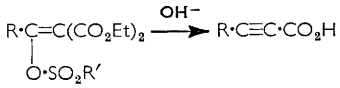
Enol Elimination Reactions. Part III.* The Scope and Limitations of Eliminations involving Enol Sulphonates

By E. J. D. Brown and John Harley-Mason

Elimination reactions of enol sulphonates have been further studied. The enol sulphonates of *p*-anisoyl-, 2-furoyl-, and 2-thenoyl-malonic esters readily gave the corresponding propiolic acids on treatment with base, whereas the enol sulphonates of *o*-, *m*-, and *p*-nitrobenzoylmalonic esters gave negligible yields. The enol sulphonates of cyclopropylcarbonylmalonate gave cyclopropylpropiolic acid, while those of trichloroacetylmalonate and fumaroylmalonate gave no acetylenic product. The enol sulphonates of tribenzoylmethane gave benzoylphenylacetylene.

In Part I [1] a number of new processes leading to acetylenes by elimination reactions of enol sulphonates were described. We now report some further examples and a series of experiments designed to show the scope and limitations of the method.

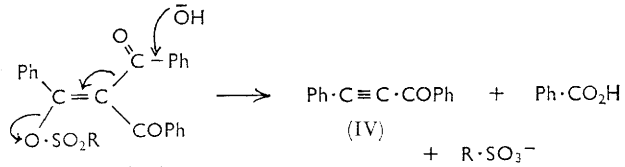


(I) (II)

2-Furyl-, 2-thienyl-, and *p*-methoxyphenyl-propiolic acids (II) were prepared in satisfactory yields from the appropriate acylmalonate enol sulphonates (I) by using sodium hydroxide in aqueous dioxan as described in Part I.

Enol sulphonates of diethyl cyclopropylcarbonylmalonate (I; R = cyclopropyl; R′ = *p*-Me·C_6H_4, *p*-Br·C_6H_4, and *p*-$C_{10}H_7$) gave cyclopropylpropiolic acid (II; R = cyclopropyl) in low yield. This case is interesting in that it is an exception to the general rule (see Part I) that a double bond or aromatic ring conjugated with the developing triple bond is essential for elimination to succeed. Apparently the cyclopropane ring is sufficiently "ethylene-like" to enable the reaction to occur, albeit in low yield.

The foregoing examples are all decarboxylative eliminations. Two examples of a related fragmentation process, involving elimination of arylsulphonate ion and a carboxylic acid, thus leading to acetylenic acids were described in Part I.[1] A further example of the latter type of process is provided by the action of alkali on the enol sulphonates (III; R = *p*-Br·C_6H_4 and

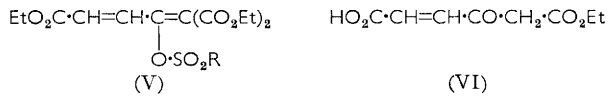


(III) (IV)

p-Me·C_6H_4) of tribenzoylmethane, giving in this case the acetylenic ketone (IV).

We now turn to a number of cases in which triple-bond formation fails, since this gives a guide to the limitations of the general preparative method. Enol sulphonates of diethyl trichloroacetylmalonate (I; R = CCl_3, R′ = *p*-Me·C_6H_4) gave no acetylenic product and only hydrolysis of the sulphonate occurred. Evidently elimination is not promoted by the very strong dipole of the trichloromethyl group. Enol sulphonates of *o*-, *m*-, and *p*-nitrobenzoylmalonates (I; R = *o*-, *m*-, and *p*-NO_2·C_6H_4, R′ = *p*-Br·C_6H_4) were readily obtained; in all three cases treatment with alkali gave only traces of acetylenic acids (detected only by the infrared spectra). This is perhaps not unexpected in the case of the *ortho*- and *para*-compounds in which the electron-withdrawing effect of the nitro-group might be expected to be inhibiting; but the failure in the case of the *meta*-compound is surprising.

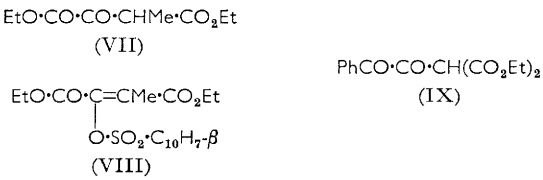
Treatment of diethyl sodiomalonate with ethylfumaroyl chloride gave triethyl fumaroylmalonate, which gave an enol toluene-*p*-sulphonate (V; R = *p*-Me·C_6H_4).



