Hetero-Cope Rearrangement *via* an Isolable Intermediate

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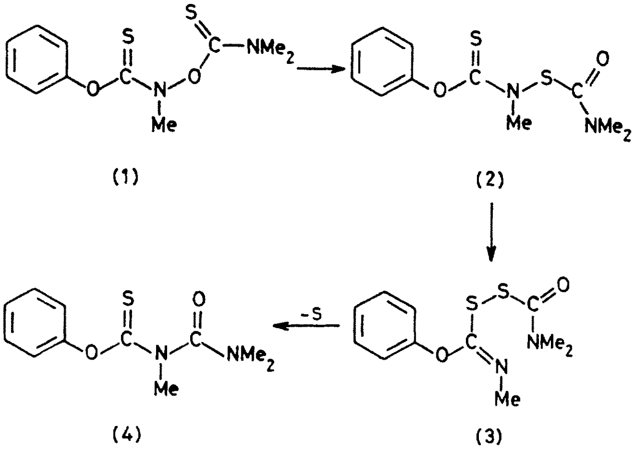
Summary The [3,3] rearrangement (**1**)–(**3**) takes place in methanol solution *via* the isolable intermediate (**2**).

Thermal molecular rearrangements in solution may proceed by a variety of mechanisms, the distinctions between ion-pair, radical-pair, and concerted processes being often difficult to determine.[1] In the hetero-Cope rearrangement,[2,3] reaction may in addition occur *via* a dipolar intermediate.[3] This report deals with an unusual [3,3] rearrangement which proceeds by way of a prior [1,3] shift.[4]

The hydroxylamine derivative (**1**) [m.p. 69—70 °C (decomp.); n.m.r. ($CDCl_3$) δ (NMe) 3·79 (3H), 3·39 (3H), and 3·24 (3H); i.r. (CCl_4) no absorption in the 1800—1600 cm^{-1} region] rearranges in methanol to the isomer (**2**) in 85—90% yield (n.m.r.) after 1 h at 25 °C, $<10\%$ of (**3**) being formed. Compound (**2**) [m.p. 114 °C (decomp.); n.m.r. ($CDCl_3$) δ (NMe) 3·69 (3H) and 2·95 (6H); i.r. (CCl_4) 1696s cm^{-1}] may be isolated in *ca.* 60% yield after two recrystallisations from cold ethanol. Pure (**2**) rearranges, however, during 4 h at 55 °C in methanol to the disulphide (**3**) [m.p. 85—86 °C (decomp.); n.m.r. ($CDCl_3$) δ (NMe) 3·18 (3H) and 3·06 (6H); i.r. (CCl_4) 1696s and 1668s cm^{-1}] which decomposes at this temperature to the stable urea derivative (**4**) [m.p. 100 °C; n.m.r. ($CDCl_3$) δ (NMe) 3·36 (3H) and 3·03 (6H); i.r. (CCl_4) 1707s cm^{-1}] with extrusion of molecular sulphur.

Pure (**3**) may be isolated with some difficulty by repeated recrystallisation in yields of *ca.* 30%; the actual yield in the conversion (**2**)–(**3**) is *ca.* 80%, as shown by the fact that the consecutive reactions (**2**)—(**4**) may be carried out in an overall yield of over 70% when (**3**) is not isolated.



Satisfactory elemental analyses were obtained for each of the four compounds described, and the structures were assigned on the basis of the n.m.r., i.r., u.v., and mass-spectral analyses.

The mechanisms of the three steps here reported are complex and will be discussed elsewhere. Essentially the same behaviour may be observed using other solvents, however, and the purpose of this communication is to draw attention to the surprising fact that the rearrangement (**1**)—(**3**) occurs only to a small extent (if at all) *via* a single concerted reaction, the step-wise route following consecutive [1,3] rearrangements being preferred.

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[1] C. Walling, H. P. Waits, J. Milovanovic, and C. G. Pappiaonnou, *J. Amer. Chem. Soc.*, 1970, **92**, 4927.

[2] E. Winterfeldt, *Topics Current Chem.*, 1970, **16** (1), 75.

[3] R. Gompper and W.-R. Ulrich, *Angew. Chem.*, 1976, **88**, 300.

[4] See W. B. Ankers, R. F. Hudson, and A. J. Lawson, *J.C.S. Perkin II*, 1974, 1826.