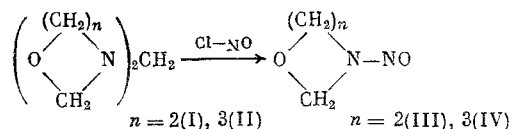


SYNTHESIS OF N-NITROSOAMINES BY THE CLEAVAGE OF AMINALS WITH NITROSYL CHLORIDE

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We are the first to report the smooth cleavage of aminals (I) [1] and (II) [2] using nitrosyl chloride to form N-nitroso-1,3-oxazolidine (III) and N-nitrosotetrahydro-1,3-oxazine (IV) which have been obtained previously by a different pathway [3-5]



The reactions were carried out with an equimolar reagent ratio in absolute ether at -40°C for 1 h and then at 20°C for 1 h. Products (III) and (IV) are yellow liquids which are mixtures of syn and anti isomers (NO relative to the NCH_2O group) due to hindered amide rotation about the N-N bond. The signals of the isomers in the PMR spectra were assigned on the basis of the shielding effect of the syn NO group.

Product (III) was obtained in 53% yield, bp $70-71^\circ\text{C}$ (1 mm), n_D^{17} 1.4832. PMR spectrum at 400 MHz in CDCl_3 relative to TMS (δ , ppm, J, Hz): anti isomer) 3.67 t (CH_2N , $^3J=6.4$), 4.20 t (CH_2O), 5.66 s (OCH_2N); syn isomer) 4.22 t (CH_2N , $^3J=6.8$), 4.43 t (CH_2O), 5.12 s (OCH_2N). The anti/syn ratio was 2. Found: C, 35.30; H, 6.28; N, 27.84%. Calculated for $\text{C}_3\text{H}_6\text{N}_2\text{O}_2$: C, 35.29; H, 5.92; N, 27.44%.

Product (IV) was obtained in 50% yield, bp $75-77^\circ\text{C}$ (1 mm), n_D^{17} 1.4900. PMR spectrum: anti isomer) 1.71 t. t(CCH_2C), 3.91 t (CH_2N , $^3J=5.9$), 3.96 t (CH_2O , $^3J=5.4$), 5.58 s (OCH_2N); syn isomer) 2.00 t. t(CCH_2C), 3.92 t (CH_2N , $^3J=3.6$), 4.41 t (CH_2O , $^3J=3.6$), 5.06 s (OCH_2N). The anti/syn ratio was 7. Found: C, 41.56; H, 6.95; N, 14.00%. Calculated for $\text{C}_4\text{H}_8\text{N}_2\text{O}_2$: C, 41.37; H, 6.94; N, 24.13%.

Saavedra [4] has reported carcinogenic and mutagenic activity of (III) and (IV) which have been detected as dangerous impurities in commercial cooling lubricants [5]. The mutagenic activity of (III) was confirmed for *Drosophila*. The percentage of lethal mutations was 3.7 for adults and 9.5 for larvae (according to the data of I. A. Rapoport).

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