Table II. Novel Azido Compounds

Compound	Reaction Temp., °C.	Reaction Time, Hrs.	Yield, %	B.P., °C./mm. (M.P.)	Index of Refraction/°C.	Analysis^a Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
Bis(2-Azidoethyl)ether	100	19	92	73/3	1.4706/27	...	...	...	...	53.83	54.11
Bis(2-Azidoethoxy)ethane	95	36	85	83/0.3	1.4672/28.5	36.00	36.54	6.0	6.19	41.98	41.48
2-Azidomethyl-5-hydroxy-1,4-pyrone	Ambient	24	63	(126–128)	...	43.12	43.14	2.99	3.02	25.15	25.15
Bis(2-Azido-1-methylethyl)ether	100	67.5	44	78/2	1.4588/30	39.23	39.07	6.56	6.56	45.62	45.40
2-Azidoethyl Azidoacetate	80	3	41	90/1.1	1.4798/30	28.24	28.52	3.85	3.61	49.40	49.87

[a] The materials containing high percentages of nitrogen were difficult to analyze as they tended to explode at high temperatures.

pending it in boiling ethanol and adding water until solution occurred. Cooling gave 18 grams crystalline material, m.p. 165–166.5°. Evaporation of the filtrate with subsequent recrystallization as above gave an additional 8 grams material. Total yield 26 grams (37%) m.p. 165–166.5° (Table I).

REACTION BENZYL AZIDE AND 3-HYDROXYBUTYNE. 1-BENZYL-4(OR 5)-(1-HYDROXYETHYL)-1,2,3-TRIAZOLE. A mixture of 133 grams (1.0 mole) of benzylazide and 70 grams (1.0 mole) 3-hydroxybutyne in 150 ml. toluene was heated at 100° on the steam bath for about 3 days. The volume was then reduced under vacuum to a viscous residue which was subsequently distilled through short (1–2-inch) column. The product possessed the properties indicated in Table I.

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Anilino Hydroquinones: Precursors to Azo Dye-Developers

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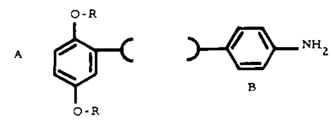
Protected hydroquinones, joined by different groups to various anilines, are used in the preparation of photographic dye-developers. In this paper the preparation and properties of these developer functions are described.

THE PREPARATION of azo dye-developers, described in the patent literature (*3, 4, 5, 12, 13*), makes use of protected hydroquinone functions joined through various structures to an anilino group. These developer-connected anilines are diazotized, coupled into appropriate couplers, and the protecting groups then removed to give the dye-developers.



The structures of these compounds were dictated by the following considerations: The redox system had to be sufficiently insulated from the chromophore so that changes in the oxidation state of the developer would not change the color of the dye. The hydroquinone had to be protected during the diazotization step from interaction with the diazonium salt (*15*) by a group that could be readily removed after coupling. Variations in the groups attached to ring A were made with a view toward modifying the photographic characteristics of the compound, or of changing some general property of the molecule, such as solubility. Substituents on ring B were generally chosen for the purpose of modifying the color of the azo dye.

In general, these compounds were synthesized by first assembling suitably chosen A and B fragments. This was frequently followed by demethylation of any methylated hydroxyl groups and replacing them with the readily removable acetate or carbethoxy functions. The amine precursor, a nitro group, was then reduced.

The reductions usually went readily at room temperature in a standard Parr apparatus. In many cases the free amine was isolated without difficulty. However, the application of heat during the evaporation of solvent following the reduction often led to amine-ester interaction, with attendant loss of product. For this reason, and because the amine was to be diazotized in the next step, we found it convenient to isolate many of our reduction products as their hydrochloride salts. The structures and physical constants of these developer moieties are indicated in the accompanying table.

The first two new intermediates described below, 2,5-dicarbethoxyhomogentisyl chloride and 2,5-dibenzyloxyphenol, were first synthesized in these laboratories by M.S. Simon and J.M. Clegg, respectively.

