2$	H	178–180 179[b]	94						
Vd	$BrCH_2$	H	H	$BrCH_2$	114–116	99	37.9	3.2	42.2	37.8	3.3	41.8
Ve	$BrCH_2$	$BrCH_2$	$BrCH_2$	H	174–176		33.0	2.7	50.8	33.4	2.8	50.5
Vf	$BrCH_2$	$BrCH_2$	$BrCH_2$	$BrCH_2$	253–255 256–257[b]	93	29.7	2.5	56.5	30.0	2.7	56.2

[a] G. Zemplén, R. Bognár, and S. Marvay, *Ber.*, **76B**, 1165 (1943); *Chem. Abstr.*, **39**, 1398 (1945). [b] H. v. Euler, E. Alder, H. Hasselquist, and M. Lundin, *Arkiv Kemi, Mineral. Geol.*, **18A**, No. 7, (1944); *Chem. Abstr.*, **39**, 3786 (1945).

TABLE VI

BROMOMETHYLCATECHOL DIACETATES



No.	R_1	R_2	R_3	R_4	M.p., °C.	Yield, %	Calcd., %			Found, %		
							C	H	Br	C	H	Br
VIa	$BrCH_2$	H	H	H	94–96	97	46.0	3.8	27.9	45.6	4.1	28.2
VIb	$BrCH_2$	H	H	$BrCH_2$	137–139	99	37.9	3.2	42.2	38.2	3.4	42.1
VIc	$BrCH_2$	$BrCH_2$	H	$BrCH_2$	160–162	96	33.0	2.8	50.8	33.1	2.7	50.5
VId	$BrCH_2$	H	C_6H_5	H	117–118	94	56.2	4.1	22.0	55.8	4.5	22.3
VIe	$BrCH_2$	H	C_6H_5	$BrCH_2$	128–129	94	47.4	3.5	35.1	47.8	3.8	35.5

the product had been washed with two 100-ml. portions of ether, it (231 g., 75%) was dried and had m.p. 201–203°.

2,3,5-Tris(morpholinomethyl)hydroquinone (Ie).—Paraformaldehyde (45 g., 1.5 moles) and morpholine (131 g., 1.5 moles) were warmed (under nitrogen) in 500 ml. of 2-(2-ethoxyethoxy)-ethanol until the mixture was homogeneous. Hydroquinone (55 g., 0.5 mole) was added and the distillate removed until the pot temperature rose to 140°. The mixture was then refluxed for 24 hr. After refrigeration for 18 hr., the crystalline product (189 g.) was separated, washed with ether, and then stirred with 1 l. of benzene. The insoluble 2,5-bis(morpholinomethyl)-hydroquinone (Ic) was removed by filtration and the filtrate evaporated to yield 68.5 g. (33%) of crude 2,3,5-tris(morpholinomethyl)hydroquinone, m.p. 154–160°. A pure sample was obtained by repeated crystallizations from ethyl acetate, m.p. 168–169° (lit.[4] m.p. 159–160°).

Tetrakis(morpholinomethyl)hydroquinone (If).—A mixture of morpholine (470 g., 5.35 moles), paraformaldehyde (160 g., 5.35 moles), 700 ml. of benzene, and 700 ml. of 2-(2-ethoxyethoxy)ethanol was heated and 500 ml. of distillate was removed. Hydroquinone (110 g., 1.0 mole) in 350 ml. of methanol was then slowly added and the distillate was again removed until the reaction temperature reached 145°. The mixture was then refluxed for 20 hr. and cooled, and the crystals were washed with ether (yield, 280 g., 55%, m.p. 254–257°). An analytical sample, m.p. 256–257°, was obtained by recrystallization from 2-(2-ethoxyethoxy)ethanol.

