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A New Chelating Polymer

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A New Chelating Polymer

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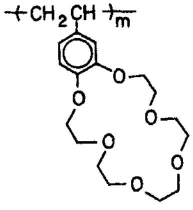
ABSTRACT

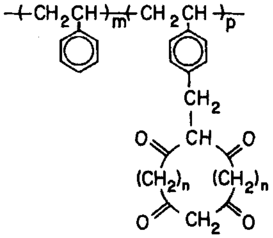
This paper reports a new synthesis of polymers in which macrocyclic bis-1,3-diketones are attached to polystyrene and then complexed with transition metals. Preparation of 22- and 26-membered macrocyclic bis-1,3-diketones was performed by Fe(III)Cl_3-induced ring expansion reaction of the corresponding tetrakis(trimethylsilyloxy)tricycloalkanes according to the procedure we reported previously. Treatment of the 22- and 26-membered macrocyclic bis-1,3-diketones with chloromethylated polystyrene in dimethylformamide in the presence of sodium hydride produced polystyrene with macrocyclic bis-1,3-diketone as pendant groups. As expected, the polystyrene carrying macrocyclic bis-1,3-diketone rings was found to form metal chelated polymer when it was treated with transition metal salts such as copper, nickel, and cobalt.

Synthesis of polymer carrying macrocyclic ligands as pendant groups on a polymer chain has been a subject of considerable interest. Recently, so-called poly(crown ether) (I), in which benzo-18-crown-6 is attached to a polymer chain, has been prepared, and its interesting behavior caused by its complexation with metal cations has been extensively investigated [1-3]. Crown ethers form complexes mainly with alkali and alkaline earth cations, depending upon their ring size. On the other hand, 1,3-diketones have been well known to form stable complexes with various transition metals although their bonding character is different from those with crown ethers. It would be expected that cyclic bis-1,3-diketones having a hole large enough to take up metal permit more effective complexation with transition metals. Unlike crown ethers, 1,3-diketones have reactive methylene groups in the molecule. Therefore, cyclic-1,3-diketone ligand may be readily introduced as a pendant group to a variety of reactive polymer by carbon-carbon bond formation.

Now we wish to report a new synthesis of polymers (II), in which macrocyclic bis-1,3-diketones are attached to polystyrene, and a preliminary result on their complexation with transition metals.



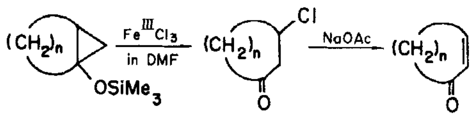
I



II

SYNTHESIS OF MACROCYCLIC BIS-1,3-DIKETONES

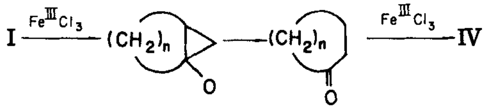
Recently we reported [4, 5] an oxidation reaction of 1-silyloxybicyclo[n.1.0]alkanes (III) with Fe(III)Cl$_3$, leading to the formation of the corresponding 2-cycloalkenone (V) via 3-chlorocycloalkanone (IV) in moderate to excellent yields according to Eq. (1). This reaction presents a new method for one-carbon ring homologation of cycloalkanones. It is of practical use, since 1-silyloxybicyclo[n.1.0]alkanes



III IV V (1)

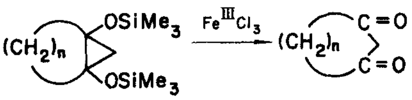
are readily prepared by the Simmons-Smith reaction of silyl enol ethers of cycloalkanones [6]. Recently, Stork has reported [7] a comparable ring homologation of cycloalkanones by the dichlorocyclopropanation of silyl enol ether followed by hydrolysis.

The reaction for one-carbon homologation of cycloalkanones in this study is mechanistically interesting in terms of the regioselectivity in the ring-opening of silyloxybicyclo[n.1.0]alkane (III), of which the bridging bond is cleaved. This is contrasted with the bromination [8] and the potassium tert-butoxide treatment [9] of 1-silyloxybicyclo-[n.1.0]alkanes producing 2-bromomethylcycloalkanones and 2-methylcycloalkanones, respectively. Based upon the extensive studies on the reaction of cyclopropanol with various halogenating reagents by DePuy and co-workers [10, 11], the present ring enlargement reaction may be well explained by a mechanism involving an alkoxy radical intermediate (VI) which undergoes the homolytic β-scission of the bridging carbon-carbon bond, and the subsequent abstraction of chlorine by the resulting carbon radical species (VII) to give 3-chlorocycloalkanone (IV) [Eq. (2)]. Detailed understanding of the reaction mechanism must await further study.



