

CXXV.—*Condensation of Phenols with Esters of the Acetylene Series. Part VI.*

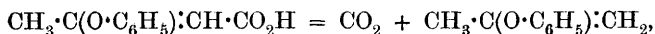
By SIEGFRIED RUHEMANN and ERNEST WRAGG, B.A.

PREVIOUS researches led to the result that ethyl acetylenedicarboxylate and ethyl chlorofumarate yield the same esters on treatment with the sodium phenolates, and that the acids formed from them on hydrolysis readily condense to derivatives of 1:4-benzopyrone under the influence of concentrated sulphuric acid. As has also been shown, the acids obtained from the products of the interaction of the sodium phenolates with ethyl phenylpropiolate cannot be thus transformed into flavone and its homologues, but on distillation lose carbon dioxide, yielding phenoxy styrene and its homologues, and on treatment with sulphuric acid decompose into carbon dioxide, acetophenone, and the corresponding phenols.

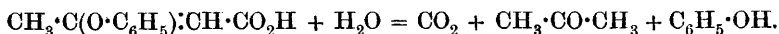
Similar is the behaviour of the substances produced from eugenol and *m*-xylenol, which is described in this paper. Although we have not been able to obtain the benzopyrone compound from eugenoxycinnamic acid, yet xylenoxycinnamic acid can readily be condensed to dimethylbenzopyronecarboxylic acid. β -*m*-Xylenoxycinnamic acid, on the other hand, is completely decomposed by sulphuric acid.

The fact that the aryl ethers of β -hydroxycinnamic acid are not transformed into benzopyrone derivatives induced us to ascertain whether this reaction is prevented from taking place only by the presence of the phenyl group, or whether hydrocarbon radicles in general

have this effect. For this purpose, we have studied ethyl β -phenoxy-crotonate, which is formed by the action of sodium phenolate on ethyl β -chlorocrotonate, and have found that the corresponding acid does not yield a benzopyrone compound, but undergoes changes similar to those observed in the case of the aryl ethers of β -hydroxycinnamic acid. On heating, it loses carbon dioxide and forms β -phenoxypropylene, thus :

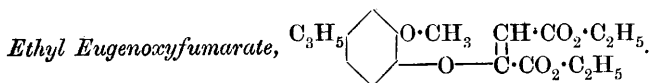


whilst under the influence of sulphuric acid it suffers the following decomposition :



With the view of testing whether the difference in the behaviour of the aryl ethers of β -hydroxycinnamic and β -hydroxycrotonic acids from that of the ethers of hydroxyfumaric acid is caused by the configuration of the unsaturated acids, we have subjected β -chloro*iso*-crotonic acid, instead of its stereoisomeride, to the action of sodium phenolate. We find, however, that the same compound is formed as when ethyl β -chlorocrotonate is used. This result may be explained by the assumption that the formation of ethyl β -phenoxy-crotonate is preceded by the addition of sodium phenolate to the chlorocrotonic esters, accompanied by the transformation of ethyl β -chlorocrotonate into ethyl β -*isochlorocrotonate*. The resulting substance would thus have the configuration $\begin{matrix} \text{CH}_3 \cdot \text{C} \cdot \text{O} \cdot \text{C}_6\text{H}_5 \\ | \\ \text{CO}_2\text{Et} \cdot \text{C} \cdot \text{H} \end{matrix}$, which on account of the axial position of phenoxy to the ester group could not yield a benzopyrone compound.

EXPERIMENTAL.



The union of eugenol with ethyl chlorofumarate takes place when the unsaturated ester (1 mol.) is gradually added to a solution of sodium (1 at.) in an excess of the phenol. The dark, viscous product is heated for a short time, and, after standing for several hours, treated as in the former cases. The ester is a yellowish oil which boils at 231—232° under 14 mm. pressure ; it possesses an aromatic odour, and at 21°/21° has the density 1·1256. On analysis :

0·2030 gave 0·4822 CO₂ and 0·1247 H₂O. C = 64·73 ; H = 6·82.

