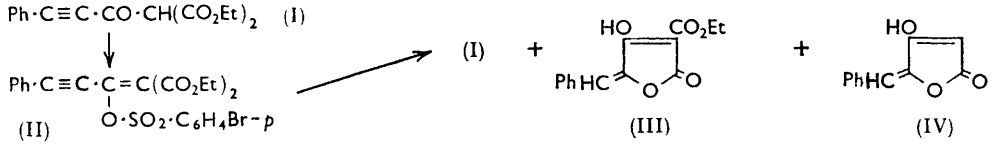
# 914. *Enol Elimination Reactions. Part II.*[1] *A New Synthesis of Tetronic Acids.**

By Ian Fleming and John Harley-Mason.

Attempts to extend the new enol elimination reaction described in the preceding paper to the synthesis of polyacetylenic acids led instead to "$\gamma$-ylidene" tetronic acids. Subsequently an improved synthesis of this class of tetronic acid was discovered, in which bromine is added to unsaturated enol *p*-bromobenzenesulphonates and the products are treated with alkali.

Having established the general synthesis of conjugated enynoic acids,[1] we attempted to extend the reaction to the synthesis of conjugated polyacetylenic acids, particularly as these are frequently found in Nature.

Diethyl phenylpropioloylmalonate (I) was made by the action of phenylpropioloyl chloride on the ethoxymagnesium salt of diethyl malonate in almost quantitative yield. Ruhemann and Merriman,[2] using the corresponding sodium salt, had been unable to make this compound; the products which they obtained were not observed with the present method. The crude ester gave a crystalline enol *p*-bromobenzenesulphonate (II) in 60% yield, which had a strong band at 2205 cm.$^{-1}$ in its infrared spectrum, characteristic of the triple bond. Treatment of this compound with alkali under similar conditions to those described in the previous paper gave three separable products, only one of which, however, the recovered hydrolysis product (I), showed a triple bond in its infrared spectrum. The reaction, therefore, had not produced the conjugated diacetylenic acid. The products obtained were formulated as $\gamma$-benzylidene-$\alpha$-ethoxycarbonyltetronic acid (III) and $\gamma$-benzylidenetetronic acid (IV) both of which were soluble in sodium hydrogen carbonate solution.



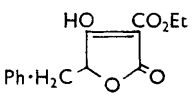

The evidence for these assignments is as follows. (i) Elemental analysis indicated $C_{14}H_{12}O_5$ and $C_{11}H_8O_3$, respectively. (ii) The $\gamma$-benzylidene-$\alpha$-ethoxycarbonyltetronic acid (III) was converted by dilute alkali into the tetronic acid (IV), thus establishing their relationship. (iii) The $\gamma$-benzylidene-$\alpha$-ethoxycarbonyltetronic acid (III) had a band at 1785 cm.$^{-1}$ in its infrared spectrum, characteristic of a vinyl ester carbonyl group. In this case the presence of a five-membered ring, which raises the frequency, and the $\alpha\beta$-unsaturation lowers the frequency, so they mutually compensate. The lowering

* Preliminary communication, *Chem. and Ind.*, 1962, 561.

[1] Part I, Fleming and Harley-Mason, preceding paper.

[2] Ruhemann and Merriman, *J.*, 1905, **87**, 1383.

