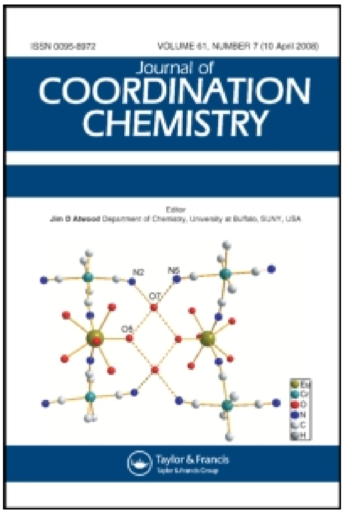
This article was downloaded by:
On: *23 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

High Pressure Approach to the Synthesis of Diazacoronands and Cryptands

Janusz Jurczak[a]; Ryszard Ostaszewski[a]
[a] Institute of Organic Chemistry, Polish Academy of Sciences, Warszawa, Poland

To cite this Article Jurczak, Janusz and Ostaszewski, Ryszard(1992) 'High Pressure Approach to the Synthesis of Diazacoronands and Cryptands', Journal of Coordination Chemistry, 27: 1, 201 — 214
To link to this Article: DOI: 10.1080/00958979209407952
URL: http://dx.doi.org/10.1080/00958979209407952

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Coord. Chem. 1992, Vol. 27, pp. 201–214
Reprints available directly from the publisher
Photocopying permitted by license only

HIGH PRESSURE APPROACH TO THE SYNTHESIS OF DIAZACORONANDS AND CRYPTANDS

JANUSZ JURCZAK* and RYSZARD OSTASZEWSKI

Institute of Organic Chemistry, Polish Academy of Sciences, 01-224 Warszawa, Poland

Application of the high-pressure technique for the synthesis of various types of molecular receptors is presented. Several aspects of this technique are discussed in the context of its further development.

INTRODUCTION

There has been growing interest in macrocyclic molecular receptors since their discovery by Pedersen.[1] The main feature of these compounds is their complexing behaviour. It was soon recognized that they form stable complexes with a wide range of species: inorganic and organic cations, uncharged molecules, C–H acids, *etc.* Therefore, studies aimed at a rational design and synthesis of more elaborated macrocyclic structures with desired complexing properties are well advanced.

Introduction of nitrogen into macrocyclic polyethers created a new class of host molecules. Diazacoronands and cryptands play a prominent role in molecular architecture; one may note that the incorporation of nitrogen-pivoting atoms into receptor molecules offers an enormous number of possible structures. Fusion of specific binding sites with a particular functional group may lead to highly sophisticated structures capable of acting as selective complexers for metal ions, and—moreover—as molecular catalysts, co-catalysts, ion carriers, enzyme mimics, metallo-enzyme active site models, allosteric systems, photoactive molecular devices, *etc.*

The number of practical applications of molecular devices is quite impressive: analytical chemistry (separation of enantiomers[2] and isotopes[3]), polymer chemistry,[4] ion-selective sensors,[5] photochemical splitting of water,[6] cancer therapy,[7] immunology,[8] *etc.*

Tailored synthesis of polyfunctional diazacoronands and cryptands is the subject of this review.

SYNTHESIS OF DIAZACORONANDS

A very versatile procedure for the synthesis of diazacoronands and cryptands commonly called "high-dilution method"—was developed by Lehn *et al.*[9] This method is based on the condensation of α,ω-diamine with an appropriate dicarboxylic acid dichloride in a large volume of inert solvent.[10] The reactants are added separately and at the same rate, preferably using a syringe pump, to the vigorously stirred solvent. This method has, however, some important drawbacks; for example, even a slight contamination of the reactants and solvent markedly deteriorates the yield.

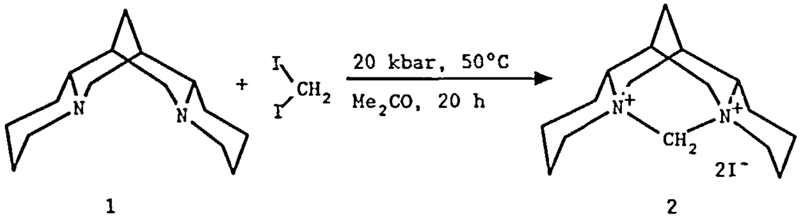
In parallel with the high-dilution technique, another alternative approach was developed; it consists of condensation of α,ω-diamines with α,ω-dihalogeno compounds in the presence of alkali metal carbonates. Kulstad and Malmsten[11] demonstrated that the nature of the metal ion substantially influences the yield of macrocyclization; therefore, the "template effect" is the driving force of these reactions. A remarkable revival and development of alkali metal ion-promoted methods were noted recently, particularly in the field of compounds comprising heterobiarylic subunits, despite the fact that the removal of metal ion may create great obstacles in obtainment of metal-free diazacoronands and cryptands.

There are also other methods which cannot be classified as high-dilution or ion-template procedures, but their practical applications are rather limited. One of these methods was based on the double-quaternization reaction proposed by Newkome *et al.*[12] We decided to reinvestigate this approach, but using the high-pressure technique.