C₁₈H₂₂O₆ requires C = 64·67 ; H = 6·58 per cent.

Eugenoxyfumaric Acid, C₃H₅(O·CH₃)^[1]C₆H₃(O·C(CO₂H))^[4]:CH·CO₂H.—The potassium salt of the acid separates as a crystalline solid on boil-

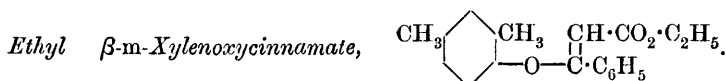
ing the ester with alcoholic potash for 2—3 hours. After the product has been freed from alcohol by distillation on the water-bath, water is added to the residue, and the solution treated with an excess of dilute sulphuric acid, when the organic acid separates as an oil. This is prevented from solidifying on account of the presence of eugenol, which is formed along with eugenoxycinnamic acid on hydrolysis of the ester. In order to remove the phenol, the ethereal solution of the oil is shaken with sodium carbonate, and an excess of dilute sulphuric acid added to the aqueous layer. The organic acid which separates is best extracted with ether, and, after complete evaporation of the latter, remains as a yellow solid, which is very soluble in ether or alcohol. It readily dissolves in boiling water, and, on cooling, crystallises in yellowish plates which melt and decompose at 172—173°. On analysis :

0·2142 gave 0·4755 CO₂ and 0·0980 H₂O. C = 60·54 ; H = 5·08.

C₁₄H₁₄O₆ requires C = 60·43 ; H = 5·03 per cent.

Eugenoxycinnamic acid dissolves in concentrated sulphuric acid, forming a dark red solution. After standing overnight, it is gradually poured into cold water, when a brownish, gelatinous precipitate is produced, which we have been unable to obtain in a crystalline form, and therefore have not further examined.

Action of the Sodium Derivative of m-Xylenol on Ethyl Phenylpropiolate.



The action of ethyl phenylpropiolate (1 mol.) on a hot solution of sodium (1 at.) in an excess of *m*-xylenol takes place very readily. The sodium derivative of the phenol, which partly separates on adding the unsaturated ester, disappears. The dark red oil which is formed sets, on cooling, to a resin. After standing for some hours, it is agitated with dilute sulphuric acid and ether ; the ethereal layer is then freed from the excess of the phenol by potash, the ether evaporated, and the remaining oil distilled in a vacuum. It boils at 225—226° under 10 mm. pressure, is colourless, and at 21°/21° has the density 1·0946. On analysis :

0·1877 gave 0·5300 CO₂ and 0·1180 H₂O. C = 77·0 ; H = 6·98.

C₁₉H₂₀O₃ requires C = 77·02 ; H = 6·76 per cent.

β-m-Xylenoxycinnamic Acid, (CH₃)₂C₆H₃^[1,3]·O·C(C₆H₅)^[4]:CH·CO₂H.—The ester is hydrolysed when it is boiled with alcoholic potash for 2 hours. On adding dilute sulphuric acid to the alkaline fluid after evaporation of the alcohol on the water-bath, *β-m*-xylenoxycinnamic

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acid is precipitated as a resin, which, on stirring with a little alcohol, sets to a solid. This dissolves in hot dilute alcohol, and the solution, on cooling, yields an emulsion from which colourless prisms gradually separate. The acid melts at 121—122° with evolution of gas. On analysis :

0·2000 gave 0·5575 CO₂ and 0·1080 H₂O. C = 76·02 ; H = 6·0.

C₁₇H₁₆O₃ requires C = 76·12 ; H = 5·97 per cent.

The *silver* salt is obtained as a white precipitate on mixing the solution of the acid in ammonia with silver nitrate ; it is neither changed on exposure to light nor decomposed on drying at 100°. On analysis :

0·2994 left, on ignition, 0·0858 Ag. Ag = 28·66.

