LETTERS TO THE EDITOR

SYNTHESIS OF FURAN DERIVATIVES FROM 1,3-ALKADIYNES

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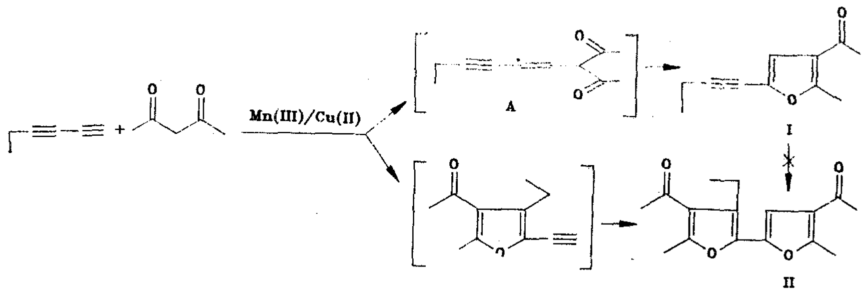
For the first time, we studied the reaction of the conjugated diacetylenes 1,3-hexadiyne, 1,3-butadiyne, and 5-methyl-1,3-hexadiyn-5-ol with acetylacetone and acetoacetic ester in the presence of the oxidative system manganese(III) acetate/copper(II) acetate. It was shown that the reaction products are substituted 5-alkynyl- and 5-(5-furyl)furans. In particular, in the reaction of 1,3-hexadiyne with acetylacetone, 3-acetyl-5-(1-butynyl)-2-methylfuran (I) and 3-acetyl-5-(3-acetyl-2-methyl-4-ethyl-5-furyl)-2-methylfuran (II) are formed in an equimolar ratio in a total yield of 33%.

Compound I is obtained as a result of attack of the acetylacetonyl radical at the $C_{(1)}$ atom of 1,3-hexadiyne with subsequent oxidative cyclization of the intermediate radical A in the presence of copper(II) acetate. By a separate experiment, it was shown that under the reaction conditions furan I is not converted to bifuryl II. Therefore, the formation of compound II is apparently due to the attack of the acetylacetonyl radical at the $C_{(4)}$ atom of 1,3-hexadiyne, leading to the reactive intermediate B, which then gives reaction product II in the reaction with a second mole of acetylacetone.

The reaction was carried out at 30°C in acetic acid with 1,3-hexadiyne—acetylacetone—$Mn(OAc)_3$—$Cu(OAc)_2$ molar ratios of 1:8:4:4. Cyclization products I and II were isolated in the individual state by column chromatography on silica gel, with hexane—ether (4:1) as the eluting agent.

3-Acetyl-5-(1-butynyl)-2-methylfuran (I). Yield, 17%; n_D^{20} 1.5380 (Silufol, hexane—ether, 1:1). IR spectrum (thin layer), ν: 3135 (C—H), 2240 (C≡C), 1680 (C=O), 1595, 1555 cm^{-1} (furan ring). Proton NMR spectrum (CCl_4), δ: 1.21 (3H, triplet, J = 7.6 Hz, CH_3), 2.28 (3H, singlet, CH_3CO), 2.42 (2H, quartet, CH_2), 2.52 (3H, singlet, 2-CH_2), 6.59 ppm (1H, singlet, 4-H).



3-Acetyl-5-(3-acetyl-2-methyl-4-ethyl-5-furyl)-2-methylfuran (II). Yield, 16%; mp 105-106°C; R_f 0.17 (Silufol, hexane—ether, 1:1). IR spectrum (mineral oil), ν: 1678, 1660 (C=O), 1597, 1578, 1512 cm^{-1} (furan ring). Proton NMR spectrum (CCl_4), δ: 1.12 (3H, triplet, J = 7.5 Hz, CH_3), 2.32 (3H, singlet, CH_3CO), 2.36 (3H, singlet, CH_3CO), 2.55 (3H, singlet, 2-CH_3), 2.58 (3H, singlet, 2-CH_3), 2.80 (2H, quartet, CH_2), 6.59 ppm (1H, singlet, 4-H), M^+ 274.

The obtained compounds had satisfactory analytical characteristics.

The reactions proceed similarly in the case of acetoacetic ester and other diacetylenic compounds.

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