The Radical-induced Cyclisations of Some Unsaturated Allylic Sulphones

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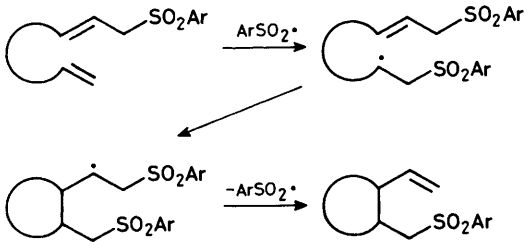
Conditions are described which promote the isomerisation of some suitably constituted unsaturated allylic sulphones to products derived apparently by a radical chain cyclisation mechanism.

Interest has burgeoned in recent years in the synthetic possibilities and mechanistic peculiarities of cyclisation reactions involving radicals.[1] We have recently described a 1,3-rearrangement of allylic sulphones, catalysed by dibenzoyl peroxide, which we believe occurs by an addition–elimination mechanism involving aryl sulphonyl radicals.[2] It seemed possible therefore that an appropriately constituted olefinic allylic sulphone might undergo cyclisation by a related chain process, as outlined in Scheme 1.

We now report examples of reactions which appear to occur in this way. The first successful attempts involved an allylic ether as the olefinic component. Thus compound (**2**), derived from the cyclohexenyl sulphone (**1**) by allylic halogenation and subsequent displacement (allyl alcohol, Et_3N), was converted into the bicyclic sulphone (**3**) (75%) (as a 5:2 mixture of stereoisomers) on treatment with dibenzoyl peroxide (5 mol %) in CCl_4 under reflux (3 h). The propynyl ether analogous to (**2**) similarly underwent ring closure to give the bicyclic vinyl sulphone (**4**) ($Z:E$ 10:1) in 74% yield.

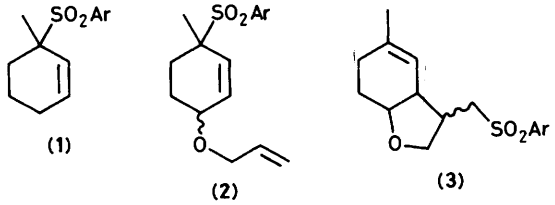
The possibility of initial 1,3-rearrangement of an allylic sulphone followed by cyclisation was investigated using



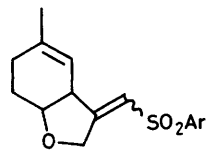
Scheme 1

olefinic allylic sulphones of type (**5**), which were obtained from simple allylic sulphones (**6**) *via* metallation (BuLi)–alkylation (pent-4-enyl bromide). Treatment of (**5a**) with $(PhCOO)_2$ (5 mol %) in CCl_4 (reflux; 3 h) gave (**7a**), as a mixture of two diastereoisomers (3:1), in 93% yield. When the reaction was monitored by n.m.r. spectroscopy, evidence for the intermediacy of (**8a**) was obtained. On prolonged treatment (24 h), the radical-catalysed addition of CCl_4 to (**7a**) to give (**9**) was observed.

Analogous results were obtained with the sulphones (**5b**), (**5c**), and (**5d**) giving cyclisation products (**7b**), (**7c**), and (**7d**) respectively. In the case of (**5b**), isomerisation–cyclisation occurred faster than for (**5a**) implying, possibly, that the

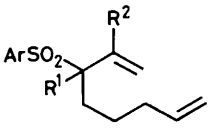


(1) (2) (3)



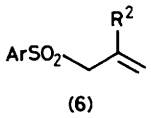
(4)

Ar = *p*-MeC_6H_4

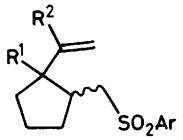


(5)

a; $R^1 = R^2 = H$
b; $R^1 = H$, $R^2 = Me$
c; $R^1 = Me$, $R^2 = H$
d; $R^1 = R^2 = Me$

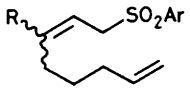


(6)



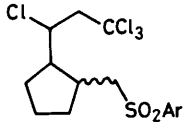
(7)

a; $R^1 = R^2 = H$
b; $R^1 = H$, $R^2 = Me$
c; $R^1 = Me$, $R^2 = H$
d; $R^1 = R^2 = Me$



(8)

a; R = H
c; R = Me



(9)

Ar = *p*-MeC_6H_4

methyl group (R^2) has a favourable influence on the radical addition steps. The successful cyclisation to (**7c**) indicates that quaternary carbon centres can be formed even though the cyclisation step would involve addition to the more substituted end of the double bond in (**8c**).

We are exploring the scope and potential of this route to vicinally disubstituted cyclopentanes where both substituents possess useful functionality for further synthetic elaboration.

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