Chinese Chemical Letters Vol. 11, No. 6, pp. 499–502, 2000

Synthesis and Properties of New-type Troponoid Dithio-Crown Ethers

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Abstract: Condensation of 3,7-dichloromethyl-5-isopropyl-2-methoxytropone **4** with bis (mercaptoethyl) ether **5a** and mono, di, and tri-ethylene glycol bis(mercaptoethyl) ethers **5b**-**5d** gave troponoid-annexed dithiocrown ethers **6a**-**6d**. Compounds **6a**-**6d** have selective and reversible mercury salt capturing ability.

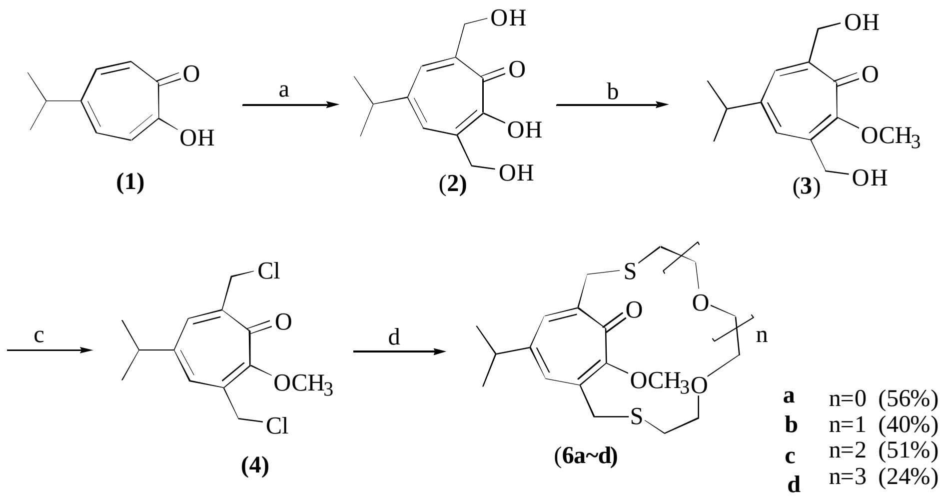
Keywords: Tropone, crown ether, complex, reversible.

Troponoid dithio-crown ethers are a kind of novel compounds. Takeshita *et al*[1-6] have reported the synthesis and mercurophilic properties of this kind of compounds. In the reported compounds, the two sulfur atoms are attached, part or all, to the tropone ring directly. Whether the dithio-crown ethers still have selective and reversible mercury salt capturing ability when the two sulfur atoms link to the benzylic-type position of tropone ring aroused our interest.

Herein, we wish to report that from the reaction of 3,7-dichloromethyl-5-isopropyl-2-methoxytropone **4** with bis (mercaptoethyl) ether **5a** and mono, di, and tri-ethylene glycol bis (mercaptoethyl) ethers **5b-5d** under high-dilution conditions with NaOMe in MeOH, the dithio-crown ethers **6a-6d** were obtained respectively. Condition of reaction, yields and some physical properties of compounds **2-6** are listed in **Scheme 1** and **Table 1.**

In **6a** and **6b**, the benzylic-type hydrogens appeared as an AX-systems in the ^{1}H-NMR spectra, suggesting that the ether ring are too short to flip from one side of tropone ring to the other. The ether ring in **6c** is long enough to flip from one side ofthe tropone ring to the other side. This was witnessed by the change of signal shape of the benzylic-type hydrogens, **6c** showed one benzylic-type signal at δ 4.44 ppm (2H, br) and another at δ 3.18ppm (1H,br) and δ 3.35ppm (1H,br), this also verified that the flipping over of the ether ring is slow. However, in **6d**, there are signals at δ 3.81ppm (2H,s) and δ 3.91ppm (5H,s) respectively. The latter signal includes the methoxy group and the benzylic-type hydrogens adjacent to the carbonyl group.The two sharp peaks may be ascribed to the quick flipping over of the ether ring.

Scheme1



a n=0 (56%)
b n=1 (40%)
c n=2 (51%)
d n=3 (24%)

a CH_2O, KOH 90% b CH_2N_2 95% c $SOCl_2$ /CH_2Cl_2 67%

d $HSCH_2CH_2O(CH_2CH_2O)_nCH_2CH_2SH$

With the expectation that the compounds synthesized also have the reversible mercury (Ⅱ) salt capturing ability, we did the mercury ion complexation experiment too. When an aqueous solution containing Hg^{2+} was shaken with a $CDCl_3$ solution of **6**, Hg^{2+}

