# SYNTHESIS OF MERCUROPHILIC DICYANOHEPTAFULVENES BY REMOTE SUBSTITUTION OF 5,8,11,14,17-PENTAOXA-2,20-DITHIABICYCLO[19.4.1]HEXACOSA-21,23,25-TRIEN-26-ONE AND ITS HOMOLOGUES WITH MALONONITRILE

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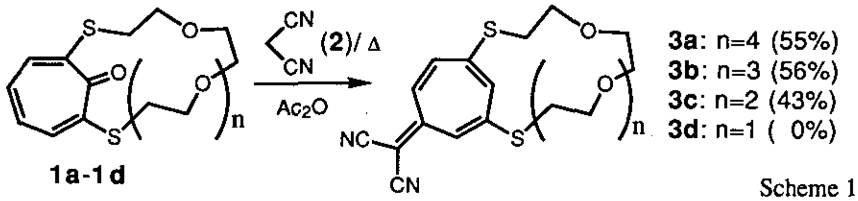
*Abstract*—5,8,11,14,17-Pentaoxa-2,20-dithiabicyclo[19.4.1]hexacosa-21,23,25-trien-26-one and its homologs gave, *via* remote substitution, dithio-crown-etherated 8,8-dicyanoheptafulvene derivatives upon heating in acetic anhydride. The dithio-crown-etherated dicyanoheptafulvenes efficiently extract and reversibly transport $Hg^{++}$ ion.

Previously, we have synthesized a remarkably efficient mercurophilic dithio-crown derivative, 5,8,11,14-tetraoxa-2,17-dithiabicyclo[16.4.1]tricosa-18,20,22-trien-23-one (**1b**) and its homologues,[1] and these compounds showed a reversible complexation, which has been explained in terms of the Coulomb cation-cation repulsive interaction between mercuric ion and a hydroxytropylium ion formed upon acid treatment. Meanwhile, we have found a remote substitution of sterically hindered tropones to 8,8-dicyanoheptafulvene derivatives upon treatment with malononitrile (**2**) in acetic anhydride.[2]

Therefore, it is desirable to extend the complexation study to heptafulvene derivatives, which also form a cycloheptatrienylium system upon acidification. Herein, we describe the results, synthesis and mercurophilic properties of such heptafulvene derivatives prepared from appropriate tropones and **2**.

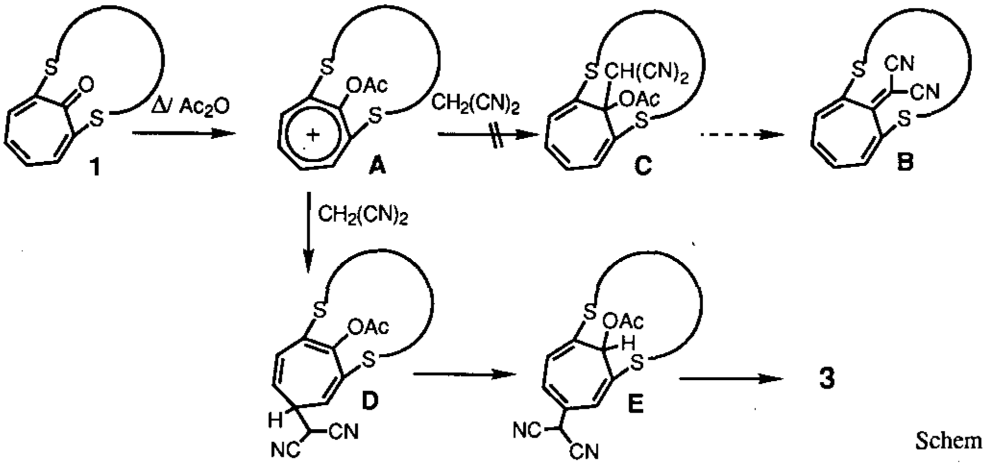
A mixture of 5,8,11,14,17-pentaoxa-2,20-dithiabicyclo[19.4.1]hexacosa-21,23,25-trien-26-one (**1a**) and **2** was heated in acetic anhydride for 1 h to give, *via* column chromatography, red-crystalline heptafulvene (**3a**), mp 70-

71 °C, in a 55% yield, which was identified to be a remote-condensation product,[2] 23-dicyanomethylene-5,8,11,14,17-pentaoxa-2,20-dithiabicyclo[19.4.1]hexacosa-1(26),21,24-triene.



