BIS(CYANOMETHYLIDENE)-1,4-DIOXANES

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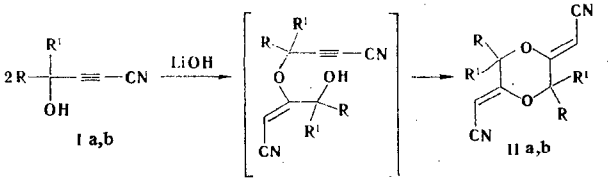
UDC 547.491:547.841

We have previously shown that tertiary cyanoacetylenic alcohols Ia,b in the presence of bases (5-10% NaOH, KOH, and CsOH) undergo cyclization to give products with an oxetane ring [1].

We found that a different reaction occurs in the presence of LiOH. Instead of the expected oxetanes we isolated 1,4-dioxanes IIa,b — products of dimerization of alcohols Ia,b.



I, II a R=R'=CH$_3$; b R+R'=(CH$_2$)$_5$

It is evident that LiOH displays lower activity in the step involving splitting out of the cyanoacetylene anion from the starting alcohol and its subsequent addition to a second molecule of alcohol I, which precede the formation of oxetanes [1]. The decomposition of alcohols Ia,b is indirectly confirmed by their absence in the reaction mixture and the moderate yields of 1,4-dioxanes IIa,b (up to 37%).

At the same time, the rather high basicity of LiOH makes it possible to realize the nucleophilic addition of a tertiary hydroxy group to an activated acetylenic bond, and the existence of a strong β-orienting effect of the nitrile group promotes the formation of a 1,4-dioxane ring. Thus 2.5 mmole of alcohols Ia,b in 0.5 ml of dioxane was added to a solution of 0.027 g of LiOH in 9.5 ml of dioxane, and the mixture was stirred for 2 h at 20°C (Ia) or 50°C (Ib). Chromatography with a column packed with Al_2O_3 in a chloroform–benzene–alcohol system (20:4:1) gave IIa (37%), with mp 213°C (from benzene), or IIb (27%) with mp 244-245°C. IR spectrum of IIa: 1145 (COC), 1640 (C=CH), and 2235 cm^{-1} (CN); the spectrum did not contain the absorption band of a hydroxy group. PMR spectrum of IIa: 4.7 (=CH) and 1.5 ppm (CH_3).

The results of elementary analysis and the data from the mass-spectral determination of the molecular mass for IIa,b were in agreement with the calculated values.

LITERATURE CITED

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Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Irkutsk 664033. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, p. 996, July, 1983. Original article submitted February 2, 1983.

 0009-3122/83/1907-0806$07.50