

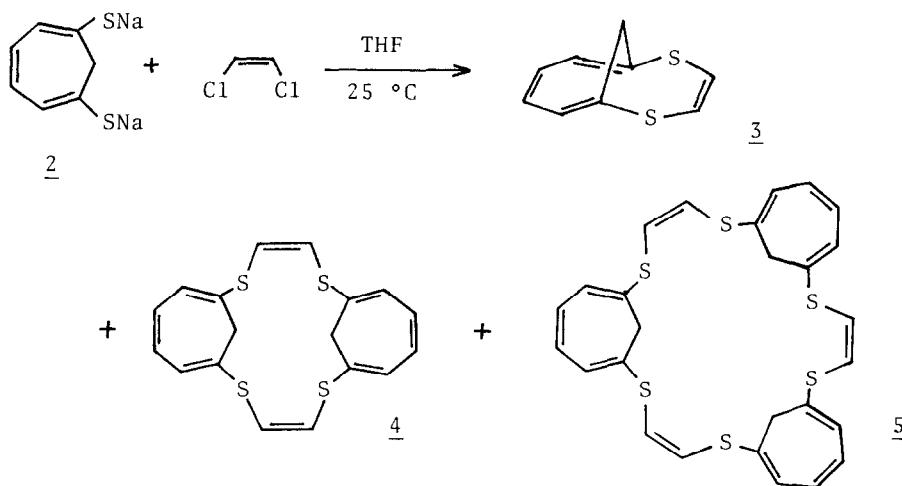
SYNTHESIS OF MACROCYCLIC COMPOUNDS CONTAINING
THE CYCLOHEPTATRIENE AND TROPYLIUM ION UNIT

Renji Okazaki,* Haruko Takai, Masaharu O-oka, and Naoki Inamoto
Department of Chemistry, Faculty of Science, The University of Tokyo,
Hongo, Bunkyo-ku, Tokyo 113, Japan

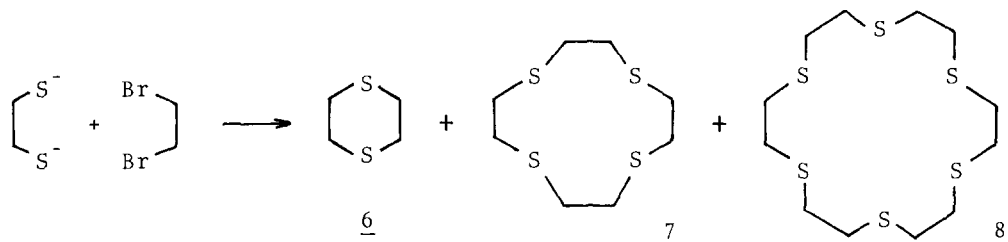
Summary Crown compounds containing the cycloheptatriene and tropylium ion unit were synthesized from 1,6-dithiocyanatocycloheptatriene

We recently described the photochemical synthesis of 1,6-dithiocyanatocycloheptatriene (1) from benzocyclopropene and thiocyanogen and its use as a starting material for some novel bridged sulfur heterocycles ¹ We report here the first synthesis of crown compounds having the cycloheptatriene and tropylium ion unit by using 1

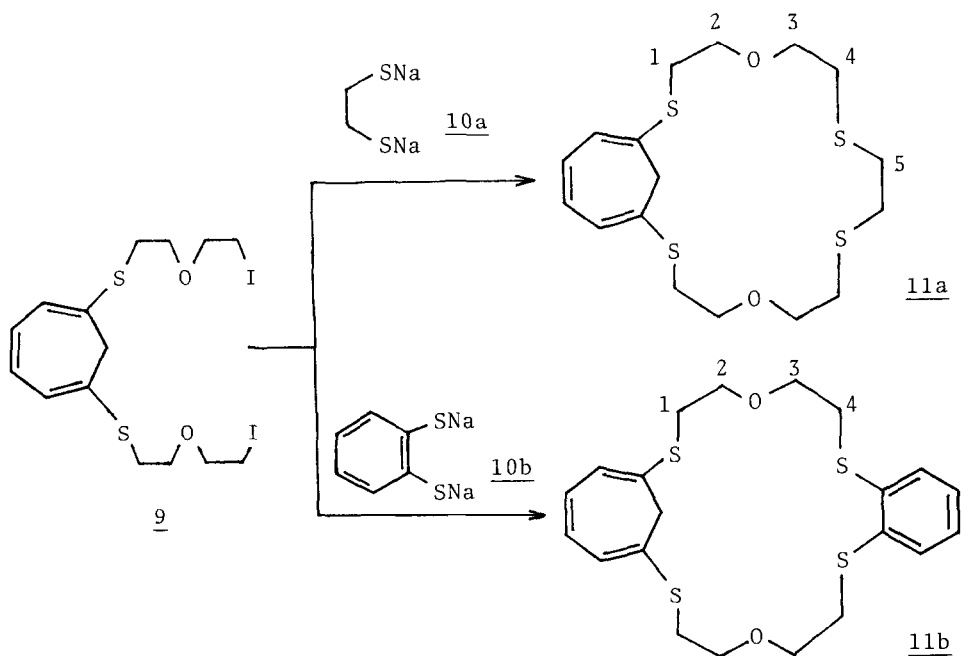
The reaction of dithiolate 2, obtained by reduction of 1 with sodium in liquid ammonia, with *cis*-dichloroethylene afforded 3 (11%), 4 (13%), and 5 (11%) ² The formation of 3, 4, and 5 in similar yields is noteworthy in view of the report that the ratios of the yields, 7/6 and 8/6, in the reaction of ethaned-



thiolate with 1,2-dibromoethane are very low (0.065 and 0.0069, respectively)³
 The *cis*-configuration of the halide used in the present reaction is probably responsible for the facile formation of the macrocycles 4 and 5

