Enol Elimination Reactions. Part IV.[1,2] Some Improvements to the Synthesis of Conjugated Acetylenic Acids

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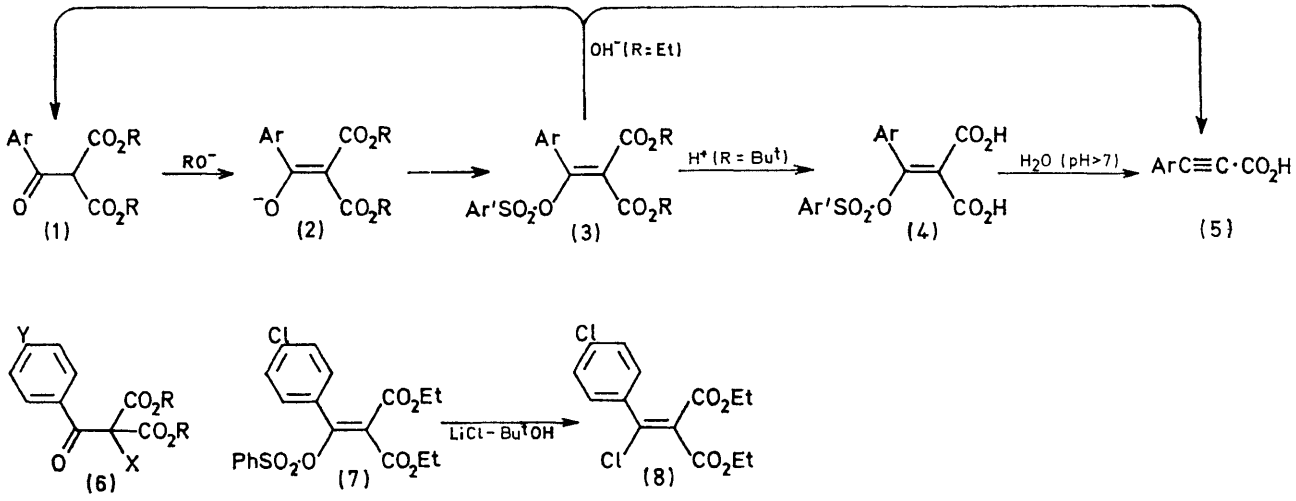
The reaction of the enolates (2) of acylmalonates with arenesulphonyl halides gives enol sulphonates in poor yield, partly because of competing halogenation which gives α-halogeno-ketones (6). The halogenation is reversible, and, because the reverse reaction leads to re-establishment of the original sulphonation conditions, it is possible to make enol sulphonates from the reaction of an α-halogeno-ketone with an arenesulphinate ion. This reaction is the sulphur equivalent of the Perkow reaction, but it is not preparatively useful. The halogenation reaction can be avoided altogether by using arenesulphonic anhydrides as sulphonating agents. The result is that the synthetic sequence: acylmalonate → enol sulphonate → acetylenic acid is now a useful one for the synthesis of conjugated acetylenic acids. For some purposes the use of t-butyl esters in place of ethyl esters has advantages.

In earlier papers on enol elimination reactions,[1,3-5] we have described the synthesis of the enol sulphonates (**3**; R = Et) of several acylmalonates (**1**; R = Et). Usually, we treated the enolate ion (**2**; R = Et) of the acylmalonate with an arenesulphonyl chloride in ethanol, but yields[3,4] averaged only about 40%. A small improvement, to an average yield of 46%, was made[1] by performing the reaction heterogeneously in dioxan. At the time, high yields were not important to us and we rather assumed that the by-products were the result of *C*-sulphonation. However, no such product ever crystallised. A second poor step in the sequence leading to the acetylenic acid (**5**) was the reaction of the enol sulphonate (**3**; R = Et) with alkali. Although the acetylenic acid was produced, it was always accompanied by the acylmalonate which had been our starting material. This product was the result of hydroxide ion attack at the conjugate position competing with ester hydrolysis.

We hoped to improve the yields of these reactions, and, in addition, for mechanistic studies described elsewhere,[6] we wanted the free acids of general formula (**4**). We reasoned that by using the t-butyl esters in place of the ethyl esters we might succeed in both our aims. The t-butyl groups could be removed with acid to give the diacids (**4**). In alkali, the diacids would undergo the usual decarboxylative elimination to give the acetylenic acids (**5**) in high yield, but in this case, with the carboxylate groups already ionised, there would be no competition from the substitution reaction, which leads back to the starting material. Secondly, the large t-butyl group should make the carbon atom of the enolate (**2**; R = Bu^t) more hindered than the oxygen atom, and we might therefore hope for more production of enol sulphonate and less *C*-sulphonation.



The di-t-butyl malonate (**1**; Ar = Ph, R = Bu^t) was prepared and the corresponding enolate (**2**) was generated with 1 equiv. of potassium t-butoxide in t-butyl alcohol. When we treated this with naphthalene-β-sulphonyl chloride, only 30% of the enol sulphonate (**3**; Ar = Ph, Ar' = β-$C_{10}H_7$, R = Bu^t) was obtained. In this case, however, we isolated a by-product (31% yield) which proved to be the chloro-compound (**6**; Y = H, X = Cl, R = Bu^t). There was no sign of *C*-sulphonation.