3-Morpholinomethylcatechol (IIa).—A mixture of paraformaldehyde (120 g., 4 moles) and morpholine (349 g., 4 moles) in 800 ml. of isopropyl alcohol was warmed cautiously on a steam bath until it was homogeneous. The resulting solution was cooled to 10°, and added to a solution of catechol (440 g., 4 moles) in 500 ml. of acetone. The mixture was concentrated on a rotary evaporator at 10° under aspirator vacuum. After approximately 6 hr., a white pasty mass remained. This was triturated with 500 ml. of ether and refrigerated overnight. The crystalline product was filtered and dried (yield, 380 g., 45.4%, m.p. 121–126°). An analytical sample was obtained after one recrystallization from ethyl acetate, m.p. 127–128°.

3,4,6-Tris(morpholinomethyl)catechol (IIc).—Paraformaldehyde (120 g., 4 moles) and morpholine (348 g., 4 moles) were refluxed in 1 l. of isopropyl alcohol until the mixture was homogeneous. Catechol (110 g., 1 mole) was added and the reaction mixture refluxed for 24 hr. The isopropyl alcohol was removed under vacuum and the crystalline product triturated in 500 ml. of ether (yield, 355 g., m.p. 128–132°). After one recrystallization from ethyl acetate 264 g. (64.8%, m.p. 139–140°) was obtained. Recrystallization of a sample from ethyl acetate gave an analytical sample, m.p. 142–143°.

3-Morpholinomethyl-5-phenylcatechol (IId).—A mixture of paraformaldehyde (36 g., 1.2 moles) and morpholine (104.5 g., 1.2 moles) in 500 ml. of isopropyl alcohol was warmed on a steam bath until it was homogeneous. To this solution was added 186 g. (1 mole) of 4-phenylcatechol. The mixture was refluxed for 15 min. during which time 3-morpholinomethyl-5-phenylcatechol crystallized. After cooling, the product (243 g., 85%) was separated, washed with ether, and dried, m.p. 172°. Recrystallization from ethyl acetate did not change the melting point.

3,6-Bis(morpholinomethyl)-4-phenylcatechol (IIe). A.—A mixture of paraformaldehyde (60 g., 2 moles) and morpholine (174 g., 2 moles) in 500 ml. of 2-(2-ethoxyethoxy)ethanol and 500 ml. of benzene was refluxed in a distillation apparatus. After 150 ml. of distillate had been removed, a solution of 4-phenylcatechol (186 g., 1.0 mole) in 250 ml. of methanol was slowly added. Distillate was removed until the reaction temperature reached 110° and then the reaction mixture was refluxed for 15 hr. The reaction mixture was cooled and the product filtered, washed with ether, and dried (236 g., 61%, m.p. 213–216°). Recrystallization from 2-(2-ethoxyethoxy)ethanol gave an analytical sample, m.p. 216–217°.

B.—A solution of 4-phenylcatechol (186 g., 1.0 mole) and isobutoxymethylmorpholine[10] (346 g., 1.0 mole) in 500 ml. of benzene was refluxed for 4 hr. The benzene was removed under reduced pressure and the product separated as a crystalline mass. Trituration with ethanol, filtration, and drying gave 315 g. (81.5%). A sample recrystallized from ethyl acetate melted at 216–217°.

2-Morpholinomethylphenol.—A mixture of phenol (188 g., 2 moles) and ethoxymethylmorpholine (290 g., 2 moles) in 500 ml. of isopropyl alcohol was concentrated on a rotary evaporator at 20° for 4 hr., and at 40° for 2 hr. The residual liquid was distilled to yield 261 g. (68%), b.p. 135° (0.07 mm.), m.p. 95–96° (lit.[11] m.p. 95–96°).

Acetolysis (Tables III and IV).—With the exception of IIIb and IIIf, the acetoxymethyl derivatives of Tables III and IV were prepared from their corresponding aminomethyl compounds of Tables I and II by a general procedure involving refluxing a mixture of 0.5 mole of the Mannich base and 500 ml. of acetic anhydride for 18 hr. In the case of IIIf, extension of the refluxing period from 18 hr. to 48 hr. increased the yield from 15 to 34%. The yield was not improved by longer reaction times.