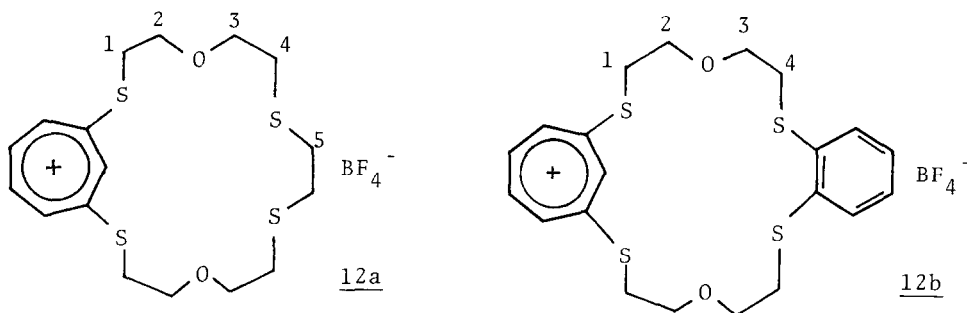


Two other sulfur containing macrocycles were also synthesized by the following reaction using diiodide 9⁴. The simultaneous addition of 1-butanol solutions of 9 and 10a,b⁵ into boiling 1-butanol under high dilution conditions afforded 11a,b (11a 42%, 11b 69%)²



In spite of recent intensive interest in the chemistry of crown compounds,⁶ there has been no report on crown compounds having the cycloheptatriene unit, and 5 and 11a,b are the first example of such type. These are interesting not only to know the relationship between the complexing ability and the structure but also to synthesize functionalized crown compounds to which much attention has recently been attracted.

Of further interest in these macrocycles is their conversion to macrocycles containing the tropylium ion unit. The reaction of 11a,b with trityl fluoroborate gave 12a,b in good yields (12a yellow crystals, 67%, 12b orange crystals, 84%)²



They are the first example of a crown compound containing a carbonium ion in its skeleton.

Although extensive studies have been done on the interaction of the macrocyclic ligand with a metal cation and an ammonium ion, there has been no report on that with a carbonium ion. The compound of type 12 is interesting in that it might provide an access to a study on the interaction of a carbonium ion with hetero atoms in the macrocyclic ring.

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REFERENCES AND NOTES

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2. The structure of these new compounds was established by spectral and analytical data 3 oil, NMR(CDCl₃) δ 2.66(d, J=12Hz, 1H, CH₂ syn to the triene), 3.92(dt, J=12Hz, 1.5Hz, 1H, CH₂ anti to the triene), 5.69(s, 2H, SCH), 6.1-6.7(m, 4H, trienic), MS m/e 180(M⁺, 15%), 147(100%) 4 mp 257 °C (dec), NMR(CS₂) δ 2.81(s, 4H, CH₂), 6.45(bs, 8H, trienic), 6.59(s, 4H, SCH), MS m/e 360(M⁺, 56%), 147(100%) 5 mp 219 °C, NMR(CS₂) δ 2.72(s, 6H, CH₂), 6.47(s, 6H, SCH), 6.15-6.55(m, 12H, trienic), MS m/e 540(M⁺, 7%), 147(100%) 11a mp 107.5-110 °C, NMR(CDCl₃) δ 2.64(s, 2H, CH₂ of cycloheptatriene), 2.69(t, J=6.0Hz, 4H, C⁴H₂), 2.85(s, 4H, C⁵H₂), 3.00(t, J=6.0Hz, 4H, C¹H₂), 3.64(t, J=6.0Hz, 8H, C²H₂, C³H₂), 6.01-6.45(m, 4H, olefinic), MS m/e 390(M⁺, 38%), 154(100%), UV λ_{\max} (log ϵ)(CH₂Cl₂) 231 nm(4.06), 252(sh 3.92), 322(3.76), 410(2.93) 11b mp 135-137 °C, NMR(CDCl₃) δ 2.57(s, 2H, CH₂ of cycloheptatriene), 2.75-3.20(m, 8H, C¹H₂, C⁴H₂), 3.40-3.78(m, 8H, C²H₂, C³H₂), 5.95-6.43(m, 4H, olefinic), 6.96-7.48(m, 4H, aromatic), MS m/e 438(M⁺, 47%), 153(100%), UV λ_{\max} (log ϵ)(CH₂Cl₂) 252 nm(sh 4.10), 290(3.71), 312(sh 3.69), 410(2.46) 12a mp 120-130 °C(dec), NMR(DMSO-d₆) δ 2.66(t, J=6.0Hz, 4H, C⁴H₂), 2.71(s, 4H, C⁵H₂), 3.46-4.00(m, 12H, C¹H₂, C²H₂, C³H₂), 7.90-8.53(m, 5H, tropylium), UV λ_{\max} (log ϵ)(CH₃CN) 239 nm(3.98), 345(4.38), 404(4.19) 12b mp 172-174 °C, NMR(DMSO-d₆) δ 3.08(t, J=5.5Hz, 4H, C⁴H₂), 3.40-3.99(m, 12H, C¹H₂, C²H₂, C³H₂), 7.05-7.50(m, 4H, aromatic), 7.86-8.63(m, 5H, tropylium), UV λ_{\max} (log ϵ)(CH₃CN) 214 nm(4.48), 345(4.38), 403(4.19)
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4. The iodide 9 was prepared by the reaction of 2 with 2-(2-chloroethoxy)ethanol followed by iodination via tosylation
5. o-Benzenedithiol was prepared by the method of Degani I. Degani and F. Fochi, *Synthesis*, 471 (1976)
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