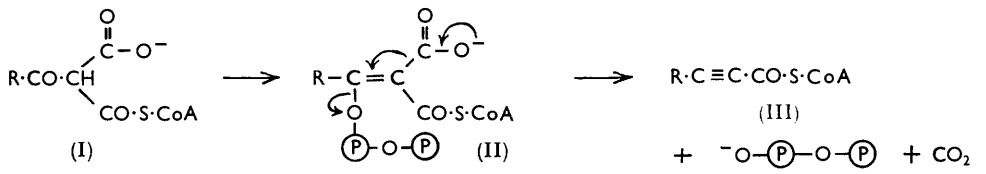
913. *Enol Elimination Reactions. Part I. A New Synthesis of Acetylenic Acids.**

By Ian Fleming and John Harley-Mason.

Decarboxylative elimination from enol sulphonate derivatives (V) of acylmalonates, in mild alkaline conditions, gives acetylenic acids when a double bond or aromatic ring is conjugated with the developing triple bond. The enol sulphonates (XII, XIII) of acylacetoacetates also give acetylenic acids, and in one case the elimination was shown to be *trans*.

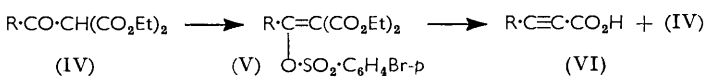
A large number of naturally occurring acetylenic compounds are now known.[1] Their biogenesis is well known to proceed from acetate units [2] but the precise mechanism whereby a $-CO\cdot CH_2-$ unit becomes dehydrated to a triple bond is obscure. There has been no laboratory analogy for the dehydration of an enol, and, furthermore, triple bonds can rarely be synthesised in the laboratory under " physiological " conditions.

The suggestion by Wakil and Ganguly [3] that the acylmalonate (I) was an intermediate in polyacetate synthesis led Jones [4] to postulate a mechanism for the biogenesis of acetylene bonds based on an enol pyrophosphate (II) of that intermediate. He suggested that the enol pyrophosphate (or phosphate) would undergo a concerted elimination-decarboxylation, (II) ⟶ (III). The loss of carbon dioxide should provide a powerful source of electrons for the developing triple bond, and the pyrophosphate ion is a good leaving group.



Decarboxylative eliminations to give acetylenic compounds are known; [5] eliminations from enols are unusual and take place under conditions very unlike those found in Nature.[6] Accordingly, it was decided to examine a model system based on Jones's postulate. The model initially chosen was the enol *p*-bromobenzenesulphonate of diethyl benzoylmalonate.

Diethyl benzoylmalonate (IV; R = Ph) gave a crystalline enol *p*-bromobenzenesulphonate (V; R = Ph) on treatment of an ethanolic solution of its sodium salt with *p*-bromobenzenesulphonyl chloride. Treatment of this sulphonate with four equivalents



of sodium hydroxide in homogeneous aqueous dioxan solution at room temperature overnight gave a mixture of diethyl benzoylmalonate and phenylpropiolic acid (VI; R = Ph), identified by comparison with an authentic specimen. The yield of the latter was greatest (73%) in the most concentrated alkali (0·175N). The use of milder conditions

* Preliminary communications: *Proc. Chem. Soc.*, 1961, 245; *Chem. and Ind.*, 1962, 560.

[1] Jones, *Proc. Chem. Soc.*, 1960, 199; Sörensen, *Proc. Chem. Soc.*, 1961, 98; Bohlmann, *Chimia (Switz.)*, 1962, **16**, 353.

[2] Bu'Lock and Gregory, *Biochem. J.*, 1959, **72**, 322.

[3] Wakil and Ganguly, *J. Amer. Chem. Soc.*, 1959, **81**, 2597.

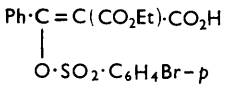
[4] Jones, *Chem. Eng. News*, 1961, **39** (No. 12), 46.

[5] Wislicenus and Henze, *Annalen*, 1900, **313**, 247; Grob, *Angew. Chem.*, 1961, **73**, 758.

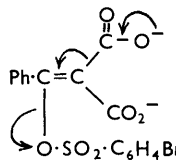
[6] Paul and Tselitcheff, *Bull. Soc. chim. France*, 1952, 808; Odaira, *Bull. Chem. Soc. Japan*, 1956, **29**, 470.

(sodium carbonate or very dilute sodium hydroxide) gave a crystalline monoethyl ester (VII) which, on further treatment with aqueous alkali, gave phenylpropiolic acid.

Presumably the reaction involves the concerted elimination and decarboxylation of an intermediate anion such as (VIII). It can be seen that the decomposition of (VIII) leading to phenylpropiolic acid, carbon dioxide, and *p*-bromobenzenesulphonate ion is remarkably similar to the sequence, (II) ⟶ (III), postulated by Jones for the biogenesis of the triple bond. The success of the reaction strongly supports Jones's hypothesis by providing a reasonably close laboratory analogy in both the structure of the compounds and the relatively mild conditions.



