J. Chem. Research (S),
1999, 522–523
J. Chem. Research (M),
1999, 2201–2217

3-Allylsalicylaldehyde and 3-Allylsalicylic Acid Derivatives: Synthesis and Conversion to Allyl-crown Compounds as New Potential Precursors for Polymer Supported Crown Compounds

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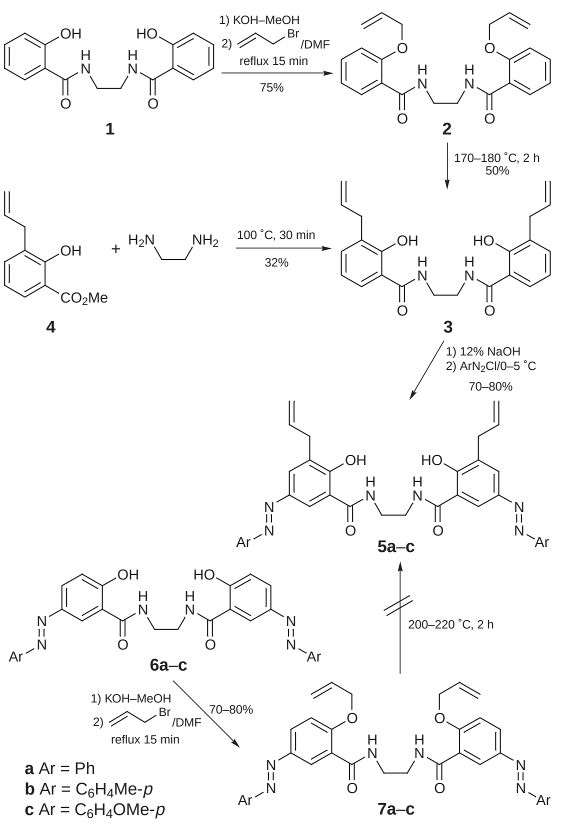
3-Allylsalicylaldehyde and methyl 3-allylsalicylate are converted in moderate to good yields into the new diallyl substituted 14–16, 23–25-membered macrocyclic crown diamides **8a–h**, **10a–c**, **15a**,**b** and the 21–23-membered dithiatetraaza-crown compounds **17a–g**, **18a–c**.

The use of crown ethers and analogous compounds on a large scale for industrial purposes is inhibited by their expense. A potentially useful way around this problem lies in attaching the complexing agent to a polymeric backbone and thus facilitating its retrieval. Large numbers of both soluble and insoluble polymers containing crown ethers have been developed and have been the subject of many reviews.[1,7,9] Their utilization in chiral recognition[10,11,13] and as phase-transfer catalysts have been discussed.[15] Also, their cation binding properties[20,21] and their use in analytical applications have been studied.[22,27]

Recently, we described the utility of salicylaldehyde and salicylic acid derivatives as efficient building blocks in the synthesis of useful crown compounds.[28–32] As a part of a program directed towards the synthesis of polymer supported crown compounds, we describe here, our studies concerning the synthetic utility of 3-allylsalicyladehyde and 3-allylsalicylic acid derivatives in the synthesis of allyl substituted crown compounds. The latter constitute potential precursors for the synthesis of polymer supported crown compounds through chemical bonding and transformations of the allyl substituents. 14–16 membered crown lactams **8a**–**f** and 23–25-membered crown lactams **10a**–**c**, **15a**,**b** with diallyl substituents were prepared as shown in Schemes 2–4 in moderate to good yields. Also, 21–23-membered dithiatetraaza-crown compounds **17a**–**g**, **18a**–**c** with allyl substituents were prepared (Scheme 5) in good to excellent yields.

The first synthetic strategy starts with the synthesis of the new 1,2-bis(3-allyl-2-hydroxybenzoylamino)ethane **3**. Two routes were investigated for the synthesis of compound **3** as shown in Scheme 1. Thus, compound **3** was obtained in 50% yield by heating 1,2-bis(2-allyloxybenzoylamino)ethane **2** at 170–180 °C (conditions were optimized to obtain the best yield). The latter was obtained by reacting the dipotassium salt of 1,2-bis(2-hydroxybenzoylamino)ethane **1** with allyl bromide. Alternatively, condensation of methyl 3-allyl-2-hydroxybenzoate **4** with ethylenediamine on a steam-bath gave compound **3** in 32% yield. Conversion of compound **3** into the bis-azo derivatives **5a**–**c** was accomplished by direct coupling with the appropriate diazonium salts in aqueous NaOH solution. Alternative attempts to rearrange the 1,2-bis(5-arylazo-2-allyloxybenzoylamino)ethanes **7a**–**c** into compounds **5a**–**c** were unsuccessful. Compounds **7a**–**c** were prepared by reacting the dipotassium salt of 1,2-bis(5-arylazo-2-hydroxybenzoylamino)ethanes **6a**–**c** with allyl bromide.



Scheme 1

Reaction of the dipotassium salts of the bis(2-hydroxybenzoylamino)ethane **3**, **5a**–**c** with the appropriate dibromo compounds in DMF gave the corresponding 14–16-membered ring macrocycles **8a**–**h** (Scheme 2). Similarly, the 24-membered macrocycles **10a**–**c** were prepared from the dipotassium salts of **3** and **5c** and 1,4-bis(2-chloromethylphenoxy)butanes **9a**,**b** (Scheme 3).

