The General Electrocyclic Rearrangement of Sulphonium Ylids: Participation of *sp*-Hybridized Bonds

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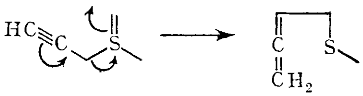
RECENTLY we reported a general electrocyclic rearrangement of sulphonium ylids[1-3] (Scheme 1) and noted[2] at that time the predictive possibilities of this interpretation. We now describe an example of such a process which was deduced from our previous treatment.

SCHEME 1

Since the acetylenic bond participates in many electrocyclic processes of carbon systems[4] we tested its participation in the general Scheme 1 which predicts the rearrangement as shown (Scheme 2). When the salt (I), ν_{max} 2220 cm.$^{-1}$, n.m.r. δ (CH_2Cl_2), 7·45 (10H, m), 4·67 (4H, s), 3·64 (2H, q) and 1·62 (3H, t), derived from the diacetylenic sulphide,[5] m.p. 46—47° (pentane–CCl_4); λ_{max} (ethanol) 243 mμ (ϵ 39,000); n.m.r. δ (CCl_4) 7·3 (10H, m) and 3·63 (4H, s), with triethyloxonium fluoroborate, was treated with n-butyl-lithium at $-70°$ in tetrahydrofuran, it was smoothly transformed into the allene (II).† The structure of (II) followed from its composition, $C_{20}H_{18}S$, and its spectral properties, ν_{max} (neat) 1935, and 860 cm.$^{-1}$; λ_{max}(ethanol) 243 mμ (ϵ 13,000) ond, 315 mμ (800); n.m.r. δ (CCl_4), 7·20 (10H, m), 5·09 (2H, d, *J* 2), 4·66 (1H, t, *J* 2),[6] 2·63 (2H, q, *J* 7), and 1·17 (3H, t, *J* 7 Hz). The presence of the acetylenic residue was not confirmed by i.r. absorption but the



SCHEME 2

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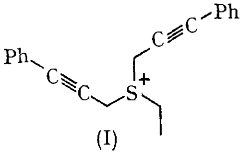
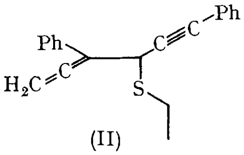
† Satisfactory analytical data has been obtained for all new compounds.

laser-Raman spectrum was unambiguous, a band at 2199 cm.$^{-1}$ being compatible with the presence of a single conjugated acetylene.‡ Final confirmation of the structural assignment was obtained by combined desulphurization and hydrogenation (Raney nickel W-4) to give the known 1,4-diphenylhexane, identical (i.r., n.m.r., and g.l.c. behaviour) with authentic material.[7]



(I)



(II)

These results support our original postulate[2] and extend the scope of the rearrangement mechanism to the production of unusual unsaturated systems.

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‡ We are indebted to Dr. T. Long of this department for his assistance in obtaining this spectrum.

[1] J. E. Baldwin, R. E. Hackler, and D. P. Kelly, *Chem. Comm.*, 1968, 537.

[2] J. E. Baldwin, R. E. Hackler, and D. P. Kelly, *Chem. Comm.*, 1968, 538.

[3] Other workers have noted specific examples of this general process, *cf.* R. B. Bates and D. Feld, *Tetrahedron Letters*, 1968, **417**; G. M. Blackburn, W. D. Ollis, J. D. Plackett, C. Smith, and I. O. Sutherland, *Chem. Comm.*, 1968, 186; B. M. Trost and R. LaRochelle, *Tetrahedron Letters*, 1968, 3327.

[4] For example, the Diels–Alder reaction, *cf.* A. Wasserman, "Diels–Alder Reactions", Elsevier, Amsterdam, 1965, p. 20.

[5] I. Iwai and I. Ide, *Chem. and Pharm. Bull.* (*Japan*), 1964, **12**, 1094.

[6] Long-range couplings in allenes are well authenticated *cf.* E. I. Snyder and J. D. Roberts, *J. Amer. Chem. Soc.*, 1962, **84**, 1582.

[7] H. Gilman and S. A. Harris, *J. Amer. Chem. Soc.*, 1932, **54**, 2072.