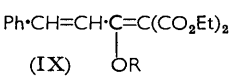
(VII)



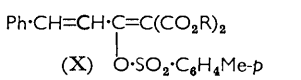
(VIII)

The good yield, the availability of acylmalonates, and the difficulty of making conjugated enynoic acids indicated that the new reaction might be useful synthetically. Accordingly its scope was extended to the preparation of other acetylenic acids. In this way 5-phenylpent-4-en-2-ynoic acid (VI; R = Ph·CH:CH) and hex-4-en-2-ynoic acid (VI; R = Me·CH:CH), as well as a new compound, octa-4,6-dien-2-ynoic acid (VI; R = Me·CH:CH·CH:CH), were prepared easily from the enol *p*-bromobenzenesulphonates of diethyl cinnamoylmalonate (IV; R = Ph·CH:CH), diethyl crotonoylmalonate (IV; R = Me·CH:CH), and diethyl sorboylmalonate (IV; R = Me·CH:CH·CH:CH), respectively. In each case some concurrent hydrolysis took place, to give back the original diethyl acylmalonate (IV), the recovery of which effectively enhanced the yield. The method, therefore, is general for the synthesis of acids of the type (VI) in which a double bond or aromatic ring is conjugated with the triple bond.

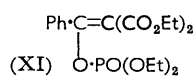
The use of leaving groups other than *p*-bromobenzenesulphonate was briefly investigated. Diethyl cinnamoylmalonate (IV; R = Ph·CH:CH) gave a crystalline enol *p*-bromobenzenesulphonate (IX; R = SO_2·C_6H_4Br-*p*), enol naphthalene-2-sulphonate (IX; R = SO_2·$C_{10}H_7$), and enol toluene-*p*-sulphonate (IX; R = SO_2·C_6H_4Me-*p*). The enol *p*-bromobenzenesulphonate underwent elimination on treatment with alkali as already described.



(IX)



(X)



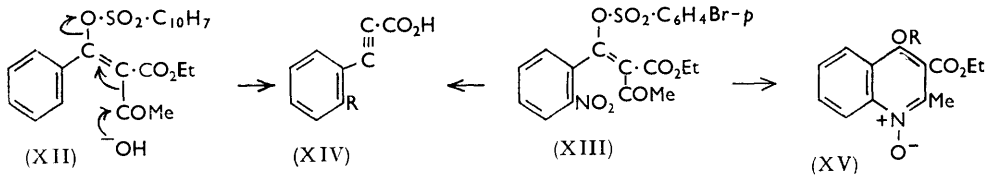
(XI)

The corresponding enol toluene-*p*-sulphonate, which has the poorer leaving group, gave, under similar conditions, a separable mixture of the enol toluene-*p*-sulphonates of cinnamoylmalonic acid (X; R = H, H) and its monoethyl ester (X; R = H, Et). Treatment of this mixture with aqueous alkali at room temperature gave 5-phenylpent-4-en-2-ynoic acid (VI; R = Ph·CH:CH) in an overall yield of 64% which compares favourably with the yield of 40% from the enol *p*-bromobenzenesulphonate, and, moreover, gave a purer product. The enol naphthalene-2-sulphonate (IX; R = SO_2·$C_{10}H_7$) was intermediate in reactivity, giving partial elimination in the first treatment, completed in the second, with an overall yield of 55%. Presumably, with the poorer leaving group, the competing substitution reaction which leads to recovered acylmalonate is also inhibited, allowing only ester hydrolysis to take place. Then, the change to the more polar solvent is probably sufficient to effect the elimination. Once ester hydrolysis has taken place the anion will be much less susceptible to hydrolysis at the enol sulphonate position; hence the higher yield.

The only other leaving group investigated was the enol diethyl phosphate (XI) made

by a Perkow[7] reaction in 97·5% yield. However, treatment with alkali under a variety of conditions gave only hydrolysis products, *i.e.*, acetophenone, benzoylacetic acid, and benzoic acid, with no triple-bond absorption in the infrared spectrum of the crude products.

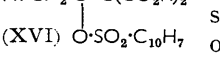
The use of acylacetoacetates in place of acylmalonates was another variation of structure which was investigated in the hope of preparing acetylenic ketones. The crystalline enol naphthalene-2-sulphonate (XII) of ethyl benzoylmalonate was prepared, in only 4% yield, from the sodium salt of diethyl benzoylacetoacetate; only one crystalline product could be isolated. Treatment of this with alkali under the same conditions as before gave, again, phenylpropiolic acid (XIV; R = H) rather than the desired acetylenic ketone. This elimination must involve attack by hydroxide ion on the ketone carbonyl group with concerted loss of acetic acid and naphthalene-2-sulphonate ion.



