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SYNTHESIS OF LARGE RING PROTON CRYPTATE
TRIDECALINO[2.2.2]CRYPTAND⊃2HI

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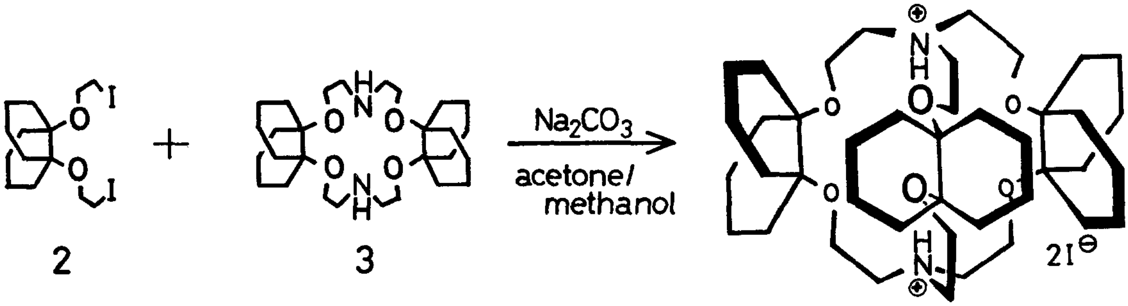
Summary. Condensation of 8,9:17,18-didecalino-4,13-diaza-18-crown-6 with 1,8-diiodo-4,5-decalino-3,6-dioxaoctane in the presence of sodium carbonate produced proton cryptate, tridecalino[2.2.2]cryptand⊃2HI.

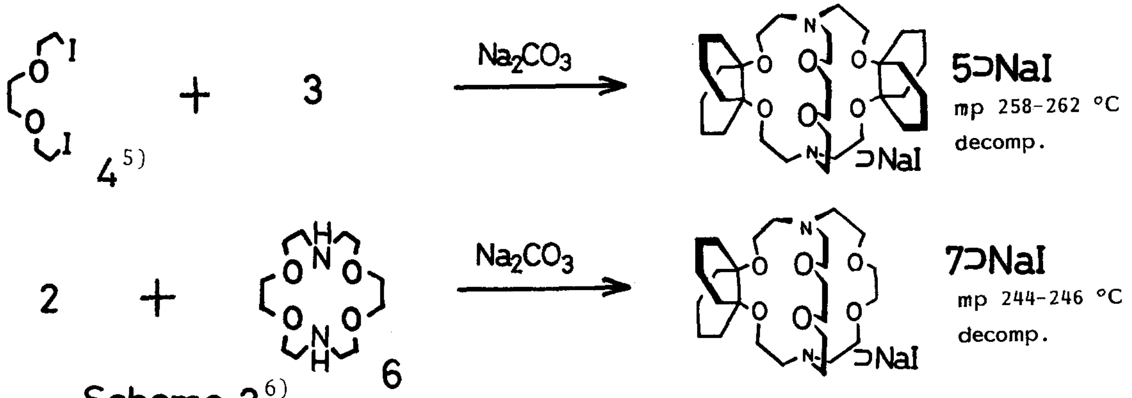
Although it has been reported that [1.1.1]cryptand having the rigid and small cavity forms the proton cryptate in which its inside proton is shielded strongly from the environment,[1] little is known about the proton cryptates in other ring systems. Based on the instructive information obtained from our studies on the embedding effect of the decalin walls,[2] we have designed a new type of spherical cryptand, tridecalino[2.2.2]cryptand (1), with the aid of CPK molecular model. This rigid molecule would form stable proton cryptates, because the configuration of the lone pairs on nitrogen atoms is fixed to endo-endo and the decalin moieties construct a spherical shell, by which the inside cavity is shielded from the attack of the outside large size anion and solvent. We now report on the formation of a large ring proton cryptate, tridecalino-[2.2.2]cryptand⊃2HI, under the basic reaction condition.

As expected, the reaction of 1,8-diiodo-4,5-decalino-3,6-dioxaoctane (2)[3] with 8,9:17,18-didecalino-4,13-diaza-18-crown-6 (3)[4] in acetone/methanol in the presence of sodium carbonate gave the diproton cryptate, 1⊃2HI, in 5% yield after recrystallization from methanol (mp 273-276 °C), as illustrated in Scheme



2 3 1⊃2HI

Scheme 1[6]



Scheme 2[6]

1.[6] The FAB-MS spectrum (m/z) showed the peak at 702 $(1+2H)^{2+}$. The ^1H NMR spectrum in $CDCl_3$ showed broad singlet at δ 10.4 ppm, indicating the existence of the N-H bonds. The anion exchange reaction of 1⊃2HI with $LiClO_4$ in H_2O/CH_2Cl_2 system produced 1⊃2$HClO_4$ in 95% yield (recrystallized from MeOH, mp 240-250 °C decomp.).

In the cases of more flexible and less-substituted [2.2.2]cryptand systems, on the other hand, sodium cryptates, 5⊃NaI and 7⊃NaI were obtained instead of the corresponding proton cryptates under the similar reaction conditions, as shown in scheme 2.[6] Three decalin moieties constructing the shell were required for the formation of isolable proton cryptate.

These results are explained as follows: The deprotonation of 1⊃2HI may be markedly depressed because endo-endo configuration of lone pairs would be preferable and the inside protone are shielded by the surrounding decalin shell from the attack of the outside carbonate anions. In the cases of less-substituted proton cryptates, 5⊃2HI and 7⊃2HI, formed under the reaction conditions, on the contrary, may be easily deprotonated by the attack of carbonate anions to give the free cryptands, which would form the sodium cryptates, 5⊃NaI and 7⊃NaI, with NaI. Interestingly, the N-H resonance in ^1H NMR spectrum of 1⊃2HI (δ 10.4 ppm) disappeared by the addition of D_2O, suggesting the smaller molecule D_2O than carbonate anion could penetrate the decalin shell.

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References and Notes

1) For example see: H. -J. Brugge, D. Carboo, K. von Deuten, A. Knochel, J. Kopf, and W. Dreissig, J. Am. Chem. Soc., 108, 107 (1986), and references cited therein.
2) For example see: K. Kobiro, M. Takahashi, S. Takada, Y. Odaira, and K. Kawasaki, Bull. Chem. Soc. Jpn., 58, 3635 (1985), and references cited therein.
3) 2 was prepared by chlorination of 4,5-didecalino-3,6-dioxaoctane-1,8-diol followed by halogen exchange reaction with NaI (oily, 77 %).
4) 3 was prepared by condensation of 2 and benzylamine in the presence of Na_2CO_3 followed by hydrogenolysis (mp 171-173 °C, 24 %).
5) V. J. Gatto and G. W. Gokel, J. Am. Chem. Soc., 106, 8240 (1985).
6) All new compounds gave satisfactory elemental analyses and spectral data.

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