(V) (VI)

On alkaline treatment no acetylenic product was obtained and only a product of hydrolysis, the half-ester (VI), was isolated. This failure is interesting in that the activating double bond is present, and the similar crotonoylmalonate enol sulphonates in which the terminal ethoxycarbonyl group of (V) is replaced by methyl gave an acetylenic acid readily (see Part I [1]). This case is clearly analogous to the nitrobenzoylmalonates above.

Diethyl oxalopropionate (VII) gave a crystalline enol naphthalene-2-sulphonate (VIII); *cis* or *trans*) in 60% yield. This, on alkaline treatment, failed to give any acetylenic acid.



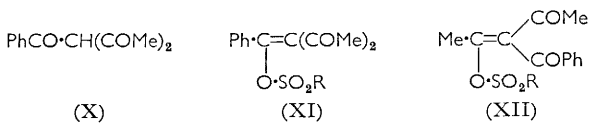
(VII) (IX) (VIII)

Crude diethyl phenylglyoxalylmalonate (IX) (prepared from phenylglyoxalyl chloride and diethyl ethoxymagnesium malonate) gave the corresponding enol *p*-bromobenzenesulphonate (I; R = PhCO, R′ = *p*-Br·C_6H_4) in very poor yield. On alkaline treatment, this, again, failed to give any acetylenic product.

* Part II, I. Fleming and J. Harley Mason, *J. Chem. Soc.*, 1963, 4778.

[1] I. Fleming and J. Harley-Mason, *J. Chem. Soc.*, 1963, 4771.

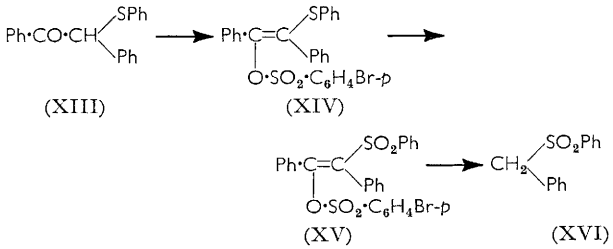
Enol sulphonates of benzoylacetylacetone (X) were next examined. Here, two structurally different products could be obtained, (XI) or (XII; *cis* or *trans*).



(X) (XI) (XII)

Only one product was actually isolated, and was shown to be (XII) by catalytic hydrogenation over platinum which yielded the known 3-benzoylpentan-2-one. As would be expected in the absence of an activating group (see above), no acetylenic product was obtained on treatment with alkali.

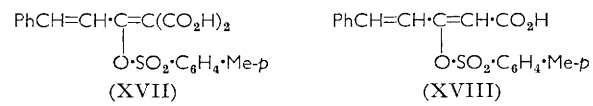
A further case was studied in an attempt to find an entirely different leaving group. α-Benzoylbenzyl phenyl sulphide (XIII) was converted into the enol *p*-bromobenzenesulphonate (XIV) which was then



(XIII) (XIV) (XV) (XVI)

oxidised to the sulphone (XV). Fragmentation of (XV) might be possible by attack of hydroxyl ion on the sulphone group, leading to elimination of benzenesulphonic acid and *p*-bromobenzenesulphonic acid giving diphenylacetylene. However, the only isolable material was found to be the hydrolysis product, benzyl phenyl sulphone (XVI).

Fleming and Harley-Mason found that very dilute base gave only ester hydrolysis with the *p*-bromobenzenesulphonate (I; R = Ph, R′ = *p*-Br·C_6H_4) of diethyl benzoylmalonate enol.[1] This would suggest that the base is directly involved in the elimination, loss of bicarbonate ion, rater than carbon dioxide, being the electron source for the developing triple bond. Similarly, loss of acetic acid on alkaline treatment of acylacetoacetate enol sulphonates [1] and the formation of benzoylphenylacetylene by elimination of benzoic acid and sulphonate ion from arylsulphonates of tribenzoylmethane enol, must involve attack of hydroxide ion on a carbonyl group, as shown in (III) ⟶ (IV). That unimolecular decomposition is indeed unlikely in the case of decarboxylative elimination was shown by examination of the behaviour of the *p*-toluenesulphonate (XVII) of cinnamoylmalonic acid enol in a non-basic



(XVII) (XVIII)

medium. When the diacid (XVII) was heated in water for 15 min., decarboxylation *without* elimination occurred, affording the toluene-*p*-sulphonate (XVIII) of cinnamoylacetic acid enol, without formation of the acetylenic acid (II; R = PhCH=CH). On the other hand, treatment of (XVII) in aqueous base is known [1] to give the acetylenic acid (II; R = PhCH=CH) by concerted elimination–decarboxylation.

