Alkene Formation through Condensation of Phenylmethanesulphonyl Fluoride with Carbonyl Compounds

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Arylmethanesulphonyl fluorides condense with aromatic, aliphatic and conjugated aldehydes and ketones in the presence of potassium carbonate and a crown ether to give aryl-substituted alkenes in satisfactory to modest yields.

Alkanesulphonyl chlorides are prone to dissociate the chloride ion readily in basic milieu. A conspicuous example of this lability is the immediate formation of the benzylsulphonylsulphene–triethylamine adduct when phenylmethanesulphonyl chloride is treated with triethylamine at −40 or −50 °C.[1] However, recently Lee *et al.* revealed that the bonding of sulphonyl fluorides was different from that of the chlorides, from studies on nucleophilic substitution reactions.[2] Phenylmethanesulphonyl fluoride has markedly smaller ρ^{x} and ρ^{y} values compared with those for the chloride in reactions with aniline. This kinetic result prompted us to examine the possibility that a carbanion can be generated at the benzyl site

$$\underset{\mathbf{1}}{RCH_2SO_2F} + \underset{\mathbf{2}}{R^1COR^2} \xrightarrow{K_2CO_3} \underset{\mathbf{3}}{RCH=CR^1R^2}$$

1a: R = Ph
1b: R = p-C_6H_4
1c: R = p-MeC_6H_4
1d: R = H

Scheme 1

Table 1 Results for condensations[a] of alkanesulphonyl fluorides (RCH_2SO_2F)[b] with carbonyl compounds (R^1COR^2)[c]

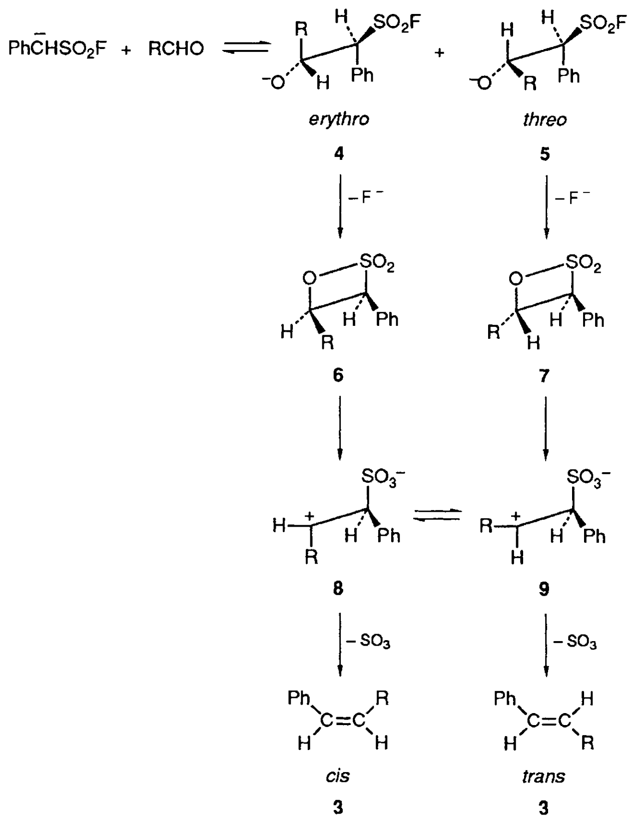
R^1	Yield(%)[d] (*cis/trans* ratio)[e]	R^1	Yield(%)[d] (*cis/trans* ratio)[e]
Ph	69 (1.2)	PhCH=CH	55 (~0)
p-ClC_6H_4	63 (1.4)	$PhCH_2$	54 (0.8)
p-MeC_6H_4	55 (0.6)	$(Me)_2CHCH_2$	48 (~0)
p-$NO_2C_6H_4$	78 (1.5)	Me[f]	40
p-$MeOC_6H_4$	42 (~0)	$(CH_2)_5$[m]	18
m-MeC_6H_4	56 (0.9)	Ph[g]	20
m-$NO_2C_6H_4$	84 (1.5)	p-ClC_6H_4[h]	72 (0.4)
m-$MeOC_6H_4$	66 (1.3)	p-MeC_6H_4[i]	68 (0.3)
o-MeC_6H_4	44 (0.6)	Ph[j]	57 (1.1)
o-$NO_2C_6H_4$	52 (0.2)	Ph[k]	70 (0.5)
α-Thienyl	53 (~0)	Ph[l]	51 (0.8)
α-Naphthyl	67 (0.5)		

