Reactions of 3-Aryl-4-bromosydnones with amines

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REACTION of 4-bromo-3-phenylsydnone[1] (I) with hot piperidine yields the amide (II), m.p. 128°. Its structure follows from analysis, its infrared spectrum with absorption peaks at 3300 (>NH) and 1640 cm.$^{-1}$ (tertiary amide), and also from its nuclear magnetic resonance spectrum: two doublets at τ 4·62 and 5·28 (NH and –CH·CO; *cf.* structure II) with a multiplet (4 H) at τ 7·4 corresponding to $-CH_2\cdot N\cdot CH_2-$ in the piperidine ring attached to CH in (II) and two multiplets at τ 6·1 and 6·6 corresponding to $-CH_2\cdot N\cdot CH_2-$ of the piperidine at >CO (*cf.* structure II). Since the halogen atom in 4-halogeno-3-phenylsydnones is not reactive to nucleophiles[2] the first stage is undoubtedly ring fission to give the amide (III). Subsequent replacement of the aliphatic halogen (III; X = Br) by piperidine as well as denitrosation (piperidine hydrobromide proved a good denitrosating agent) are feasible steps to the product (II).

Treatment of the bromosydnone (IV; X = H) with cyclohexylamine gave an unforeseen result. The main product was the Schiff base (VI) m.p. 114°, because on reduction (5% Pd–charcoal in ethanol and hydrogen) it gave material identical with authentic *NN'*-dicyclohexylglycinamide (VIII). The unexpected cleavage course of the heterocycle (IV) is rationally interpreted as a relief of a 1 : 6 interaction between the nitroso-oxygen and the amino-hydrogen in the intermediate amide (V) leading to the observed azomethine (VI) and the phenyl diazohydroxide (VII; X = H). Such an internal elimination reaction is precluded in the nitroso-intermediate (III; X = NC_5H_{10}) derived from piperidine because of absence of a suitably positioned hydrogen. The intermediacy of the diazohydroxide (VII) and with it support for the postulated mechanism was established in two ways. In one case, 4-bromo-3-*p*-chlorophenylsydnone (IV; X = *p*-Cl) was made to react with cyclohexylamine and furnished, in addition to the Schiff base (VI), chlorobenzene. This product is obviously formed by homolysis of the diazo-compound (VII; X = *p*-Cl) to give a chlorophenyl radical (route *a*) which subsequently abstracts hydrogen. In the second case, fluorine was used as a chemical label[3] by employing the *p*-fluorophenylsydnone (IV: X = *p*-F) for the

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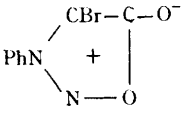
[1] J. C. Earl, *Rec. Trav. chim.*, 1956, **75**, 1080.

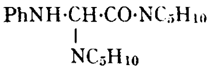
[2] H. Kato and M. Ohta, *Bull. Chem. Soc. Japan*, 1957, **30**, 210. M. Bellas and H. Suschitzky, unpublished result.

[3] P. Miles and H. Suschitzky, *Tetrahedron*, 1963, **19**, 385; 1962, **18**, 1369. I. K. Barben and H. Suschitzky, *J. Chem. Soc.*, 1960, 2735.

reaction. The reaction mixture contained, apart from the Schiff base (VI), ionic fluorine. Its presence is explained by route (*b*): The covalent diazohydroxide (VII; X = *p*-F) gives rise to an ion pair (X = *p*-F) in which the fluorine is rendered labile to anionic attack through the agency of a *p*-diazonium group.[3] It thus suffers replacement by any of the surrounding nucleophiles. Route (*a*) and (*b*) are both in keeping with the normal behaviour of aryl radicals. Evolution of nitrogen was also observed (*cf.* route *a*).

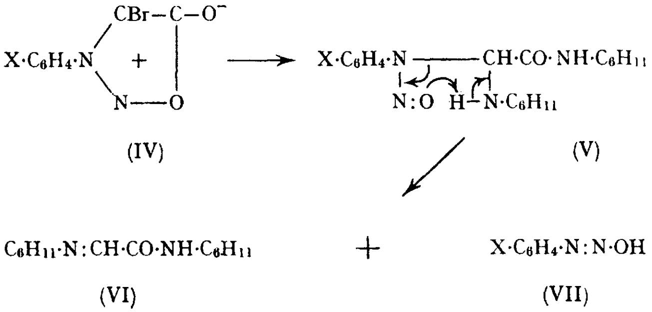


(I)



$\mathrm{PhNH{\cdot}CH(NC_5H_{10}){\cdot}CO{\cdot}NC_5H_{10}}$ (II)

$\mathrm{PhN(NO){\cdot}CHX{\cdot}CO{\cdot}NC_5H_{10}}$ (III)



The preparative scope of this multicentre type of elimination and of the reaction with secondary amines to give the apparently unknown diamino-acid amides of type (II) is under investigation.

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