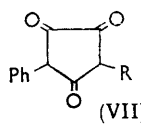
of this absorption to 1713 cm.$^{-1}$ in the free tetronic acid (IV) is normal.[3] The latter, having an unsubstituted α-position, may participate in intermolecular hydrogen bonding, as in the case of dimedone,[4] where the carbonyl absorption is 70 cm.$^{-1}$ below the normal value for an αβ-unsaturated ketone. The other infrared bands are also consistent (see Experimental section); in particular, the presence of more bands in the 1500—1800 cm.$^{-1}$ region than there are structural features to account for them is typical of tetronic acids.[3] (iv) The nuclear magnetic resonance spectrum of the free tetronic acid (IV) showed an aromatic multiplet, and the two aliphatic protons as separate singlets. (v) Hydrogenation of the γ-benzylidene-α-ethoxycarbonyltetronic acid (III) was effected with difficulty and gave γ-benzyl-α-ethoxycarbonyltetronic acid (V) whose m. p. agreed with literature values,[5,6] and whose infrared and ultraviolet spectra showed the expected features. Hydrogenation of γ-benzylidenetetronic acid (V) was effected with even more difficulty, and the single isolated product showed only end-absorption in the ultraviolet spectrum, and hydroxyl and saturated carboxylic acid carbonyl frequencies in its infrared spectrum. It was formulated as the hydrogenation and hydrogenolysis product, 3-hydroxy-5-phenylpentanoic acid (VI), the reported [7] m. p. of which agreed with that found. (vi) The p$K_a$ of the γ-benzylidene-α-ethoxycarbonyltetronic acid (III) was 2·5, and that of the γ-benzylidenetetronic acid (IV) was 4·15, both measured in aqueous methanol. The difference in these values parallels the difference found for other pairs of tetronic acids.[8] (vii) The method of synthesis is strongly in favour of the structures (III) and (IV). The only reasonable alternatives, the cyclopentanetriones (VII; R = $CO_2Et$ or H) and the



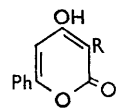

(V)

$Ph{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2H$

(VI)




(VII)




(VIII)

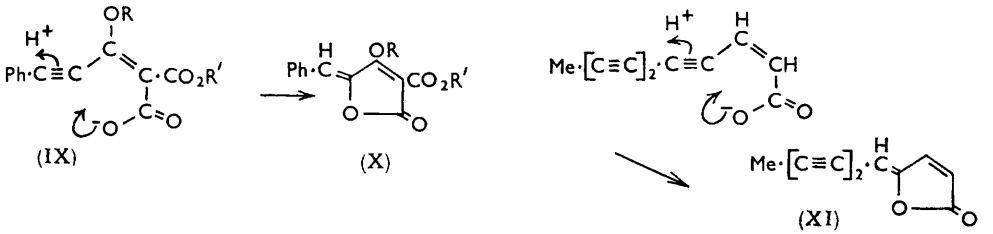
hydroxypyrones (VIII; R = $CO_2Et$ or H) were unlikely from the above evidence. Since the reported [9] m. p. of the free phenylcyclopentanetrione (VII; R = H) was similar to that observed for the $C_{11}H_8O_3$ product, this compound was prepared, and found to be different. Subsequently, the hydroxypyrones (VIII; R = $CO_2Et$ or H) were also prepared (see below) and found to be different from our products, as expected from the m. p.'s in the literature.[10,11]

Presumably the reaction proceeds through ester hydrolysis and intramolecular attack by the carboxylate ion on the triple bond or the protonated triple bond, (IX) ⟶ (X). An analogous process was observed by Jones and his co-workers [12] when they saponified the dehydromatricaria ester. The presence in this molecule of the *cis*-double bond enabled intramolecular attack on the triple bond, with formation of the lactone (XI), to take place.

The only other "γ-ylidene" tetronic acids known are the natural products related to pulvinic acid and vulpinic acid,[13] pulvinone,[14] and an intermediate in Raphael's synthesis of penicilloic acid.[15]

[3] Duncanson, *J.*, 1953, 1207.
[4] Rasmussen, Tunnicliff, and Brattain, *J. Amer. Chem. Soc.*, 1949, **71**, 1068.
[5] Pons and Veldstra, *Rec. Trav. chim.*, 1955, **74**, 1217.
[6] Reid and Ruby, *J. Amer. Chem. Soc.*, 1951, **73**, 1060.
[7] Fittig and Hofmann, *Annalen*, 1894, **283**, 309.
[8] Haynes and Plimmer, *Quart. Rev.*, 1960, **14**, 292.
[9] Wislicenus and Melius, *Annalen*, 1924, **436**, 101.
[10] Macierewicz and Janiszewska-Broziek, *Roczniki Chem.*, 1950, **24**, 167.
[11] Arndt, Eistert, Scholz, and Aron, *Chem. Ber.*, 1936, **69**, 2308.
[12] Christensen, Sørensen, Bell, Jones, and Whiting, "Festschrift Arthur Stoll," 1957, 545.
[13] Meyer and Cook, "The Chemistry of Natural Colouring Matters," Reinhold, New York, 1943, p. 156.
[14] Claisen and Ewan, *Annalen*, 1895, **284**, 278.
[15] Raphael, *J.*, 1948, 1508.