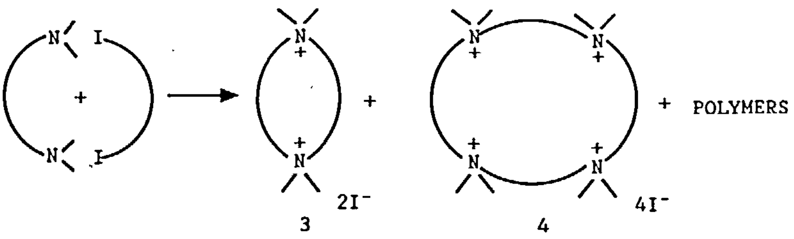
The formatin of charged products from neutral substrates usually results in increased solvation. Thus, when the charge develops along the reaction coordinate the activation volume is often large and negative. For example, the formation of quaternary ammonium salt from a tertiary amine and alkylating agent (the Menshutkin reaction) has an activation volume within the range of −20 to −50 cm^3/mol.[13] Such reactions should be dramatically accelerated by pressure. High pressure not only accelerates the Menshutkin reaction, but also influences the reaction selectivity, as shown in Scheme 1 for double quaternization of the alkaloid spartein (**1**). Double quaternization of **1** with methylene iodide under high pressure furnished the corresponding bis-quaternary salt **2** in a quantitative yield.[14]

The results presented above inspired further investigations involving the application of the Menshutkin reaction in the synthesis of N,N′-dimethyl diazacoronands. The general synthetic concept is presented in Scheme 2.

It was expected that an N,N′-tetramethyl α,ω-diamine would react under high-pressure conditions with an α,ω-diiodo compound to form the macrocyclic



Scheme 1



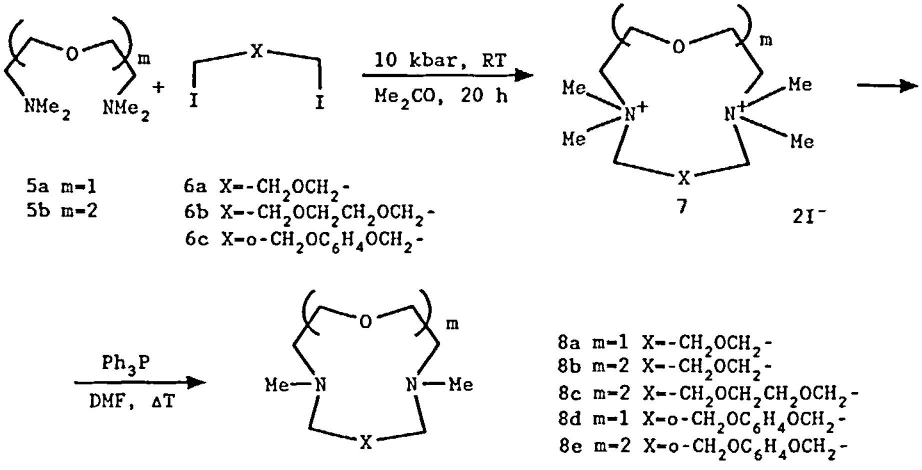
Scheme 2

quaternary salts 3 and 4. Indeed, the reaction of tertiary amines of type 5 with diiodo derivatives 6 under a 10 kbar pressure afforded the desired crystalline bis-quaternary salts of the type 7 in a quantitative yield (Scheme 3).[15]

Subsequent demethylation of compounds 7 by treatment with triphenylphosphine in boiling dimethylformamide gave N,N'-dimethyl diazacoronands of general structure 8 in a good yield (Table 1).[15]

The influence of changes in pressure on the yield of the double-quaternization reaction was also studied.[16] Under atmospheric pressure the reaction failed to give the bis-quaternary salt even when the reaction time was prolonged to several days. Under moderate pressure (2–4 kbar) the yields were very poor, and the bis-quaternary salt was accompanied by polymeric materials. Upon application of much high pressure (8–10 kbar), the crystalline product was almost free from polymers.

These findings indicate that this reaction is stepwise and consists of two pressure-accelerated processes: the first intermolecular quaternization is slow, and the second intramolecular quaternization is fast. The linear conformation of the quaternary salt formed at the first stage is in an equilibrium with the quasi-cyclic

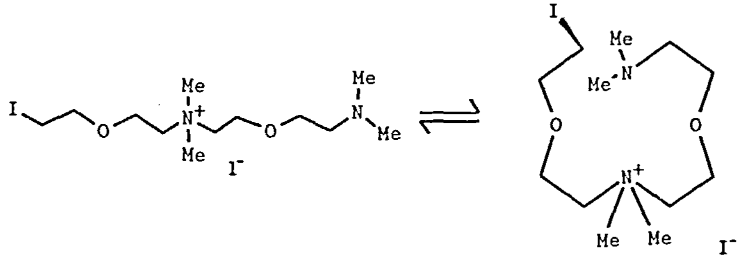


Scheme 3

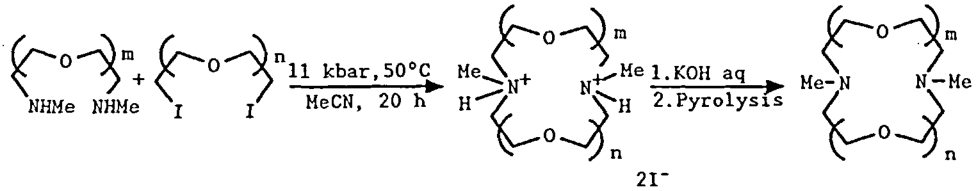
TABLE I

Yields of bis-quarternary salts obtained from N,N'-tetramethyl α,ω-diamines and α,ω-diiodoethers.