Ethyl *o*-nitrobenzoylacetoacetate gave, again, only one crystalline enol *p*-bromobenzenesulphonate (XIII), in 10% yield. On treatment of this derivative with alkali as before, *o*-nitrophenylpropiolic acid (XIV; R = NO_2) was obtained in 65% yield and identified from its melting point, elemental analysis, and infrared spectrum. The only other product of the reaction was ethyl *o*-nitrobenzoylacetoacetate formed by the usual hydrolysis. In this case it was possible to confirm that the elimination is a *trans*-process, as we have assumed in the cases of the acids (II) and (VIII). Reductive cyclisation of the enol *p*-bromobenzenesulphonate of ethyl benzoylacetoacetate was achieved, by using ferrous sulphate and ammonia, to give the quinaldine *N*-oxide (XV; R = $SO_2{\cdot}C_6H_4Br$-*p*), identical with a specimen prepared by treatment of the sodium salt of the quinaldine *N*-oxide (XV; R = H) with *p*-bromobenzenesulphonyl chloride.

Natural acetylenic compounds frequently contain conjugated polyacetylenic groupings, and frequently triple bonds are not conjugated with double bonds.[1] The scope of the laboratory reaction was investigated in these two directions. Polyacetylenic compounds could not be made because of the formation of tetronic acids (see the following paper[8]). It also appears that enol sulphonates of the type of (V) in which R does not contain a double bond or aromatic ring conjugated with the enol double-bond fail to undergo the elimination reaction.

The crystalline enol naphthalene-2-sulphonate (XVI; R = Et) of diethyl phenylacetylmalonate was prepared, but treatment with alkali, under conditions which gave successful elimination in the previous examples, gave an acidic oil whose infrared and ultraviolet spectra closely resembled those of the starting ester. The oil was formulated as the diacid (XVI; R = H), since its infrared spectrum showed only one peak due to a carbonyl group; the half-ester (XVI; R = H, Et) would probably show two such bands. This formulation was supported by treatment of the oil with an excess of diazoethane which gave the starting ester (XVI; R = Et). All attempts to convert the diacid into benzylpropiolic acid failed; the only products isolated under a variety of conditions were phenylacetone and phenylacetic acid, the result of hydrolysis rather than elimination.



(XVI)

Jones[9] prepared the enol *p*-bromobenzenesulphonate and enol toluene-*p*-sulphonate of diethyl acetylmalonate but these compounds, which were oils, also failed to undergo elimination on treatment with alkali.

[7] Lichtenthaler, *Chem. Rev.*, 1961, **61**, 607; Kirby, Ph.D. dissertation, Cambridge, 1962.
[8] Fleming and Harley-Mason, following paper.
[9] Jones, personal communication.

Since the present work was completed, interest in enol elimination has been shown in other laboratories. Cymerman Craig and Moyle [10] have studied elimination from vinyl diethyl phosphates, using sodamide in liquid ammonia, and have found that acetylenic compounds are readily produced only when a double bond or aromatic ring is conjugated with the vinyl phosphate group. Some of their work has been duplicated by Nakagawa, Nakaminami, Ogura, and Ono,[11] who, in addition, have shown that elimination takes place from vinyl sulphonates and phosphates in the presence of sodium t-butoxide in benzene. A new synthesis of acetylenic acids, developed by Märkl [12] and by Gough and Trippett,[13] by an extension of the Wittig olefin synthesis, has also been reported.

All these reactions require conjugation of the developing triple bond with an existing double bond or aromatic ring. We suggest that conjugation of the existing π-orbital of this double bond with the π-orbital of the developing bond is necessary in the transition state. This means that the transition state is twisted so that this double bond and the enol double bond are not co-planar, as they would be expected to be in the ground state. A scale model of the enol *p*-bromobenzenesulphonate of diethyl benzoylmalonate shows that conjugation in the ground state is not possible without severe strain. This is confirmed by the ultraviolet spectrum, which resembles that of the unconjugated enol naphthalene-2-sulphonate (XVI) of diethyl phenylacetylmalonate. Thus, in this case the desired incipient conjugation is already set up for successful elimination, which may account for the relatively high yield (73%) compared with the yields of the sterically less constrained enol *p*-bromobenzenesulphonates of diethyl cinnamoylmalonate (40%), crotonoylmalonate (57%), and sorboylmalonate (30%).

Experimental

The infrared spectra were determined on a Perkin-Elmer 21 spectrometer with sodium chloride prism, using Nujol and hexachlorobutadiene mulls for the solid products and liquid films for the liquids. Ultraviolet spectra were determined for 95% ethanol solutions on a Cary recording spectrophotometer.