Accordingly, the synthesis of this class of compound was studied briefly. In the first place, it was found that the presence of the *p*-bromobenzenesulphonyl group was unnecessary in the method used above. Treatment of diethyl phenylpropioloylmalonate (I) with dilute sodium hydroxide at room temperature gave starting material (26%),



(IX) (X) (XI)

γ-benzylidene-α-ethoxycarbonyltetronic acid (III) (13%), and γ-benzylidenetetronic acid (IV) (13%). Similar treatment with alkali, but boiling the solution for two hours, gave only γ-benzylidenetetronic acid (IV) (34%). Little attempt was made to improve these yields, since an alternative route was discovered.

Addition of bromine to 1-(diethoxycarbonylmethylene)-3-phenylprop-2-enyl *p*-bromobenzenesulphonate (preceding paper:[1] V; R = Ph·CH:CH) gave 2,3-dibromo-1-(diethoxycarbonylmethylene)-3-phenylpropyl *p*-bromobenzenesulphonate (XII; R = Ph). Treatment of this compound with alkali in aqueous dioxan gave γ-benzylidene-α-ethoxycarbonyltetronic acid (III) in 52% yield. This route, besides giving a better yield, avoids the relatively expensive acetylenic starting material of the previous route.

The reaction appears to be general. Addition of bromine to 1-(diethoxycarbonylmethylene)but-2-enyl *p*-bromobenzenesulphonate (preceding paper: V; R = Me·CH:CH) gave 2,3-dibromo-1-(diethoxycarbonylmethylene)butyl *p*-bromobenzenesulphonate (XII; R = Me), and treatment of this product with alkali, as before, gave a compound, formulated, by analogy, as α-ethoxycarbonyl-γ-ethylidenetetronic acid (XIII; R = $CO_2Et$) in 34% yield. This structure was confirmed by the following evidence. (i) Elemental analysis corresponded with $C_9H_{10}O_5$. (ii) The infrared spectrum showed strong absorption at 1775 cm.$^{-1}$ (lactone C:O). (iii) The nuclear magnetic resonance spectrum showed the *O*-ethyl group, and a low-intensity quartet and high-intensity

(XII) (XIII)

doublet due to the ethylidene group. The alternative formulation, as a hydroxy-methylpyrone (VIII; Me for Ph, and R = $CO_2Et$), was, therefore, ruled out. (iv) The p$K_a$ was 2·3. (v) Treatment with aqueous 10% sodium hydroxide at room temperature gave a compound, $C_6H_6O_3$, formulated as γ-ethylidenetetronic acid (XIII; R = H), which had a different ultraviolet spectrum and p$K_a$ from those of the known isomer, 4-hydroxy-6-methyl-2-pyrone[16] (VIII; Me for Ph, and R = H). In one experiment, a small amount of material, with the analysis of $C_7H_6O_5$, was produced, presumably the free carboxylic acid (XIII; R = $CO_2H$). On melting at 127° it effervesced, rapidly resolidified, and finally melted just below the melting point of γ-ethylidenetetronic acid (XIII; R = H). This appears to be the first isolation of an α-carboxytetronic acid.

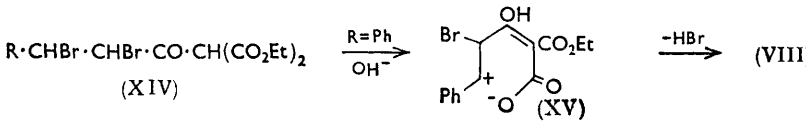
In the case of diethyl crotonoylmalonate the *p*-bromobenzenesulphonate group was not necessary for tetronic acid synthesis. Addition of bromine directly to diethyl crotonoylmalonate (preceding paper: IV; R = Me·CH:CH) and treatment of the crude product

[16] Berson, *J. Amer. Chem. Soc.*, 1952, **74**, 5172.

