2. The replacement of triphenylphosphine by triferrocenylphosphine in an organogold complex affects the direction of the reaction, but does not change its stereochemical result.

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SYNTHESIS OF A NEW PHOSPHORUS-CONTAINING MACROCYCLE

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Heterocyclic compounds that contain at least two P atoms in the ring [1-3], especially macrocyclic structures [4-7], are available only with difficulty, and have received little study. At the same time, a large number of quite readily available macrocyclic polyethers (crown ethers), which possess complexing properties, is known [8].

The synthesis of a 15-membered macrocyclic compound, which contains both phosphine oxide groupings and polyether units, is described in the present paper. The complexing properties of such systems are of definite interest [9].

The scheme for the synthesis of the macrocycle includes obtaining a phosphorus-containing diphenol, which then can be used in the cyclization step with the dihalo derivatives of polyglycols via the method for the synthesis of crown ethers.

From o-bromo(methoxymethoxy)benzene (I), which was obtained from o-bromophenol, we prepared the Grignard reagent, which when reacted with ethylenebis(phenylphosphinic chloride) [10] gives ethylenebis[phenyl(o-methoxymethoxyphenyl)phosphine oxide] (II). The basic properties of this dioxide were studied by the method of potentiometric titration with HClO4 in nitromethane solution [11]; the found value was pK_{q} (CH₃NO₂) = 6.57. Treatment of dioxide (II) with alcoholic HCl solution gives ethylenebis[phenyl(o-hydroxyphenyl)phosphine oxide] (III), which is insoluble in water and most organic solvents. The IR spectrum of (III) has a very broad absorption band in the 2300-3200-cm⁻¹ region that corresponds to the stretching vibration of phenolic OH groups, which take part in strong H bonding. The stretching vibra-tions of the P=O group gives a quite broad band around 1140-1150 cm⁻¹. The treatment of (III) with sodium ethoxide, and then with β,β '-dichlorodiethyl ether in dimethylformamide (DMF) at high dilution gives 1,2,7,8-dibenzo-3,6-diphospha-3,6-dioxo-3,6-dipheny1-15-crown-5 (IV). This compound is readily soluble in alcohol or chloroform, and less readily soluble in benzene. The molecular weight of macrocycle (IV), determined in an analytical ultracentrifuge, is 540; the calculated mol.wt. is 532.5. The IR spectrum of (IV) lacks absorption in the vibration region of phenolic OH groups, while the $v_{P=0}$ (shoulder at 1170 cm⁻¹). The basicity of dioxide (IV) is pK_{α} (CH₃NO₂) = 6.84. The ³¹P-{¹H} NMR spectrum of (IV) represents a narnow singlet line, which, relative to the signal of 85% H₃PO₄, is shifted downfield by 35.7 ppm.

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EXPERIMENTAL

o-Bromo (methoxymethoxy) benzene (I). With stirring, to 51.9 g of o-bromophenol in 150 ml of hot toluene was added dropwise a solution of 6.9 g of Na in 150 ml of alcohol. The mixture was heated to reflux and the alcohol was removed, with the simultaneous addition of toluene so as to maintain the volume of the mixture at \sim 250 ml. After removal of the alcohol, 24.0 g of methyl chloromethyl ether was added dropwise in 20 min at 0-5°C, and after 12 h we added 50 ml of 5 N NaOH solution. The organic layer was separated, washed with water, dried over Na₂SO₄, concentrated *in vacuo*, and the residue was distilled. We obtained 34.5 g (53%) of (I), bp 87-89° (1 mm); $n_{\rm D}^{2°}$ 1.5504, $d_4^{2°}$ 1.4597. Found (%): C 44.1, H 4.4, Br 36.3. C₈H₉BrO₂. Calculated (%): C 44.3, H 4.2, Br 36.8.

