On the Ring-Opening Reactions of the Furan Compounds. I. The Synthesis of 1,4-Pentadien-3-one-1,5-dicarboxylic Acid from 2-Furanacrylic Acid

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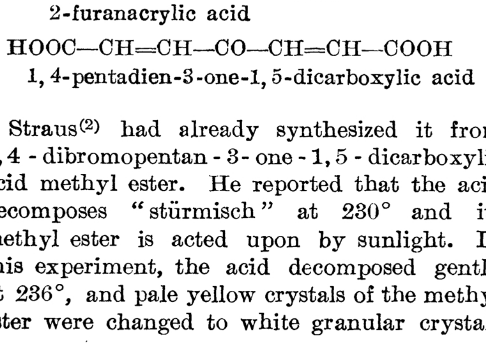
In the ring opening of furan compounds by hydrogen peroxide, 2-furanacrylic acid behaved peculiarly, by giving 1,4-pentadien-3-one-1,5-dicarboxylic acid in fairly good yield. This reaction is analogous to the bromine and subsequent silver oxide oxidation⁽¹⁾ by which 2-furanpropionic acid gives furonic acid as illustrated below:



$\text{—}CH_2\text{—}CH_2\text{—}COOH \xrightarrow{Br_2}$

2-furanpropionic acid

$OHC\text{—}CH{=}CH\text{—}CO\text{—}CH_2\text{—}CH_2\text{—}COOH$

$\downarrow Ag_2O$

$HOOC\text{—}CH{=}CH\text{—}CO\text{—}CH_2\text{—}CH_2\text{—}COOH$

furonic acid

$\text{—}CH{=}CH\text{—}COOH \xrightarrow[HCl]{H_2O_2}$

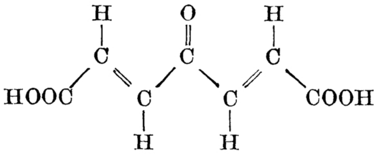
2-furanacrylic acid

$HOOC\text{—}CH{=}CH\text{—}CO\text{—}CH{=}CH\text{—}COOH$

1,4-pentadien-3-one-1,5-dicarboxylic acid

Straus⁽²⁾ had already synthesized it from 2,4-dibromopentan-3-one-1,5-dicarboxylic acid methyl ester. He reported that the acid decomposes "stürmisch" at 230° and its methyl ester is acted upon by sunlight. In this experiment, the acid decomposed gently at 236°, and pale yellow crystals of the methyl ester were changed to white granular crystals by exposure to direct sunlight. But the photochemical change took place also with the free acid. That is to say, the acid of pale yellow crystals was changed to an acid of hygroscopic white powder by direct sunlight, the methyl ester of which was identified with the 1,4-pentadien-3-one-1,5-dicarboxylic acid methyl ester exposed to direct sunlight. Since it had already been reported that the methyl ester is polymerised to a dimer by direct sunlight,⁽³⁾ the free acid may be polymerised to a dimer.

On reducing the acid by aluminium amalgam, γ-ketopimelic acid was obtained. By potassium permanganate oxidation, the acid gave oxalic acid and fumaric acid, but no maleic acid. It is assumed, therefore, that two double bonds of the acid have the trans structure as follow:



Its carbonyl group reacted upon phenylhydrazine with formation of phenylhydrazone.

α-Methyl-β-(2-furyl)-acrylic-acid, α-phenyl-β-(2-furyl)-acrylic acid and α-cyano-β-(2-furyl)-acrylic acid did not undergo such a furan ring opening by hydrogen peroxide.

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(1) A. Baeyer, *Ber.*, **10**, 695 (1877).

(2) F. Straus, *Ber.*, **37**, 3297 (1904).

(3) H. Stobbe and E. Färber, *Ber.*, **58**, 1551 (1925).

Experimental

1, 4-Pentadien-3-one-1, 5-dicarboxylic acid.—Furanacrylic acid 4.8 g. was suspended in a mixture of 40 cc. 35% aqueous hydrogen peroxide and 5 cc. conc. hydrochloric acid, and the vessel was kept for five days in water at room temperature (about 28°), when orange crystals were formed at the bottom. The cyrstals were filtered and washed with methanol to remove unchanged furanacrylic acid. Yield, 2.2 g. From the filtrate was obtained 0.3 g. of the acid by concentration on the water-bath. The resulting acid was dissolved in boiling water, decolourized by active charcoal and crystallised in pale yellow hexagonal plates on cooling. It melted at 236° with decomposition.

