The Condensation of Furfural with Methyl Ethyl Ketone by Aqueous Sodium Hydroxide

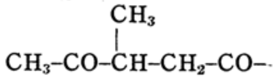
By Hiroshi MIDORIKAWA

(Received December 7, 1953)

In the previous paper[1], it was reported that, in the condensation of furfural with methyl ethyl ketone by aqueous sodium hydroxide, a mixture of two furfurylidene ketones was obtained and one of those was 4-(2-furyl)-3-methyl-3-buten-2-one (I), and the other was considered to be 1-(2-furyl)-1-penten-3-one (II). In the present experiment, these furfurylidene ketones were completely separated from each other, and the results[1] previously obtained were confirmed.

The condensation was carried out at the reaction temperature 60∼63°. The resulting condensation product gave a mixture of three species of semicarbazone, foliated crystals (m.p. 212∼213°), needle crystals (m.p. 183∼184°) and tabular crystls (m.p. 166∼167°).

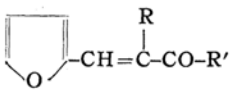
The semicarbazone of foliated crystals (m.p. 212∼213°), separating from the other two species by the less solubility in methanol, regenerated a ketone, a pale yellow oil, on heating with dilute hydrochloric acid. This oil afforded α-methyl-2-furanacrylic acid (III) in a good yield on sodium hypochlorite oxidation. Consequently it is evident that this oil is 4-(2-furyl)-3-methyl-3-buten-2-one (I). The reactions are illustrated in the formulation shown below.

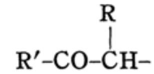
By refluxing with alcoholic hydrochloric acid, this ketone did not give γ, ζ-dioxo-ε-methylcaprylic acid,  $CH_3-CO-\overset{CH_3}{\overset{|}{CH}}-CH_2-CO-CH_2-CH_2-COOH$, which was considered to be obtained by the furan ring opening. This result corresponds to the noteworthy fact

---

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

that the furfurylidene ketone

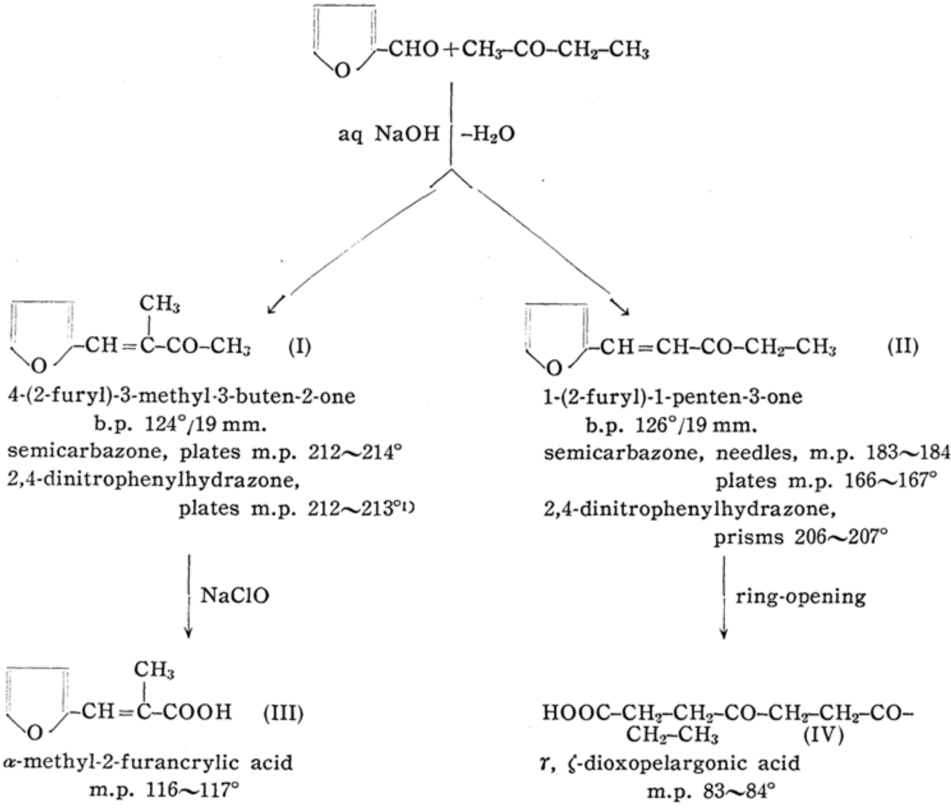


which possesses the alkyl group (R) at the carbon atom joining its carbonyl and furfurylidene groups, as in this keton, does not give the dioxocarboxylic acid  $R'\text{-CO-}\overset{R}{\overset{|}{C}}\text{H-}CH_2\text{-CO-}CH_2\text{-}CH_2\text{-COOH}$ by the cleavage of the furan ring when refluxed with alcoholic hydrochloric acid²⁾, although there are a few exceptions³⁾.

The semicarbazones of needle crystals (m.p. 183~184°) and tabular crystals (166~167°) which were more soluble in methanol were selected from each other, after several recrystallisations. The latter crystals were not detected in the previous experiment¹⁾. The needle crystals appeared to shift to the tabular crystals comparatively less soluble in methanol on repeated recrystallisation by methanol-water. These two species of crystals were converted into the identical 2,4-dinitrophenylhydrazone of carmine needles (m.p. 206~207°), when reacted with 2,4-dinitrophenylhydrazine in alcoholic sulfuric acid. Obviously, one species of ketone gave the two species of semicarbazone, although it was not clear whether these two species are two forms in dimorphism or in syn-anti isomerism.

