A Sulphur Equivalent of the Perkow Reaction

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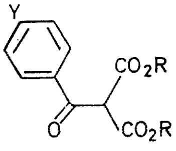
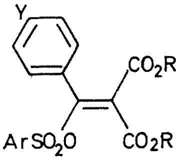
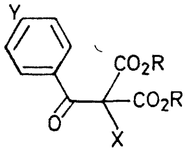
Summary The reaction of α-halogeno-acylmalonates with arsenesulphinate ion gives the corresponding enol sulphonate in a reaction which is, in effect, the sulphur equivalent of the Perkow reaction.

THE reaction[1] of the enolate of an acylmalonate (**1**) with an arenesulphonyl halide has generally given us poor yields of the enol sulphonates (**2**). We now find that the major by-product, with the t-butyl esters (**1**; R = Bu^t), is the α-halogenoketone (**3**; R = Bu^t, X = Br or Cl). Halogenation of enolate ions by sulphonyl halides is precedented.[2] The possibility of achieving the reverse reaction attracted our attention because sulphinate ion is known[3] to be capable of dehalogenating vicinal dibromides.


(1)


(2)


(3)

When the α-bromo-ketone (**3**; R = Et, X = Br, Y = Cl) was heated with sodium benzenesulphinate in wet t-butyl alcohol for 3 h, the acylmalonate (**1**; R = Et, Y = Cl) was isolated in 40% yield. Similarly, the α-chloro-ketone (**3**; R = Bu^t, X = Cl, Y = H) was converted into the acylmalonate (**1**; R = Bu^t, Y = H) with sodium toluene-*p*-sulphinate ion.

When these reactions were carried out in dry t-butyl alcohol, however, the enol sulphonates (**2**; R = Et, Y = Cl, Ar = Ph) and (**2**; R = Bu^t, Y = H, Ar = *p*-MeC$_6$H$_4$), respectively, were isolated (in 14% and 11% yields) as well as the acylmalonates (**1**). We have not yet been able to make this reaction preparatively useful. The best yield was obtained when the α-bromo-ketone (**3**; R = Bu^t, X = Br, Y = H) was heated with sodium benzenesulphinate in dry t-butyl alcohol for 5 h: a 40% yield of the enol sulphonate (**2**; R = Bu^t, Y = H, Ar = Ph) and 50% of recovered α-bromo-ketone were isolated.

This reaction, the conversion of an α-halogeno-ketone into an enol sulphonate is the first example of the sulphur equivalent of a well known reaction in phosphorus chemistry, the Perkow reaction.[4] Because we can isolate the intermediate malonate when the reaction is done in wet t-butyl alcohol, we can be fairly sure that the reaction is initiated by attack of sulphinate on bromine, followed by *O*-sulphonation by the resultant sulphonyl bromide. This is analogous to the mechanism of the reaction of triphenylphosphines with α-halogeno-ketones giving enol phosphonium salts[5] but it is not the mechanism of the Perkow reaction proper, in which trialkyl phosphites attack either at carbonyl carbon or at carbonyl oxygen to give enol phosphates.[5]

Having identified the by-product of the sulphonation reaction as the α-halogeno-ketone, we now know how to avoid the unwanted reaction. Reaction of the enolate of (**1**) with an arenesulphonic anhydride gives good yields of the enol sulphonate.

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