Competitive Cyclopropanation and Aromatization of an Intermediate of the Sommelet–Hauser Rearrangement

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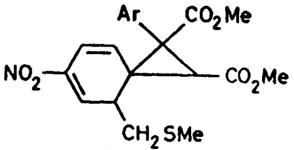
Summary The non-aromatic intermediate of the Sommelet–Hauser rearrangement of a stabilized methoxycarbonyl sulphur ylide gives not only the expected rearranged product, but also reacts with the starting ylide to give the corresponding cyclopropane.

THE Sommelet–Hauser rearrangement of aryl sulphonium ylides is a well known reaction.[1,2] The intermediate postulated for this reaction aromatizes when the *ortho* positions are free,[3] but to our knowledge such an intermediate has never been isolated or trapped. We describe here the cyclopropanation of the Sommelet–Hauser intermediate formed from the sulphur ylide (**1**; X = NO$_2$).[4]

The ylide (**1**) was stable in boiling anhydrous tetrahydrofuran but readily gave a mixture of the ester (**4**; X = NO$_2$) (m.p. 59 °C, yield 53%) and the cyclopropane (**5**) (m.p. 154 °C, yield 6%) in boiling methanol. As already suggested for other sulphur ylides,[1,5] a protic solvent such as methanol may favour the tautomeric form (**2**; X = NO$_2$) which is the only form able to give this 2,3 sigmatropic rearrangement.

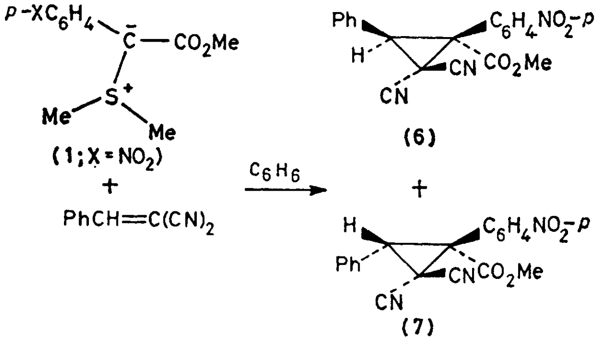
The structures of (**4**)[4] and (**5**) were assigned from their u.v., i.r., ^{1}H n.m.r., ^{13}C n.m.r., and mass spectra. Particularly significant were the i.r. and ^{1}H n.m.r. spectra of (**5**).

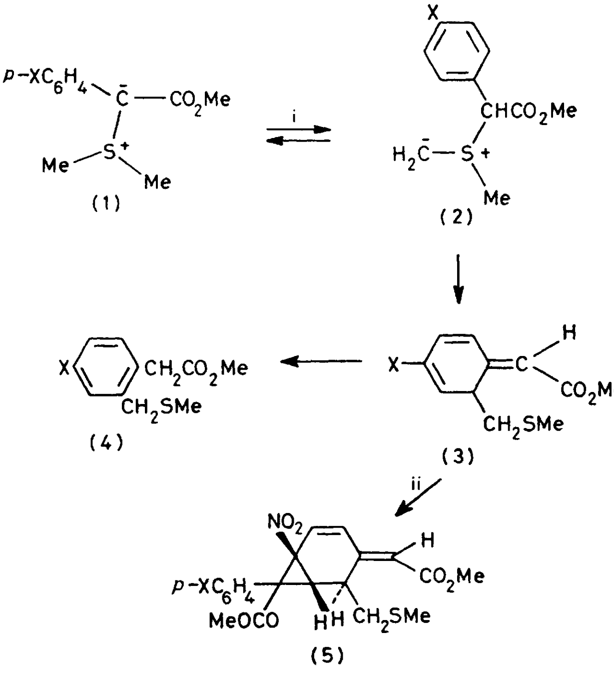


(**5′**)