We tried several other arenesulphonyl chlorides, and

[1] Part III, E. J. D. Brown and J. Harley-Mason, *J. Chem. Soc.* (*C*), 1966, 1390.
[2] A small part of the present work was reported in preliminary form: I. Fleming and C. R. Owen, *Chem. Comm.*, 1970, 1402.
[3] I. Fleming and J. Harley-Mason, *J. Chem. Soc.*, 1963, 4771.
[4] I. Fleming and J. Harley-Mason, *J. Chem. Soc.*, 1963, 4778.
[5] Reviewed in J. Cymerman Craig, M. D. Bergenthal, I. Fleming, and J. Harley-Mason, *Angew. Chem. Internat. Edn.*, 1969, **8**, 429.
[6] I. Fleming and C. R. Owen, *J. Chem. Soc.* (*B*), in the press.

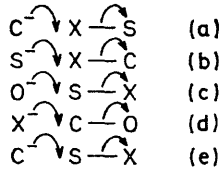
in each case obtained comparable yields of the chloro-compound (6) and the enol sulphonate (3; Ar = Ph, R = Bu^t, Ar′ = *p*-MeC_6H_4, *p*-BrC_6H_4, or *p*-$NO_2C_6H_4$). With toluene-*p*-sulphonyl bromide in place of the chloride, the corresponding bromo-derivative (6; R = Bu^t, Y = H, X = Br) was obtained in 30% yield, but this time there was little (8%) of the enol sulphonate (3; Ar = Ph, R = Bu^t, Ar′ = *p*-MeC_6H_4). When we tried diethyl esters in place of the di-t-butyl esters, we did not observe chlorination (although about 3% of diethyl chloromalonate was isolated, indicating that some *C*-chlorination had taken place), but the reaction of a diethyl ester (2; R = Et, Ar = *p*-ClC_6H_4) with benzenesulphonyl bromide gave the bromo-compound (6; R = Et, Y = Cl, X = Br) in 27% yield, along with 4% of the enol sulphonate.

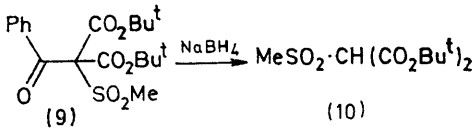
The action of arenesulphonyl halides as *C*-halogenating agents has precedent in the reaction [7-9] of β-keto-ester anions with sulphonyl halides. It seemed likely that the reverse reaction would be easy, since dehalogenation of vicinal dibromides by sulphinate ion was known.[10] If the reverse reaction could be achieved, it would generate our starting materials. It was therefore possible that the yields of enol sulphonates could be enhanced simply by heating the original sulphonation mixture for longer periods.

When we refluxed the bromo-ketone (6; R = Et, X = Br, Y = Cl) with sodium benzenesulphinate for 3 hr. in t-butyl alcohol in the presence of water, debromination occurred to give the acylmalonate (1; R = Et, Ar = *p*-ClC_6H_4). When we repeated the reaction in anhydrous t-butyl alcohol, we again obtained the acylmalonate (11%), but in addition we isolated the enol sulphonate (3; Ar = *p*-ClC_6H_4, Ar′ = Ph, R = Et) (14%). This reaction, the conversion of an α-halogeno-ketone into an enol sulphonate, is the first example to be reported of the sulphur equivalent of the Perkow reaction. Because we can isolate the intermediate malonate when the reaction is done in wet t-butyl alcohol, we infer that the reaction is initiated by attack of sulphinate on the bromine atom, 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,[11] but it is not the mechanism of the Perkow reaction proper, in which trialkyl phosphites attack either at carbonyl carbon or carbonyl oxygen atoms to give enol phosphates.[11]

In the reaction in dry t-butyl alcohol, the only other product was unchanged α-bromo-ketone. We therefore hoped that use of longer reflux times would increase the yields. This was not the case, and we have not yet been able to make the reaction preparatively useful. The best yield was obtained with the di-t-butyl ester (6; X = Br, Y = H, R = Bu^t); the reaction was very clean: after 5 hr. under reflux a 40% yield of the sulphonate and 50% yield of recovered (6) was obtained. With a chloro-ketone (6; X = Cl, Y = H, R = Bu^t) and toluene-*p*-sulphinate, only a low yield (11%) of the enol sulphonate was obtained, along with the acylmalonate (1; Ar = Ph, R = Bu^t) (30%), even after 2 days under reflux in dry t-butyl alcohol.