Diamine	Diiodo compound	Macrocyclization yield	Demethylation yield	Product obtained
5a	**6a**	99%	81%	**8a**
5b	**6a**	95%	74%	**8b**
5a	**6b**	95%	—	**8b**
5b	**6b**	97%	59%	**8c**
5a	**6c**	96%	70%	**8d**
5b	**6c**	99%	64%	**8e**



Scheme 4



9a m=1
9b m=2

6a n=1
6b n=2

10a m=n=1
10b m=1 n=2
10c m=n=2

8

Scheme 5

conformation which should be favoured by high pressure and could easily react intramolecularly (Scheme 4).[17]

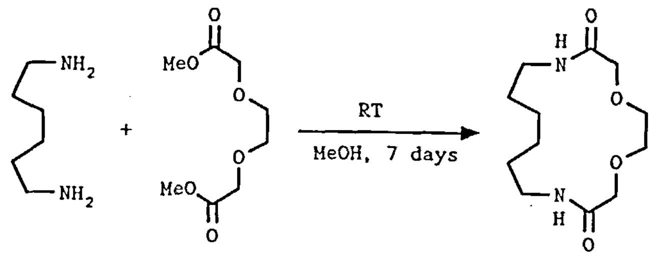
On the other hand, the linear conformation may react with a second molecule of the compound **6a** to form the linear bis-quaternary salt. However, under increasingly high pressure, the reaction leading to linear polymers should be disfavoured because of the increasing viscosity that would prevent intermolecular collisions.

The above-presented findings demonstrate that the high-pressure double-quaternization reaction, carried out in aprotic solvents, is characterized by a complex mechanism in which—apart from molecular processes like conformational changes of substrates and/or intermediates—some macroscopic processes, *e.g.* changes in viscosity of the reaction media, play a prominent role.[17]

N,N'-Dimethyl diazacoronands were also obtained by a double-alkylation reaction involving secondary α,ω-diamines (**9**) and typical α,ω-diiodo compounds (**6**). For example, the secondary amines of the type **9** reacted with diiodo ethers **6** under high-pressure conditions (acetonitrile as solvent, 11 kbar, 50°C, 20 h) to give the respective salts of the type **10** in a very good yield (Scheme 5).[18]

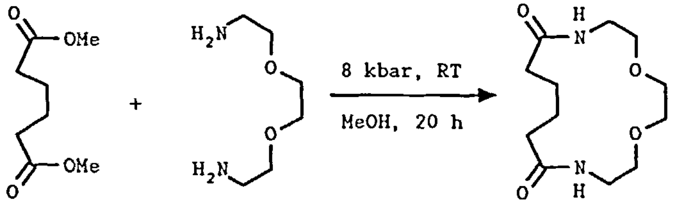
Neutralization of salts **10** by potassium hydroxide, followed by pyrolysis of obtained crown complex formed, lead to the desired N,N'-dimethyl diazacoronand of the type **8** in a good overall yield.[18]

Another useful method for the synthesis of diazacoronands is the reaction between primary α,ω-diamines and dimethyl ester of α,ω-diacids. It was found that 1,6-diaminohexane (**11**) reacts with 1 equivalent of diester **12** under ambient conditions (methanol as a solvent, 25°C, 7 days [reagents] 0.1 M) to give the respective macrocyclic diamide **13** in 38% yield (Scheme 6).[19]



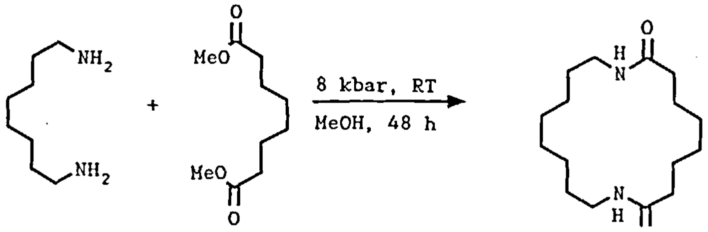
11 12 13

Scheme 6



14 15 16

Scheme 7



17 18 19

Scheme 8

Several attempts were made in order to prepare a similar amide **16** under the same conditions, starting from adipic acid dimethyl ester (**14**) and diamine **15**. Unfortunately, the reaction failed, even when a reaction mixture was heated at reflux for several days. Finally, the reaction was forced by application of high pressure to afford the desired macrocyclic amide **16** in 27% yield (Scheme 7).[19]

The high-pressure reaction of 1,8-diaminooctane (**17**) with dimethyl ester of suberic acid (**18**) afforded the macrocyclic amide **19** in 15% yield (Scheme 8).[19]

It is noteworthy that efficiency of the synthesis of macrocycles *via* amide bond formation depends on the structure of substrates used. Thus, when both, α,ω-diamine and α,ω-diester have ether functionalities, the reaction can be carried out at atmospheric pressure. Even the presence of the ether group only in α,ω-diester is sufficient for realization of this reaction under ambient conditions. In all other cases application of the high-pressure technique is necessary.[19]

SYNTHESIS OF CRYPTANDS

A representative example of the double-quaternization reaction for the synthesis of simple cryptands is illustrated in Scheme 9.[20] An equimolar mixture of N,N'-dimethyl diazacoronand **8a** and bis(2-iodoethyl) ether (**6a**), dissolved in acetone, was exposed to 10 kbar pressure at room temperature for 20 hours. During the reaction the bis-quaternary salt precipitated quantitatively.