The diethyl acylmalonates were prepared by the method of Reynolds and Hauser,[14] their sequence being interrupted by distillation of the crude acylmalonate left after evaporation of the ether. The preparation of the only new example, diethyl sorboylmalonate, illustrates the general method, which gave excellent yields.

Diethyl Sorboylmalonate (IV; R = Me·CH:CH·CH:CH).—Sorboyl chloride (23 g.) was added to the ethoxymagnesium salt of diethyl malonate during 15 min. as in the method of Reynolds and Hauser.[14] The ethereal solution of the product was washed with aqueous acid, sodium hydrogen carbonate solution, and water; the solution was dried (Na_2SO_4) and the ether evaporated. The *ester* was a pale yellow liquid (36·6 g., 94%), b. p. 128—130°/0·6 mm., n_D^{32} 1·549 (Found: C, 61·7; H, 7·6. $C_{13}H_{18}O_5$ requires C, 61·5; H, 7·1%); $\nu_{max.}$ 1720s (unsat. ester C:O), 1623s and 1556s (chelated and conjuated C:O) cm.$^{-1}$; $\lambda_{max.}$ 311 mμ (ε 28,400); $\lambda_{min.}$ 242 mμ (ε 4000).

Enol Sulphonates.—These were prepared by the following general method. To the diethyl acylmalonate or ethyl acylacetoacetate (0·02 mole) in ethanol (20 ml.) a solution of sodium ethoxide [from sodium (0·02 mole) and ethanol (15 ml.)] was added. A cooled solution of the sulphonyl chloride (0·02 mole) in ethanol (40 ml.) was added and the mixture kept at room temperature overnight. The precipitated sodium chloride was removed, the mother-liquors evaporated, dissolved in ether, and extracted with dilute alkali, and the ether evaporated. The oily residue was kept in ethanol until crystallisation occurred. Sometimes the crystalline product separated from the reaction mixture with the sodium chloride. In all cases the product [all colourless except for the yellow sulphonate (XIII)] crystallised from ethanol as

[10] Cymerman Craig and Moyle, *Proc. Chem. Soc.*, 1962, 149.
[11] Nakagawa, Nakaminami, Ogura, and Ono, *Bull. Chem. Soc. Japan*, 1962, **35**, 1485, 1488; Nakaminami, *ibid.*, 1962, **35**, 1629.
[12] Märkl, *Chem. Ber.*, 1961, **94**, 3005.
[13] Gough and Trippett, *J.*, 1962, 2333, 2337.
[14] Reynolds and Hauser, *Org. Synth.*, 1950, **30**, 70.

