

DIDECALINO-14-CROWN-4. HIGHLY LITHIUM ION SELECTIVE EXTRACTANT

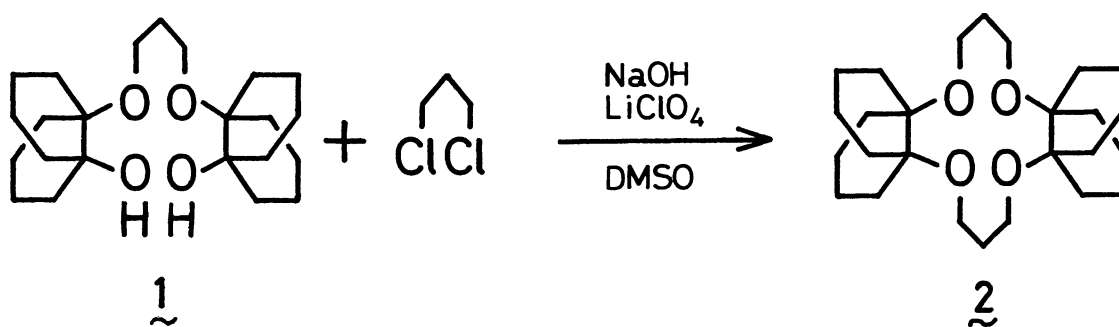
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Didecalino-14-crown-4 has been synthesized and found to have the conspicuous extractability as well as selectivity for lithium ion.

Increasing attention has been paid on lithium ion selective complexing agent.¹⁾ But little is known about the organic host molecules which are able to extract lithium ion from water with high selectivity and efficacy.^{1f)} Recently, we have synthesized cylindrical crown ether, tridecalino-18-crown-6, which showed high complexing ability and selectivity for potassium ion owing to conspicuous embedding effect of the decalin walls.²⁾ In this connection, we have designed the highly lipophilic cylindrical crown ether with small cavity, didecalino-14-crown-4 (2), in expectation of lithium ion selective extractant. We now report on synthesis and alkali metal ion extractability of 2.

The title compound was synthesized in 5% yield (mp 179-180 °C, recrystallized from 1,2-dimethoxyethane) by the reaction of 1,2;8,9-didecalino-3,7-dioxanonane-1,9-diol (1)³⁾ and 1,3-dichloropropane in DMSO at 110 °C for 36 h using sodium hydroxide as a base and lithium perchlorate as a template,⁴⁾ as shown in Scheme 1.⁵⁾



Scheme 1.

In order to make clear the effect of decalin moieties on the extraction of alkali metal ion, solvent extractions were carried out in the water/dichloromethane system⁶⁾ as shown in Fig. 1. As expected, the title compound 2 shows high extractability toward lithium ion. Interestingly, 2 exhibits quantitative extrac-

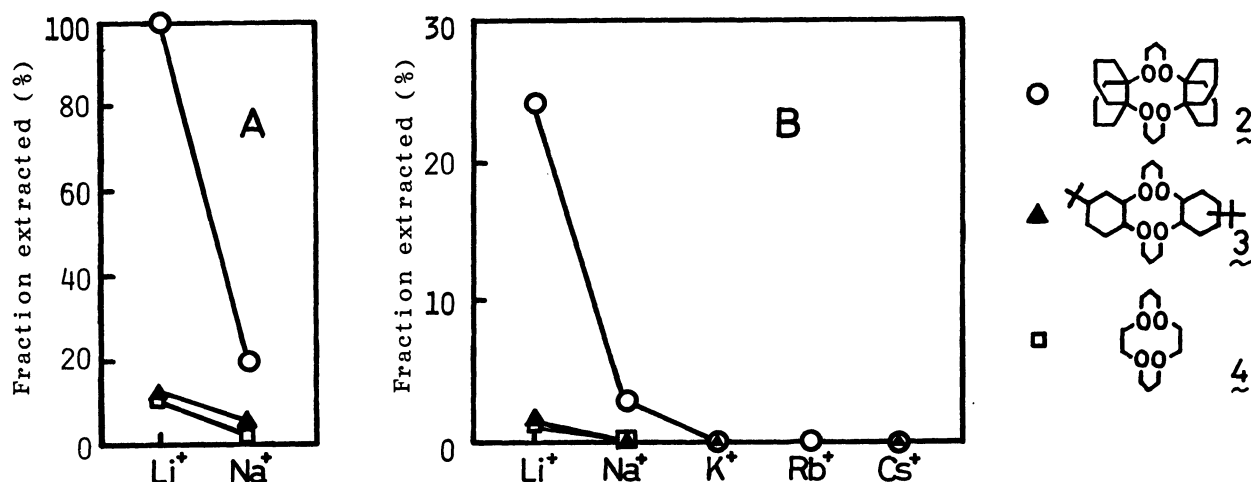


Fig. 1. Extraction of picrates into dichloromethane by crown ethers, 2, 3,⁶⁾ and 4.⁷⁾
 A: [picric acid]= 7.0×10^{-5} M, [crown ether]= 7.0×10^{-4} M, [metal hydroxyde]=0.1 M.
 B: [picric acid]=[crown ether]= 7.0×10^{-5} M, [metal hydroxide]=0.1 M.

tion toward lithium ion under the condition A using tenfold excess crown ether compared with lithium picrate. Even under the condition B using a 1/10 amount of crown ether (7.0×10^{-5} M) compared with that of the condition of A (7×10^{-4} M), 2 exhibits high extractability toward lithium ion, while the reference 14-crown-4 derivatives, 3 and 4, exhibit quite low one toward lithium ion. We infer that the high extractability of 2 for lithium ion is derived from the embedding effect and the increase of lipophilicity by incorporation of the decalin moieties.

Moreover, the Li⁺/Na⁺ selectivity of 2 is very high compared with those of the 3 and 4. Concerning this high selectivity of 2, we ascribe it to the fixation of four oxygens of the ether ring at the favorable position for complexation with lithium ion by introduction of the decalin moieties, as pointed out by CPK molecular model examination.

References

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- 14-Crown-4 (4) was prepared from 3,7-dioxanonane-1,9-diol ditosylate and 1,3-propanediol by the method similar to that described by Kimura^{1d)} in 19% yield (mp 25.0-27.0 °C).

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