(presumably XIV; R = Me) with aqueous alkali at room temperature gave the same product, α-ethoxycarbonyl-γ-ethylidenetetronic acid (XIII; R = $CO_2Et$) in 46% yield.

However, the same technique, of adding bromine and treating the product with aqueous alkali, on diethyl cinnamoylmalonate (preceding paper: IV; R = Ph·CH:CH) gave 3-ethoxycarbonyl-4-hydroxy-6-phenyl-2-pyrone (VIII; R = $CO_2Et$) in 36% yield, identified by its melting point and comparison of its degradation product, 4-hydroxy-6-phenyl-2-pyrone (VIII; R = H), with an authentic sample.[10,11]

It is probable that in the latter case the formation of a benzyl carbonium ion (XV) is encouraged in the more polar medium, water, and that this carbonium ion is attacked by the carboxylate anion resulting from ester hydrolysis. In the less polar medium, aqueous dioxan, used for the corresponding enol *p*-bromobenzenesulphonate, formation of the carbonium ion is not so encouraged and direct displacement of bromide ion takes place in what is, presumably, the geometrically favoured position.




In the case of the diethyl αβ-dibromobutyrylmalonate (XIV; R = Me), the corresponding carbonium ion (XV; Me for Ph) is not stabilised by conjugation with a benzene ring and is evidently not formed to an appreciable extent even in water.

## Experimental

For details of the determination of the infrared and ultraviolet spectra see the preceding paper.[1] Nuclear magnetic resonance (n.m.r.) spectra were determined by using a Perkin-Elmer nuclear magnetic resonance spectrometer operating at 40 Mc./sec. Throughout, the signals are referred on the τ scale, with tetramethylsilane (τ = 10·00) as an internal reference

*Diethyl Phenylpropioloylmalonate* (I).—This was prepared by the method of Reynolds and Hauser [17] as used for diethyl sorboylmalonate in the preceding paper.[1] The yield of undistilled *ester* was " 100%." A sample, after molecular distillation, had $n_D^{25}$ 1·573 (Found: C, 66·7; H, 6·2. $C_{16}H_{16}O_5$ requires C, 66·7; H, 5·6%); $\nu_{max.}$ 2230s (C:C), 1727s (ester C:O), 1648m, 1605m, 1538s, and 1495w (enol, keto, and aryl absorptions) cm.$^{-1}$. 1-(*Diethoxycarbonylmethylene*)-3-*phenylprop*-2-*ynyl* p-*bromobenzenesulphonate* (II) was prepared by the general method described in the preceding paper, from the crude acylmalonate directly. The yield of the *vinyl sulphonate* was 60%; it formed prisms, m. p. 61—62° (Found: C, 57·5; H, 3·4. $C_{22}H_{19}BrO_7S$ requires C, 57·2; H, 3·75%); $\nu_{max.}$ 2205m (C:C), 1725s (unsat. ester C:O), 1631s (C:C), 1594m, 1577m, and 1492m (Ar) cm.$^{-1}$; $\lambda_{max.}$ 236 and 313 mμ (ε 26,150 and 22,120); $\lambda_{min.}$ 217 and 264 mμ (ε 19,620 and 10,860).

