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

Janusz Jurczak,* Ryszard Ostaszewski, and Piotr Salański
Institute of Organic Chemistry, Polish Academy of Sciences, 01-224 Warszawa, Poland

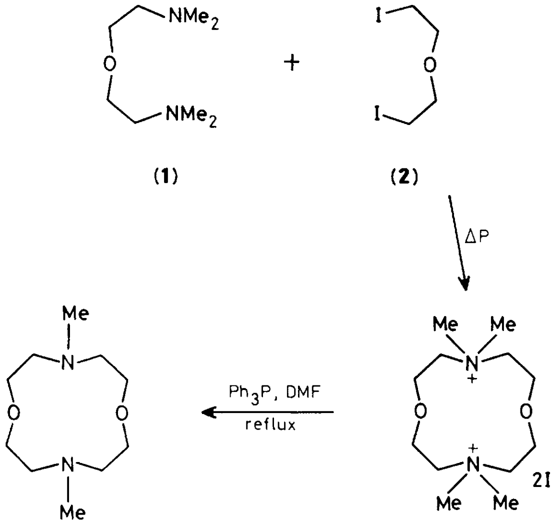
α,ω-Tertiary diamines react under high pressure with α,ω-di-iodo compounds to give the cyclic bis-quaternary salts in almost quantitative yields and their subsequent demethylation with triphenylphosphine affords *N,N'*-dimethyl diazacoronands in high yield.

The methods for the formation of diazacoronands have recently been reviewed.[1] In principle, high-dilution techniques[2] 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

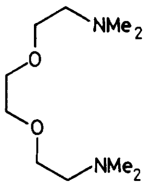
Table 1. Synthesis of *N*,*N*′-dimethyl diazacoronands.

Diamine	Di-iodo compound	Bis-quaternary salt[a]	Yield, %	Diazacoronand[b]	Yield, %
(**1**)	(**2**)	(**3**)	99	$Me_2(12)$-N_2O_2	81
(**1**)	(**6**)	(**8**)	95	$Me_2(15)$-N_2O_3	74
(**5**)	(**2**)	(**8**)	95	$Me_2(15)$-N_2O_3	77
(**5**)	(**6**)	(**9**)	97	$Me_2(18)$-N_2O_4	59
(**1**)	(**7**)	(**10**)	96	$Me_2B(15)$-N_2O_3	70
(**5**)	(**7**)	(**11**)	99	$Me_2B(18)$-N_2O_4	64

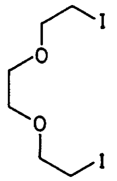
[a] All double quaternizations were carried out under 1100 MPa at 25 °C in acetonitrile solution during 20 h. [b] Demethylation was performed in boiling dimethylformamide (DMF) using triphenylphosphine as a nucleophile.



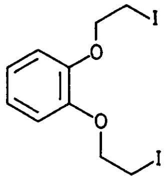
(**4**) (**3**)



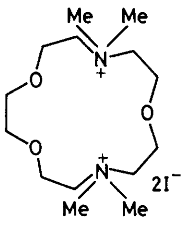
(**5**)



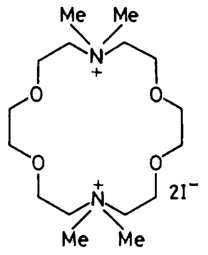
(**6**)



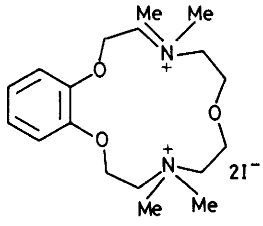
(**7**)



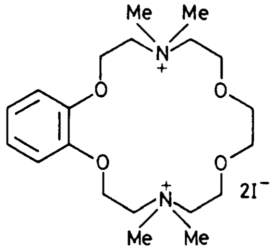
(**8**)



(**9**)



(**10**)



(**11**)

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,† 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).‡ Demethylation followed by treatment with triphenylphosphine[6] (boiling dimethylformamide, 24 h) afforded the *N*,*N*′-dimethyl diazacoronand $Me_2(12)$-N_2O_2 (**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.

This work was supported by the Polish Academy of Sciences CPBP 01.13 grant.

Received, 31st August 1988; Com. 8/03497D

References

1 G. W. Gokel and S. H. Korzeniowski, 'Macrocyclic Polyether Syntheses,' Springer Verlag, Berlin, 1982.
2 B. Dietrich, J.-M. Lehn, and J.-P. Sauvage, *Tetrahedron Lett.*, 1969, 2885.
3 J. Jurczak and M. Pietraszkiewicz, *Top. Curr. Chem.*, 1985, **130**, 183.
4 J. Jurczak, R. Ostaszewski, M. Pietraszkiewicz, and P. Sałański, *J. Incl. Phenom.*, 1987, **5**, 553.
5 J. Jurczak, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 3438.
6 Tse-Lok Ho, *Synth. Commun.*, 1973, **3**, 99.
7 K. Suwińska, to be published.

---

† For the high-pressure experiments we used the piston–cylinder type apparatus described earlier.[5]

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

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