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XXIII. The Condensation of Acetoacetic Ester with Butyndial Tetramethylacetal*

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The reaction of butyndial tetramethylacetal with acetoacetic ester in the presence of boron trifluoride etherate is investigated, and is shown to give 5, 5'-dimethyl-4, 4'-dicarbethoxy-2, 2'-difuryl. The reaction is extended to synthesize some difuran derivatives.

We previously made a detailed investigation of a new reaction of acetals of saturated and acetylenic aldehydes with acetoacetic ester under the action of boron trifluoride etherate, which resulted in formation of alkoxy keto-esters [1].

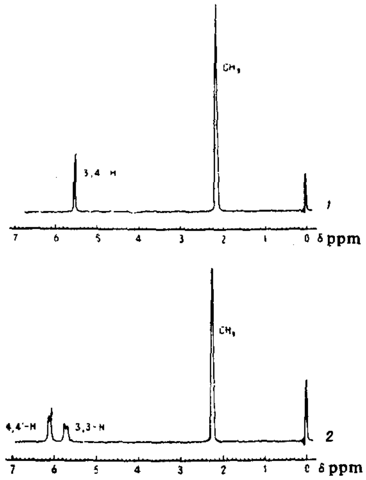
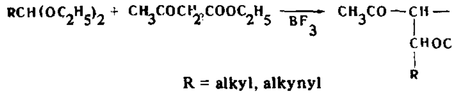


Fig. 1. NMR spectra: 1) 2, 5-dimethylfuran; 2) 5, 5'-dimethyl-2, 2'-difuryl.



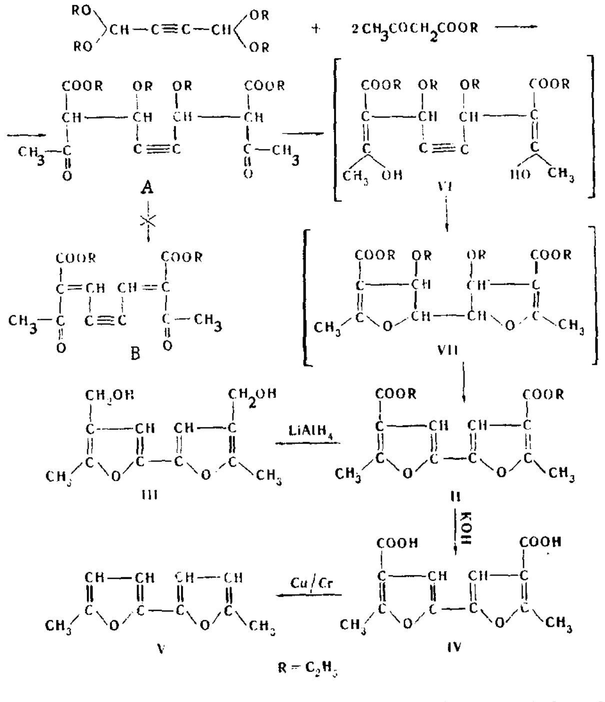
$$RCH(OC_2H_5)_2 + CH_3COCH_2COOC_2H_5 \xrightarrow[BF_3]{} CH_3CO-\underset{\underset{\displaystyle R}{|}}{\underset{\displaystyle CHOC_2H_5}{\underset{|}{CH}}}-COOC_2H_5$$

R = alkyl, alkynyl

It was of interest to carry out the acetoacetic ester reaction with a bifunctional acetal, e. g., butyndial tetramethylacetal (I). However, we found this to give, along with the expected ester A, a 46% yield of a substance whose elementary analysis and molecular weight corresponded to the divinylacetylene diketodiester B, formed by splitting off two molecules of alcohol from diester A. The chemical and spectroscopic properties of this substance did not, however, correspond to a divinylacetylene diketone structure for it [2], but corresponded to 5, 5'-dimethyl-4, 4'-dicarbethoxy-2, 2'-difuryl (II), corresponding to a class of difuryl derivatives almost unstudied in the literature. The sole representative of this series of compounds, 2, 2'-difuryl, has been obtained from ethylfuroylacetate [3].