I. NEW INTERMEDIATES

2,5-Dicarbethoxyhomogentisyl Chloride. Homogentisic lactone was carbethoxylated (method 5) to give dicarbethoxyhomogentisic acid, m.p. 95-97°, white crystals from hexane.

ANAL. Calcd. for $C_{14}H_{16}O_8$: C, 53.8; H, 5.1. Found: C, 53.8; H, 5.1. Treatment of the acid with refluxing thionyl chloride gave the acid chloride, m.p. 53-54°, from benzene-hexane.

ANAL. Calcd. for $C_{14}H_{15}ClO_7$: C, 50.9; H, 4.5; Cl, 10.6. Found: C, 50.9; H, 4.7; Cl, 10.7.

2,5-Dibenzyloxyphenol. Acetylhydroquinone (0.2*M*) was benzylated by refluxing with benzyl iodide (0.55*M*) in 450 ml. of acetone over 0.9*M* of anhydrous potassium carbonate for 36 hours, keeping the reaction mixture blanketed with nitrogen throughout. The acetone was distilled off and the residue crystallized from ethanol, to give a 66% yield of white crystals, m.p. 74-76°.

ANAL. Calcd. for $C_{22}H_{20}O_3$: C, 79.5; H, 6.0. Found: C, 79.2; H, 5.8.

The benzylated ketone was oxidized to the phenol ester by the following procedure (*2*). To 16.6 grams of 2,5-dibenzyloxyacetophenone (.05*M*) in 40 ml. of acetic acid was added 11.5 grams of 40% peracetic acid. The mixture was heated at 60° C. with stirring for 0.5 hour, cooled, and the product filtered off. Yield of white, crystalline 2,5-dibenzyloxyphenyl acetate, m.p. 121-124° was 60.5%. Analytical sample was recrystallized from ethanol.

ANAL. Calcd. for $C_{22}H_{20}O_4$: C, 75.8; H, 5.7. Found: C, 75.6; H, 5.6.

A mixture of 17.4 grams of 2,5-dibenzyloxyphenyl acetate (0.05*M*), 100 ml. of 5*N* NaOH, and 100 ml. of ethanol was stirred and refluxed three hours. After evaporating the ethanol in vacuo, the precipitated sodium 2,5-dibenzyloxyphenolate was filtered off. The product was washed with ether to remove starting material, then slurried with dilute HCl and filtered. The 2,5-dibenzyloxyphenol was recrystallized from ethanol, to give 7.9 grams (51.5%) of pink-white crystals, m.p. 92-95°.

ANAL. Calcd. for $C_{20}H_{18}O_3$: C, 78.5; H, 5.9. Found: C, 78.3; H, 6.1.

***p*-Carboxyphenylhydroquinone Dicarbethoxy Ester.** Carbethoxylation of *p*-carboxyphenylhydroquinone (*14*) by method 5 gave a 50% yield of white solid, m.p. 174-175° (from aqueous ethanol and benzene-hexane).

ANAL. Calcd. for $C_{19}H_{18}O_8$: C, 61.0; H, 4.8. Found: C, 61.2; H, 5.0.

The acid chloride, prepared from the acid and thionyl chloride, was an oil which did not solidify at room temperature. It was based directly in the preparation of compound 43.

2,5-Dimethoxy-4′-nitrostilbene. A mixture of 24.5 grams of *p*-nitrophenylacetic acid (0.135*M*), 18 grams of 2,5-dimethoxybenzaldehyde (0.108*M*), and 6 ml. of piperidine was refluxed (130° C.) for 3.5 hrs. The piperidine was distilled off and the temperatures was raised to 160° C. for three hours. The mixture, on cooling, was diluted with 25 ml. of acetic acid, then poured into 125 ml. of water.