One possible cause of the failure to increase the yields is a subsequent reaction of the enol sulphonate with the halide ion now in the solution. For example, when the enol sulphonate (7) was refluxed in t-butyl alcohol with lithium chloride, it gave the vinyl chloride (8). However, this addition–elimination reaction is not general under these conditions; a bromide ion does not seem to displace sulphonate so easily, and the t-butyl esters corresponding to (7) are also less reactive. We would nevertheless like to draw attention to the multifarious kinds of displacement reactions which we have observed in the foregoing experiments: (*a*) displacement of sulphinate by attack of carbanion on halogen, (*b*) displacement of enolate ion by attack of sulphinate on halogen, (*c*) displacement of halide ion by attack of oxyanion on sulphur, and (*d*) displacement of sulphonate by attack of halide on carbon. A final case, (*e*) displacement of halide ion by attack of carbanion on sulphur, was the only example of *C*-sulphonation we observed. When we treated the enolate (2; Ar = Ph, R = Bu^t) with methanesulphonyl chloride in t-butyl alcohol, we obtained the sulphone (9). The structure of this compound was confirmed by reducing it with sodium borohydride; under these conditions, the first-formed alcohol underwent a reverse aldol-type of reaction to give the sulphonylmalonate (10).





(9) (10)

Having failed to obtain good yields of enol sulphonates from Perkow-like reactions, we tried sulphonic anhydrides as sulphonating agents which would not have competing halogenation. These were uniformly successful, and we recommend their use in the preparation of the enol sulphonates of readily enolised ketones. For reasons which we have not yet fathomed, the reaction of the enolates (2) with arenesulphonic anhydrides in t-

[7] E. v. Meyer and T. v. Findeisen, *J. prakt. Chem.*, 1902, [2], **65**, 529.
[8] J. W. Bruhl, *Ber.*, 1902, **35**, 4113; R. Truchet, *Ann. chim.* (*France*), 1931, **16**, 309.
[9] F. B. LaForge and S. B. Soloway, *J. Amer. Chem. Soc.*, 1947, **69**, 2934.
[10] R. Otto, *J. prakt. Chem.*, 1896, **53**, 1; R. Otto and F. Stoffel, *Ber.*, 1897, **30**, 1799.
[11] A. J. Kirby and S. G. Warren, ' The Organic Chemistry of Phosphorus,' Elsevier, London, 1967, pp. 118—131.

butyl alcohol always gives about 10% unchanged acylmalonate (1). However, the effective yield is generally about 85% with both diethyl and di-t-butyl esters, and this under conditions which are not necessarily optimum.

The next step in the synthetic sequence was the removal of the t-butyl groups from the enol sulphonates (3; R = Bu^t). This proved to be easy with toluene-*p*-sulphonic acid in boiling benzene for 1 hr., and, in one case only, in neat trifluoroacetic acid at room temperature for 2·5 min. The yields were unpredictable, and in the range 40—78%. Although it is possible that conditions which would give a high yield could be found for any individual case, they would be different for each compound and would be partly dependent on the ease with which the diacids (4) crystallised from the hot benzene. We already know, from work described in Part III,[3] that heating the diacids (4) under acidic conditions leads to monodecarboxylation without elimination. We have also found that in the trifluoroacetic acid case (with Ar = Ph, and Ar′ = β-$C_{10}H_7$) the ester 'hydrolysis' is accompanied by formation of naphthalene-β-sulphonic anhydride. In both solvents, then, removal of the ester group was not much faster than other reactions, and we were therefore pessimistic about the possibility of improvement in the yields. This route did, nevertheless, provide us with all the diacids (4) used in the kinetic work.

In aqueous alkali the decarboxylative elimination reaction of these acids is essentially quantitative; this route to the acetylenic acids (5) is therefore good and is less than satisfactory only in the step in which the t-butyl ester groups are removed. In terms of overall yield, however, the original route, involving use of alkali on the diethyl esters (3; R = Et), is still the best. Although the reaction gives unchanged acylmalonate, it is clean, and the effective yield of acid (5) is high. As a result of the improvement in the sulphonation step already described, the overall yield in the sequence (1) ⟶ (5) can now be expected to be about 80% based on starting material consumed in both steps. With further work in any individual case, this should be improved upon; we now claim, therefore, that this route to acetylenic acids (5) is preparatively useful, provided, of course, that the group Ar is one which permits the decarboxylative elimination reaction to take place. As a result of our earlier exploratory work, and particularly of our recent kinetic study,[6] we deduce that the decarboxylative elimination will take place whenever the group occupying the position Ar in (3) is as good as, or better than, a *p*-nitrophenyl group in supporting positive charge on an adjacent carbon atom.

The decarboxylative elimination from the diethyl esters has to be done in a mixed solvent such as aqueous dioxan, and in dilute solution, which leads to cumbersome operations if the scale is large. The decarboxylative elimination from compounds (4) does not need the dioxan and is therefore easily done in more concentrated solution in aqueous alkali. Thus in some cases it may be that the use of the t-butyl esters in place of the ethyl esters will be advantageous, especially if the removal of the t-butyl group is relatively smooth, if the sulphonation step is relatively poor, and if large quantities are to be handled.

[12] D. S. Breslow, F. Baumgarten, and C. R. Hauser, *J. Amer. Chem. Soc.*, 1944, **66**, 1288.

