

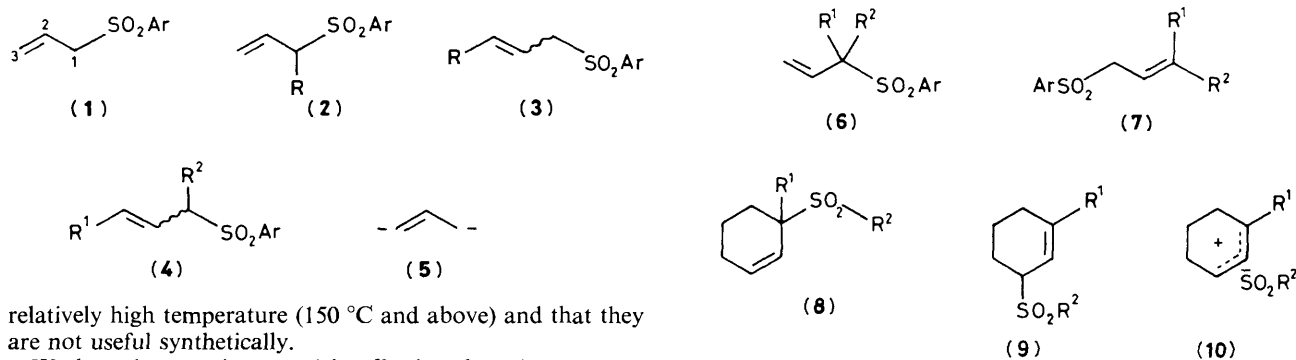
1,3-Rearrangements of Allylic Sulphones

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Three sets of conditions which promote the 1,3-rearrangement of certain allylic sulphones are described.

There have been scattered reports in the literature which indicate more¹ or less² directly that substituted allylic sulphones can undergo 1,3-rearrangement. However the implication is that such rearrangements occur thermally at



relatively high temperature (150 °C and above) and that they are not useful synthetically.

We have become interested in effecting the 1,3-rearrangement of allylic sulphones under controlled conditions since the possibility of performing metallation-alkylation, followed by 1,3-rearrangement, then a further metallation-alkylation [*i.e.* (1) → (2) → (3) → (4)], and finally regioselective reduction of the sulphone (4) would allow, *e.g.* allyl sulphone, to be used as a reagent corresponding to the allyl dianion synthon (5). The recent publication by Kocienski³ describing 1,3-rearrangement accompanying epoxidation of certain allylic sulphones bearing a substituent at C-2 on treatment with *m*-chloroperbenzoic acid in aqueous NaHCO₃ prompts us to report our observations.

We have found, depending on the constitution of the allylic sulphone, three types of conditions which can be used to promote 1,3-rearrangement.

Conditions (A), applicable to rearrangement of acyclic allylic sulphones (Ar = *p*-tolyl) such as (2, R = Me, PhCH₂, CH₂=CHCH₂, or Me₃Si) to the corresponding (3) and of (6, R¹ = R² = Me) and (6, R¹ = Me, R² = Me₃Si) to the corresponding (7), involve heating under reflux in CCl₄ containing (PhCO₂)₂ (5 mol %). Rearrangement is complete after 18 h and isomers (3) are obtained as (*E*)-(*Z*) mixtures (*ca.* 3:1) with the exception of (3, R = Me₃Si) where only the (*E*)-isomer was detected. The products (3) and (7) with the more substituted double bond are clearly more stable thermodynamically than their precursors, and we suggest a chain mechanism for the rearrangement involving addition-elimination of ArSO₂• radicals.

Conditions (B), applicable to rearrangement of cyclohexenyl sulphones (8, R² = *p*-tolyl; R¹ = Me, Et, or PhCH₂)† to their isomers (9), involve heating (100 °C; 8 h) in AcOH-H₂O (6:4 v/v). Under these conditions acyclic allylic sulphones of types (2) and (6) do not rearrange nor does (8, R² = *p*-tolyl, R¹ = ²H). We propose a mechanism involving

† These sulphones rearrange only very sluggishly under conditions (A).

a fairly tight ion-pair, *cf.* (10). Apparently the allylic cation must be both cyclic and have a secondary-tertiary substitution pattern. An ion-pair mechanism is supported by cross-over experiments involving rearrangement of (8, R² = *p*-tolyl, R¹ = Me) in the presence of PhSO₂Na. (8, R² = Bu^t, R¹ = Me) rearranges even more readily under solvolytic conditions, *i.e.* H₂O-tetrahydrofuran (1:1) under reflux or AcOH-H₂O (6:4) at 20 °C to give (9, R² = Bu^t, R¹ = Me).

Conditions (C) involve heating (100 °C; 8 h) the allylic sulphone in AcOH-H₂O (6:4) containing ArSO₂Na (up to 7 mol. equiv.). The acyclic sulphones (Ar = *p*-tolyl) of types (2) and (6) which are unaffected by heating in AcOH-H₂O in the absence of ArSO₂Na, undergo 1,3-rearrangement to (3) and (7) respectively; also (8, R² = *p*-tolyl, R¹ = ²H) is equilibrated (1:1 mixture) with (9, R² = *p*-tolyl, R¹ = ²H). We are hesitant at present to suggest a mechanism for the sulphinate induced rearrangement. Possibilities include (a) some sort of nucleophile assisted ion-pair process and (b) an S_{RN1} mechanism.^{4,5} However the reaction is not inhibited by *m*-dinitrobenzene, a known⁴ radical anion trap. It is possible that Kocienski's rearrangements³ induced by sodium *m*-chloroperbenzoate are related processes.

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