2,4-DICHLOROMETHYL-1,5-DIPHENOXY-3-THIAPENTANE IN THE SYNTHESIS OF OXATHIANE CROWN ETHERS

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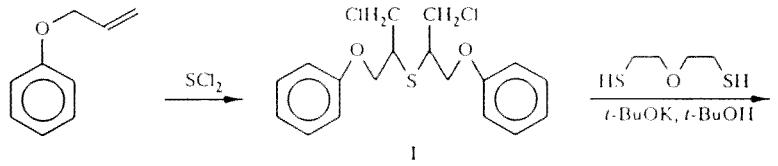
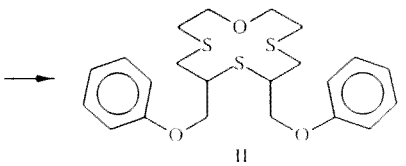
The most common method for the synthesis of macrocycles containing sulfur is the interaction of dihalogenoderivatives with dithiols of various structures [1-3]. We are the first to use for the synthesis of thiacrown ethers 2,4-dichloromethyl-1,5-diphenoxy-3-thiapentane (I) made in high yield and regioselectivity by the reaction of sulfur dichloride with allyl phenyl ether [4]:



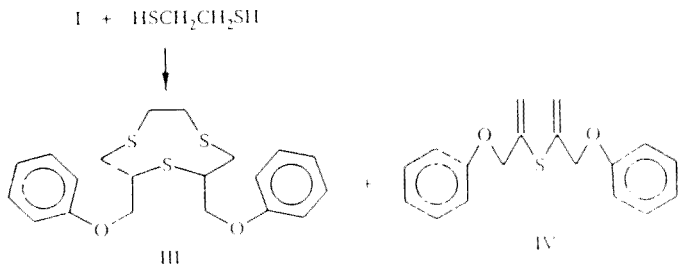
I



II

Compound I was treated with 2,2′-dimercaptoethyl ether by boiling with potassium *tert*-butoxide in *tert*-butanol for 6 h. 6,8-Diphenoxymethyl-1-oxa-3,7,10-trithiacyclododecane (II) was isolated from the reaction mixture in 31% yield after treatment with ether and water. The ^{1}H NMR spectrum of this compound contains signals at 3.1-3.5 (10H, m, CHS, CH_2S), 4.0-4.2 (8H, m. CH_2O), 6.95, 7.20 ppm (10H, m, ArH). The mass spectrum contained peaks with *m/z* 329 $(M-PhO)^+$ and 222 $(M-2PhO)^+$ but no molecular ion. Elemental analysis: calc. for $C_{22}H_{28}O_3S_3$: C 60.52, H 6.46%. Found: C 59.57, H 6.12%.

Reaction of the dichlorosulfide I with 1,2-ethanedithiol under the same conditions gave the corresponding 9-membered heterocycle, 2,9-diphenoxymethyl-1,4,7-trithiacyclononane (III), in very low yield (5%), contaminated with the divinylsulfide (IV) which arises from dehydrochlorination of the initial dichlorosulfide I:



III IV

The ^{1}H NMR spectrum of compound III contains signals at 3.0-3.4 (m, CHS, CH_2S), 4.35 (m, CH_2O), 5.3-6.2 (m, $CH_2=$), 6.95 and 7.30 ppm (m, ArH).

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