970. *Reactions of Some Substituted Benzo*-1,2,3-*triazines.*

By E. W. Parnell.

The product obtained from the diazotisation of *o*-aminobenzamidoxime is not the hydroxylamine (I; R = NH·OH), but is probably 4-aminobenzo-1,2,3-triazine 3-oxide (VIIa). The reactions of 4-hydrazinobenzo-1,2,3-triazine with copper salts have been studied.

A compound alleged to be the hydroxylamine (I; R = NH·OH) was first prepared by diazotisation of *o*-aminobenzamidoxime by Pinnow and Sämann.[1] When reduced with stannous chloride it gave a base, $C_7H_7N_3$, which was formulated as 1,2-dihydrobenzo-1,2,3-triazine (II). Gabriel[2] obtained this compound by diazotisation and reduction of *o*-aminobenzonitrile and assigned to it the structure (III; R = $NH·NH_2$), but recently Aron and Elvidge,[3] and Cooper,[4] have shown that the product from both reactions is in fact 3-aminoindazole (IV; R = NH_2).

The "hydroxylamine" of Pinnow and Sämann[1] has now been reduced catalytically (Raney nickel), giving ammonia, *o*-aminobenzonitrile (III; R = NH_2), and 3-aminoindazole (IV; R = NH_2). Grundmann and Ulrich[5] noted that reduction of the corresponding 7-chloro-derivative by sodium borohydride yielded only 2-amino-4-chlorobenzonitrile. A novel transformation of the "hydroxylamine" has also been observed on fusion with ammonium acetate; *o*-azidobenzonitrile (III; R = N_3) was formed in high yield. The reduction of the "hydroxylamine" to 3-aminoindazole, and the conversion into the azide, closely resemble the reactions of 4-methylbenzo-1,2,3-triazine 3-oxide (V),

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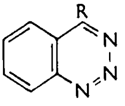
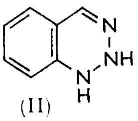
[1] Pinnow and Sämann, *Ber.*, 1896, **29**, 623.
[2] Gabriel, *Ber.*, 1903, **36**, 805.
[3] Aron and Elvidge, *Chem. and Ind.*, 1958, **38**, 1234.
[4] Cooper, *J.*, 1958, 4212.
[5] Grundmann and Ulrich, *J. Org. Chem.*, 1959, **24**, 272.

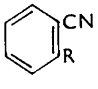
prepared by Meisenheimer, Senn, and Zimmermann[6] by diazotisation of *o*-aminoacetophenone oxime. In this instance reduction gave 3-methylindazole (IV; R = Me) and treatment with dilute sulphuric acid or a mixture of phosphorus tri- and penta-chloride gave *o*-azidoacetophenone (VI). These similarities suggested that Pinnow and Sämann's compound might be the *N*-oxide (VIIa) or its tautomer (VIIb). Further evidence was



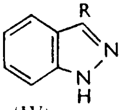
(I)



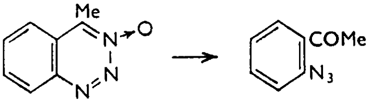
(II)



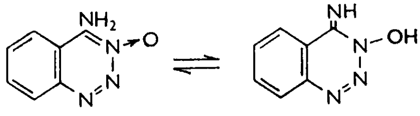
(III)



(IV)



(V) (VI)



(VIIa) (VIIb)

obtained by treatment of the thiol (I; R = SH) with hydroxylamine, affording the authentic compound (I; R = NH·OH). This differed in physical properties and ultraviolet and infrared absorption spectra from Pinnow and Sämann's compound, which therefore in all probability has structure (VII). The compounds prepared by Grundmann and Ulrich[5] from 2-amino-4-chloro- and 2-amino-4-methoxy-benzamidoximes must hence be derivatives of (VII).

The compounds (I; R = NH_2 and R = NH·NH_2) have previously been prepared[5] from the methylthio-derivative (I; R = SMe). They have now been obtained directly from the thiol (I; R = SH); and the amine (I; R = NH_2) has been made by diazotisation of *o*-aminobenzamidine.