*Action of Alkali on* 1-(*Diethoxycarbonylmethylene*)-3-*phenylprop*-2-*ynyl* p-*Bromobenzenesulphonate*.—The compound (2 g.), in purified dioxan (45 ml.), was mixed with 0·465N-aqueous sodium hydroxide (35 ml.; whole is 0·2N) and kept overnight at room temperature. Working up, as in the preparation of the acetylenic acids, gave diethyl phenylpropioloylmalonate (0·47 g., 41%) in the sodium hydrogen carbonate-insoluble, alkali-soluble, fraction. The crude sodium hydrogen carbonate-insoluble fraction showed no C:C absorption in its infrared spectrum. It was boiled for 5 min. with chloroform (4 ml.) and filtered. The filtrate slowly deposited pale yellow prisms (110 mg., 11%) which gave colourless prisms, decomposing and darkening at 175—180°, finally melting at 196° (from benzene, ethanol, or ethyl acetate), of γ-*benzylidene*-α-*ethoxycarbonyltetronic acid* (III) (Found: C, 65·0; H, 4·7. $C_{14}H_{12}O_5$ requires C, 64·7; H, 4·6%); $\nu_{max.}$ 3210m (OH, not chelated), 1785s (αβ-unsat. vinyl γ-lactone C:O), 1670s (doubly conjugated ester C:O), 1630m, 1602s, and 1502w (Ar) cm.$^{-1}$; $\lambda_{max.}$ 226 and 300 mμ (ε 18,660 and 22,600); $\lambda_{min.}$ 246 mμ (ε 4890); p$K_a$ (in 62·5% v/v methanol–water) 2·5 (Equiv. weight, by titration, 274. $C_{14}H_{12}O_5$ requires 260).

The chloroform mother-liquors were evaporated; the residue crystallised from benzene as a mixture of fine white needles, m. p. 157°, and pale yellow plates, m. p. 166° (50 mg., 7%).

[17] Reynolds and Hauser, *Org. Synth.*, 1955, **30**, 70.

The ultraviolet and infrared spectra of the forms were virtually identical and recrystallisation of hand-separated plates gave again the mixture of plates and needles, indicating that they were different crystalline modifications of the same compound, *γ-benzylidenetetronic acid* (IV) (in subsequent experiments the mixture of crystalline modifications was used) (Found: C, 70·1; H, 4·8. $C_{11}H_8O_3$ requires C, 70·3; H, 4·3%); $\nu_{max.}$ for the plates 2690w (OH, of acid), 1713s (intermolecularly chelated αβ-unsturated vinyl γ-lactone C:O), 1688 and 1663m (C:C) 1570s (conjugate and chelated C:O), and for the needles an extra band at 1604s (Ar) cm.$^{-1}$; $\lambda_{max.}$ 220, 227, 233, and 312 mμ (ε 9450, 9000, 7900, and 19,150); $\lambda_{min.}$ 225, 232, and 244 mμ (ε 8500, 7720, and 2850) [*M* (cryoscopy in dioxan) 206; (by titration) 190. $C_{11}H_8O_3$ requires 188]; p$K_a$ (in 62·5% v/v methanol–water) 4·15. The n.m.r. spectrum, taken in acetone solution, showed a complex multiplet centred at τ 2·4 due to the aromatic protons, a singlet at τ 3·65 due to the exocyclic vinyl proton, and a singlet at τ 4·72 due to the α-proton.

*Action of Alkali on γ-Benzylidene-α-ethoxycarbonyltetronic Acid.*—γ-Benzylidene-α-ethoxycarbonyltetronic acid (30 mg.) was kept in 0·5N-aqueous sodium hydroxide (5 ml.) for 2 days at room temperature. Extraction with ether after acidification, evaporation of the ether, and crystallisation of the resultant oil (24 mg.) gave pale yellow prisms (7 mg., 22%), m. p. 165°. The infrared spectrum was identical with that of γ-benzylidenetetronic acid obtained from 1-(diethoxycarbonylmethylene)-3-phenylprop-2-ynyl *p*-bromobenzenesulphonate.