Ethylenebis[phenyl(o-methoxymethoxyphenyl)phosphine Oxide] (II). With stirring, to a mixture of 1.95 g of Mg and 40 ml of THF were added dropwise 1.5 g of (I), and then at 40-50° a solution of 13.8 g of (I) in 30 ml of THF. The mixture was stirred for 1 h at 50°, diluted with 70 ml of THF, 10.4 g of ethylenebis(pheny-phosphinic chloride) (mp 180°) was added in small portions at 0°, and the mixture was stirred for 2 h at 60-65°. After 12 h 100 ml of 2 N NH₄Cl solution was added dropwise to the mixture at 0°, and then 100 ml of chloroform was added at 20°. The organic layer was separated, washed with 100 ml of 2 N NaOH solution, then with water, dried over Na₂SO₄, concentrated *in vacuo*, and the residue was recrystallized from benzene to give 8.2 g (50%) of (II), mp 197-199°. Found (%): C 65.6, H 5.8, P 11.5. $C_{30}H_{32}P_2O_6$. Calculated (%): C 65.6, H 5.9, P 11.3.

 $\frac{\text{Ethylenebis[phenyl(o-hydroxyphenyl)phosphine oxide] (III).}{\text{of } 3.4 \text{ g of (II)} \text{ in } 25 \text{ ml of alcohol was added } 20 \text{ ml of conc. HCl and the mixture was refluxed for 3 min.} The precipitate was separated and washed with boiling alcohol. We obtained 2.4 g (83%) of (III), mp 342-344°. Found (%): C 67.4, H 5.4, P. 13.5. C_{26}H_{24}P_{2}O_{4}. Calculated (%): C 67.5, H 5.2, P. 13.4.}$

1,2,7,8-Dibenzo-3,6-diphospha-3,6-dioxo-3,6-diphenyl-15-crown-5 (IV). A mixture of 2.2 g of (III), 15 ml of DMF, and a solution of 0.22 g of Na in 5 ml of alcohol was heated for 2 h at 100-110° (N₂), after which a solution of 0.68 g of β,β' -dichlorodiethyl ether in 40 ml of DMF was added and the mixture was heated for 18 h at 115-120°. The precipitates were separated and the filtrate was concentrated *in vacuo*. The residue was dissolved in 100 ml of chloroform, washed with 50 ml of 3 N NaOH solution, then with water, and dried over Na₂SO₄. The solvent was removed, and the residue was extracted with boiling benzene. We obtained 1.1 g (43.5%) of (IV), mp 224-225°. Found (%): C 67.4, H 5.8, P 11.7. C₃₀H₃₀P₂O₅. Calculated (%): C 67.7, H 5.7, P 11.6.

CONCLUSIONS

We synthesized a 15-membered organophosphorus macrocycle with twophosphine oxide groupings and polyether units, and specifically 1,2,7,8-dibenzo-3,6-diphospha-3,6-dioxo-3,6dipheny1-15-crown-5.

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POLARIZABILITY ANISOTROPY OF ETHYLENE OXIDE AND ETHYLENE SULFIDE

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A study of three-membered rings, including those that contain a heteroatom, is of great interest due to the practical significance of their derivatives, as well as the specific traits of the electronic structure, and consequently the chemical and physical properties of small rings. One of the more important characteristics of molecules and bonds is the polarizability anisotropy. Relative to the polarizability ellipsoids (PE) of ethylene oxide (I) and ethylene sulfide (II) it was indicated that they cannot be expressed as the tensor sums of the usual additive parameters of the bonds in the ring [1-4]. Consequently, the PE of these molecules have to be determined as a whole, independent of their additive components. The PE of (I) and (II) are characterized by three major mutually perpendicular axes: b₁) along the axis of symmetry of the ring, b₂) in the plane of the ring, and b₃) perpendicular to the plane of the ring. In order to determine the values of the axes of the PE of molecules it is necessary to solve a system of three equations, which include the total polarizability, the Kerr constant (KC), and the molecular anisotropy (MA), which is determined from the degree of polarization of the Rayleigh light-scattering [5, 6].

Due to the difficult availability of data on light depolarization, indirect methods were used previously, which were based on deriving the values of the major axes of the PE from an examination of the molecular refractions and KC of (I) and (II), and of their derivatives with polar substituents of known structure [1, 2, 4, 7]. This means that any possible manifestations of intramolecular interactions in the polarizability anisotropy are neglected. At the present time it has become possible to determine the PE of (I) and (II) directly by employing the data on the MA.

We determined the KC and MA of (I) and (II). The total polarizabilities were calculated from the experimentally found values of the molecular refractions as reported in [5]. The obtained results are given in Table 1.

As can be seen from Table 1, the KC of (I) and (II) practically coincide with those determined previously. The dipole moments of the studied compounds are well known [11], and consequently were not redetermined.

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