Tetrahedron Letters,Vol.29,No.22,pp 2735-2736,1988 0040-4039/88 $3.00 + .00
Printed in Great Britain Pergamon Press plc

NITRATION BY OXIDES OF NITROGEN, PART 2: PREPARATION OF NITRAMINES BY REACTION OF STRAINED-RING NITROGEN HETEROCYCLES WITH DINITROGEN PENTOXIDE

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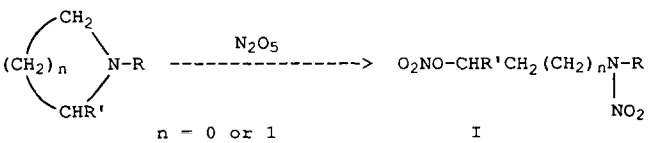
Summary: Several aziridines and three azetidines have been found to yield nitramine-nitrates in good to excellent yield by ring opening with dinitrogen pentoxide.

The preparation of nitrate esters by the cleavage of small-ring oxygen heterocycles (epoxides and oxetanes) by dinitrogen pentoxide (N_2O_5) has already been described[1]. We wish now to describe the extension of this route to small-ring nitrogen heterocycles, aziridines and azetidines, which offer the possibility of a novel and convenient synthesis of nitramines, particularly (although not exclusively) aliphatic nitramines. This class of compound, which is widely encountered in explosive and propellant technology, is commonly prepared by the reaction of secondary amides with nitric acid in dehydrating media such as acetic anhydride[2], by the addition of nitrate salts of secondary amines to such a medium in the presence of a catalyst, eg chloride ion[3], by direct interaction of an amine with N_2O_5[4], or by nitrolysis of gem-diamines with nitric acid-acetic anhydride[5,6]. More recently developed methods include the reaction of N,N-dialkylamides with nitronium tetrafluoroborate[7], the reaction of t-butylamines with nitric acid or N_2O_5[8], and the the action of nitric acid-acetic anhydride on *tert.* amines with *in situ* oxidation of the resulting nitrosamines with peracetic acid[9]. (Routes involving oxidation of isolated nitrosamines have been disregarded owing to the high toxicity of these compounds.)

Certain of these routes suffer from contamination of the product by nitrosamines which are awkward to remove[10]; others have the disadvantage of using reagents which are not available cheaply on an industrial scale (eg NO_2BF_4), while some produce co-products which are difficult to dispose of (eg *t*-butyl nitrate). For these reasons, we sought a novel method to overcome these difficulties, based on the reaction of strained-ring compounds mentioned above.

We prepared a series of aziridines and azetidines, the nitrogen analogues of epoxides and oxetanes (Table), and reacted them with N_2O_5 in halogenated solvents under conditions similar to those described earlier[1]. (Only those compounds with N-substituents are described here; those unsubstituted on nitrogen behaved in an entirely different manner which will be described fully elsewhere.) In many cases ring opening took place cleanly with the generation of nitramine-nitrates (I) by cleavage of the ring C-N bond and addition of N_2O_5 (Eqn 1), and the products were isolated without difficulty.



n = 0 or 1 I ---------- 1

Competing reactions, principally cationic ring-opening polymerisations, took place rarely, generally only when a) the nitrogen heterocycle possessed labile hydrogen (eg hydroxyl, amino or unsubstituted aryl groups), leading to formation of nitric acid during the reaction with consequent polymerisation *via* quaternised species, or b) the nitrogen heterocycle was appreciably basic - some N-alkyl aziridines showed this tendency. It was also essential that the reactions were carried out under scrupulously dry conditions to prevent generation of nitric acid, and that the

TABLE

Entry	Heterocycle R	R'	Mol N_2O_5: substrate	Solvent	Temp. °C	Yield %
	A. Aziridines					
1	CH_2CH_2CN	Me	1.25:1	CH_2Cl_2	-10 to -5	70
2	CH_2CH_2CN	H	1.1:1	CH_2Cl_2	-10 to 0	56
3	n-Bu	H	1.0:1	$CDCl_3$	-2 to 2	69[11]
4	Picryl	H	1.13:1	$CDCl_3$	-2 to 2	76[12]
5	EtO_2C	H	1.1:1	$CDCl_3$	-5 to 0	82
	B. Azetidines					
6	CH_2CH_2CN	-	1.16:1	CH_2Cl_2	-10 to 5	79
7	n-Bu	-	1.1:1	$CDCl_3$	-10 to -5	41
8	EtO_2C	-	1.1:1	CH_2Cl_2	-10 to -5	88

Notes

Reaction time was 0.5 to 1 hr. All yields are isolated yields.
All products showed spectra (^1H nmr and i.r.) consistent with the assigned structures, and gave satisfactory elemental analysis or accurate mass figures.

N_2O_5 be free from this contaminant. The necessity for ring strain in the substrate molecule was illustrated by the inertness of a cyclic amine with a five-membered ring (N-methylpyrrolidine) - no nitramine was obtained.

In conclusion, the reaction of N_2O_5 with strained-ring nitrogen heterocycles has been shown to provide a simple and versatile route to nitramine products and to possess significant advantages over existing methods. The versatility of the technique is emphasised by the fact that only two of the products listed in the table (entries 3 & 4) have been previously prepared. A fuller account of the synthetic potential and mechanistic aspects of these reactions will be presented in future publications.

Acknowledgements

Thanks are due to Dr A V Cunliffe and Mr R Morrell for assistance with nmr spectroscopy, Mr J Rowley for mass spectrometric measurements, and Mr I Bird for synthesis of heterocyclic precursors.

References and Notes

1. See accompanying article.
2. T Urbanski, "Chemistry and Technology of Explosives", Vol. 3, Pergamon Press, Oxford, 1967
3. W J Chute, K G Herring, L E Tombs and G F Wright, *Canad J Res.*, 26B, 89-103 (1948)
4. W D Emmons, A S Pagano and T E Stevens, *J. Org. Chem.*, 23, 311 (1958)
5. F Chapman, *J Chem Soc* 1631 (1949)
6. For further details, see a) ref. 2, b) P A S Smith "Open Chain Nitrogen Compounds", Vol 2, Chapter 15, Benjamin, New York, 1966
7. S A Andreev, L A Novik, B A Lebedeev, I V Tselinskii and B V Gidaspov, *J. Org. Chem. USSR*, 14(2), 221 (1978)
8. D A Cichra and H G Adolph, *J. Org. Chem.*, 47(12), 2474 (1982)
9. J H Boyer, T P Pillai and V T Ramakrishnan, *Synthesis*, 677 (1985)
10. For detailed discussion of this problem see: J C Bottaro, R J Schmitt and C D Bedford, *J. Org. Chem.*, 52(11) 2292 (1987)
11. W Plesch and M Wiessler, *Liebig's Annalen*, 1494 (1984)
12. L V Clark, *Ind. Eng. Chem.*, 25, 1385 (1933)

(Received in UK 6 April 1988)