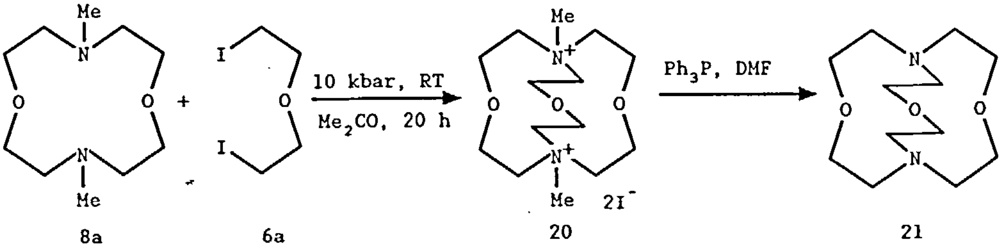
An additional experiment was performed using two equivalents of bis(2-iodoethyl) ether (**6a**) under exactly the same conditions; the product was identical with the former one. The conclusion is that under these conditions the transition state leading to the cryptand skeleton is highly favoured over the formation of linear polymers. Finally, [1.1.1] cryptand (**21**) was obtained by treatment of the bis-quaternary salt **20** with triphenylphospine in boiling dimethylformamide in 59% yield.[20]

The scope and utility of this method were demonstrated using series of N,N'-dimethyl diazacoronands. Four N,N'-dimethyl diazacoronands were selected as model compounds: $Me_2[12]\text{-}N_2O_2$ (**8a**), $Me_2[15]\text{-}N_2O_3$ (**8b**), $Me_2[18]\text{-}N_2O_4$ (**8c**) and $Me_2B[18]\text{-}N_2O_4$ (**8e**). Bis(2-iodoethyl) ether (**6a**) and 1,2-bis(2-iodethoxy)ethane (**6b**) served as bridging components.

All double-quaternizatin reactions were performed under the same conditions, *e.g.* in a *ca.* 0.08 M solution in acetone, at ambient temperature, for 20 hours, at 10 kbar pressure was maintained during the reaction. As in the case shown in Scheme 9, without exception, colourless crystalline solids precipitated in the reaction cell. After simple work-up (washing with hexane and drying under vacuum) analytically pure bis-quaternary salts were obtained. Demethylation was carried out by heating the respective salt with triphenylphosphine in boiling dimethylformamide, followed by column chromatography on alumina. The yield obtained for the double-quaternization and demethylation reactions are listed in Table 2.[20]

These encouragingly good results stimulated more systematic studies in this field. First of all, it was interesting to test the influence of the length of the bridging component on the yield of the double-quaternization reaction. The above-mentioned N,N'-dimethyl dizacoronands were applied, and several α,ω-diiodoalkanes (from C_3 to C_{10} except for C_7 and C_9) were used as bridging components. A typical example is provided in Scheme 10.[21]

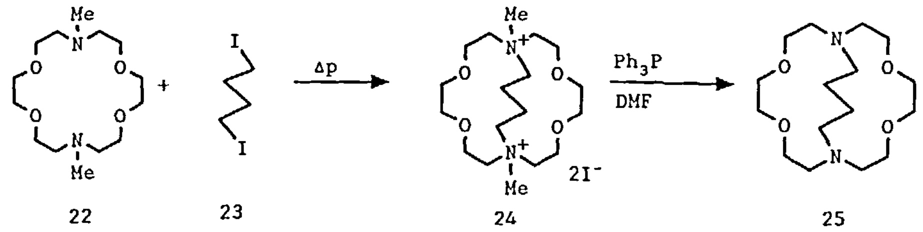
Diazacoronand $Me_2[18]\text{-}N_2O_4$ (**22**) reacted with 1,4-diiodobutane (**23**) under high-pressure conditions to give the bis-quaternary salt **24** as a precipitate which was demethylated in the usual manner to afford [2.2.C_4] cryptand **25** in 97% yield. All reactions were carried out under the same conditions, *e.g.* in a *ca.* 0.08 M solution



Scheme 9

TABLE II
Synthesis of simple cryptands.

Diazocoronand	Diiodoether	Resulting cryptand	Quaternization yield	Demethylation yield
Me$_2$[12]-N$_2$O$_4$	**6a**	[1.1.1]	95%	59%
Me$_2$[12]-N$_2$O$_4$	**6b**	[2.1.1]	81%	51%
Me$_2$[15]-N$_2$O$_3$	**6a**	[2.1.1]	91%	72%
Me$_2$[15]-N$_2$O$_3$	**6b**	[2.2.1]	82%	62%
Me$_2$[18]-N$_2$O$_4$	**6a**	[2.2.1]	91%	80%
Me$_2$[18]-N$_2$O$_4$	**6b**	[2.2.2]	94%	65%
Me$_2$B[18]-N$_2$O$_4$	**6a**	[2$_B$.2.1]	100%	87%
Me$_2$B[18]-N$_2$O$_4$	**6b**	[2$_B$.2.2]	100%	71%



Scheme 10

in acetone, at ambient temperature, for 20 hours, and under 10 kbar pressure. In this way 22 different bis-quaternary salts were obtained. The yields are presented in Table 3.[21]

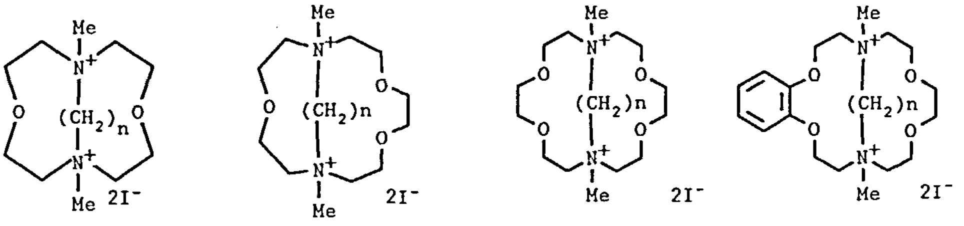
It is clear that yields drop substantially when longer bridging components are used. This means that usefulness of the high-pressure procedure is somewhat limited to bridging compounds longer than those comparable in size to 10-methylene units.