A dark red oil separated. The supernatant liquid was decanted and the residual oil solidified on treatment with 25 ml. of ethanol. The solid was filtered off and recrystallized from 300 ml. of ethanol, to give 11.5 grams of yellow needles, m.p. 115-116° (37%). A sample recrystallized for analysis melted at 116.5-117°.

ANAL. Calcd. for $C_{16}H_{15}NO_4$: C, 67.4; H, 5.3; N, 4.9. Found: C, 67.4; H, 5.5; N, 4.9.

II. SYNTHETIC METHODS

Method 1. Sulfones. Compounds 17 and 20. To a warm, saturated solution of *p*-benzoquinone in water was added a warm aqueous solution containing one equivalent of the sulfinic acid (*8, 6*). The sulfone precipitated immediately. After heating briefly on the steambath, the product was filtered off, desiccated, and recrystallized.

Method 2. Diaryl Thioethers. Compounds 11 and 14. To an ethanolic solution of *p*-nitrothiophenol (*16*) was slowly added a concentrated solution of one equivalent of the quinone in alcohol. The color of the quinone was discharged immediately on admixture. The ethanol solution was either evaporated to dryness (compound 14) or drowned in water (compound 11) and the precipitated product filtered off. The dried crude product was crystallized.

Method 3. Alkyl-aryl Thioethers. Compounds 5 and 8. A deaerated solution of 4 grams of NaOH (0.1*M*) in 100 ml. of MeOH was added under nitrogen to a mixture of 0.1*M* each of the mercaptohydroquinone (*1, 7*) and of *p*-nitro phenylethyl bromide (*10*). The solution was refluxed one hour under nitrogen, chilled and acidified with conc. HCl. Precipitated sodium bromide was filtered off. The methanolic filtrate was evaporated to dryness, and the residue taken up in ether and water. The ether was dried and evaporated, and the residual product recrystallized.

Method 4. Alkyl-aryl Ether. 4′-NITROPHENYLPROPYL-2,5-DIBENZYLOXY PHENYL ETHER. Compound 23. A mixture of 0.03*M* of 2,5-dibenzyloxyphenol, 0.03*M* of *p*-nitrophenylpropyl bromide (*9*), and a solution of 0.03*M* of NaOH in 100 ml. of ethanol and 50 ml. of water was refluxed eight hours, then allowed to cool overnight. The precipitate that separated was filtered off and crystallized from ethanol, yielding 63% of near-white needles, m.p. 100-102° C. A sample recrystallized for analysis melted at 106-107° C.

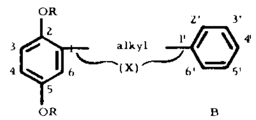
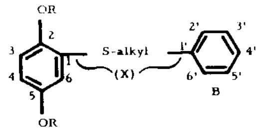
Method 5. Carbethoxylation. Compound 21. To a deaerated solution of 0.4*M* of NaOH in water (5%) was added 0.1*M* of dihydroxy compound under a nitrogen atmosphere. The solution was cooled to 0° C. and 0.3*M* of ethyl chloroformate was added at a rate slow enough to keep the temperature from rising (ca. 0.5 hour). The mixture was stirred at 0-5° C. for one hour after the addition, keeping the pH at 8 by addition of 50% NaOH as needed. The product was brought down by acidification with dilute HCl, extracted with ether, and isolated in the usual manner.

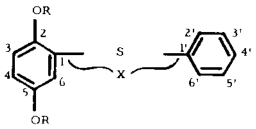
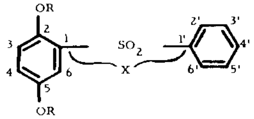
Method 6. Demethylations. METHOD A. COMPOUND 28. A mixture of 3.5 grams of 2,5-dimethoxy-4′-nitrophenyl ether, 40 ml. of acetic acid, and 40 ml. of 48% HBr was refluxed under nitrogen. After four hours the condenser was adjusted for downward distillation, and excess reagent was distilled off. After 5.5 hours (total) aspirator suction was applied and the mixture evaporated to dryness. The residual product was desiccated in vacuo over KOH and recrystallized.

