

Synthesis of the first tris(crown formazan)

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Abstract—A synthesis of tris(crown formazan) **2** from the corresponding hexakis(acetamidophenoxymethyl)benzene **11** by hydrolysis with an ethanolic solution containing hydrochloric acid followed by diazotization and subsequent coupling with cyanoacetic acid in pyridine containing CuSO_4 is described.

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The chemistry and diverse applications of acyclic formazans as well as monocyclic crown-formazans have received much attention and are the subject of a large number of reviews.¹ Many macrocyclic formazans have been synthesized and their applications in selective metal extraction² and determination³ were studied. Such applications depend mainly on the cavity size of the macrocyclic crown formazans as well as on the substituents in the macrocycle. In this respect we recently reported the synthesis of macrocyclic formazans **1** and studied their behavior in spectrophotometric determination of lithium as well as carriers in cesium ion selective electrodes.⁴

Moreover, interest has recently been directed towards the synthesis of multi-site crown compounds.⁵ These multi-site molecular receptors are capable of binding

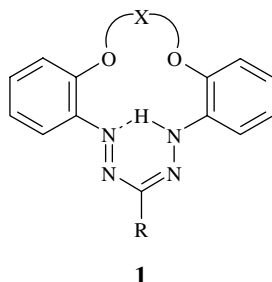
two or more guest metal cations. In continuation of these studies we report here the first synthesis of the tris(crown formazan) **2**, which is expected to be useful analytically on account of its ability to bind more than one metal ion.

Two strategies have been investigated for the synthesis of the target compound **2**. In the first strategy (Scheme 1) we studied the synthesis of crown formazan **3**, which should undergo cyclotrimerization upon heating with a catalytic amount of $\text{CpCo}(\text{CO})_2$ to give the target compound **2**.⁶

For this purpose the bis(acetamido) derivative **6** was prepared in 70% yield as outlined in Scheme 2, by reacting the K-salt **5** (obtained upon treatment of acetamidophenol **4** with KOH) with 1,4-dibromo-2-butyne in boiling DMF. Compound **6** underwent acid hydrolysis upon treatment with an ethanolic solution containing hydrochloric acid to give an 85% yield of the corresponding bis(amine hydrochloride) **7**. Unfortunately, diazotization of **7** with NaNO_2 in hydrochloric acid followed by coupling with cyanoacetic acid in pyridine containing CuSO_4 did not yield the corresponding macrocyclic formazan **3**. The reaction instead gave a mixture of products that were difficult to separate and were not characterized.

It is also noteworthy that the macrocyclic formazan **9** could not be obtained by coupling of the corresponding bis(diazonium salt) **8**^{7,8} with cyanoacetic acid (Scheme 3).

In search of an expedient pathway to prepare **2** our attention focused on compound **12** as a precursor, which should undergo diazotization and subsequent coupling

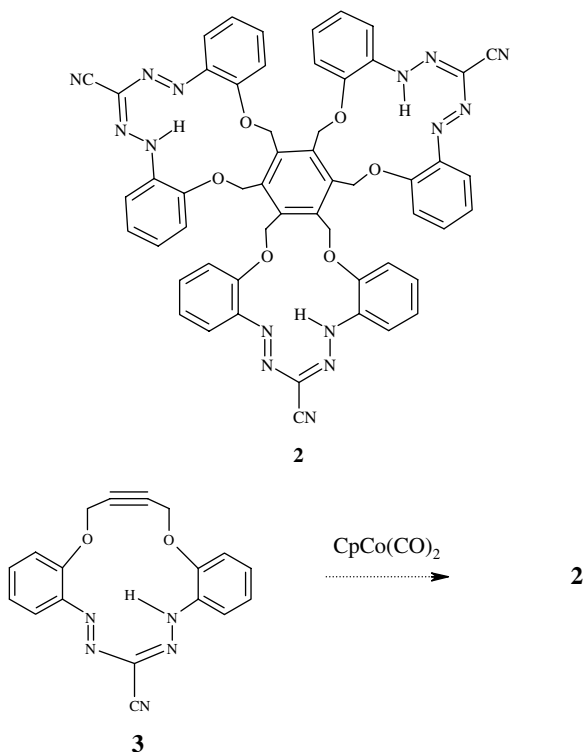


1

X, = $(\text{CH}_2)_3$, $(\text{CH}_2)_4$, $\text{CH}_2\text{C}(\text{=CH}_2)\text{CH}_2$, $\text{CH}_2\text{CH}(\text{OH})\text{CH}_2$,
 $(\text{CH}_2)_2\text{-O-(CH}_2)_2$, R = H, Ph, CN, ArSO_2

Keywords: Alkylation; Diazotization; Coupling; Macrocyclic formazan.