EXPERIMENTAL

Infrared spectra were determined on a Perkin-Elmer 21 spectrometer with sodium chloride prisms, Nujol mulls being used for solid products. The nuclear magnetic resonance spectra were determined by use of a Perkin-Elmer spectrometer operating at 40 and 60 Mc./sec. Positions of references are quoted as chemical shifts on the τ scale and have been measured against tetramethylsilane (τ = 10) as internal reference.

M. p.s and b. p.s are not corrected.

The following new diethyl acylmalonates were prepared by the methods of Bowman [2] or Reynolds and Hauser.[3] They were distilled and analytical samples were subsequently obtained by molecular distillation (130—140°/10^{-2} mm.) of the purified product. The yields and physical properties of each were as follows: *diethyl 2-furoylmalonate* (76%, Bowman), b. p. 148°/10^{-2} mm. (Found: C, 56·5; H, 5·9. $C_{12}H_{14}O_6$ requires C, 56·7; H 5·5%); $\nu_{max.}$ 3140m and sharp, 2990vs (C–H), 1735vs and broad (ester CO), 1677s (ketonic CO), and 1570s (C=C) cm.$^{-1}$; *diethyl 2-thenoylmalonate*, (99%, Bowman), pale yellow solid, m. p. 36—45° (Found: C, 53·6; H, 5·4. $C_{12}H_{14}O_5S$ requires C, 53·4; H, 5·2%); $\nu_{max.}$ 1740vs (ester CO) and 1665vs (ketonic CO) cm.$^{-1}$; *diethyl cyclopropylcarbonylmalonate*, (86%, Reynolds and Hauser), b. p. 124°/1 mm. (Found: C, 58·1; H, 7·3. $C_{11}H_{16}O_5$ requires C, 57·9; H, 7·0%); $\nu_{max.}$ 3400—2700 broad and flat (chelated enolic OH), 1735s, 1710s (ester CO), 1635 (ketonic CO), 1590s (enolic C=C). These infrared results suggest the presence of a mixture of keto and enol forms, which was confirmed by the n.m.r. spectrum in carbon tetrachloride. The n.m.r. spectrum showed a singlet at τ −3·8 (conjugated and chelated OH), two singlets at 6·6 and 6·8, two multiplets centred at 5·8 (–CH_2– of the ester groups) and 8·9 (CH_3 of the ester groups and presumably also the cyclopropyl –CH_2–) and a broad flat multiplet centred at 7·9 (presumably due to the CH– of the cyclopropyl ring). The complete absence of absorption between τ 3 and 5·5 (olefinic protons) shows that isomerisation of the cyclopropyl ring has not occurred; *diethyl trichloroacetylmalonate* (68·5%, Reynolds and Hauser), b. p. 115—120°/1 mm. (Found: C, 35·55; H, 3·7; Cl; 34·7. $C_9H_{11}Cl_3O_5$ requires C, 35·4; H, 3·6; Cl, 34·9%); $\nu_{max.}$ 1772s (ester CO) and 1740s (α-halogen substituted ketone) cm.$^{-1}$.

Diethyl m-*Nitrobenzoylmalonate*.—(100%, Bowman). The crude *compound* was crystallised from aqueous ethanol and an analytical sample was subsequently obtained by molecular distillation; it had m. p. 42—54°. The indefinite m. p. suggests the presence of a mixture of keto and enol forms (Found: C, 54·35; H, 5·2; N, 4·7. $C_{14}H_{15}NO_7$ requires C, 54·4; H, 4·85; N, 4·5%); $\nu_{max.}$ 3400—2600 (chelated and conjugated OH), 1740vs, 1730vs (ester CO), 1700s (ketonic CO), 1612s (C=C), and 1527vs (NO_2) cm.$^{-1}$.

Diethyl Phenylglyoxalylmalonate.—Phenylglyoxylic acid (40 g.; recrystallised from benzene–light petroleum) was dissolved in a mixture of purified thionyl chloride

[2] R. E. Bowman, *J. Chem. Soc.*, 1950, 322.
[3] G. A. Reynolds and C. R. Hauser, *Org. Synth.*, 1950, **30**, 70.