Scheme 1

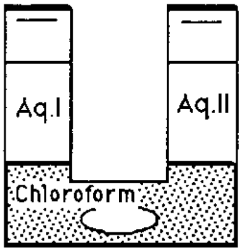
Similar treatment of 5,8,11,14-tetraoxa-2,17-dithiabicyclo[16.4.1]tricosa-18,20,22-trien-23-one (**1b**) and 5,8,11-trioxa-2,14-dithiabicyclo[13.4.1]cosa-15,17,19-trien-20-one (**1c**) with **2** also gave red crystals, 20-(dicyanomethylene)-5,8,11,14-tetraoxa-2,17-dithiabicyclo[16.4.1]tricosa-1(23),18,21-triene (**3b**), mp 133-134 °C, and 17-dicyanomethylene-5,8,11-trioxa-2,14-dithiabicyclo[13.4.1]cosa-1(20),15,18-triene (**3c**), mp 175-177 °C, in 56 and 43% yields, respectively, but 5,8-dioxa-2,11-dithiabicyclo[10.4.1]heptadeca-12,14,16-trien-17-one (**1d**)[3] was unreactive under those conditions. Therefore, the reaction of 5-oxa-2,8-dithiabicyclo[7.4.1]tetradeca-9,11,13-trien-14-one (**1e**) with **2** was not even attempted. For the reaction mechanism, provided is Scheme 2, where the first step of the reaction is a formation of an acetoxytropylium ion (A), and the absence of *ipso*-product (**B**) might be attributable to the steric hindrance in the intermediate (**C**). On the other hand, an intermediate (**D**) leading to the remote-condensate is eligible for a thermally-allowed 1,5-hydrogen shift to an intermediate (**E**).[4]



Scheme 2

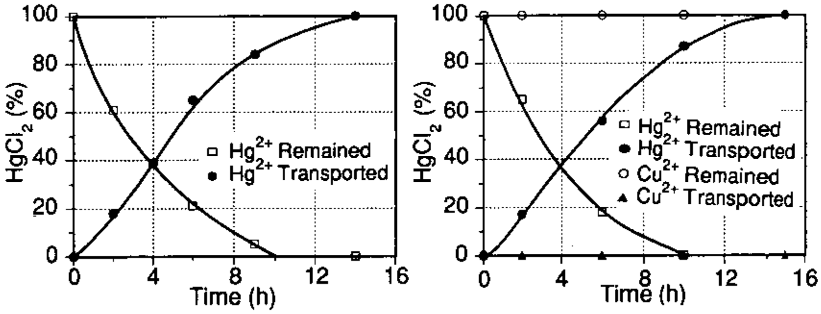
As like as the troponoid analogues,[5] these heptafulvenes formed crystalline complexes with $Hg^{++}$ ion. Extraction of $Hg^{++}$ ion into chloroform-*d* containing (**3a-c**) was checked by $^1H$ nmr spectroscopy; **3a** and **3b** revealed clear

$^1H$ nmr change due to the complexation, but the change of **3c** by complexation was not conclusive. However, according to the experiments using a *U*-type cell (Figure 1),[6] all these **3a-c** transported $Hg^{++}$ ion selectively, and, in parallel to that with **1**, the $Cu^{++}$ ion did not interfere the transportation of $Hg^{++}$. The extraction into an organic layer containing the crown ethers and the reverse-extraction into an aqueous layer (2M HCl) occurred quite smoothly. Indeed, the most satisfactory results obtained with **3a** is far better than any previous ones ever studied. The results are summarized in Figure 2. It is also worthy to note that the efficiency of the transportation sharply dropped when **3b** or **3c** was used; under the same conditions, the transportation rate for **3b** or **3c** was less than 30% to that for **3a**.



Aq. I (10 $cm^3$) : $HgCl_2$ (≈5 mg)
Aq. II(10 $cm^3$) : 2M HCl
$CHCl_3$(20 $cm^3$) : **3**(≈20 mg)

Figure 1. The *U*-type cell.



i) $Hg^{++}$ ion without $Cu^{++}$ ion ii) $Hg^{++}$ ion with $Cu^{++}$

Figure 2. Transportation of $Hg^{++}$ ion with **3a**.

In the case of troponoid analogues, **1b** is better than **1a**. The difference in the fitted ring sizes between **1** and **3** must be due to a difference in their substitution patterns; *i.e.*, in **3**, the electronegative dicyanomethylene, a terminal of conjugated π-system, is distant from the sulfur atoms, other site of coordination. In this respect, the $^{13}C$ nmr of **3a** induced a significant complexation shifts (Δδ) in the chemical shifts for aromatic carbon signals, but not with the cyano groups, to suggest a role of its π-system for the complexation.[3] However, informations deduced from the nmr data should be carefully taken into account, and the structure of 3a-$Hg^{++}$ complex should be discussed after the X-ray analysis.[7]

The markedly selective and reversible complex formation with $Hg^{++}$ observed in **1** is now extended to **3**. The results clearly show that the protonation is responsible to a ready liberation of $Hg^{++}$ ion by acidification to generate 6π-cationic system for the seven-membered ring and to cause the Coulomb repulsion with complexed $Hg^{++}$ ion. This may be attributed to the difference with the benzenoid counterpart.

