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1,3-Rearrangements of Allylic Sulphones

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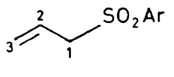
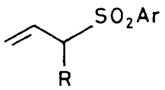
Three sets of conditions which promote the 1,3-rearrangement of certain allylic sulphones are described.

There have been scattered reports in the literature which indicate more[1] or less[2] directly that substituted allylic sulphones can undergo 1,3-rearrangement. However the implication is that such rearrangements occur thermally at



(**1**)



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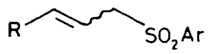

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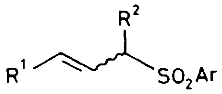

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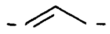

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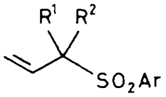

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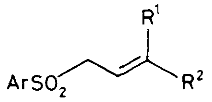

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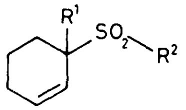
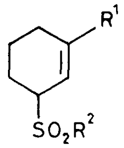
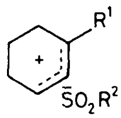


(**8**)



(**9**)



(**10**)

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 Kocienski[3] describing 1,3-rearrangement accompanying epoxidation of certain allylic sulphones bearing a substituent at C-2 on treatment with *m*-chloroperbenzoic acid in aqueous $NaHCO_3$ 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, $PhCH_2$, $CH_2{=}CHCH_2$, or Me_3Si) to the corresponding (**3**) and of (**6**, R^1 = R^2 = Me) and (**6**, R^1 = Me, R^2 = Me_3Si) to the corresponding (**7**), involve heating under reflux in CCl_4 containing $(PhCO_2)_2$ (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 = Me_3Si) 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 $ArSO_2\cdot$ radicals.

Conditions (B), applicable to rearrangement of cyclohexenyl sulphones (**8**, R^2 = *p*-tolyl; R^1 = Me, Et, or $PhCH_2$)† to their isomers (**9**), involve heating (100 °C; 8 h) in AcOH–H_2O (6:4 v/v). Under these conditions acyclic allylic sulphones of types (**2**) and (**6**) do not rearrange nor does (**8**, R^2 = *p*-tolyl, R^1 = ^2H). We propose a mechanism involving 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**, R^2 = *p*-tolyl, R^1 = Me) in the presence of $PhSO_2Na$. (**8**, R^2 = Bu^t, R^1 = Me) rearranges even more readily under solvolytic conditions, *i.e.* H_2O–tetrahydrofuran (1:1) under reflux or AcOH–H_2O (6:4) at 20 °C to give (**9**, R^2 = Bu^t, R^1 = Me).

Conditions (C) involve heating (100 °C; 8 h) the allylic sulphone in AcOH–H_2O (6:4) containing $ArSO_2Na$ (up to 7 mol. equiv.). The acyclic sulphones (Ar = *p*-tolyl) of types (**2**) and (**6**) which are unaffected by heating in AcOH–H_2O in the absence of $ArSO_2Na$, undergo 1,3-rearrangement to (**3**) and (**7**) respectively; also (**8**, R^2 = *p*-tolyl, R^1 = ^2H) is equilibrated (1:1 mixture) with (**9**, R^2 = *p*-tolyl, R^1 = ^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 $S_{RN}1$ mechanism.[4,5] However the reaction is not inhibited by *m*-dinitrobenzene, a known[4] radical anion trap. It is possible that Kocienski's rearrangements[3] induced by sodium *m*-chloroperbenzoate are related processes.

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

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