prisms. The yields and physical properties of each are as follows. 2,2-*Diethoxycarbonyl*-1-*phenylvinyl* p-*bromobenzenesulphonate* (V; R = Ph) (29%), m. p. 91—91·5° (Found: C, 49·6; H, 3·55. $C_{20}H_{19}BrO_7S$ requires C, 49·7; H, 3·95%); $\nu_{max.}$ 1737s (unsat. ester C:O), 1635s (C:C), and 1575s (Ar) cm.$^{-1}$; $\lambda_{max.}$ 240 mμ (ε 23,200); $\lambda_{min.}$ 220 mμ (ε 14,900); $\lambda_{infl.}$ 258—270m (ε 12,000). 1-(*Diethoxycarbonylmethylene*)-3-*phenylprop*-2-*enyl* p-*bromobenzenesulphonate* (V; R = Ph·CH:CH) (52%), m. p. 98—99° (Found: C, 51·85; H, 4·2. $C_{22}H_{21}BrO_7S$ requires C, 51·9; H, 4·15%); $\nu_{max.}$ 1727 and 1710s (unsymm. unsat. ester C:O), 1624s (C:C), 1599s (C:C), and 1578m (Ar) cm.$^{-1}$; $\lambda_{max.}$ 236 and 327 mμ (ε 25,900 and 28,800); $\lambda_{min.}$ 216 and 270 mμ (ε 14,000 and 5330). 1-(*Diethoxycarbonylmethylene*)*but*-2-*enyl* p-*bromobenzenesulphonate* (V; R = Me·CH:CH) (45%), m. p. 71° (Found: C, 46·05; H, 4·3. $C_{17}H_{19}BrO_7S$ requires C, 45·7; H, 4·3%); $\nu_{max.}$ 3110w (C:CH), 1739 and 1713s (unsat. ester C:O), 1648 and 1610s (C:C), and 1574s (Ar) cm.$^{-1}$; $\lambda_{max.}$ 239 and 268 mμ (ε 20,400 and 19,800); $\lambda_{min.}$ 217 and 253 mμ (11,000 and 16,000). 1-(*Diethoxycarbonylmethylene*)*hexa*-2,4-*dienyl* p-*bromobenzenesulphonate* (V; R = Me·CH:CH·CH:CH) (61%), m. p. 112—113° (Found: C, 48·25; H, 4·8. $C_{19}H_{21}BrO_7S$ requires C, 48·3; H, 4·5%); $\nu_{max.}$ 1735s and 1714s (unsat. ester C:O), 1614s (C:C), and 1578m (Ar) cm.$^{-1}$; $\lambda_{max.}$ 235 and 322 mμ (ε 24,200 and 33,300); $\lambda_{min.}$ 261 mμ (ε 10,100). 1-*Diethoxycarbonylmethylene*)-3-*phenylprop*-2-*enyl toluene*-p-*sulphonate* (IX; R = SO_2·C_6H_4Me-*p*) (72%), m. p. 131·5—132° (Found: C, 61·9; H, 5·45. $C_{23}H_{24}O_7S$ requires C, 62·3; H, 5·45%); $\nu_{max.}$ 1728 and 1714s (unsat. ester C:O), 1627s (C:C), and 1598m (Ar) cm.$^{-1}$; $\lambda_{max.}$ 226 and 326 mμ (ε 23,050 and 27,600); $\lambda_{min.}$ 212 and 267 mμ (ε 17,150 and 5060). 1-(*Diethoxycarbonylmethylene*)-3-*phenylprop*-2-*enyl naphthalene*-2-*sulphonate* (IX; R = SO_2·$C_{10}H_7$) (68%), m. p. 95·6° (Found: C, 65·1; H, 5·0. $C_{26}H_{24}O_7S$ requires C, 65·0; H, 5·05%); $\nu_{max.}$ 1723 and 1710s (unsat. ester C:O), 1622s (C:C), and 1596s (Ar) cm.$^{-1}$; $\lambda_{max.}$ 230 and 328 mμ (ε 31,600 and 60,900); $\lambda_{min.}$ 260 mμ (ε 8450). 1-*Benzyl*-2,2-*diethoxycarbonylvinyl naphthalene*-2-*sulphonate* (XVI; R = Et) (21%), m. p. 88° (Found: C, 64·25; H, 5·05. $C_{25}H_{24}O_7S$ requires C, 64·25; H, 5·15%); $\nu_{max.}$ 1728s (unsat. ester C:O), 1659s (C:C), 1625w, 1605w, 1590w, and 1500m (Ar) cm.$^{-1}$; $\lambda_{max.}$ 231, 317, and 329 mμ (ε 70,500, 1420, and 1660); $\lambda_{min.}$ 305 and 323 mμ (ε 9500 and 1180); $\lambda_{infl.}$ 265 and 278 mμ (ε 6750 and 6150). 2-*Acetyl*-2-*ethoxycarbonyl*-1-*phenylvinyl naphthalene*-2-*sulphonate* (XII) (4%), m. p. 136° (Found: C, 65·65; H, 4·85. $C_{23}H_{20}O_6S$ requires C, 65·3; H, 4·75%); $\nu_{max.}$ 1733s (unsat. ester C:O), 1670s (unsat. ketone C:O), and 1625s (C:C) cm.$^{-1}$. 2-*Acetyl*-2-*ethoxycarbonyl*-1-o-*nitrophenylvinyl* p-*bromobenzenesulphonate* (XIII) (10%), yellow plates, m. p. 89—92° (Found: C, 46·05; H, 3·15; N, 2·95. $C_{19}H_{16}BrNO_8S$ requires C, 45·8; H, 3·2; N, 2·8%); $\nu_{max.}$ 1727s (unsat. ester C:O), 1703s (ketone C:O), 1653w (C:C), 1608w and 1578m (Ar), and 1536s (NO_2) cm.$^{-1}$.