The mixture of these needle and tabular crystals of semicarbazone, on heating with dilute hydrochloric acid, generated a faintly yellow oil. This oil was considered to be 1-(2-furyl)-1-penten-3-one (II), since it generated no heat and gave no chloroform on treatment with aqueous sodium hypochlorite. This ketone gave the dioxocarboxylic acid (m.p. 83~84°) in a good yield, on refluxing with alcoholic hydrochloric acid. It seemed certain that this dioxocarboxylic acid is γ, ζ-dioxopelargonic acid (IV).

The reactions described above are illustrated in the following formulation.



Experimental

Condensation of furfural with methyl ethyl ketone Furfural (60 g.) and methyl ethyl ketone 120 g.) were dissolved in water (1000 cc.), and 10% aqueous sodium hydroxide (50 cc.) was at once run in at 60° with stirring. After prolonged

---

[2] H. Midorikawa: This Bulletin, **26**, 317 (1953).

[3] D. L. Turner: *J. Am. Chem. Soc.*, **71**, 612 (1949).

stirring for 1 hr. at 60°, the reaction mixture was worked up in the same manner as in the case of the previous report[1] to give a pale yellow oil (70 g.) distilling at 126∼127°/20 mm.

This fraction (30 g.) was suspended in a solution of semicarbazide hydrochloride (30 g.) and sodium acetate (50 g.) in water (40 cc.) and methanol added, until a homogeneous solution was obtained. On standing overnight, crystals (40 g.) of semicarbazone separated out.

The crystals (40 g.) of semicarbazone were heated with methanol (200 cc.) on a water-bath, and, on cooling, a fraction(16 g.) of crystals melting at 205∼210° was obtained. This fraction was once more washed with hot methanol (50 cc.) to give colourless crystals (15 g.) melting at 211∼213°. From the filtrate pale yellow crystals (25 g.) melting at 130∼140° were obtained by addition of a sufficient quantity of water. Several recrystallisations of these crystals from methanol gave a mixture (15 g.) of needles (m.p. 183∼184°) previously reported[1] and plates (m.p. 166∼167°), which were picked out from each other. On repetition of the recrystallisation, the needle crystals appeared to shift to the tabular crystals less soluble in methanol. Analysis of the tabular crystals (m.p. 166∼167°): Found: C, 57.75, H, 6.12, N, 20.16. Calcd. for $C_{10}H_{13}O_2N_3$: C, 57.94, H, 6.32, N, 20.28%.

Both needle and tabular crystals were converted into the 2,4-dinitrophenylhydrazone (m.p. 206∼207°), which showed no depression of the mixed melting point with 2,4-dinitrophenylhydrazone (m.p. 205∼206°) obtained in the previous experiment[1].

4-(2-Furyl)-3-methyl-3-buten-2-one (I) The crystals (12 g.) melting at 211∼213° were suspended in a mixture of conc. hydrochloric acid (20 cc.) and water (40 cc.), and heated for a brief time in the water-bath. The liberated oil, on extraction with ether, dehydration over calcium chloride and fractionation, gave a pale yellow oil (7 g.) distilling at 124°/19 mm. This sweet smelling ketone did not solidify at room temperature, and colourised on standing. Found: C, 71.53, H, 6.55. Calcd. for $C_9H_{10}O_2$: C, 71.96, H, 6.71%.

This ketone (1 g.) was suspended in sodium hypochlorite solution[1] (10 cc.) and the vessel kept in water at ordinary temperature for 2 days, with occasional shaking. The resulting chloroform was removed and the aqueous solution acidified with dilute hydrochloric acid to yield α-methyl-2-furanacrylic acid (III) (0.6 g.).

This ketone (2 g.) was refluxed with conc. hydrochloric acid (1.5 cc.) and alcohol (5 cc.) on the water-bath for 3 hrs. The reaction mixture, worked up in the same manner as previously reported,[1] did not give any dioxocarboxylic acid.

1-(2-Furyl)-1-penten-3-one (II) A semicarbazone mixture (12 g.) of the needle crystals (m.p. 183∼184°) and tabular crystals (m.p. 166∼167°) was treated with dilute hydrochloric acid in the same manner as in the case of 4-(2furyl)-3-methyl-3-buten-2-one (I) to give a pale yellow oil (7 g.) distilling at 126°/19 mm. This sweet smelling ketone also did not solidify at room temperature and colourised on standing. Found: C, 71.34, H, 6.57. Calcd. for $C_9H_{10}O_2$: C, 71.96, H, 6.71%.

This ketone, on suspencion in sodium hypochlorite solution at room temperature for 2 days, did not undergo any reaction.

This ketone (2 g.) was refluxed with conc. hydrochloric acid (1.5 cc.) and alcohol (5 cc.) for 3 hrs. in the water-bath. The reaction mixture, worked up in the same manner as previously reported, gave the dioxocarboxylic acid (0.8 g.) melting at 83∼84° which was considered to be γ, ζ-dioxopelargonic acid (IV).

Summary

From the condensation product of furfural with methyl ethyl ketone by aqueous sodium hydroxide were isolated 4-(2-furyl)-3-methyl-3-buten-2-one (I) and 1-(2-furyl)-1-penten-3-one (II).

The former ketone (I) was oxidised by sodium hypochlorite to yield α-methyl-2-furanacrylic acid, (III) but gave no γ, ζ-dioxo-ε-methylcaprylic acid by refluxion with alcoholic hydrochloric acid.

The latter ketone (II) gave γ, ζ-dioxopelargonic acid (IV) by refluxion with alcoholic hydrochloric acid, but was no acted upon by sodium hypochlorite.

The semicarbazone of 1-(2-furyl)-1-penten-3-one (II) existed in two forms of the needle crystals melting at 183∼184° and the tabular crystals melting at 166∼167°.

The author expresses his sincere thanks to Dr. T. Hayashi for his kind advice.

Scientific Research Institute, Komagome,
Bunkyo-ku, Tokyo