

MACROCYCLIC HEXAKETONE AS A SPECIFIC HOST OF URANYL ION

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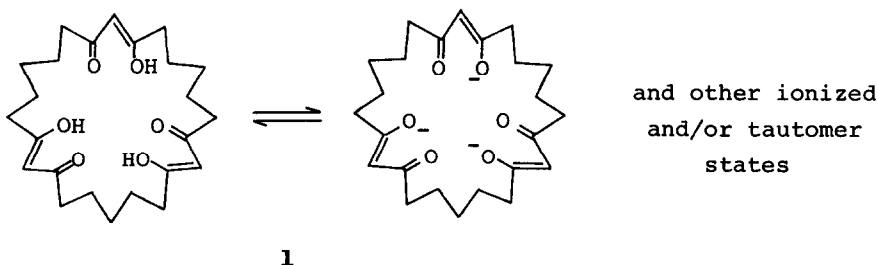
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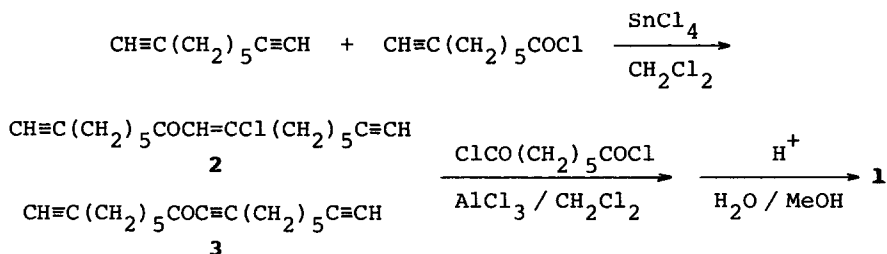
A novel synthetic method was described for a new macrocyclic hexaketone, 1,3,9,11,17,19-hexaoxocyclotetacosane, which extracted 98 % of uranyl ion into benzene phase from a dilute (10 ppm) aqueous solution of pH 8.

Extraction of uranium from sea water is one of the most significant and fascinating problems to be challenged but severely hampered by the presence of a large excess of competing ionic species. The ligand to extract uranium is required to be specific enough to discriminate uranyl ( $UO_2^{2+}$ ) ion from other metal cations such as  $Mg^{2+}$  which is in a  $3.8 \times 10^6$  molar excess. It is fortunate, however, that the crystallographic study on uranyl salts elucidated their coordination structure to be a quasi planar hexadentate, which is so unique that one might synthesize a specific host of uranyl ion by the arrangement of six ligands in near coplanarity and at a proper distance from the center of gravity of the host molecule. The other minor problem arises from the fact that the uranyl ion exists as a stable carbonate complex in sea water. Carbonate may easily be driven out by a stronger ligand possibly with negative charge, e.g., enolate form of  $\beta$ -diketone.

Combination of the indispensable requisites described above led us to design a macrocyclic compound 1, in which three  $\beta$ -diketone units are located symmetrically around the  $C_3$  axis of a 24-membered macrocycle. The CPK molecular model of enolate of the assumed structure 1 strongly suggests that the six oxygen atoms can direct toward the inside of the ring and its cavity is appropriately designed to accommodate the uranyl ion.



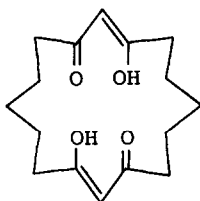
Incorporation of  $\beta$ -diketone unit in macrocycles has been performed by Cram *et al.*<sup>2</sup> and Ito *et al.*<sup>3</sup> Cram's procedures may or may not be applicable to the preparation of **1**. By the latter method,<sup>4</sup> no appreciable amount of cyclic trimer was detectable in the attempted condensation of diethyl pimelate. Here we report a novel and versatile synthesis of  $\beta$ -diketones from the addition products of acid chlorides to terminal acetylenes in the presence of Lewis acid catalyst.<sup>5</sup> The product was a mixture of conjugated  $\beta$ -chloroenone and ynone<sup>6</sup> which behaved as protected forms of the  $\beta$ -diketone functionality and survived during the subsequent reaction conditions and was finally converted smoothly to the corresponding  $\beta$ -diketone by the treatment with aqueous acid or base. The synthetic scheme of **1** is as follows:



