Synthesis of *o*- and *p*-Diazophenol

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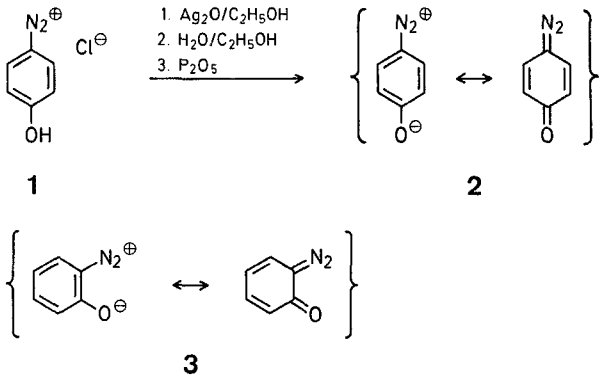
High yield syntheses of *p*-diazophenol (4-diazoniophenoxide) in tetrahydrate and anhydrous forms (**2**) and of *o*-diazophenol have been developed. Previous syntheses[2,3,4] of *p*-diazophenol have been in low yield and previously published syntheses of *o*-diazophenol (**3**) have been uncertain[4] or lack details[6]. The N.M.R. spectra of these compounds supplement previous investigations.



1 **2**

3

p-Diazophenol Tetrahydrate:

p-Diazophenol hydrochloride[1] (**1**; 4.0 g) was dissolved in absolute ethanol (100 ml). Freshly prepared silver oxide [from silver nitrate (8 g) and sodium hydroxide (1.5 g), washed with water and then with absolute ethanol] was added while stirring and keeping the mixture at 0°. It was stirred and kept at this temperature for 3 hr after which a green solution was filtered off and evaporated to ~ 20 ml at temperatures below 20°. The solution was passed through a short alumina column with 1:2 absolute ethanol/ether. The yellow eluate was evaporated to an oil. 80% aqueous ethanol (30 ml) was added, followed by sufficient ether to crystallize the product out below −20°. After recrystallization from 90% aqueous ethanol, 4.6 g (94%) of *p*-diazophenol tetrahydrate were obtained. The whole procedure was carried out in the absence of direct light. The elemental analysis and N. M. R. confirmed that the form was a tetrahydrate. A broad OH stretch peak in the I. R. spectrum (Nujol; 3390 cm^{-1}) of the product also indicated the presence of water. Otherwise, the I. R.[6] and U. V.[3,4] spectra and other properties[2,3] agreed with previous reports.

$C_6H_{12}N_2O_5$	calc.	C 37.49	H 6.29	N 14.57
	found	37.67	6.18	14.80

N.M.R. (DMSO-d_6): 2:1 intensity ratio of H_2O to aromatic proton peaks (see N. M. R. of anhydrous form).

Anhydrous *p*-Diazophenol (2):

The anhydrous form was quantitatively prepared from the tetrahydrate by dehydration in vacuum over phosphorus pentoxide (keeping the sample cool and dark) for 24 hr. The dehydrated material was recrystallized from an absolute ethanol-ether solution. It crystallized as orange prisms and decomposed over 100°.

$C_6H_4N_2O$	calc.	C 59.99	H 3.35	N 23.32
	found	59.40	3.68	22.82

N.M.R. (DMSO-d_6): 2 doublets of equal total intensity (δ = 6,17, 7.78) with additional fine structure.

***o*-Diazophenol (3):**

o-Diazophenol hydrochloride[1] (2.0 g) was suspended in absolute ethanol (25 ml). Freshly prepared silver oxide was added in a

manner similar to the preparation of the *p*-diazophenol. After 2 hr, the mixture was passed through a Hyflo filter and quickly evaporated to dryness at temperatures below 10°. The dark mass was dissolved in cold ether and passed through a short alumina column with cold ether. The product was crystallized from the eluent at −50°. This preparation was also performed in the absence of direct light. Yield: 1 g (65%) of *o*-diazophenol in the form of yellow plates or prisms. It readily sublimed and it decomposed above the m.p. 66°. It decomposed in a few hours at room temperature in the presence of light, but it may be stored for several weeks at −50° in the dark. The I. R. spectrum agreed with a previous report[6]. The U. V. spectrum was in reasonable agreement with that reported[4] for the diazotization product of *o*-aminophenol. The N.M.R., I.R., and the elemental analysis confirmed the absence of water.

$C_6H_4N_2O$	calc.	C 59.99	H 3.35	N 23.32
	found	60.06	3.64	23.16

N. M. R. (CCl_4): 4 multiplets of equal total intensity, 2 doublets ($\delta = 6.95$, 7.51); 2 triplets ($\delta = 6.66$, 7.38), with additional fine structure.

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[1] The hydrochloride was prepared by diazotization of the aminophenol.

[2] A. HANTZSCH, W. B. DAVIDSON, Chem. Ber. **29**, 1528 (1896).

[3] L. C. ANDERSON, M. J. ROEDEL, J. Amer. Chem. Soc. **67**, 955 (1945).

[4] J. D. C. ANDERSON, R. J. W. LE FÈVRE, I. R. WILSON, J. Chem. Soc. **1949**, 2083.

[5] J. D. C. ANDERSON, R. J. W. LE FÈVRE, Nature **162**, 449 (1948).

[6] K. B. WHETSEL, G. F. HAWKINS, F. E. JOHNSON, J. Amer. Chem. Soc. **78**, 3360 (1956).