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A FOUR-MEMBERED CYCLIC NITRONE AND THE P.M.R. SPECTRA OF CYCLIC NITRONES

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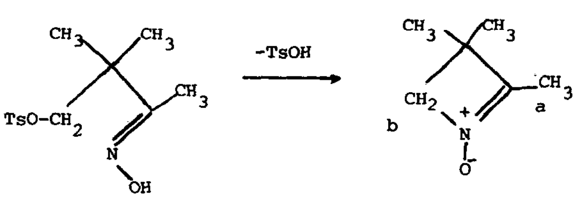
Many five-membered cyclic nitrones (1-pyrroline 1-oxides) and a few six-membered compounds have been used in the study of the nitrone group[1,2], but we know of no previous report of a four-membered cyclic nitrone. We have now prepared 2,3,3-trimethyl-1-azetine-1-oxide, 2.

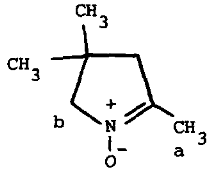
The hydroxyketone $HOCH_2CMe_2COMe$[3] was tosylated and converted to the oxime 1, assumed to be the E isomer shown. Pyrroline 1-oxides have been prepared by the base-catalysed cyclisation of γ-tosyloxy[4] or γ-chloro ketoximes[5], but all attempts to cyclise 1 with common bases (pyridine, K_2CO_3, NaOEt, NaH) failed. However, when 1 was heated with one equivalent of 1,8-bis(dimethylamino)naphthalene in refluxing anhydrous benzene the azetine 1-oxide 2 was obtained as a colourless hygroscopic oil (ca. 30% yield). Small amounts of 2 have been distilled at 110° (bath)/0.5 mm, and it is stable during the period of ordinary spectroscopic measurements, but neat samples decompose in a few days at room temperature. The structure 2 is supported by the following spectroscopic evidence: I.r. spectrum: 1627 cm^{-1} ($C{=}N^{+}{-}O^{-}$). U.v. spectrum (EtOH): λ_{max} 225 nm (ε_{max} ca. 7300). P.m.r. spectrum ($CDCl_3$): δ 1.30, s, C(ch$_3$)$_2$; 1.90, t, 2-CH_3; 3.92, q, 4-CH2 (coupling constant shown below). Mass spectrum: molecular ion at m/e 113. This evidence, particularly the ultraviolet spectrum, is not compatible with an alternative isoxazoline structure.[5]



1

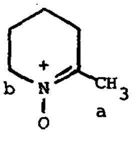
2

$^5J_{ab}$ = 1.95±0.05 Hz



3

$^5J_{ab}$ = 1.84±0.05 Hz



4

$^5J_{ab}$ = 1.50±0.1 Hz

The literature contains very few PMR data and no systematic investigations concerning simple nitrones. The 100 MHz PMR spectra of 2, 3, and 4 were examined in detail to test trends in homoallylic coupling. It can be seen that the trends previously observed in homoallylic coupling[6] are indeed retained in transoid coupling across the nitrone system; more detailed comment will be made elsewhere.

References

1. J. Hamer and A. Maculoso, Chem. Rev., 64, 473 (1964).
2. G. R. Delpierre and M. Lamchen, Quart. Rev., 19, 329 (1965).
3. J. E. Dubois, Ann. Chim., 6, 406 (1951).
4. G. Stork. S. D. Darling, I. T. Harrison, and P. S. Wharton, J. Amer. Chem. Soc., 84, 2019 (1962).
5. H. A. Brandman and R. T. Conley, J. Org. Chem., 38, 2236 (1973).
6. M. Barfield and S. Sternhell, J. Amer. Chem. Soc., 94, 1905 (1972) and references therein.