In an attempt to prepare the unknown parent base, benzo-1,2,3-triazine, the 4-hydrazino-compound was heated with aqueous cupric sulphate;[7] nitrogen was evolved but only benzaldehyde and salicylonitrile were isolated. The nitrile is probably formed by hydrolysis of a *o*-cyanobenzenediazonium salt (cf. Buckley and Gibson[8]) and this is in agreement with the many observations[9] that benzo-1,2,3-triazines often behave as diazonium salts. The formation of benzaldehyde may be explained by oxidation of the hydrazine (I; R = NH·NH_2) to benzo-1,2,3-triazine, (I; R = H), ring fission to a benzaldimine-*o*-diazonium salt, reduction by hydrazine,[10] and finally hydrolysis to benzaldehyde. These two schemes suggested that in the presence of cuprous chloride *o*-chlorobenzonitrile and *o*-chlorobenzaldehyde might be formed. This was so; about 40% of the nitrile and a trace of aldehyde were produced. Benzo-1,2,3-triazine could not be isolated from any of these reactions.

EXPERIMENTAL

4-*Aminobenzo*-1,2,3-*triazine*.—(*a*) *o*-Aminobenzamidine dihydrochloride[11] (2·0 g.), dissolved in water (10 ml.) and 2N-hydrochloric acid (5 ml.), was treated at 0° with sodium nitrite (0·73 g.) in water (3 ml.). A solid soon separated and was redissolved by warming the mixture to 20° and diluting it with water. Addition of concentrated aqueous ammonia gave the crude product (1·3 g., quant.), m. p. 254—260° (decomp.), which crystallised from ethanol as pale yellow plates,[12] m. p. 266° (decomp.) (Found: C, 57·5; H, 4·4; N, 39·0. Calc. for $C_7H_6N_4$: C, 57·5;

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[6] Meisenheimer, Senn, and Zimmermann, *Ber.*, 1927, **60**, 1736.

[7] Schofield and Swain, *J.*, 1950, 392.

[8] Buckley and Gibson, *J.*, 1956, 3242.

[9] Erickson, Wiley, and Wystrach (1956). "The 1,2,3- and 1,2,4-triazines, tetrazines, and pentazines," New York, Wiley.

[10] Hantzsch and Vock, *Ber.*, 1903, **36**, 2066.

[11] Carrington, *J.*, 1955, 2527.

[12] The m. p.s of the benzo-1,2,3-triazines vary greatly with the rate of heating.

H, 4·1; N, 38·4%). The *picrate*, yellow prisms from water, had m. p. 237—238° (decomp.) (Found: N, 26·1. $C_7H_6N_4,C_6H_3N_3O_7$ requires N, 26·2%). The amino-compound evolved nitrogen when warmed with aqueous sodium hydroxide. Treatment with methyl iodide in methanol gave a *methiodide* as slender yellow needles (from ethanol), m. p. 216—217° (decomp.) (Found: N, 19·1; I, 43·8. $C_8H_9IN_4$ requires N, 19·4; I, 44·1%).

(*b*) 4-Mercaptobenzo-1,2,3-triazine [2] (1·0 g.) was ground with mercuric chloride (2·5 g.) to a fine powder, and the mixture kept with liquid ammonia (10 ml.) in a sealed tube at room temperature for 48 hr. The ammonia was then evaporated, the residue dissolved in dilute hydrochloric acid, and mercury precipitated as the sulphide. After being filtered, the solution was made alkaline with concentrated aqueous ammonia to give a pink solid (0·6 g., 67%) which crystallised from ethanol as plates, m. p. 266° (decomp.), identical with the product from (*a*).

o-Aminobenzamidoxime was diazotised by the method of Pinnow and Sämann [2] and the product crystallised as bright yellow needles (from ethanol), m. p. 191° (decomp.).

Catalytic Reduction of Pinnow and Sämann's "4-Hydroxyaminobenzo-1,2,3-triazine."—The compound [2] (10 g.) was catalytically reduced in methanol (100 ml.) at 60°/400 lb. per sq. in. in the presence of Raney nickel (*ca.* 1·0 g.). After the absorption of 1 mol. of hydrogen the catalyst was filtered off; ammonia was detected in the filtrate. Evaporation of the solvent gave an oil which slowly crystallised and, after being triturated with benzene, the solid (2·0 g.) was crystallised from propan-2-ol and then from benzene to give 3-aminoindazole, m. p. 157—158° (Found: C, 62·8; H, 5·6; N, 32·7. Calc. for $C_7H_7N_3$: C, 63·2; H, 5·3; N, 31·6%). *o*-Aminobenzonitrile was also isolated as the hydrochloride, m. p. 197° (decomp.), from the oily reduction product (Found: C, 53·7; H, 4·4; Cl, 22·6; N, 18·2. Calc. for $C_7H_6N_2,HCl$: C, 54·3; H, 4·5; Cl, 23·0; N, 18·1%).