VI VII (2)

This reaction for one-carbon homologation of cycloalkanones is also applicable to bis(trimethylsilyloxy)bicyclo[n.1.0]alkanes (VIII) which are prepared by the cyclopropanation of bis(silyloxy)enediol derived from the silylacyloin synthesis [12]. This reaction provides a new route to cycloalkane-1,3-diones (IX). Some results of cycloalkane-1, 3-dione synthesis are summarized in Table 1.

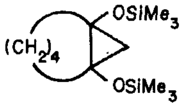
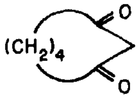
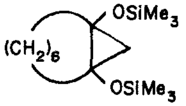
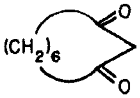
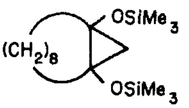
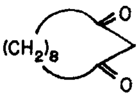
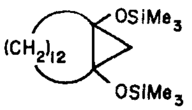
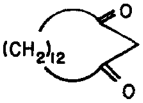


VIII IX (3)

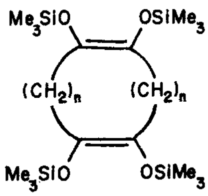
On the basis of the findings mentioned above, we wish to describe a new and versatile synthesis of macrocyclic compounds, in which two 1,3-diketone units are symmetrically located in the ring.

The synthesis of the macrocyclic tetraketones (XII) started with tetrakis(trimethylsilyloxy)cycloalkadienes (X), cyclic silylacyloin

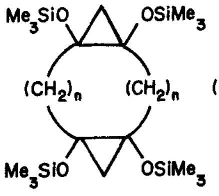
TABLE 1. Synthesis of Cyclic 1,3-Diketones

No.	Bis(trimethylsilyloxy)-bicyclo[n.1.0]alkane	Cyclic 1,3-diketone	Yield (%)
1			68
2			72
3			73
4			88

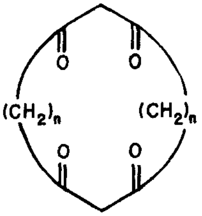
dimers, which are derived from the silyl-acyloin condensation of aliphatic dicarboesters such as dimethyl nonanedioate, dimethyl decanedioate, dimethyl dodecanedioate, and dimethyl tetradecanedioate. Tetrakis(trimethylsilyloxy)cycloalkadienes (X) were prepared according to the following procedure. To a suspension of sodium dispersion (0.45 g-atom) and trimethylchlorosilane (0.5 mole) in xylene (300 ml), dimethyl decanedioate (0.1 mole) in xylene (30 ml) was added dropwise with vigorous stirring over 3 hr at 40-50°C. Then the mixture was heated at 80°C for 3 hr and allowed to stand overnight at room temperature. After the reaction mixture was filtered, the filtrate was distilled in vacuo. Removal of 1,2-bis(trimethylsilyloxy)cyclodecene by Kugelrohr distillation left a viscous liquid, which was slowly solidified and recrystallized from ether to give pure Xb, mp 89-90°C (lit. [12] mp 90-90.5°C), in 47% yield. Compounds Xa, Xc, and Xd were separated from 1,2-bis(trimethylsilyloxy)cyclononene, 1,2-bis(trimethylsilyloxy)cyclododecene, and 1,2-bis(trimethylsilyloxy)-cyclotetradecene, respectively, by Kugelrohr distillation and subjected to the subsequent cyclopropanation without further purification. Cyclopropanation of X with diethylzinc and methylene diiodide afforded tetrakis(trimethylsilyloxy)tricycloalkanes (XI), which were then treated with $FeCl_3$ in DMF [4] to produce the desired macrocyclic tetraketones XII in satisfactory yields.



