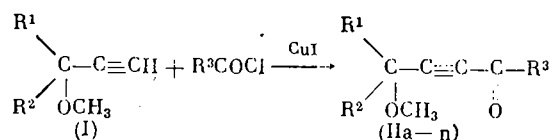


REACTION OF TERMINAL ACETYLENES WITH ACID CHLORIDES IN THE PRESENCE OF COPPER SALTS

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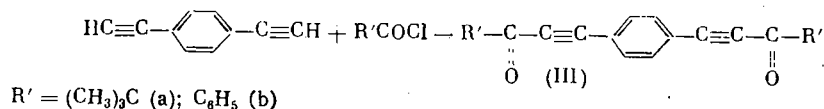
Up to now the α -acetylenic ketones were obtained mainly by the condensation of either the acid chlorides or anhydrides of acids with Na, Li, Cu, etc. acetylides. Previously it was shown by us that this reaction can be run without prior preparation of the acetylides, since it proceeds successfully in the presence of CuI in aprotic solvents if equimolar amounts of triethylamine are used [1]. In the present paper this method was used to acylate ethers of acetylenic alcohols and p-diethynylbenzene.



The reaction was run in either benzene or toluene solution at 45–80°C in an inert gas stream. To absorb the formed HCl we used triethylamine in a 1:1 mole ratio to the acid chloride. The amount of CuI was varied from 0.01 to 1 mole per mole of acetylenic compound.

The highest yields (70–85%) of the acetylenic ketones [(IIId), (IIg), and (IIIm)] were obtained when the ethers of tertiary acetylenic carbinols are reacted with benzoyl chloride. The acylation of the methyl ether of propargyl alcohol proceeds in lower yields, but in the presence of the complex Pd-Cu catalyst proposed in [2], this reaction in general does not go (Table 1).

p-Diethynylbenzene actively reacts with acid chlorides to give diketones (IIIa) and (IIIb) in 70–77% yields.



Previously similar diketones were obtained by the oxidation of secondary acetylenic glycols [3] in 20% yield.


A further study of this reaction disclosed that the acylation of terminal acetylenes can be run in the presence of catalytic amounts of CuCl, in which connection, contrary to all of the previous concepts, the latter proved to be much more active than CuI. Thus, the reaction of 3-methyl-3-methoxy-1-nonyne (Ia) with isobutyryl chloride proceeded exothermally in 15 min and the yield of acetylenic ketone (IIk) was 78%, whereas to complete this reaction using CuI required 5 h. The amount of CuCl was varied from 0.5 mole to 0.025 mole per mole of acetylenic compound. The reaction proceeded briskly in all cases, while the yield of the end product (IIk) reached 73–78%. The yield dropped to 44% only when the amount of CuCl was decreased to 0.01 mole per mole of acetylenic ether. Ether (Ia) also reacted actively with benzoyl chloride, and here the yield of ketone (IIg) was 86.4%.

The structure of the obtained compounds was proved by both analytical and spectral methods; the IR spectra had adsorption bands in the 1650–1670 cm^{-1} and 2230 cm^{-1} regions, which testify to conjugation of the acetylenic fragment with the carbonyl group.

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TABLE 1. Reaction Conditions and Properties of Acetylenic Ketones*

$$\begin{array}{c}
 R^1 \\
 | \\
 R^2 - C - C \equiv C - R^3 \\
 | \quad \quad \quad || \\
 OCH_3 \quad \quad O
 \end{array}$$

