LI.—*Condensation of Phenols with Esters of the Acetylene Series. Part IV. Benzo- γ -pyrone and its Homologues.*

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RUHEMANN and STAPLETON (Trans., 1900, 77, 1184) have shown that phenoxyfumaric acid, under the influence of concentrated sulphuric acid, loses water and condenses to benzo- γ -pyronemonocarboxylic acid which, on distillation, loses carbon dioxide and yields benzo- γ -pyrone. We have applied this reaction to the cresoxyfumaric acids and thus obtained the isomeric toluo- γ -pyrones which are described in this paper. Benzo- γ -pyrone and its methyl derivatives dissolve in alcohol and ether as well as in boiling water, and their solutions in concentrated sulphuric acid show a blue fluorescence; they also possess an aromatic odour which is especially apparent on heating them with water.

Our attempts to transform benzo- γ -pyrone and its homologues into hydroxyquinolines according to the equation

have as yet been unsuccessful, since, at the ordinary temperature, they seem to form additive compounds with ammonia, which, however, on heating readily dissociate into their components. From benzo- γ -pyronecarboxylic acid, an additive product of this kind has been obtained which most probably has the formula

On boiling this substance with water, however, it loses ammonia, as also does the compound obtained by the action of aqueous ammonia on ethyl benzo- γ -pyronecarboxylate. By acting on the ester with alcoholic ammonia, an additive compound does not seem to be formed, or, if so, only to a small extent, and in its stead the amide of benzo- γ -pyronecarboxylic acid is obtained. When heated with alcoholic or aqueous ammonia at 160°, benzo- γ -pyrone and its homologues suffer decomposition.

EXPERIMENTAL.

Benzo- γ -pyronecarboxylic Acid.

When analysed previously (Ruhemann and Stapleton, *loc. cit.*), the silver salt seemed to contain one molecular proportion of water; we now find that this result was due to impurity, as the pure salt, obtained by crystallisation, is anhydrous. On analysis:

0.2217 left on ignition 0.0804 Ag. Ag = 36.27.

$\text{C}_{10}\text{H}_5\text{O}_4\text{Ag}$ requires Ag = 36.36 per cent.

Benzo- γ -pyronecarboxylic acid dissolves in concentrated aqueous ammonia, forming a yellow solution. After standing overnight, this is freed from ammonia by heating it under diminished pressure; on slightly acidifying the solution with dilute hydrochloric acid, a yellowish solid is precipitated which, after washing with water, is dried in a vacuum over sulphuric acid. On analysis:

0.2799 gave 15.5 c.c. moist nitrogen at 17° and 752 mm. N = 6.35.

$\text{C}_{10}\text{H}_9\text{O}_4\text{N}$ requires N = 6.76 per cent.

As already pointed out above, this result indicates that the compound is an additive product of ammonia with benzo- γ -pyronecarboxylic acid. This view is supported by the facts that the yellowish solution of the substance in alcohol becomes colourless and evolves ammonia on boiling, and that the solution on cooling deposits colourless

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needles which melt and decompose at 251° and are identical with benzo- γ -pyronecarboxylic acid.

The behaviour of the acid towards ammonia is similar to that of its ester.

Ethyl Benzo- γ -pyronecarboxylate, $\text{CO}_2\text{C}_2\text{H}_5 \cdot \text{C} \begin{smallmatrix} \text{=CH} \\ \text{O} \cdot \text{C}_6\text{H}_4 \end{smallmatrix} > \text{CO}$, is obtained

by boiling the solution of the acid in absolute alcohol with a few c.c. of concentrated sulphuric acid for six hours on the water-bath. After mixing the cold solution with water, it is shaken with ether and the ethereal layer freed from unchanged acid by sodium carbonate. On evaporating the ether, a solid remains which crystallises from dilute alcohol in long, colourless, silky needles melting at $69-70^{\circ}$. On analysis:

0.1907 gave 0.4615 CO_2 and 0.0819 H_2O . C = 66.00; H = 4.77.

$\text{C}_{12}\text{H}_{10}\text{O}_4$ requires C = 66.06; H = 4.59 per cent.

Amide of Benzo- γ -pyronecarboxylic Acid, $\text{NH}_2 \cdot \text{CO} \cdot \text{C} \begin{smallmatrix} \text{=CH} \\ \text{O} \cdot \text{C}_6\text{H}_4 \end{smallmatrix} > \text{CO}$.—

Ethyl benzo- γ -pyronecarboxylate dissolves in alcoholic ammonia, and, after a few minutes, the yellowish solution deposits an almost colourless solid which increases in quantity on standing overnight. This dissolves only sparingly in water or alcohol, and crystallises from the hot solutions in slightly yellow prisms which soften at about 230° and melt to a dark liquid at 252° . On analysis:

0.2122 gave 14.2 c.c. moist nitrogen at 19° and 744 mm. N = 7.52.

$\text{C}_{10}\text{H}_7\text{O}_3\text{N}$ requires N = 7.41 per cent.

The formation of the amide seems to be preceded by that of its additive compound with ammonia; the latter, however, is unstable, and if the ester remains in contact with an aqueous instead of with an alcoholic solution of ammonia, a yellow product is obtained which, on boiling with water, loses ammonia and yields the amide.