X



XI

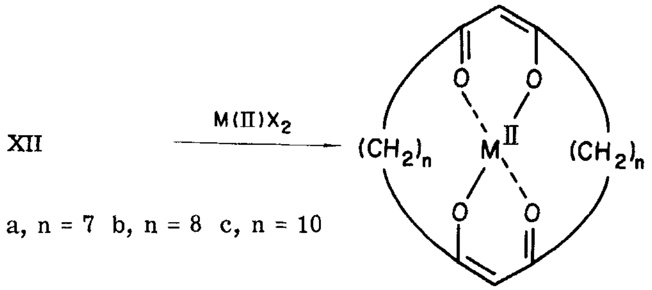


XII

a, n = 7 b, n = 8 c, n = 10 d, n = 12

A typical experimental procedure for the preparation of the macrocyclic tetraketones XII is as follows. Under a nitrogen atmosphere, 40.2 g (150 mmole) of methylene diiodide was added dropwise to a stirring mixture of 16.5 g (26 mmole) of Xb and 15.7 g (130 mmole) of diethylzinc in 100 ml of benzene at room temperature. The mixture was then heated at reflux for 3 hr. The standard work-up of the reaction mixture [13] gave 12.5 g of a viscous liquid (XIb), whose IR spectrum exhibited an absorption band at 3050 cm^{-1} characteristic of cyclopropane ring at the expense of a band at 1665 cm^{-1} ascribable to the carbon-carbon double bond of the starting material of Xb. The viscous liquid of XIb without further purification was subjected to the $FeCl_3$-induced ring enlargement reaction [4, 5], i. e., 12.5 g (19 mmole) of XIb was added dropwise to a solution of 12.4 g (76 mmole) of anhydrous $FeCl_3$ in 40 ml of DMF at room temperature, and then, the mixture was heated with stirring at 65°C for 4 hr. The reaction mixture was poured into 10% HCl aqueous solution and extracted with chloroform. The chloroform extract was washed with water, dried over $MgSO_4$, and evaporated. The residue was chromatographed on silica gel eluting with chloroform to furnish 4.4 g of 22-membered cyclic tetraketone XIIb (47% yield based on Xb used) as a keto-enol tautomer mixture. The structure of XIIb was confirmed by elemental analysis and spectral data. IR (neat) showed bands at 1710, 1610 cm^{-1}; UV ($CHCl_3$) showed absorption at 275 nm (ϵ 5500). NMR ($CDCl_3$ with Me_4Si) showed δ 0.90-2.00 (br s, 24H), 2.00-2.60 (m, 8H), 3.55 (s) + 5.55 (s) + 15.0 (br s) = 4 H. The mass spectrum showed a M^+ peak at 364. Similarly, 20-, 26- and 30-membered cyclic tetraketones XIIa, XIIc and XIId were synthesized in 33, 43, and 35% isolated yields from tetrakis(trimethylsilyloxy)cycloalkadienes Xa, Xc, and Xd, respectively.

The CPK molecular model indicated that the macrocyclic tetraketones XII thus prepared are capable of taking a conformation in which the four carbonyl oxygens are directed toward the inside of the ring and are on the same plane with a cavity large enough to take up some transition metals. Now it was found that 1:1 chelating metal



