[Contribution from the Department of Chemistry, Ontario Agricultural College]

The Condensation of 3-Pentanone with Furan

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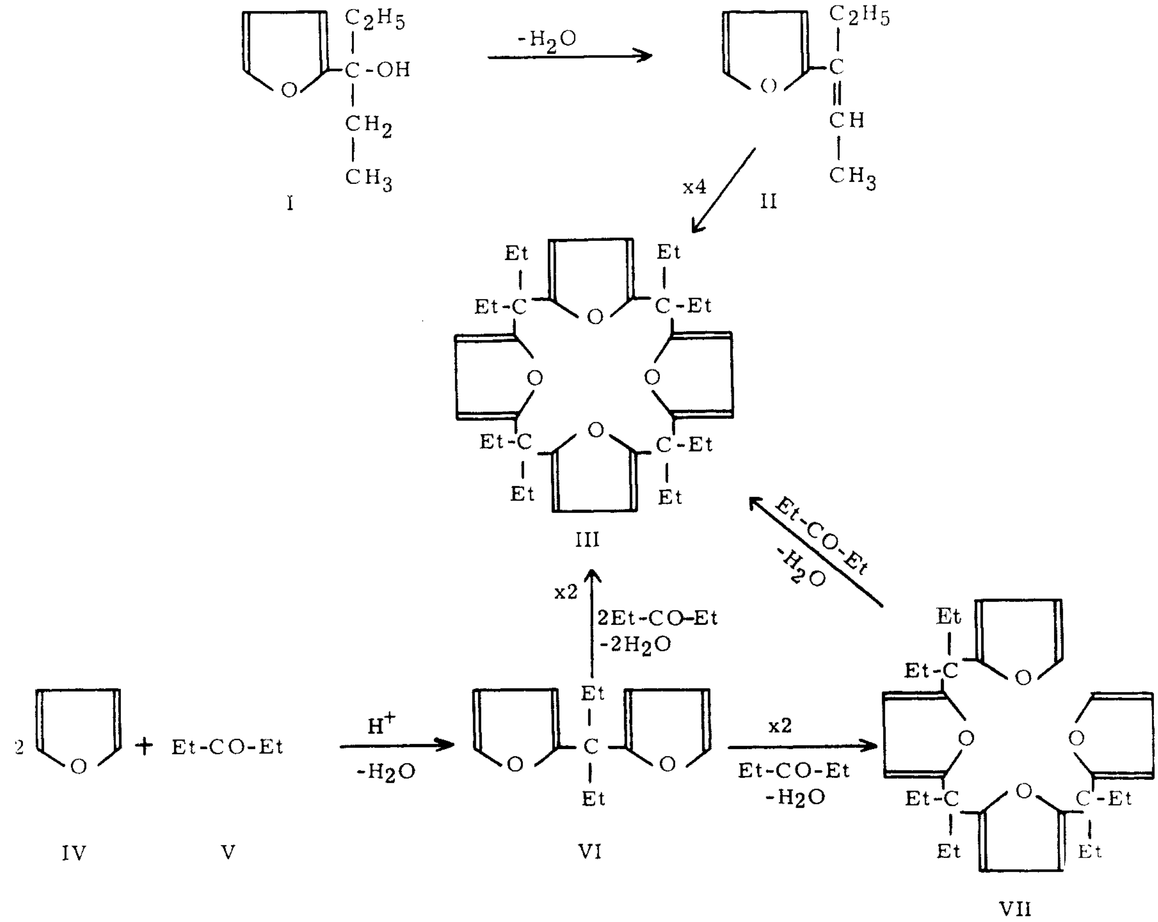
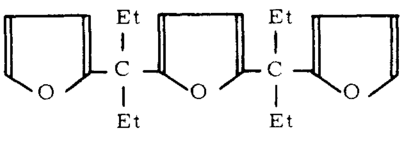
Polycondensation occurs when furan and 3-pentanone are treated with hydrochloric acid. The products are (a) 3,3-difurylpentane, (b) 2,5-*bis*(diethylfurfuryl)furan, (c) 3,3-pentylidene *bis*[5-(diethylfurfuryl)furan], and (d) a cyclic anhydrotetramer of 3-furyl-3-pentanol.

The anhydrotetramer of 3-furyl-3-pentanol derived from furan and 3-pentanone is identical with the compound obtained when 3-furyl-3-pentanol is deliberately synthesized and dehydrated in a vacuum over phosphorus pentoxide. The compound is designated as 2,2,7,7,12,12,17,17-octaethyl-21,22,23,24-tetroxaquaterene.

Recently, Ackman, Brown, and Wright[2] reported that methyl ketones condense with furan in the presence of hydrochloric acid to form the corresponding difurylalkanes. Subsequent reaction of two molecules of the difurylalkane with two molecules of the parent methyl ketone leads to the formation of a cyclic compound composed of four each of furan and methyl ketone residues.

These cyclic compounds, which have been named "Tetroxaquaterenes," may be looked upon as anhydrotetramers of the corresponding substituted furfuryl alcohols. It is not surprising then, that the





VIII

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[2] Ackman, Brown, and Wright, *J. Org. Chem.*, **20**, 1147 (1955).

compound which Hale, McNally, and Pater[3] obtained by the dehydration of 3-furyl-3-pentanol (I) is not 3-furyl-2-pentene (II), as reported by them, but rather its cyclic tetramer, 2,2,7,7,12,12,-17,17-octaethyl-21,22,23,24-tetroxaquaterene (III).