*Hydrogenation of γ-Benzylidene-α-ethoxycarbonyltetronic Acid.*—γ-Benzylidene-α-ethoxycarbonyltetronic acid (200 mg.) in ethyl acetate (20 ml.) was hydrogenated at room temperature and atmospheric pressure with Adams catalyst (27 mg.) for 2·5 hr., after which 3 equiv. of hydrogen (56 ml.) had been absorbed. Filtration, evaporation, and crystallisation from benzene–light petroleum (b. p. 60—80°) gave crystals (80 mg., 25%). A sublimed sample had m. p. 110—116°, and m. p. 129—130° (from ethanol) (lit.,[5,6] 122—130° and 126·5—128°); $\nu_{max.}$ 1760s (conjugated γ-lactone), 1702m (C:C), and 1608s (chelated C:O) cm.$^{-1}$; $\lambda_{max.}$ 241 mμ (ε 9460); $\lambda_{min.}$ 219 mμ (ε 6600), consistent with the formulation as γ-benzyl-α-ethoxycarbonyl tetronic acid (V).

*Hydrogenation of γ-Benzylidenetetronic Acid.*—γ-Benzylidenetetronic acid (100 mg.) in ethyl acetate (10 ml.) was hydrogenated at room temperature and atmospheric pressure with Adams catalyst (11 mg.) for 40 min., after which 1·5 equiv. of hydrogen had been steadily absorbed. Filtration, evaporation, and crystallisation from benzene gave some starting material (10 mg.), m. p. 162—164° (identical infrared spectrum). A second crop of starting material (5 mg.) separated during several days; when this had been removed the residue deposited white crystals (20 mg.), m. p. 128—129·5°; $\nu_{max.}$ 3220m (bonded OH), 2640w (carboxyl OH), 1680s (bonded acid C:O), 1610 and 1497w (unconjugated Ar) cm.$^{-1}$. The ultraviolet spectrum showed no absorption above 220 mμ in neutral, acid, and alkaline solutions. The material was formulated as 3-hydroxy-5-phenylpentanoic acid (VI) (lit.,[7] m. p. 130°).

*Action of Alkali on Diethyl Phenylpropioloylmalonate.*—Diethyl phenylpropioloylmalonate (1·15 g.) was kept in 2·5N-aqueous sodium hydroxide (4 ml.) at room temperature for 1 week. Water was added (30 ml.) and the mixture acidified (HCl) and extracted with ethyl acetate (220 ml.). The ethyl acetate layer was extracted with sodium hydrogen carbonate solution and the organic layer evaporated, to give starting material (0·3 g., 26%), identified by its infrared spectrum. The carbonate extract was acidified, and extracted with ethyl acetate (2 × 20 ml.), and the organic layer dried ($Na_2SO_4$) and partially evaporated. On storage, γ-benzylidene-α-ethoxycarbonyltetronic acid separated (140 mg., 13%), softening and darkening at 176° and finally melting at 195°. Evaporation of the mother-liquors and crystallisation of the residue from benzene gave γ-benzylidenetetronic acid (100 mg., 13%), m. p. 158—162°. The infrared spectra of both products were identical with those of products formed by alkali from 1-(diethoxycarbonylmethylene)-3-phenylprop-2-ynyl *p*-bromobenzenesulphonate. A similar experiment to the above, but refluxing the mixture for 2 hr., gave no starting material, no ethoxycarbonyltetronic acid but γ-benzylidenetetronic acid (IV) (240 mg., 34%).

2,3-*Dibromo*-1-(*diethoxycarbonylmethylene*)-3-*phenylpropyl* p-*Bromobenzenesulphonate* (XII; R = Ph).—1-(Diethoxycarbonylmethylene)-3-phenylprop-2-enyl *p*-bromobenzenesulphonate (1·6 g.) in glacial acetic acid (20 ml.) was mixed with bromine (0·12 ml.) and kept at room temperature for 24 hr. Evaporation of the solvent and crystallisation of the residue gave needles of the *dibromide* (0·66 g., 31%), m. p. 155° (from ethanol) (Found: C, 39·5; H, 3·0. $C_{22}H_{21}Br_3O_7S$ requires C, 39·6; H, 3·2%); $\nu_{max.}$ 1723s (unsat. ester C:O), 1574m (Ar) cm.$^{-1}$; $\lambda_{max.}$ 240 mμ (ε 25,100); $\lambda_{min.}$ 221 mμ (ε 20,900).

