

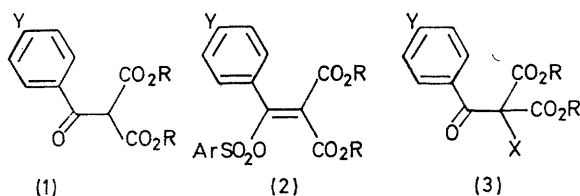
A Sulphur Equivalent of the Perkow Reaction

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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 reaction¹ 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 known³ to be capable of dehalogenating vicinal dibromides.



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*-MeC₆H₄), 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 salts⁵ 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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¹ I. Fleming and J. Harley-Mason, *J. Chem. Soc.*, 1963, 4771 and 4778; E. J. D. Brown and J. Harley-Mason, *J. Chem. Soc. (C)*, 1966, 1390; reviewed in J. Cymerman Craig, M. D. Bergenthal, I. Fleming, and J. Harley-Mason, *Angew. Chem. Internat. Edn.*, 1969, 8, 429.

² Houben-Weyl, "Methoden der organischen Chemie, Thieme Verlag, Stuttgart, 1962, V (3), p. 897.

³ R. Otto, *J. prakt. Chem.*, 1896, 53, 1; R. Otto and F. Stoffel, *Ber.*, 1897, 30, 1799.

⁴ F. W. Lichtenthaler, *Chem. Rev.*, 1961, 61, 607.

⁵ A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus," Elsevier, London, 1967, pp. 118–131.