The reaction mixture was concentrated under reduced pressure to a sirup. Acetates IIIa and IVa were isolated by distillation. The other acetates were poured into 2 l. of cold water. With the exception of IIIe, trituration of the resulting sirup induced crystallization. The crystals were washed with two 500-ml. portions of water and recrystallized from ethanol–ligroin (b.p. 30–60°). It was advantageous to slurry benzene solutions of IIIe and IIIf with small amounts of Micro-Cel "C"[12] to remove dark-colored impurities prior to their recrystallization.

2,3-Bis(acetoxymethyl)hydroquinone Diacetate (IIIb).—The starting bisoxazine VII was prepared in 70% yield from hydroquinone, formaldehyde, and methylamine following a recently described procedure.[5] Bisoxazine VII (44 g., 0.2 mole) and 200 ml. of 90% formic acid were refluxed for 16 hr. on a steam bath. Concentration of the reaction mixture under reduced pressure yielded a viscous sirup. This was dissolved in 200 ml. of benzene and reconcentrated free of solvent. A mixture of the sirup, 250 ml. of acetic anhydride, and 50 g. of anhydrous sodium acetate was refluxed for 16 hr. (Caution! Carbon monoxide is evolved.), concentrated under reduced pressure to *ca.* 250 ml., and poured into 1 l. of cold water. The desired product (IIIb) crystallized, was filtered, and dried. A dark-colored impurity was removed by slurrying a solution of the product in 700 ml. of benzene with 30 g. of Micro-Cel "C",[12] followed by filtration. The filtrate was concentrated to *ca.* 100 ml. and diluted with ligroin (b.p. 30–60°) to cloudiness. After refrigeration overnight, 33.7 g. (49.9%) of crystals were isolated, m.p. 106–108° (lit.[5] m.p. 106–108°).

2-Acetoxymethylphenyl Acetate.—A mixture of 2-morpholinomethylphenol (260 g., 1.35 moles) and 800 ml. of acetic anhydride was refluxed for 8 hr. Distillation yielded 218 g. (78%) of product identical with the product obtained by acetylation of 2-hydroxybenzyl alcohol, b.p. 90° (0.1 mm.), $n^{25}\text{D}$ 1.4975.

Bromide Substitution (Tables V and VI).—The following example is illustrative of the general procedure followed in preparing 2-bromomethylphenyl acetate, 2,4,6-tris(bromomethyl)phenyl acetate, and the bromomethyl compounds of Tables V and VI. A slight modification in procedure was necessary for the synthesis of VIb and is described in a succeeding section.

A mixture of 2,5-bis(acetoxymethyl)hydroquinone diacetate (IIIc, 33.8 g., 0.1 mole) and 100 ml. of 30% hydrogen bromide–acetic acid in 175 ml. of methylene chloride stood overnight at room temperature. Acetic anhydride (100 ml.) was added and the solution was concentrated under reduced pressure to a crystalline mass. The product was slurried in 100 ml. of ether and 400 ml. of ligroin (b.p. 30–60°) and refrigerated overnight at 5° to complete the crystallization. A first crop (32.8 g., m.p. 178–180°) and a second crop (3.0 g., m.p. 176–179°) of 2,5-bis(bromomethyl)hydroquinone diacetate (Vc, total yield, 94%) was obtained. Recrystallization from benzene gave an analytical sample, m.p. 178–180°.

2-Bromomethylphenyl Acetate.—The general procedure in this case gave a liquid which was distilled at 83° (0.1 mm.) to give the product in 92% yield, $n^{25}\text{D}$ 1.5493.

Anal. Calcd. for $C_9H_9BrO_2$: C, 47.2; H, 3.9; Br, 34.9. Found: C, 47.5; H, 3.7; Br, 34.8.

2,4,6-Tris(bromomethyl)phenyl acetate, m.p. 147–149°, was prepared in 95% yield from 2,4,6-tris(acetoxymethyl)phenyl acetate.[8]

Anal. Calcd. for $C_{11}H_{11}Br_3O_2$: C, 31.8; H, 2.7; Br, 57.8. Found: C, 32.0; H, 2.8; Br, 57.7.

