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SYNTHESIS AND PROPERTIES OF THE FIRST INTRAMOLECULAR ARENEDIAZONIUM CATION-CROWN ETHER COMPLEX

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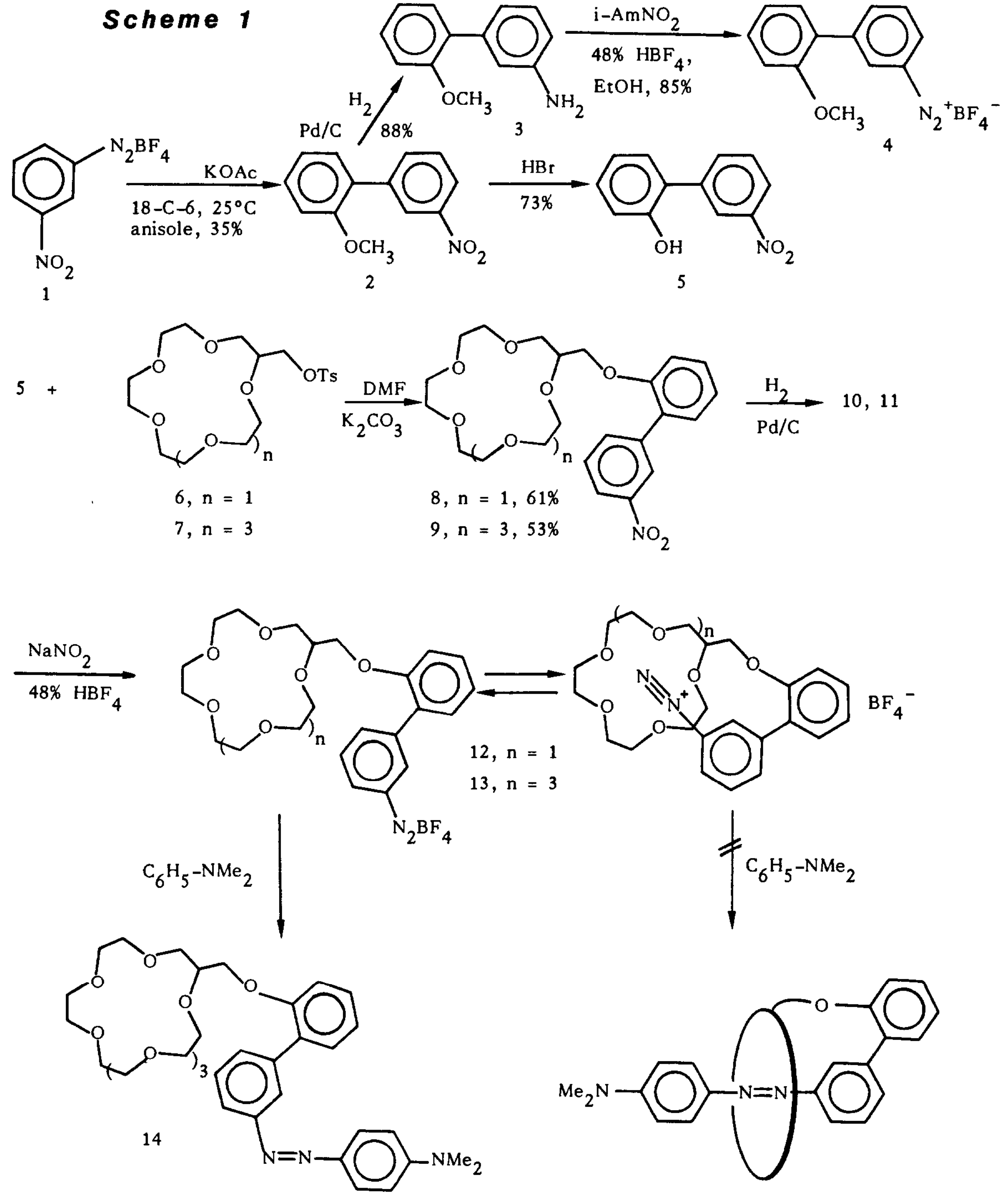
Summary: The first intramolecular arenediazonium cation-crown ether complex is reported along with attempts to form a molecular knot from it.

In the first report of arenediazonium cation complexation, it was noted that attempts to synthesize an azoarene threaded through the crown hole had failed.[1] Only non-encircled, conventional products were obtained. This was apparently due to the highly dynamic character of such complexes in solution which precluded formation of the desired rotaxane.[2] It is only in the solid phase that the complexes appear to be stable.[3] A further difficulty is that crown complexation diminishes the reactivity of the bound arenediazonium cation in several reactions[4] including azo-coupling.[5] We originally thought that intramolecular complexation of an arenediazonium cation might sufficiently enhance complex stability that hitherto unsuccessful arenediazonium cation coupling reactions might lead to a rotaxane or molecular knot. Similar tethering strategies have been successfully employed in recent rotaxane syntheses.[6] The purpose of this study was therefore to prepare the first intramolecular arenediazonium-crown ether complex based on lariat ether chemistry[7] and to attempt formation of a molecular knot from it. We report the results of that effort here.

