1.93 (3 H, s), 2.3–2.6 (5 H, m), 3.93 (2 H, s), 5.0 (1 H, s), 5.23 (1 H, s). HRMS: $C_{11}H_{15}O$ (M^+ – Br) requires 163.1123, found 163.1157. Further elution of the column furnished a 2:1 diastereomeric mixture of the acetoxy bromo enones **11b** (806 mg, 46%) as an oil.

6-Methoxy-1,2,6-trimethylbicyclo[3.2.1]octan-3-one (12a and 13a). Radical cyclization of bromo enone **11a** (275 mg, 1 mmol) in 55 mL of benzene with TBTH (0.3 mL, 1.1 mmol) and AIBN (catalytic) for 1.5 h as described for **2a** and purification over 15 g of silica gel furnished the cyclized compounds **12a** and **13a** (1:1, 146 mg, 75%) as oils. These were further purified by bulb-to-bulb distillation (bath temperature 135 °C/10 Torr).

6-Acetoxy-1,2,6-trimethylbicyclo[3.2.1]octan-3-one (12b and 13b). Radical cyclization of bromo enone **11b** (303 mg, 1 mmol) in 55 mL of benzene with TBTH (0.3 mL, 1.1 mmol) and AIBN (catalytic) for 1.5 h and purification over 15 g of silica gel with 3:1 ethyl acetate–hexane as eluent furnished first the acetoxy-migrated product **14** (50 mg, 22%) as an oil. IR (neat): 1740, 1670, 1380, 1240, 1040 cm^{-1}. ^1H NMR (60 MHz, CCl_4): δ 0.95 (3 H, d, J = 6.5 Hz), 1.7 (3 H, s), 1.92 (3 H, s), 2.0 (3 H, s), 2.0–2.4 (5 H, m), 3.9 (2 H, m). Further elution of the column furnished the cyclized acetates **12b** and **13b** (163 mg, 73%) as oils. These were further purified by bulb-to-bulb distillation (bath temperature 155 °C/10 Torr).

Acknowledgment. We thank the INSA, New Delhi, for the financial support and one of us (P.H.) wishes to thank the CSIR, New Delhi, for the award of a research fellowship. We also thank Professor G. S. Krishna Rao for the generous gift of the (*S*)-carvone used in this work.

Registry No. 1, 2244-16-8; **2a** (isomer 1), 127400-19-5; **2a** (isomer 2), 127400-27-5; **2b** (isomer 1), 127400-33-3; **2b** (isomer 2), 127400-35-5; **2c** (isomer 1), 127400-29-7; **2c** (isomer 2), 127400-36-6; **2d** (isomer 1), 127400-30-0; **2d** (isomer 2), 127400-37-7; **2e** (isomer 1), 127400-31-1; **2e** (isomer 2), 127400-38-8; **2f**, 127400-26-4; **3a**, 127470-66-0; **3b**, 127400-34-4; **3c**, 127400-39-9; **3d**, 127470-74-0; **3e**, 127470-75-1; **4a**, 127470-67-1; **4b**, 127470-71-7; **4c**, 127470-72-8; **4d**, 127400-42-4; **4e**, 127400-43-5; **5**, 127400-20-8; **6**, 127400-21-9; **7**, 127470-68-2; **8**, 127400-22-0; **9**, 127470-69-3; **10**, 85710-66-3; **11a** (isomer 1), 127400-23-1; **11a** (isomer 2), 127400-32-2; **11b** (isomer 1), 127400-28-6; **11b** (isomer 2), 127400-40-2; **12a**, 127400-24-2; **12b**, 127400-41-3; **13a**, 127470-70-6; **13b**, 127470-73-9; **14**, 127400-25-3.

Supplementary Material Available: Spectral data and HRMS (or analytical data) for the compounds **2b–e**, **3b–e**, **4b–e**, **11a–b**, **12a–b**, and **13a–b** (4 pages). Ordering information is given on any current masthead page.

The Development of a New Nitrating Agent: The Unusual Regioselective Nitration of Diphenylpolyethylene Glycols and Phenylpolyethylene Glycols with Trimethylsilyl Nitrate–BF_3OEt_2

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We have investigated the nitration of the following podands, 1-phenoxy-8-(2′-nitrophenoxy)-, 1-phenoxy-8-(4′-nitrophenoxy)-, and 1-(2′,4′-dinitrophenoxy)-8-phenoxy-3,6-dioxaoctane (**1**, **2**, and **3**), and 1-(2′,4′-dinitrophenoxy)-11-phenoxy-3,6,9-trioxaundecane (**4**), 1-phenoxy-3,6,9-trioxadecane (**5**), and 1-phenoxy-3,6,9,12-tetraoxatridecane (**6**), with trimethylsilyl nitrate catalyzed by BF_3OEt_2, which is soluble in nonpolar solvents. The reaction selectivity was measured by the ortho:para ratio of the nitrated products and was unusually large in CCl_4. The structures of all isolated products, 1,8-bis(2′-nitrophenoxy)-, 1-(2′-nitrophenoxy)-8-(4′-nitrophenoxy)-, 1,8-bis(4′-nitrophenoxy)-, 1-(2′,4′-dinitrophenoxy)-8-(2′-nitrophenoxy)-, and 1-(2′,4′-dinitrophenoxy)-8-(4′-nitrophenoxy)-3,6-dioxaoctane (**7**, **8**, **9**, **10**, and **11**), 1-(2′,4′-dinitrophenoxy)-11-(2′-nitrophenoxy)- and 1-(2′,4′-dinitrophenoxy)-11-(4′-nitrophenoxy)-3,6,9-trioxaundecane (**12** and **13**), 1-(2′-nitrophenoxy)- and 1-(4′-nitrophenoxy)-3,6,9-trioxadecane (**14** and **15**), and 1-(2′-nitrophenoxy)- and 1-(4′-nitrophenoxy)-3,6,9,12-tetraoxatridecane (**16** and **17**), were confirmed by the independent preparation of these compounds using a modification of Joeger's method. We have invented a new nitrating system (trimethylsilyl nitrate and BF_3OEt_2) and have shown that the selectivity (o/p ratio of nitrated products) is unusually high in CCl_4.