Fusion of "4-Hydroxyaminobenzo-1,2,3-triazine" with Ammonium Acetate.—The compound [2] (1·0 g.) and ammonium acetate (5·0 g.) were heated at 135° during 5 min. The yellow colour of the starting material faded and an oil separated from the melt. After a further 3 min. the mixture was cooled and water (10 ml.) added. The oil solidified and was filtered off. Crystallisation of this solid (0·75 g., 84%) from light petroleum gave pure *o*-azidobenzonitrile, m. p. 54—55° (Found: C, 57·8; H, 2·76; N, 39·7. Calc. for $C_7H_4N_4$: C, 58·2; H, 2·78; N, 38·9%).

4-Hydrazinobenzo-1,2,3-triazine.—4-Mercaptobenzo-1,2,3-triazine (26 g.) was added to hydrazine hydrate (130 ml.; 60% w/v solution) cooled in ice. Hydrogen sulphide was evolved, the solid dissolved, and the product separated and after 16 hr. at room temperature was filtered off. The crude product (21 g.), m. p. 186° (decomp.), crystallised from methanol as brown needles, m. p. 188° (decomp.) (Found: C, 52·0; H, 4·0; N, 43·8. Calc. for $C_7H_7N_5$: C, 52·2; H, 4·35; N, 43·5%). The *methanesulphonate* crystallised from methanol–ether as silvery plates, m. p. 166—167° (decomp.) (Found: N, 27·0; S, 12·8. $C_7H_7N_5,CH_4O_3S$ requires N, 27·2; S, 12·4%).

Authentic 4-Hydroxyaminobenzo-1,2,3-triazine.—4-Mercaptobenzo-1,2,3-triazine (2·0 g.), hydroxylamine hydrochloride (0·94 g.), sodium acetate (1·1 g.), and ethanol (40 ml.) were refluxed together overnight. The hot mixture was filtered, the filtrate evaporated to low bulk, and the residue triturated with water. Crystallisation of the residue (1·45 g., 73%), m. p. 170° (decomp.), from aqueous methanol or nitromethane gave the pure compound as fine cream-coloured needles, m. p. 175° (decomp.) (Found: C, 52·0; H, 4·0; N, 34·0. Calc. for $C_7H_6N_4O$: C, 51·9; H, 3·7; N, 34·0%).

Reaction of 4-Hydrazinobenzo-1,2,3-triazine with Cupric Sulphate.—4-Hydrazinobenzo-1,2,3-triazine methanesulphonate (1·0 g.), dissolved in water (5 ml.), was added to cupric sulphate pentahydrate (10 g.), dissolved in water (45 ml.). The resultant suspension was boiled, and distilled until the distillate was clear (*ca.* 5 min.). The oil isolated from the distillate was neutral and was converted into its 2,4-dinitrophenylhydrazone (50 mg.) which, crystallised from acetic acid, had m. p. 243°, undepressed by admixture with benzaldehyde 2,4-dinitrophenylhydrazone. The residual reaction solution was extracted with ether, and the phenolic component isolated from the extract by alkali as a solid (*ca.* 20 mg.), m. p. 87—91°. This crystallised from light petroleum (b. p. 60—80°), and had m. p. 93—95°, undepressed by authentic salicylonitrile.

Reaction of 4-Hydrazinobenzo-1,2,3-triazine and Cupric Chloride.–Cuprous Chloride.—4-Hydrazinobenzo-1,2,3-triazine methanesulphonate (1·0 g.), in water (5 ml.), was added to cupric sulphate pentahydrate (10 g.), cuprous chloride (1·0 g.), and concentrated hydrochloric acid (10 ml.), in water (40 ml.). The resultant suspension was boiled and distilled until no more solid distilled with the steam. The solid, *o*-chlorobenzonitrile (0·25 g.), m. p. 40—42°, crystallised from light petroleum (b. p. 40—60°) and then had m. p. and mixed m. p. 42—43°. The residual reaction solution was extracted with ether, yielding a trace of oil which gave *o*-chlorobenzaldehyde 2,4-dinitrophenylhydrazone (*ca.* 10 mg.), m. p. and mixed m. p. 211° (from acetic acid).

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