An Unusual Ring-enlargement in the Reaction of Acetylenic Esters and Ketones with *N,N*-Dimethylaminoallene

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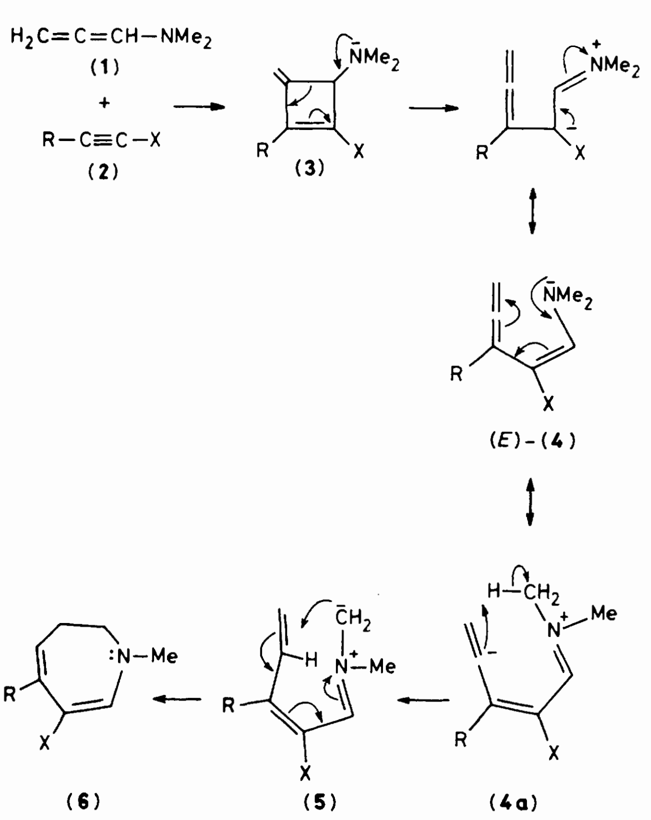
The four-membered ring compounds formed from *N,N*-dimethylaminoallene and acetylenic esters or ketones are converted into derivatives of 2,3-dihydroazepine upon heating.

In the course of our study of the reactivity of allenic amines $H_2C{=}C{=}CH{-}NR_2$[1] we investigated the reaction between *N,N*-dimethylaminoallene (**1**) and acetylenic esters (**2**). Slow addition at 50 °C of (**1**) to a twofold excess of methyl but-2-ynoate afforded, after removal of the excess of acetylenic ester by distillation, the expected four-membered ring compound



R = H or Me, X = CO_2Me or COMe
or
R = H, X = COMe or COPr^n

Scheme 1

(3) in good yield. When the same procedure was carried out at −40 °C for methyl propiolate, heating during distillation of (3) gave rise to a different compound. The structure of this compound was shown by ^{1}H and ^{13}C n.m.r., i.r., and mass spectroscopy to be (**6**).† Heating a solution of (**3**; R=Me) in tetrachloroethene under reflux (121 °C) for 3 h, led to complete conversion into (**6**). On cooling the solution obtained after conversion (at 105 °C) of 25% of the starting compound (3), the allenic derivative (4) was detected in the mixture; a maximal accumulation of 10% could be attained. The presence of the allene was detected in the i.r. (C=C=C at 1957 cm^{-1}) and ^{1}H n.m.r. spectra. Only the *E*-isomer was present. Similar results were obtained for acetylenic *ketones*. The ring opening took place readily at room temperature and upon heating (66 °C) the allenic compound (**4**) closed smoothly to give the seven-membered ring (**6**). On the basis of these observations we propose the reaction course shown in Scheme 1.

The relatively easy opening of the four-membered ring (3), may be explained by the simultaneous presence of the pushing NMe_2 and the pulling substituent X ('push-pull system'). Closely analogous systems, lacking either the NMe_2 (**3**; X = CO_2Me_3, H in place of NMe_2) or the appropriate X group (**3**; X = CH_2OH), did not open on heating for 2—3 h at 120 °C.

The allenic compound (**4**), formed by ring opening of (**3**) can be written as the mesomeric zwitterion structure (**4a**), in which one of the methyl protons is transferred to the negatively charged carbon atom of the original allenic system. The ylide structure (**5**) finally undergoes a cyclization with charge neutralization and formation of (**6**).

To our knowledge this unusual ring transformation has no related precedents.

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Reference

1 H. D. Verkruijsse, H. J. T. Bos, L. J. de Noten, and L. Brandsma, *Recl. Trav. Chim. Pays-Bas*, 1981, **100**, 244.

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† The ^{1}H n.m.r. spectra of (6) showed signals, *inter alia*, at δ 7.3 (7-H), 6.4—6.5 (5-H), and 5.3—5.5 (4-H).