*Action of Alkali on* 2,3-*Dibromo*-1-(*diethoxycarbonylmethylene*)-3-*phenylpropyl* p-*Bromobenzenesulphonate*.—The dibromo-compound (0·54 g.) in purified dioxan (16 ml.) was mixed with 0·25N-aqueous sodium hydroxide solution (10 ml.; whole is 0·104N) and kept at room temperature overnight. Working up as in its preparation above gave γ-benzylidene-α-ethoxycarbonyltetronic acid (120 mg., 52%). Recrystallisation from ethyl acetate gave 53 mg. of pure material, softening and darkening at 175°, m. p. 196°. The infrared spectrum and mixed m. p. were identical with those of the previously obtained samples.

2,3-*Dibromo*-1-(*diethoxycarbonylmethylene*)*butyl* p-*Bromobenzenesulphonate* (XII; R = Me).—1-(Diethoxycarbonylmethylene)but-2-enyl *p*-bromobenzenesulphonate (0·56 g.) in carbon tetrachloride (10 ml.) was mixed with bromine (0·073 ml.) and kept at room temperature for 2 hr. Evaporation of the solvent gave the *dibromo-compound*, prisms, m. p. 153—154° (from ethanol) (0·49 g., 65%) (Found: C, 33·7; H, 3·1. $C_{17}H_{19}BrO_7S$ requires C, 33·6; H, 3·2%); $\nu_{max.}$ 1725s (ester C:O), 1636s (C:C), 1577s and 1501w (Ar) cm.$^{-1}$; $\lambda_{max.}$ 241 mμ (ε 21,500); $\lambda_{mm.}$ 220 mμ (ε 15,400).

α-*Ethoxycarbonyl*-γ-*ethylidenetetronic Acid* (XIII; R = $CO_2Et$).—2,3-Dibromo-1-(diethoxycarbonylmethylene)butyl *p*-bromobenzenesulphonate (1·8 g.) in purified dioxan (46 ml.) was mixed with 0·4175N-aqueous sodium hydroxide (30 ml.; whole is 0·165N and 4 equiv.) and kept at room temperature overnight. Working up as in the preparation of the acetylenic acids gave crude crystalline material (0·51 g., 86%) in the sodium hydrogen carbonate-soluble fraction. Crystallisation from benzene with addition of light petroleum (b. p. 40—60°) and leaving the mixture at 0° gave needles of α-ethoxycarbonyl-γ-ethylidenetetronic acid (200 mg., 34%), m. p. 125—127° (Found: C, 54·2; H, 4·9. $C_9H_{10}O_5$ requires C, 54·5; H, 5·1%). On a larger scale it was possible to obtain needles of the *tetronic acid*, m. p. 134—136° (from ethanol); $\nu_{max.}$ 3205m (OH) 1775s (unsat. vinyl lactone C:O), 1690m, 1665s (doubly conjugate ester C:O), 1615s (C:C) cm.$^{-1}$; $\lambda_{max.}$ 230, 248, and 286 mμ (ε 14,260, 14,700, and 9870); $\lambda_{min.}$ 238 and 271 mμ (ε 14,000 and 8590). The n.m.r. spectrum taken in carbon tetrachloride solution showed a weak quartet centred at τ 4·25 (vinyl proton), a medium intensity quartet centred at τ 5·65 (ester $CH_2$), a strong doublet centred at τ 8·07 (methyl group attached to the exocyclic double bond), and a strong triplet centred at τ 8·60 (ester $CH_3$ group). The spectrum is not consistent with the alternative formulation as a δ-lactone. The p$K_a$ (in water with a trace of methanol) was 2·3. *M* (titration) was 208. ($C_9H_{10}O_5$ requires 198.)

