Chinese Chemical Letters Vol. 10, No. 8, pp. 665–666, 1999

Synthesis of Arsamacrocyclic Polyethers

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Abstract: The synthesis of eight new arsamacrocyclic Polyethers was described. The structures of these compounds were characterized by elemental analysis, IR, ^{1}H-NMR and MS.

Keywords: Macrocyclic compound, arsamacrocyclic polyether, synthesis.

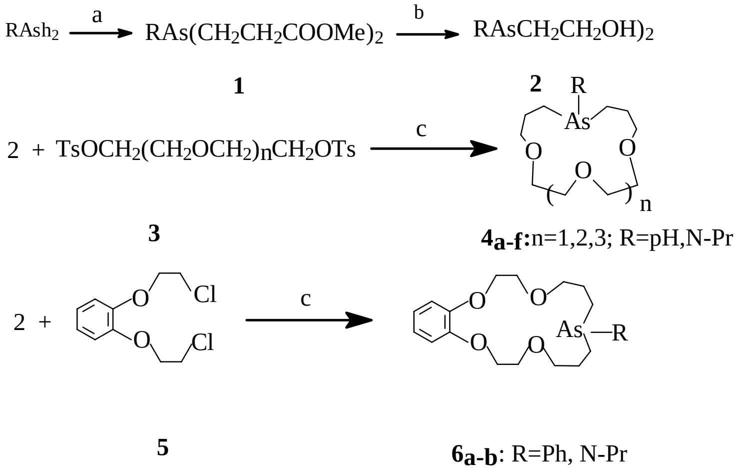
The synthesis of macrocyclic compounds and the study of guest complexation behavior of such hosts have been an active area of research in recent years. Our interest has been focussed on heteromacrocyclic polyethers which have soft ligating sites, appropriate for coordination of transition metals. In particular, heteromacrocycles which contain tricoordinated arsenic atoms as soft ligating sites not only possess a high complex-forming capacity but can also stabilize transition metals in their lowest valence states. A series of arsamacrocyclic polyethers have been synthesized by introducing tricoordinated arsenic atoms into the ring of crown ethers.

The synthesis of the title compounds are reported in this paper. **Scheme1**outlines the synthesis of these compounds. Among them, the compounds **4** were prepared by cyclocondensation of 4-phenyl-4-arsa-1,7-heptanediol **2** with the appropriate ditosylate $T_SOCH_2(CH_2OCH_2)_nCH_2OT_S$ **3** under high-dilution conditions[1] in the presence of organic alkali in dry THF. Similarly, the reaction of the intermediate **2** with *o-bis* (2-chloroethoxy) benzene **5** results in the formation of compounds **6** under the same conditions.

2 was prepared by treatment of dimethyl 4-phenyl-4-arsaheptanediate **1** with $LiAlH_4$ in dry ether [2]. In the presence of sodium ethanolate in absolute ethanol, the compound **1** was prepared by addition reaction of methyl acrylate with phenylarsine. Because phenylarsine is not commercially available, it was obtained by reducing the corresponding arsonic acid with zinc amalgam under acidic conditions. The intermediates **3** and **5** can be easily prepared [3].

Typical experimental procedure: The diol **2** (10mmol) and t-BuONa (22mmol) in THF (100mL) and the ditosylate **3** (10mmol) in THF (100mL) were added dropwise simultaneously from separate constant addition funnels to a round-bottom flask initially charged with 0.5L of boiling THF with vigorous stirring. Keep refluxing for 36 h after the addition was completed. The reaction mixture was concentrated in vaccum. The re-

Scheme 1



Conditions: a. CH_2=CHCOOMe, b. $LiAlH_4$, c. t-BuONa/THF

Table I Melting points and yields of title compounds

Compd	n	R	Formula	Mp,°C	Yield,%
4a	1	Ph	$C_{16}H_{25}AsO_3$	69-70.5	41
4b	2	Ph	$C_{18}H_{29}AsO_4$	42-44	32
4c	3	Ph	$C_{20}H_{33}AsO_5$	below 25	32
4d	1	n-Pr	$C_{13}H_{27}AsO_3$	below 25	24
4e	2	n-Pr	$C_{15}H_{31}AsO_4$	below 25	22
4f	3	n-Pr	$C_{17}H_{35}AsO_5$	below 25	17
6a	-	Ph	$C_{22}H_{29}AsO_4$	112-113	37
6b	-	n-Pr	$C_{19}H_{31}AsO_4$	66-67	26

sidue was dissolved in ether (200mL) and washed with saturated aqueous ammonium chloride(100mL),water(2×100mL), dried over $MgSO_4$. The solution was concentrated under reduced pressure to give an oil or solid which was chromatographed on silica gel with benzene/ether (9:1 v/v) as eluent to yield the products. residue was dissolved in ether (200mL) and washed with saturated aqueous ammonium The above operations must be performed under dry nitrogen or argon atmosphere and in absolute anhydrous conditions. The yields of cyclization were in 27-40%, and eight new title compounds have been identified by elemental analysis, IR, ^{1}H-NMR and MS.

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Received 2 February 1999