In order to gain more knowledge about the nature of the double-quaternization reactions, several additional experiments were performed. The influence of solvent was studied for the reaction of Me$_2$B[18]-N$_2$O$_4$ (**8e**) with bis(2-iodoethyl) ether (**6a**) in a 1:1 ratio. Six different aprotic solvents were chosen as the reaction medium. All reactions were performed under a 10 kbar pressure at 30°C. The yields of the bis-quaternary salts are collected in Table 4.[22]

In all cases, except for dimethylformamide and acetonitrile, white crystalline salts precipitated during the reaction. All reactions were completed after 20 hours. The yields differed substantially after 4 hours, thus indicating that high-pressure double quaternization was greatly accelerated in polar solvents like dimethylformamide or acetonitrile. From a practical point of view, it would be desirable to perform a double-quaternization reaction in dimethylformamide within a short time and to demethylate directly the resulting bis-quaternary salt, since dimethylformamide is a good reaction medium for the following demethylation reaction.[22]

The influence of the leaving group was demonstrated in a set of experiments. Again, Me$_2$B[18]-N$_2$O$_4$ (**8e**) was the model compound reacting with four bridging

TABLE III
Yields of bis-quaternary salts obtained from N,N'-dimethyl diazocoronands and α,ω-diiodoalkanes.



n	Yield	n	Yield	n	Yield	n	Yield
3	91%	3	90%	3	100%	3	87%
4	86%	4	96%	4	97%	4	89%
5	72%	5	89%	5	76%	5	91%
6	70%	6	93%	6	63%	6	92%
8	59%	8	58%	8	58%	8	54%
				10	56%	10	55%

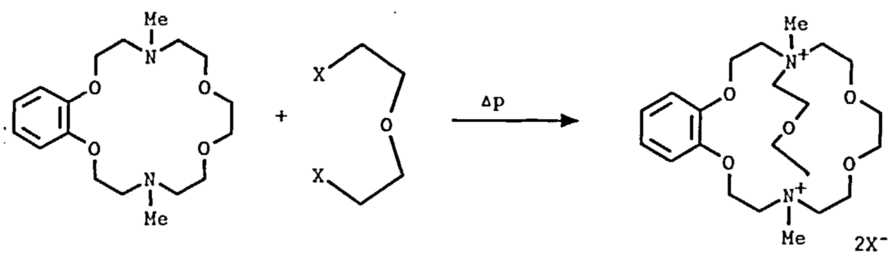
TABLE IV
The influence of solvent on double quaternization of $Me_2B[18]$-N_2O_4 (**8e**) with bis(2-iodoethyl) ether (**6a**).

	Reaction time/yield	
Solvent	20 h	4 h
Dimethylformamide	100%	100%
Acetonitrile	100%	95%
Acetone	100%	65%
Ethyl acetate	100%	53%
Diethyl ether	100%	30%
Toluene	100%	44%

components **6a** and **26b–d** in acetone and acetonitrile under standard conditions: 10 kbar, 30°C, 20 h (Scheme 11). The yields of the respective bis-quaternary salts are listed in Table 5.[22]

It is clear that the results are in good agreement with the well known order of reactivity I > Br > Tos ≫ Cl. Evidently, bis(2-iodoethyl) ether (**6a**) is the best bridging component. It not only affords the best yield of a bis-quaternary salt, but moreover diiodide **27a** can be demethylated easier than the corresponding dibromide **27b**, dichloride **27c** or bis-tosylate **27d**. Furthermore, the bis-quaternary diiodides are nonhygroscopic solids which allow all analytical treatment without problems.[22]

Simple cryptands were also obtained in a double-alkylation reaction involving diazacoronands with secondary-amino functionalities and diiodo bridging components.[23] For example, [18]-N_2O_4 (**28**) was reacted with bis(2-iodoethyl) ether (**6a**)

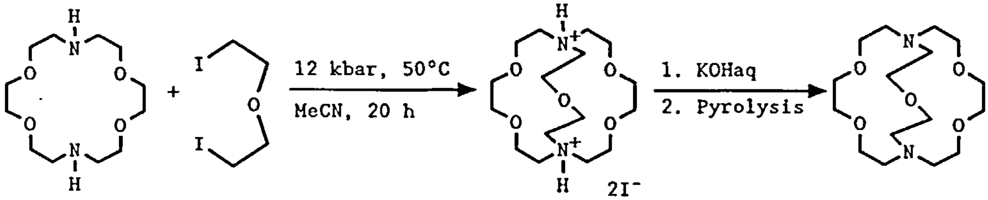


8e 6a X=I 26c X=Cl 26b X=Br 26d X=OTs 27

Scheme 11

TABLE V
The influence of leaving groups on the double-quaternization reaction of **8e** with compounds **6a** and **26b–d**.