The structure of the 5, 5'-dimethyl-4, 4'-dicarbethoxy-2, 2'-difuryl (II) which we have prepared is confirmed by the chemical reactions, elementary analyses, and spectroscopic and physicochemical data of the compounds prepared from it.

5, 5'-Dimethyl-4, 4'-dicarbethoxy-2, 2'-difuryl (II) does not form an oxime or 2, 4-dinitrophenylhydrazone, showing that it does not contain a keto group. It does not undergo hydrogenation in ethanol using Adam's catalyst, and it does not form a maleic anhydride adduct. Reduction with $LiAlH_4$ gives diol III in high yield. Saponification of II with alcoholic alkali gives diacid IV, and using the method worked out for 3-furancarboxylic acid [4], IV is decarboxylated to give an 80% yield of 5, 5'-dimethyl-2, 2'-difuryl (V).



Like 2, 2'-difuryl [3], 5, 5'-dimethyl-2, 2'-difuryl does not give a maleic anhydride adduct; it is not hydrogenated in ethyl acetate using Adam's catalyst, but with the same catalyst in acetic acid it absorbs 5.7 moles hydrogen to give a complex mixture of hydrogenolysis products. UV and IR* spectra of V (λ_{max} 285 mm,

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*For Part XXII see [7].

*IR spectra were measured by L. V. Orlova, on a DS-301 instrument, and using a 0.07 mm layer of $CHCl_3$ solution.

ε 20 000; ν 1578, 1593, 1699 cm^{-1}) confirm the presence of two double bonds in the furan ring.

Comparison of the NMR spectra* of 5, 5'-dimethyl-2, 2'-difuryl (V) and 2, 5-dimethylfuran, conclusively confirmed structure V.

The 2, 5-dimethylfuran spectrum shows a methyl group signal at 2.12 ppm, and a singlet signal due to protons at positions 3 and 4 at 5.55 ppm, and as their chemical shifts are the same, it is not split.

In the NMR spectrum of V the 2.21 ppm signal, intensity 6 proton units, belongs to methyl groups, and the signals at 5.71 and 6.09 ppm, intensity 2 proton units each, are split into doublets belonging respectively to protons at positions 4, 4' and 3, 3'.

The signal of the protons at positions 4, 4' is further split because of the CH_3 group, so that its spectrum is broad compared with the signal from the 3, 3' protons.

Formation of 5, 5'-dimethyl-4, 4'-dicarbethoxy-2, 2'-difuryl (II) can be considered to take place as described above.

The first stage of this scheme is the ordinary reaction between butyndial acetal and acetoacetic ester, proceeding analogously to the reaction of monoacetals [1], and giving diketodiester A, which in its enol form VI then undergoes cyclization involving the acetylenic bond, to give compound VII. Splitting off two molecules of alcohol from VII gives II.

Thus, in the condensation of acetoacetic ester with butyndial tetraethylacetal, the first step is reaction of the acetal at its mobile hydrogen, i.e., here too the type of reaction involved is the one which we previously studied for acetals of saturated and acetylenic aldehydes.

EXPERIMENTAL

GLC analysis of the reaction products used a chromatograph with a flame ionization detector, a stream of hydrogen, and a 2 meter column packed with 1% polymethylsiloxane on NaCl [5].

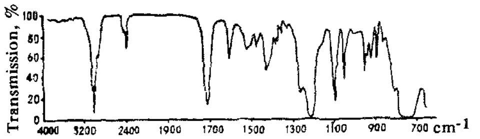

Fig. 2. IR spectrum of 5, 5'-dimethyl-4, 4'-dicarbethoxy-2, 2'-difuryl.