(56 ml.) and benzene (80 ml.), and the solution was refluxed for 2½ hr. Benzene and excess of thionyl chloride were removed under reduced pressure and the residue of crude phenylglyoxalyl chloride was distilled under vacuum, yielding a yellow oil (36·5 g., 81%) which had b. p. 60—65°/0·3 mm. (lit.,[4] b. p. 91°/9·5 mm.); $\nu_{max.}$ 1780s (COCl), 1690s (CO), and 1600m (aromatic ring) cm.$^{-1}$. Diethyl phenylglyoxalylmalonate was subsequently prepared by the method of Reynolds and Hauser, from the above acyl chloride and freshly distilled ethyl malonate. The desired enol was isolated as a thick yellow oil and was used without further purification since it decomposed on attempted distillation; it had $\nu_{max.}$ 1780s, 1730s (ester CO), 1670s, 1630s (ketonic CO), and 1600m (aromatic ring) cm.$^{-1}$.

Enol Arylsulphonates.—These were prepared by the following method. To the enol dissolved in ethanol, sodium ethoxide (1 equiv.) in ethanol was added. After removal of the ethanol, the dry enol salt was dissolved or suspended in a suitable solvent, the arylsulphonyl chloride (1·2 equiv.) was added, and the resulting mixture was kept at room temperature for several days (or heated on the water-bath for several hours). The solvent used and the time needed for reaction are given below for each enol sulphonate. The enol sulphonates were isolated from the reaction mixture as described in Part I [1] and were kept in ethanol until crystallisation occurred. The yields and physical properties of each were as follows.

2,2-*Diethoxycarbonyl*-1-2′-*furylvinyl* p-*bromobenzenesulphonate* (I; R = 2-furyl; R′ = *p*-Br·C_6H_4). Prepared in ethanol, kept overnight at room temperature, in 12% yield, this *sulphonate* had m. p. 56—58° (Found: C, 45·7; H, 4·0. $C_{18}H_{17}BrO_8S$ requires C, 45·65; H, 3·6%); $\nu_{max.}$ 1740s, 1720vs (ester CO), 1617vs (C=C), 1572m, 1550m (aromatic ring), and 1395vs (sulphonate) cm.$^{-1}$.

2,2-*Diethoxycarbonyl*-1-2′-*furylvinyl naphthalene*-2-*sulphonate* (I; R = 2-furyl; R′ = β-$C_{10}H_7$). Prepared in dioxan, kept for two weeks at room temperature, in 51·5% yield, this *sulphonate* had m. p. 69—71° (Found: C, 59·6; H, 5·0. $C_{22}H_{20}O_8S$ requires C, 59·5; H, 4·5%); $\nu_{max.}$ 1725vs (ester CO), 1618vs (C=C), 1547m (aromatic ring), and 1392vs (sulphonate) cm.$^{-1}$.

2,2-*Diethoxycarbonyl*-1-2′-*thenoylvinyl* p-*bromobenzenesulphonate* (I; R = 2-thienyl; R′ = *p*-Br·C_6H_4). Prepared in dry tetrahydrofuran, refluxed for 6 hr. and kept overnight at room temperature, in 26·6% yield, this *sulphonate* had m. p. 89—91° (Found: C, 44·8; H, 4·0. $C_{18}H_{17}BrO_7S_2$ requires C, 44·2; H, 3·45%); $\nu_{max.}$ 1743vs, 1700vs (unsat. ester CO), 1622s (C=C), 1575vs (aromatic ring), and 1395vs (aromatic sulphonate) cm.$^{-1}$.

1-p-*Anisoyl*-2,2-*diethoxycarbonylvinyl* p-*bromobenzenesulphonate* (I; R = *p*-MeO·C_6H_4; R′ = *p*-Br·C_6H_4). Prepared in dioxan, kept for 3 days at room temperature and heated at 100° for 4 hr., in 38% yield, this *sulphonate* formed felted needles, m. p. 101·5—103·5°, from aqueous ethanol (Found: C, 49·3; H, 4·2; Br, 15·5. $C_{21}H_{21}BrO_8S$ requires C, 49·15; H, 4·1; Br, 15·6%); $\nu_{max.}$ 1735s, 1695vs (unsat. ester CO), 1635m (C=C), 1605m, 1575m (aromatic ring), and 1375s (sulphonate) cm.$^{-1}$.

2,2-*Dibenzoyl*-1-*phenylvinyl* p-*bromobenzenesulphonate* (III; R = *p*-Br·C_6H_4). Prepared in dry dioxan, heated at 100° for 3 hr. and kept overnight at room temperature, in 47% yield, this *sulphonate* had m. p. 141—142° (Found: C, 61·4; H, 3·34; Br, 14·7. $C_{28}H_{19}BrO_5S$ requires C, 61·4; H, 3·5; Br, 14·6%); $\nu_{max.}$ 1655s, 1640s (ketonic CO), 1595m, 1570m (aromatic ring), and 1385vs (−SO_2−O−) cm.$^{-1}$.