EXPERIMENTAL

Acylmalonates (1).—Diethyl benzoylmalonates were prepared as described earlier.[3] Di-t-butyl benzoylmalonates were prepared by the method of Breslow and his coworkers [12] except that the product was purified and characterised. Acidification of the reaction mixture, extraction with ether, washing with sodium hydrogen carbonate solution, and concentration *in vacuo* gave the acylmalonates; the yield was usually about 80%. The following acylmalonates were prepared by this method: *di-t-butyl benzoylmalonate*, m.p. 73—75° (Found: C, 67·2; H, 7·25. $C_{18}H_{24}O_4$ requires C, 67·45; H, 7·55%), $\nu_{max.}$ (KBr) 2800—3050m, 1750s, 1730s, and 1690s cm.$^{-1}$, $\lambda_{max.}$ (EtOH) 247 and 280 nm. (ε 13,110 and 2310), τ (CCl_4) 2·2 (5H, m), 5·17 (0·8H, s), and 8·45, 8·59, and 8·68 (18H, s); *di-t-butyl* p-*methoxybenzoylmalonate*, m.p. 114·5—115·5° (Found: C, 65·2; H, 7·5. $C_{19}H_{26}O_6$ requires C, 65·05; H, 7·5%); *di-t-butyl* p-*methylbenzoylmalonate*, m.p. 80—81° (Found: C, 68·5; H, 7·9. $C_{19}H_{26}O_5$ requires C, 68·3; H, 7·8%); *di-t-butyl* p-*fluorobenzoylmalonate*, m.p. 84—86° (Found: C, 64·05; H, 6·9. $C_{18}H_{23}FO_5$ requires C, 63·9; H, 6·8%); *di-t-butyl* p-*phenylbenzoylmalonate*, m.p. 105—107° (Found: C, 72·9; H, 8·35. $C_{24}H_{28}O_5$ requires C, 72·7; H, 8·35%); *di-t-butyl* p-*chlorobenzoylmalonate*, m.p. 103—104° (Found: C, 60·95; H, 6·35; Cl, 9·85. $C_{18}H_{23}ClO_5$ requires, C, 60·95; H, 6·5; Cl, 10·0%); *di-t-butyl* 3,4-*dichlorobenzoylmalonate*, m.p. 80—81·5° (Found: C, 55·7; H, 5·95. $C_{18}H_{22}Cl_2O_5$ requires C, 55·5; H, 5·7%); and *di-t-butyl* p-*nitrobenzoylmalonate*, m.p. 104—106° (Found: C, 59·0; H, 6·3; N, 3·85. $C_{18}H_{23}NO_7$ requires C, 59·15; H, 6·35; N, 3·85%).

Enol Sulphonates (3).—The benzoylmalonate (1) (25 mmoles) was added to a stirred solution of potassium (25 mmoles) in t-butyl alcohol (150 ml.). The arenesulphonic anhydride [13] (27·5 mmoles) was added and the mixture was heated under reflux for 2 hr. The solvent was removed *in vacuo*, and the residue was shaken with ether and dilute sodium hydroxide solution. The aqueous layer yielded unchanged benzoylmalonate (*ca.* 10%), which could be recovered after acidification. The ether layer was dried (Na_2SO_4) and evaporated, and the residue of enol sulphonate was crystallised from ethanol. The yield was usually about 75% (effectively 83%). The following enol sulphonates were prepared by this method: 1-*benzoyl*-2,2-*di-t-butoxycarbonylvinyl naphthalene*-β-*sulphonate*, m.p. 137—138° (Found: C, 66·1; H, 6·0. $C_{28}H_{30}O_7S$ requires C, 65·9; H, 5·9%), $\nu_{max.}$ (KBr) 1725s, 1700s, 1642m, 1590w, 1575w, 1385s, and 1185s cm.$^{-1}$, $\lambda_{max.}$ (EtOH) 233, 267, 313, and 329 nm. (ε 67,400, 14,020, 1308, and 1370), τ 2·4 (12H, m), and 8·45 and 8·75 (18H, s); 1-p-*methoxyphenyl*-2,2-*di-t-butoxycarbonylvinyl naphthalene*-β-*sulphonate*, m.p. 139—140° (Found: C, 64·3; H, 5·9. $C_{29}H_{32}O_8S$ requires C, 64·45; H, 6·0%); 2,2-*di-t-butoxycarbonyl*-1-p-*tolylvinyl naphthalene*-β-*sulphonate*, m.p. 138—139° (Found: C, 66·4; H, 5·8. $C_{29}H_{32}O_7S$ requires C, 66·4; H, 6·1%); 1-p-*fluorophenyl*-2,2-*di-t-butoxycarbonylvinyl naphthalene*-β-*sulphonate*, m.p. 132—134°

[13] V. O. Lukashevitch, *Doklady Akad. Nauk S.S.S.R.*, 1957, **114**, 1025 (*Chem. Abs.*, 1958, **52**, 3717e).

