SYNTHESIS OF Y-METHOXYALKYNYL KETONES

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Acetylenic ketones with functional groups can be synthesized by reacting acetylenic ketones with carbonyl compounds under the conditions of either the Nef [1] or the Favorskii [2] reaction, by the oxidation of secondary-tertiary acetylenic γ -glycols [3], and by the partial hydration of the ethers of diacetylenic carbinols [4].

We tried to obtain γ -methoxyalkynyl ketones by using benzoyl chloride to acylate the methyl ethers of tertiary acetylenic carbinols in triethylamine in the presence of catalytic amounts of $[P(C_6H_5)_3]_2PdCl_2/CuI$ catalyst [5]. The reaction is slow (20-25 h) under the conditions of this method, and the yields of the γ -methoxyalkynyl ketones are 20-50%. In our opinion, the reason for the unsatisfactory progress of the reaction is the fact that the quaternary salts, formed by the reaction of the tertiary amine with the acid chloride, are difficultly soluble in triethylamine.

Taking into account the fact that the activity of the acetylenic carbanion increases strongly in the presence of Pd catalyst, while the formation of the acetylide anion is facilitated by the presence of aprotic solvents [6], we came to the conclusion that the acylation of terminal acetylenic compounds must be run in either benzene or toluene. In such case the triethylamine can be used either in equimolar amount or in slight excess.

Thus, for example, the acylation of the methyl ether of dimethylethynylcarbinol with benzoyl chloride in the presence of catalytic amounts of $[P(C_6H_5)_3]_2PdCl_2/CuI$ in benzene, using an equimolar amount of triethylamine, proved to be exothermic and was ended in 15 min, while the yield of the acetylenic ketone was 92%. Under the same conditions the reaction of PhCOCl with phenylacetylene is exothermic, quantitative, and is ended in 1 h (instead of the 15 h by the method given in [5]). As a result, under our conditions the reaction of acyl halides with the methyl ethers of tertiary acetylenic carbinols is an efficient method for obtaining γ -methoxyalkynyl ketones.



The reaction course and the yield of some of the γ -methoxyalkynyl ketones depend on the order of adding the reactants. Thus, when acetylenic ketone (III1) was obtained by adding the methyl ether of dimethylethynylcarbinol to a triethylamine—isobutyryl chloride mixture in benzene in the presence of (PPh₃)₂PdCl₂/CuI we isolated, besides ketone (III1) (48.8% yield), also tetramethylcyclobutane-1,3-dione in 40.0% yield (when based on acid chloride). The formation of the latter is easily explained by the dimerization of the ketene (CH₃)₂C= C=0, which is formed by the dehydrochlorination of isobutyryl chloride. Under analogous conditions, the yield of ketone (III1) was 76.5% when isobutyryl chloride is added to a mixture of triethylamine and the methyl ether of dimethylethynylcarbinol in benzene.

The presence of absorption bands at 2220 cm⁻¹ (C=C) and 1690 cm⁻¹ (C=O) in the IR spectra of ketones (IIIa-r), the absence of absorption bands at 3300 cm⁻¹ (=CH), and also the elemental analysis and GLC data confirm the structure of our synthesized compounds.

EXPERIMENTAL

The IR spectra of the compounds in $CHCl_3$ solution were recorded on a UR-20 spectrometer. The GLC was run on a Chrom-4 instrument, using a 120 \times 0.4 cm column packed with 0.5% of

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		R ³ Yield,
(p, mm 1	-	=
91,6 113-11		\mathbf{Ph}
88,1 128-13		\mathbf{Ph}
86,4 163		Ρh
93,8 166–16		\mathbf{h}
80,0 $122-12$		m-MeC ₆ H ₄
95,0 $148-15$		m-MeC ₆ H ₄
86,0 156-15		m-MeC ₆ H ₄
80.0 $164-16$		$m-MeC_6H_4$
87,0 157-15		p-MeOC ₆ H ₄
87,0 188-19		<i>p</i> -MeOC ₆ H₄
76,5 $95-96$		CHMe ₂
76,6 96		CHMe2
70,2 $111-11$		$CHMe_2$
69,7 (2)		CMe ₃
76,0		p-NO2CoH4
74,6 171 (2)		Ô

TABLE 1. γ -Methoxyalkynyl Ketones $\frac{R^{1}}{R^{2}}$, $\frac{C}{C}$ -C=C- R^{3}

1723

PEGA deposited on glass (0.2-0.25 mm), nitrogen as the carrier gas, and a temperature of 110-160°. The methyl ethers of the tertiary acetylenic carbinols were obtained as described in [7]. The yields and constants of the obtained compounds are given in Table 1.

<u>4-Methyl-4-methoxy-1-phenyl-2-pentyn-1-one (IIIa)</u>. With stirring, in an inert gas stream, to a mixture of 0.2 g of CuI, 0.2 g of (PPh₃)₂PdCl₂ and 30 g of Et₃N in 200 ml of benzene were added in succession 29 g of PhCOC1 and 19.6 g of 3-methyl-3-methoxy-1-butyne (Ia); the mixture was heated for 10 min at 74°. Then the mixture was cooled to about 20°, decomposed with water, and extracted with benzene. The benzene layer was washed with water and dried over K_2CO_3 . We obtained 36.8 g (91.7%) of (IIIa). Ketones (IIIb-r) were obtained in a similar manner.

CONCLUSIONS

A convenient method was proposed for the synthesis of γ -methoxyalkynyl ketones, which is based on the catalytic acylation of the appropriate acetylenic compounds with carboxylic acid chlorides.

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HYDROMAGNESATION OF UNSATURATED COMPOUNDS USING DIETHYLAMINO-

MAGNESIUM HYDRIDE, CATALYZED BY TRANSITION METAL COMPLEXES

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As a continuation of the study of the catalytic hydrometallation of unsaturated compounds by Al [1, 2] and Mg [3] hydrides, we studied the reaction of diethylaminomagnesium hydride (DAMH) [4] with olefins and dienes of variable structure in the presence of transition metal complexes.

Of the heteroorganic compounds tested by us, the best catalyst for the hydromagnesation of olefins proved to be Cp_2TiCl_2 , whereas the Fe, Ni, and Zr compounds were considerably less active, while TiCl₄ was inactive (Table 1). Thus, the hydromagnesation of 1-hexene, 1-octene, 1-decene. and 1-undecene with an equimolar amount of DAMH in the presence of Cp_2TiCl_2 at 60° leads to the corresponding diethylaminomagnesium alkylates (I)-(IV) in high yields. As can be seen from Table 2, the yield of the hydromagnesation products decreases slightly with in-



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