The second synthetic strategy depends upon the synthesis of the new bis(6-allyl-2-chloromethylphenoxy)alkanes **14a**–**c**. The latter were prepared as shown in Scheme 4 starting with 3-allyl-2-hydroxybenzaldehyde **11**. Thus, reacting the dipotassium salt of **11** with the appropriate dibromoalkanes in DMF gave the corresponding bis(carbonyl)ethers **12a**–**c**. Sodium tetrahydroborate reduction of the latter gave the corresponding bis(hydroxymethyl)ethers **13a**–**c**. Reaction of the latter with

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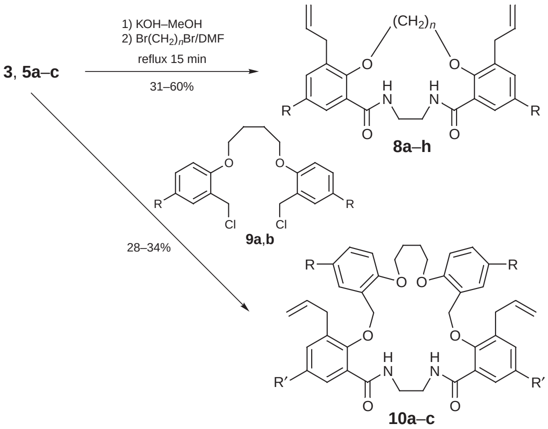
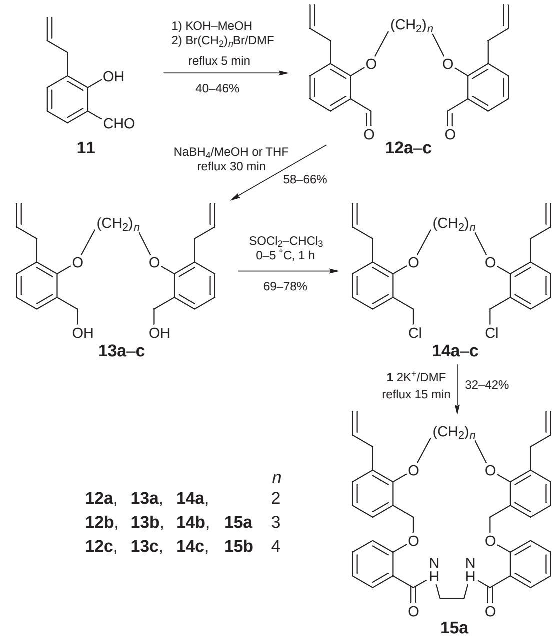


	n	R
8a	2	H
8b	3	H
8c	2	p-MeC$_6$H$_4$N$_2$
8d	2	p-MeOC$_6$H$_4$N$_2$
8e	3	PhN$_2$
8f	3	p-MeC$_6$H$_4$N$_2$
8g	3	p-MeOC$_6$H$_4$N$_2$
8h	4	p-MeOC$_6$H$_4$N$_2$

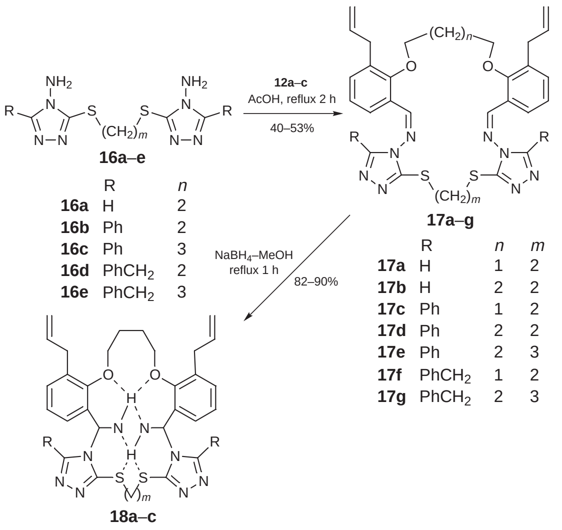
	R	R′
9a	Cl	
9b	p-MeC$_6$H$_4$N$_2$	
10a	Cl	H
10b	Cl	p-MeOC$_6$H$_4$N$_2$
10c	p-MeC$_6$H$_4$N$_2$	H

Schemes 2, 3



	n
12a, **13a**, **14a**,	2
12b, **13b**, **14b**, **15a**	3
12c, **13c**, **14c**, **15b**	4

Scheme 4



	R	n
16a	H	2
16b	Ph	2
16c	Ph	3
16d	PhCH$_2$	2
16e	PhCH$_2$	3

	R	n	m
17a	H	1	2
17b	H	2	2
17c	Ph	1	2
17d	Ph	2	2
17e	Ph	2	3
17f	PhCH$_2$	1	2
17g	PhCH$_2$	2	3

	R	m
18a	H	2
18b	Ph	2
18c	Ph	3

Scheme 5

thionyl chloride in CHCl$_3$ gave the desired bis(chloromethyl)ethers **14a**–**c**. Reaction of the latter with the dipotassium salt of **1** in DMF gave the bis-allyl 23,24 membered macrocycles **15a**,**b** (Scheme 4).

Similarly to our recent reported[31] synthetic approaches towards thiaazacrown compounds, condensation of the bis(carbonyl) ethers **12a**–**c** with the appropriate bis(4-amino-1,2,4-triazol-3-ylsulfanyl)alkanes **16a**–**e** in acetic acid gave the corresponding bis-allyl 21–23-membered macrocycles **17a**–**g**. Sodium tetrahydroborate reduction of **17b**, **d**,**e** gave high yields of the corresponding diallyldioxadithiatetraaza macrocycles **18a**–**c** (Scheme 5). Since our attempts to acylate the latter under different conditions were unsuccessful we believe that these compounds exist in the hydrogen bonded form shown.

The structures of all new acyclic and macrocyclic compounds are consistent with data obtained from MS, IR, ^{1}H, ^{13}C NMR and elemental analyses.

Techniques used: ^{1}H, ^{13}NMR, IR, MS

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Received, 8th March 1999; Accepted, 18th May 1999
Paper E/9/01795J

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