There have been several reports in the literature concerning aromatic nitration with unusual positional selectivity using naked nitronium ion generated in polar solvents.[1,2] Nonpolar solvents are usually preferable for the generation of naked nitronium ion, but examples of well-controlled aromatic nitrations in nonpolar solvents are rare.[1b] The nitrating agents commonly used are nitric acid in the presence of other acids, nitronium salts,[3] and nitrate esters.[1b,4,6] The nitronium ion (NO_2^+) generated from these agents is known to exist as a solvated species in most aromatic nitrations. When these reagents are used in solvents with heteroatoms, the reactivity and selectivity vary with the size of the solvated nitronium ion. In particular, it has been found that the interaction between nitronium ions and oxygen atoms is an important consideration in regioselective nitrations. For example, Olah et al. recorded the highest ortho selectivity (ortho/para ratio = o/p = 2.7 or 3.0) in the nitrations of anisole with NO_2PF_6–OEt_2 and *N*-nitro-2,4,6-collidinium tetrafluoroborate, respectively.[1,5] Benzene derivatives with properly placed oxygen atoms in side chains seem to promote the

(1) (a) Olah, G. A.; Lin, H. C.; Olah, J. A.; Narang, S. C. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 545. (b) Sparks, A. K. *J. Org. Chem.* **1966**, *31*, 2299.
(2) Eberson, L.; Radner, F. *Acc. Chem. Res.* **1987**, *20*, 53.
(3) Olah, G.; Kuhn, S.; Milinko, A. *J. Chem. Soc.* **1956**, *78*, 4257.
(4) Bordwell, F. G.; Garbisch, W., Jr. *J. Am. Chem. Soc.* **1960**, *82*, 3588. Kurz, M. E.; Yang, L. T. A.; Zahora, E. P.; Adams, R. C. *J. Org. Chem.* **1973**, *38*, 2271; **1981**, *46*, 3533.
(5) Cacace, F.; Giacomello, P.; Wolf, A. P. *J. Am. Chem. Soc.* **1980**, *102*, 3511.
(6) Knowless, J. R.; Norman, R. O. C. *J. Chem. Soc.* **1961**, 3888.

0022-3263/90/1955-4887$02.50/0

Table I. Distribution of Products in the Nitration of 1[a]

nitrating agent	Lewis acid	solv	2	3	8	9	10	o/p[b]
HNO_3/H_2SO_4 (20 equiv)	-	-	8.8	6.1	14.5	49.3	21.3	0.89
NO_2BF_4 (3 equiv)	-	CCl_4	26.7	49.6	8.3	10.7	4.7	0.65
NO_2BF_4 (3 equiv)	BF_3OEt_2 (1 equiv)	MeCN	31.6	22.9	27.7	14.1	3.6	1.66
Me_3SiONO_2 (3 equiv)	BF_3OEt_2 (1 equiv)	MeCN	43.5	29.0	13.8	11.0	2.8	1.80

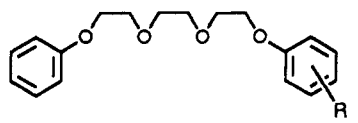
[a] Concentration of 1 is 0.17 mmol. [b] o/p = (2 + 8(2) + 9)/(3 + 9 + 10(2)).

Table II. The Selectivity for the Nitration of 2[a] under Various Conditions

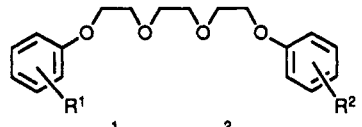
nitrating agent (mmol)	solv	selectivity o/p	isolated total yield, %
NO_2BF_4 (0.51)	CCl_4	0.37	20>
NO_2BF_4 (0.51)	CCl_4[b]	0.47	20>
NO_2BF_4 (0.34)	MeCN	1.70	25
NO_2BF_4 (0.34)	MeCN[b]	3.54	22
$AcONO_2$ (3.40)	MeCN[b]	1.52	84
HNO_3/H_2SO_4 (3.40)	-	0 .64	39
Me_3SiONO_2 (3.40)	MeCN[b]	4.02	84

[a] Concentration of 2 is 0.17 mmol. [b] Addition of BF_3OEt_2 0.51 mmol. [c] o/p = 8(yield)/9(yield) = 8/9.

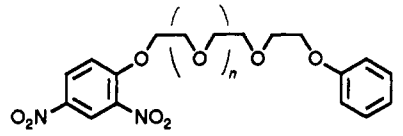
Chart I. The Podands



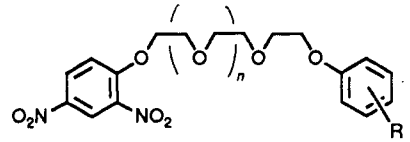
1: R = H
2. R = o-NO_2
3: R = p-NO_2



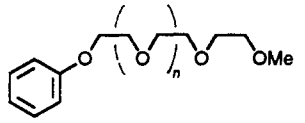
8: R^1 = o-NO_2; R^2 = o-NO_2
9: R^1 = o-NO_2; R^2 = p-NO_2
10: R^1 = p-NO_2; R^2 = p-NO_2



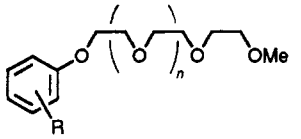
4: n = 1
5: n = 2



11: n = 1; R = o-NO_2
12: n = 1; R = p-NO_2
13: n = 2; R = o-NO_2
14: n = 2; R = p-NO_2



6. n = 1
7: n = 2



15: n = 1; R = o-NO_2
16: n = 1; R = p-NO_2
17: n = 2; R = o-NO_2
18: n = 2; R = p-NO_2

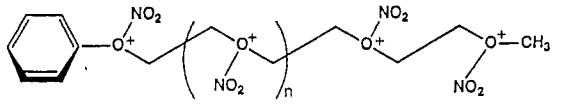
regioselective nitrations.[6] On the other hand, Masci reported that the naked nitronium ion in association with several of the oxygen atoms of a crown ether gave a new nitrating agent with para selectivity.[7] When benzene

Table III. The Selectivity for the Nitration of Podands with Me_3SiONO_2

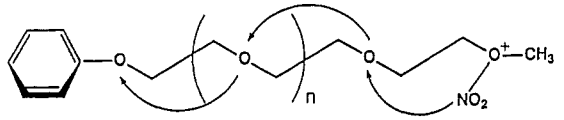
substr[a]	solvent	Lewis acid	selectivity (o/p ratio)
2	CCl_4	BF_3OEt_2	7.37[b]
	MeCN	BF_3OEt_2	4.02[b]
	MeCN	$AlCl_3$	2.43[b]
	MeCN	$TiCl_4$	4.41[b]
3	CCl_4	BF_3OEt_2	5.65[c]
	MeCN	BF_3OEt_2	4.81[c]
	MeCN	$AlCl_3$	2.16[c]
4	CCl_4	BF_3OEt_2	4.50[d]
	MeCN	BF_3OEt_2	3.60[d]
5	CCl_4	BF_3OEt_2	3.50[e]
	MeCN	BF_3OEt_2	2.60[e]
6	CCl_4	BF_3OEt_2	3.50[f]
	MeCN	BF_3OEt_2	2.30[f]
7	CCl_4	BF_3OEt_2	6.69[g]
	MeCN	BF_3OEt_2	1.95[g]

[a] Concentration of substrate, TMSN, and Lewis acid is 0.017, 0.051, and 0.10 mmol, respectively. o/p ratio is calculated as follows. [b] o/p = 8(yield)/9(yield) = 8/9. [c] o/p = 9/10. [d] o/p = 11/12. [e] o/p = 13/14. [f] o/p = 15/16. [g] o/p = 17/18.

