

Intermolecular Carbon–Carbon Bond forming Reactions involving Allylic Sulphones

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Adducts (**3**) are formed in satisfactory yield from allylic sulphones (**2**) and monosubstituted alkenes (**1**) under free radical conditions provided that the X substituent in the sulphone is electron withdrawing.

The potential in organic synthesis of free radical reactions, particularly those leading to the formation of carbon–carbon bonds, has attracted much attention in recent years.¹ Our investigations have been concerned with free radical addition–elimination reactions of allylic sulphones, and we have

previously described 1,3-rearrangement reactions of allylic sulphones² and cyclisations of suitably constituted unsaturated allylic sulphones³ occurring *via* this type of process. The cyclisation reactions involve intramolecular interaction between a double bond and an allylic sulphone. We report

Table 1. The reactions of β -substituted allylic sulphones with vinyl acetate.

Sulphone (2)	Conditions ^a solvent/time (h)	Product	Yield/%
X = H	CCl ₄ /32	No adduct	—
X = Me	CCl ₄ /24	No adduct	—
X = SAr	CCl ₄ /14	No adduct	—
X = S(O)Ar	CDCl ₃ /32	No adduct	—
X = SO ₂ Ar	CDCl ₃ /32	(3) R = OCOMe, X = SO ₂ Ar	48
X = CO ₂ Me	CCl ₄ /6	(3) R = OCOMe, X = CO ₂ Me	66
X = CN	CDCl ₃ /32	(3) R = OCOMe, X = CN	77

^a All reactions carried out with BPO/heat.

Table 2. The reactions of sulphone (2) (X = CO₂Me) with alkenes.

Alkene (1)	Conditions ^a time/h	Product	Yield/%
R = OCOMe	6	(3) R = OCOMe, X = CO ₂ Me	66
R = n-C ₆ H ₁₃	12	(3) R = n-C ₆ H ₁₃ , X = CO ₂ Me	62
R = Ph	8	(3) R = Ph, X = CO ₂ Me	58
R = CO ₂ Me	8	(3) R = CO ₂ Me, X = CO ₂ Me	69
Isopropenyl acetate	16	No adduct	—
Cyclohexene	16	No adduct	—
Phenylacetylene	32	(4)	70 ^b

^aAll reactions carried out in CCl₄/BPO/heat. ^b Estimated. Pure material isolated for microanalysis.

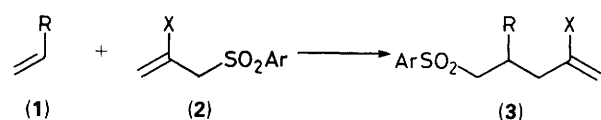
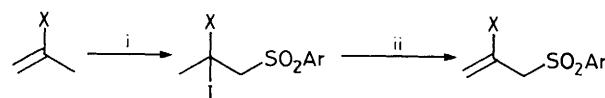
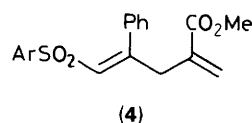
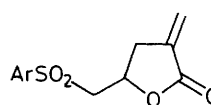
here results of investigations into analogous intermolecular processes of the type outlined in Scheme 1.†

Consideration of the normal influence of substituent effects on free radical reactions⁴ led to the expectation that the process was more likely to be successful when the R group of the alkene (1) was electron donating, and the X group of the allylic sulphone (2) was electron withdrawing: addition of an electrophilic sulphonyl radical⁵ should occur more readily to an electron rich alkene, and the resulting nucleophilic alkyl radical should add more readily to an electron deficient allylic sulphone. Allylic sulphones (2) in which the X group is electron withdrawing can be conveniently prepared from methacrylate derivatives by addition of toluene-*p*-sulphonyl iodide⁶ followed by base-induced dehydroiodination/isomerisation (Scheme 2).

We initially studied the reaction of sulphone (2) (X = CO₂Me) with vinyl acetate. Treatment of the sulphone (3 equiv.) and alkene (1 equiv.) with dibenzoyl peroxide (BPO) (5 mol%) in carbon tetrachloride under reflux (6 h) gave the adduct (3) (R = OCOMe, X = CO₂Me) in 66% yield.

The reactions of sulphones (2) with vinyl acetate were then studied in order to determine the role of the X group in influencing the success of the intermolecular process. The results of these studies are summarised in Table 1. As expected, adducts (3) were only formed in cases where the X group was electron withdrawing.

Sulphone (2) (X = CO₂Me) was used to compare the suitability of various alkenes in the intermolecular process. The results of these studies are summarised in Table 2. In all attempted cases, adducts (3) were isolated where the alkene (1) was monosubstituted, but adducts were not formed in cases where the alkene was disubstituted. The electronic influence of the R group in the alkene seems not to be as

**Scheme 1****Scheme 2.** Reagents and conditions: i, ArSO₂I, hv; ii, Et₃N.**(4)****(5)**

crucial to the success of the reaction as that of the X group in the allylic sulphone. However, since adduct formation is not successful with disubstituted alkenes, it appears that steric factors are important. Reaction of (2) (X = CO₂Me) with phenyl acetylene gave adduct (4) as a single isomer, the *Z* stereochemistry of which was confirmed in a nuclear Overhauser enhancement experiment.

The intermolecular addition process described here could potentially be used in synthesis for further elaboration starting from a compound with a terminal carbon-carbon multiple bond. The adduct (3) (R = OCOMe, X = CO₂Me), on treatment with catalytic amounts of toluene-*p*-sulphonic acid and methanol under reflux (6 h) in benzene, was converted into the α -methylene- γ -lactone (5) in 76% yield. The overall process (2) (X = CO₂Me) \rightarrow (5) represents a concise construction of this important lactone functionality. Previous examples of preparatively useful S_H2' reactions are cited in ref. 7.

We are continuing investigations into the scope of intermolecular free radical addition reactions of this type.

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† Throughout this paper Ar = *p*-tolyl.