This acid is prepared in the same manner as benzo- γ -pyronecarboxylic acid, namely, by dissolving *o*-cresoxyfumaric acid (Ruhemann and Beddow, *Trans.*, 1900, **77**, 1124) in concentrated sulphuric acid, allowing the solution to stand for a day, and then gradually adding it to ice-cold water. The white solid which is thus precipitated crystallises from rectified spirit in silky needles which melt and decompose at $255-256^{\circ}$. On analysis:

0.1769 gave 0.4192 CO₂ and 0.0630 H₂O. C = 64.63 ; H = 3.96.

C₁₁H₈O₄ requires C = 64.71 ; H = 3.92 per cent.

The silver salt obtained as a white precipitate on mixing a solution of the acid in ammonia with silver nitrate, dissolves with difficulty in boiling water, and on cooling crystallises in colourless needles. On analysis :

0.2815 left, on ignition, 0.0977 Ag. Ag = 34.71.

C₁₁H₇O₄Ag requires Ag = 34.73 per cent.

o-Toluo- γ -pyronecarboxylic acid, when heated above its melting point, loses carbon dioxide, and an oil distils over which soon sets to a solid. This dissolves in light petroleum (b. p. 70–80°), leaving behind a small quantity of unaltered *o*-toluo- γ -pyronecarboxylic acid. From the solution on cooling, colourless needles of *o*-toluo- γ -pyrone separate which melt at 84–85°. On analysis :

0.1868 gave 0.5135 CO₂ and 0.0838 H₂O. C = 74.97 ; H = 4.98.

C₁₀H₈O₂ requires C = 75.00 ; H = 5.00 per cent.

o-Toluo- γ -pyrone dissolves with the greatest ease in alcohol, but less readily in hot water ; it has an aromatic odour, which is especially noticeable on boiling the aqueous solution. The solution of *o*-toluo- γ -pyrone in concentrated sulphuric acid shows a fluorescence similar to that of its lower homologue.

m-Cresoxyfumaric acid (Ruhemann and Beddow, Trans., 1900, 77, 1124), on treatment with concentrated sulphuric acid, as in the former cases, loses water and condenses to the pyrone compound. This crystallises from dilute alcohol in colourless plates which soften at about 222° and melt at 233–234° with decomposition. On analysis :

0.1775 gave 0.4204 CO₂ and 0.0655 H₂O. C = 64.59 ; H = 4.10.

C₁₁H₈O₄ requires C = 64.71 ; H = 3.92 per cent.

This compound is obtained by heating the acid, and distils at about 280° as a yellowish oil which, on cooling, solidifies. It is readily soluble in alcohol, ether, chloroform, or light petroleum, but only

sparingly so in boiling water, and crystallises from the aqueous solution in colourless needles melting at 72—73°. On analysis :

0.1696 gave 0.4653 CO₂ and 0.0788 H₂O. C = 74.82 ; H = 5.16.

C₁₀H₈O₂ requires C = 75.00 ; H = 5.00 per cent.

m-Toluo- γ -pyrone also has a pleasant, aromatic odour, and its solution in concentrated sulphuric acid shows a faint blue fluorescence.

p-Cresoxyfumaric acid, CO₂H·C(O·C₆H₄·CH₃)₂·CH·CO₂H, which is required for the preparation of the above acid, has not been recorded before. We have obtained it by the hydrolysis of ethyl *p*-cresoxyfumarate (Ruhemann and Beddow, Trans., 1900, 77, 1125) with alcoholic potash. It forms yellowish plates which dissolve in boiling water and melt with decomposition at 197°. On analysis :

0.1948 gave 0.4250 CO₂ and 0.0784 H₂O. C = 59.50 ; H = 4.47.

C₁₁H₁₀O₅ requires C = 59.46 ; H = 4.50 per cent.

This acid readily dissolves in cold concentrated sulphuric acid ; after standing overnight, the dark solution is added to ice-cold water, when *p*-toluo- γ -pyronecarboxylic acid is precipitated as a white solid which crystallises from dilute alcohol in colourless needles and melts and decomposes at 258°. On analysis :

0.1939 gave 0.4594 CO₂ and 0.0631 H₂O. C = 64.62 ; H = 3.62.

0.1747 „ 0.4164 CO₂ „ 0.0614 H₂O. C = 65.00 ; H = 3.90.

C₁₁H₈O₄ requires C = 64.71 ; H = 3.92 per cent.

This compound, formed on heating *p*-toluo- γ -pyronecarboxylic acid, crystallises from boiling water in colourless needles melting at 88—89°. On analysis :

0.1823 gave 0.5005 CO₂ and 0.0838 H₂O. C = 74.88 ; H = 5.11.

C₁₀H₈O₂ requires C = 75.00 ; H = 5.00 per cent.

p-Toluo- γ -pyrone is odourless, but on boiling its aqueous solution a pleasant aromatic odour is developed. The substance is readily soluble in alcohol or light petroleum, and its solution in concentrated sulphuric acid shows a blue fluorescence.

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