CXLIII.—*The Properties of Conjugated Compounds. Part II. Addition to Butadiene Esters.*

By Ernest Harold Farmer and Alfred Thomas Healey.

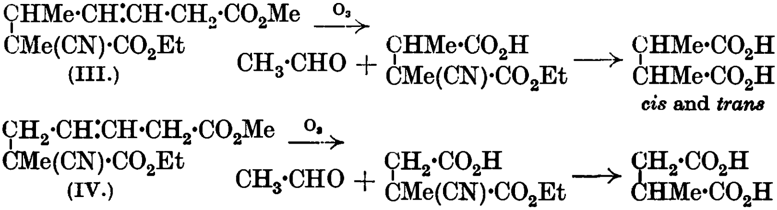
It has been established that the addition of esters to αβ-unsaturated esters and ketones can take place reversibly in two ways, yielding products of the normal and the abnormal type $\cdot CHX\cdot CH_2\cdot CO$ and $CH_2\cdot CHX\cdot CO$ [$X{=}CH(CO_2Et)_2$, etc.], respectively, although generally one type of addition may be favoured to the practical exclusion of the other. The formation of one or other (or both) of the additive products in a given case is dependent on a system of connected equilibria which vary with the experimental conditions but are not greatly affected by the polar condition of the reactants (compare E. H. Ingold, J., 1925, **127**, 469; Cooper, Ingold, and Ingold, J., 1926, 1868). With conjugated esters of the type $CH{:}CH\cdot CH{:}CH\cdot C{:}O$, however, the possible modes of additive reaction are more numerous. Vorländer, in securing the attachment of the malonic residue at the δ-carbon atom of methyl sorbate (*Annalen*, 1906, **345**, 227), experimentally demonstrated that they are not confined to αβ-addition, and it is possible that attachment of the components of the addendum may occur simultaneously or alternately in two or more ways.

In seeking evidence of the variability or otherwise of addition to butadiene derivatives, the additive properties of sorbic and β-vinylacrylic acids were studied. The addition of methyl sodiomalonate to the esters of these acids has recently been examined by Kohler and Butler (*J. Amer. Chem. Soc.*, 1926, **48**, 1036), who obtained in the respective cases excellent yields of the compounds $(MeO_2C)_2CH\cdot CHMe\cdot CH{:}CH\cdot CH_2\cdot CO_2Me$ (I) and

$(MeO_2C)_2CH\cdot CH_2\cdot CH{:}CH\cdot CH_2\cdot CO_2Me$ (II),

which appeared to be the sole products of addition. Our experiments, carried out before the appearance of Kohler and Butler's paper, gave results concerning the formation and constitution of these compounds in complete agreement with those of the latter authors, and in the case of methyl β-vinylacrylate, particularly, the absence of any but the minutest traces of a second additive product was readily demonstrable. Further, an examination of (II) showed it to be non-mobile : it neither suffered double-bond displacement by the action of sodium methoxide nor showed any tendency to undergo further condensation with esters like methyl cyanoacetate. Therefore its formation by a process of $\gamma\delta$-addition—a possibility not usually considered but which would be somewhat analogous to the formation of γ-oxalyl derivatives of $\beta\beta$-dimethylacrylic ester (Higginbotham and Lapworth, J., 1923, **123**, 1325)—followed by double-bond displacement is out of the question. The additions are indubitably and completely of $\alpha\delta$-type.

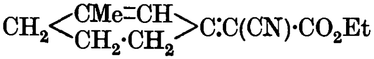
Attempts to obtain a different result by varying the experimental conditions of condensation failed entirely, but the limits of variation with substances so prone to polymerisation as sorbic and β-vinylacrylic esters were necessarily narrow. Attention was therefore directed to the effect of varying the ester-addendum, as, for instance, by alkylation. Few cases of the employment of alkylated malonic and cyanoacetic esters in the Michael reaction are recorded in the literature. Thorpe observed (J., 1900, **77**, 932) that during reaction between ethyl $\beta\beta$-dimethylacrylate and ethyl methylsodiocyanoacetate the addendum appeared to suffer an unusual partition, CH_3—¦—$C(CN){:}C(ONa){\cdot}OEt$, leading to the formation of the methylable sodio-derivative of an ester $EtO_2C{\cdot}CHMe{\cdot}CMe_2{\cdot}CH(CN){\cdot}CO_2Et$. E. H. Ingold has interpreted the observations of Bone and Sprankling (J., 1899, **75**, 839) concerning the interaction of ethyl ethylsodiomalonate and ethyl α-bromo*iso*butyrate in a manner involving reversible Michael additions, whereby the effect of the alkyl group of the addendum is to favour the abnormal type of $\alpha\beta$-addition. With both sorbic and β-vinylacrylic esters, however, the addition of ethyl methylcyanoacetate, which readily takes place, follows the same course as with ethyl malonate; the esters (III) and (IV) are exclusively produced in the respective cases, the constitutions following from the nature of the ozone degradation products as shown below.



