

A Simple New Synthesis of Furans by the Addition of Enolate Anions to Allenic Sulphonium Salts

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Summary Furans are obtained by addition of enolate ions to allenic sulphonium salts.

ADDITION of a variety of nucleophiles to allenic sulphonium salts has been reported.^{1,2} We now report a furan synthesis which involves this type of reaction.

Dimethylprop-2-ynylsulphonium bromide¹ (I) isomerises rapidly to the allene (II) in ethanol. Addition of an ethanolic solution of a β -ketoester, β -ketosulphone, or β -diketone (1 mol) and sodium ethoxide (1 mol) rapidly gives the furan (IV) in high yield (Table).

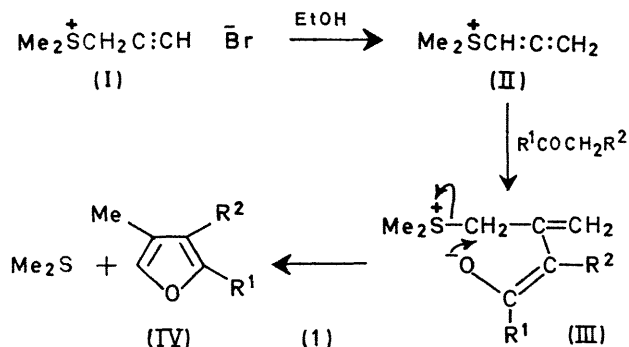
| Addend | Furan (IV) | Yield (%) |
|-------------------------------------------------------|----------------------------------------------------------------------------------------|-----------------------|
| MeCOCH ₂ CO ₂ Et | R ² =CO ₂ Et, R ¹ =Me | 86 |
| MeCOCH ₂ SO ₂ - <i>p</i> -Tolyl | R ² = <i>p</i> -Tolyl SO ₂ , R ¹ =Me | 78 |
| PhCOCH ₂ COPh | R ² =COPh, R ¹ =Ph | 72 |
| MeCOCH ₂ COMe | R ² =COMe, R ¹ =Me | 89 |
| PhCOCH ₂ COMe | { R ² =COPh, R ¹ =Me R ² =COMe, R ¹ =Ph | 83 (50:50 mixture) |

In a convenient modification of this simple method, the sulphonium salt may be preformed in acetonitrile and the other reagents added thereafter without isolation of the salt.

The mechanism is probably as shown in equation (1).

In accordance with this representation, the γ -substituted salt, $\text{Me}_2\text{S}^+\text{CH}=\text{C}=\text{CHPh}^- \text{Br}$, with sodioacetoacetate gives 2-methyl-4-benzyl-3-carbethoxyfuran (63%).

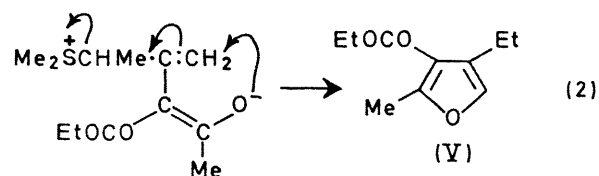
By contrast, treatment of the salt $\text{Me}_2\text{S}^+\text{C}(\text{Me})\text{:C}:\text{CH}_2^- \text{Br}$ with ethyl sodioacetoacetate gives the furan (V) indicating



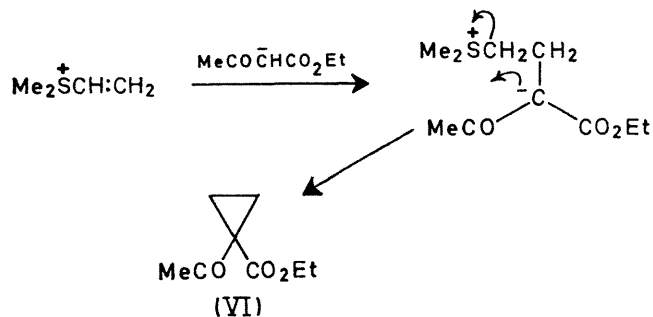
the operation of an intramolecular $\text{S}_\text{N}2'$ pathway [equation (2)].

Furans are not obtained when dimethylvinylsulphonium bromide (generated *in situ* from dimethyl-2-phenoxyethylsulphonium bromide and sodium ethoxide³) is used. With ethyl acetoacetate the cyclopropane (VI) (61%) was obtained in accordance with previous work on vinylsulphonium salts.⁴ Evidently, oxygen is the preferred

nucleophile at the allylic centre in the adduct (III) while



carbon is preferred for the saturated system developed in the vinyl sulphonium salt.⁵



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⁵ Cf. R. G. Pearson, *Survey of Progress in Chem.*, 1969, 5, 1.