A New Route to N-*Substituted* o-*Phenylenediamines.*

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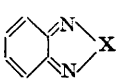
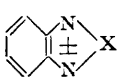
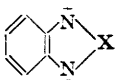
Phenyl-lithium reacts with benzo-2 : 1 : 3-thiadiazole or its selenium analogue to give diphenyl sulphide (or selenide) and *N*-phenyl-*o*-phenylenediamine. With the oxygen analogue, further substitution can occur and 2-anilinotriphenylamine has been obtained. A tentative reaction scheme is proposed to account for the formation of these compounds.

Direct *N*-substitution of *o*-diamines has received little attention. *N*-Methylation of *o*-phenylenediamine by methyl iodide has been carried out by Brown and Nelson (*J. Amer. Chem. Soc.*, 1953, **75**, 24) but the method has not been extended to higher homologues and is inapplicable to aryl substituents. The method presented below provides a new route to *N*-substituted *o*-diamines and involves the reaction of phenyl-lithium with benzo-2 : 1 : 3-thiadiazole (I; X = S) or its selenium and oxygen analogues. With the first it gives


(I)


(I*a*)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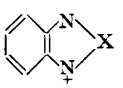
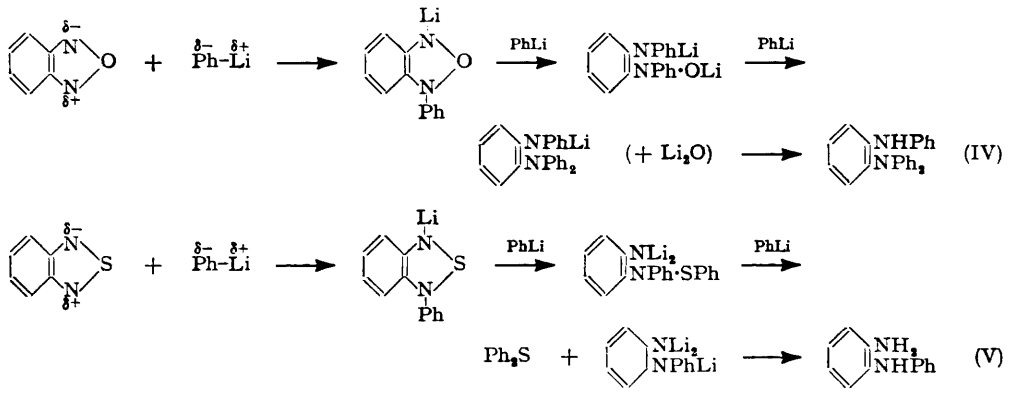

(III)

diphenyl sulphide and *N*-phenyl-*o*-phenylenediamine (V), and with benzo-2 : 1 : 3-selenadiazole (I; X = Se) it gives diphenyl selenide and the diamine (V). With 4 : 7-diethoxybenzo-2 : 1 : 3-selenadiazole it gives diphenyl selenide and 2-amino-3-anilinoquinol diethyl ether. Use of a larger proportion of phenyl-lithium did not cause further substitution of the *o*-diamine. Benzofurazan (I; X = O) and an excess of phenyl-lithium gave a small quantity of diphenyl and 55% of 2-anilinotriphenylamine (IV), the only convenient route to this compound.

The normal mode of addition of an organometallic compound to an organic system places the organic residue on the most positive atom. Pauling (" Nature of the Chemical Bond," Cornell Univ. Press, New York, 1949, p. 60) gives as the order of decreasing electronegativities: O 3·5, N 3·0, S 2·5, Se 2·4, so reactions with phenyl-lithium should be: $\geq$N·O– ⟶ $\geq$NPh + LiO–; $\geq$N·S– ⟶ $\geq$NLi + RS–; $\geq$N·Se– ⟶ $\geq$NLi + RSe–. If it is assumed that the structures (II) and (III) provide a major portion of the canonical forms contributing to the hybrid (I*a*),* then the annexed reactions account for the products

* This is not an improbable assumption. The compounds involved are partially mesoionic (Baker, Ollis, and Poole, *J.*, 1950, 1546) and the hybrid will contain a large ionic contribution, particularly in the polarised state of the transition complex.

isolated. Selenium would be expected to behave similarly to sulphur as their electronegativities are nearly equal. A higher yield is obtained from the sulphur compound than from the selenium compound but this may be offset by the relatively easier accessibility of



the latter which is conveniently prepared in very good yields by reaction of *o*-diamines with selenious acid (Hinsberg, *Ber.*, 1889, **22**, 863, 2897; 1890, **23**, 1397; Heinemann, D.-R.P. 261,412; Lane and Williams, *J.*, 1954, 2978).

Experimental

The equivalent weights of the amines described below were determined by titration in glacial acetic acid with 0·1N-perchloric acid, with crystal-violet as indicator. The equivalent weight of the *N*-phenyl-*o*-phenylenediamine hydrochloride was determined by titration in dimethylformamide with sodium methoxide in benzene–methanol with thymol-blue as indicator.

