LETTERS TO THE EDITOR

ALKYLATION OF BENZOCROWN ETHERS BY CERTAIN ALCOHOLS

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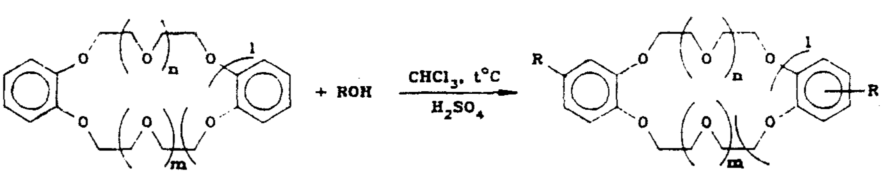
Methods for preparing alkyl-substituted benzocrown ethers by condensation of alkylpyrocatechols [1], reduction of the corresponding derivatives [2], or alkylation of benzocrown ethers by alcohols in polyphosphoric acid [3, 4] are known. In the last case, substantial differences in the reactivity of crown ethers as a function of their structure were not noted.

We first found that benzo-12-crown-4 (I), benzo-15-crown-5 (II), dibenzo-21-crown-7 (III), and dibenzo-24-crown-8 (IV) are quantitatively alkylated by tert-butanol in boiling $CHCl_3$ in the presence of concentrated H_2SO_4 [ratio of crown ether–tert-butanol–acid 1:5 (or 10 for dibenzocrown ethers):2 (or 4) moles]. The large differences in crown ether reactivities in this reaction were unexpected. Thus, whereas crowns I and II yield 90-94% of the corresponding 4-tert-butyl derivatives after 1-2 h, crowns III and IV convert 100% into a mixture of mono- and dialkylated products. Dibenzo-18-crown-6 (V) converts only half way, forming exclusively the 4-tert-butyl derivative. However, benzo-18-crown-6 (VI) is not alkylated by this reaction. Under analogous conditions, crowns III and IV are alkylated by benzyl alcohol to form mono-substituted or a mixture of the corresponding mono- and di-substituted products. Crown ether II is not alkylated.



R = $(CH_3)_3C$, $C_6H_5CH_2$; I $l=n=0$, $m=1$; II $l=0$; $n=m=1$; III $l=n=1$, $m=2$; IV $l=1$, $n=m=2$; V $l=m=n=1$; VI $l=0$, $m=1$, $n=2$

Carrying out the reaction in the presence of a 1.5- to 3-fold excess (relative to crown ether) of Na or K perchlorate significantly increases the degree of conversion for tert-butanol. For example, crown ether V yields 95% of the 4-tert-butyl derivative, whereas the degree of conversion for VI is less than 15%. An analogous increase in yield is seen for benzyl alcohol (crown ether II under the experimental conditions is highly reactive and converts quantitatively into a mixture of mono- and di-tert-butyl-II in a 70:30 ratio).

Alkylation by this method is much poorer for crown ethers I-VI in benzene, xylene, n-heptane, and in excess tert-butanol or does not occur with 50% H_2SO_4 in water. These crown ethers are not alkylated under the experimental conditions by normal- or isoaliphatic alcohols. The simplest benzocrown-ether analog, benzo-1,4-dioxane (VII), is readily and quantitatively alkylated under these conditions by tert-butyl and benzyl alcohols.

It can be proposed that the factor controlling the reaction is complex formation between the crown ethers and the alkyl (aralkyl) cation, which should differ markedly on changing the size of the macrocycle. The fact that the yield of mono- and dialkyl derivatives increases sharply with use of Na (K) perchlorates, which readily form complexes with crown ethers, is consistent with this. The noted difference in reactivity of crown ethers I, II, and VI indicated that it was necessary to examine alkylation of dioxane VII by tert-butanol under the conditions given above and at ratios of reagents using a 1.5-fold excess (in crown ether) of the aliphatic analogs of crown ethers II and VI, namely 15-crown-5 (VIII) and 18-crown-6 (IX). It was found that dioxane VII in the presence of crown ether VIII, as expected, was quantitatively alkylated, whereas for crown ether IX dioxane VII is not alkylated. A similar surprising suppression of the alkylation, also not seen earlier, confirms in our opinion the hypothetical possibility of complex formation between benzocrown ethers and the alkylating cation.

The product purity and composition of the reaction mixture were monitored by GLC using reference samples prepared by the methods of [1, 3, 4]. The structure and composition of the compounds synthesized were confirmed using IR and PMR spectroscopies, mass spectrometry, and elemental analysis.

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STRUCTURE OF 1,2-TETRANAPHTHOPORPHINE

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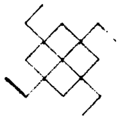
The common method of synthesizing tetrapyrrole macroheterocycles by template tetramerization of asymmetrically substituted porphinogens around a coordinated metal atom frequently produces a mixture of isomers, the number of which approaches or equals the number of fragment combinations possible. For example, isomers were formed during synthesis of metal complexes of 1,2-naphthalocyanine from 1,2-dicyanonaphthalene [1] and of tetra (tert-butyl)porphyrazine from tert-butylmaleonitrile [2]. In the latter case, preparative high-pressure liquid chromatography (HPLC) was used to separate the three isomers.

Earlier we prepared tetra-1,2-naphthoporphine (I) and its Zn complex [3], in which it is theoretically possible to propose the presence of four isomers Ia-d.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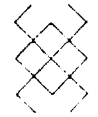
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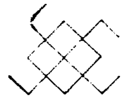
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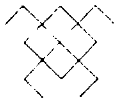
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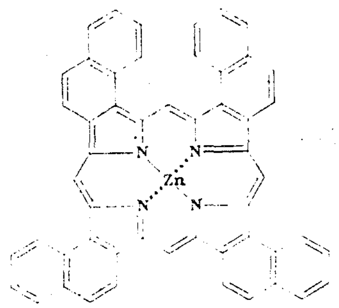

A preliminary conclusion about formation of primarily one low-symmetry isomer was made on the basis of polarized fluorescence spectra [4]. However, its structure was not determined. Due to steric hindrances between the aromatic fragments, formation of isomer Ib (cf. [2]) is not likely. Only one isomer with a retention time 10.07 min was found by HPLC for the Zn complex of I (Kratos instrument, 25-cm column, 4.6-mm inner diameter, silica gel sorbent, 637 nm spectrophotometric detection, isopropyl alcohol mobile phase, 1 ml/min flow rate). The structure of this isomer was elucidated by ^{13}C NMR spectroscopy. Three signals at 102.90, 99.07, and 95.84 ppm in the ratio 1:2:1 are seen for the meso-carbon atoms in the spectrum of the Zn complex in DMF at 25°C. This enabled the isomer to be assigned to type Id, since an isomer of type Ic should have four signals from meso-carbon atoms according to symmetry. Thus, template tetramerization yielding the Zn complex of the tetranaphthoporphine produces only one isomer of type Id. This can be explained using a synthesis scheme for tetraarenoporphines [5] that passes through an intermediate bisisoindole.

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