(Found: C, 63·6; H, 5·7. $C_{28}H_{29}FO_7S$ requires C, 63·6; H, 5·5%); 1-*biphenyl-4-yl*-2,2-*di-t-butoxycarbonylvinyl naphthalene*-β-*sulphonate*, m.p. 130—132° (Found: C, 69·7; H, 6·05. $C_{34}H_{34}O_7S$ requires C, 69·6; H, 5·8%); 1-p-*chlorophenyl*-2,2-*di-t-butoxycarbonylvinyl naphthalene*-β-*sulphonate*, m.p. 135·5—136° (Found: C, 61·9; H, 5·3; Cl, 6·75. $C_{28}H_{29}ClO_7S$ requires C, 61·7; H, 5·3; Cl, 6·5%); 1-(3,4-*dichlorophenyl*)-2,2-*di-t-butoxycarbonylvinyl naphthalene*-β-*sulphonate*, m.p. 120·5—121·5° (Found: C, 58·1; H, 5·0. $C_{28}H_{28}Cl_2O_7S$ requires C, 58·0; H, 4·9%); 1-p-*nitrophenyl*-2,2-*di-t-butoxycarbonylvinyl naphthalene*-β-*sulphonate*, m.p. 141·5—142° (Found: C, 60·5; H, 5·4; N, 2·2. $C_{28}H_{29}NO_9S$ requires C, 60·5; H, 5·3; N, 2·5%); 2,2-*di-t-butoxycarbonyl*-1-p-*tolylvinyl benzenesulphonate*, m.p. 129·5—130·5° (Found: C, 63·5; H, 6·55. $C_{25}H_{30}O_7S$ requires C, 63·3; H, 6·3%); 2,2-*di-t-butoxycarbonyl*-1-p-*tolylvinyl toluene*-p-*sulphonate*, m.p. 103·5—104·5° (Found: C, 64·0; H, 6·45. $C_{26}H_{32}O_7S$ requires C, 63·9; H, 6·55%); 2,2-*di-t-butoxycarbonyl*-1-p-*tolylvinyl* p-*nitrobenzenesulphonate*, m.p. 123·5—124·5° (Found: C, 58·05; H, 5·6; N, 2·7. $C_{25}H_{29}NO_9S$ requires C, 57·8; H, 5·6; N, 2·7%); and 1-p-*methoxyphenyl*-2,2-*di-t-butoxycarbonylvinyl benzenesulphonate*, m.p. 124—125° (Found: C, 61·45; H, 5·95. $C_{25}H_{30}O_8S$ requires C, 61·2; H, 6·1%).

Decarboxylative Elimination.—The hydrolysis and concurrent decarboxylative elimination of the diethyl esters (3; R = Et) was carried out as described earlier;[3] the yields of the acetylenic acids (5) were between 70 and 90% (for *p*-substituents with $\sigma^+ \leqslant 0{\cdot}114$). Unchanged benzoylmalonates (1) usually made up most of the remainder, the effective yield being at least 95%.