*Action of Phenyl-lithium on Benzo-*2 : 1 : 3-*thiadiazole.*—Benzo-2 : 1 : 3-thiadiazole (27·2 g., 0·2 mole) in ether (100 ml.) was added dropwise to a stirred solution of phenyl-lithium (59 g., 0·7 mole) in ether (100 ml.) under nitrogen. After 2 hr., water (100 ml.) was added to the deep green solution. The red ether layer was run off and evaporated; the residual red tar was distilled and collected in the following fractions: (i) (36 g.) b. p. 132—136°/1 mm., n_D^{21} 1·6314; (ii) b. p. 136—160°/1 mm., a mixture of (i) and (iii); (iii) (27 g.) b. p. 162—166°/1 mm., m. p. 78°. Fraction (i) was diphenyl sulphide (b. p. 148·5—149·5°/12 mm., $n_D^{18·5}$ 1·635); oxidation with hydrogen peroxide in acetic acid gave diphenyl sulphone, m. p. and mixed m. p. 128°. Fraction (ii) was purified by shaking its ethereal solution with 10% hydrochloric acid; a crystalline precipitate of N-*phenyl-*o-*phenylenediamine hydrochloride*, m. p. 115·5—117° (decomp.), was filtered off (Found: N, 12·7; Cl, 16·35%; equiv., 222. $C_{12}H_{13}N_2Cl$ requires N, 12·7; Cl, 16·1%; equiv., 220); a small quantity of diphenyl sulphide, b. p. 294—295°/760 mm., was obtained on distillation of the filtrate. Fraction (iii) was purified by crystallisation from ethanol; *N*-phenyl-*o*-phenylenediamine had m. p. 79—80° (Found: C, 78·3; H, 6·4; N, 15·3%; equiv., 183. Calc. for $C_{12}H_{12}N_2$: C, 78·3; H, 6·5; N, 15·2%; equiv., 184); heating it with lead oxide gave phenazine, m. p. and mixed m. p. 171—172° (Found: N, 15·3. Calc. for $C_{12}H_8N_2$: N, 15·55%).

*Action of Phenyl-lithium on Benzo-*2 : 1 : 3-*selenadiazole.*—Benzo-2 : 1 : 3-selenadiazole (18·3 g., 0·1 mole) in ether (120 ml.) was similarly treated with phenyl-lithium (29·4 g., 0·35 mole) and worked up, giving fractions: (i) b. p. 88—110°/0·5 mm.; (ii) (21 g.) b. p. 112—136°/0·5 mm.; and (iii) (10 g.) b. p. 138—140°/0·5 mm. Fraction (i) was a small amount of unchanged material; fraction (ii) was redistilled and gave as a main fraction, b. p. 120°/2·5 mm., diphenyl selenide (Found: C, 62·0; H, 3·9. Calc. for $C_{12}H_{10}Se$: C, 61·8; H, 4·3%), characterised by conversion into the dibromide, m. p. 151° (decomp.) (Found: C, 37·3; H, 2·6; Br, 41·3. Calc. for $C_{12}H_{10}Br_2Se$: C, 36·7; H, 2·55; Br, 40·6%) [Edwards, Gaythwaite, Kenyon, and Phillips (*J.*, 1928, 2302) gave m. p. 154° (decomp.)]. Fraction (iii), crystallised from ethanol, had m. p. 79—80° (equiv., 183), not depressed on admixture with authentic *N*-phenyl-*o*-phenylenediamine.

4 : 7-*Diethoxybenzo-*2 : 1 : 3-*selenadiazole.*—Equimolar amounts of 2 : 3-diaminoquinol diethyl ether hydrochloride (Lane and Williams, *J.*, 1953, 4187) and selenious acid were heated together in water (steam-bath) for 1 hr., giving a quantitative yield of this *base*, m. p. 152—152·5° (yellow

platelets from benzene) (Found: C, 44·3; H, 4·1; N, 10·3. $C_{10}H_{12}O_2N_2Se$ requires C, 44·3; H, 4·4; N, 10·3%).

2-*Amino*-3-*anilinoquinol Diethyl Ether*.—The foregoing compound (6·4 g., 0·024 mole) was treated as described above with phenyl-lithium (8·4 g., 0·1 mole). Working up as before gave diphenyl selenide (5 g.) and the above *amino-ether* (2·5 g.), m. p. 77—79° (from ethanol) (Found: C, 70·6; H, 7·3; N, 10·3%; equiv., 275. $C_{16}H_{20}O_2N_2$ requires C, 70·5; H, 7·35; N, 10·3%; equiv., 272). The *monoperchlorate* had m. p. 153·5—155° (from acetic acid–ether) (Found: N, 7·65; Cl, 9·7. $C_{16}H_{21}O_6N_2Cl$ requires N, 7·5; Cl, 9·5%).

2-*Anilinotriphenylamine*.—Benzofurazan (8·4 g., 0·07 mole) was similarly treated with phenyl-lithium (42·0 g., 0·5 mole). Vacuum-distillation of the residue from the ether layer gave only diphenyl (m. p. and mixed m. p.) and a main fraction (13 g.), b. p. 226—230/2 mm., solidifying to a yellow solid. After 4 crystallisations from ethanol the base named had m. p. 94·5—95·5° (colourless plates) (Found: C, 85·1; H, 5·85; N, 8·4. Calc. for $C_{24}H_{20}N_2$: C, 85·6; H, 5·95; N, 8·3%). It was insufficiently basic for titration with perchloric acid in glacial acetic acid and gave a deep blue Liebermann reaction. Wieland (*Annalen*, 1911, **381**, 206) obtained it as a thermal decomposition product of tetraphenylhydrazine and described it as "amorphous," m. p. "about 85°."

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