

NOTE.

Attempts to prepare a Compound containing the Group $-\overset{\nearrow}{\text{N}}\begin{matrix} \text{S} \\ \parallel \\ \text{O} \end{matrix}$. *By R. J. W.*

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IN view of the rapid transformation of PhNO by H₂O₂ in alk. soln. (Bamberger, *Ber.*, 1900, **33**, 113) into its *N*-oxide (PhNO₂), it seemed of interest to attempt to prepare the corresponding thio-compound (annexed formula). The following

types of expt. were made: PhNO was treated with freshly liberated hydrogen polysulphides, with Na polysulphides, with nascent S from $\text{Na}_2\text{S}_2\text{O}_3$ and acid, with HgS at various temps., with S directly at 100° , and with S in $\text{C}_5\text{H}_5\text{N}$. The first four methods were largely without effect but appeared to cause some reduction to PhNH_2 (identified by diazotisation and coupling with β -naphthol). The chief recognisable product from the last three processes was azoxybenzene, the yield of which was improved by working in a CO_2 atm. No indication was obtained in any of the expts. of the desired co-ordination. Azoxybenzene is the major thermal decomp. product of PhNO (Bamberger, *Ber.*, 1902, **35**, 1606).

No co-ordination could be observed between PhNO and alc. ZnCl_2 , alc. FeCl_3 , MeI, or Me_2SO_4 . Further, the properties of copper *o*-nitrosobenzoate are not those of a co-ordinated Cu compound (colour and solubility). Aromatic nitroso-compounds do not form salts with the hydrogen halides or H_2SO_4 but, instead, undergo decomp.

PhNO is evidently inadequately represented as a tercovalent N-containing mol.

S was without action on alkyl nitrites either alone or in $\text{C}_5\text{H}_5\text{N}$ solution. These esters underwent loss of HNO_2 when mixtures with $\text{C}_5\text{H}_5\text{N}$ or $\text{C}_9\text{H}_7\text{N}$ were kept in contact with air for a few days, the nitrate of the base and the alcohol being produced. The reaction apparently consists of hydrolysis by moisture present in the atm., followed by oxidation of (presumably) pyridine or quinoline nitrite, since similar results are not obtained when a mixture of the constituents, previously well dried, is left in a desiccator or when a mixture of the ordinary moist liquids is left in a sealed tube.

Solubility of Sulphur in Pyridine.—"Flowers of sulphur" were twice recryst. from boiling $\text{C}_5\text{H}_5\text{N}$, pure S, m. p. 119° (sharp), being thus obtained as long yellow needles. 19.6 G. of a boiling sat. soln. and 14.0 g. of a sat. soln. at room temp. gave on evapn. 7.6 g. and 0.2 g. of S respectively, whence 100 g. of $\text{C}_5\text{H}_5\text{N}$ dissolve 63 g. and 1.5 g. at the two temps.

Action of Pyridine on Amyl and cycloHexyl Nitrites.—(a) Equal vols. of $\text{C}_5\text{H}_5\text{N}$ and amyl nitrite were boiled under reflux for 5 hrs. and then distilled. The fraction, b. p. 100 – 110° , on standing deposited colourless crystals, m. p. 107 – 114° (Found: N, 19.9. Calc. for $\text{C}_5\text{H}_6\text{N}_2\text{O}_3$: N, 19.7%), evidently of pyridine nitrate, since they would not diazotise PhNH_2 but gave a positive reaction with NHPH_2 – H_2SO_4 , and were identical with the product obtained by treating $\text{C}_5\text{H}_5\text{N}$ with HNO_3 in CHCl_3 . The fraction, b. p. 120 – 130° , contained amyl alcohol.

(b) A mixture of amyl nitrite (50 g.) and $\text{C}_5\text{H}_5\text{N}$ (100 g.) was left in a loosely-stoppered flask for 5 days. Pyridine nitrate (3.1 g.) was then obtained on filtration.

(c) *cycloHexyl* nitrite (2 c.c.) and $\text{C}_5\text{H}_5\text{N}$ (4 c.c.) after a week afforded pyridine nitrate (0.2 g.) similarly.—UNIVERSITY COLLEGE, UNIVERSITY OF LONDON. [Received, May 4th, 1932.]