The Formation of Azides by the Reaction of Amine Anions with Nitrous Oxide

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THE preparation of azides by the diazo-transfer[1] reaction of toluene-*p*-sulphonyl azide (II) with anions of amines has recently been reported.[2] To develop mild methods to introduce the azide and diazo-group[3,4] into organic compounds, we have examined another potential diazo-transfer agent, nitrous oxide.

The electronic structure of nitrous oxide (I) is related closely to that of toluene-*p*-sulphonyl azide (II). In both cases, the loss of a stable anion is possible and the 1,3-dipolar form in which the terminal nitrogen carries a positive charge, is a main contributor to the structure of both nitrous oxide and toluene-*p*-sulphonyl azide.

Nitrous oxide has been used as a diazo-transfer agent previously. Müller and Rundel[5,6] have shown that nitrous oxide reacted with methyllithium and triphenylphosphine methylene to give diazomethane.[7] Earlier, Beringer, Farr, and Sands[8] had reported the reaction of various organolithium compounds with nitrous oxide. Although the expected initial products were not obtained, the compounds isolated could be rationalized *via* the formation of the corresponding diazo-compounds. Meier and Frank investigated the reaction of anions of some amines and hydrazines with nitrous oxide. With aniline anion, nitrous oxide gave about 57% yield of azobenzene and a small amount of a yellow oil, believed to be phenyl azide.[9]

In view of the advantage offered by the easy removal of excess or unreacted nitrous oxide from the reaction mixture, the reaction of nitrous oxide with amine anions was re-investigated.

Our initial experiment was carried out by bubbling nitrous oxide through a solution of the anion of aniline for 20 hr. at 0°. Upon aqueous work-up of the reaction mixture, a dark residue was obtained from the neutral fraction. It exhibited only an extremely weak absorption at 2120 cm.$^{-1}$ ($-N_3$). When the time of passage of nitrous oxide was increased to 70 hr., a 10% yield of phenyl azide was obtained. It is of interest to note that *p*-anisyl azide was formed in 19% yield

Azides from the reaction of nitrous oxide with amine anions[a]

Azide	Pressure (lb./in.^{2})	Recovered amine (g.)	Time (hr.)	Yield (theor.)	(%) Net[b]
PhN_3[c]	30—40	7·3	5·0	9(10)	39
PhN_3	80	4·4	70·0	18	32
PhN_3[f]	80	1·5	42·0	35	51
p-$MeC_6H_4{\cdot}N_3$	50—55	7·0	2·5	16	46
p-$MeO{\cdot}C_6H_4{\cdot}N$[c,d]	50—55	3·3	4·5	25(19)	35
cyclo-$C_6H_{11}N_3$[e]	30—50	2·9	5·0	10	15

[a] The amount of starting amine was 0·10 mole in each case, except as otherwise noted. The anions were prepared by the reaction of the amine with methyl-lithium.

[b] Based on the amount of unrecovered amine.

[c] Values in parenthesis refer to initial runs carried out by bubbling nitrous oxide through the reaction mixture (see Text).

[d] Azoanisole was isolated in 4·5% yield.

[e] Identified by its boiling point and its infrared spectrum.

[f] Fifty millimoles of aniline and two equivalents of methyl-lithium were used.

after only 20 hr. Similarly, cyclohexyl azide could be isolated after 20 hr.

When amine anions were treated at room temperature under a pressure of 30—50 lb./in.^{2} with nitrous oxide, equal and often better conversions were obtained after 5 hr. or less (see Table). All the azides reported were characterized by their boiling points, their infrared spectra, and by the formation of adducts with triphenylphosphine.†

Preliminary experiments with benzophenone and fluorenone hydrazones indicated that, under the same conditions, the diazoalkanes are generated. *NN*-Diphenylhydrazine anion reacted easily with nitrous oxide but neither of the anticipated products, *N*-azidodiphenylamine and/or tetraphenyltetrazene, were isolated. Instead, diphenylamine was obtained in 89% conversion. The formation of diphenylamine may be rationalized as arising from further reaction of *N*-azidodiphenylamine [or the *N*-nitrene therefrom] with the anion followed by fragmentation of diphenylamine.

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† See footnote e of the Table.

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