On the Ring-opening Reactions of the Furan Compounds. IV. The Condensation Products of Furfural with Methyl Propyl Ketone, Methyl Isopropyl Ketone and Pinacolin by Alkali

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In the previous paper[1] it was reported that, in the condensation of furfural and benzaldehyde with methyl ethyl ketone by alkali, the lowered reaction temperature (0～5°) favored the aldol condensation at the α-methylene group of the ketone and the elevated reaction temperature (60～65°) the condensation at the α-methyl group of the ketone. In the present work were studied the condensation of furfural with methyl propyl ketone by alkali and the ring-opening of the condensation products of furfural with methyl isopropyl ketone and pinacolin.

The condensation of furfural with methyl propyl ketone was carried out in two cases of lowered and elevated reaction temperatures, 0～5° and 60～63°.

In both cases, the condensation products afforded two species of semicarbazone—a greater amount of colorless needle crystals melting at 143～144° and a much smaller amount of colorless needles melting at 223～225°. The ratios of the semicarbazone melting at 143～144° to that melting at 223～225° in the two cases were nearly equal. Considered from the analysis, the condensation product at the lowered reaction temperature appeared to contain a small quantity of the aldol condensation product which corresponds to that of furfural with methyl ethyl ketone.

The condensation product at the reaction temperature 0～5°, after heating with dilute hydrochloric acid in order to dehydrate the aldol[2] which was considered to be contained, was oxidized by sodium hypochlorite to give α-ethyl-2-furanacrylic acid (IV), in the fol-

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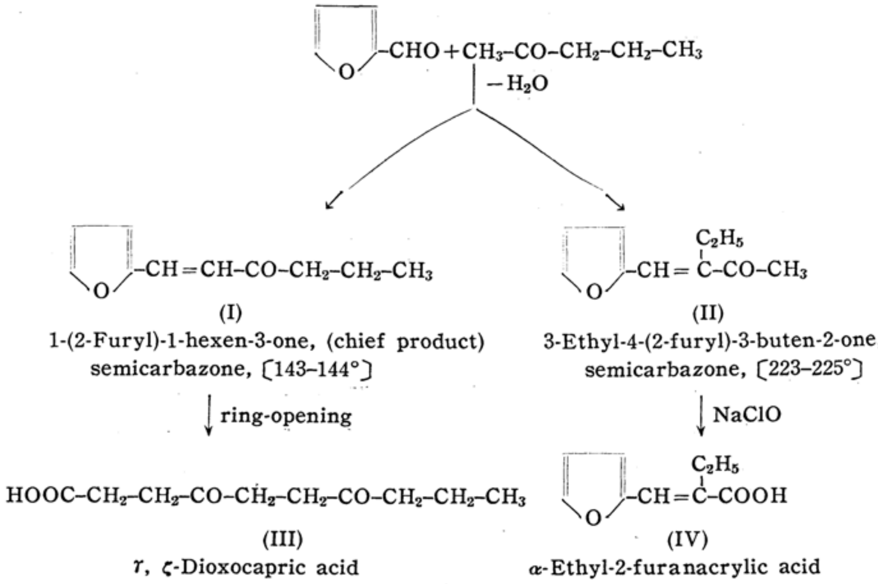
[1] H. Midorikawa: This Bulletin, **26**, 460 (1953).

[2] H. Midorikawa: This Bulletin, **26**, 462 (1953).

lowing formulation, although in a very poor yield. Consequently it is evident that 3-ethyl-4-(2-furyl)-3-buten-2-one (II) is contained in it and methyl propyl ketone reacts with furfural at the α-methylene group of the ketone. The condensation product at the reaction temperature 0~5°, after being heated with dilute hydrochloric acid, gave a mixture of a larger proportion of the semicarbazone melting at 143~144° and a much smaller proportion of that melting at 223~225°.

The condensation product at the reaction temperature 60~63°, on the ring-opening in alcoholic hydrochloric acid[3], gave a dioxocarboxylic acid in a good yield. This acid was considered to be identical with the dioxocarboxylic acid which was reported as γ, ζ-dioxocapric acid (III) by Breusch and Ulusoy[4].