[a] The reactions were carried out under the conditions described in the text unless otherwise state. [b] R = Ph unless otherwise state. [c] R^2 = H unless otherwise stated. [d] Isolated yields. [e] The ratios were determined using GLC. [f] Acetone was also used as the solvent; 12 h reflux; R^2 = Me. [g] R = H; the molar ratio of methanesulphonyl fluoride: potassium carbonate: benzaldehyde was 3 : 12 : 1, 10 h reflux. [h] R = p-MeC_6H_4. [i] R = p-ClC_6H_4. [j] The solvent used was toluene. [k,l] Without the catalyst; the solvent used was HMPA and DMSO, respectively. [m] $R^1R^2 = (CH_2)_5$.

of **1a** and may react with electrophiles before leaving the fluoride ion.† The present work deals with a new strategy for C=C bond formation by condensation of carbonyl compounds with the fluorosulphonylmethyl anion generated by treatment with potassium carbonate and a crown ether catalyst (Scheme 1). Particular attention has been given to the stereochemical course of the reaction together with factors influencing the reaction rate.

When an equimolar mixture of **1a**‡ and benzaldehyde in acetonitrile was treated with potassium carbonate (4 mol dm^{-3}) and dibenzo-18-crown-6 (0.05 mol dm^{-3}) and stirred at ambient temperature for three hours, stilbene **3a** was isolated in 69% yield, slightly enriched in the *cis*-isomer. Similarly **1a** condensed smoothly with other aromatic aldehydes to give the corresponding alkenes in satisfactory yields (see Table 1). The products can be simply separated by elution of the reaction mixture with benzene through a short column followed by recrystallisation or distillation. Stereoisomerisation of the alkenes was not observed during this experimental procedure and self-condensation of the starting carbonyl compounds was only a trace reaction under the conditions used.

It is noteworthy that in the condensation reactions with **1a** the aromatic aldehydes with electron-withdrawing substituents showed enhanced reaction rates compared with those with electron-donating groups. The stereochemistry of the stilbenes formed from the *para*- and *meta*-substituted aromatic aldehydes showed an increase in the proportion of *cis*-product by the use of more electrophilic carbonyl reactants. However, *ortho*-substituted benzaldehydes, thiophene-2-carbaldehyde, 1-naphthaldehyde and conjugated cinnamaldehyde, after reaction with **1a**, gave *trans*-isomers preferentially independently of the electronic nature of the substituents. The degree of stereoselectivity was also influenced by the nature of the reaction medium; reaction in toluene exhibited a similar stereochemical trend as in the case of acetonitrile. However interestingly, the use of aprotic polar solvents like hexamethylphosphoramide (HMPA) or dimethyl sulphoxide (DMSO) with **1a**, **1b** or **1c** yielded benzaldehydes with a larger proportion of the *trans*-isomer. For the reaction of **1a** with aliphatic aldehydes such as phenylacetaldehyde or isobutyraldehyde, somewhat stronger conditions are required to drive the condensations and reaction of **1a** with ketones gave alkenes in poor yields. The aliphatic methanesulphonyl fluoride **1d** condensed with benzaldehyde only slightly.



Scheme 2

A provisional condensation mechanism is shown in Scheme 2; carbanion attack at the carbonyl bonds forms the oxide ions **4** and **5**; the formation of the *erythro*-isomer **4** is favoured in which the more electrophilic aldehydes are more reactive. Both isomers close individually to give four-membered cyclic sultones **6** and **7**, which following dissociation leads to the equilibrium zwitterionic mixture (**8** and **9**). In the case of the reaction with aldehydes with electron-releasing substituents or conjugated ones, the equilibrium between the rotamers (**8** and **9**) will be established almost completely by stabilisation of the carbonium ion and in favour of **9**, which then gives the alkenes. Ion stabilisation will also be effected by the use of polar solvents. However, the zwitterions with electron-deficient groups dissociate rapidly to the alkenes as soon as they are formed; in these cases the stereochemistry of the initially formed intermediates **4** and **5** will determine the isomeric ratio of the final products.

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† Tokura and his coworkers have reported the reaction of **1a** and **d** with strong bases, phenyllithium and phenylmagnesium bromide to yield mainly $PhCH_2SO_2CHPhSO_2Ph$ or $PhCH_2SO_2Ph$, respectively; Y. Shirota, T. Nagai and N. Tokura, *Tetrahedron*, 1969, **25**, 3193.

‡ The sulphonyl fluorides **1a–d** were prepared according to the procedure by Tullock *et al.*[3]

We are investigating the mechanism and scope of this mild and practical method for alkene synthesis in more detail.

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