| Compound | R ¹ | R ² | R ³ | Amount of Cul, moles | T°, C | Time, hr | Yield, % | Bp, °C (p, mm of Hg) | n _D (°C) | Found Calculated, % | | Empirical formula |
|----------|--------------------------------------|--------------------------------|--|----------------------|-------|----------|----------|----------------------|---------------------|---------------------|----------------|---|
| | | | | | | | | | | C | H | |
| (IIa) | H | H | C ₆ H ₅ | 0.1 | 45 | 6 | 25.0 | 128 (3) | 1.5550 (21.5) | 75.57 75.84 | 5.73 5.79 | C ₁₁ H ₁₀ O ₂ |
| (IIb) | H | H | m-CH ₃ -C ₆ H ₄ | 0.1 | 45 | 5 | 30.0 | 138 (1.5) | 1.5500 (21.5) | 76.37 76.51 | 6.44 6.31 | C ₁₂ H ₁₂ O ₂ |
| (IIc) | H | H | (CH ₃) ₂ CH | 0.05 | 60 | 4 | 56.4 | 62 (5) | 1.4450 (20) | 68.64 68.54 | 8.62 8.63 | C ₈ H ₁₂ O ₂ |
| (IId) | CH ₃ | C ₄ H ₉ | C ₆ H ₅ | 0.01 | 70 | 7 | 70.9 | 128-130 (1) | 1.5230 (22) | 78.61 78.65 | 8.20 8.25 | C ₁₆ H ₂₀ O ₂ |
| (IIe) | CH ₃ | C ₄ H ₉ | m-CH ₃ -C ₆ H ₄ | 0.01 | 80 | 18 | 56.1 | 143 (1) | 1.5183 (24) | 78.95 79.03 | 8.56 8.58 | C ₁₇ H ₂₂ O ₂ |
| (II f) | CH ₃ | C ₄ H ₉ | (CH ₃) ₂ CH | 0.02 | 80 | 3.5 | 58.1 | 96 (1) | 1.4470 (20) | 74.34 74.29 | 10.68 10.68 | C ₁₃ H ₂₂ O ₂ |
| (IIg) | CH ₃ | C ₆ H ₁₃ | C ₆ H ₅ | 0.01 | 80 | 7 | 77.2 | 103 (2) | 1.5165 (17) | 79.40 79.37 | 8.93 8.88 | C ₁₈ H ₂₄ O ₂ |
| (IIh) † | CH ₃ | C ₆ H ₁₃ | p-NO ₂ -C ₆ H ₄ | 0.005 | 70 | 10 | 50.0 | - | - | 68.10 68.12 | 7.44 7.30 | C ₁₈ H ₂₃ NO ₄ |
| (II i) | CH ₃ | C ₆ H ₁₃ |  (CH ₃) ₂ CH | 0.05 | 70 | 8 | 35.0 | 171 (2) | 1.5050 (20) | 73.40 73.25 | 8.37 8.45 | C ₁₆ H ₂₂ O ₃ |
| (IIk) | CH ₃ | C ₆ H ₁₃ | (CH ₃) ₂ CH | 0.1 | 45 | 5 | 70.2 | 102 (1) | 1.4530 (20) | 75.76 75.58 | 10.77 11.00 | C ₁₅ H ₂₆ O ₂ |
| (II l) | CH ₃ | C ₆ H ₁₃ | (CH ₃) ₃ C | 0.01 | 60 | 6 | 69.7 | 127 (2) | 1.4520 (20) | 76.06 76.14 | 10.97 11.18 | C ₁₆ H ₂₈ O ₂ |
| (II m) | -(-CH ₂ -) ₅ - | | C ₆ H ₅ | 0.015 | 70 | 5 | 88.0 | 166-168 (4) | 1.5510 (22) | 79.17 79.31 | 7.21 7.49 | C ₁₆ H ₁₈ O ₂ |
| (II n) | -(-CH ₂ -) ₅ - | | (CH ₃) ₂ CH | 0.02 | 70 | 4 | 40.9 | 100-102 (1) | 1.4730 (20) | 74.85 74.96 | 9.71 9.68 | C ₁₃ H ₂₀ O ₂ |

*Amount of starting acetylenic ether = 0.1 mole.

†Mp 76-78°C (from alcohol), Found: N 4.58%; Calculated: N 4.41%.

EXPERIMENTAL

The GLC was run on a Chrom-4 chromatograph using a 250 cm × 3.0 mm column, packed with 5% PEGA deposited on Sterchamol, and nitrogen as the carrier gas. The IR spectra were taken on a UR-20 spectrometer. The methyl ethers of the tertiary acetylenic alcohols were obtained as described in [4].

2,2,6-Trimethyl-6-methoxy-4-dodecyn-3-one (IIk). To 1.9 g (0.01 mole) of CuI and 12.6 g (0.125 mole) of Et₃N in 50 ml of toluene were added 16.8 g (0.1 mole) of ether (Ia) and 15 g (0.125 mole) of trimethylacetyl chloride, and the mixture was stirred for 6 h at 60°C in an argon stream. The reaction course was followed using GLC. The reaction mixture was decomposed with water, extracted with ether, and dried over MgSO₄. We isolated 17.5 g (69.7%) of ketone (IIk). The reaction conditions and properties of the acetylenic ketones (IIa-n) are given in Table 1.

Under analogous conditions, from 3.15 g (0.025 mole) of p-diethynylbenzene, 6 g of (0.05 mole) of pivalyl chloride, 5.05 g (0.05 mole) of Et₃N, and 9.5 g (0.05 mole) of CuI in 100 toluene we obtained 5.1 g (69.4%) of 1,4-bis(2,2-dimethyl-4-pentyn-3-one)benzene (IIIa), mp 143-144°C (from alcohol). Found: C 81.56; H 7.70%. C₂₀H₂₂O₂. Calculated: C 81.60; H 7.53%.

We also synthesized 1,4-bis(3-phenyl-1-propyn-3-one)benzene (IIIb) in 77.2% yield; mp 191°C (from benzene). Found: C 85.93; H 4.23%. C₂₄H₁₄O₂. Calculated: C 86.21, H 4.22%, cf. [3].

Preparation of 2,6-Dimethyl-6-methoxy-4-dodecyn-3-one (IIk) in the Presence of CuCl. To a mixture of 10.1 g of Et₃N, 16.8 g of ether (Ia), and 1 g of CuCl in 75 ml of benzene was added 10.6 g of isobutyryl chloride in an argon atmosphere. The temperature of the reaction mixture rose to 55°C, and after 15 min the starting ether (Ia) was absent in the mixture (GLC data). After 45 min the mixture was decomposed and we isolated 18.5 g (77.7%) of ketone (IIk). Under the same conditions we obtained ketone (IIg) in 86.4% yield.

CONCLUSIONS

A method was developed for the synthesis of acetylenic ketones by the acylation of terminal acetylenic compounds with acid chlorides in the presence of CuCl.

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