*Preparation of, and Action of Alkali on, Diethyl* αβ-*Dibromobutyryl Malonate*.—Diethyl crotonoylmalonate (1·67 g.) in carbon tetrachloride (10 ml.) was treated at 0° with bromine (0·38 ml.) in carbon tetrachloride (5 ml.) as rapidly as the colour was discharged. The solvent was evaporated and the residue dissolved in 2·5N-aqueous sodium hydroxide solution (9 ml.) and diluted with water (10 ml.). The mixture was extracted with ether and the aqueous layer kept at room temperature overnight. Acidification (HCl), extraction with ether, and extraction of the ether with sodium hydrogen carbonate solution, acidification, extraction with ether, and evaporation of the ether layer gave α-ethoxycarbonyl-γ-ethylidene tetronic acid (660 mg., 46%). Sublimation under a vacuum at 100° gave a reasonably pure product, m. p. 122—125°, whose infrared spectrum was identical with the sample obtained previously from 2,3-dibromo-1-(diethoxycarbonylmethylene)butyl *p*-bromobenzenesulphonate.

γ-*Ethylidenetetronic acid* (XIII; R = H).—α-Ethoxycarbonyl-γ-ethylidenetetronic acid (180 mg.) was dissolved in 2·5N-sodium hydroxide solution (3 ml.) and kept at room temperature for 2 days. Acidification, extraction with ether, extraction of the ether layer with sodium hydrogen carbonate solution, reacidification, and extraction with ether gave, after evaporation of the ether, γ-*ethylidenetetronic acid* (80 mg., 70%), m. p. 182—185° (from benzene with a little ethanol) (Found: C, 56·9; H, 5·0. $C_6H_6O_3$ requires C, 57·2; H, 4·8%); $\nu_{max.}$ 2680 and 2540m (acid OH), 1724s (lactone C:O, lowered by intermolecular hydrogen bonding), 1693s, 1643m, and 1612s (C:C), and 1550s (chelated C:O) cm.$^{-1}$; $\lambda_{max.}$ 257 mμ (ε 16,900); p$K_a$ (in water) 3·85 [*M* (titration), 133. $C_6H_6O_3$ requires 126]. 6-Methyl-4-hydroxy-2-pyrone [16] has m. p. 186—186·5°, p$K_a$ 5·00, and $\lambda_{max.}$ 283 and 345 mμ (log ε 3·78 and 2·45).

*Preparation of, and Action of Alkali on, Diethyl* αβ-*Dibromo*-β-*phenylpropionylmalonate* (XIV; R = Ph).—Diethyl cinnamoylmalonate (2·0 g.) in carbon tetrachloride (20 ml.) was cooled to 0° and a solution of bromine (0·35 ml.) in carbon tetrachloride (5 ml.) added as rapidly as the colour was discharged. Evaporation of the solvent, addition of N-aqueous sodium hydroxide (22·5 ml.), extraction with ether, and keeping the aqueous layer overnight gave, after working up as in the corresponding reaction with diethyl crotonoylmalonate, in the carbonate-soluble

fraction needles of 3-ethoxycarbonyl-4-hydroxy-6-phenyl-2-pyrone (0·64 g., 36%), m. p. 132° (lit.,[10] m. p. 134—135°) (Found: C, 64·7; H, 4·6. Calc. for $C_{14}H_{12}O_5$: C, 64·7; H, 4·6%); $\nu_{max.}$ 1745s (lactone C:O), 1714m (conjugated ester C:O), 1640s (chelated C:O), 1567s (C:C), and 1502m (Ar) cm.$^{-1}$; $\lambda_{max.}$ 216 and 328 mμ (ε 18,100 and 17,600); $\lambda_{min.}$ 254 mμ (ε 3780); $\lambda_{infl.}$ 233 and 277 mμ (ε 12,000 and 5260). The assignment of structure was confirmed by treatment of the product with sulphuric acid by the method of Macierewicz and Janiszewska-Broziek [10] which gave 6-phenyl-4-hydroxy-2-pyrone (VIII; R = H), m. p. 262—263° with decomposition and sintering at 245—250° (lit.,[10,11] decomp. with melting 245—247°). In view of the m. p. discrepancy, 6-phenyl-4-hydroxy-2-pyrone was prepared from dehydrobenzoylacetic acid by the method of Arndt, Eistert, Scholz, and Aron [11] and found to be identical with the product obtained as above, in m. p., mixed m. p., and infrared spectrum.

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