METHOD B. COMPOUND 2. A mixture of 8.55 grams of 2,5-dimethoxy-4′-nitrostilbene (0.03*M*) and 40 grams of pyridine hydrochloride was refluxed 0.5 hour under nitrogen and poured (warm) into ice water. The precipitate that separated was filtered off, dried, and recrystallized.

Method 7. Acetylations. COMPOUNDS 3, 6, 9, 12, 15, 18, 25 AND 29. A mixture of 4 grams of dihydroxy compound, 40 ml. of acetyl chloride, and 4 drops of H_2SO_4 was refluxed 1.5 hours. The solution was either evaporated to dryness

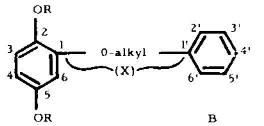
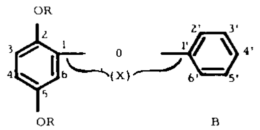
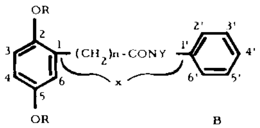
Table I. Anilino Hydroquinone Esters and Intermediates

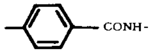
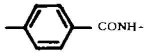
No.	Name	R	A Substituent(s)	X	B Substituent(s)	Method Yield, %	M.P.[a] Cryst.[b] Solvent	Analyses %[c]		
									Calcd.	Found
	Alkyl Compounds A									
1	2,5-Dimethoxy-4′-nitrostilbene	CH_3—	...	—CH=CH—	4′—NO_2	30	115°–116° A	C H N	67.4 5.3 4.9	67.4 5.5 4.9
2	2,5-Dihydroxy-4′-nitrostilbene	—H	...	—CH=CH—	4′—NO_2	6(B) 59	231°–235° B	C H N	65.4 4.3 5.4	65.2 4.3 5.3
3	2,5-Diacetoxy-4′-nitrostilbene	—$COCH_3$	...	—CH=CH—	4′—NO_2	7 83	192°–194° C	C H N	63.3 4.4 4.1	63.1 4.4 4.1
4	α-(2,5-Diacetoxyphenyl)-β-(4′-aminophenyl)-ethane hydrochloride	—$COCH_3$	...	—CH_2-CH_2—	4′—$NH_2 \cdot HCl$	11 88	154°–158° dec. K	C H N	61.8 5.8 4.0	62.0 5.9 3.6
	Alkyl-Aryl Thio Ethers A									
5	2,5-Dihydroxyphenyl-4′-nitrophenyl-ethylthio ether	—H	...	—S-CH_2CH_2	4′—NO_2	3 71	120°–122° D	C H N	57.7 4.5 4.8	57.7 4.6 4.8
6	2,5-Diacetoxyphenyl-4′-nitrophenyl-ethylthio ether	—$COCH_3$	...	—S-CH_2-CH_2—	4′—NO_2	7 84	105°–107° E	C H N	57.6 4.6 3.7	57.6 4.6 3.7
7	2,5-Diacetoxyphenyl-4′-amino-phenyl-ethylthio ether	—$COCH_3$	...	—S-CH_2-CH_2—	4′—NH_2	not obtained crystalline[d]				
8	2,5-Dihydroxy-4-methylphenyl-4′-nitro-phenylethylthio ether	—H	4-CH_3	—S-CH_2-CH_2—	4′—NO_2	3 60	121–123° D	C H N	59.0 4.9 4.6	59.3 5.1 4.5
9	2,5-Diacetoxy-4-methylphenyl-4′-nitro-phenylethylthio ether	—$COCH_3$	4-CH_3	—S-CH_2-CH_2—	4′—NO_2	7 87	89°–91° E	C H N	58.6 4.9 3.6	58.7 4.9 3.3
10	2,5-Diacetoxy-4-methylphenyl-4′-amino-phenylethyl thio ether	—$COCH_3$	4-CH_3	—S-CH_2-CH_2—	4′—NH_2	not obtained crystalline[d]				