From the stand-point of the poor yield of α-ethyl-2-furanacrylic acid (IV) and the good yield of γ, ζ-dioxocapric acid (III), it was infered that 3-ethyl-4-(2-furyl)-3-buten-2-one(II), which furnished the former acid on the treatment with sodium hypochlorite, gave the semicarbazone of colourless needles (m. p. 223~225°), and the furfurylidene ketone which gave the semicarbazone of colorless minute needles (m. p. 143~144°) was 1-(2-furyl)-1-hexen-3-one (I) yielding γ, ζ-dioxocapric acid (III) by the ring-opening, as shown below.



(I)
1-(2-Furyl)-1-hexen-3-one, (chief product)
semicarbazone, [143–144°]

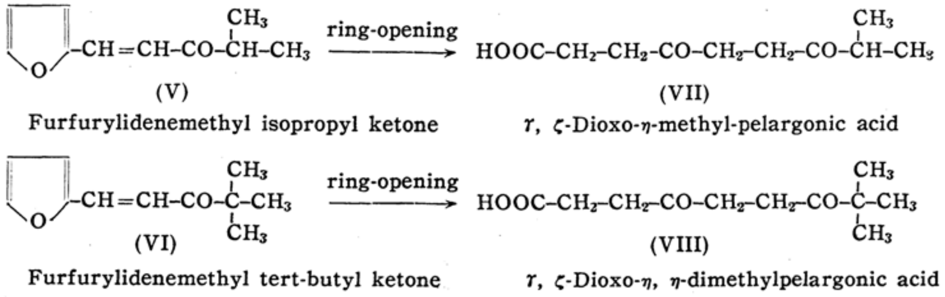
(II)
3-Ethyl-4-(2-furyl)-3-buten-2-one,
semicarbazone, [223–225°]

(III)
γ, ζ-Dioxocapric acid

(IV)
α-Ethyl-2-furanacrylic acid

The poor yield of α-ethyl-2-furanacrylic acid (IV) appeared to reveal a weaker reactivity of the α-methylene group of methyl propyl ketone in comparison with that of methyl ethyl ketone.

The condensation products of furfural with methyl isopropyl ketone and pinacolin by alkali, furfurylidenemethyl isopropyl ketone (V) and furfurylidene-methyl tert-butyl ketone (VI), gave γ, ζ-dioxo-η-methylpelargonic acid (VII) and γ, ζ-dioxo-η, η-dimethylpelargonic acid (VIII) respectively, on the ring-opening in alcoholic hydrochloric acid. These reactions are illustrated as follows:



(V)
Furfurylidenemethyl isopropyl ketone

(VII)
γ, ζ-Dioxo-η-methyl-pelargonic acid

(VI)
Furfurylidenemethyl tert-butyl ketone

(VIII)
γ, ζ-Dioxo-η, η-dimethylpelargonic acid

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[3] E. A. Kehrer and P. Igler: *Ber.*, **32**, 1177 (1899).

[4] F. L. Breusch and E. Ulusoy: *C. A.*, **42**, 5850 (1948).

[5] I. Kashiwagi: This Bulletin, **1**, 94 (1926).

Experimental

Condensation of Furfural with Methyl Propyl Ketone Into a stirred suspension of methyl propyl ketone (13 g.) and furfural (7 g.) in water (150 cc.) was at once introduced 5 % aqueous sodium hydroxide (10 cc.) at 60~63°. The reaction was complete after stirring for 2.5 hrs. at 60~63°. The reaction mixture was neutralised with dilute sulfuric acid. The oily layer was separated and the aqueous solution extracted twice with ether. The combined ethereal solution of the oily layer and the ether extract, after drying over anhydrous sodium sulfate, was fractionated to give a yellow liquid (7 g.), b. p. 119~121°/8 mm.

This fraction was considered to consist of 1-(2-furyl)-1-hexen-3-one (I) in a larger proportion and 3-ethyl-4-(2-furyl)-3-buten-2-one (II) in a much smaller proportion.