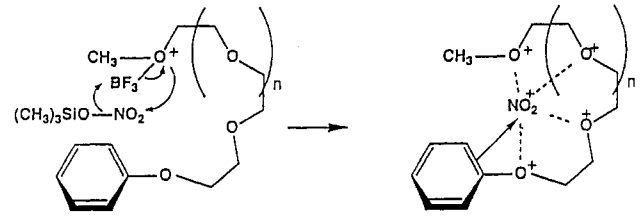
substrates possess a side chain that has several arranged oxygen atoms, the question arises whether nitronium ions might be collected along the chain symbolized in A, for the



A



B

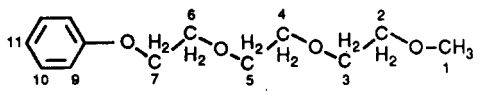


purpose of achieving higher ortho selectivity. Alternatively, the trapped nitronium ion might assume a suitable position for ortho attack through the properly situated oxygen bridge (B). Podands (noncyclic crown type compounds, Chart I)[8] would appear to be ideal substrates to provide an answer to this question. With this experiment in mind, we prepared α,γ-diphenylpolyethylene glycols (podands 1–5) and phenylpolyethylene glycols (podands 6 and 7).

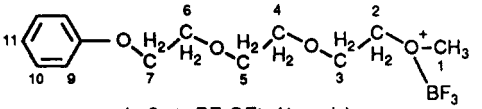
(7) As an example of solvation models, it should be noted that the naked nitronium ion in several oxygen atoms of crown ether gave a new nitrating agent with para selectivity. Masci, B. *J. Chem. Soc., Chem. Commun.* **1982**, 1261. Masci, B. *J. Org. Chem.* **1985**, *50*, 4081. There is an interesting example of the nitration of dibenzo-18-crown-6. Feigenbaum, W. H.; Michel, R. H. *J. Poly. Sci.* **1971**, A-1, 9, 817.

(8) Voegtle, F.; Weber, E. *Angew. Chem., Int. Ed. Engl.* **1979**, *8*, 376.

Table IV. Spin–Lattice Relaxation Time, T_1 (s), Chemical Shift of ^{13}C NMR (125 MHz), and Chemical Shift of ^1H NMR (500 MHz) of 6 and 6-BF_3 (1:1) in $CDCl_3$[a]



a: 6 in $CDCl_3$



b: 6 + BF_3OEt_2 (1 equiv)

		no. of position										
		1	2	3	4	5	6	7	8	9	10	11
a	T_1, s	5.9	3.27	3.04	2.13	2.09	1.92	1.97	18.47	3.66	3.63	1.98
	^{13}C, ppm	58.95	71.85	70.49	70.58	70.74	69.69	67.20	158.67	114.53	129.32	120.74
	^1H, ppm	3.36	3.53	3.63	3.67	3.72	3.84	4.11	–	6.90	7.25	6.92
b	T_1, s	3.40	1.54	3.10	2.02	2.17	2.24	1.65	22.00	3.77	3.88	2.29
	^{13}C, ppm	58.92	71.83	70.20	70.45	70.77	67.19	69.72	158.60	114.49	129.31	120.76
	^1H, ppm	3.85	3.90–4.09 (broad)		4.02	4.09	4.21	4.46	–	7.22	7.60	7.26

[a] These samples were not degassed and were measured at room temperature.

The product distribution and selectivities (defined in o/p)[9] for the nitration of the podands with several nitrating reagents are summarized in Tables I–III. As shown in Table I, the product distribution of 1 is complicated and the reaction system is not suitable for evaluation of the selectivity. In order to simplify the determination, we chose nitrated podands (2–5), 6, and 7 for the following examination. It is notable that the selectivity increases in the presence of BF_3OEt_2, implying Friedel–Crafts type nitration catalyzed by BF_3 (Table II).[10] In the case of NO_2BF_4 the selectivity and yields are lower in CCl_4, due to poor solubility of the nitrating agent in the nonpolar solvent (Table II). Compound 2 was selected as the representative substrate for the study of solvent effects and Lewis acid effects on the selectivity of nitrating agents in Table II. The selectivity is highly dependent on the nitrating reagent used, probably reflecting the size of the solvated nitronium ion (Table II).[7] The solubility and solvation may perturb the selectivity of nitration with nitronium ion. If possible, we wanted to formulate an ideal nitrating reagent that would be soluble even in nonpolar solvents and avoid the solvation problem. We present herein trimethylsilyl nitrate (TMSN),[11] a new ideal nitrating reagent and demonstrate how this unique reagent reacts with the podands. This reagent is catalyzed by Lewis acids; the nitration rate was very slow without added Lewis acid.

The selectivity in the nitration of the podands with both common nitrating agents and TMSN are summarized in Table II. As the selectivity is higher in the case of 2 (Table III), we chose 2 as a standard substrate for measuring the selectivity. The order of selectivity (o/p) for nitrating agents in CH_3CN was found to be TMSN–BF_3OEt_2 > NO_2BF_4 > acetyl nitrate > H_2SO_4–HNO_3. TMSN–BF_3OEt_2 is a more selective nitrating system than the other nitrating agents in CH_3CN. The selectivity in CCl_4 is higher than that in CH_3CN (Table III). The order of efficiency of the Lewis acids as catalysts was $TiCl_4$ > $BF_3OEt_2 \gg AlCl_3$ for the selectivity and the yield of their nitration with TMSN (Table III). The highest selectivity (o/p = 7.4) was recorded in the case of 2 with this new nitrating system in CCl_4. Probably, the generated naked nitronium ions are trapped by oxygen atoms in podands, and the ions can approach the ortho position via the properly arranged oxygen bridge. Therefore, this highly selective nitration is interpreted in terms of a pseudointramolecular nitration.

In order to clarify the nature of the BF_3–podand interaction, substrate 6 was selected due to both its higher selectivity and its simple structure. We examined 2D HETCOR (Figure 1) and ^{13}C NMR spectra (Figure 1) of 6, as well as the spin–lattice relaxation times (T_1) of the carbons in 6. As indicated by the ^{13}C NMR spectra of 6 with or without BF_3OEt_2 (1 equiv), it is the oxygen atom in the methoxy group that is primally involved in this interaction in CD_3Cl (Figure 1 and Table IV), as evidenced by the broadening for the C-2, C-3, and methyl carbons and protons which was observed. Furthermore, T_1's of the carbon resonances with and without BF_3OEt_2 show perturbations on the carbon atoms of the methyl group and those next to the methoxy group due to the complex formation (Table IV). From the titration of 6 with BF_3OEt_2, the formation of a 1:1 complex between BF_3OEt_2 and the podand was confirmed (Figure 2). Consequently, a picture of the selective nitration mechanism may be drawn as follows: The oxygen atom of the methoxy group in 6 traps BF_3 first, then a nitronium ion is generated by catalytic N–O bond fission as shown in C, initiating the regioselective pseudointernal nitration. A parallel study with 7 afforded higher ortho selectivity (o/p = 6.8) compared to that of 6, probably due to a higher concentration of trapped nitronium ion in the longer arm with more oxygen atoms which should favor the ortho selective nitration even more highly. As shown herein, TMSN–BF_3OEt_2 is an interesting nitrating agent for the investigation of the nitration of aromatic compounds with oxygen side chains bearing specifically arranged oxygen atoms.