a, n = 7 b, n = 8 c, n = 10

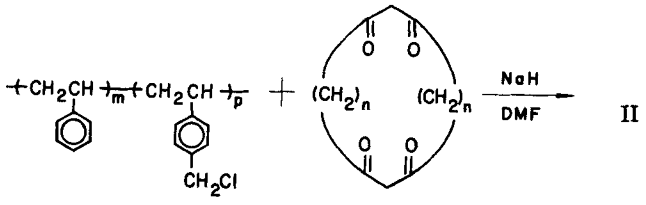
XIII

complexes XIII were isolated in the reaction of XIIa, XIIb, and XIIc with transition metals such as Cu(II), Ni(II), and Co(II). To a solution of 100 mg (0.55 mmole) of anhydrous $Cu(II)(OAc)_2$ in 10 ml of ethyl alcohol was added 200 mg (0.55 mmole) of XIIb in 3 ml of ethyl alcohol at room temperature and the mixture was stirred for 1 hr under nitrogen. A precipitated light blue solid (230 mg) was collected and recrystallized from benzene. The solid was assigned to the 1:1 chelating Cu(II) complex (XIIIb·Cu) by the following spectral data and elemental analysis. The IR spectra (KBr disk, 1565, 1515 cm^{-1}) and UV spectra [$CHCl_3$ solvent, λ_{max} 295 nm (ϵ 9500), 250 (9000)] are similar to those of $Cu(acac)_2$. The mass spectrum exhibited four parent peaks at 425, 426, 427, and 428 with relative intensity of 100:23.86:47.68:10.51 due to the isotopic distribution, which is consistent with the calculated value [calculated relative intensity: 425 (100), 426 (24.39), 427 (48.07), 428 (11.06)], based on the 1:1 chelating Cu(II) complex, XIIIb·Cu. According to the same procedure, 1:1 chelating Cu(II) complexes XIIIa·Cu and XIIIc·Cu were prepared [14].

The related nickel(II) and cobalt(II) complexes (XIII·Ni and XIII·Co) were prepared by the reaction of XII with anhydrous $NiCl_2$ and with anhydrous $CoCl_2$ in the presence of triethylamine.

SYNTHESIS OF POLYSTYRENE HAVING MACROCYCLIC BIS-1,3-DIKETONE RINGS AND ITS COMPLEXATION WITH TRANSITION METALS

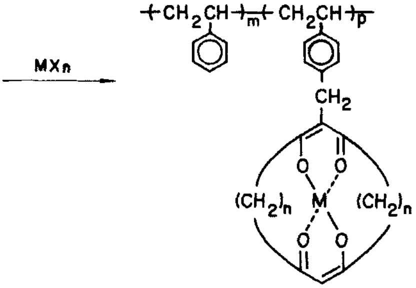
The macrocyclic bis-1,3-diketones XII prepared according to the above procedure may be introduced to a variety of so-called reactive polymer through their active methylene groups. We now found that chloromethylated polystyrene (XIV) was treated with macrocyclic bis-1,3-diketone XII in the presence of sodium hydride to produce a new chelating polymer (II) having cyclic bis-1,3-diketone ring as pendant group.



XIV XII

Synthesis of polymer II was carried out as follows. Noncross linked chloromethylated polystyrene ($\overline{M}_n = 1.7 \times 10^4$), where 20% of the phenyl group was chloromethylated, was treated with 1.2 equivalents of sodium 22-membered cyclic-bis-1,3-diketone, which was prepared from 22-membered cyclic-bis-1,3-diketone (XIIb) and 1 equivalent of sodium hydride in dimethylformamide for 24 hr. The reaction mixture was poured into chloroform and washed with 10% HCl aqueous solution and then water. The chloroform solution was concentrated and poured into a large amount of hexane. The precipitated polymer IIb was collected by filtration and washed with methanol (85% yield). Elemental analysis of polymer IIb indicated that 70% of chloromethyl groups in the polymer bound the 22-membered cyclic bis-1,3-diketone XIIb. The value corresponds to a styrene unit/22-membered cyclic bis-1,3-diketone ratio of 7, since the content of chloromethyl group in the starting chloromethylated polystyrene is 20%. The infrared spectrum of polymer IIb exhibited a strong absorption band at 1710 cm^{-1} but did not exhibit any band around 1600 cm^{-1} characteristic of enolizable 1,3-diketone. This observation indicates that the cyclic bis-1,3-diketone attached to the polymer IIb exists as the keto tautomer. This finding was supported by the UV spectrum of the polymer IIb in chloroform; i. e., no absorption band at 275 nm due to the enol tautomer of cyclic bis-1,3-diketone XIIb was observed. Similar results were obtained with polymer IIc. When the polymer IIb was treated with $Cu(II)(OAc)_2$ in a mixed solvent of THF and ethyl alcohol, Cu(II) chelating polymer (XVb·Cu) was formed in 80% yield. As expected, the UV spectrum of Cu(II) chelating polymer (XVb·Cu) in chloroform showed an absorption band at λ_{max} 307 nm which is comparable with that of XIIIb·Cu (λ_{max} 295 nm). Cu(II) chelating polymer (XVb·Cu) was also prepared by shaking a chloroform solution of polymer IIb with an aqueous solution of cupric acetate, as judged by UV spectrum.

II



XV

On treatment with 10% aqueous HCl, copper(II) ion was completely removed from the copper(II) chelating polymer XV·Cu, reproducing polymer II.

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