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HIGH-PRESSURE SYNTHESIS OF CRYPTANDS WITH ALIPHATIC BRIDGING UNITS

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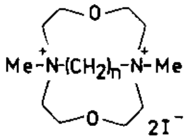
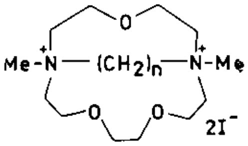
Abstract — N,N'-Dimethyl diazacoronands react with α,ω-diiodoalkanes under high pressure (10 kbar) to give the bis-quaternary salts which are transformed into cryptands via demethylation with triphenylphosphine.

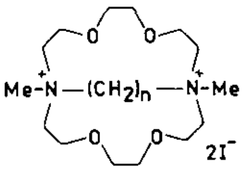
We have already published syntheses of cryptands either simple[1] and more elaborated[2,3] by high-pressure double quaternization of N,N'-dimethyl diazacoronands followed by demethylation. Now we report on the influence of the length of the bridging unit on high-pressure double quaternization. We selected four diazacoronands: (12)-N_2O_2,[4] (15)-N_2O_3,[5] (18)-N_2O_4,[5] and B(18)-N_2O_4[5] and a range of α,ω-diiodoalkanes.[6] Equimolar amounts of substrates (ca. 0.08M solution in acetone) were exposed to the pressure of 10 kbar for 20h at 25°C, in the apparatus described earlier.[7] In all cases the white precipitate of quaternary salt was observed.



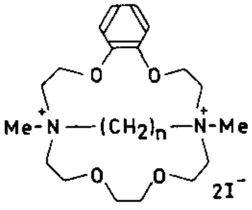
		Yield
1:	n=3	90%
2:	n=4	86%
3:	n=5	72%
4:	n=6	70%
5:	n=8	59%



		Yield
6:	n=3	91%
7:	n=4	96%
8:	n=5	89%
9:	n=6	93%
10:	n=8	58%



		Yield
11:	n=3	100%
12:	n=4	97%
13:	n=5	76%
14:	n=6	63%
15:	n=8	58%
16:	n=10	56%



		Yield
17:	n=3	87%
18:	n=4	89%
19:	n=5	91%
20:	n=6	92%
21:	n=8	54%
22:	n=10	55%

The bis-quaternary salts were demethylated with triphenylphosphine in boiling DMF[8] to give the cryptands with aliphatic bridging units.[9] The very high yield and selectivity of the reactions presented here makes this method very attractive for the synthesis of modified cryptands. However, the yield of double-quaternization reactions depends significantly on the bridging unit length, therefore the method presented herein possesses a practical value for the aliphatic bridges having up to six methylene groups.

ACKNOWLEDGEMENTS

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2. M.Pietraszkiewicz, P.Sałański, and J.Jurczak, Tetrahedron, 40, 2971 (1984).
3. M.Pietraszkiewicz, P.Sałański, and J.Jurczak, J.Chem.Soc.,Chem.Commun., 1184 (1983).
4. (12)-N_2O_2 was prepared from N-p-toluenesulphonyl-N-benzyl-1,7-diaza-4,10-dioxacyclododecane by detosylation with $LiAlH_4$, removal of benzyl group by hydrogenation on Pd/C, and methylation with HCO_2H/HCHO.
5. Other diazacoronands were prepared by routine methods, for example: L.C.Hodgkinson, M.R.Johnson, S.J.Leigh, N.Spencer, I.O.Sutherland, and R.F.Newton, J.Chem.Soc.,Perkin I, 2193 (1979).
6. α,ω-Diiodoalkanes were obtained in Filkenstein method with respective α,ω-dichloroalkanes and sodium iodide in boiling acetone, see: C.S.Gibson and J.D.A. Johnson, J.Am.Chem.Soc., 52, 2525 (1930).
7. J.Jurczak, Bull.Chem.Soc.Jpn, 52, 3438 (1979).
8. Tse-Lok Ho, Synth.Commun., 3, 99 (1973).
9. Typically, compound 8 was demethylated with triphenylphosphine in boiling DMF for 5h to give [2.1.C_5]cryptand (80% yield). MS (17 eV) M^+ 286(2); ^{1}H NMR, $CDCl_3$, δ (ppm): 3.9-3.4 (m,12H,OCH_2), 2.9-2.4 (m,12H,NCH_2), 1.8-1.4 (m,6H,C-CH_2-C).

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