Experimental Section

All melting points were measured with a Yanaco micro melting point apparatus and are uncorrected. Infrares spectra were obtained on a JASCO IRA-1 spectrometer. Ultraviolet spectra were measured with a Hitachi UV-200 spectrometer. ^1H NMR spectra were recorded on a JEOL JNMPX 60 instrument unless otherwise denoted at 500 MHz and on a Varian XL-500 spectrometer in $CDCl_3$. ^{13}C NMR spectra were recorded on a Varian XL-500 spectrometer (125 MHz) in $CDCl_3$.

Materials (Chart II). 1,8-Dichloro-3,6-dioxaoctane (A1) was prepared by the method of Pedersen:[12] 95% yield; colorless oil;

(9) The o/p measurements of nitration of podands (1–6) were carried out on a HPLC (Cosmosil 5C-18, 4.6 × 150 mm, 70% methanol, 225 nm), which was calibrated before each set of measurements.

(10) Friedel–Crafts type nitrations: Kuhn, S. J.; Olah, G. A. *J. Am. Chem. Soc.* **1961**, *83*, 4564. Olah, G. A.; Lin, C. H. *Synthesis* **1973**, 491. Olah, G. A.; Fung, A. P.; Narang, S. C.; Olah, J. A. *J. Org. Chem.* **1981**, *46*, 3533. Narang, S. C.; Thompson, M. J. *Aust. J. Chem.* **1978**, *31*, 1839.

(11) (a) Schmidt, M.; Schmidbaur, H. *Angew. Chem.* **1959**, *71*, 220. (b) Drake, J. E.; Henderson, H. E. *J. Inorg. Neucl. Chem.* **1978**, *40*, 137. (c) Voronkov, M. G.; Roman, V. K.; Maletina, E. A. *Synthesis* **1982**, 277. The NMR spectrum of TMSN shows a methyl peak at 0.40 ppm. The IR spectrum of neat TMSN shows 1600 ($-NO_2$), 1300 (NO_2), 830 ($-NO_3$), and 1050 (Si–O–R) cm^{-1}. (d) The Ph.D. Thesis of Narang, S. C. Flinders University, Adelaide, South Austraila, 1975.

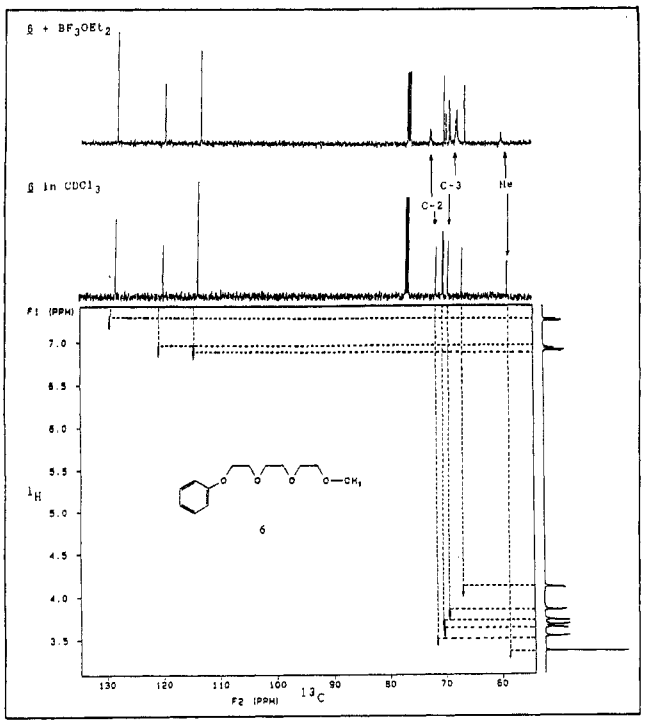


Figure 1. D-HETCOR contour plot of **6** in $CDCl_3$; ^1H NMR = 500 MHz, ^{13}C NMR = 125 MHz, at room temperature, chemical shift of ^{13}CMR (125 MHz) of **6** and **6**–BF_3OEt_2 (1:1) omitted one carbon bearing no hydrogen in the benzene part.

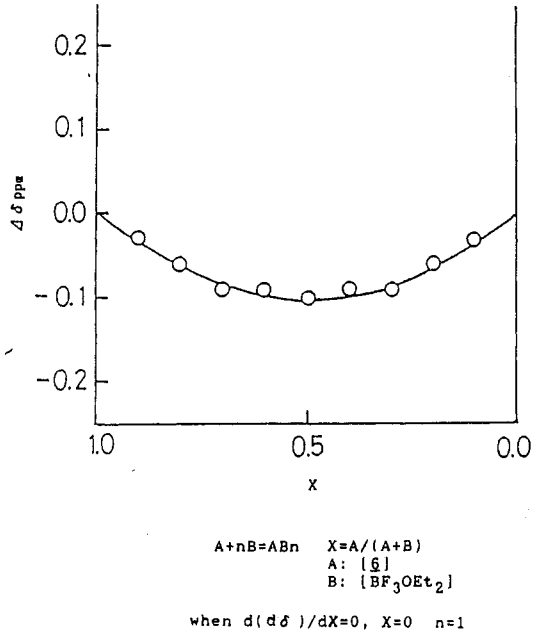


Figure 2. Titration of **6** with BF_3OEt_2 for determination of the molar ratio between **6** and BF_3OEt_2 for their complexation.

bp 152–155 °C (70 mmHg); ^1H NMR ($CDCl_3$) 3.61 ppm (br s, 12 H). 2-Nitrofluorobenzene, 4-nitrofluorobenzene, 2,4-dinitrofluorobenzene, phenol, triethylene glycol, tetraethylene glycol, and triethylene glycol monoethyl ether are available from commercial products. 1,8-Diphenoxy-3,6-dioxaoctane (**1**) was prepared from **A1** and phenol in 87% yield by the method of Joeger and Whitney:[13] mp 44–45 °C (ethanol) (lit. mp 43.5–44 °C); ^1H NMR δ 3.64 (s, 4 H), 3.70–4.18 (m, 8 H), and 6.7–7.4 ppm (m, 10 H, phenyl); ^{13}C NMR ($CDCl_3$) δ 67.276, 69.802, 70.892, 114.596 (phenyl), 120.815 (phenyl), 129.383 (phenyl), and 158.723 ppm

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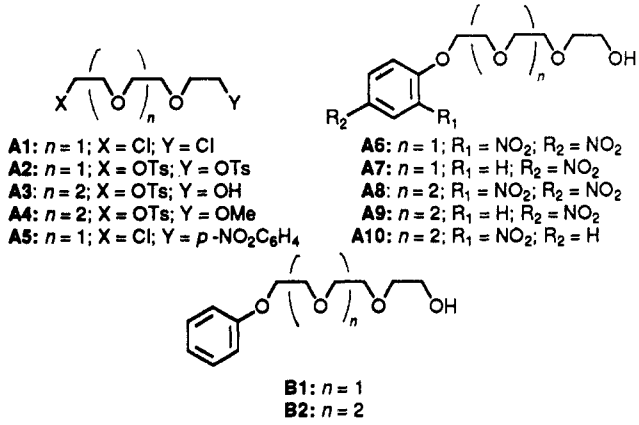
Chart II. Starting Materials



