9. *Benz*cyclo*octatetraenes. Part II. The Action of Acetic Anhydride on δ-Benzylidenelœvulic Acids.*

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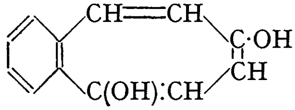
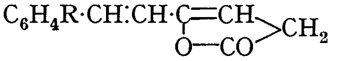
The dehydration products obtainable from δ-benzylidenelævulic acids by the action of acetic anhydride are shown to be almost certainly *2-keto-5-styryl-2 : 3-dihydrofuran* derivatives and not 1 : 2-benz-$\Delta^{1:3}$-*cyclo*octadiene-5 : 8-diones as stated by Sen and Roy (*J. Indian Chem. Soc.*, 1930, **7**, 401). Benzoylation of these dehydration products by the Schotten–Baumann method yielded *dibenzoyl* derivatives, one benzoyl group being presumably linked to carbon. Attempts to obtain corresponding dibenzoyl derivatives from the Δ^1- and Δ^2-angelicalactones failed.

Sen and Roy (*loc. cit.*) prepared a number of coloured substances by the action of acetic anhydride on δ-benzylidenelævulic acid and its derivatives. They examined none of these coloured compounds in detail, but presumably because the product (A) from δ-benzylidenelævulic acid gave a dibenzoyl derivative in the Schotten–Baumann reaction with benzoyl chloride, they formulated this and all the analogous compounds as 1 : 2-benz-$\Delta^{1:3}$-*cyclo*octadiene-5 : 8-diones, benzoylation of (A) being pictured as occurring through the corresponding dienolic structure (I).

We have submitted two of the substances described by Sen and Roy, namely, those from δ-benzylidenelævulic acid and δ-*p*-methoxybenzylidenelævulic acid, to further study and have found their reactions and properties much more in accord with their formulation as 2-*keto*-5-*styryl*-2 : 3-*dihydrofurans* (II, R = H and R = OMe respectively). In our view the dehydration of the δ-benzylidenelævulic acids

(I.)





$$\begin{array}{l}C_6H_4R\cdot CH{:}CH\cdot C{=\!=}CH\diagdown \\ \qquad\qquad\qquad\qquad\;\; | \qquad\qquad\; CH_2 \\ \qquad\qquad\qquad\qquad\;\, O{-\!-}CO\diagup\end{array}$$

(II.)

by acetic anhydride is to be compared with the dehydration of lævulic acid under analogous conditions to yield Δ^2-angelicalactone (Thiele, *Annalen*, 1901, **319**, 184). Thus oxidation of (A) with alkaline potassium permanganate yielded benzoic acid, and although its equivalent weight determination was made difficult because of its deep colour, it behaved more like a lactone than a di-enol. The lactonic behaviour was confirmed by its catalytic hydrogenation, four hydrogen atoms being taken up to yield a liquid product in which the lactonic function was not to be mistaken. The product from δ-*p*-methoxybenzylidenelævulic acid behaved in an exactly analogous manner.

In the light of these results it was expected that the product of the benzoylation of (A) by the Schotten–Baumann method, which was recorded as a dibenzoyl derivative by Sen and Roy (*loc. cit.*), would prove to be a monobenzoyl derivative of the enolic form of (II). Especially was this the case as the analytical figures for the two structures lie close together, and because the melting point of the product as reported by these workers was far below that of the purified material as handled by us. We have, however, been able to confirm Sen and Roy's characterisation of this substance as a dibenzoyl derivative by further analyses, as well as by the preparation of the analogous *di*-o-*chlorobenzoyl* and *di*-o-*iodobenzoyl* compounds. Since the dibenzoylated material gave no phthalic acid on oxidation, however, Sen and Roy's formulation of it must be in error, and it would appear as if one of the benzoyl groups is directly linked to carbon. No experimental evidence of this has been obtained, but benzoylation on carbon by the Schotten–Baumann method is not unknown (cf. *J. Amer. Chem. Soc.*, 1941, **63**, 1143). In this connection it is perhaps significant that the above products could not be obtained when pyridine was used in place of aqueous sodium hydroxide as condensing agent.

A *dibenzoyl* derivative of (II, R = OMe) is also described. No analogous compounds could be obtained, however, from the Δ^1- and Δ^2-angelicalactones by the Schotten–Baumann method.

EXPERIMENTAL.

δ-*Benzylidenelævulic Acid*.—The method of Erlenmeyer (*Ber.*, 1890, **23**, 74) was improved as follows: Benzaldehyde (41 c.c.), dissolved in alcohol (100 c.c.), was added simultaneously with 2N-sodium hydroxide (280 c.c.) to lævulic acid (42 c.c.). The mixture was shaken, placed in a boiling water-bath until homogeneous (8—10 mins.), and the solution then cooled rapidly by addition of ice. The crystals which separated on addition of dilute (1 : 1) hydrochloric acid (120 c.c.) were collected, dried by exposure to air, and recrystallised from benzene (3 vols.)–light petroleum (1 vol.). Yield, 32 g.