The Dicarboxylic Acids (4).—The enol sulphonates (3; R = Bu^t) (2 mmoles) were heated under reflux in benzene (100 ml.) with toluene-*p*-sulphonic acid (100 mg.) for 1 hr. The diacids (4) crystallised directly, or on cooling, or on the addition of light petroleum (b.p. 30—40°). They were purified by dissolving them in ether and adding light petroleum (b.p. 30—40°). Some of them retained solvent of crystallisation, but all were dried at 50° over phosphorus pentoxide and paraffin wax at 0·2 Torr for 2 days. The following acids were prepared by this method: 2,2-*dicarboxy*-1-*phenylvinyl naphthalene*-β-*sulphonate*, m.p. 105—105·5° (decomp.) [from chloroform–light petroleum (b.p. 60—80°)] (Found: C, 60·1; H, 3·7. $C_{20}H_{14}O_7S$ requires C, 60·3; H, 3·5%), $\nu_{max.}$ (KBr) 3200—2600m, 1707s, 1672s, 1632m, 1594w, 1502w, 1385m, and 1182s cm.$^{-1}$, $\lambda_{max.}$ (EtOH) 232, 268, and 329 nm. (ε 67,200, 13,700, and 1460), $\lambda_{infl.}$ 313 nm. (ε 1540); 2,2-*dicarboxy*-1-p-*methoxyphenylvinyl naphthalene*-β-*sulphonate*, m.p. 115—116° (decomp.) [from ether–light petroleum (b.p. 30—40°)] (Found: C, 59·0; H, 3·9. $C_{21}H_{16}O_8S$ requires C, 58·9; H, 3·8%); 2,2-*dicarboxy*-1-p-*methoxyphenylvinyl benzenesulphonate*, m.p. 117—118° (decomp.) [from ether–light petroleum (b.p. 60—80°) (Found: C, 54·2; H, 4·0. $C_{17}H_{14}O_8S$ requires C, 54·0; H, 3·7%); 2,2-*dicarboxy*-1-p-*methoxyphenylvinyl toluene*-p-*sulphonate*, m.p. 113—115° (decomp.) [from ether–light petroleum (b.p. 60—80°)] (Found: C, 54·8; H, 4·2. $C_{18}H_{16}O_8S$ requires C, 55·1; H, 4·1%); 2,2-*dicarboxy*-1-p-*nitrophenylvinyl naphthalene*-β-*sulphonate*, m.p. 115—116° (decomp.) [from ether–light petroleum (b.p. 30—40°)] (Found: C, 51·9; H, 3·2; N, 3·4. $C_{20}H_{13}NO_9S,H_2O$ requires C, 52·1; H, 3·2; N, 3·1%); 2,2-*dicarboxy*-1-p-*chlorophenylvinyl naphthalene*-β-*sulphonate*, m.p. 112—113° (decomp.) [from ether–light petroleum (b.p. 30—40°)] (Found: C, 55·6; H, 3·1. $C_{20}H_{13}ClO_7S$ requires C, 55·5; H, 3·0%); 2,2-*dicarboxy*-1-p-*tolylvinyl naphthalene*-β-*sulphonate*, m.p. 129—130° (decomp.) [from ether–light petroleum (b.p. 60—80°)] (Found: C, 60·9; H, 4·0. $C_{21}H_{16}O_7S$ requires C, 61·1; H, 3·9%); 2,2-*dicarboxy*-1-p-*tolylvinyl benzenesulphonate*, m.p. 106—107° (decomp.) (from benzene) (Found: C, 56·4; H, 4·1. $C_{17}H_{14}O_7S$ requires C, 56·4; H, 3·9%); 2,2-*dicarboxy*-1-p-*tolylvinyl toluene*-p-*sulphonate*, m.p. 106·5—108° (decomp.) (from benzene) (Found: C, 57·5; H, 4·5. $C_{18}H_{16}O_7S$ requires C, 57·4; H, 4·3%); 2,2-*dicarboxy*-1-p-*tolylvinyl* p-*nitrobenzenesulphonate*, m.p. 105—106° (decomp.) [from ether–light petroleum (b.p. 60—80°)] (Found: C, 48·1; H, 3·7; N, 3·0. $C_{17}H_{13}NO_9S,H_2O$ requires C, 48·0; H, 3·5; H, 3·3%); 2,2-*dicarboxy*-1-p-*fluorophenylvinyl naphthalene*-β-*sulphonate*, m.p. 110—112° (decomp.) [from ether–light petroleum (b.p. 30—40°)] (Found: C, 57·6; H, 3·5. $C_{20}H_{13}FO_7S$ requires C, 57·7; H, 3·2%); 2,2-*dicarboxy*-1-*biphenyl*-4-*ylvinyl naphthalene*-β-*sulphonate*, m.p. 87·5—89° (decomp.) (from benzene) (Found: C, 69·8; H, 4·3. $C_{26}H_{18}O_7S,C_6H_6$ requires C, 69·6; H, 4·3%); and 2,2-*dicarboxy*-1-(3,4-*dichlorophenyl*)-*vinyl naphthalene*-β-*sulphonate*, m.p. 88—90° (decomp.) (from benzene) (Found: C, 51·2; H, 2·8. $C_{20}H_{12}Cl_2O_7S$ requires C, 51·4; H, 2·6%).

The first of these acids was also prepared by treating the enol sulphonate (3; R = Bu^t, Ar = Ph, Ar′ = β-$C_{10}H_7$) (0·25 g.) with trifluoroacetic acid (1·5 ml.) at room temperature for 2 min. The solution was poured into water; the acid (0·17 g., 91%) crystallised slowly. If the solution in trifluoroacetic acid was kept for 30 min., naphthalene-β-sulphonic anhydride (m.p. 185°; lit.,[13] 185—190°) precipitated. Although this method gave a good yield of the dicarboxylic acid in this case, it proved to be generally less reliable than the method using toluene-*p*-sulphonic acid in benzene.

The Acetylenic Acids (5) *from the Dicarboxylic Acids* (4).—The dicarboxylic acid (4) (2 mmoles) was dissolved in a saturated solution of sodium hydrogen carbonate (10 ml.) and kept at room temperature for between 3 min. (Ar = *p*-MeO·C_6H_4) and 10 months (Ar = *p*-O_2N·C_6H_4), the times being based on our knowledge of the rates.[6] The acetylenic acid crystallised upon acidification in essentially quantitative yield (for $\sigma^+ \leqslant 0{\cdot}114$). The m.p.s were in agreement with the values reported and all the acids had strong i.r. bands in the acetylene region. The only new acetylenic acid was biphenyl-4-ylpropiolic acid, m.p. 175—176° (decomp.) (from benzene) (Found: C, 80·9; H, 4·75. $C_{15}H_{10}O_2$ requires C, 81·1; H, 4·5%), $\nu_{max.}$ (KBr) 3200—2750m, 2224, 2206s, and 1670s cm.$^{-1}$, $\lambda_{max.}$ (EtOH) 289 nm. (ε 30,500). For yields in 3,4-dichloro- and *p*-nitro- cases, see ref. 6.

