

Alkylation of the inverted porphyrin nickel(II) complex by dihalogenalkanes: formation of monomeric and dimeric derivatives.

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An efficient and simple method of modification of “inverted” porphyrin is provided by reactions of 5,10,15,20-tetraaryl-2-aza-21-carbaporphyrinatonicel(II) **2** with dihalogenalkanes under basic conditions. The substituents are bound to the internal carbon or external nitrogen of the inverted pyrrole depending on dihalogenalkane and basic catalyst. The monomeric 2- or 21-ethoxymethyl-substituted species are formed in the reaction of **2** with dihalomethanes and sodium ethoxide or ethanol in the presence of K_2CO_3 . A novel, dimeric 21,21'-ethylene-linked derivative **11** is obtained from **2** and ethylene bromide in dichloromethane in the presence of potassium carbonate and ethanol, while application of potassium *tert*-butoxide promotes formation of *N*-bromoethyl-substituted monomer **12**. Reaction of **2** with propylene bromide in the presence of proton scavenger efficiently leads to the 21-allyl-substituted monomer **14** that is a product of the HBr elimination from a transient 21-bromopropyl-substituted species. The new compounds have been identified and characterized by means of mass spectrometry and optical and NMR spectroscopies. A single-crystal X-ray analysis performed for **12** allows discussion of structural parameters concerning the macrocycle and coordination core. Formation of deprotonated species $[2]^-$, which is proposed as a key intermediate in the alkylation reaction, has been observed spectroscopically. Chirality of the *N*-substituted derivatives induced by protonation of the internal carbon is observed by NMR at low temperatures.

Adres publiczny

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<https://www.acs.org/content/acs/en.html>