The 21-crown-7 system was chosen for the macroring portion of the complex because this unit is known to form the most stable complexes with arenediazonium cations.[3,4] An examination of C-P-K molecular models suggested that an ortho-linkage might have geometrical advantages, but ortho-substituted arenediazonium cations form unstable complexes with crowns. The point

Scheme 1


N$_2$BF$_4$
NO$_2$
1
KOAc
18-C-6, 25°C
anisole, 35%
H$_2$
Pd/C
88%
OCH$_3$
NH$_2$
3
i-AmNO$_2$
48% HBF$_4$,
EtOH, 85%
OCH$_3$
N$_2^+$BF$_4^-$
4
OCH$_3$
NO$_2$
2
HBr
73%
OH
NO$_2$
5
5 +
OTs
6, n = 1
7, n = 3
DMF
K$_2$CO$_3$
8, n = 1, 61%
9, n = 3, 53%
NO$_2$
H$_2$
Pd/C
10, 11
NaNO$_2$
48% HBF$_4$
N$_2$BF$_4$
12, n = 1
13, n = 3
BF$_4^-$
C$_6$H$_5$-NMe$_2$
C$_6$H$_5$-NMe$_2$
14
NMe$_2$
Me$_2$N

of attachment to the aromatic ring was therefore made the meta position. Our experience with lariat ethers[9] suggested that the most effective tether would be a flexible one. This would allow preparation of an arylamine which was first accessible to diazotizing reagents and could then rotate into position for crown complexation. The synthesis of an intramolecular crown-diazonium cation complex, based on the 2-hydroxy-3'-nitrobiphenyl system, is shown in scheme 1.

2-Methoxy-3'-nitrobiphenyl (2) was prepared was prepared in 35% yield by the phase transfer Gomberg Bachmann reaction.[8] Demethylation[9] gave 2-hydroxy-3'-nitrobiphenyl (5) which was allowed to react with $TsOCH_2$-15-crown-5 (6) or -21-crown-7 (7), prepared in the usual fashion from the corresponding hydroxymethyl crown.[7a,10] The nitrobiphenylated lariat ethers, 8 and 9, were reduced (95%, 98%) to obtain the free amines. Diazotization of these amines gave 12 as a red gum [IR($CHCl_3$) 2272 cm^{-1}], and 13 as a colorless foam [glass transition 45-50°C, decomposition, 70-73°C, IR ($CHCl_3$) 2290 cm^{-1}].[11] Compound 4 was prepared to facilitate spectral comparison. We refer to the intramolecular complex as an "ostrich complex" because of the popular belief that this bird puts its head in a hole when endangered.

Evidence for ostrich complexation was obtained using ^1H-NMR and infrared analysis. The proton spectrum of 12 in $CDCl_3$ showed a relatively sharp $-OCH_2CH_2-$ band in the 3-5 PPM region while that for 13 was considerably broadened and contained numerous shoulders. Such behavior is characteristic of crown ether arenediazonium cation complexation.[3] Fifteen-membered 12 exhibited an IR absorption ($CHCl_3$) at 2272 cm^{-1} which shifted to 2302 cm^{-1} when one equivalent of 18-crown-6 was added. In contrast, the diazonium vibration of 13 was observed at 2290 cm^{-1} in either the presence or absence of added crown. Unfortunately, all attempts to prepare a molecular knot from 13 by coupling with N,N-dimethylaniline led only to the expected azo-crown, 14.[12] The failure of the ostrich complex (13) to convert to a knot was confirmed by examining the ^1H-NMR spectrum of azo compound 14 in the presence and absence of $Eu(fod)_3$. The macroring of 14 shifted from 3.65 to 7.05-7.15 ppm. Had an azo linkage been threaded through the hole, no such shift would have been observed.

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11. Compound 13: ^{1}H-NMR ($CDCl_3$): 2.53 (br s, imp); 3.27-4.20 (m, 29H, spikes at 3.30, 3.53, 3.67); 6.80-7.60 (m, 4H); 7.97-8.67 (m, 3H), 9.70 (s, 1H). Anal, Calcd for $C_{27}H_{37}BF_4N_2O_8$: C, 53.65%, H, 6.16%. Found, 51.19%; H, 6.51%. Since the diazonium compounds are difficult to purify and characterize, full analytical data were obtained at the amine stage. Anal. for 10: $C_{23}H_{31}NO_6$: C, 66.17%; H, 7.48%; N, 3.35%. Found: C, 66.10; H, 7.25; N, 3.33. Anal for 11: $C_{27}H_{39}NO_8$: C, 64.14; H, 7.77; N, 2.77. Found: C, 64.02; H, 7.63; N, 2.47.

12. Red oil, 14. ^{1}H-NMR ($CDCl_3$): 3.10 (s, 6H); 3.57-4.10 (m, 29H, spikes at 3.60, 3.67, 3.70); 6.83-8.70 (m, 8H). IR (neat) 1600, 1370, 1120 (br), 760 cm^{-1}.

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