2,2-*Dibenzyl*-1-*phenylvinyl toluene*-p-*sulphonate* (III; R = *p*-Me·C_6H_4). Prepared in dry dioxan, heated at 100° for 3 hr. and kept for 3 days at room temperature, in 30% yield, this *sulphonate* had m. p. 123—124° (Found: C, 72·2; H, 5·0. $C_{29}H_{22}O_5S$ requires C, 72·2; H, 4·6%); $\nu_{max.}$ 1660s, 1630s (ketonic CO), 1595s (C=C), 1580m (aromatic ring), and 1360vs (−SO_2−O−) cm.$^{-1}$.

2-2-*Diethoxycarbonyl*-1-*trichloroacetylvinyltoluene*-p-*sulphonate* (I; R = CCl_3; R′ = *p*-Me·C_6H_4). This, prepared in dioxan, kept for 2 days at room temperature and heated at 100° for 3 hr., was a colourless *liquid* which could not be distilled without decomposition (Found: C, 42·5; H, 4·5; Cl, 21·7. $C_{16}H_{17}Cl_3O_7S$ requires C, 41·75; H, 3·7; Cl, 23·2%), indicated that the material was somewhat impure; $\nu_{max.}$ 1750s (ester CO), 1590m(C=C), 1370s and 1180s (−SO_2−O−) cm.$^{-1}$.

2,2-*Diethoxycarbonyl*-p-*nitrobenzoylvinyl* p-*bromobenzenesulphonate* (I; R = *p*-NO_2·C_6H_4; R′ = *p*-Br·C_6H_4). Prepared in ethanol, kept overnight at room temperature, in 60% yield, this *sulphonate* had m. p. 125—126° (Found: C, 45·6; H, 3·4; Br, 14·8; N, 2·7. $C_{20}H_{18}BrNO_9S$ requires C, 45·45; H, 3·4; Br, 15·15; N, 2·65%); $\nu_{max.}$ 1735vs (unsat. ester CO), 1637m (C=C), 1600w, 1757w (aromatic ring), and 1523s (NO_2 group) cm.$^{-1}$.

2,2-*Diethoxycarbonyl*-o-*nitrobenzoylvinyl* p-*bromobenzenesulphonate* (I; R = *o*-NO_2·C_6H_4; R′ = *p*-Br·C_6H_4). Prepared in dioxan, heated at 100° for 7 hr. and kept overnight at room temperature, in 64% yield), this formed *needles*, m. p. 125—127° (Found: C, 45·6; H, 3·8; Br, 14·8; N, 2·6. $C_{20}H_{18}BrNO_9S$ requires C, 45·45; H, 3·4; Br, 15·15; N, 2·65%); $\nu_{max.}$ 1740vs, 1700vs (conjugated ester CO), 1637w (C=C), 1607mw, 1573m (benzene ring), 1530vs (NO_2) cm.$^{-1}$.

2-2-*Diethoxycarbonyl*-o-*nitrobenzoylvinyl naphthalene*-2-*sulphonate* (I; R = *o*-NO_2·C_6H_4; R′ = β-$C_{10}H_7$). Prepared in dioxan, heated at 100° for 5 hr. and kept overnight at room temperature, in 53% yield, this formed *needles*, m. p. 106·5—108° (Found: C, 57·9; H, 4·7; N, 2·8. $C_{24}H_{21}NO_9S$ requires C, 57·7; H, 4–2; N, 2·8%); $\nu_{max.}$ 1740vs, 1700s (unsat. ester CO), 1640w (C=C), 1605w, 1574w (naphthalene rings), and 1535s (NO_2 group) cm.$^{-1}$.

2,2-*Diethoxycarbonyl*-m-*nitrobenzoylvinyl* p-*bromobenzenesulphonate* (I; R = *m*-NO_2·C_6H_4; R′ = *p*-Br·C_6H_4). Prepared in ethanol, kept overnight at room temperature, in 40·8% yield, this *sulphonate* formed felted plates, m. p. 72·5—74° (Found: C, 45·5; H, 3·7; Br, 15·3; N, 2·8. $C_{20}H_{18}BrNO_9S$ requires C, 45·45; H, 3·4; Br, 15·15; N, 2·65%); $\nu_{max.}$ 1750vs, 1707s (unsat. ester CO), 1640m (C=C), 1575m (aromatic ring), and 1532vs (NO_2 group) cm.$^{-1}$.