	H	C
Anal. Calcd. for $C_7H_6O_5$:	3.55	49.39
Found:	3.53	49.38

When the acid dissolved in a mixture of phenylhydrazine and acetic acid was left overnight, the phenylhydrazone crystallised out. It formed red needles by recrystallisation from a mixture of methanol and water; m. p. 182-3°.

	H	C	N
Anal. Calcd. for $C_{13}H_{12}O_4N_2$:	4.61	59.97	10.76
Found:	4.52	59.48	10.56

1, 4-Pentadien-3-one - 1, 5 - dicarboxylic acid methyl ester.—0.5 g. of the acid was esterified by refluxing for thirty minutes with 3 cc. methanol and 0.2 g. conc. sulfuric acid. On cooling the whole the methyl ester was separated out and recrystallised in pale greenish yellow needles from ethyl acetate; m. p. 171-2°.

	H	C
Anal. Calcd. for $C_9H_{10}O_5$:	5.08	54.52
Found:	5.01	54.57

Its phenylhydrazone was obtained by the same method as the acid, and recrystallised from methanol; lustrous yellow leaflets; m. p. 153-4°.

	H	C	N
Anal. Calcd. for $C_{15}H_{16}O_4N_2$:	5.59	62.45	9.71
Found:	5.25	62.11	9.48

3-Pentanone-1, 5-dicarboxylic acid (**γ-ketopimelic acid**).—To the 20 cc. aqueous solution of the 1 g. acid neutralised by sodium carbonate, was added 0.2 g. aluminium amalgam and left at room temperature for a day. After filtering off aluminium hydroxide, the filtrate was acidified with hydrochloric acid and evaporated to dryness on the water-bath. From the residue, γ-ketopimelic acid was extracted with methanol and recrystallised from a mixture of methanol and chloroform. Yield, about 0.1 g., m. p. 142-3°.

	H	C
Anal. Calcd. for $C_7H_{10}O_5$:	5.79	48.25
Found:	5.57	48.25

Oxidation of 1, 4-pentadien-3-one-1, 5-dicarboxylic acid.—To 1.7 g. of the acid suspended in 50 cc. water was added drop by drop with stirring at about 15° a potassium permanganate solution which consisted of 5 g. potassium permanganate and 70 cc. water. After about thirty minutes, the reaction was over. The reaction mixture was filtered, neutralised with acid, concentrated on the water-bath and shaken up with ether upon acidification. From the ether solution were obtained two compounds. The one was soluble in water and melted at 100-1°. Yield, 0.1 g.. The mixed melting point of oxalic acid with it showed no depression. The other was insoluble in water and melted at 275° in a sealed tube. Yield, 0.1 g. It was identified with fumaric acid.

	H	C
Anal. Calcd. for $C_4H_4O_4$:	3.47	41.36
Found:	3.73	41.39

Photochemical changes of 1, 4-pentadien-3-one-1, 5-dicarboxylic acid and its methyl ester.—The methyl ester placed in a covered glass vessel was exposed to direct sunlight for a few hours with frequent stirring. The pale greenish yellow crystals of methyl ester changed into a white powder. It was recrystallised in colourless rhombs from ethyl acetate and melted at 239° with decomposition as reported by Straus. Similarly, the acid changed into a hygroscopic white powder by exposure to direct sunlight. The recrystallisation was unsuccessful. It melted at about 221° with decomposition.

	H	C
Anal. Calcd. for $C_7H_6O_5$:	3.55	49.39
Found:	3.87	48.59

0.5 g. of the acid sufficiently exposed to sunlight was esterified by refluxing for thirty minutes with 3 cc. of methanol and 0.3 g. of conc. sulfuric acid. The methyl ester crystallised out and was recrystallised from ethyl acetate. It formed colourless rhombs and melted at 237° with decomposition.

	H	C
Anal. Calcd. for $C_9H_{10}O_5$:	5.08	54.52
Found:	4.86	54.00

The mixed melting point of this methyl ester and the photochemically changed methyl ester showed no depression.

Summary

2-Furanacrylic acid gave 1, 4-pentadien-3-one-1, 5-dicarboxylic acid in a fairly good yield by treatment with aqueous hydrogen peroxide containing hydrochloric acid. This acid underwent the same photochemical change by direct sunlight as its methyl ester.

This acid was reduced to γ-ketopimelic acid by aluminium amalgam, and oxidised to fumaric and oxalic acids by potassium permanganate. It is assumed that the two double bond have the trans structure. The phenylhydrazones of the acid and the methyl ester were obtained.

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