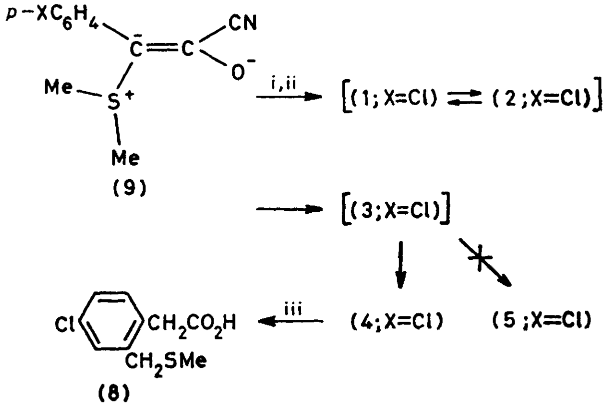
In agreement with the presence of a saturated and an unsaturated ester group, two strong ν_{CO} bands (1742 and 1706 cm^{-1}) were observed in the i.r. spectrum (Nujol) of (**5**),† and its n.m.r. spectrum (CDCl$_3$) showed δ 3·56 (s, 3H, OCH$_3$), 3·80 (s, 3H), 2·70 (middle of the AB part of an ABX system, 2H, SCH$_2$), 2·39 (s, 3H, SCH$_3$), 6·25 [d, 1H, CH (sp^2, cyclohexene)], 7·14 (d, 1H), 4·68 (middle of the X part of an ABX system, slightly broadened by a vicinal *trans* proton, 1H, C*H*–CH$_2$SMe), 4·06 [s slightly broadened by a vicinal *trans* proton, 1H, CH (cyclopropane)], 5·88 (s, 1H), 7·60 (d, 2H, Ar), and 8·20 (d, 2H). Only one isomer was detected from the ^{1}H n.m.r. spectrum of the crude product. As the two vicinal sp^3 cyclohexene protons showed a very low coupling constant, they must be *trans* to each other, as indicated in structure (**5**). The relative configurations of the other asymmetric carbons were not determined.

The structure of the cyclopropane (**5**) is best explained by an intermolecular reaction of the Sommelet–Hauser intermediate (**3**; X = NO$_2$) with the sulphur ylide (**1**; X = NO$_2$) (Scheme 1). Such an unusual reaction may be assisted by two favourable factors. On the one hand the intermediate (**3**) is a Michael acceptor activated by both the nitro and ester groups, and the ylide (**1**; X = NO$_2$) is a Michael donor which reacts readily, for instance, with 1,1-dicyano-2-phenylethene to give equal amounts of the two isomeric cyclopropanes (**6**) [m.p. 162 °C; i.r. (Nujol) 2251 and 1734 cm^{-1}; δ (CDCl$_3$) 3·82 (s, 3H), 4·14 (s, 1H), and 6·80—8·30 (m, 9H)] and (**7**) [incompletely purified, δ (CDCl$_3$) 3·62 (s, 3H) and 3·84 (s, 1H), δ$_{Ar}$ masked by the Ar of the isomer (**6**)]. On the other hand, the aromatization of the Sommelet–Hauser intermediate requires proton abstraction followed by reprotonation.[1] The reaction leading to (**4**) and (**5**) was carried out in the absence of an added base and so the lifetime of the intermediate should be increased and an intermolecular reaction could compete with the aromatization.





SCHEME 1. X = NO$_2$; i, MeOH, ii (**1**; X = NO$_2$).



SCHEME 2. i, CF$_3$CO$_2$H–MeOH, ii, NaOH, iii, HCl.

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† The u.v. spectra, λ_{max} = 280 nm, ϵ = 23 980, confirm also the structure of (**5**). We thank the referees for suggesting structure (**5**) rather than the isomeric (**5′**).

In an attempt to prepare the sulphur ylide (**1**; X = Cl) according to a previously described procedure,[4] we isolated only the rearranged product (**4**; X = Cl). In the presence of aqueous NaOH, (**4**) was hydrolysed the acid (**8**) (Scheme 2) [m.p. 104 °C; yield 79% from (**9**); i.r. (Nujol) 1692 and 3000—3400 cm^{-1}; δ ($CDCl_3$) 3·65 (s, 2H), 3·75 (s, 2H), 1·99 (s, 3H), and 7·20 (m, 3H)]. It is of interest that in this case no trace of the cyclopropane (**5**; X = Cl) was observed in the crude product by ^{1}H n.m.r. spectroscopy.

The higher activity of the ylide (**1**; X = Cl) compared with the ylide (**1**; X = NO_2) may be accounted for by a displacement toward the right of the equilibrium between the isomers (**1**) and (**2**) (Scheme 1).

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