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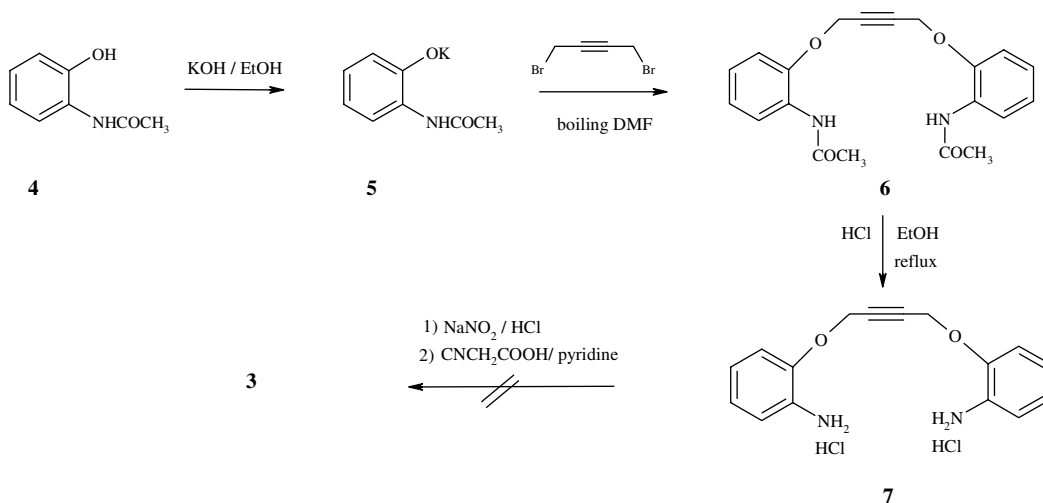


Scheme 1.

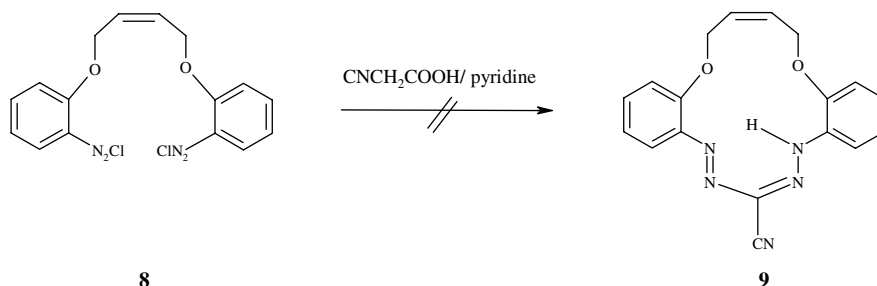
with cyanoacetic acid to furnish the target molecule **2** (Scheme 4). Thus, six-fold substitution of hexakis(bromomethyl)benzene **10**⁹ with 6 equiv of the potassium salt **5** in refluxing DMF gave an 82% yield of the corresponding hexakis(acetamidophenoxymethyl)benzene **11** as colourless crystals. Treatment of the latter with an ethanolic solution containing hydrochloric acid gave the corresponding hexakis(amine hydrochloride) **12** in 78% yield. Diazotization with NaNO₂ in hydrochloric acid followed by coupling with cyanoacetic acid in pyridine containing CuSO₄ and subsequent purification gave the corresponding tris(crown formazan) **2** as deep red crystals in 10% yield.¹⁰

The structure of **2** was confirmed by IR, NMR and MS as well as elemental analysis. The symmetry of compound **2** is manifested by a singlet characteristic of the six equivalent OCH₂ groups in the ¹H NMR spectrum. The structure of compound **2** was further confirmed by comparison with those of the related crown formazans **13** and **14**.

Compound **13** was synthesized as described^{4c} by coupling of the corresponding bis(diazonium salt) with cyanoacetic acid in pyridine containing CuSO₄. Compound **14** was prepared as outlined in Scheme 5. Thus, reaction of the K-salt **5** with 1,3-bis(bromomethyl)benzene **15** in boiling DMF yielded 75% of the correspond-



Scheme 2.



Scheme 3.

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