$$\begin{array}{l} \text{CHMe}{\cdot}\text{CH}{:}\text{CH}{\cdot}\text{CH}_2{\cdot}\text{CO}_2\text{Me} \\ | \\ \text{CMe(CN)}{\cdot}\text{CO}_2\text{Et} \\ \quad\text{(III.)} \end{array} \xrightarrow{O_3} \text{CH}_3{\cdot}\text{CHO} + \begin{array}{l} \text{CHMe}{\cdot}\text{CO}_2\text{H} \\ | \\ \text{CMe(CN)}{\cdot}\text{CO}_2\text{Et} \end{array} \longrightarrow \begin{array}{l} \text{CHMe}{\cdot}\text{CO}_2\text{H} \\ | \\ \text{CHMe}{\cdot}\text{CO}_2\text{H} \\ \textit{cis}\ \text{and}\ \textit{trans} \end{array}$$

$$\begin{array}{l} \text{CH}_2{\cdot}\text{CH}{:}\text{CH}{\cdot}\text{CH}_2{\cdot}\text{CO}_2\text{Me} \\ | \\ \text{CMe(CN)}{\cdot}\text{CO}_2\text{Et} \\ \quad\text{(IV.)} \end{array} \xrightarrow{O_3} \text{CH}_3{\cdot}\text{CHO} + \begin{array}{l} \text{CH}_2{\cdot}\text{CO}_2\text{H} \\ | \\ \text{CMe(CN)}{\cdot}\text{CO}_2\text{Et} \end{array} \longrightarrow \begin{array}{l} \text{CH}_2{\cdot}\text{CO}_2\text{H} \\ | \\ \text{CHMe}{\cdot}\text{CO}_2\text{H} \end{array}$$

Indeed in no experiment could any divergence from the type of ester-addition be observed, and in particular there is little doubt of the entire absence of αβ-products. Consequently, any representation such as that of Kohler and Butler (1 : 4-additive product $\rightleftharpoons CH_2{:}CH{\cdot}CH{:}CH{\cdot}CO_2Me + Na[CH(CO_2Me)_2] \rightleftharpoons$ 1 : 6-additive product) is at present purely speculative. In view of the foregoing results, the observation that ethyl methyl*cyclo*hexenylidenecyanoacetate (V) under Guareschi's conditions adds on the components of

(V.) 

$$CH_2{<}\begin{matrix}CMe{:}CH\\CH_2{\cdot}CH_2\end{matrix}{>}C{:}C(CN){\cdot}CO_2Et$$

$$CH_3{\cdot}CH{:}CH{\cdot}CH{:}C(CO_2Et)_2$$

(VI.)

ethyl cyanoacetate at the αβ-carbon atoms (Farmer and Ross, J., 1926, 1577) is of interest; this substance may be regarded as a substituted sorbic ester in which both spatial and polar conditions are modified—a modification which causes complete change of additive mode. With the α-carboxysorbic ester (VI) addition of esters could not be secured.

It was shown by Auwers and Heyna (*Annalen*, 1923, **434**, 140) that sorbic acid adds on bromine at the γδ-double bond. β-Vinylacrylic acid behaves similarly. The crude dibromide consisted of a mixture of crystalline and liquid material, each portion of which yielded with diethylamine a crystalline bromovinylacrylic acid. The identity or otherwise of these two products could not be satisfactorily determined, since both polymerised on heating and neither could be satisfactorily reduced. The bromination product was, however, constitutionally homogeneous, both solid and liquid portions yielding acraldehyde dibromide (identified by conversion into α-bromoacraldehyde) and oxalic acid. No trace of material derived by αβ- or βγ-addition could be isolated.

EXPERIMENTAL.