Leaving group X	Yield of the double-quaternization reaction in	
	Acetone	Acetonitrile
I	100%	100%
Br	85%	100%
Cl	8%	52%
OTs	70%	100%



28 6a 29 30

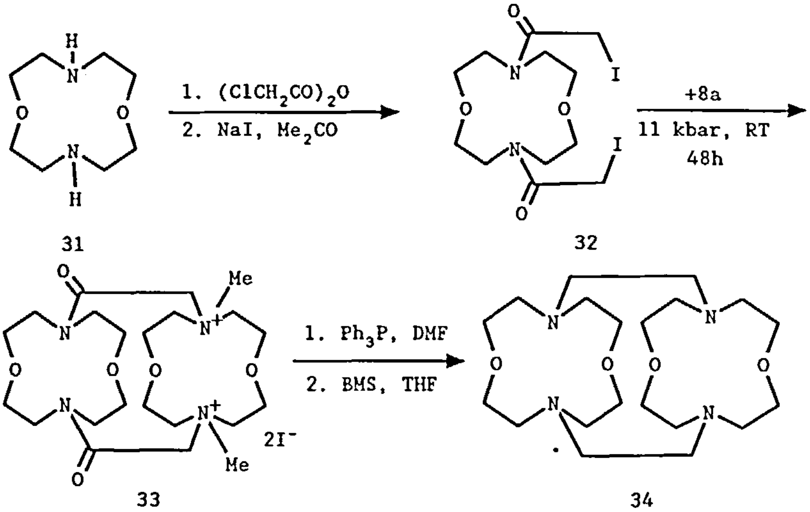
Scheme 12

under high-pressure conditions (acetonitrile as a solvent, 12 kbar, 50°C, 20 h) to afford in a quantitative yield the respective salt **29**. The latter compound was then neutralized with potassium hydroxide to form a cryptate which was immediately decomposed thermally under vacuum, giving the desired [2.2.1] cryptand (**30**) as shown in Scheme 12. Under similar conditions, three other cryptands were prepared. The results are presented in Table 6.[23]

The above procedure requires application of higher pressure, as compared with the double-quaternization reaction, but in some instances it may be useful for the solving some particular synthetic problems.

TABLE VI
Synthesis of cryptands via alkylation of diazocoronands.

Diazacoronand	Diiodo compound	Alkylation yield	Cryptand obtained	Overall yield
[12]-N_2O_2	6a	79%	[1.1.1]	65%
[12]-N_2O_2	6b	92%	[2.1.1]	73%
[15]-N_2O_3	6a	96%	[2.1.1]	78%
[15]-N_2O_3	6b	92%	[2.2.1]	83%
[18]-N_2O_4	6a	89%	[2.2.1]	80%
[18]-N_2O_4	6b	92%	[2.2.2]	65%

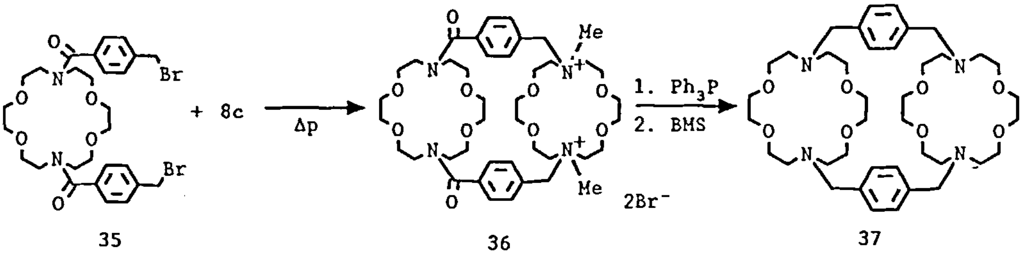


Scheme 13

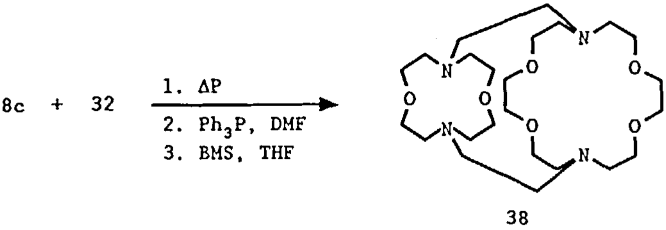
Undoubtedly, cryptands are a very promising class of macrobicyclic and macropolycyclic molecular receptors. The number of their possible structures is practically unlimited and depends on the researcher's imagination and creativity. The high-pressure metod offers excellent possibilities with respect to the design and synthesis of more elaborated polyfunctionalized macropolycyclic cryptands. A convenient high-pressure approach to the synthesis of tricyclic cryptand-related compounds is exemplified in Scheme 13.[24]

Alkylation of diazacoronand **31** using chloroacetyl anhydride, followed by exchange of chlorine by iodine, afforded the respective bis-amide **32** in 44% overall yield. The high-pressure double-quaternization reaction of diiodo compound **32** with N,N'-dimethyl diazacoronand **8a** furnished the bis-quaternary salt **33** in 62% yield. Final demethylation, followed by reduction of amide functionalities, afforded the desired tricyclic cryptand **34** in 14% yield.

In the same manner another symmetric tricyclic cryptand **37** has been synthesized in 18% overall yield, starting from the diazacoronand derivative **35** and N,N'-dimethyl diazacoronand **8c**, as shown in Scheme 14.[24]



