Synthesis of a [10]-(2,6)-Pyridinophane

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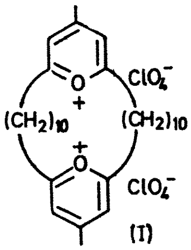
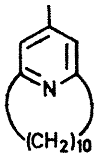
Summary The reaction of isobutene with 1,12-dodecanedioic dichloride in the presence of aluminium chloride leads to a dimeric pyrylium salt (I), though by modifying the conditions of the reaction a mixture is obtained which, after amminolysis, gives mainly the monomeric [10]-(2,6)-pyridinophane (II).

WHILE studying the synthesis of new types of transition-metal ligands we encountered the problem of preparing a [10]-(2,6)-pyridinophane (II) in a simple way. Apart from the total synthesis of muscopyridine[1] we found only one report[2] on the preparation of (2,6)-pyridinophanes. A re-investigation of this work gave the following results.

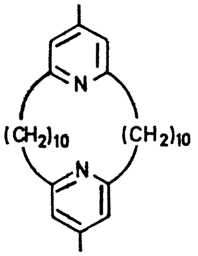
The experimental procedure[2] described for the condensation of isobutene and dodecanedioic dichloride in the presence of aluminium chloride afforded in 2% yield a pyrylium perchlorate (I), the physical constants of which were identical with those reported by Balaban *et al.*[2] Treatment of the product with ammonia in t-butyl alcohol gave a pyridine having the reported m.p. (103—105°), microanalysis, and i.r. spectra.[2] However, the mass spectrum of the product showed a base peak at m/e 462, proving its dimeric nature. A second independent determination of the molecular weight by the vaporimetric



(I)



(II)



(III)

method[3] gave the value of 509 which, within the limits of error, corresponds to the dimeric compound (III).

With the assumption that during the condensation reaction some monomeric pyrylium salt must also have been formed, we submitted the total reaction mixture to a more thorough investigation. After removing the organic solvent and the gummy polymeric material the aqueous solution of the pyrylium salts was freeze-dried and treated with an excess of ammonia. All basic products were extracted from the alkaline solution with ether and separated by chromatography on silica gel (hexane–EtOAc, 10:1). Beside the crystalline dimeric pyridinophane (III) (R_F 0·31) an oily pyridine derivative† (R_F 0·45) was isolated, λ_{max} (ethanol) 216 (ϵ 4075) and 265 nm (3120); ν_{max} ($CHCl_3$) 2933 (*vs*), 2860 (s), 1606 (s), 1565 (m), 1446 (m), and 861 (w) cm^{-1}; ($CDCl_3$) 1·18 (s, 12 H), 1·80 (m, 4 H), 2·28 (s, 3 H), 2·80 (m, 4 H), and 6·76 p.p.m. (s, 2 H); (M^+) *m/e* 231; molecular weight[3] 235 (calc. 231).

In order to raise the yield (*ca.* 0·5%) of the monomeric pyridinophane (II) we carried out the preparation of the pyrylium salt[2] at 50°, and stopped the reaction as soon as all the reactants had been added. In this case, after amminolysis, the yield of the monomeric pyridinophane (II) increased to 1%, whereas practically no dimeric material could be isolated.

We thank the Schweizerischer Nationalfonds for financial support.

(*Received, November 4th,* 1970; *Com.* 1916.)

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† The compound gave satisfactory analytical data.

[1] K. Biemann, G. Büchi, and B. H. Walker, *J. Amer. Chem. Soc.*, 1957, **79**, 5558.
[2] A. T. Balaban, M. Gavat, and C. D. Nenitzescu, *Tetrahedron*, 1962, **18**, 1079.
[3] Ch. Chylewski and W. Simon, *Helv. Chim. Acta*, 1964, **47**, 515.