A. Derivatives of β-*Vinylacrylic and Sorbic Acids.*

β-Vinylacrylic acid, prepared by Doebner's method (*Ber.*, 1902, **35**, 1137), was purified by solution in ether and extraction with dilute aqueous sodium carbonate. The acid obtained by re-extracting the alkaline liquid was drained on porous tiles and recrystallised from petroleum. It formed colourless, prismatic needles, m. p. 80° (Doebner, m. p. 80°; Kohler and Butler, m. p. 72°).

The *dibromide* was obtained in the usual way, carbon disulphide being used as diluent. The crude product, thoroughly freed from carbon disulphide, partly solidified when cooled in an ice–salt mixture. The semi-solid mass was spread on porous tiles; these absorbed the oily matter, leaving a solid which separated from petroleum in tufts of colourless needles, m. p. 47° (Found : Br, 61·55. $C_5H_6O_2Br_2$ requires Br, 62·0%). The *methyl* ester, obtained by the action of methyl alcohol and sulphuric acid on the solid dibromide, was a pale yellow oil, b. p. 136°/10 mm. (Found: Br, 58·6. $C_6H_8O_2Br_2$ requires Br, 58·8%).

Extraction of the porous tiles with ether yielded a brown oil (about one-fifth of the total product) from which no further solid matter could be obtained. From this dibromo-acid (Found: Br, 61·6%), which was examined separately, the *methyl* ester was obtained as a pale yellow oil, b. p. 134—136°/12 mm. (Found: Br, 59·1%).

Bromo-β-vinylacrylic Acid.—The solid dibromide (10 g.), dissolved in absolute ether (150 c.c.), was gradually treated with an ethereal solution of diethylamine (8 g.) at 0°. Diethylamine hydrobromide separated rapidly; when separation had ended, the ethereal liquor was filtered, agitated several times with dilute sulphuric acid, and finally dried. Removal of the solvent yielded an acid which crystallised from benzene–petroleum in long, colourless needles (Found: Br, 44·9. $C_5H_5O_2Br$ requires Br, 45·2%). When this substance was heated, it changed without melting or evident degradation to a yellow, apparently amorphous, solid which gradually darkened in colour as the temperature rose. A similar yellow solid, doubtless a polymeride of bromovinylacrylic acid, was obtained when boiling pyridine was employed in place of diethylamine. Pure crystalline bromovinylacrylic acid could not be kept; invariably it changed, in less than 2 days, to a brown, amorphous mass. The *methyl* ester, obtained in similar fashion from the ester of the solid portion of the dibromide (above), was a pale yellow oil which solidified on cooling to 0° (m. p. about 10°), but polymerised to a thick jelly on standing for 2 hours at room temperature.

Removal of hydrogen bromide from the liquid portion of the dibromide (using ethereal diethylamine) yielded a bromovinylacrylic acid which crystallised from benzene–petroleum in colourless plates (Found: Br, 44·9%). When heated, this acid behaved like the above described monobromo-acid; when allowed to stand, the crystalline form was gradually lost, the change becoming marked after 7—8 days. The *methyl* ester obtained in a similar way from the ester of the liquid portion of the dibromide (above) was a yellow oil, b. p. 95—98°/16 mm., which polymerised within 8 hours of distillation (Found: Br, 41·7. $C_6H_7O_2Br$ requires Br, 41·9%). Attempts to establish the identity of the two specimens of bromovinylacrylic acid did not succeed; reduction to vinylacrylic acid could not be effected.

Sorbic Acid Dibromide.—Bromination of sorbic acid yielded a crude dibromide which consisted of a solid, m. p. 94—95°, and a yellow liquid (compare Kachel and Fittig, *Annalen*, 1873, **168**, 287; Auwers and Heyna, *loc. cit.*). From the liquid, however, further large quantities of the solid dibromide separated, and it is probable that the very small liquid residue consisted almost entirely of the solid form, since it did not yield a distinctive bromosorbic acid on treatment with diethylamine. Esterification of the solid dibromide yielded the *methyl* ester, a pleasant-smelling liquid, b. p. 146°/12 mm. (Found: Br, 56·0. $C_7H_{10}O_2Br_2$ requires Br, 55·9%). The same compound was obtained by addition of bromine to pure methyl sorbate.