2-*Keto*-5-*styryl*-2 : 3-*dihydrofuran* (II, R = H).—The red product obtained from δ-benzylidenelævulic acid by the action of acetic anhydride was less contaminated by resinous materials, and the yield was very much improved, when the conditions used for its preparation by Sen and Roy (*loc. cit.*) were made rather less drastic. Acetyl chloride could not be substituted for acetic anhydride in the reaction. The acid (10 g.) was heated for 30 minutes in a boiling water-bath with acetic anhydride (20 g.). The red solid which remained after the reaction mixture had been stirred with an excess of saturated sodium bicarbonate solution was collected and recrystallised from methyl alcohol. The product (7·3 g., 80%) had m. p. 95·5° and not 196° as stated by the above authors. It was slowly soluble in sodium hydroxide solution, but addition of mineral acid to its solution so obtained yielded a viscous red oil which was not identical with the starting material, since it dissolved in sodium bicarbonate solution. Oxidised in the usual way with alkaline potassium permanganate, it yielded benzoic acid. Accurate values for the equivalent weight (found by solution in excess of sodium hydroxide and back-titration) were not possible on account of the deep red colour of the solution (Found: equiv., 197·2. Calc. for $C_{12}H_{10}O_2$: equiv., 186). The material was somewhat unstable on protracted storage in the light, being gradually converted into a pale brown, resinous substance of lower m. p. It was unchanged after being kept for a fortnight or longer, however, in a vacuum desiccator in the dark.

2-*Keto*-5-β-*phenylethyltetrahydrofuran*.—The above material, dissolved in alcohol, was treated with a palladium–strontium carbonate catalyst and shaken with hydrogen at 1—2 atms. The *product* was a faintly yellow liquid, b. p. 173—175°/7 mm., which could not be further hydrogenated (Found: C, 75·3; H, 7·5;

equiv. by back-titration, 187·8. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·4%; equiv., 190). It was insoluble in sodium bicarbonate solution, but soluble in aqueous sodium hydroxide. Addition of mineral acid to its solution in sodium hydroxide yielded an oil which, although immediately soluble in sodium bicarbonate solution, soon lost this solubility on standing.

Behaviour of 2-Keto-5-styryl-2 : 3-dihydrofuran in the Schotten–Baumann Reaction.—The material (3·7 g., 1 mol.) was treated in quick succession with benzoyl chloride (14 g., 5 mols.) and excess of 2N-sodium hydroxide (200 c.c.), and the flask vigorously shaken under running water. The *dibenzoyl* derivative crystallised almost immediately. When the smell of benzoyl chloride could no longer be detected, the aqueous solution was decanted, and the product washed several times with water by decantation and finally recrystallised from slightly aqueous acetone (charcoal). It formed fine yellow needles, m. p. 177·5—178·5° (Sen and Roy, *loc. cit.*, describe a light yellow powder, m. p. 160°) [Found: C, 79·2; H, 4·6; *M* (Rast), 390. $C_{26}H_{18}O_4$ requires C, 79·2; H, 4·6%; *M*, 394. Calc. for $C_{19}H_{14}O_3$: C, 78·6; H, 4·8%; *M*, 290]. Oxidised in the usual way with alkaline potassium permanganate, this dibenzoyl derivative yielded benzoic acid, and attempts to establish the simultaneous formation of phthalic acid failed. Benzoylation could not be effected by the use of pyridine as condensing agent.

When *o*-chlorobenzoyl chloride was used in the above reaction, the *di-o-chlorobenzoyl* derivative was obtained in brilliant yellow, flat, elongated prisms from aqueous acetone, m. p. 159·5—160° (Found: C, 67·2; H, 3·5. $C_{26}H_{16}O_4Cl_2$ requires C, 67·4; H, 3·5%. Calc. for $C_{19}H_{13}O_3Cl$: C, 70·3; H, 4·0%).

The *di-o-iodobenzoyl* derivative, obtained by an analogous procedure, formed small, yellow, transparent prisms of rhombohedral outline from slightly aqueous dioxan, m. p. 192—193° (Found: C, 48·3; H, 2·5. $C_{26}H_{16}O_4I_2$ requires C, 48·3; H, 2·5%. Calc. for $C_{19}H_{13}O_3I$: C, 54·8; H, 3·1%).

2-Keto-5-p-methoxystyryl-2 : 3-dihydrofuran (II, R = OMe).—This substance was obtained by a procedure analogous to that described above for the preparation of the corresponding benzylidene derivative. Recrystallised from methyl alcohol, it formed brick-red prisms, m. p. 115—115·5°, and not 78° as reported by Sen and Roy (*loc. cit.*) (Found: C, 72·2; H, 5·3. Calc. for $C_{13}H_{12}O_3$: C, 72·2; H, 5·6%). The material was unstable, and after exposure to light for as short a period as 24 hours, it had undergone considerable decomposition, sintering at 82° and forming a meniscus at 100°. It kept better in a vacuum desiccator in the dark. In other respects its properties agreed with those found for the above benzylidene derivative. It yielded with benzoyl chloride in the Schotten–Baumann reaction a *dibenzoyl* derivative, which formed lustrous, deep orange-coloured prisms from aqueous acetone, m. p. 170—171° (Found: C, 76·1; H, 4·9. $C_{27}H_{20}O_5$ requires C, 76·4; H, 4·7%. Calc. for $C_{20}H_{16}O_4$: C, 75·0; H, 5·0%). It gave anisic acid on oxidation in the usual way with alkaline potassium permanganate. When it was hydrogenated by a procedure analogous to that described above for the benzylidene derivative, *2-keto-5-β-p-methoxyphenylethyltetrahydrofuran* was produced as an oil, b. p. 195—200°/5 mm., soluble in aqueous sodium hydroxide, but insoluble in sodium bicarbonate solution (Found: equiv. by back-titration, 222. $C_{13}H_{16}O_3$ requires equiv., 220).

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