THE SYNTHESIS OF ACETYLENIC ACETALS

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Zinc chloride on silica gel is an active catalyst for the condensation of ethyl orthoformate with terminal acetylenes.

The Howk reaction is a well known method for the synthesis of acetylenic acetals. The hydrolysis of these derivatives gives acetylenic aldehydes. However, this reaction proceeds in a complex manner and the acetal yield depends on the structure of the acetylenic compound and condensing agent and drops with increasing reaction time [1]

$$\underset{(I)}{R{-}C{\equiv}CH} + HC(OEt)_3 \longrightarrow \underset{(II)}{R{-}C{\equiv}C{-}CH(OEt)_2} \xrightarrow{H^+} \underset{(III)}{R{-}C{\equiv}C{-}CHO}$$

$$R = Ph\ (a);\ n\text{-}C_6H_{13}C(OMe)Me\ (b).$$

Indeed, acetal (IIb) was obtained in 30% yield upon the condensation of acetylene (Ib) with ethyl orthoformate in the presence of $ZnCl_2$. In addition, the starting reagents and a tarry residue were obtained from the reaction mass. The fraction of the tarry residue increased with increasing condensation time.

We have found that this reaction proceeds much more efficiently when $ZnCl_2$ supported on silica gel is used as the catalyst. In this case, the yield of (IIb) was increased to 70% and the procedure for isolation of the reaction product was simplified. In the case of the synthesis of (IIa), we found that the catalyst is not altered during the reaction and may be reused. The hydrolysis of acetals (IIa) and (IIb) was carried out in the presence of sulfuric acid in aqueous acetic acid. Aldehyde (IIIb) was isolated in 92% yield, while aldehyde (IIIa) was subjected to further chemical transformations without isolation.

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrometer in CCl_4. The preparation of acetylenic ether (Ib) was described in our previous work [2]. KSK silica gel was ground in a porcelain mortar and 10% $ZnCl_2$ was added. Water was added and the mixture was thoroughly mixed. The water was evaporated and the catalyst was roasted for 5 h and 170-180°C.

1,1-Diethoxy-3-phenyl-2-propyne (IIa). A mixture of 51 g (0.5 mole) phenylacetylene, 74 g (0.5 mole) $HC(OEt)_3$, and 10 g catalyst was stirred for 2 h, increasing the temperature from 130 to 180°C. The ethanol liberated was collected in a Dean—Stark trap. The reaction mixture was cooled. The catalyst was filtered off and the residue was distilled to give 73.5 g (72%) acetal (II), bp 91-92°C (2 mm), n_D^{21} 1.5181 [1].

The yield of acetal (IIa) was virtually the same when the catalyst was reused.

An analogous procedure gave 1,1-diethoxy-4-methyl-4-methoxy-2-decyne (IIb) in 68% yield, bp 131-132°C (3 mm), n_D^{18} 1.4442. Found: C, 70.96; H, 11.12%. Calculated for $C_{16}H_{30}O_3$: C, 71.07; H, 11.18%. IR spectrum (ν, cm^{-1}): 1080 (C—O), 1050, 1120 (C—O—C—O—C).

4-Methyl-4-methoxy-2-decyn-1-al (IIIb). A mixture of 28.4 g acetal (IIb), 20 ml 5% H_2SO_4, and 20 ml acetic acid was stirred in a rotary evaporator on a steam bath using a water pump for 1 h. The reaction mixture was cooled, washed with aqueous $NaHCO_3$ and water and dried over $MgSO_4$. Distillation gave 18.1 g (92%) aldehyde (IIIb), bp 73-74°C (15 mm), $n_D^{20.5}$ 1.4560. Found: C, 73.22; H, 10.24%. Calculated for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27%. IR spectrum (ν, cm^{-1}): 2215 ($-C{\equiv}C-$), 1680 (C=O), 1080 (C—O).

LITERATURE CITED

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2. A. S. Zanina, I. L. Kotlyarevskii, S. I. Shergina, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 7, 1636 (1977).

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