A1: $n = 1$; X = Cl; Y = Cl
A2: $n = 1$; X = OTs; Y = OTs
A3: $n = 2$; X = OTs; Y = OH
A4: $n = 2$; X = OTs; Y = OMe
A5: $n = 1$; X = Cl; Y = p-$NO_2C_6H_4$
A6: $n = 1$; $R_1 = NO_2$; $R_2 = NO_2$
A7: $n = 1$; $R_1 = H$; $R_2 = NO_2$
A8: $n = 2$; $R_1 = NO_2$; $R_2 = NO_2$
A9: $n = 2$; $R_1 = H$; $R_2 = NO_2$
A10: $n = 2$; $R_1 = NO_2$; $R_2 = H$

B1: $n = 1$
B2: $n = 2$

(phenyl); UV (EtOH) λ_{max} (log ε) 220 (4.17), 272 (3.47), 278 nm (3.39). 1-(2′-Nitrophenoxy)-8-phenoxy-3,6-dioxaoctane (**2**), 1-(4′-nitrophenoxy)-8-phenoxy-3,6-dioxaoctane (**3**), and 1-(2′,4′-dinitrophenoxy)-8-phenoxy-3,6-dioxaoctane (**4**) were prepared through the following three steps.

Bis(*p*-tolylsulfonyl)-1,4,7,10-tetraoxadecane (A2). **A2** was prepared in 71% yield by the method of Dale and Kristiansen:[14] mp 75–77 °C (lit. mp 78 °C); ^1H NMR δ 2.43 (br s, 6 H), 3.5–3.7 (m, 10 H), 4.0–4.2 (m, 2 H), 7.27 (d, 4 H, J = 8 Hz), 7.73 ppm (d, 4 H, J = 8 Hz); IR (Nujol) ν 1160 cm^{-1} (–SO_2–O–).

8-Hydroxy-1-phenoxy-3,6-dioxaoctane (B1).[20] A suspension of **A2** (17.5 g, 34.6 mmol), phenol (6.5 g, 69 mmol), and anhydrous potassium carbonate (9.5 g, 69 mmol) in 50 mL of dry benzene was refluxed under an atmosphere of nitrogen for 73 h. After neutralization of the reaction mixture with 1 N HCl, the reaction mixture was extracted with chloroform (3 × 100 mL). The solution was then dried under reduced pressure, and the residue was chromatographed on silica gel, eluting with a benzene–ethyl acetate gradient solvent (from pure benzene to pure ethyl acetate). Fractions containing **B1** were combined, and the solvent was removed under reduced pressure to give pure **B1** in 71% yield: colorless oil; ^1H NMR δ 2.8 (br s, 1 H, OH), 3.5–3.9 (m, 10 H), 4.0–4.2 (m, 2 H), 6.7–7.4 ppm (m, 5 H, phenyl); IR (neat) ν 3400 cm^{-1}.

1-(2′-Nitrophenoxy)-8-phenoxy-3,6-dioxaoctane (2). A suspension of **B1** (2.33 g, 10.3 mmol), 2-fluoronitrobenzene (1.78 g, 12.6 mmol), and anhydrous potassium carbonate (1.42 g, 10.3 mmol) in benzene (50 mL) was refluxed and stirred for 43 h under an atmosphere of nitrogen. After workup, a crude yellow oil was obtained. Purification of the oil by column chromatography (silica gel, benzene–ethyl acetate, 1:1, as eluent) and tube distillation [range of bath temperature 155–160 °C (0.4 mmHg)] gave pure **2** in 72% yield: ^1H NMR δ 3.77 (br s, 4 H), 3.8–3.9 (m, 4 H), 3.9–4.3 (m, 4 H), and 6.7–7.8 ppm (m, 9 H, phenyl and *o*-nitrophenyl); ^{13}C NMR δ 67.26, 69.318, 69.591, 69.750, 70.854, 71.132, 114.591, 114.956, 120.552, 120.782, 125.543, 129.372, 134.012, 140.000, 152.257, and 158.733 ppm; IR (neat) ν 1520, 1340 (–NO_2) cm^{-1}; UV (MeCN) λ_{max} (log ε) 216 (4.27), 266 (3.57), 271 (3.55), 279 (3.42), 322 nm (3.28). Anal. Calcd for $C_{18}H_{21}NO_6$: C, 62.2; H, 6.10; N, 4.03. Found: C, 62.0; H, 5.84; N, 3.84.

1-(4′-Nitrophenoxy)-8-phenoxy-3,6-dioxaoctane (3) was prepared by a similar method as above using **B1** and 4-nitrofluorobenzene: yield 41%; mp 52–53 °C (ethanol); ^1H NMR δ 3.69 (br s, 4 H), 3.7–3.9 (m, 4 H), 6.7–7.4 (m, 4 H), 8.04 ppm (d, 2 H); ^{13}C NMR (CCl_4–$CDCl_3$, 10:1) δ 67.205, 68.159, 69,560, 69.941, 71.082, 71.143, 114.471, 114.578, 120.949, 125.766, 129.42, 142.337,

(14) Dale, J.; Kristiansen, P. O. *Acta Chem. Scand.* **1892**, *26*, 1471.
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(17) Dutasta, J.-P.; Declercq, J.-P.; Esteban-Carderon, C.; Tinant, B. *J. Am. Chem. Soc.* **1989**, *111*, 7130.
(18) George, L.; Doelling, G. L.; Adams, K. H. U.S. Patent 2,585,750 Feb 1952.
(19) Neeman, M. *J. Am. Chem. Soc.* **1962**, *84*, 989.
(20) This was used for the next step in the synthesis without further purification.

158.820, 163.595 ppm; IR (neat) ν 1490, 1330 ($-NO_2$) cm^{-1}; UV (MeCN) λ_{max} (log ϵ) 221 (4.16), 272 (3.73), 280 (3.81), 308 nm (4.05). Anal. Calcd for $C_{18}H_{21}NO_6$: C, 62.2; H, 6.09; N, 4.03. Found: C, 61.8; H, 6.14; N, 3.97.

1-(2',4'-Dinitrophenoxy)-8-phenoxy-3,6-dioxaoctane (4) was prepared by a similar method for **1** and **3** using **B1** and 2,4-dinitrofluorobenzene: pale yellow oil; yield 80%; ^1H NMR δ 3.6–4.1 (m, 10 H), 4.2–4.5 (m, 2 H), 6.7–7.4 (m, 6 H), 8.27 (dd, 1 H, J = 10 Hz and J = 3 Hz), 8.57 ppm (d, 1 H, J = 3 Hz); IR (neat) 1520, and 1340 cm^{-1} ($-NO_2$); UV (MeCN) λ_{max} (log ϵ) 218 (4.27), 259 (3.82), 272 (3.91), 279 (3.97), and 295 nm (4.02). Anal. Calcd for $C_{18}H_{20}N_2O_8$: C, 55.10; H, 5.14; N, 7.14. Found: C, 54.79; H, 5.33; N, 7.10.