Acetylenic Acids.—The enol *p*-bromobenzenesulphonate (about 0·002 mole) was dissolved in purified dioxan (30 ml.) and 0·4N-aqueous sodium hydroxide (20 ml., 4 equiv.) added. The homogeneous mixture was kept at room temperature overnight, ether (30 ml.) and water (20 ml.) were added, and the aqueous layer was separated, cooled in ice, and carefully acidified. Extraction with ether, treatment of the extract with sodium hydrogen carbonate solution, acidification at 0°, and re-extraction with ether gave the acetylenic acid (VI) in the ether layer. The recovered hydrolysis product, the starting diethyl acylmalonate (IV), could be isolated from the ethereal layer left after the carbonate extraction. The method of purification, yields, and physical properties of the acids are as follows. Phenylpropiolic acid (VI; R = Ph), recrystallised from carbon tetrachloride and vacuum sublimed, 73% yield, m. p. 137—138·5° (lit., 136—137°), mixed m. p. 137—138° (Found: C, 74·1; H, 4·3. Calc. for $C_9H_6O_2$: C, 74·0; H, 4·1%). The infrared spectra of the product and the authentic material were identical. *trans*-5-Phenylpent-4-en-2-ynoic acid (VI; R = Ph·CH:CH) 40% yield from 1-(diethoxycarbonylmethylene)-3-phenylprop-2-enyl *p*-bromobenzenesulphonate, 55% yield from the corresponding naphthalene-2-sulphonate, and 64% yield from the corresponding toluene-p-sulphonate as described below. The last product was the purest and had m. p. 151—152° (from benzene) (lit.,[12] m. p. 151—153°) (Found: C, 77·25; H, 5·33. Calc. for $C_{11}H_8O_2$: C, 76·9; H, 4·65%); $\nu_{max.}$ 2225s and 2190s (C:C), 1667s (unsat. acid C:O), 1605s (C:C), 1575 (Ar), and 964s (*trans*-CH:CH) cm.$^{-1}$; $\lambda_{max.}$ 221 and 298 mμ (ε 9833 and 22,510); $\lambda_{min.}$ 212 and 240 mμ (ε 8015 and 2612). *trans*-Hex-4-en-2-ynoic acid (VI; R = Me·CH:CH) (57%) sublimed under a vacuum, m. p. 127—130° (lit.,[15] 126—130°) then recrystallised from light petroleum (b. p. 80—100°), m. p. 131—133° (lit.,[15] 130·5—132·5°) (Found: C, 65·4; H, 5·95. Calc. for $C_6H_6O_2$: C,

[15] Allan, Jones, and Whiting, *J.*, 1955, 1862.

65·5; H, 5·45%). trans, trans-*Octa*-4,6-*dien*-2-*ynoic acid* (VI; R = Me·CH:CH·CH:CH) (30%) recrystallised from benzene–cyclohexane followed by vacuum sublimation to give prisms of the *acid*, m. p. 118—121° (Found: C, 71·2; H, 6·0. $C_8H_8O_2$ requires C, 70·7; H, 5·9%); $\nu_{max.}$ 2235w, 2205, and 2188s (C:C), 1674s (unsat. acid C:O), and 1635m (C:C) cm.$^{-1}$; $\lambda_{max.}$ 270 mμ (ε 24,000); $\lambda_{min.}$ 227m (ε 6550).

Similar treatment of the enol sulphonates of diethyl benzoylacetoacetate (XII) and diethyl *o*-nitrobenzoylacetoacetate (XIII) gave phenylpropiolic acid and *o*-nitrophenylpropiolic acid in 43% and 65% yield, respectively. The former had identical m. p., mixed m. p., and infrared spectrum with the previously obtained sample. The latter had m. p. 157—159° (lit.,[16] m. p. 155—156°); $\nu_{max.}$ 2240s (C:C), 1719s (acid C:O), and 1527s and 1345s (NO_2) cm.$^{-1}$.

Action of Alkali on 1-(*Diethoxycarbonylmethylene*)-3-*phenylprop*-2-*enyl Toluene*-p-*sulphonate*.—The compound (5·8 g.), dissolved in dioxan (240 ml.), was mixed with 0·3N-sodium hydroxide (110 ml., 2·5 equiv., making the total concentration 0·095M in alkali), and the mixture kept at room temperature for 18 hr. Extraction, as for the preparation of phenylpropiolic acid, gave an oil (4·64 g.) in the sodium hydrogen carbonate-soluble fraction, which crystallised from benzene (10 ml.)–hexane (1 ml.) (3·51 g.). Addition of hexane to the mother-liquors gave more crystals (0·5 g.). A little of the first crop was boiled with benzene for 2 min., then filtered, and the residue dissolved in ether and precipitated with light petroleum (b. p. 40—60°). The crystals which separated were a mixture of white and yellow prisms. The former appeared to be purer but otherwise not significantly different from the latter and were formulated as 1-(*dicarboxymethylene*)-3-*phenylprop*-2-*enyl toluene*-p-*sulphonate*, m. p. 123—124° (decomp. and gas evolution) (Found: C, 59·3; H, 4·2. $C_{19}H_{16}O_7S$ requires C, 58·8; H, 4·1%). The material lost weight during the weighing, presumably owing to loss of carbon dioxide; $\nu_{max.}$ 2635w (carboxyl OH), 1715s and 1683s (unsat. acid C:O), 1620s (C:C), 1585s (Ar), and 982s (*trans*-CH:CH) cm.$^{-1}$; $\lambda_{max.}$ 227 and 322 mμ (ε 19,970 and 26,870); $\lambda_{min.}$ 212 and 261 mμ (ε 13,815 and 4017).

