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THE REACTION OF PHOSGENE WITH 4-(4'-NITROBENZYL) PYRIDINE

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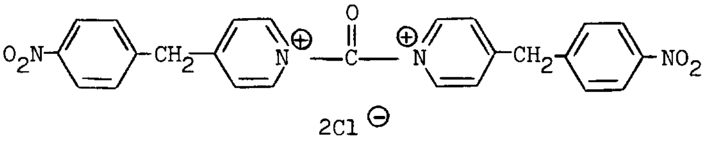
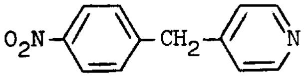
4-(4'-Nitrobenzyl) pyridine (IIa) is widely used as a reagent for the quantitative estimation of microgram levels of phosgene [1-3]. During recent work on the determination of phosgene in tetrahydrofuran solvent we had cause to investigate the nature of the orange chromophoric species produced when phosgene reacts with IIa.

Following the reported method of Lamouroux [1] for isolation of the product from phosgene with IIa, we obtained a pale yellow crystalline material of melting point 210° (decomp.). Lamouroux quotes m.p. 212° and gives analytical data for chlorine and nitrogen in fair agreement with the proposed structure (I, incorrectly drawn in the original paper as an aniline and not a pyridine derivative). No spectroscopic information was included.



I

Our spectroscopic evidence (strong amine hydrochloride band at 3050-2050 cm^{-1} and no carbonyl absorption in the infrared; no peak in the ultraviolet corresponding to the orange chromophore, λ = 440 nm.) and micro-analytical data, were not in agreement with I but suggested that the product was IIb, i.e. the hydrochloride of the nitrobenzyl pyridine reagent. Lamouroux's analytical data for Cl and N is, in fact, in much better agreement with IIb than I.

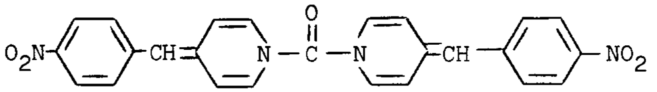


IIa free base

IIb hydrochloride

The identity was confirmed by synthesis of an authentic sample of IIb by treating an ethereal solution of IIa with dry hydrogen chloride gas. The two samples were identical in all physical and spectroscopic properties.

In order to isolate the authentic chromophoric species we have treated phosgene (>99% purity) with IIa in dry ether and an atmosphere of nitrogen, filtered off the deep purple coloured precipitate and washed it with ice-cold hydrochloric acid (0.001N) to remove traces of IIa and IIb. The product was a deep purple solid of m.p. 138-138.5° giving a negative test for ionic chloride and having carbonyl infrared absorption at 1658 cm^{-1}. and ultraviolet absorption in agreement with that of the chromophoric species. The extensive conjugation (and hence deep colour) of the product can be rationalised on the basis of the structure III which resembles that proposed [4] for, but not isolated from, the reaction of phosgene with other acylating species.



III

Found: C=66.4, H=3.99, N=12.25% $C_{25}H_{18}N_4O_5$ requires: C=66.1, H=3.99, N=12.3%

The mass spectrum of III has its greatest m/e at 426 (M-CO) and a base peak at 213.

A sample of the complex III is stable in ethanol solution but is very rapidly decolourised by addition of hydrochloric acid to give IIb. This observation accounts for the isolation of IIb in Lamouroux's preparation.

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