Calcd. for $C_{10}H_{12}O_2$: C, 73.12, H, 7.37 %; Found: C, 72.92, H, 7.60 %.

This oil gave a mixture of two species of semicarbazone. The greater part consisted of colorless microscopic needles, which were fairly soluble in methanol and melted at 143~144° on recrystallisation from methanol-water. In addition, fewer colorless needles, which were sparingly soluble in cold methanol and recrystallised from methanol, m.p. 223~225°, were obtained.

The semicarbazone melting at 143~144° was considered to be that of 1-(2-furyl)-1-hexen-3-one (I).

Calcd. for $C_{11}H_{15}O_2N_3$: C, 59.69, H, 6.83, N, 18.99 %; Found: C, 59.55, H, 6.86, N, 19.12 %.

In a solution of 2, 4-dinitrophenylhydrazine in methanolic sulfuric acid, this semicarbazone was converted to a 2, 4-dinitrophenylhydrazone, which was recrystallised from pyridine in red foliated crystals, m. p. 171~172°.

Calcd. for $C_{16}H_{16}O_5N_4$: C, 55.79, H, 4.68, N, 16.27 %; Found: C, 55.74, H, 4.43, N, 16.57 %.

The semicarbazone melting at 223~225° was considered to be the one of 3-ethyl-4-(2-furyl)-3-buten-2-one (II).

Calcd. for $C_{11}H_{15}O_2N_3$: C, 59.69, H, 6.83, N, 18.99 %; Found: C, 59.69, H, 6.89, N, 18.79 %.

This semicarbazone was also converted to 2, 4-dinitrophenylhydrazone which was recrystallised from pyridine in carmine prisms, m. p. 183~184°.

Calcd. for $C_{16}H_{16}O_5N_4$: C, 55.79, H, 4.68, N, 16.27 %; Found: C, 55.81, H, 4.45, N, 16,21 %.

The condensation at 0~5° also was carried out by stirring a mixture of methyl propyl ketone (15 g.), furfural (8 g.), water (150 cc.) and 10 % aqueous sodium hydroxide (10 cc.) for 7 hrs. The reaction mixture was kept overnight below 10°, and then worked up in the same manner as in the condensation at 60~63°. A fraction (7.5 g.) distilling at 119~123°/8 mm was collected.

Calcd. for $C_{10}H_{12}O_2$: C, 73.12, H, 7.37 %; Found: C, 70.34, H, 7.62 %. (This analysis seems to show that this fraction contains a small amount of the aldol condensation product, $C_4H_3O\cdot CH(OH)CH(CH_3)\cdot CO\text{–}CH_3$, which requires C, 65.89 %; H, 7.74 %.)

This fraction gave the same semicarbazones as the condensation product at the reaction temperature 60~63°.

Ring-opening of the Condensation Product of Furfural with Methyl Propyl Ketone The condensation product (2 g.) at the reaction temperature 60—63° was refluxed with conc. hydrochloric acid (1.5 cc.) and alcohol (5 cc.) for 3 hrs. The reaction mixture was evaporated till dry in the water-bath, and a small quantity of dil. hydrochloric acid was added to evaporate till dry once more. The residue was extracted with a sufficient quantity of water, and the extract was concentrated on the water-bath to give the dioxocarboxylic acid which was considered to be γ, ζ-dioxocapric acid (III) (0.7 g.). The acid was recrystallised from ligroin as colorless hexagonal plates, m.p. 83~84°; lit.,4) m.p. 83~84°.

Calcd. for $C_{10}H_{16}O_4$: C, 59.96, H, 8.00 %; Found: C, 60.40, H, 8.14 %.