			Diaryl Thio Ethers							
11	*p*-Nitrophenylthiohydroquinone	—H	. . .	—S—	4′—NO_2	2 76	186°-187° F	C H N	54.8 3.5 5.3	55.0 3.5 5.3
12	*p*-Nitrophenylthiohydroquinone diacetate	—$COCH_3$	. . .	—S—	4′—NO_2	7 96	113°-115° E	C H N	55.8 3.8 4.0	55.5 4.1 4.1
13	*p*-Aminophenylthiohydroquinone diacetate	—$COCH_3$	. . .	—S—	4′—NH_2	11 66	112.5°- 124° F	C H N	60.6 4.8 4.4	60.5 4.7 4.4
14	4′-Nitrophenyl-2,5-dihydroxy-3,6-dimethylphenylthio ether	—H	2,5-$(CH_3)_2$	—S—	4′—NO_2	2 75	168°-172° G	C H N S	57.7 4.5 4.8 11.0	57.8 4.6 4.6 10.9
15	4′-Nitrophenyl-2,5-diacetoxy-3,6-dimethylphenylthio ether	—$COCH_3$	2,5-$(CH_3)_2$	—S—	4′—NO_2	7 85	116°-118° A	C H N S	57.6 4.5 3.7 8.5	57.7 4.8 3.5 8.8
16	4′-Aminophenyl-2,5-diacetoxy-3,6-dimethylphenylthio ether	—$COCH_3$	2,5-$(CH_3)_2$	—S—	4′—$NH_2 \cdot HCl$	11 90	120° dec. K	C H N	56.6 5.3 3.7	56.2 5.3 3.6
			Sulfones							
17	2,5-Dihydroxyphenyl-4′-nitrophenyl sulfone	—H	. . .	—SO_2—	4′—NO_2	1 98	213°-214° H	C H N S	48.8 3.1 4.7 10.9	48.9 3.3 4.7 10.8
18	2,5-Diacetoxyphenyl-4′-nitrophenyl sulfone	—$COCH_3$	. . .	—SO_2—	4′—NO_2	7 77	169°-171° G	C H N S	50.7 3.5 3.7 8.4	51.0 3.4 3.7 8.6
19	2,5-Diacetoxyphenyl-4′-aminophenyl sulfone	—$COCH_3$	. . .	—SO_2—	4′—NH_2	11 73	179°-180° A	C H N	55.0 4.3 4.0	55.1 4.0 4.0
20	2,5-Dihydroxyphenyl-2′,5′-dimethoxy-3′-nitrophenyl sulfone	—H	. . .	—SO_4	2′,5′—$(OCH_3)_2$— 3′—NO_2	1 A	212°-213° E	C H N S	47.3 3.7 3.9 9.0	47.5 3.9 4.0 9.2
21	2,5-Bis(ethoxycarbonyloxy)-phenyl-2′,5′-dimethoxy-3′-nitrophenyl sulfone	—$CO_2C_2H_5$	. . .	—SO_2—	2′,5′—$(OCH_3)_2$— 3′—NO_2	5 9.6	170°-172° L	C H N S	48.2 4.2 2.8 6.4	48.5 4.4 2.5 6.7
22	2,5-Bis(ethoxycarbonyloxy)-phenyl-2′,5′-dimethoxy-3′-aminophenyl sulfone	—$CO_2C_2H_5$	. . .	—SO_2—	2′,5′ -$(OCH_3)_2$ 3′—NH_2	11 40	140°-142° A	C H N S	51.2 4.9 3.0 6.8	51.3 5.1 3.2 6.7

(Continued on page 236)

Table I. Anilino Hydroquinone Esters and Intermediates (Continued)

