LETTERS TO THE EDITOR

NOVEL THIACROWN ETHERS INCORPORATING THIOACETAL GROUPS

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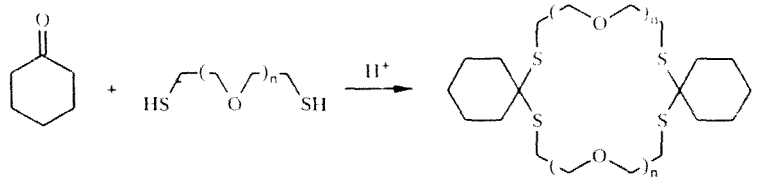
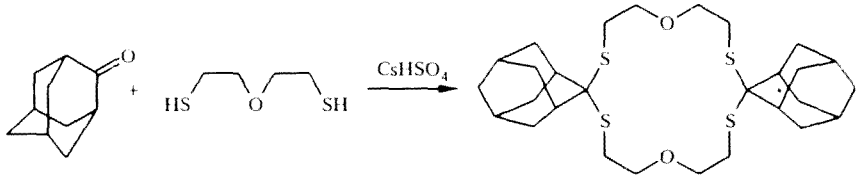
Thiacrown ethers are of considerable interest as selective complexing agents for heavy metal ions [1, 2]. However some of their structural types, particularly thioacetals, are represented by single examples [1-5]. Their conformational properties [4, 5] and the possibility of introducing highly lipophilic substituents into the S–C–S unit [5] are interesting. In this paper we report the syntheses of new lipophilic thiacrown ethers of this type starting from cyclic ketones (cyclohexanone, adamantanone) and dithiols prepared from the corresponding oligoethylene glycols.



I n=1; II n=2



III

Cyclization of equimolar amounts of the reagents was carried out by dehydration on boiling in benzene in the presence of TsOH (method A) or with a new reagent, cesium hydrogen sulfate, which was prepared by reaction of a 1:2 molar ratio of cesium carbonate and sulfuric acid (method B). Use of $CsHSO_4$, which is both an acid catalyst and a template reagent, thanks to the presence of the large cesium ion, increased the yield of thiacrown ether I and permitted the preparation of compound III which could not be isolated when TsOH was used. Compounds I and II were separated by column chromatography (silica gel, eluents chloroform and 1:1 chloroform–ethanol) while compound III was purified by crystallization from benzene.

Thiacrown Ether (I, $C_{20}H_{36}O_2S_4$). Viscous oil; yield 40% (A) and 80% (B). ^1H NMR Spectrum (250 MHz, $CDCl_3$): 1.43 (4H, m, CH_2), 1.62 (8H, m, CH_2), 1.82 (8H, m, CH_2), 2.79 (8H, t, J = 7 Hz, CH_2S), 3.60 (8H, t, J = 7 Hz, CH_2O). Mass spectrum, m/z (relative intensity, %): 436 (1, M^+), 219 (22), 185 (1), 159 (12), 141 (100), 114 (60), 81 (65), 61 (75).

Thiacrown Ether (II, $C_{24}H_{44}O_4S_4$). Viscous oil, yield 48% (A). ^1H NMR Spectrum (250 MHz, $CDCl_3$): 1.41 (4H, m, CH_2), 1.60 (8H, m, CH_2), 1.79 (8H, m, CH_2), 2.78 (8H, t, J = 7 Hz, CH_2S), 3.60 (16H, m, CH_2O). Mass spectrum, m/z (relative intensity, %): 442 (3), 360 (63), 301 (15), 212 (22), 180 (32), 124 (43), 103 (54), 45 (100).

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Thiacrown Ether (III, $C_{28}H_{44}O_2S_4$). Yield 50% (B). M.p. 224°C. ^{1}H NMR Spectrum (360 MHz, $CDCl_3$): 1.62 (8H, m, CH_2), 1.70 (4H, br.s, CH), 1.89 (8H, m, CH_2), 2.52 (8H, m, CH, CH_2), 2.84 (8H, t, J = 6.5 Hz, CH_2S), 3.71 (8H, t, J = 6.5 Hz, CH_2O). Mass spectrum *m/z* (relative intensity, %): 540 (3), 404 (2), 270 (22), 238 (13), 202 (5), 166 (100).

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