1-(2',4'-Dinitrophenoxy)-11-phenoxy-3,6,9-trioxaundecane (5) and 1-methoxy-11-phenoxy-3,6,9-trioxaundecane (7) were prepared by a similar method employed for **4** in the following three steps.

1-Hydroxy-3,6,9-trioxaundecyl *p*-toluenesulfonate (A3).[20] **A3** was prepared by the method used for **A2**: colorless oil; 77% yield; ^1H NMR δ 3.5–3.8 (m, 14 H), 4.1–4.3 (m, 2 H), 7.33 (d, 2 H, J = 7 Hz), and 7.78 ppm (d, 2 H, J = 7 Hz).

1-Hydroxy-11-phenoxy-3,6,9-trioxaundecane (B2). B2 was prepared by a similar method employed for **B1**: yield 62%; ^1H NMR δ 2.7 (br s, 1 H, OH), 3.5–3.9 (m, 14 H), 4.0–4.3 (m, 2 H), 6.7–7.4 ppm (m, 5 H, phenyl); IR (neat) ν 3420 cm^{-1} (–OH).

7 was prepared quantitatively by treatment of **B2** with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide:[15] colorless oil; ^1H NMR δ 3.35 (s, 3 H), 3.5–3.7 (m, 12 H), 3.84 (t, 2 H, J = 4.9 Hz), 4.11 (t, 2 H, J = 4.9 Hz), and 6.9–7.3 ppm (m, 5 H); IR (neat) ν 1050 and 1230 (C–O–C) cm^{-1}. Anal. Calcd for $C_{15}H_{24}O_5$: C, 61.7; H, 8.88. Found: C, 61.6; H, 8.85.

5 was prepared by the parallel method of **4** with **B2**: yield 81%; ^1H NMR δ 3.6–4.5 (m, 16 H), 6.7–7.4 (m, 6 H), 8.30 (dd, 1 H, J = 10 Hz and J = 3 Hz), and 8.60 (d, 1 H, J = 3 Hz); IR (neat) ν 1340, 1520 ($-NO_2$) cm^{-1}; UV (MeCN) λ_{max} (log ϵ) 218 (4.26), 259 (3.82), 270 (3.90), 281 (3.97), and 294 nm (4.02). Anal. Calcd for $C_{20}H_{24}N_2O_9$: C, 55.0; H, 5.54; N, 6.41. Found: C, 54.7; H, 5.50; N, 6.26.

1-Methoxy-3,6-dioxaoctyl *p*-toluenesulfonate (A4) was prepared by the parallel method for **A2**:[16,20] colorless oil; 84% yield; ^1H NMR δ 2.43 (s, 3 H), 3.33 (s, 3 H), 3.5–3.8 (m, 10 H), 4.1–4.3 (m, 2 H), 7.2 (d, 2 H, J = 8 Hz), and 7.8 ppm (d, 2 H, J = 8 Hz); IR (neat) ν 1160 cm^{-1} ($-SO_2-O-$).

1-Methoxy-8-phenoxy-3,6-dioxaoctane (6) was prepared using triethylene glycol monomethyl ether as follows: **6** was prepared by the treatment of **A4** and phenol with potasium carbonate in refluxed benzene for 24 h under an atmosphere of nitrogen: colorless oil; yield 85%; ^1H NMR δ 3.33 (s, 3 H), 3.5–4.2 (m, 12 H), and 6.7–7.4 ppm (m, 5 H, phenyl); ^{13}C NMR ($CDCl_3$) δ 59.027, 67.283, 69.759, 70.592, 70.656, 70.819, 71.925, 114.600, 120.816, 129.389, and 158.745 ppm; IR (neat) ν 1220 and 1100 cm^{-1} (R–O–R). Anal. Calcd for $C_{13}H_{29}O_4$: C, 64.9; H, 8.38. Found: C, 64.5; H, 8.12.

1-(2'-Nitrophenoxy)-8-methoxy-3,6-dioxaoctane (15) and 1-(4'-nitrophenoxy)-8-methoxy-3,6-dioxaoctane (16) were prepared by the parallel method for **2**. **15**: yellow oil; yield 90%; ^1H NMR δ 3.37 (s, 3 H), 3.5–3.7 (m, 8 H), 3.91 (t, 2 H, J = 4.8 Hz), 4.26 (t, 2 H, J = 4.8 Hz), 7.03 (t, 1 H, J = 8 Hz), 7.11 (d, J = 8 Hz), 7.51 (t, 1 H, J = 8 Hz), and 7.82 ppm (d, 1 H, J = 8 Hz); IR (neat) ν 1520, 1340 ($-NO_2$), 1240, 1035 cm^{-1} (R–O–R). Anal. Calcd for $C_{13}H_{19}NO_6$: C, 54.7; H, 6.71; N, 4.91. Found: C, 54.7; H, 6.68; N, 4.72.

16: ^1H NMR (500 MHz) δ 3.37 (s, 3 H), 3.5–3.7 (m, 8 H), 3.89 (t, 2 H, J = 4.8 Hz), 4.21 (t, 2 H, J = 4.8 Hz), 6.97 (d, 2 H, J = 9.2 Hz), and 8.18 ppm (d, 2 H, J = 9.2 Hz); IR (neat) ν 1505, 1330 ($-NO_2$), 1250, 1040 cm^{-1} (R–O–R); UV (MeCN) λ_{max} (log ϵ) 221 (3.91) and 308 nm (4.04). Anal. Calcd for $C_{13}H_{19}NO_6$: C, 54.7; H, 6.71; N, 4.91. Found: C, 54.8; H, 6.7; N, 5.00.

Bis(2'-nitrophenoxy)-3,6-dioxaoctane (8) and bis(4'-nitrophenoxy)-3,6-dioxaoctane (10) were prepared by the parallel method for **1** starting from **A1**. The reaction of **A1** and 2-nitrophenol gave **8**. **8**:[17] yellow needles; 26% yield; mp 46–47 °C (lit. mp 63 °C); ^1H NMR δ 3.67 (s, 3 H), 3.7–3.9 (m, 4 H), 3.1–4.3 (m, 4 H), and 6.9–7.9 ppm (m, 8 H, phenyl); IR (Nujol) ν 1520 and 1340 cm^{-1} ($-NO_2$); UV (MeCN) λ_{max} (log ϵ) 213 (4.45), 260 (3.9), and 326 (3.64).

10:[18] pale yellow needles; mp 95–96 °C; ^1H NMR δ 3.72 (s, 4 H), 3.8–3.9 (m, 4 H), 4.1–4.3 (m, 4 H), 6.91 (d, 4 H, J = 9 Hz), and 8.11 ppm (d, 4 H, J = 9 Hz); IR (Nujol) ν 1490 and 1325 cm^{-1}; UV(MeCN) λ_{max} (log ϵ) 222 (4.15) and 305 nm (4.34).

1-(2'-Nitrophenoxy)-8-(4'-nitrophenoxy)-3,6-dioxaoctane (9) was prepared as follows.