The second crop crystallised from benzene–hexane (above) as needles, m. p. 131—133° (from benzene) (decomp. and gas evolution) and was formulated as 1-(*carboxyethoxycarbonylmethylene*)-3-*phenylprop*-2-*enyl toluene*-p-*sulphonate* (Found: C, 60·8; H, 5·4. $C_{21}H_{20}O_7S$ requires C, 60·6; H, 4·8%); $\nu_{max.}$ 1737s (unsat. ester C:O), 1715 and 1660m (C:C), 1613s and 1565s (Ar), 1392s and 1174s (SO_2·O), and 964s (*trans*-CH:CH) cm.$^{-1}$; $\lambda_{max.}$ 227 and 320 mμ (ε 20,950 and 25,815); $\lambda_{min.}$ 212 and 260 mμ (ε 15,750 and 5370).

The crude mixture of diacid (X; R = H, H) and monoethyl ester (X; R = H, Et) (1 g.) was dissolved in 2·4N-sodium hydroxide (5 ml.) and water was added (10 ml.). The mixture was kept in the dark for 48 hr. at room temperature, acidified at 0°, and extracted with ether. Evaporation of the ether layer gave crude yellow crystals [360 mg., 64% based on 1-(diethoxycarbonylmethylene-3-phenylprop-2-enyl toluene-*p*-sulphonate].

2-*Carboxy*-2-*ethoxycarbonyl*-1-*phenylvinyl* p-*Bromobenzenesulphonate* (VII).—2,2-Diethoxycarbonyl-1-phenylvinyl *p*-bromobenzenesulphonate (1 g.) was dissolved in dioxan (220 ml.), and a mixture of 2·9N-sodium hydroxide (3 ml.) and water (212 ml.) was added, making the total concentration N/50 in alkali. The mixture was kept at room temperature for 42 hr. The acidic (sodium hydrogen carbonate-soluble) fraction (370 mg. of an oil) was obtained as in the preparation of phenylpropiolic acid. The oil crystallised as needles of the half-ester, m. p. 128—129° (decomp. with gas evolution) [from benzene–light petroleum (b. p. 40—60°)] (Found: C, 47·45; H, 3·15. $C_{18}H_{15}BrO_7S$ requires C, 47·5; H, 3·3%); $\nu_{max.}$ 1726s (unsat. ester C:O), 1714s (unsat. acid C:O), 1615s (C:C), 1577s (Ar) cm.$^{-1}$; $\lambda_{max.}$ 239 mμ (ε 22,055); $\lambda_{min.}$ 219 mμ (ε 13,640); $\lambda_{infl.}$ 258—268 mμ (ε 10,340). Further treatment of the acid with aqueous sodium hydroxide solution overnight gave phenylpropiolic acid, identical with the sample obtained previously.

2,2-*Diethoxycarbonyl*-1-*phenylvinyl Diethyl Phosphate* (XI).—Bromine (0·94 ml., 1 equiv.) was added with stirring to diethyl benzoylmalonate (4·82 g.) in carbon tetrachloride (30 ml.) and the mixture kept at room temperature for 2 hr. The solvent was evaporated under a vacuum, leaving a colourless oil. A sample of the oil was crystallised to give pure *diethyl* α-*benzoyl*-α-*bromomalonate*, m. p. 64° [from light petroleum (b. p. 60—80°)] (Found: C, 49·4; H, 4·4. $C_{14}H_{15}BrO_5$ requires C, 49·0; H, 4·4%). The crude oil was dissolved in dry ether (50 ml.) and cooled in an ice-bath. Triethyl phosphite (3 g.) was run in with stirring during

[16] Baeyer, *Ber.*, 1880, **13**, 2258.

½ hr. and the mixture allowed to reach room temperature. Evaporation of the ether gave a pale yellow oil of the *phosphate* (7·12 g., 97·5%). A sample obtained by distillation (b. p. 185—190°/6 × 10^{-4} mm.), followed by molecular distillation, had n_D^{24} 1·498 (Found: C, 54·05; H, 6·4. $C_{18}H_{25}O_8P$ requires C, 54·0; H, 6·25%); $\nu_{max.}$ 1727s (unsat. ester C:O), 1637m (C:C), 1603, 1582, and 1497m (Ar), 1286s (P:O), and 1030s (P–O–C) cm.$^{-1}$.

Action of Alkali on Diethyl 2,2-Diethoxycarbonyl-1-phenylvinyl Phosphate.—(*a*) The phosphate (14 g.) in purified dioxan (30 ml.) was mixed with 0·83N-aqueous sodium hydroxide (30 ml.) (whole is 0·29N) and kept overnight at room temperature. Working up gave a mixture of benzoic acid and benzoylacetic acid in the bicarbonate-soluble fraction (160 mg.); the former was identified from the infrared spectrum of the mixture and the latter by crystallisation of the mixture from ether–light petroleum (40 mg., 7%), m. p. 99—100° (lit., 102—103°). The infrared spectra of the product and authentic material were identical.