Ackman, Brown, and Wright were unsuccessful in preparing the same compound (III) by the condensation of furan (IV) with 3-pentanone (V). We have now succeeded in preparing the cyclic tetramer, III, as well as the intermediates, 3,3-difurylpentane (VI) and 3,3-pentylidene *bis* [5-(diethylfurfuryl)furan] (VII), from these reagents.

The tetroxaquaterene, III, prepared by our procedure, is identical with the one prepared according to the directions of Hale, McNally, and Pater,[3] as shown by mixture melting point. The structure of 3,3-difurylpentane (VI) is supported by permanganate oxidation to yield the expected diethylmalonic acid.

A third compound, thought to be 2,5-*bis*(diethylfurfuryl)furan (VIII), is also a product of the condensation of furan with 3-pentanone. It is not a direct intermediate in the formation of the tetroxaquaterene (III).

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EXPERIMENTAL

All melting points have been corrected against reliable standards. Molecular weights were determined by the Rast method.

3,3-Difurylpentane (VI). A mixture of 226 g. (3.32 moles) of furan and 140 ml. of 37% hydrochloric acid in 125 ml. of 95% ethanol was treated with 286 g. (3.32 moles) of 3-pentanone (EK 1330), the latter being added dropwise while stirring. After being stirred for 113 hours the mixture took on a deep reddish-purple color. The organic phase was separated, washed with 10% aqueous sodium bicarbonate solution until neutral, and then dried over magnesium sulfate. The excess furan was flashed off and the excess 3-pentanone was removed by simple distillation. The remaining oil was distilled under diminished pressure.

The first fraction, a colorless oil, b.p. 76–77°/2 mm., m.p. −9 to −8°, weighed 58.5 g. (17%) n^{20}_{D} 1.4978, d^{20}_{4} 1.023.

Anal. Calc'd for $C_{13}H_{16}O_2$: C, 76.5; H, 7.84; Mol. wt., 204. Found: C, 76.6; H, 7.93; Mol. wt., 197.

2,5-Bis(diethylfurfuryl)furan (VIII). A second fraction from the preceding distillation boiled at 162–163°/1–2 mm. It was a pale green liquid which weighed 106 g. (28%) and had n^{20}_{D} 1.5089; d^{20}_{4} 1.028.

Anal. Calc'd for $C_{22}H_{28}O_3$: C, 77.6; H, 8.23; Mol. wt., 340. Found: C, 78.3; H, 8.44; Mol. wt., 306.

3,3-Pentylidene bis[5-(diethylfurfuryl)furan] (VII). A third fraction from the preceding distillation boiled at 212–215°/1–2 mm. It was a greenish-yellow oil weighing 14.0 g. (3.5%) and had n_{D}^{20} 1.5199; d_{4}^{20} 1.034.

Anal. Calc'd for $C_{31}H_{40}O_4$: C, 78.1; H, 8.40; Mol. wt., 476. Found: C, 77.8; H, 8.45; Mol. wt., 465.

2,2,7,7,12,12,17,17-Octaethyl-21,22,23,24-tetroxaquaterene (III). (*a*) *From 3,3-difurylpentane and 3-pentanone.* A solution of 1.53 g. (0.0075 mole) of 3,3-difurylpentane and 1.02 g. (0.012 mole) of 3-pentanone in 10 ml. of absolute ethanol was treated with dry hydrogen chloride gas for 15 minutes, at the end of which time the solution had become deep purple in color and a solid had separated. The solid was removed by filtration and washed twice with 10 ml. of cold absolute ethanol. Crystallization from acetone (200 ml./g.) gave 0.4 g. (20%) of long white needles, m.p. 249°. If the needles are left in contact with the mother liquor they change to white plates, m.p. 249°. A mixture melting point of this compound, melting at 249° and the compound prepared by the procedure of Hale, McNally, and Pater[3] also melting at 249°, showed no depression.

Anal. Calc'd for $C_{36}H_{48}O_4$: Mol. wt., 545. Found: Mol. wt., 544.

(*b*) *From 3,3-pentylidene bis[5-(diethylfurfuryl)furan]* (VII) *and 3-pentanone.* A solution of 0.39 g. (0.00082 mole) of VII and 2.5 g. (0.029 mole) of 3-pentanone in 10 ml. of absolute ethanol was treated with dry hydrogen chloride gas for 20 minutes at which time the solution was deep purple in color and a solid had separated. The solid was removed by filtration, washed twice with 10 ml. of cold absolute ethanol, and crystallized from acetone (200 ml./g.). The crystallized product, 0.18 g. (29%), formed first as long white needles, slowly changing to white plates, m.p. 249°. A mixture melting point of this compound with the compound from (*a*) showed no depression.

Oxidation of 3,3-difurylpentane (VI). When 2.04 g. (0.010 mole) of 3,3-difurylpentane was stirred with 13.0 g. (0.0824 mole) of potassium permanganate dissolved in 200 ml. of water, heat was evolved over a period of two hours. Stirring was continued for another 15 hours at room temperature. At the end of this time, all the permanganate had been consumed. After filtering off the manganese dioxide, the filtrate was acidified with hydrochloric acid to *p*H 1. The filtrate then was heated to 60° and 0.1 *molar* potassium permanganate solution was added dropwise until a pink color persisted. The solution was filtered and continuously extracted with 100 ml. of ether for 24 hours. When the ether solution was dried over sodium sulfate and the ether was flashed off, there remained 0.25 g. of a reddish oil which partially crystallized after standing for 30 days. The solid was removed by filtration and on crystallization from chloroform yielded 0.1 g. (6.6%) of white needles, m.p. 124°. A mixture melting point with authentic diethylmalonic acid showed no depression.

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[3] Hale, McNally and Pater, *Am. Chem. J.*, **35**, 72 (1906).