Scheme 14



Scheme 15

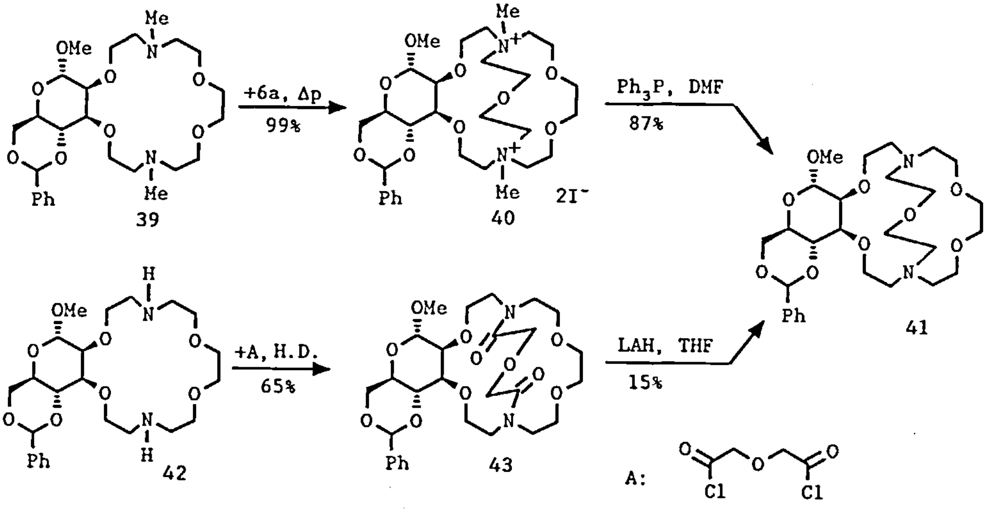
Another example characteristic of this approach is presented in Scheme 15. Starting from $Me_2[18]-N_2O_4$ (**8c**) and the N,N'-disubstituted derivative **32** of $[12-N_2O_2$, the nonsymmetric tricyclic cryptand **38** was obtained in *ca.* 20% overall yield.[24]

All the above examples of application of the high-pressure technique illustrate the great advantages of this method for the tricyclic cryptand synthesis.

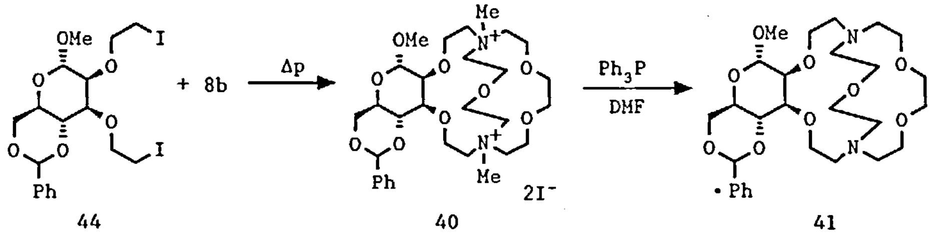
SYNTHESIS OF CHIRAL CRYPTANDS

All chiral crown ethers incorporating one carbohydrate subunit possess two diastereotopic faces of the macrocyclic ring. They are able to form diastereotopic complexes with primary alkylammonium cations. These properties may be followed by the fusion of the cryptand framework and the chiral unit. In our first synthesis of chiral cryptands, N,N'-dimethyl diazacoronands incorporating suitably protected D-manno-, D-gluco-, and D-galacto-pyranosidic subunits[25] served as substrates in the double-quaternization reactions.[26] The double quaternization of these diazacoronands with bis(2-iodoethyl) ether (**6a**) afforded in quantitative yields the corresponding bis-quaternary salts. Demethylation was followed in the usual manner to give the desired chiral cryptands. The comparison of two approaches—high-pressure double quaternization and the high-dilution method—to the synthesis of chiral [2.2.1] cryptand incorporating D-manno-pyranosidic unit (**41**) is shown in Scheme 16.[26]

The above-presented methodology requires the use as a substrate of chiral N,N'-dimethyl diazacoronands whose preparation is difficult and not very efficient.



Scheme 16



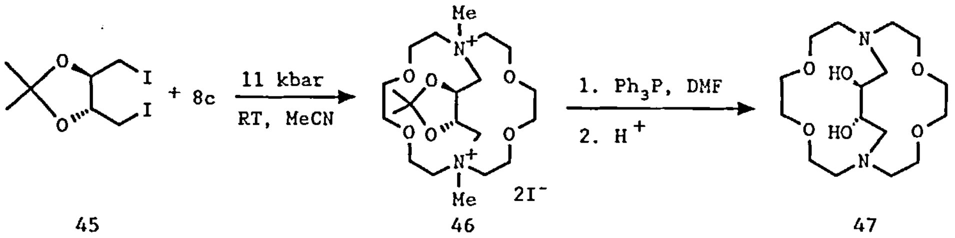
Scheme 17

On these grounds we resolved to change the strategy of the chiral cryptand synthesis. According to this new approach, the substrates consist of achiral N,N′-dimethyl diazacoronands and chiral bridging components. An example of the high-pressure synthesis of the chiral cryptand **41** by this method is illustrated in Scheme 17.[27]

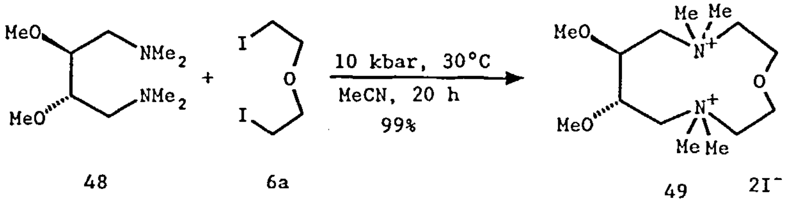
The high-pressure reaction of N,N′-dimethyl-1, 7-diaza-15-crown-5 (**8b**) with a properly protected, readily available D-mannopyranose derivative **44** provided the desired chiral [2.2.1] cryptand **41** in a very good overall yield.