Bromosorbic acid was obtained by treating an ethereal solution of solid sorbic acid dibromide with diethylamine. It crystallised from benzene–petroleum in white plates, m. p. 140° (Found: Br, 41·8. $C_6H_7O_2Br$ requires Br, 41·9%). The *methyl* ester of this acid was obtained in similar fashion from the methyl ester of solid sorbic acid dibromide (above). It was a pleasant-smelling, yellow oil, b. p. 104—106°/10 mm. (Found: Br, 38·8. $C_7H_9O_2Br$ requires Br, 39·0%).

Removal of hydrogen bromide from the small liquid residue obtained in the bromination of sorbic acid yielded a bromosorbic acid, m. p. 140°, identical with that described above.

Reduction of Bromosorbic Acid.—When this acid was reduced in the usual way with zinc dust and acetic acid, a halogen-free, brown oil was obtained which soon solidified. After recrystallisation, it melted at 140° and was identical with ordinary sorbic acid. To avoid geometrical inversion which had possibly occurred, milder reducing agents were tried, but reduction could not be effected therewith.

B. Addition of Esters.

Methyl β-methyl-Δ^{γ}-pentene-$\alpha\alpha\epsilon$-tricarboxylate was obtained, in 60—70% yield, by addition of methyl malonate to methyl sorbate under essentially the conditions described by Kohler and Butler (*loc. cit.*). The ester corresponded in boiling point with that obtained by Kohler and Butler.

Condensation was also attempted under other conditions. Employment of an ethereal, alcohol-free suspension of ethyl sodiomalonate with methyl sorbate at room temperature yielded a product containing methyl methylpentenetricarboxylate, products derived therefrom by internal condensation, and polymeric products from methyl sorbate. With diethylamine as condensing agent and methyl cyanoacetate as addendum, no addition occurred; there was a similar result when these substances were brought together under Guareschi's conditions. When alcoholic methyl sodiomalonate was employed, subsidiary condensations proceeded too far to allow isolation of any pure product.

Methyl Δ^{γ}-pentene-$\alpha\alpha\epsilon$-tricarboxylate was obtained in a similar way by adding methyl malonate to methyl β-vinylacrylate. This ester, prepared by esterification of the pure acid with methyl alcohol and sulphuric acid, could be stabilised for a considerable time by addition of a small quantity of quinol immediately after distillation. In most of the condensations no appreciable quantity of the latter ester was recovered unchanged. The addition product distilled at 178—180°/17 mm. (172°/13 mm. on redistillation. Kohler and Butler give a lower b. p., 147—151°/11 mm.). The *triamide* was formed in almost quantitative yield when the ester was allowed to stand with alcoholic ammonia. It formed colourless prisms, m. p. 213° (Found : C, 48·5; H, 6·7. $C_8H_{13}O_3N_3$ requires C, 48·2; H, 6·5%).

Methyl Ethyl β-Cyano-γ-methyl-Δ^{δ}-hexene-βζ-dicarboxylate.—To a solution of sodium (2·3 g.) in the minimal quantity of absolute methyl alcohol, ethyl methylcyanoacetate (12·8 g.) and sufficient dry ether to produce a permanent turbidity were added. Methyl sorbate (12·6 g.) was then dissolved in the solution, and the whole refluxed on a steam-bath for 6 hours. More ether was added to the cooled product, which was then poured into water and worked up in the usual way. The oil so obtained yielded unchanged esters and a product (2 g.) of b. p. 185—188°/16 mm. In each of three such additions, a similar yield was obtained. When, however, only one-eighth of the sodium theoretically required was used and the refluxing continued for 5 hours, the yield of addition product rose to 60—70%. The latter was a pale yellow, mobile oil (Found : C, 61·8; H, 7·4. $C_{13}H_{19}O_4N$ requires C, 61·6; H, 7·5%).

Methyl ethyl β-cyano-Δ^{δ}-hexene-βζ-dicarboxylate was prepared in similar fashion to the preceding ester, ethyl methylcyanoacetate (2 mols.), methyl β-vinylacrylate (1 mol.), and sodium (1/8 atom) being used. Refluxing for more than 5 hours resulted in a diminished yield. The ester was a pale yellow, mobile oil, b. p. 182—185°/16 mm. (Found : C, 60·3; H, 7·0. $C_{12}H_{17}O_4N$ requires C, 60·25; H, 7·1%).