Figure 1 Change in ^1H-NMR spectrum of **6c** caused by Hg^{2+}

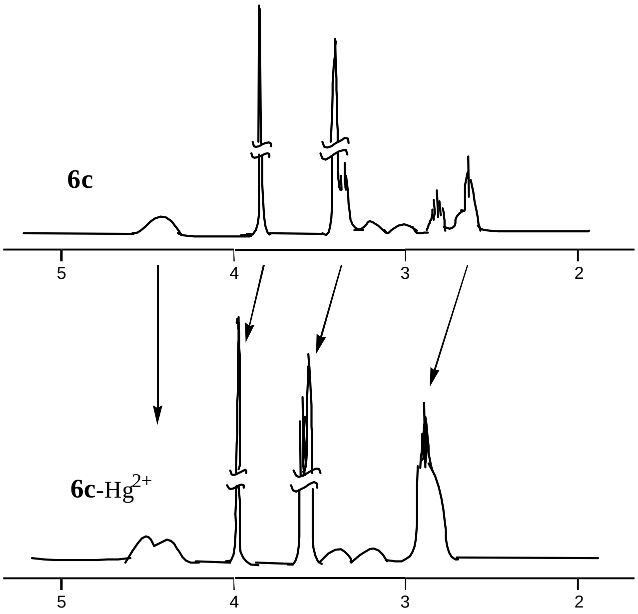


Table 1 Phycical properties of the new compounds

Compound	Colour and state	mp°C
2	brown needle	108-110
3	pale yellow oil	
4	pale yellow oil	
6a	pale yellow needle	106-108
6b	yellow prism	68-71
6c	pale yellow oil	
6d	pale yellow oil	

was extracted into the $CDCl_3$ layer, this was tested by the change of chemical shift of the relevant hydrogens in ^{1}H-NMR spectra. For example, particulary diagnostic for Hg^{2+}-complexed **6c** is the appearance of two broad signals, one at δ 3.20ppm and 3.36ppm, other at δ 4.45 and 4.52ppm. The methylene signals of **6c** shift downfield to some extent (see **Figure 1**). The mercury ion included could be liberated quantitatively by treatment with aqueous 2mol/L HCl solution. But Cu^{2+}could not be extracted from the solution containing Hg^{2+} and Cu^{2+} on the basis of ^{1}H-NMR evidence, thus achieving an effective transportation of Hg^{2+}. More detailed complexing experiment are underway.

Experimental

3,7-dihydroxymethyl-5-isopropyltropolone **2** was prepared by general method[7], 3,7-dihydroxymethyl-5-isopropyl-2-methoxytropone **3** was synthesized from compound **2** and new-prepared diazomethane in ethyl ether. Compound **4** was obtained by general method[7]used thionyl chloride as chloro reagent.

Reaction of compound 4 with compounds 5a-5d.

General procedure

To a mixture of benzene (15 mL) and methanol (10 mL), **4** (190 mg,0.69 mmol) was added (solution A). Sodium metal (31.8 mg,1.38 mmol) was added to methanol (10 mL), after the sodium metal disappeared, a solution of **5a** (95 mg,0.69 mmol) in methanol (15 mL) was added and stirred for 0.5 hr at room temperature (solution B). To a 500 mL four neck flask , 300 mL methanol was added and heated to reflux gently under nitrogen and stirring. Then solution A and solution B were added dropwise simultaneously and gradually from two side and keep the equal speed (*ca*. 3 hr), the reaction continued for 18 hr. After cooling, the solvent was removed in vacuo, 20mL water was added to the residue and acidified to weak acidity with hydrogen chloride, the mixture was extracted several times with chloroform and dried over anhydrous sodium sulfate, and then the solvent was removed, the residue was column chromatographed with petroleum ether-ethyl acetate (6:1) to give **6a**.

Acknowledgments

We warmly thank the National Natural Science Foundation of China for financial aid and Professor Akira Mori and Mr. Kanji Kubo (Institute of Advanced Material Study, Kyushu University, Japan) for their measurements of the high-resolution mass spectra and elemental analysis.

References and **Notes**

1. H.Takeshita, A. Mori, S.Hirayama, *J .Chem.Soc., Chem Commun.*, **1989**, (9), 564.
2. A. Mori, B. Z. Yin, H. Takeshita, *Chemistry Express*, **1992**, *7*(4), 313.
3. K..Kubo, A.Mori, H.Takeshita, *Heterocycles*, **1993**, *36*(9), 1941.
4. H. Takeshita, B. Z.Yin, K.Kubo, A.Mori, *Bull. Chem. Soc. Jpn.*, **1993**, *66*, 3451.
5. A. Mori, K. Kubo, H.Takeshita, *Bull.Chem.Soc.Jpn.*, **1994**, *67*(4), 1094.
6. K.Kanji, M.Akira, H. Takeshita, *Bull. Chem. Soc. Jpn.*, **1997**, *70*(1), 231.
7. T. Nozoe, T.Mukai, K.Takase, *Sci. Rep. Tohoku Univ., Ser. I*, **1952**, *36*, 40.
8. Compounds (**2**) was confirmed by ^{1}H-NMR, IR and elemental analysis; (**3**), (**4**) and (**6a-6d**) were verified by ^{1}H-NMR and HR-MS, in agreement with the assigned structures.

Received 6 July 1999
Revised 3 April 2000