VIb from IVb.—The reaction was conducted in the identical manner just described. However, monoacetate XVI separated from solution and, owing to its low solubility, was not acetylated during the subsequent treatment with acetic anhydride. Warming the mixture of VIb and XVI in acetic anhydride with 2 drops of concentrated sulfuric acid gave a 99% yield of 3,6-bis(bromomethyl)catechol diacetate (VIb).

VIb and XVI from IVb.—3,6-Bis(acetoxymethyl)catechol diacetate (IVb, 42.3 g., 0.125 mole) was dissolved in 100 ml. of 30% hydrogen bromide–acetic acid and allowed to stand 16 hr. at room temperature. A crystalline product separated from solution during this period. The reaction mixture was concentrated free of solvents. The crystalline residue was slurried with 100 ml. of methylene chloride and filtered. The insoluble portion was washed with two 25-ml. portions of methylene chloride and dried, to yield 11.0 g. (26%) of XVI, m.p. 167° dec.

Anal. Calcd. for $C_{10}H_{10}Br_2O_3$: C, 35.5; H, 3.0; Br, 47.3. Found: C, 35.8; H, 3.2; Br, 47.5.

Acetylation of XVI with acetic anhydride and a drop of sulfuric acid gave VIb in quantitative yield.

The combined methylene chloride filtrates were concentrated to one-half volume, diluted to cloudiness with ligroin (b.p. 30–60°) and refrigerated overnight at −20°. Diacetate VI crystallized and was isolated in 70.7% yield (33.6 g.).

A tris(bromomethyl)catechol monoacetate, m.p. 183–184°, was isolated in analogous fashion from IVc.

Anal. Calcd. for $C_{11}H_{11}Br_3O_3$: C, 30.6; H, 2.6; Br, 55.6. Found: C, 30.9; H, 2.9; Br, 55.9.

XVI from VIb.—A mixture of VIb (34 g., 0.9 mole), 100 ml. of 30% hydrogen bromide–acetic acid, 150 ml. of methylene chloride, and 250 ml. of benzene was allowed to stand overnight at room temperature and then concentrated to a crystalline solid. The product was slurried in 100 ml. of methylene chloride

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[10] J. P. Mason and M. Zief, *J. Am. Chem. Soc.*, **62**, 1450 (1940).

[11] H. A. Bruson, U. S. Patent 2,040,039 (1935).

[12] A synthetic calcium silicate manufactured by the Johns-Manville Co., New York, N. Y.

and filtered; the residual crystals (XVI) were washed with two 25-ml. portions of methylene chloride, giving 21.8 g. (72%) of XVI, m.p. 167° dec.

An amount of 8.3 g. (24%) of unchanged VIb was recovered from the filtrate.

8-Hydroxy-3-methyl-6-phenyl-3,4-dihydro-2H-1-oxa-3-azanaphthalene (IX).—4-Phenylcatechol (93 g., 0.5 mole) in 200 ml. of ethanol was added to a refluxing solution of bis(isobutoxymethyl)methylamine[5] (203 g., 1.0 mole) in 250 ml. of benzene. The mixture was refluxed for 30 min. and then concentrated to a white, crystalline mass. The product was dissolved in 300 ml. of benzene and chromatographed on a column (5 × 45 cm.) of alumina, with 4 l. of benzene as a developer. The effluent was concentrated to *ca.* 400 ml., diluted to cloudiness with ligroin (b.p. 30–60°), and refrigerated overnight. The resulting crystals (52.8 g.) had m.p. 157–158°.

Anal. Calcd. for $C_{15}H_{15}NO_2$: C, 74.7; H, 6.2; N, 5.8. Found: C, 75.0; H, 6.6; N, 5.8.

2,7-Dimethyl-1,2,3,6,7,8,-hexahydro-4,5-dioxa-2,7-diazaphenanthrene (VIII), m.p. 205–207° dec., was prepared in 77% yield by the condensation of catechol (55 g., 0.5 mole) with bis(isobutoxymethyl)methylamine (203 g., 1.0 mole) following the procedure described for the preparation of IX.

Anal. Calcd. for $C_{12}H_{16}N_2O_2$: C, 65.4; H, 7.3; N, 12.7. Found: C, 65.5; H, 7.7; N, 12.7.