1-*Diethoxycarbonylmethylene*-3-*ethoxycarbonylallyl toluene*-p-*sulphonate* (V; R = *p*-Me·C_6H_4). Prepared in dioxan, kept for 3 days at room temperature, in 73% yield, this *sulphonate* had m. p. 71—73° from aqueous ethanol (Found: C, 54·5; H, 5·1. $C_{20}H_{24}O_9S$ requires C, 54·55; H, 5·45%); $\nu_{max.}$ 1740s and 1730s (ester CO), 1645m and 1610s (C=C), 1370s and 1180s (aromatic sulphonate) cm.$^{-1}$.

1,2-*Diethoxycarbonylprop*-1-*enyl Naphthalene*-2-*sulphonate* (VIII).—Prepared in dioxan, during two weeks at room temperature, in 60% yield, this *sulphonate* had m. p. 91—93° (Found: C, 58·1; H, 5·1. $C_{19}H_{20}O_7S$ requires C, 58·2; H, 5·1%); $\nu_{max.}$ 1725s (ester CO), 1660m (C=C), 1625w, 1595w,

[4] M. S. Kharasch, C. S. S. Kane, and H. C. Brown, *J. Amer. Chem. Soc.*, 1942, **64**, 332.

and 1505m (naphthalene rings), 1380s and 1190s (aromatic sulphonate) cm.$^{-1}$.

1-*Benzoyl*-2,2-*diethoxycarbonylvinyl* p-*bromobenzene-sulphonate* (I; R = PhCO; R′ = *p*-Br·C_6H_4). Prepared in ethanol, kept for 5 days at room temperature, in 0·5% yield, this *sulphonate* had m. p. 144—146° (Found: C, 49·2; H, 3·6. $C_{21}H_{19}BrO_8S$ requires C, 49·35; H, 3·7%); $\nu_{max.}$ 1750s (ester CO), 1630s (ketonic CO), 1560s (C=C), and 1395s (sulphonate) cm.$^{-1}$.

2-*Acetyl*-2-*benzoyl*-1-*methylvinyl* p-*bromobenzenesulphonate* (XII; R = *p*-Br·C_6H_4). Prepared in dry acetone, kept overnight at 0°, in 24% yield, this *sulphonate* had m. p. 83—85° (Found: C, 51·45; H, 3·62. $C_{18}H_{15}BrO_5S$ requires C, 51·1; H, 3·55%); $\nu_{max.}$ 1700s, 1680s, 1660s (ketonic CO), 1610m (C=C), and 1590s (aromatic ring) cm.$^{-1}$. The n.m.r. spectrum taken in CCl_4 solution showed two multiplets centred at τ 2·15 and 2·4 (aromatic ring) and two singlets at τ 7·85 and 8·05 (methyl groups).

α-*Phenyl*-β-*phenylthiostyryl* p-*Bromobenzenesulphonate* (XIV).—Sodium hydride (50% dispersion in oil, 2·4 g.) was added in small portions to desyl phenyl sulphide (XIII) [5,6] (14·6 g.) in dry acetone (200 ml.), with ice cooling. After 30 min., *p*-bromobenzenesulphonyl chloride (13 g.) in dry acetone (100 ml.) was added and the mixture was refluxed for 2 hr. and kept overnight at room temperature. Working-up afforded 10 g. (40%) the p-*bromobenzenesulphonate* (XIV), m. p. 128·5—131·5° (from ethanol) (Found: 59·7; H, 3·7; Br, 15·4. $C_{26}H_{19}BrO_3S_2$ requires C, 59·6; H, 3·6; Br, 15·3%); $\nu_{max.}$ 1570m (C=C), 1375s and 1185s (−SO_2−O−) cm.$^{-1}$.

α-*Phenyl*-β-*phenylsulphonylstyryl* p-*Bromobenzenesulphonate* (XV).—Hydrogen peroxide (30%, 15 ml.) was added to α-phenyl-β-phenylthiostyryl *p*-bromobenzenesulphonate (XIV) (5 g.) in glacial acetic acid (100 ml.) and the mixture was heated at 90° for ½ hr. After cooling, water was added dropwise, the white solid material which separated was collected, washed with water and recrystallised from a mixture of ethanol (200 ml.) and acetone (50 ml.), yielding quantitatively the *sulphone* (XV), m. p. 170—173° (decomp.) (Found: C, 56·1, 56·2; H, 3·71, 3·38; Br, 14·51. $C_{26}H_{19}BrO_5S_2$ requires C, 56·25; H, 3·4; Br, 14·4%); $\nu_{max.}$ 1640m, 1615w, 1570m (C=C and aromatic ring), 1360s and 1165s (sulphone and sulphonate) cm.$^{-1}$.