Attempted Addition of Esters to Methyl Δ^{γ}-Pentene-ααε-tricarboxylate.—In order to ascertain the mobility or fixity of the double bond in methyl pentenetricarboxylate, attempts were made to secure addition of methyl cyanoacetate, (1) using sodium as condensing agent under the conditions described above, and (2) under Guareschi's conditions. In neither case did addition take place.

Attempted Addition of Methyl Malonate and Methyl Cyanoacetate to Methyl Crotonylidenemalonate.—Methyl crotonylidenemalonate was synthesised by the method of Meerwein (*Annalen*, 1908, **358**, 82). All attempts by the above-described methods to secure its condensation with methyl malonate failed. Condensation with methyl cyanoacetate under Guareschi's conditions also did not succeed. Attempts to prepare by Meerwein's method the probably more reactive methyl crotonylidenecyanoacetate were unsuccessful.

C. Oxidations.

Ozonisation of Vinylacrylic Acid Dibromide.—Through a solution of the solid dibromide (10 g.) (p. 1062) in 60 c.c. of chloroform, mixed with 10 c.c. of water, a rapid stream of ozonised oxygen was passed for 6 hours. The issuing gases were led through aqueous ammonia to absorb any formaldehyde carried from the decomposition vessel. The absence of formaldehyde was demonstrated by the hexamethylenetetramine test. The aqueous and the chloroformic layer were separated. A portion of the former, acidified with acetic acid, yielded with calcium chloride a thick precipitate of calcium oxalate; from the remainder a quantity of pure oxalic acid was isolated. The chloroformic layer was evaporated at room temperature. The residue, a pale yellow oil, was warmed for $\frac{1}{2}$ hour with aqueous potassium acetate (8 g. in 12 c.c. of water). The deep yellow, lachrymatory α-*bromoacraldehyde* so produced was distilled in steam and extracted with ether; it was obtained, after removal of the solvent and distillation, as a pale yellow oil, b. p. 58°/21 mm. (Found: Br, 59·2. C_3H_3OBr requires Br, 59·25%). It yielded a *semicarbazone*, m. p. 160°, which was identical with that obtained from a specimen of α-bromoacraldehyde synthesised by the method of Auwers and Heyna (*loc. cit.*).

The liquid dibromide also was oxidised in a similar way and yielded the same degradation products. No compounds arising from αβ- or αδ-dibromides could be found among the oxidation products.

Ozonisation of Methyl Methylpentenetricarboxylate (I) *and Methyl Pentenetricarboxylate* (II).—The oxidation of these substances was conducted in a similar way to that described by Kohler and Butler (*loc. cit.*) and yielded precisely similar results.

Ozonisation of Methyl Ethyl Cyanomethylhexenedicarboxylate (III).—The ester (10 g.), dissolved in dry chloroform (30 c.c.), was submitted to a current of ozonised oxygen for 36 hours. On evaporation of the chloroform under diminished pressure, the ozonide was obtained as a viscous, faintly yellow oil. This was decomposed by heating with water (30 c.c.) for 2 hours, the escaping vapours being passed into a solution of *p*-nitrophenylhydrazine hydrochloride. The yellow precipitate (m. p. 126° after recrystallisation) which formed in the latter was identified as acetaldehyde-*p*-nitrophenylhydrazone by comparison with an authentic specimen.

The aqueous liquor was mixed with 30% hydrogen peroxide

(50 c.c.). After 12 hours, the aqueous portion was decanted, and the oil hydrolysed by boiling with 40% potassium hydroxide solution (30 c.c.) until no more ammonia was evolved (5 hours). The cooled alkaline liquid yielded, on acidification and extraction, a gummy acid which partly crystallised. This was esterified with alcohol and sulphuric acid and distilled. The colourless ester, b. p. 125—132°/12 mm., was re-hydrolysed with alcoholic potassium hydroxide; a solid potassium salt separated which yielded an acid, m. p. 123°, and the alcoholic liquor yielded a second acid, m. p. 195°. These acids were identified by their basicity and by comparison with authentic specimens as *cis*- and *trans*-forms, respectively, of *s*-dimethylsuccinic acid.

Ozonisation of Methyl Ethyl Cyanohexenedicarboxylate (IV).—The method was that employed in the preceding oxidation. The only substances that could be isolated were acetaldehyde (identified as the *p*-nitrophenylhydrazone, m. p. 126°) and a cyano-ester which yielded a considerable quantity of methylsuccinic acid, m. p. 112° (identified by basicity and comparison with an authentic specimen).

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