5, 5'-Dimethyl-4, 4'-dicarbethoxy-2, 2'-difuryl (II). A mixture of 38 g (0.29 mole) acetoacetic ester and 18.8 ml BF_3 etherate was stirred, and at room temperature 16.8 g (0.0703 mole) butyndial diacetal (I) was added gradually. Then the mixture was stirred for 30 min more at the same temperature, and for 15 min at 35°, ether was added, and the solution treated with sodium carbonate. The ether solution was washed with water, dried over $MgSO_4$, and the ether taken off. After 7.3 g crystalline product was separated off and excess acetoacetic ester distilled off, the residue was vacuum distilled. There was obtained a 4.6 g fraction with bp 75°–82° C (0.6 mm), n_D^{20} 1.4400 which GLC showed to consist mainly of starting I, and a 3 g fraction with 160°–175° C (0.35 mm), which solidified after distilling. TLC showed it to be identical with the compound previously isolated (R_f 0.53; Al_2O_3 grade III activity, hexane–acetone 9:1), and so did GLC. Mp 95.5°–97° C (crystallized twice ex acetone). λ_{max} 276 nm, ε 25 000 (in EtOH). Found: C 62.76; 62.73; H 5.93; 5.87%; M 289.2 (ebullioscopic), calculated for $C_{16}H_{18}O_6$: C 62.74; H 5.92%; M 306.3.

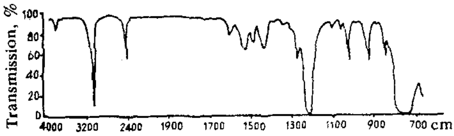

Fig. 3. IR spectrum of 5, 5'-dimethyl-2, 2'-difuryl.

5, 5'-Dimethyl-4, 4'-hydroxymethyl-2, 2'-difuryl (III). A solution of 1.2 g (0.004 mole) diester II in 10 ml tetrahydrofuran was added over a period of 35 min, at room temperature, to 15 ml of an ether solution of 0.015 mole $LiAlH_4$. The next day the mixture was treated with ammonium chloride solution, the organic layer washed with water, dried, and evaporated, to give 0.98 g colorless crystalline diol III, mp 136°–138° C (ex acetone). R_f 0.23 (SiO_2 benzene–ethyl acetate 2:1). IR spectrum: 3180, 3284 cm^{-1}. Found: C 64.98; 64.78; H 6.49; 6.35%; M 210.1 (ebullioscopic), calculated for $C_{12}H_{14}O_4$: C 64.85; H 6.35%; M 222.2.

5, 5'-Dimethyl-4, 4'-dicarboxy-2, 2'-difuryl (IV). A mixture of 8 g (0.026 mole) diester II, 120 ml 20% ethanolic KOH, and 80 ml absolute EtOH was refluxed for 2 hr. The ethanol was distilled off, the residue dissolved in water, and extracted twice with ether. The aqueous solution was acidified with dilute H_2SO_4, and a colorless precipitate formed. This was separated off, washed repeatedly with water, and dried. Yield was 6 g diacid IV, very sparingly soluble in organic solvents, mp 300° C (ex dioxane). Found: C 57.20; 57.29; H 4.27; 4.24%, equiv. wt. 123.6, calculated for $C_{12}H_{10}O_6$: C 57.60; H 4.03%, equiv. wt. 125.1. λ_{max} of the K salt of IV 286 nm (ε 20 650); 295.5 nm (ε 21 200).

5, 5'-Dimethyl-2, 2'-difuryl (V). A mixture of 6 g (0.024 mole) diacid IV, 12 ml quinoline, and 1.2 g Cu chromite [6] was held at 190°–200° C for 80 min, while 1050 ml (87%) CO_2 evolved. Next a mixture of quinoline and decarboxylation product was distilled over at 80°–92° C (10 mm). The distillate was diluted with ether, the ether solution washed a few times with HCl (1:1), then with $NaHCO_3$ solution, and finally with water, then dried over $MgSO_4$ and evaporated. Yield was 3.05 g (80%) 5, 5'-dimethyl-2, 2'-difuryl (V), colorless crystals mp 37°–39° C (ex MeOH); bp 92°–94° (10 mm), n_D^{40} 1.5460; R_f 0.83 (Al_2O_3 grade III activity, hexane–acetone 9:1). GLC confirmed that the substance was an individual compound. Found C 73.86; 73.90; H 6.10; 6.23%, calculated for $C_{10}H_{10}O_2$: C 74.05; H 6.18%. λ_{max} 285 mm, ε 20 000 (in EtOH).

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*The spectra were determined in CCl_4 solution, with an INM-C-60 instrument, the internal standard being tetramethylsilane.

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