2,7-Dimethyl-9-phenyl-1,2,3,6,7,8-hexahydro-4,5-dioxa-2,7-diazaphenanthrene (XV).—A solution of 4-phenylcatechol (46.5 g., 0.25 mole) and bis(isobutoxymethyl)methylamine (101.5 g., 0.5 mole) in 400 ml. of toluene was refluxed for 18 hr. Removal of solvents gave a crystalline product which was dissolved in 500 ml. of benzene and chromatographed on a column (5 × 45 cm.) of alumina, with 1 l. of benzene as a developer. Recrystallization of the effluent solids from acetone yielded 31 g. of the desired product, m.p. 179–181°.

Anal. Calcd. for $C_{18}H_{20}N_2O_2$: C, 73.0; H, 6.8; N, 9.5. Found: C, 72.6; H, 7.2; N, 9.3.

IVd from IX, IVb from VIII, and IVe from XV.—In a typical experiment a solution of 25 g. (0.1 mole) of IX in 250 ml. of 90% formic acid was heated on a steam bath for 18 hr. The reaction mixture was concentrated to a sirup. A mixture of the sirup, 250 ml. of acetic anhydride, and 40 g. of sodium acetate was refluxed for 16 hr. The cooled solution, when poured into 1 l. of cold water, gave a sirup which slowly crystallized. The crystals were recrystallized twice from ethanol and had m.p. 111-113°. The melting point and infrared spectrum were identical with those of the product obtained by the acetolysis of IId. The mixture melting point was undepressed.

In similar manner, VIII was converted to the same tetraacetate (IVb), m.p. 113–114°, as was obtained by the acetolysis of IIb, and XV afforded the same tetraacetate (IVe), m.p. 99–101°, obtained by the acetolysis of IIe.

2-Morpholinomethyl-4-phenylphenol (XI).—A mixture of 153 g. (5.1 moles) of paraformaldehyde, 444 g. (5.1 moles) of morpholine, and 1950 ml. of ethanol was stirred until the initial exothermic reaction subsided and a nearly homogeneous solution resulted. A slurry of 845 g. (5 moles) of *p*-phenylphenol in 1 l. of ethanol was then added and the mixture was refluxed for 18 hr. Distillation of 1500 ml. of ethanol left a heavy liquid which crystallized to yield 747 g. (55%) of 2-morpholinomethyl-4-phenylphenol, m.p. 86–88.5° (lit.[13] m.p. 91°).

2-Chloro-6-morpholinomethyl-4-phenylphenol (XIV).—A mixture of 352 g. (4.05 moles) of morpholine, 121.5 g. (4.05 moles) of paraformaldehyde, and 1 l. of ethanol was stirred until the initial exothermic reaction subsided and a nearly homogeneous solution resulted. A solution of 783 g. (3.83 moles) of 2-chloro-4-phenylphenol in 1 l. of warm ethanol was added and the resulting solution was refluxed for 2 hr. Distillation of 960 ml. of ethanol gave a pot liquor which, on standing, deposited 760 g. of product, m.p. 126–130°. A 245-g. second crop (86% total yield) was also obtained. Two recrystallizations from ethanol gave an analytical sample, m.p. 130–132.5°.

Anal. Calcd. for $C_{17}H_{18}ClNO_2$: C, 67.2; H, 5.9; Cl, 11.7; N, 4.6. Found: C, 67.3; H, 6.2; Cl, 11.9; N, 4.7.

2-Methyl-4-phenylphenol (XII) from XIV.—A mixture of 30.4 g. (0.1 mole) of XIV, 10 g. of 10% palladium on charcoal, and 200 ml. of ethanol was hydrogenated at 80° and 71 p.s.i. (initial pressure) in a Parr shaker. The reactor was stopped after 5 min. when the pressure drop indicated the consumption of 0.19 mole of hydrogen. Filtration, followed by removal of the solvent, gave a white solid which was washed with water, 5% hydrochloric acid, and then water. Crystallization from methanol–water gave 14 g. (70%) of product, m.p. 111.5–112.5°. Recrystallization from methanol gave an analytical sample, m.p. 112–114° (lit.[14] m.p. 115°).

