

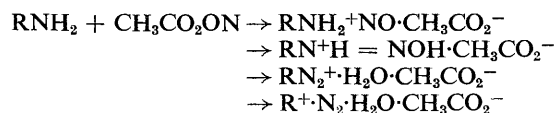
Acetyl Nitrite: a Useful Nitrosating Reagent

Andrew B. Kyte, Richard Jones-Parry and David Whittaker*

The Robert Robinson Laboratories, University of Liverpool, Liverpool L69 3BX, U.K.

Acetyl nitrite has been prepared, and shown to be a useful reagent for the study of the mechanism of deamination of primary amines.

It has been suggested by Collins¹ that nitrosation of amines with sodium nitrite in acetic acid may involve preliminary formation of acetyl nitrite which then nitrosates the amine. If this is the case, then the counterion involved in the reaction would also be derived from the nitrite (Scheme 1). If acetyl



Scheme 1.

nitrite could be isolated and then used for deamination in solvents other than acetic acid the results obtained should aid understanding of ion pairing in deamination reactions;² the reagent itself would also be of value in nitrosation studies in general.³

Acetyl nitrite had not previously been prepared, but was readily obtained by mixing an excess of solid silver acetate with nitrosyl chloride at liquid nitrogen temperature and allowing the mixture to warm up to room temperature, a method similar to that used in making trifluoroacetyl nitrite.⁴ Acetyl nitrite was then distilled off *in vacuo*. It is a green solid at -196°C , a green liquid at -78°C , and a pale brown liquid at room temperature. The ^1H n.m.r. spectrum of a solution in CDCl_3 shows a single peak at δ 2.18, and the ^{13}C n.m.r. spectrum of the neat liquid at -20°C had peaks at 173.7 and 19.9 p.p.m. The mass spectrum was mainly that of biacetyl. Microanalysis of the volatile, unstable material was not possible.

Acetyl nitrite decomposed rapidly in water, giving a solution free of chloride ions. It reacted with octan-1-ol in pyridine at room temperature to give octyl nitrite, with no trace of octyl acetate. It readily deaminated octylamine in acetic acid, giving a product composition identical to that obtained by

Table 1. Deamination of octylamine at room temperature in anhydrous acetic acid.

Products (%)	Reagent	
	Sodium nitrite	Acetyl nitrite
Total octenes	18	15
1-Methylheptan-1-ol	6	6
1-Methylheptyl acetate	22	20
Octan-1-ol	2	3
Octyl acetate	50	48

reaction of the amine with sodium nitrite in acetic acid, as shown by the results in Table 1. Other aliphatic primary amines behave similarly. In most cases product compositions were identical for reaction with either reagent, the only exception to date being 2α -H-pinane- 3α -ylamine, where reaction with acetyl nitrite gave a large increase in the yields of alcohol products, formed by capture of the water molecule produced when the diazotic acid is decomposed, over reaction with sodium nitrite. Product differences were also observed in reactions of the amine hydrochloride rather than the amine.

Deamination of an optically active amine has been used to determine the relative amounts of product formation *via* a diazonium ion and *via* a carbocation, on the assumption that the former pathway yields an inverted product while the latter yields a racemic product.⁵ Such branching of the reaction pathway should be sensitive to counterion, so we repeated the work, deaminating optically active *s*-butylamine with sodium nitrite in acetic acid to yield *s*-butyl acetate as the main product, 32% inverted relative to starting material, in reasonable agreement with the reported 28% inversion.⁵ Using acetyl nitrite in acetic acid, the product showed 30% inversion, identical within the accuracy of the experiment.

Although these data show that the deamination of amines with sodium nitrite in acetic acid is more complex than simple

formation of acetyl nitrite followed by nitrosation and decomposition of the intermediate, the similarity of the products in many cases suggests that acetyl nitrite probably has an important role. We therefore sought to extend the experiments of Whiting,² by deaminating amines with acetyl nitrite in propionic acid, to compare the amounts of acetates, formed by ion-pair collapse, with the amounts of propionates, formed by capture of the intermediate by solvent. However, with the n- and s-butylamines, only trace amounts of acetate products were observed; octylamine gave a propionate/acetate ratio of 17, while 1-methylheptylamine gave a propionate/acetate ratio of 22.

Clearly, acetyl nitrite is providing the counterion in amine deamination reactions, but capture by intermediates is much less important than in the deaminations studied by Whiting, so the results are not comparable. A possible explanation is

that the lifetime of the diazotic acid is sufficient to permit exchange of the counterion in this reaction, and this is being investigated.

Received, 8th October 1981; Com. 1192

References

- 1 C. J. Collins, *Acc. Chem. Res.*, 1971, **4**, 315.
 - 2 H. Maskill, R. M. Southam, and M. C. Whiting, *Chem. Commun.*, 1965, 496; E. H. White and K. W. Field, *J. Am. Chem. Soc.*, 1975, **97**, 2148.
 - 3 B. C. Challis and D. E. G. Shuker, *J. Chem. Soc., Perkin Trans. 2*, 1979, 1020.
 - 4 C. W. Taylor, T. J. Brice, and R. L. Wear, *J. Org. Chem.*, 1962, **27**, 1064.
 - 5 A. Streitwieser and W. D. Schaeffer, *J. Am. Chem. Soc.*, 1957, **79**, 2888 and 2893.
-