Action of Alkali on 1,2-*Diethoxycarbonylprop*-1-*enyl*, 2,2-*Diethoxycarbonyl*-1-*trichloroacetylvinyl*, 2,2-*Diethoxy-carbonyl*-o-, -m-, *and* -p-*nitrobenzoylvinyl, and* 2,2-*Diethoxy-carbonyl*-1-*trichloroacetylvinyl Sulphonates*.—These were treated with 0·2N-sodium hydroxide in aqueous dioxan as described in Part I.[1] In all cases, no acetylenic acid could be isolated: only hydrolysis products were obtained, with no triple bond absorption in the infrared spectrum of the crude reaction products except in the case of the three nitrobenzoyl malonates where a weak band at 2210—2240 cm.$^{-1}$ was present.

Investigation of the Product obtained by Alkaline Treatment of 1-*Diethoxycarbonylmethylene*-3-*ethoxycarbonylallyl Tolu-ene*-p-*sulphonate* (V).—The enol sulphonate (V) failed to give any acetylenic product on alkaline treatment, but a small quantity of a crystalline acid was obtained which had m. p. 137—139° after sublimation at 110°/0·5 mm. This compound was formulated as *ethyl* trans-β-*carboxy-acryloylacetate* (VI), on the basis of analytical and infrared data (Found: C, 51·5; H, 5·4. $C_8H_{10}O_5$ requires C, 51·6; H, 5·4%); $\nu_{max.}$ 3200w and broad (OH), 2700w, 2600w (carboxylic acid), 1710s (ester CO), 1660s (carboxylic CO), and 1600s (C=C) cm.$^{-1}$.

Action of Alkali on α-*Phenyl*-β-*phenylsulphonylstyryl* p-*Bromobenzenesulphonate* (XV).—The enol-sulphonate (XV) was treated with NaOH in aqueous dioxan as described in Part I [1] but failed to give any diphenylacetylene. Working up gave a crystalline residue which was subsequently recrystallised from ethanol and proved to be benzyl phenyl sulphone, having the same m. p. 150—153° and mixed m. p. (lit.,[7] m. p. 148—149°) and the same infrared spectrum.

Preparation of 2-*Furyl*-, 2-*Thienyl*-, *and* p-*Methoxyphenyl-propiolic Acids* (II; R = 2-furyl, 2-thienyl, and *p*-methoxy-phenyl).—These were prepared by alkaline treatment of the corresponding enol sulphonates (I) as described in Part I. The method of purification, yields and physical properties are as follows: 2-furylpropiolic acid (II; R = 2-furyl), recrystallised from chloroform–light petroleum, 48% yield, m. p. 106—111° (decomp.) (lit.,[8] m. p. 109—110°); $\nu_{max.}$ 3200—2600w and broad (acidic OH), 2220vs (C≡C), 1665vs (CO_2H), and 1565m (C=C) cm.$^{-1}$; 2-Thienylpropiolic acid (II; R = 2-thienyl), recrystallised from carbon tetrachloride, 51·5% yield, m. p. 133—135° (lit.,[9] m. p. 130—133°) (Found: C, 55·1; H, 3·3. Calc. for $C_7H_4O_2S$: C, 55·25; H, 2·6%). $\nu_{max.}$ 3200—2500w and broad (carboxylic OH), 2210vs (C≡C), 1670vs and broad (carboxylic CO), 1515w (C=C) cm.$^{-1}$; *p*-methoxyphenylpropiolic acid (II; R = *p*-MeO·C_6H_4), white needles from benzene–light petroleum, 70% yield, m. p. 141—142° (decomp.) (lit.,[9,10] m. p. 141—143°, 144—144·4°) (Found: C, 68·2; H, 4·8. Calc. for $C_{10}H_8O_3$: C, 68·25; H, 4·5%); $\nu_{max.}$ 3300—2600w and broad (acidic OH), 2240m, 2200vs (C≡C), 1665vs and rather broad (CO_2H), and 1600s (aromatic ring) cm.$^{-1}$.