(*b*) A similar experiment, but with refluxing for 10 min., gave acetophenone (identified as its 2,4-dinitrophenylhydrazone and by the identity of its infrared spectrum with an authentic sample) and benzoic acid only.

(*c*) A similar experiment in methanol–water at room temperature gave crude acetophenone (42%) and pure benzoic acid (48%).

In none of these runs was there any sign of a triple-bond frequency in the infrared spectra of the crude products.

4-p-Bromobenzenesulphonyloxy-3-ethoxycarbonyl-2-methylquinoline N-Oxide (XV; R = SO_2·C_6H_4Br-*p*).—(*a*) 3-Ethoxycarbonyl-4-hydroxy-2-methylquinoline *N*-oxide [17] (50 mg.) was dissolved in an aqueous solution of sodium hydrogen carbonate (15 mg.) and the water evaporated. The residue was dissolved in hot ethanol, *p*-bromobenzenesulphonyl chloride (55 mg.) added, and the mixture kept at room temperature overnight. On evaporation and extraction of the residue with ether and aqueous alkali, the ether layer gave an oil which formed prisms of the N-*oxide*, m. p. 226° (from ethanol) (Found: C, 49·1; H, 3·95. $C_{19}H_{16}BrNO_6$ requires C, 48·9; H, 3·45%).

(*b*) From 2-acetyl-2-ethoxycarbonyl-1-*o*-nitrophenylvinyl *p*-bromobenzenesulphonate (with Mr. E. J. D. Brown). 2-Acetyl-2-ethoxycarbonyl-1-*o*-nitrophenylvinyl *p*-bromobenzenesulphonate (0·4 g.) in dioxan (80 ml.) was mixed first with a solution of ferrous sulphate (1·8 g., heptahydrate) in water (60 ml.). Aqueous ammonia (6 ml.; *d* 0·88) was added; the mixture was warmed to 60° for 5 min., kept at room temperature for 5 hr., and the black precipitate was removed and thoroughly washed with acetone. The combined filtrates were evaporated at reduced pressure, the residue was washed with a little ether and then dissolved in ethyl acetate–water. The ethyl acetate layer was dried (Na_2SO_4) and evaporated, leaving an oily residue which crystallised from ethanol as prisms, m. p. and mixed m. p. with the sample obtained above 225—226°. The two samples had identical infrared spectra.

Action of Alkali on 2,2-Diethoxycarbonyl-1-benzylvinyl Naphthalene-2-sulphonate.—The naphthalene-2-sulphonate (XVI; R = Et) (1·0 g.) in purified dioxan (30 ml.) was mixed with 2·5N-aqueous sodium hydroxide (4 ml.) and water (16 ml.) (whole is 0·2N) and kept at room temperature overnight. Working up as for the acetylenic acids gave no unchanged starting material, but diethyl phenylacetylmalonate (220 mg., 37%) and an oil (290 mg., 33%) in the carbonate-soluble fraction. The oil did not crystallise; its infrared spectrum had no triple-bond absorption and only a singlet at about 1725 cm.$^{-1}$ in the carbonyl region; it had $\lambda_{max.}$ 228 mμ (ε 55,500) and $\lambda_{min.}$ 212 mμ (ε 29,900), resembling the starting material. It was therefore formulated as 1-benzyl-2,2-dicarboxyvinyl naphthalene-2-sulphonate (XVI; R = H). Treatment of a fraction (120 mg.) with an excess of diazoethane in ether gave starting material (50 mg., 37%), m. p. 88° (from ethanol), with an identical infrared spectrum. The remainder (240 mg.) was dissolved in 2·5N-aqueous sodium hydroxide (16 ml.) and water (10 ml.) and kept for 48 hr. at room temperature. Working up as usual gave an oil (70 mg.) whose infrared spectrum strongly resembled that of the starting oil and showed no triple-bond frequency. More crude 1-benzyl-2,2-dicarboxyvinyl naphthalene-2-sulphonate (125 mg.) was prepared as above and refluxed in 2·5N-aqueous sodium hydroxide solution (3 ml.) for 2 hr. Ether extraction gave an oil whose infrared spectrum was identical with that of phenylacetone and which gave a 2,4-dinitrophenylhydrazone, m. p. 155° (lit., 156°). Acidification of the alkali layer, and extraction, gave an oil (21 mg., 51%) whose infrared spectrum was identical with

[17] McCluskey, *J. Amer. Chem. Soc.*, 1922, **44**, 1575.

that of phenylacetic acid. Refluxing of a further 125 mg. of the acid in pyridine gave only impure phenylacetone (identified by its infrared spectrum). Pyrolysis of a further 125 mg. at 150° gave a sublimate of phenylacetic acid (identified by its infrared spectrum) and a second, unidentified product which showed neither C:C nor C:C:C absorption in its infrared spectrum.

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