

High-pressure Approach to the Synthesis of *N,N'*-Dimethyl Diazacoronands

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α,ω -Tertiary diamines react under high pressure with α,ω -di-iodo compounds to give the cyclic bis-quaternary salts in almost quantitative yields and their subsequent demethylation with triphenylphosphine affords *N,N'*-dimethyl diazacoronands in high yield.

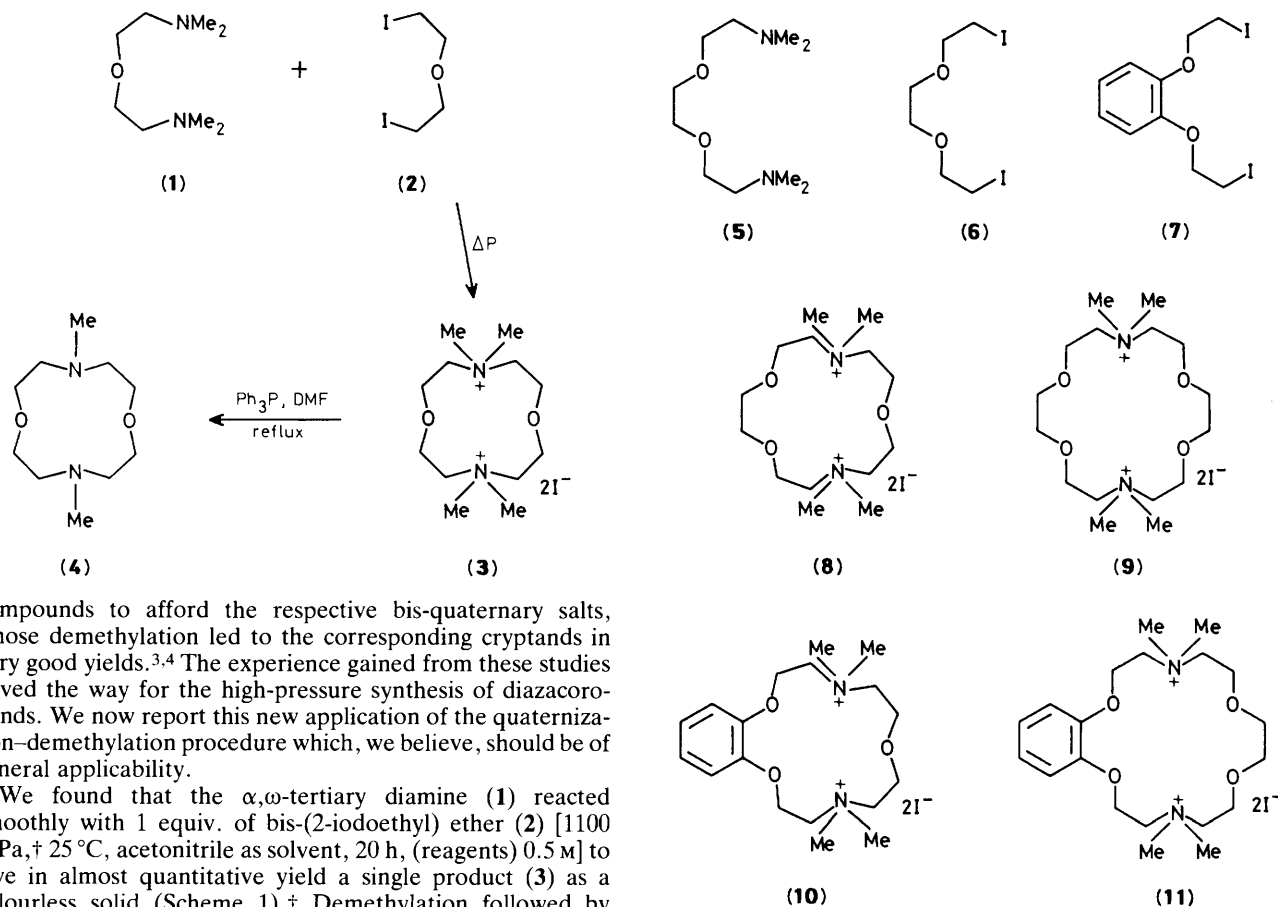
The methods for the formation of diazacoronands have recently been reviewed.¹ In principle, high-dilution techniques² provide the most useful method. However, this method is limited to compounds possessing no reducible groups. Furthermore, even a slight contamination of the

reactants and/or solvent has a marked influence on the reaction yield. To avoid these difficulties our attempts focused on high-pressure double-quaternization reactions. It was recently found that *N,N'*-dimethyl diazacoronands reacted under high-pressure conditions with various α,ω -di-iodo

Table 1. Synthesis of *N,N'*-dimethyl diazacoronands.

Diamine	Di-iodo compound	Bis-quaternary salt ^a	Yield, %	Diazacoronand ^b	Yield, %
(1)	(2)	(3)	99	Me ₂ (12)-N ₂ O ₂	81
(1)	(6)	(8)	95	Me ₂ (15)-N ₂ O ₃	74
(5)	(2)	(8)	95	Me ₂ (15)-N ₂ O ₃	77
(5)	(6)	(9)	97	Me ₂ (18)-N ₂ O ₄	59
(1)	(7)	(10)	96	Me ₂ B(15)-N ₂ O ₃	70
(5)	(7)	(11)	99	Me ₂ B(18)-N ₂ O ₄	64

^a All double quaternizations were carried out under 1100 MPa at 25 °C in acetonitrile solution during 20 h. ^b Demethylation was performed in boiling dimethylformamide (DMF) using triphenylphosphine as a nucleophile.



compounds to afford the respective bis-quaternary salts, whose demethylation led to the corresponding cryptands in very good yields.^{3,4} The experience gained from these studies paved the way for the high-pressure synthesis of diazacoronands. We now report this new application of the quaternization-demethylation procedure which, we believe, should be of general applicability.

We found that the α,ω -tertiary diamine (1) reacted smoothly with 1 equiv. of bis-(2-iodoethyl) ether (2) [1100 MPa, \dagger 25 °C, acetonitrile as solvent, 20 h, (reagents) 0.5 M] to give in almost quantitative yield a single product (3) as a colourless solid (Scheme 1). \ddagger Demethylation followed by treatment with triphenylphosphine⁶ (boiling dimethylformamide, 24 h) afforded the *N,N'*-dimethyl diazacoronand Me₂(12)-N₂O₂ (4) in 81% yield.

Four other bis-quaternary salts (8), (9), § (10), and (11) were obtained under the same conditions, starting from tertiary α,ω -diamines (1) and (5), and from α,ω -di-iodo compounds (2), (6), and (7). The results are presented in Table 1.

This method should be useful, particularly for the syntheses of more elaborate *N,N'*-dimethyl diazacoronands, including chiral compounds.

\dagger For the high-pressure experiments we used the piston-cylinder type apparatus described earlier.⁵

\ddagger Satisfactory analyses and spectral data were obtained for all new compounds.

§ The structure of compound (9) was independently confirmed by X-ray analysis.⁷

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