## REFERENCES

1. K. Kubo, A. Mori, and H. Takeshita, *Chem. Express*, 1992, **7**, 945.
2. A. Mori, B. Z. Yin, A. Endo, and H. Takeshita, *Chem. Lett.*, **1992**, 855.
3. The nmr spectral data (270 MHz for $^{1}$H and 67.5 MHz for $^{13}$C spectra in $CDCl_3$), as well as electronic spectra, of new heptafulvenes are listed below:

   **3a**: δ(H)=3.15(2H, t, *J*=6.6 Hz), 3.21(2H, t, *J*=5.5 Hz), 3.67(16H, s), 3.77(2H, t, *J*=6.6 Hz), 3.84(2H, t, *J*=5.5 Hz), 6.65(1H, dd, *J*=12.5, 2.2 Hz), 6.76(1H, br s), 6.90(1H, dd, *J*=2.2, 1.8 Hz), and 7.07(1H, dd *J*=12.5, 2.2 Hz). δ(C)=32.5, 32.9, 66.3, 68.3, 69.5, 70.7(3C), 71.0(4C), 71.2, 115.5, 115.6, 121.6, 127.3, 132.3, 137.5, 149.1, 154.5, and 158.5. $\lambda_{max}^{CHCl_3}$=313 nm (ε=23300), 332 (17600), and 439 (23300).

   **3a**-Hg$^{++}$: δ(H)=3.15(2H, t, *J*=7.0 Hz), 3.28(2H, t, *J*=5.5 Hz), 3.66-3.84(20H, m), 6.63(1H, dd, *J*=12.8, 2.2 Hz), 6.65(1H, dd, br s), 6.85(1H, br s), and 7.09(1H, dd *J*=12.8, 2.2 Hz). δ(C)=31.4, 33.3, 67.1, 67.7, 68.1, 70.0(4C), 70.2(2C), 70.5, 70.6, 115.3, 115.5, 122.1, 126.7, 132.6, 137.5, 148.8, 152.4, and 158.6.

   **3b**: δ(H)=3.14(2H, t, *J*=5.9 Hz), 3.21(2H, t, *J*=5.5 Hz), 3.62-3.71(12H, m), 3.76(2H, t, *J*=5.9 Hz), 3.84 (2H, t, *J*=5.5 Hz), 6.64(1H, dd, *J*=12.5, 1.8 Hz), 6.88(2H, br s), and 7.10(1H, dd, *J*=12.5, 2.2 Hz). δ(C)= 32.7, 33.9, 66.2, 67.8, 70.2, 70.3, 70.6, 70.8, 71.0, 71.1, 71.2, 115.6, 115.7, 121.3, 128.0, 132.1, 137.5, 148.8, 154.8, and 158.6. $\lambda_{max}^{CHCl_3}$=312 nm (ε=16900), 332 (16800), and 438 (23300).

   **3c**: δ(H)=3.21(2H, t, *J*=5.5 Hz), 3.23(2H, t, *J*=5.5 Hz), 3.56-3.68(8H, m), 3.77(2H, t, *J*=5.5 Hz), 3.83 (2H, t, *J*=5.5 Hz), 6.71(1H, dd, *J*=12.1, 2.2 Hz), 7.02(1H, br s), 7.09(1H, dd, *J*=12.1, 2.2 Hz), and 7.13 (1H, dd, *J*=2.2, 1.5 Hz). δ(C)=33.3, 33.9, 65.8, 68.9, 70.4, 70.5, 70.9, 71.2, 71.5, 115.6, 115.7, 124.9, 128.6, 132.6, 137.7, 150.0, 153.3, and 158.6. $\lambda_{max}^{CHCl_3}$=314 nm (ε=9400), 337(9400), 446 (14000).
4. S. Sugiyama and H. Takeshita, *Chem. Lett.*, **1986**, 1203; *Kyushu Daigaku Sogo Rikogaku Kenkyuka Hokoku*, 1990, **12**, 301.
5. H. Takeshita, A. Mori, and S. Hirayama, *J. Chem. Soc., Chem. Commun.*, **1989**, 564; A. Mori, B. Z. Yin, and H. Takeshita, *Chem. Express*, 1992, **7**, 313.
6. The *U*-type cell used was the same as the previous apparatus, described in ref. 1.
7. According to the X-ray crystallographic study with **1c**-Hg$^{++}$ complex, which will be reported in future, nearly perpendicular geometry of the tropone ring to the dithio-crown ring was observed, and the Hg$^{++}$ is on the one side of carbonyl oxygen and the sulfur atoms. However, in the $^{1}$H nmr spectrum, its α-methylene protons of thioether groups appeared as magnetically-equivalent 2H triplets, and Hg$^{++}$ is in the equilibrium conditions. Also, this should be the case for **3a** as could be judged from the nmr data.

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