No.	Name	*R*	*A* Substituent(s)	*X*	*B* Substituent(s)	Method Yield, %	M.P.[a] Cryst.[b] Solvent	Analyses %[c]	Calcd.	Found
			Alkyl Aryl Ethers							
23	4′-Nitrophenylpropyl-2,5-dibenzyloxyphenyl ether	—CH$_2$-C$_6$H$_5$	. . .	—O-(CH$_2$)$_3$—	4′—NO$_2$	4 63	106°-107° A	C H N	74.2 5.8 3.0	74.1 5.8 3.2
24	4′-Nitrophenylpropyl-2,5-dihydroxyphenyl ether	—H	. . .	—O-(CH$_2$)$_3$—	4′—NO$_2$	9 62	155°-157° G	C H N	62.3 5.2 4.8	62.4 5.2 5.0
25	4′-Nitrophenylpropyl-2,5-diacetoxyphenyl ether	—COCH$_3$	. . .	—O-(CH$_2$)$_3$—	4′—NO$_2$	7 54	92°-95° E	C H N	61.1 5.1 3.8	61.1 5.2 3.8
26	4′-Aminophenylpropyl-2,5-diacetoxy phenyl ether	—COCH$_3$	. . .	—O-(CH$_2$)$_3$	4′—NH$_2$·HCl	11 59	138°-140° J	C H Cl	60.1 5.8 9.3	60.0 5.8 9.2
			Diaryl Ethers							
27	4′-Nitrophenyl-2,5-dimethoxyphenyl ether	CH$_3$—	. . .	—O—	4′—NO$_2$	10 70	76°-76.5° A	C H N	61.1 4.8 5.1	61.0 4.9 5.2
28	4′-Nitrophenyl-2,5-dihydroxyphenyl ether	—H	. . .	—O	4′—NO$_2$	6(A) 58	162°-164° H	C H N	58.3 3.7 5.7	58.2 3.7 5.7
29	4′-Nitrophenyl-2,5-diacetoxyphenyl ether	—COCH$_3$	. . .	—O—	4′—NO$_2$	7 66	111°-113° A	C H N	58.0 4.0 4.2	57.9 3.9 4.4
30	4′-Aminophenyl-2,5-diacetoxyphenyl ether	—COCH$_3$	. . .	—O—	4′—NH$_2$	11 74	112°-113° A	C H N	63.8 5.0 4.7	63.8 5.3 4.7
			Amides							
31	2,5-Diacetoxy-4′-nitrobenzanilide	—COCH$_3$	. . .	—CONH—	4′—NO$_2$	8(B) 67	152°-153° A	C H N	57.0 3.9 7.8	57.0 3.8 7.8
32	2,5-Diacetoxy-4′-Aminobenzanilide	—COCH$_3$	. . .	—CONH—	4′—NH$_2$	11 73	251°-252° A	C H N	62.2 4.9 8.5	62.3 4.9 8.5
33	2,5-Diacetoxy-4′-nitro-*N*-methylbenzanilide	—COCH$_3$	. . .	—CON(CH$_3$)—	4′—NO$_2$	8(B) 81	139°-140° A	C H N	58.1 4.3 7.5	58.0 4.2 7.5