To a stirred solution of 8.8 g (73 mmol) of 1,8-nonadiyne and 1.4 g (8.8 mmol) of 7-octynoyl chloride in 10 ml of  $\text{CH}_2\text{Cl}_2$ , stannic chloride, 3.45 g (13.2 mmol), was added dropwise at 15°C and the mixture was stirred for 10 min. The reaction was quenched and excess 1,8-nonadiyne was recovered *via* distillation *in vacuo*. The residual oil was chromatographed on basic alumina (activity II) to afford 0.48 g (20 %) of  $\beta$ -chloroenone **2** and 0.64 g (30 %) of ynone **3**. Either **2** or **3**, or their mixture (1.0 mmol) was treated with 0.20 g (1.0 mmol) of

pimeloyl chloride in the presence of 0.53 g (4.0 mmol) of  $\text{AlCl}_3$  in 200 ml of  $\text{CH}_2\text{Cl}_2$  at room temperature. After 10 hrs, the reaction was quenched and evaporation of the solvent afforded an oily material, which was heated to reflux in 30 ml of aqueous methanol (1 : 2) in the presence of a few drops of sulfuric acid (5 hrs). After usual work-up, the mixture was chromatographed on Silica Gel. Cyclic hexaketone **1** was obtained as more than 95 % enol form, 0.12 g (29 % based on **2** and/or **3** used), colorless needles; mp  $59^\circ\text{C}$ . Anal. Found: C, 68.25; H, 8.74. Calcd: C, 68.55; H, 8.63. The structure of **1** was confirmed by spectroscopic analyses: IR(KBr)  $1600\text{ cm}^{-1}$ , NMR ( $\text{CDCl}_3$  with  $\text{Me}_4\text{Si}$ )  $\delta$  1.1—1.9 (m, 18H), 2.1—2.5 (t, 12H), 3.54 (s) + 5.48 (s) + 14.2 (br s) = 6H, mass spectrum m/e 420 ( $\text{M}^+$ ), 402, 385, and 125 (base).

The synthetic method described here can be successfully extended toward the synthesis of macrocyclic polyketones which usually require an elaborate combination of multi-step reactions. One of the successful applications is visualized in the synthesis of cyclic tetraketone **4** which was prepared in 34 % yield by the addition of pimeloyl chloride to 1,8-nonadiyne followed by the hydrolysis, Colorless needles; mp  $125^\circ\text{C}$ . IR(KBr)  $1600\text{ cm}^{-1}$ , NMR ( $\text{CDCl}_3$  with  $\text{Me}_4\text{Si}$ )  $\delta$  1.0—1.9 (m, 12H), 2.1—2.5 (t, 8H), 3.53 (s) + 5.45 (s) + 14.5 (br s) = 4H, mass spectrum m/e 280 ( $\text{M}^+$ ), 262, 245, and 125 (base).

**4**

Hexaketone thus prepared extracted uranyl ion almost quantitatively into an organic phase from a dilute aqueous solution. A solution of hexaketone **1** in benzene (4.2 mM, 1 ml) was stirred with 10 ppm solution of uranyl acetate (pH 8, 5 ml) at room temperature. After 20 hrs, the residual concentration of uranyl ion in the aqueous phase was determined to be  $0.2\text{ ppm}^7$  (98 % extraction). Dicyclohexyl-18-crown-6 left uranyl ion in the aqueous solution as an uncomplexed form in the concentration as high as 8.4 ppm under the same condition. Hexa-

ketone 1 is calculated to be 260 times more effective than dicyclohexyl-18-crown-6 estimated from their extraction equilibrium constants.<sup>8</sup> The benzene extract liberated uranyl ion quantitatively within 1 hr on treatment with a 1 N HCl aqueous solution. Further studies on the complexation behaviors of 1 and extension of the preparation to a series of macrocyclic polyketones are now under way.

## REFERENCES AND NOTES

1. (a) I. Fankuchen, Z. Krystallogr. **91**, 473 (1935); (b) W. H. Zachariasen, Acta Cryst., **1**, 277, 281 (1948).
2. (a) A. H. Alberts and D. J. Cram, J. Chem. Soc., Chem. Commun., 958 (1976); (b) A. H. Alberts and D. J. Cram, J. Am. Chem. Soc., **99**, 3880 (1977).
3. Y. Ito, T. Sugaya, M. Nakatsuka, and T. Saegusa, J. Am. Chem. Soc., **99**, 8366 (1977).
4. K. Ruhlmann, Synthesis, 236 (1971).
5. (a) C. C. Price and J. A. Pappalardo, Org. Syn. Coll. Vol., **4**, 186 (1963); (b) W. R. Benson and A. E. Pohland, J. Org. Chem., **29**, 385 (1964); (c) H. Martens and G. Hoornaert, Tetrahedron Letters, 1821 (1970).
6. Conjugated allenic ketone also formed in the zinc chloride catalyzed reaction.
7. The most part of  $1-UO_2^{2+}$  complex partitioned into the benzene layer but a small fraction seems to remain in the aqueous layer to cause "non extractable" uranyl even after repeated extraction with benzene (2 ml x 8). Analysis of  $UO_2^{2+}$  concentration in the aqueous solution was made by the 665 nm absorption after treatment with Arsenazo III reagent. See H. Onishi and Y. Toita, Bunseki Kagaku, **14**, 1141 (1965).
8. The stability constant of  $1-UO_2^{2+}$  complex seems to be very high judging from the general comparison of partition and stability constants.

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