Another example confirming the validity of the strategy adapted involves the synthesis of a chiral cryptand **47** (Scheme 18). The double-quaternization reaction of N,N′-dimethyl-1, 10-diaza-18-crown-6 (**8c**) with the chiral 1,4-diiodo compound **45** obtained from d-tartaric acid, afforded under high-pressure conditions, the desired cryptand framework **46** in a very good yield.[27]

In the same manner several chiral diazacoronands were prepared. For example, the chiral diamine **48** derived from D-tartaric acid was reacted with bis(2-iodoethyl) ether (**6a**) under a 10 kbar pressure to afford the chiral bis-quaternary salt **49** in a quantitative yield (Scheme 19).[28]



Scheme 18



Scheme 19

Summing up, it can be stated that the high-pressure approach adds to the versatility of the synthesis of chiral diazacoronands and cryptands with—moreover—its marked simplification.

CONCLUSIONS

The above-presented high-pressure methods seem to be important contribution to modern synthetic chemistry. The essential points are that the double-quaternization reaction afford high yields and analytical-purity products. Secondly, the easy and mild work-up of the bis-quaternary salts greatly extends the scope of the potential applications for the preparation of much more elaborated, polyfunctional structures including chiral compounds. The high-pressure double-alkylation and double-amidation reactions are also very promising in the synthesis of diazacoronands and cryptands.

REFERENCES

1. C.J. Pedersen, *J. Am. Chem. Soc.*, **89**, 7017 (1967).
2. G.D.Y. Soagh and D.J. Cram, *J. Am. Chem. Soc.*, **101**, 3035 (1979); L.R. Sousa, G.D.Y. Soagh, D.H. Hofman and D.J. Cram, *J. Am. Chem. Soc.*, **100**, 4569 (1978); T. Shinbo, T. Yamaguchi, K. Nishimura and M. Sugiura, *J. Chromatogr.*, **405**, 145 (1987).
3. K.G. Heumann, *Top. Curr. Chem.*, **127**, 77 (1985).
4. P. Sigwalt and S. Boileau, *J. Polymer Sci.: Polymer Symp.*, **62**, 51 (1978); P. Hemery, W. Warzelhan and S. Boileau, *Polymer*, **21**, 77 (1980).
5. S.J. Pace, *Sensors and Actuators*, **1**, 475 (1981).

6. M. Kirch, J.M. Lehn and J.P. Sauvage, *Helv. Chim. Acta*, **62**, 449, 1345 (1977); J.M. Lehn and J.P. Sauvage, *Nouv, J. Chem.*, **1**, 449 (1977); J.M. Lehn, J.P. Sauvage and R. Ziessel, *Nouv, J. Chem.*, **4**, 623 (1980).
7. M.K. Moi, M. Yanuck, S.V. Desphande, H. Hope, S.J. De Wardo and C.F. Meares, *Inorg. Chem.*, **26**, 3458 (1987).
8. B. Alpha, V. Balzani, J.M. Lehn, S. Parathoner and N. Sabatini, *Angew. Chem. Int. Ed. Engl.*, **26**, 1266 (1987).
9. B. Dietrich, J.M. Lehn and J.P. Sauvage, *Tetrahedron Lett.*, 2885 (1969); *Tetrahedron*, **29**, 1647 (1973).
10. A.H. Alberts, R. Annunziata and J.M. Lehn, *J. Am. Chem. Soc.*, **99**, 8502 (1977).
11. S. Kulstad and L.A. Malmsten, *Acta Chim. Scand.*, **B 33**, 469 (1970); *Tetrahedron*, **36**, 521 (1980).
12. G.R. Newkome, V.K. Majestic and F.R. Fronczek, *Tetrahedron Lett.*, **22** 3039 (1981).
13. G. Jenner, *Angew. Chem. Int. Ed. Engl.*, **14**, 137 (1975).
14. J. Jurczak and M. Pietraszkiewicz, *Top. Curr. Chem.*, **130**, 183 (1985).
15. J. Jurczak, R. Ostaszewski and P. Sałański, *J. Chem. Soc., Chem. Commun.*, 184 (1989).
16. R. Ostaszewski, Dissertation, *Institute of Organic Chemistry*, Warszawa (1988).
17. J. Jurczak, S. Kasprzyk, M. Mąkosza, R. Ostaszewski and P. Sałański, *High Press, Rese.*, **5**, 641 (1990).
18. J. Jurczak and R. Ostaszewski, *Synthetic Commun.*, **19**, 2175 (1989).
19. J. Jurczak, S. Kasprzyk, P. Sałański and T. Stankiewicz, to be published.
20. M. Pietraszkiewicz, P. Sałański and J. Jurczak, *Bull. Pol. Ac.: Chem.*, **33**, 433 (1985).
21. M. Pietraszkiewicz, P. Sałański and J. Jurczak, *Heterocycles*, **23**, 547 (1985).
22. M. Pietraszkiewicz, P. Sałański, R. Ostaszewski and J. Jurczak, *Heterocycles*, **24**, 1203 (1986).
23. J. Jurczak, R. Ostaszewski and P. Sałański, *Bull. Pol. Ac.: Chem.*, in press.
24. J. Jurczak and R. Ostaszewski, unpublished results.
25. M. Pietraszkiewicz and J. Jurczak, *J. Chem. Soc., Chem. Commun.*, 132 (1983).
26. M. Pietraszkiewicz, P. Sałański and J. Jurczak, *J. Chem. Soc., Chem. Commun.*, 1184 (1983); *Tetrahedron*, **40**, 2971 (1984); M. Pietraszkiewicz and J. Jurczak, *J. Carbohydr. Chem.*, **4**, 429 (1985).
27. R. Ostaszewski, U. Jacobsson and J. Jurczak, *Bull. Pol. Ac.: Chem.*, **37**, 347 (1989).
28. J. Jurczak and R. Ostaszewski, to be published.