34	2,5-Diacetoxy-4′-amino-*N*-methylbenzanilide	—COCH$_3$	. . .	—CON— | CH$_3$	4′—NH$_2$	11 82	139°-140° A	C H N	63.1 5.3 8.2	63.1 5.2 8.2
35	2,5-Dicarbethoxy-4′-nitrohomogentisanilide	—CO$_2$C$_2$H$_5$	. . .	—CH$_2$CONH—	4′—NO$_2$	8(A) 87	158°-159° H	C H N	55.6 4.7 6.5	55.9 4.4 6.7
36	2,5-Dicarbethoxy-4′-aminohomogentisanilide hydrochloride	—CO$_2$C$_2$H$_5$	. . .	—CH$_2$CONH—	4′—NH$_2$·HCl	11 79	205° dec. K	C H N	54.8 5.3 6.4	54.6 5.4 6.6
37	2,5-Dicarbethoxy-4′-nitro-2′,6′-dichlorohomogentisanilide	—CO$_2$C$_2$H$_5$	. . .	—CH$_2$CONH—	4′—NO$_2$— 2′,6′—(Cl)$_2$	8(A) 33	187°-188° D	C H N	48.0 3.6 5.6	48.2 3.7 5.6
38	2,5-Dicarbethoxy-4′-amino-2′,6′-dichlorohomogentisanilide	—CO$_2$C$_2$H$_5$	. . .	—CH$_2$CONH—	4′—NH$_2$ 2′,6′—(Cl)$_2$	11 42.5	172°-174° D	C H N Cl	50.9 4.2 5.9 15.1	50.7 4.5 5.6 14.8
39	2,5-Dicarbethoxy-4′-nitro-2′,5′-dichlorohomogentisanilide	—CO$_2$C$_2$H$_5$	. . .	—CH$_2$-CONH—	4′—NO$_2$— 2′,5′—(Cl$_2$)$_2$	8(A) 50	133° A	C H N	48.0 3.6 5.6	48.2 3.6 5.5
40	2,5-Dicarbethoxy-4′-amino-2′,5′-dichlorohomogentisanilide	—CO$_2$C$_2$H$_5$	. . .	—CH$_2$—CONH—	4′—NH$_2$— 2′,5′—(Cl$_2$)$_2$	11 39.5	175°-177° E	C H N Cl	51.0 4.3 5.9 15.1	50.9 4.2 5.7 14.8
41	2,5-Dicarbethoxy-4′-nitro-2′,5′-dimethoxyhomogentisanilide	—CO$_2$C$_2$H$_5$	. . .	—CH$_2$—CONH—	4′—NO$_2$—2′,5′— (OCH$_3$)$_2$	8(A) 54	144°-145° A	C H N	53.7 4.9 5.7	53.8 4.7 5.6
42	2,5-Dicarbethoxy-4′-amino-2′,5′-dimethoxyhomogentisanilide hydrochloride	—CO$_2$C$_2$H$_5$	. . .	—CH$_2$—CONH—	4′—NH$_2$·HCl 2′,5′—(OCH$_3$)$_2$	11 100	216° dec. K	C H N	53.1 5.5 5.6	53.0 5.7 5.6
43	4-[2″,5″-Bis(carbethoxy)phenyl]-4′-nitrobenzanilide	—CO$_2$C$_2$H$_5$	. . .		4′—NO$_2$	8(B) 38	133°-136° A	C H N	60.7 4.5 5.7	61.1 4.5 5.7
44	4-[2″,5″-Bis(carbethoxy)phenyl]-4′-aminobenzanilide hydrochloride	—CO$_2$C$_2$H$_5$	. .		4′—NH$_2$ ·HCl	11 67	203° dec. K	C H N Cl	59.9 5.6 5.6 7.1	59.9 5.8 5.8 6.9

[a] Melting points are uncorrected and were taken on a Mel-Temp capillary melting point apparatus. [b] Crystallization solvents: A, ethanol; B, anisole; C, *n*-propyl alcohol; D, benzene; E, isopropyl alcohol; F, benzene-hexane; G, toluene; H, xylene; I, acetic acid; J, ethanol-ether; K, not recrystallized; L, cyclohexane-benzene. [c] We are indebted to Dr. Carol Fitz of Needham, Massachusetts, for the microanalyses. [d] The aminophenylethylthio ethers (and their hydrochloride salts) were non-crystallizable syrups. They were dissolved in dilute HCl, diazotized, and coupled immediately. The azo dyes obtained from these couplings gave correct analyses for the expected dyes.

in vacuo or quenched in ice water. Residual or precipitated product was dried and recrystallized.