The Reaction of the Enolates (2) with *Arenesulphonyl Halides*.—The benzoylmalonate (1) (25 mmoles) was added to a stirred solution of potassium (25 mmoles) in t-butyl alcohol (150 ml.). The arenesulphonyl halide (25 mmoles) was added and the mixture was heated under reflux for 2 hr. The solvent was removed *in vacuo* and the residue was shaken with ether and dilute sodium hydroxide solution. The ether layer was dried (Na_2SO_4) and evaporated, and the residue was chromatographed on silica gel, with light petroleum (b.p. 30—40°) containing ethyl acetate (3%) as eluant. The first compound eluted was the α-halogenomalonate and the second the enol sulphonate. All the crystalline products were recrystallised from ethanol. Di-t-butyl benzoylmalonate was treated by this method with each of the following sulphonyl halides.

(*a*) Naphthalene-β-sulphonyl chloride gave *di-t-butyl α-benzoyl-α-chloromalonate* (31%), m.p. 138° (Found: C, 61·1; H, 6·35; Cl, 10·25. $C_{18}H_{23}ClO_5$ requires C, 60·9; H, 6·5; Cl, 10·0%), $\nu_{max.}$ (KBr) 1762s, 1737s, 1680s, 1597m, and 1580m cm.$^{-1}$, $\lambda_{max.}$ (EtOH) 255 nm. (ε 11,500), $\lambda_{infl.}$ 290 nm. (ε 1162), τ (CCl_4) 2·1 (2H, m), 2·6 (3H, m), and 8·5 (18H, s), *m/e* 300 and 298 (2%, $M - C_4H_8$), and 105 (100%, PhCO); and the enol sulphonate (30%) (already described).

(*b*) Toluene-*p*-sulphonyl chloride gave the same chloromalonate (25%) and the enol sulphonate (31%), *1-phenyl-2,2-di-t-butoxycarbonylvinyl toluene*-p-*sulphonate*, m.p. 114—115° (Found: C, 63·4; H, 6·3. $C_{25}H_{30}O_7S$ requires C, 63·3; H, 6·4%).

(*c*) *p*-Bromobenzenesulphonyl chloride gave the same chloromalonate (30%) and *1-phenyl-2,2-di-t-butoxycarbonylvinyl* p-*bromobenzenesulphonate* (30%), m.p. 127·5—128° (Found: C, 53·25; H, 5·3. $C_{24}H_{27}BrO_7S$ requires C, 53·4; H, 5·05%).

(*d*) *p*-Nitrobenzenesulphonyl chloride gave the same chloromalonate (25%) and *1-phenyl-2,2-di-t-butoxycarbonylvinyl* p-*nitrobenzenesulphonate* (18%), m.p. 121·5—122° (Found: C, 56·9; H, 5·4; N, 2·5. $C_{24}H_{27}NO_9S$ requires C, 57·0; H, 5·4; N, 2·8%).

(*e*) Toluene-*p*-sulphonyl bromide gave *di-t-butyl α-benzoyl-α-bromomalonate* (30%), m.p. 139° (Found: C, 54·2; H, 5·8; Br, 19·9. $C_{18}H_{23}BrO_5$ requires C, 54·1; H, 5·8; Br, 20·0%); and the corresponding enol sulphonate (8%).

Diethyl *p*-chlorobenzoylmalonate was treated by the same method with the following sulphonyl halides.

(*a*) Benzenesulphonyl bromide gave *diethyl α-bromo-α-p-chlorobenzoylmalonate* (27%) as a viscous liquid (Found: C, 44·2; H, 3·6. $C_{14}H_{14}BrClO_5$ requires C, 44·5; H, 3·7%), and *1-p-chlorophenyl-2,2-diethoxycarbonylvinyl benzenesulphonate* (4%), m.p. 77—77·5° (Found: C, 55·0; H, 4·35. $C_{20}H_{19}ClO_7S$ requires C, 54·7; H, 4·3%).

(*b*) Benzenesulphonyl chloride gave no detectable α-chloromalonate (which we prepared for comparison purposes as described later), the enol sulphonate (described before) (51%), the starting acylmalonate (26%; obtained from the sodium hydroxide solution), and diethyl α-chloromalonate (3%), identical (i.r. and n.m.r. spectra) with a commercial sample.

Authentic α-Halogenomalonates (6).—For comparison with the foregoing samples, each of the new α-halogeno-malonates was prepared by dissolving the acylmalonate (1) (20 mmoles) in carbon tetrachloride (50 ml.) at 0° and adding, during 2 hr., either sulphuryl chloride (22 mmoles) or bromine (20 mmoles) in carbon tetrachloride (30 ml.) with stirring. The mixture was set aside overnight, the solvent was removed *in vacuo*, and the residue taken up in ether, washed with sodium hydroxide solution, dried ($MgSO_4$), and evaporated. The residue was recrystallised from ethanol (when R = Bu^t) or molecularly distilled (when R = Et). Yields were generally greater than 90% and in each case the products were identical (i.r. and n.m.r. spectra, t.l.c. and m.p.) with the compounds obtained from the sulphonyl halides. The only one not already described is *diethyl α-chloro-α-p-chlorobenzoylmalonate*, a viscous liquid (Found: C, 50·2; H, 4·2. $C_{14}H_{14}Cl_2O_5$ requires C, 50·5; H, 4·2%).

