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SYNTHESIS OF ACETYLENIC KETONES FROM STRAIGHT-CHAIN ACID CHLORIDES

I. L. Kotlyarevskii, S. I. Shergina, I. E. Sokolov, and A. S. Zanina

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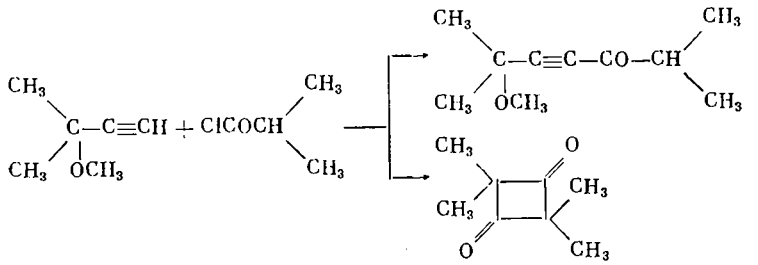
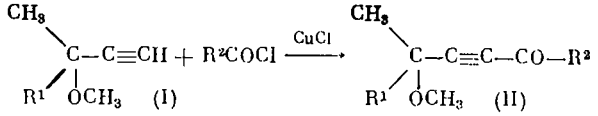
Acetylenic ketones have become more readily available in recent years [1, 2] due to the development of such synthesis methods as the acylation of terminal acetylenic compounds in the presence of a complex Cu-Pd catalyst [3, 4] and CuI [5]. However, in both cases only the acid chlorides of either aromatic or α-branched aliphatic acids can be used as the acylating agents. Attempts [3] to react the acid chlorides of the acetic, propionic, and butyric acids proved unsuccessful. The same negative result was obtained when the acid chlorides of the higher straight-chain acids were used.

When the acylation of 2-methyl-2-methoxy-3-butyne with isobutyryl chloride was studied it proved that, besides 2,6-dimethyl-6-methoxy-4-heptyn-3-one, a small amount of 2,2,4,4-tetramethyl-1,3-cyclobutanedione is formed.



The formation of a ketene dimer permitted us to postulate that triethylamine cleaves an α-proton from the acid chloride molecule to give the corresponding ketene, which is easily polymerized and copolymerizes with the acetylene under the reaction conditions. In this connection we postulated that for successful reaction it is necessary to use a stoichiometric amount (with respect to the acetylene and acid chloride) of the CuCl complex with the aliphatic amine.

The experimental results confirmed our postulations. The acylation of acetylenic ethers (I) with the acid chlorides of the acetic, propionic, valeric, and decanoic acids in the presence of equimolar amounts of CuCl and triethylamine in aprotic solvents gave acetylenic



(I) (II)

$R^1 = R^2 = CH_3$ (a); $R^1 = CH_3$, $R^2 = C_2H_5$ (b); $R^1 = CH_3$; $R^2 = n\text{-}C_4H_9$ (c); $R^1 = n\text{-}C_6H_{13}$ $R^2 = n\text{-}C_9H_{19}$ (d).

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ketones (IIa-d) in 35-50% yields, whose structure was proved by both analytical and spectral methods. The IR spectra of the (II) ketones have absorption bands in the 1650-1670 and 2230 cm^{-1} regions, which are characteristic for a conjugated carbonyl group and triple bond.

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrometer in CCl_4 solution. The GLC was run on a Chrom-4 chromatograph using an 0.25 mm × 3 mm column packed with 5% PEGA deposited on Sterchamol (0.25-0.36 mm).

2-Methyl-2-methoxy-3-nonyn-5-one (IIc). To a mixture of 100 ml of benzene and 10 g of CuCl were added in an argon stream 10.1 g of Et_3N, 9.8 g of ether (I), and 12 g of valeryl chloride. The temperature of the mixture rose to 40°C. After 1.5 h the organic layer was decanted, washed with water, and dried over $MgSO_4$. We obtained 9.2 g (50.5%) of (IIc), bp 70-71° (1 mm), n_D^{22}1.4455. Found: C 72.38, H 9.93%. $C_{11}H_{18}O_2$. Calculated: C 72.49; H 9.96%.

Similarly were obtained: 6.0 g (42.8%) of 5-methyl-5-methoxy-3-hexyn-2-one (IIa), bp 67-68° (16 mm), n_D^{20} 1.4420 [6]; 5.4 g (35.0%) of 6-methyl-6-methoxy-4-heptyn-3-one (IIb), bp 54.5-55° (2 mm), n_D^{22} 1.4452. Found: C 70.02; H 9.29%. $C_9H_{14}O_2$. Calculated: C 70.10; H 9.15%; 13-methyl-13-methoxy-11-nonadecyn-10-one (IId), bp 163° (1 mm), n_D^{22} 1.4575. Found: C 78.02; H 11.84%. $C_{21}H_{38}O_2$. Calculated: C 78.20; H 11.88%.

CONCLUSIONS

A method for the catalytic condensation of acetylenes with the acid chlorides of unbranched aliphatic acids was found.

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