SYNTHESIS OF β-SUBSTITUTED FURANS BY THE ALKYLATION OF β-DICARBONYL COMPOUNDS BY 1,2,3-TRIHALOPROPANES

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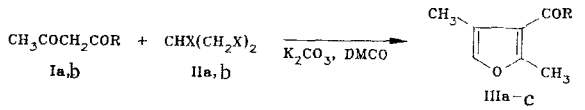
The alkylation of β-dicarbonyl compounds by dibromoethane in the presence of potassium carbonate in dimethyl sulfoxide results in the formation of cyclopropane derivatives with a high yield [1].

We found that the alkylation of β-dicarbonyl compounds by 1,2,3-trihalopropanes under similar conditions produces β-substituted furans with 60-70% yields. For example, when a mixture of acetylacetone (Ia), 1,2,3-tribromopropane (IIa), and K_2CO_3 in a 4:1:2 ratio is heated in dimethyl sulfoxide at 70°C for 12 h, 2,4-dimethyl-3-acetylfuran (IIIa) forms with a 70% yield. Compound IIIb is obtained in a similar manner with a 62% yield from acetoacetic ester (Ib) at 110°C.

The use of 1,2,3-trichloropropane in the alkylation reaction requires more severe conditions and gives the same compounds IIIa and b.



I a R=CH_3, b R=OC_2H_5; II a X=Br, b X=Cl; III a R=CH_3, b R=OC_2H_5, c R=OH

The structures of the β-substituted furans obtained (IIIa-c) were confirmed by the PMR spectra, elemental analysis, and the agreement of the constants with the literature data [2, 3]. 2,4-Dimethyl-3-acetylfuran: bp 74-76°C (10 mm Hg), n_D^{20} 1.4930. PMR spectrum (CCl_4): 2.10 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 7.23 ppm (s, 1H, CH=). Ethyl 2,4-dimethyl-3-furancarboxylate: bp 85-86°C (14 mm Hg), n_D^{20} 1.4678. PMR spectrum (CCl_4): 1.33 (t, 3H, CH_3), 2.10 (s, 3H, CH_3), 4.23 (q, 2H, CH_2), 6.87 ppm (s, 1H, CH=). 2,4-Dimethyl-3-furancarboxylic acid: mp 116-117°C (from aqueous ethanol). PMR spectrum ($CDCl_3$): 2.17 (s, 3H, CH_3), 2.57 (s, 3H, CH_3), 7.13 (s, 1H, CH=), 12.9 ppm (s, 1H, OH).

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