Method 8. Amides. METHOD A. COMPOUNDS 35, 37, 39 AND 41. A mixture of 0.1*M* of dicarbethoxyhomogentisyl chloride and 0.1*M* of the nitroaniline was refluxed one hour in *o*-dichlorobenzene. The product usually separated on cooling. Those that did not separate were precipitated by pouring the reaction mixture into hexane. The product was filtered off and recrystallized.

METHOD B. COMPOUNDS 31, 33 AND 43. A mixture of 0.02*M* of 2,5-diacetoxybenzoyl chloride, 0.02*M* of the nitroaniline, 0.02*M* of pyridine, and 60 ml. of ethylene dichloride was refluxed one hour. The cooled mixture was washed with water to remove pyridine hydrochloride. The organic layer was dried and evaporated to dryness in vacuo. Residual product was recrystallized.

Method 9. Debenzylation. COMPOUND 24. To a gently boiling solution of 15 grams of 4′-nitrophenylpropyl-2,5-dibenzyloxy phenyl ether in 150 ml. of acetic acid was slowly added 35 ml. of conc. HCl. The mixture was refluxed for 20 minutes after the addition, then poured into a liter of ice water. The brown gummy solid that separated was filtered off, and washed free of benzyl chloride with hexane on the Büchner funnel. The solid was crystallized from 30 ml. of toluene (charcoal) to give 5.5 grams of yellow crystals. m.p. 155–157°.

Method 10. Diaryl ethers. COMPOUND 27. A mixture of 25 grams of 2,5-dimethoxy potassium phenoxide, 0.13*M* (*11*), 25 grams of *p*-fluoronitrobenzene, 0.175*M* (*17*), 0.5 grams of 2,5-dimethoxyphenol (*11*), and 0.2 grams of copper powder was heated in a metal bath at 155–160° for one hour. The melt was poured into alkaline ice water. An oil separated which soon solidified, was filtered off, and recrystallized (filtering off the copper at this stage) from ethanol.

Method 11. Reductions. The nitro compound was dissolved or suspended in ethanol, the more insoluble ones in ethyl acetate, and hydrogenated in a Parr shaker over 10% Pd on $BaSO_4$ at room temperature. Theoretical uptake of hydrogen took from 15 minutes to four hours. After removal of catalyst, the free bases were isolated by vacuum evaporation of solvent; hydrochlorides were precipitated by adding one equivalent of conc. HCl to the amine in ethyl acetate.

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Syntheses of 1,2,3,4-Tetra-O-Acetyl-6-O-Benzhydryl-β-D-Glucose

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The benzhydrylation of 1,2,3,4-tetra-O-acetyl-β-D-glucose and the benzhydrylation of D-glucose followed by acetylation are described. Data presented indicate that both processes lead to the production of 1,2,3,4-tetra-O-acetyl-6-O-benzhydryl-β-D-glucose.

DURING A STUDY in this laboratory of the distribution of substituents in benzhydrylated cotton cellulose, the need arose for a D-glucose derivative having the benzhydryl group in the 6-position. A literature search showed that while Ohle and Tessmar (*4*) had attempted to prepare such a derivative by reacting benzhydryl alcohol with 5,6-anhydro-1,2-*O*-isopropylidene-α- D-glucose, they has not been successful. No other reference to such a compound was found.

The recent use of benzhydryl bromide in lutidine as a method for the benzhydrylation of cotton cellulose (*6*) suggested that the benzhydrylation of a D-glucose derivative or even D-glucose itself might be feasible. Following this lead, a sample of 1,2,3,4-tetra-*O*-acetyl-β-D-glucose was prepared according to the method of Reynolds and Evans (*5*). This in turn was treated with benzhydryl bromide in 2,6-lutidine. Chemical analysis of the product indicated the presence of four acetyl groups and one benzhydryl group.

The infrared spectrum of the product (in a potassium bromide pressing) has an absorption band near 11.2μ which is associated with a β-D-anomer, but no band at