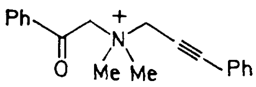
Rearrangement Reactions of Acetylenic Ammonium Ylides

By S. MAGESWARAN, W. D. OLLIS,* and I. O. SUTHERLAND
(*Department of Chemistry, The University, Sheffield* S3 7HF)

Summary The base-catalysed rearrangement of the ammonium bromide (**1**) gives a mixture of the allene (**3**) and the ylide (**5**); the implications of this result are discussed.

THE base-catalysed rearrangement of the 3-phenylprop-2-ynyl ammonium salt (**1**) was originally reported[1] to give the rearrangement product (**2**), but we recently noted[2] that this reaction gave as the major product the allene (**3**), together with a stable, crystalline ylide which we formulated as the unrearranged acetylenic ylide (**4**). We now discuss the reformulation of the ylide product and the general implications of its formation.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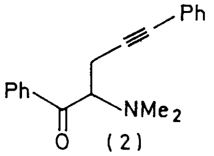
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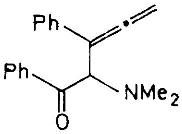
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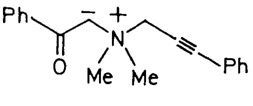
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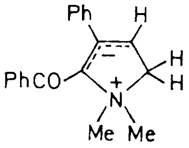
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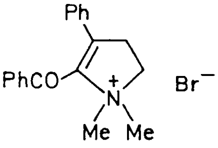
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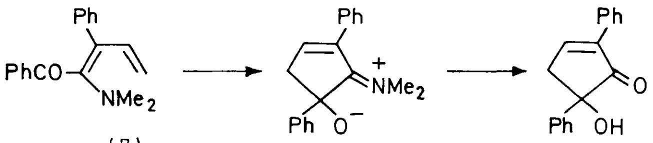
The crystalline ylide, m.p. 80°, obtained (*ca.* 25%) by the reaction of the salt (**1**) with aqueous sodium hydroxide at 0°, had the molecular formula $C_{19}H_{19}NO$ (high resolution mass spectrum); the lack of C=O absorption in its i.r. spectrum indicated an ylide structure. The n.m.r. spectrum showed, in addition to signals associated with the Ph and $\overset{+}{N}Me_2$ groups, an AX_2 system (τ_A 5·27, τ_X 5·79, J_{AX} 2 Hz). Reaction of the ylide with aqueous hydrobromic acid in tetrahydrofuran at 0° gave a crystalline hydrobromide, $C_{19}H_{20}BrNO$ (60%), which had spectroscopic properties (ν_{max} 1645 cm^{-1}; n.m.r. A_2X_2 system, τ_A 5·61, τ_X 6·34, J_{AX} 7 Hz) consistent with the formation of the pyrrolinium salt (**6**). The ylide (**5**) could be regenerated from the salt (**6**) by treatment with aqueous sodium hydroxide at 0°. Further confirmation of the constitution (**5**) for the ylide was obtained by its thermolysis (5 h, boiling benzene) followed by hydrolysis which gave as the major product a compound $C_{17}H_{14}O_2$, m.p. 112°, formulated as the hydroxycyclopentenone (**8**) (ν_{max} 3500 and 1715 cm^{-1}; n.m.r. AX_2 system, ν_A 2·18, τ_X 6·97, J_{AX} 3 Hz). This product (**8**) may be derived from the ylide (**5**) by the sequence (**5**) → (**7**) → (**8**).

Thermal isomerisation of the allene (**3**) (9 h; 55°) gave (*cf.* ref. 3) the unstable dimethylaminofuran (**9**) (τ 1·98—2·82, m, 10H; 7·23, s, 6H; 7·89, s, 3H) which was transformed on exposure to air and light[4] to give the *cis*-isomer of the vinylogous amide (**10**) ($C_{19}H_{19}NO_2$; ν_{max} 1660 cm^{-1}, τ 7·27, broad s, 6H, giving two signals at low temperatures and a sharp singlet at high temperatures)† together with a low yield of the corresponding *trans*-isomer. Hydrolysis of the intermediate dimethylaminofuran (**9**) also yielded the furan (**11**) ($C_{17}H_{14}O_2$, ν_{max} 1755 cm^{-1}; n.m.r. τ 2·44—2·86, m, 10H; τ 4·33, s, 1H; τ 8·10, s, 3H).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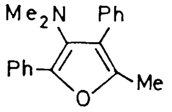
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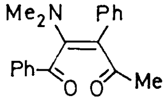
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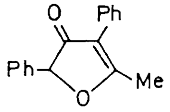
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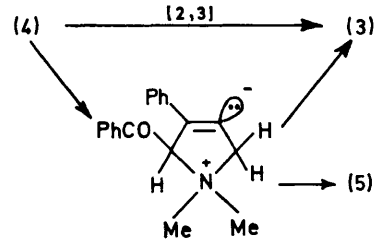

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SCHEME

The simultaneous formation of the allene (**3**) and the ylide (**5**) indicates that the acetylenic ylide (**4**) could be transformed at 0° by two possible reaction pathways (Scheme): (i) a concerted [2,3]-sigmatropic rearrangement leading directly to the allene (**3**) and (ii) an intramolecular nucleophilic addition[5] to the triple bond giving the betaine (**12**). This betaine (**12**) could then rearrange prototropically to the ylide (**5**) or undergo *anti*-elimination giving the allene (**3**) by an alternative pathway. These reaction pathways (i) and (ii) represent the limiting mechanisms for allene formation, and the existence of these two alternative mechanisms has implications regarding the base-catalysed rearrangements of other acetylenic ammonium salts[6] and

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† Details of the rotational isomerism of this compound will be given in the full paper.

related compounds [7] These implications are being further studied The stability of the ylide (**5**) has to be considered in relation to an elimination reaction which could give the diene (**7**) directly In this connection it may be noted that the normal steric requirements for the direct elimination reaction (**5**) → (**7**) cannot be satisfied in the five-membered ring system because the π-orbitals of the allyl system are related to the σ-orbitals of the $CH_2-\overset{+}{N}$ bond in (**5**) by a torsion angle of *ca* 90° (*cf* ref 8)

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