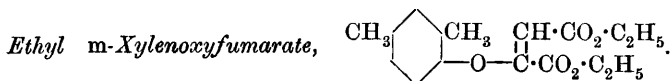
C₁₇H₁₅O₃ Ag requires Ag = 28·80 per cent.

β-m-Xylenoxystyrene, (CH₃)₂C₆H₃·^[1:3]O·C(C₆H₅)·^[4]CH₂.—*β-m-Xylenoxy-cinnamic acid*, on heating, loses carbon dioxide, and *β-m-xylenoxystyrene* is formed. It is a colourless oil with an aromatic odour, distils at 178° under 15 mm. pressure, and at 21°/21° has the density 1·0353. On analysis :

0·1700 gave 0·5343 CO₂ and 0·1090 H₂O. C = 85·71 ; H = 7·12.

C₁₆H₁₆O requires C = 85·71 ; H = 7·14 per cent.

Action of the Sodium Derivative of m-Xylenol on Ethyl Chlorofumarate.



This compound is formed in a similar manner to the other aryl ethers of ethyl hydroxyfumarate, that is, by gradually adding ethyl chlorofumarate (1 mol.) to a hot solution of sodium (1 at.) in an excess of *m*-xylenol. The dark product, after treatment as in the former cases, yields a yellowish oil which boils at 202—203° under 17 mm. pressure, and at 21°/21° has the density 1·0978. On analysis :

0·2033 gave 0·4892 CO₂ and 0·1263 H₂O. C = 65·62 ; H = 6·92.

C₁₆H₂₀O₅ requires C = 65·75 ; H = 6·85 per cent.

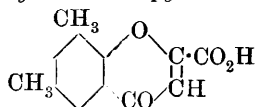
m-Xylenoxyfumaric Acid, (CH₃)₂C₆H₃·^[1:3]O·C(CO₂H)·^[4]CH·CO₂H.—The ester is readily hydrolysed by boiling it with alcoholic potash. After the alkaline solution has been freed from alcohol by distillation on the water-bath, water is added to the residue, and then an excess of dilute sulphuric acid. The solid, which is precipitated, dissolves in boiling water with difficulty, but with great ease in alcohol or ether,

and crystallises from dilute alcohol in yellowish prisms which melt and decompose at 210°. On analysis :

0·2025 gave 0·4539 CO₂ and 0·0955 H₂O. C = 61·13 ; H = 5·24.

C₁₂H₁₂O₅ requires C = 61·01 ; H = 5·08 per cent.

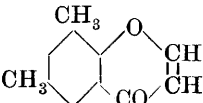
6 : 8-Dimethyl-1 : 4-benzopyrone-2-carboxylic Acid,



m-Xylenoxyfumaric acid dissolves in cold concentrated sulphuric acid, forming a red solution. After standing overnight, this is gradually poured into cold water, when a white, gelatinous precipitate is formed, which crystallises from dilute alcohol in colourless prisms. These melt and decompose at 278°, and are freely soluble in alcohol but insoluble in water. On analysis :

0·2028 gave 0·4916 CO₂ and 0·0860 H₂O. C = 61·11 ; H = 4·71.

C₁₂H₁₀O₄ requires C = 66·05 ; H = 4·59 per cent.

6 : 8-Dimethyl-1 : 4-benzopyrone, —On heating the

dimethylbenzopyronecarboxylic acid, it loses carbon dioxide, and a yellowish oil distils over which rapidly solidifies. The solid is freed from a small quantity of the acid which it contains by shaking the ethereal solution of the distillate with sodium carbonate. On evaporation of the ether, the dimethylpyrone remains behind ; it crystallises from dilute alcohol in colourless needles which melt at 80—81° and dissolve in concentrated sulphuric acid, forming a colourless solution with a bluish fluorescence. On analysis :

0·1974 gave 0·5482 CO₂ and 0·1047 H₂O. C = 75·73 ; H = 5·89.

C₁₁H₁₀O₂ requires C = 75·80 ; H = 5·75 per cent.

Action of Sodium Phenolate on the Esters of β-Chlorocrotonic and β-Chloroisocrotonic Acids.