1-Chloro-8-(2'-nitrophenoxy)-3,6-dioxaoctane (A5).[20] A suspension of 2-nitrophenol (5.0 g, 36 mmol), Na metal (0.83 g, 36 mmol), and **A1** (10.1 g, 54 mmol) in 1-butanol (100 mL) was refluxed for 94 h under an atmosphere of nitrogen. After the usual workup, the crude product was purified by column chromatography (silica gel, 10% ethyl acetate in benzene) to give **A5** (2.4 g, 6.1 mmol): a pale yellow oil; 23% yield; ^1H NMR δ 3.5–4.3 (m, 12 H), 6.7–7.7 ppm (m, 4 H); IR (neat) ν 1325, 1520 cm^{-1} ($-NO_2$).

The reaction of **A5** and 4-nitrophenol by the parallel method for **1** gave **9**. **9**: yellow needles; mp 67–68 °C (ethanol); 21% yield; ^1H NMR 3.67 (s, 4 H), 3.8–4.0 (m, 4 H), 4.2–4.4 (m, 4 H), 6.90 (d, 2 H, J = 9 Hz), 7.0–7.7 (m, 4 H), and 8.00 ppm (d, 2 H, J = 9 Hz); IR (Nujol) ν 1510, 1340 cm^{-1} ($-NO_2$); UV (MeCN) λ_{max} (log ϵ) 214 (4.26), 261 (3.66), and 305 nm (4.11). Anal. Calcd for $C_{18}H_{20}N_2O_8$: C, 55.1; H, 5.14; N, 7.14. Found: C, 54.8; H, 5.03; N, 7.20.

1-(2',4'-Dinitrophenoxy)-8-(2'-nitrophenoxy)-3,6-dioxaoctane (11) was prepared through the following sequence starting from triethylene glycol.

1-(2',4'-Dinitrophenoxy)-8-hydroxy-3,6-dioxaoatane (A6).[20] **A6** was prepared by the parallel method for **2** using 2,4-dinitrofluorobenzene, in quantitative yield: yellow oil; ^1H NMR δ 2.50 (br s, 1 H), 3.5–4.5 (m, 12 H), 7.28 (d, 1 H, J = 9 Hz), 8.37 (dd, 1 H, J = 3 Hz and J = 9 Hz), and 8.65 ppm (d, 1 H, J = 3 Hz); IR (neat) 3400, 1520, 1340 cm^{-1}.

The reaction of 2-nitrofluorobenzene and **A6** by the parallel method for **A6** gave **11**. **11**: pale yellow needles; 39% yield; mp 44–45 °C; ^1H NMR δ 3.7–4.0 (m, 8 H), 4.1–4.5 (m, 4 H), 6.8–7.38 (m, 2 H), 7.32 (d, 1 H, J = 9 Hz), 7.4–7.9 (m, 2 H), 8.33 (dd, 1 H, J = 9 Hz), 8.62 ppm (d, 1 H, J = 3 Hz); IR (Nujol) ν 1520 and 1340 cm^{-1}; UV (MeCN) λ_{max} (log ϵ) 214 (4.39), 258 (3.96), and 296 nm (4.07). Anal. Calcd for $C_{18}H_{19}N_3O_{10}$: C, 49.4; H, 4.38; N, 9.60. Found: C, 49.5; H, 4.51; N, 9.47.

1-(2',4'-Dinitrophenoxy)-8-(4'-nitrophenoxy)-3,6-dioxaoctane (12) was prepared by the following sequence starting from triethylene glycol.

1-Hydroxy-8-(4'-nitrophenoxy)-3,6-dioxaoctane (A7). A7 was prepared by the parallel method for **A6**:[20] pale yellow oil; 92% yield; ^1H NMR δ 2.63 (br s, 1 H), 3.5–4.0 (m, 10 H), 4.1–4.3 (m, 2 H), 6.92 (d, 2 H, J = 9 Hz), and 8.08 ppm (d, 2 H, J = 9 Hz); IR (neat) ν 1330, 1510 ($-NO_2$), and 3420 cm^{-1} (–OH).

The reaction of 2,4-dinitrofluorobenzene and **A7** by the parallel method for **11** gave **12**. **12**: 49% yield; yellow crystals; mp 56–57 °C; ^1H NMR δ 3.71 (m, 4 H), 3.8–4.1 (m, 4 H), 4.1–4.5 (m, 4 H), 6.97 (d, 2 H, J = 9 Hz), 7.33 (d, 1 H, J = 9 Hz), 8.17 (d, 2 H, J = 9 Hz), 8.40 (dd, 1 H, J = 3 Hz and J = 9 Hz), and 8.67 ppm (1 H, J = 3 Hz); IR (Nujol) ν 1520 and 1340 cm^{-1}; UV (MeCN) λ_{max} (log ϵ) 217 (4.23), and 302 nm (4.28). Anal. Calcd for $C_{18}H_{19}N_3O_{10}$: C, 49.4; H, 4.38; N, 9.60. Found: C, 49.2; H, 4.16; N, 9.33.

1-(2',4'-Dinitrophenoxy)-11-(2'-nitrophenoxy)-3,6,9-trioxaundecane (13) was prepared through the following two steps using tetraethylene glycol.

1-Hydroxy-11-(2',4'-dinitrophenoxy)-3,6,9-trioxaundecane (A8).[20] **8** was prepared by the parallel method for **A6** using 2,4-dinitrofluorobenzene: yellow oil; quantitative yield; ^1H NMR δ 2.57 (br s, 1 H), 3.5–4.0 (m, 14 H), 4.3–4.5 (m, 2 H), 7.31 (d, 1 H, J = 9 Hz), 8.39 (dd, 1 H, J = 3 Hz and J = 9 Hz), and 8.68 ppm (d, 1 H, J = 3 Hz); IR (neat) ν 1340, 1520 ($-NO_2$), 3420 cm^{-1} (–OH). The reaction of **A8** and 2-fluoronitrobenzene by the parallel method for **11** gave **13** in 43% yield. **13**: pale yellow needles; mp 94.5–95.5 °C, ^1H NMR δ 3.5–4.0 (m, 12 H), 4.1–4.4 (m, 4 H), 6.8–7.3 (m, 2 H), 7.30 (d, 1 H, J = 9 Hz), 7.4–7.8 (m, 2 H), 8.32 (dd, 1 H, J = 3 Hz and J = 9 Hz), and 8.58 ppm (d, 1 H, J = 3 Hz); IR (Nujol) ν 1510, and 1330 cm^{-1} ($-NO_2$); UV (MeCN) λ_{max} (log ϵ) 213 (4.42), 257 (3.98), and 296 nm (4.09). Anal. Calcd for $C_{20}H_{23}N_3O_{11}$: C, 49.9; H, 4.82; N, 8.74. Found: C, 50.0; H, 4.88; N, 8.67.

1-(2',4'-Dinitrophenoxy)-11-(4'-nitrophenoxy)-3,6,9-trioxaundecane (14) was prepared by the parallel method for **12**

starting from tetraethylene glycol.