Sodium Hypochlorite Oxidation of the Condensation Product of Furfural with Methyl Propyl Ketone The condensation product(2.3g.) at the reaction temperature 0~5° was suspended in 6 % hydrochloric acid (5 cc.) and heated by shaking in the water-bath for a short time. The separated oil was suspended in the aqueous sodium hypochlorite solution2) (15 cc.) and kept at ordinary temperature for two days, with occasional shaking. The reaction mixture was freed of the oily matter by extraction with ether and acidified with dilute hydrochloric acid to yield a small number of crystals, which were dissolved in a requisite quantity of hot water, decolorised with active charcoal and crystallised as colorless needles on cooling, m.p. 95~96°. This specimen showed no depression on admixture with α-ethyl-2-furanacrylic acid which was synthesised by the reaction of furfural with butyric anhydride and anhydrous sodium butyrate.6)

Ring-openings of Furfurylidenemethyl Isopropyl Ketone (V) and Furfurylidenemethyl *tert*-Butyl Ketone (VI) Furfurylidenemethyl isopropyl ketone (V) and furfurylidenemethyl *tert*-butyl ketone (VI) were respectively synthesised by the condensations of furfural with methyl isopropyl ketone and pinacolin, using sodium hydroxide as the condensing agent.5)

Furfurylidenemethyl isopropyl ketone (b.p. 101~102°/5 mm.) gave a semicarbazone crystallising from methanol-water as colorless needles, m.p. 148~149°, and a 2, 4-dinitrophenylhydrazone crystallising from pyridine as orange needles, m.p. 175~176°.

Semicarbazone. Calcd. for $C_{11}H_{15}O_2N_3$: C, 59.69, H, 6.83, N, 18.99 %; Found: C,59.98, H, 6.89, N, 18.97 %. *2, 4-Dinitrophenylhydrazone* Calcd. for $C_{16}H_{16}O_5N_4$: C, 55.79, H, 4.68, N, 16.27 %; Found: C, 55.57, H, 4.33, N, 16.30 %.

Furfurylidenemethyl *tert*-butyl ketone (b.p. 101~102°/5 mm.) gave no semicarbazone, as reported by Kashiwagi,5) but gave a 2, 4-dinitrophenylhydrazone crystallising from pyridine-methanol as scarlet lustrous needles, m.p. 121~123°.

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6) A. S. Carter: *J. Am. Chem. Soc.*, 50, 2299 (1928).

Calcd. for $C_{17}H_{18}O_5N_4$: C, 56.98, H, 5.07, N, 15.63 %; Found: C, 57.03, H, 5.03, N, 15.62 %.

The ring-opening of furfurylidenemethyl isopropyl ketone (2 g.) was carried out by refluxing with conc. hydrochloric acid (1.5 cc.) and alcohol (5 cc.) for 3 hrs. By the same procedure as in the case of the foregoing ring-opening reaction was obtained γ, ζ-dioxo-η-methylpelargonic acid, which was recrystallised from ligroin as colorless needles, m.p. 72~73°.

Calcd. for $C_{10}H_{16}O_4$: C, 59.96, H, 8.00 %; Found: C, 59.93, H, 7.89 %.

The ring-opening reaction of furfurylidenemethyl *tert*-butyl ketone to γ, ζ-dioxo-η, η-dimethylpelargonic acid (VIII) was performed by the same procedure as in the case of furfurylidenemethyl isopropyl ketone. The ketone (2 g.) gave the crude acid (0.5 g.) as a viscous oil. It was recrystallised from ligroin as colorless leaflets, m.p. 46~47°.

Calcd. for $C_{11}H_{18}O_4$: C, 61.64, H, 8.47 %; Found: C, 61.57, H, 8.39 %.

Summary

Methyl propyl ketone condensed with furfural by alkali both at the α-methyl and α-methylene groups of the ketone, giving 1-(2-furyl)-1-hexen-3-one (I) in a larger proportion and 3-ethyl-4-(2-furyl)-3-buten-2-one (II) in a much smaller proportion.

The former furfurylidene ketone (I) gave γ, ζ-dioxocapric acid (III) on the ring-opening in alcoholic hydrochloric acid, and the latter (II) was oxidized by sodium hypochlorite to α-ethyl-2-furanacrylic acid (IV).

The ring-opening of furfurylidenemethyl isopropyl ketone (V) and furfurylidenemethyl *tert*-butyl ketone (VI) in alcoholic hydrochloric acid gave γ, ζ-dioxo-η-methylpelargonic acid (VII) and γ, ζ-dioxo-η, η-dimethylpelargonic acid (VIII) respectively.

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