Anal. Calcd. for $C_{13}H_{12}O$: C, 84.7; H, 6.5. Found: C, 85.1; H, 6.3.

From XI.—A mixture of 26.9 g. (0.1 mole) of XI, 10 g. of 10% palladium on charcoal, and 200 ml. of ethanol was hydrogenated at 80° and 72.5 p.s.i. (initial pressure) for 16 min. in a Parr shaker. Filtration, followed by removal of the solvent, gave a heavy liquid. The liquid was dissolved in 50 ml. of methanol and concentrated hydrochloric acid was added until the solution was acidic. Addition of 500 ml. of water gave a white solid which was washed free of acid and dried, to yield 16.8 g. (91%) of 2-methyl-4-phenylphenol (XII), m.p. 110.5–113°, whose infrared spectrum was identical with that of the material prepared from XIV.

2-Chloro-6-methyl-4-phenylphenol (XIII).—A solution of 78 g. (1.1 moles) of chlorine in 1500 ml. of chloroform was added in a thin stream to a stirred suspension of 184 g. (1.0 mole) of XII in 750 ml. of chloroform. The temperature was kept below 25° during the addition. The resulting homogeneous solution was then aerated until it was essentially free of hydrogen chloride and chlorine. Removal of the solvent gave a crystalline solid which was distilled, b.p. 170.5–171.5° (7 mm.). The distillate crystallized at room temperature to give 198 g. (91%) of product, m.p. 65.5–67.5°. Recrystallization from ligroin (b.p. 66–75°), followed by cyclohexane, gave an analytical sample, m.p. 63–67.5°.

Anal. Calcd. for $C_{13}H_{11}ClO$: C, 71.5; H, 5.0; Cl, 16.3. Found: C, 71.1; H, 5.2; Cl, 16.5.

3-Methyl-5-phenylcatechol (X) from IIb.—A mixture of 392 g. (1.38 moles) of IIb, 25 g. of 10% palladium on charcoal, and 1.5 l. of alcohol was hydrogenated at 80° and 60 p.s.i. (initial pressure) until the theoretical amount of hydrogen was taken up. The reaction mixture was filtered directly into 120 ml. of concentrated hydrochloric acid. Removal of the solvent gave a white solid which was dissolved in 2 l. of ether and washed with water, 5% sodium bicarbonate solution, and then water. The ether solution was dried with sodium sulfate and the solvent removed to give 273 g. of product, m.p. 107–108°. Crystallization from benzene–ligroin (b.p. 66–75°) gave 205 g. of material, m.p. 108.5–111°. A second crop (14 g., 80% total yield, m.p. 107–110°) was obtained from the mother liquor. Recrystallization from the same solvent system gave an analytical sample, m.p. 109.5–110°.

Anal. Calcd. for $C_{13}H_{12}O_2$: C, 78.0; H, 6.0. Found: C, 77.5; H, 6.2.

From XIII.—A mixture of 109.2 g. (0.5 mole) of XIII, 60 g. (1.5 moles) of sodium hydroxide, 158 g. (0.5 mole) of barium hydroxide octahydrate, 2.5 g. of copper sulfate pentahydrate, and 240 ml. of water was placed in an autoclave under 400 p.s.i. nitrogen. The mixture was then heated at 200° for 19 hr., with agitation. The autoclave was rinsed with 1 l. of water. After addition of 240 ml. of concentrated hydrochloric acid, the reaction mixture was heated at 80° for 30 min. The mixture was then extracted with four 250-ml. portions of ether and once with 250 ml. of benzene. The combined extracts were then filtered through cotton, washed with water, and dried with sodium sulfate. Removal of the solvent gave a black oil. A short-path distillation gave 67.1 g. of a light yellow liquid, b.p. 181–225° (7–18 mm.), which crystallized at room temperature.

Vapor phase chromatography[15] indicated this solid to contain 73% of the starting material (3.64[16]), 11% of the desired product (6.04[16]), 9% of II (3.06[15]), and 6.8% of unidentified material (2.76[16]).

