Rearrangement of Prop-2-ynylic *N*-Oxides to *O*-Allenyl Hydroxylamines

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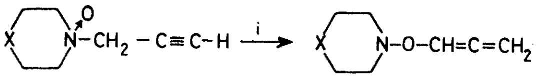
Summary Rearrangement of *N*-prop-2-ynylpiperidine *N*-oxide and *N*-prop-2-ynylmorpholine *N*-oxide to the corresponding *O*-allenyl hydroxylamines is reported; this rearrangement appears to be intramolecular proceeding by a cyclic mechanism.

As part of the pharmacological evaluation of some acetylenic amines related to oxotremorine,[1] their metabolism is being investigated.[2] The *N*-oxides sometimes appear as distinct metabolites[3] but they are thermally unstable and we have accordingly investigated the thermal rearrangement of the model *N*-oxides (I) and (II), containing both a triple bond and a cyclic amine function.

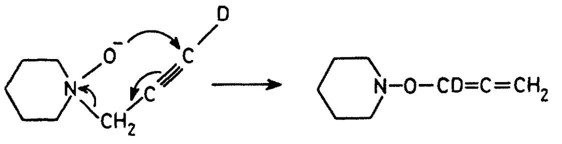
The tertiary amines were prepared from the corresponding secondary amines and prop-2-ynyl bromide or toluene-*p*-sulphonate. Subsequent oxidation with either *m*-chloroperbenzoic acid[4] or H_2O_2–MeOH afforded the *N*-oxides in fair yields. When a suspension of the compounds in dry ether was stirred under reflux until the solid disappeared, distillation *in vacuo* yielded colourless oils, identified by n.m.r. and i.r.† spectroscopy as the *N*-allenoxy-piperidine (III) (b.p. 42 °C at 0·6 mmHg) and -morpholine (IV) (b.p. 52 °C at 0·7 mmHg) (Scheme 1), respectively.



(I) X = CH_2
(II) X = O
(III) X = CH_2
(IV) X = O

Scheme 1. i, dry ether, reflux.

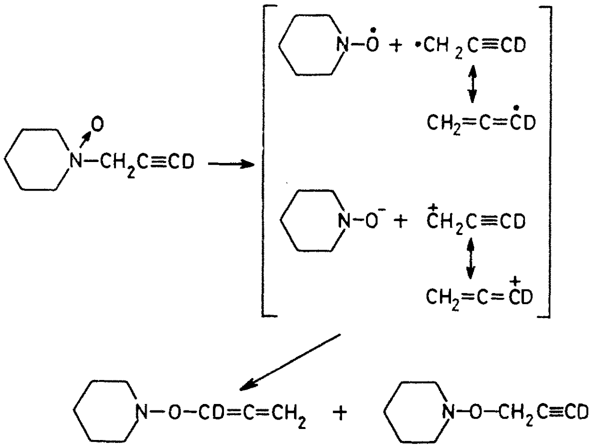
The formation of the allenic function is clearly indicated from the i.r. and n.m.r. data. The thermal rearrangement observed is reminiscent of the Meisenheimer[5] rearrangement in which a group migrates from N to O in tertiary amine oxides. The migrating groups include allyl,[6] benzyl,[7] neopentyl,[8] tetrachloropyridyl,[9] and homoadamantyl,[10] and recently,[11] one of us reported on the migration of a benzene nucleus bearing an electron withdrawing substituent. The migration of a prop-2-ynylic group has not been reported hitherto.‡



(V)

Scheme 2.

The mechanism for the migration can be explained as an intramolecular cyclic process. Accordingly deuterium substituted (I) gave the *O*-allenyl hydroxylamine (V) labelled at the α-carbon (Scheme 2), the n.m.r. spectrum of which showed a singlet at δ 5·4 for the $=CH_2$ protons.



Scheme 3.

The involvement of the alternative mechanisms of radical or heterolytic dissociation (Scheme 3) is less likely since (V) was the only product found, and no deuterium scrambling was observed.

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† I.r.: $C\equiv C$ stretch 2100s (I) and 2120s (II) cm^{-1}; $\equiv C\text{–}H$ stretch 3320m (I) and 3280m (II) cm^{-1}; $C=C=C$ stretch 1962s cm^{-1} for (III) and (IV) (*cf.* D. R. Taylor, *Chem. Rev.*, 1967, **67**, 317). N.m.r.: (I), δ 3·02 (1H, t, *J* 2·5 Hz) and 4·1 (2H, d, *J* 2·5 Hz); (II), δ 2·8 (1H, t, *J* 2·5 Hz) and 4·1 (2H, d, *J* 2·5 Hz); (III), δ 5·36 (2H, d, *J* 6 Hz) and 6·78 (1H, t, *J* 6 Hz); (IV), δ 5·3 (2H, d, *J* 6 Hz) and 6·70 (1H, t, *J* 6 Hz). Elemental analyses could not be obtained for (III) and (IV) owing to their instability.

‡ *Added in proof.* While this work was in preparation, J. C. Craig *et al.* reported on a similar rearrangement: Proc. 2nd Internat. Symp. on Acetylenes, Allenes and Cumulenes, Nottingham, Sept. 1977.

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