Ethyl β-Phenoxycrotonate, CH₃·C(O·C₆H₅) : CH·CO₂·C₂H₅.—Sodium phenolate reacts with ethyl β-chlorocrotonate as readily as with ethyl chlorofumarate on adding the ester (1 mol.) to a hot solution of sodium (1 at.) in an excess of phenol. The dark oily product, when subjected to the same treatment as in the former cases, yields a colourless oil with a pleasant aromatic odour, which distils at 147—148°

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under 14 mm. pressure, and at $21^{\circ}/21^{\circ}$ has the density 1.0726. On analysis :

0.1980 gave 0.5065 CO_2 and 0.1236 H_2O . C = 69.76 ; H = 6.93.

$\text{C}_{12}\text{H}_{14}\text{O}_3$ requires C = 69.90 ; H = 6.80 per cent.

The ester, on hydrolysis with alcoholic potash, is transformed into β -phenoxyacrotic acid, $\text{CH}_3\cdot\text{C}(\text{O}\cdot\text{C}_6\text{H}_5)\cdot\text{CH}\cdot\text{CO}_2\text{H}$. On adding dilute sulphuric acid to the alkaline solution, after evaporation of the alcohol, the acid is precipitated as a white solid which dissolves in ether or alcohol with great ease, but only sparingly in water, and crystallises from dilute alcohol in colourless needles melting at 155° . On analysis :

0.2105 gave 0.4971 CO_2 and 0.1062 H_2O . C = 67.28 ; H = 5.85.

$\text{C}_{10}\text{H}_{10}\text{O}_3$ requires C = 67.41 ; H = 5.62 per cent.

The *silver* salt is formed as a white precipitate, which is first gelatinous, but gradually becomes curdy, on adding silver nitrate to the solution of the acid in ammonia. The salt is insoluble in water, and has to be dried in a vacuum, since it turns brown when heated at 100° . On analysis :

0.2805 left, on ignition, 0.1065 Ag. Ag = 37.96.

$\text{C}_{10}\text{H}_9\text{O}_3\text{Ag}$ requires Ag = 37.89 per cent.

β -Phenoxyacrotic acid, as has been mentioned (p. 1186), when dissolved in concentrated sulphuric acid, or when boiled with dilute sulphuric acid, suffers a decomposition similar to that of the aryl ethers of β -hydroxycinnamic acid, and furnishes carbon dioxide, phenol, and acetone.

β -Phenoxypropylene, $\text{CH}_3\cdot\text{C}(\text{O}\cdot\text{C}_6\text{H}_5)\cdot\text{CH}_2$.—On heating β -phenoxyacrotic acid in a vacuum, it distils with partial decomposition ; this, however, is complete on distillation under the atmospheric pressure. The colourless oil so obtained, boils at 170° , and has an odour resembling that of phenyl mustard oil. On analysis :

0.2400 gave 0.7118 CO_2 and 0.1610 H_2O . C = 80.88 ; H = 7.45.

$\text{C}_9\text{H}_{10}\text{O}$ requires C = 80.60 ; H = 7.46 per cent.

As stated on p. 1186, ethyl β -chloroisocrotonate yields the same product as ethyl β -chlorocrotonate, when it is treated with sodium phenolate. The substance obtained from the former ester distils at 152° under 18 mm. pressure, as compared with 147 — 148° (under 14 mm. pressure) which we have found for the sample prepared from ethyl chlorocrotonate. Its composition, moreover, has been verified by the following analysis :

0.1938 gave 0.4960 CO_2 and 0.1178 H_2O . C = 69.80 ; H = 6.75.

$\text{C}_{12}\text{H}_{14}\text{O}_3$ requires C = 69.90 ; H = 6.80 per cent.

THE HYDROBROMIDES OF UNDECYLENIC ACID. 1191

The identity of both specimens of ethyl β -phenoxyacrylate is also supported by the fact that the acids formed from them on hydrolysis have the same crystalline forms and melting points.

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