A 10-g. sample of the distilled solid was stirred for 15 min. with 400 ml. of a saturated borax solution. Filtration gave 8.9 g. (89% recovery) of a white solid, m.p. 52–59°, m.m.p. 54–65° with authentic 2-chloro-6-methyl-4-phenylphenol. The pink filtrate was mixed with 400 ml. of a saturated mannitol solution,

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(13) J. H. Burckhalter, F. H. Tendick, E. M. Jones, W. F. Holcomb, and A. L. Rawlins, *J. Am. Chem. Soc.*, **68**, 1894 (1946).

(14) J. C. Colbert and R. M. Lacy, *ibid.*, **68**, 270 (1946).

(15) Chromatographed on a 4-ft. column containing 25% of Dow-Corning Silicone Fluid No. 200, on acid- and base-washed Celite 545; column temperature was 229°, flow rate 100 ml./min.

(16) Retention time relative to dimethylphthalate.

and the resulting cloudy solution was extracted with four 100-ml. portions of ether. The ether extracts were dried with sodium sulfate and the solvent was removed to yield a bright yellow, oily solid. Crystallization from benzene–petroleum ether (b.p. 30–60°) gave 0.6 g. of a yellow solid, m.p. 97–101° (sintering). Two recrystallizations from cyclohexane, followed by one from ethanol–water (decolorized with Darco), gave an off-white solid having m.p. 108–109° (sintering), m.m.p. 109.5–110.5° (sintering) with authentic X as prepared above, and an infrared spectrum identical with that of X.

3,6-Dimethylcatechol from IIb.—A mixture of 30.8 g. (0.1 mole) of 3,6-bis(morpholinomethyl)catechol (IIb), 10 g. of 10% palladium on charcoal, and 200 ml. of ethanol was hydrogenated at 70° and 63 p.s.i. (initial pressure) in a Parr shaker. Reaction was complete in 7 hr., as indicated by a pressure drop equivalent to the consumption of 0.18 mole of hydrogen. Concentrated hydrochloric acid (20 ml.) was added to the reaction mixture which was then filtered. Removal of the solvent and addition of 300 ml. of water to the resulting oil gave a solid. The mixture was filtered and the solid washed with 100 ml. of water to yield, after drying, 4.6 g. of product, m.p. 99–100°. The combined filtrate and washings were extracted with three 100-ml. portions of ether. The ether extract, after it had been washed with 10 ml. of 5% sodium bicarbonate solution, was dried with sodium sulfate and stripped, to yield 7.4 g. (total yield 87%) of product, m.p. 95.5–99°. Recrystallization from benzene–ligroin (b.p. 66–75) gave pure material, m.p. 98.5–99.5° (lit.[17] m.p. 101°).

The **dibenzoate** was prepared and found to have m.p. 93–94.5° (lit.[17] m.p. 101°).

Anal. Calcd. for $C_{22}H_{18}O_4$: C, 76.3; H, 5.2. Found: C, 75.9; H, 5.3.

3-Methylcatechol from IVa.—A mixture of 133 g. (0.5 mole) of 3-acetoxymethylcatechol diacetate, 10 g. of 10% palladium on charcoal, and 100 ml. of ethanol was hydrogenated at 80° and 70 p.s.i. (initial pressure) in a Parr shaker for 5.5 hr. Filtration and removal of the solvent gave a light yellow oil. This was dissolved in 200 ml. of 5% methanolic hydrogen chloride which was then removed on a steam bath under reduced pressure. This was repeated using methanol and once again using methanol at atmospheric pressure. The resulting dark oil was distilled to give 43 g. of crude product, b.p. 120–134° (8 mm.). Seeding with authentic 3-methylcatechol gave a pasty solid which was recrystallized from benzene and then cyclohexane to give a white solid, m.p. 63–64.5°, whose infrared spectrum was superimposable on that of authentic 3-methylcatechol. The dibenzoate was prepared (m.p. 119–120.5°) and its infrared spectrum was found to be identical with that of an authentic sample (see below).