Cyclopropylpropiolic Acid (II; R = Cyclopropyl).—The dry sodium salt of diethyl cyclopropylcarbonylmalonate was added to the arylsulphonyl chloride (1·3 equiv.) in dry acetone and the resulting mixture was kept for 2 weeks at room temperature. Working-up in the usual manner afforded oils which could not be crystallised, but which were formulated as 1-cyclopropylcarbonyl-2,2-diethoxy-carbonylvinylarylsulphonates (I; R = Cyclopropyl; R′ = *p*-Me·C_6H_4, *p*-Br·C_6H_4, and β-$C_{10}H_7$), on the basis of their infrared spectra and behaviour in alkaline conditions; $\nu_{max.}$ 1750—1710s (ester CO), 1620m (C=C), 1570m (aromatic ring), and 1380s (sulphonate) cm.$^{-1}$. The crude aryl-sulphonates were treated with sodium hydroxide in aqueous dioxan as described in Part I [1] and the acidic reaction products were isolated in the usual manner. In each case, a pale yellow oil was obtained which was formulated as cyclopropylpropiolic acid (II; R = cyclopropyl); $\nu_{max.}$ (for the crude product) 3200w, 2600w, 2230vs (C≡C), and 1700s (CO_2H) cm.$^{-1}$. The compound decomposed on attempted vacuum distillation and was characterised as the S-*benzylthiouronium salt*, m. p. 195—198° (decomp.) (Found: C, 60·3; H, 6·4; N, 9·9. $C_{14}H_{16}N_2O_2S$ requires C, 60·85; H, 5·8; N, 10·15%).

Benzoylphenylacetylene (IV).—The enol sulphonate (III; R = *p*-Br·C_6H_4) (1·8 g.) was dissolved in a mixture of dioxan (35 ml.), water (11 ml.), and 2·5N-sodium hydroxide solution (4 ml.) and kept overnight at room temperature.

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After acidification, the mixture was evaporated under reduced pressure, and the residue was distributed between $CHCl_3$ and dilute sodium hydroxide solution. Evaporation of the dried (Na_2SO_4) chloroform extract gave an oily material which was boiled with light petroleum and filtered. The insoluble substance (700 mg.) was tribenzoylmethane. On keeping at 0° the filtrate deposited crystals of benzoylphenylacetylene (200 mg., 29%), m. p. 47—49° (lit.,[11] m. p. 49—50°), whose infrared spectrum was identical with that of an authentic specimen; $\nu_{max.}$ 2210s (C≡C), 1650s (ketonic CO), 1610m, 1580m (aromatic ring) cm.$^{-1}$. Alkaline treatment of 2,2-dibenzoyl-1-phenylvinyl *p*-toluene-sulphonate (III; R = *p*-Me·C_6H_4) under similar conditions gave the same result.

Reactions of 2-*Acetyl*-2-*benzoyl*-1-*methylvinyl* p-*bromobenzenesulphonate* (XII; R = *p*-Br·C_6H_4, *cis* or *trans*).—On treatment with 3 equivs. of 0·25N-sodium hydroxide in aqueous dioxan, this enol-sulphonate failed to give any acetylenic product (there was no band between 2400 and 2100 cm.$^{-1}$ in the infrared spectrum of the crude reaction products).

The enol-sulphonate (2 g.) in ethanol was hydrogenated at atmospheric pressure for 6 hr. over Adams catalyst. The uptake was 250 ml. (approximately 2 moles of hydrogen per mole of reactant). The ethanol was removed and the residue treated with ether and water. The ether extract was evaporated, yielding a mobile oily residue whose infrared spectrum showed 2 strong CO bands at 1720 and 1680 cm.$^{-1}$ and 2 weak bands at 1600 and 1580 cm.$^{-1}$ (benzene ring). The residue was treated with a saturated aqueous solution of copper acetate, some aqueous ammonia was added and the mixture shaken for 3 hr. and kept overnight at room temperature. The dark green precipitate was collected and recrystallised twice from benzene, giving green needles (decomp.), m. p. 210°. This compound was identical with the copper salt of 3-benzoylpentan-2-one (mixed m. p. and infrared spectrum).

Decarboxylation of 2,2-*Dicarboxy*-1-*styrylvinyl Toluene*-p-*sulphonate* (XVII).—Purified cinnamoylmalonic acid enol-*p*-toluenesulphonate [1] (XVII) (1 g.) was suspended in water (20 ml.) and the mixture boiled for 15 min. The smallest amount of acetone was added for dissolution and the solution was then refluxed for 1 hr. Evaporation of the acetone (reduced pressure) followed by extraction with ether afforded 2-*carboxy*-1-*styrylvinyl toluene*-p-*sulphonate* (XVIII) (0·5 g., 50%) (Found: C, 62·76; H, 5·04% M, 345. $C_{18}H_{16}O_5S$ requires C, 62·8; H, 4·65%; *M*, 344); $\nu_{max.}$ 3200—2700w and broad (acidic OH), 1680s (carboxylic acid), 1620s (C=C), and 1590s (benzene ring) cm.$^{-1}$, m. p. 151—152° from benzene–light petroleum.

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