The Reaction of α-Halogenomalonates (6) *with Sodium Arenesulphinates*.—The α-bromomalonate (6; R = Et, X = Br, Y = Cl) (1·0 g.) was heated under reflux in t-butyl alcohol (150 ml.) with sodium benzenesulphinate (0·53 g.; dihydrate) for 3 hr. The solvent was removed *in vacuo* and the residue was worked up as already described for the reaction of the enolates (2) with arenesulphonyl halides. The alkali layer gave diethyl *p*-chlorobenzoylmalonate (0·32 g., 40%), but the ether contained no enol sulphonate. On repetition, but with anhydrous sodium benzenesulphinate, the alkali layer contained 11% of the acylmalonate and the ether layer contained 14% of the enol sulphonate already described. A longer reflux time (19 hr.) gave none of the enol sulphonate. The α-chloromalonate (6; R = Bu^t, X = Cl, Y = H) heated under reflux with anhydrous sodium toluene-*p*-sulphinate as already described, but for 2 days, gave di-t-butylbenzoylmalonate (30%) and the enol sulphonate (11%). The α-bromomalonate (6; R = Bu^t, X = Br, Y = H) was heated under reflux with anhydrous sodium benzenesulphinate as already described, but for 5 hr., and gave unchanged malonate (6) (50%) and *1-phenyl-2,2-di-t-butoxycarbonylvinyl benzenesulphonate*, m.p. 111·5—113° (Found: C, 62·4; H, 6·1. $C_{24}H_{28}O_7S$ requires C, 62·6; H, 6·1%) (40%), separated by chromatography on silica gel.

The Reaction of Lithium Chloride with the Enol Sulphonate (7).—The enol sulphonate (7) (1·0 g.) was heated under reflux in dry t-butyl alcohol (50 ml.) with lithium chloride (so that solid lithium chloride was always present) for 24 hr. The solution was worked up as described for the reaction of the enolates (2) with arenesulphonyl halides and gave (100% crude) *1-p-chlorophenyl-2,2-diethoxycarbonylvinyl chloride* (8), n_D^{20} 1·5380 (Found: C, 52·85; H, 4·4. $C_{14}H_{14}Cl_2O_4$ requires C, 53·0; H, 4·45%), $\nu_{max.}$ (film) 1735s, 1620m, and 1593m cm.$^{-1}$, $\lambda_{max.}$ (EtOH) 272 nm. (ε 10,400), τ (CCl_4) 2·66 (4H, s), 5·7, and 6·0 (each 2H, q), and 8·7 and 9·0 (each 3H, t), *m/e* 316, 318, and 320 (63%, M^+), and 163 and 165 (100%).

The Reaction of Methanesulphonyl Chloride with Di-t-butyl Benzoylmalonate.—Di-t-butyl benzoylmalonate (4·5 g.) was added to a stirred solution of potassium (0·55 g.) in t-butyl alcohol (50 ml.). Methanesulphonyl chloride (1·6 g.) was added with stirring and the mixture was heated under reflux for 2 hr. The solvent was removed *in vacuo* and the residue was taken up in ether, washed with sodium hydroxide solution, dried (Na_2SO_4), and evaporated. An n.m.r. spectrum of the residue indicated that it contained the sulphone (9) and the corresponding enol sulphonate in the ratio 3 : 1. The latter, however, was never isolated pure. The former, *di-t-butyl α-benzoyl-α-methylsulphonylmalonate*, crystallised from ethanol (yield 1·2 g., 21%); m.p. 136·5—138° (Found: C, 57·55; H, 6·5. $C_{19}H_{26}O_7S$ requires C, 57·25; H, 6·6%), $\nu_{max.}$ (KBr) 1776s, 1693m, 1598, 1580w, and 1333s cm.$^{-1}$, $\lambda_{max.}$ (EtOH) 252 nm. (ε 10,400), $\lambda_{infl.}$ 281 nm. (ε 1390), τ (CCl_4) 2·2 (5H, m), 6·76 (3H, s), and 8·51 (18H, s).

Di-t-butyl α-Methylsulphonylmalonate (10).—The sulphonylmalonate (9) (0·4 g.) was suspended in ethanol (5 ml.) and sodium borohydride (100 mg.) was added with stirring at room temperature. The clear solution was poured into dilute sulphuric acid (6N; 10 ml.) and ether (50 ml.). The ether layer was dried (Na_2SO_4), and the ether was removed *in vacuo*; the residue of *sulphonylmalonate* (10) crystallised from light petroleum (b.p. 60—80°) (yield 0·15 g., 50%), m.p. 89—89·5° (Found: C, 48·95; H, 7·3. $C_{12}H_{22}O_6S$ requires C, 48·95; H, 7·5%), $\nu_{max.}$ 1747s, 1724s, 1333s, and 1121s cm.$^{-1}$, τ (CCl_4) 5·64 (1H, s), 6·9 (3H, s), and 8·49 (18H, s).

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