3-Methylcatechol[18] was purified by distillation, followed by recrystallization from benzene, and had m.p. 65–66.5° (lit.[19] m.p. 58–62°). The **dibenzoate** was prepared and had m.p. 120–122° (lit.[20] m.p. 122°).

Anal. Calcd. for $C_{21}H_{16}O_4$: C, 75.9; H, 4.8. Found: C, 75.6; H, 5.0.

4-Methylcatechol[17] (m.p. 63.5–67°) was converted to the dibenzoate, m.p. 63–65°.

Anal. Calcd. for $C_{21}H_{16}O_4$: C, 75.9; H, 4.8. Found: C, 75.5; H, 4.9.

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[17] W. Baker, H. F. Bondy, J. Gumb, and D. Miles, *J. Chem. Soc.*, 1615 (1953).

[18] Purchased from Aldrich Chemical Co.

[19] D. H. Rosenblatt, J. Epstein, and M. Levitch, *J. Am. Chem. Soc.*, **75**, 3277 (1953).

[20] L. Vargha and G. Ocskay, *Tetrahedron*, **2**, 151 (1958).

London Force Interactions in the Reactions of Benzyl Chlorides

DAVID L. DALRYMPLE, JOHN D. REINHEIMER,[1] DONALD BARNES, AND RICHARD BAKER

Department of Chemistry, College of Wooster, Wooster, Ohio

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The rates of reaction of the nucleophiles I^-, $C_6H_5S^-$, and CH_3O^- with substituted benzyl chlorides have been determined. Calculations of the magnitude of London forces operative in the transition state indicate that the changes in rate ratios may be attributed to these forces for *ortho* substituents.

The effect of London forces on equilibria and reaction rates has been recognized by a number of authors. Pitzer and Donath[2] have refined the calculations of conformation and strain energy of hydrocarbons by including interactions of nonbonded atoms. Bunnett[3] suggested the operation of these forces in nucleophilic substitution reactions in a theoretical paper, and Reinheimer and Bunnett[4] and Lewis and Suhr[5] invoked London forces to explain reaction rate ratios and the order of halogen replacements in aromatic nucleophilic substitutions, respectively. Quantitative estimates of these forces in the transition states of halogen-exchange reactions of methyl halides were given by Spinner.[6] Bunnett and Reinheimer[7] have estimated these forces in the reactions of *ortho*-substituted benzyl chlorides with methoxide, thiophenoxide, and iodide ions. This paper reports the results of studies of the reactions of these nucleophiles with the isomeric *meta*- and *para*-substituted benzyl chlorides, and, by a new method of comparing the rates, a better correlation of theory and experiment is obtained.

Results

The reaction rate constants and thermodynamic properties of the nucleophilic displacements of chloride from *meta*- and *para*-substituted benzyl chlorides are given in Tables I and II. The results of duplicate runs are given and indicate that the reproducibility is about ±2%. Comparison of the results with the literature shows moderate agreement. Extrapolated results of Bennett and Jones[8] give $k_2 = 144 \times 10^{-5}$ l./mole sec. for the reaction of KI with *p*-bromobenzyl chloride and 115×10^{-5} for the reaction with the *m*-bromo compound at 25°. Our values of 108×10^{-5} and 98×10^{-5} l./mole sec. are somewhat lower. Charlton and Hughes[9] give 5.1×10^{-5} and 5.46×10^{-5} l./mole sec. for the same reaction with the *p*-methyl

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[1] Support of the National Science Foundation, Grant NSF-G3112, is gratefully acknowledged.

[2] K. S. Pitzer and W. E. Donath, *J. Am. Chem. Soc.*, **81**, 3213 (1939).

[3] J. F. Bunnett, *ibid.*, **79**, 5969 (1957).

[4] J. D. Reinheimer and J. F. Bunnett, *ibid.*, **81**, 315 (1959).

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[6] E. Spinner, *Australian J. Chem.*, **13**, 218 (1960).

[7] J. F. Bunnett and J. D. Reinheimer, *J. Am. Chem. Soc.*, **84**, 3284 (1962).

[8] G. M. Bennett and B. Jones, *J. Chem. Soc.*, 1815 (1935).

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