On the Ring-Opening Reactions of the Furan Compounds. II. The Synthesis of γ, ζ, ι-Triketobrassylic Acid from Difurfurylideneacetone

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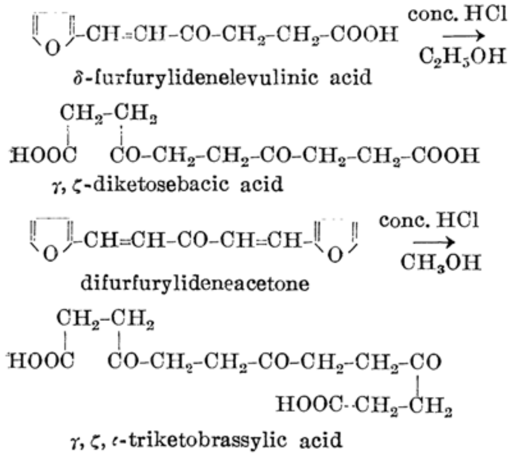
It had already been found that furfurylideneacetone yields γ, ζ-diketocaplyric acid⁽¹⁾ by refluxing with alcoholic hydrochloric acid. By a similar furan ring opening, γ, ζ-diketosebacic acid was synthesized from δ-furfurylidenelevulinic acid.⁽²⁾ In the present report, γ, ζ, ι-triketobrassylic acid was obtained from difurfurylideneacetone by the same procedure. This reaction is illustrated below.



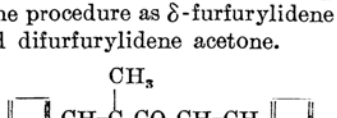
δ-furfurylidenelevulinic acid

γ, ζ-diketosebacic acid

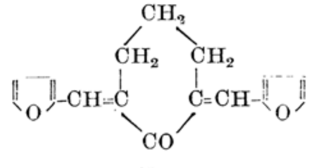
difurfurylideneacetone

γ, ζ, ι-triketobrassylic acid

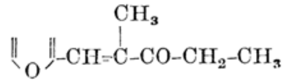
This acid gave an oily matter when combined with phenylhydrazine.* The semicarbazone and the hydrazone of this acid did not crystallize out. It was readily esterified by refluxing with alcohol and sulfuric acid. In the case of difurfurylidene-methyl-ethyl ketone (I), difurfurylidenecyclohexanone (II) and furfurylidenediethyl ketone (III), the similar ring opening reaction did not take place with the same procedure as δ-furfurylidene levulinic acid and difurfurylidene acetone.



I



II



III

These furfurylidene ketones have a branched chain at the carbon atom between the furfurylidene and the carbonyl goups. It seems that the ring opening is hindered by the presence of the branched chain.

Experimental

Difurfurylideneacetone.—20 g. furfural and 6 g. acetone were dissolved in 270 cc. water, and 30 g. 10% aqueous caustic soda solution was introduced at once. After stirring for four and a half hours, the reaction was over. Then, neutralised with sulfuric acid, it was left overnight and solidified. Yield, 20g.. It was recrystallized from ligroin; yellow prisms; m. p. 60—1°; lit.⁽³⁾ m. p. 60—1°.

γ, ζ, ι-Triketobrassylic Acid.—A mixture of 13 g. difurfurylidene acetone, 130 cc. conc. hydrochloric acid and 200 cc. methanol was refluxed on the water-bath for three hours. The reaction mixture was evaporated on the water-bath to remove hydrogen chloride, water being repeatedly added to it. The residue was extracted with a sufficient quantity of boiling water, and the extract was concentrated on the water-bath, after being decolorized with active charcoal. On cooling, colorless foliated crystals separated out from it, and were recrystallized from water. Yield, 1.5 g.; m. p. 168—9°; readily soluble in water, methanol and acetic acid on heating; insoluble in benzene, chloroform, acetone and ether.

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(1) E. A. Kehrer and P. Igler, *Ber.*, **32**, 1177 (1899).

(2) E. A. Kehrer and E. Hofacker, *Ann.*. **294**, 167 (1897).

* Kehrer and Hofacker had reported that the diphenylhydrazone of γ, ζ-diketosebacic acid is difficult to crystallize.

(3) L. Claisen and A. C. Ponder, *Ann.*, **223**, 146 (1884).

	C	H
Anal. Calcd. for $C_{13}H_{18}O_7$:	54.52	6.33
Found:	54.59	6.23

Esterification of γ, ζ, ι-Triketobrassylic Acid. —0.5g. of the acid was boiled in a mixture of 2 cc. methanol and 0.1 cc. conc. sulfuric acid for thirty minutes. On cooling the reaction mixture, the methyl ester was separated out. It was recrystallized from water. Yield, 0.4 g.; colorless needles; m. p. 92—3°.

	C	H
Anal. Calcd. for $C_{15}H_{22}O_7$:	57.29	7.06
Found:	57.20	7.20

0.3 g. of the acid was esterified by refluxing with 2 cc. ethanol and 0.1 cc. conc. sulfuric acid for thirty minutes. The ethyl ester was recrystallized from water; colorless leaflets: m. p. 63—4°.

	C	H
Anal. Calcd. for $C_{17}H_{26}O_7$:	59.61	7.63
Found:	59.66	7.36

Difurfurylidenecyclohexanone, difurfurylidene-methyl-ethyl ketone and furfurylidene diethyl ketone were synthesized by the same method as difurfurylidene acetone.

Summary

The γ, ζ, ι-triketobrassylic acid which is a new triketo-dicarboxylic acid was obtained from difurfurylidene acetone by the ring opening.

The similar ring opening did not take place in difurfurylidene cyclohexanone, difurfurylidene-methyl-ethyl ketone and furfurylidene-diethyl ketone which have a branched chain at the carbon atom between the furfurylidene and the carbonyl groups. It seems that the ring opening reaction is hindered by the presence of the branched chain.

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