1-Hydroxy-11-(4'-nitrophenoxy)-3,6,9-trioxaundecane (A9).[20] **A9** was prepared by the parallel method for **A7** using tetraethylene glycol and 4-fluoronitrobenzene in 92% yield: yellow oil; ^{1}H NMR δ 2.91 (br s, 1 H), 3.5–4.0 (m, 14 H), 4.1–4.3 (m, 2 H), 6.94 (d, 2 H, J = 9 Hz), and 8.15 ppm (d, 2 H, J = 9 Hz); IR (neat) ν 1340, 1510 ($-NO_2$), and 3420 (-OH) cm^{-1}.

The reaction of **A8** and 2,4-dinitrofluorobenzene gave **14** in 65% yield. **14**: yellow crystals; mp 60.5–61.5 °C; ^{1}H NMR δ 3.5–4.5 (m, 16 H), 6.97 (d, 2 H, J = 9 Hz), 7.32 (d, 1 H, J = 9 Hz), 8.15 (d, 2 H, J = 9 Hz), 8.40 (dd, 1 H, J = 3 Hz and J = 9 Hz), and 8.76 ppm (d, 1 H, J = 3 Hz); IR (Nujol) 1340 and 1510 ($-NO_2$) cm^{-1}; UV (MeCN) λ_{max} (log ϵ) 217 (4.21) and 301 nm (4.26). Anal. Calcd for $C_{20}H_{23}N_3O_{11}$: C, 49.9; H, 4.82; N, 8.74. Found: C, 50.1; H, 4.92; N, 8.65.

1-Methoxy-11-(2'-nitrophenoxy)-3,6,9-trioxaundecane (17) was prepared through the following two steps starting from tetraethylene glycol.

1-Hydroxy-11-(2'-nitrophenoxy)-3,6,9-trioxaundecane (A10).[20] A suspension of 4-nitrofluorobenzene (500 mg, 3.5 mmol), potassium carbonate (735 mg, 5.3 mmol), and tetraethylene glycol (6.9 g, 35 mmol) was heated for 22 h under an atmosphere of nitrogen gas. After the usual workup, the crude product (1.2 g) was isolated and purified by column chromatography on silica gel eluting with 10% ethyl acetate to give pure **A10** (1.0 g, 3.2 mmol): yellow oil; 90% yield; ^{1}H NMR δ 2.63 (br s, 1 H), 3.4–4.0 (m, 14 H), 4.1–4.3 (m, 2 H), 6.8–7.8 ppm (m, 4 H); IR (neat) ν 1340, 1520 cm^{-1} ($-NO_2$).

17 was prepared by the methylation of **A10** with diazomethane in ether:[19] ^{1}H NMR (500 MHz) δ 3.37 (s, 3 H), 3.5–3.7 (m, 12 H), 3.90 (t, 2 H, J = 4.8 Hz), 4.26 (t, 2 H, J = 4.8 Hz), 7.03 (pseudo t, 1 H, J = 7.8 Hz), 7.11 (d, 1 H, J = 8.5 Hz), 7.51 (pseudo t, 1 H, J = 7.8 Hz), and 7.82 ppm (d, 1 H, J = 8.1 Hz); IR (neat) ν 1520, 1340, 1240, and 1035 cm^{-1}; UV (MeCN) λ_{max} (log ϵ) 260 (3.51) and 326 nm (3.35).

1-Methoxy-11-(4'-nitrophenoxy)-3,6,9-trioxaundecane (18) was prepared by the method for **17**: yellow oil; ^{1}H NMR (500 Mz) δ 3.37 (s, 3 H), 3.5–3.7 (m, 12 H), 3.89 (t, 2 H, J = 4.8 Hz), 4.22 (t, 2 H, J = 4.8 Hz), 6.98 (d, 2 H, J = 9.3 Hz), and 8.19 ppm (d, 2 H, J = 9.3 Hz); IR (neat) 1505, 1330, 1250, and 1040 cm^{-1}; UV (MeCN) λ_{max} (log ϵ) 227 (3.98) and 308 nm (4.18). Anal. Calcd for $C_{15}H_{23}NO_7$: C, 54.7; H, 7.04; N, 4.21. Found: C, 54.8; H, 7.10; N, 4.33.

Trimethylsilyl Nitrate (TMSN). (a) Silver nitrate (1 g, 5.9 mmol) and trimethylsilyl chloride (540 μL, 5.6 mmol) were mixed at -5 °C (ice-salt bath) and stirred for 30 min under an atmosphere of nitrogen at 0 °C (ice bath) in a dark room. Decantation of the reaction mixture gave pure trimethylsilyl nitrate in quantitative yield (0.68 g, 5.6 mmol, 93%): IR and NMR spectra were shown in ref 11c. Anal. Calcd for $C_3H_9NO_3Si$: C, 26.7; H, 6.71; N, 10.36. Found: C, 26.2; H, 7.10; N, 10.12. (b) A practical procedure for the preparation of a CH_3CN solution of TMSN (0.42 mM): A solution of silver nitrate (73.2 mg, 0.42 mmol) and trimethylsilyl chloride (69 μL, 0.54 mmol) in CH_3CN (2 mL) was stirred for 2 h at 0 °C in a dark room. Silver chloride formed was removed by decantation. The CH_3CN layer is a pure trimethylsilyl nitrate solution, the concentration of which was measured to be 0.4 ± 0.02 mM by comparison of the corresponding methyl peak integration area with that of a standard solution of TMSN prepared by the above (a) method in CH_3CN.

General Method for Nitration of Podands with TMSN. To a solution of podands in CCl_4 or CH_3CN (20 mL) in the presence of Lewis acids was added a freshly prepared CH_3CN solution (2 mL) of TMSN over 1 min via glass pipet. After stirring for 3 h at 0 °C under N_2 in a dark room, the reaction mixture was diluted with 20 mL of $CHCl_3$ and washed with 50 mL of water three times. The $CHCl_3$ layer was separated and dried over $MgSO_4$. Evaporation of the solvent gave a residue which was chromatographed by HPLC (COSMOSIL, methanol) to give nitrated podands.[9]

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Regioselective Ring Opening of Polycyclic Aromatic Hydrocarbon Epoxides by Polymer-Supported N_3^- Anion

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The benzylic ring opening of some polycyclic aromatic hydrocarbon (PAH) tetrahydro epoxides and one diol epoxide has been achieved by Amberlite supported N_3^- ion, in a regio- and stereoselective manner. The resulting azidohydrins have been converted to the corresponding β-acyloxy amines and/or amino alcohols. The β-acyloxy amino compounds are suitable for incorporation into synthetic oligonucleotides, whereas the amino alcohols were synthesized in order to establish the regiochemistry of the ring-opening step. The tetrahydro models studied were the naphthalene (Np), benz[c]acridine (BcAr), benzo[a]pyrene (BaP), and benzo[e]pyrene (BeP) epoxides. In the Np and BcAr cases, the amino group is equatorial whereas in the BaP and BeP cases, it is axial. In the final stage of these ring-opening reactions, the racemic diol epoxide of benzo[a]pyrene (BaPDE) **24** was converted to the corresponding amines. In each of the cases studied, the attack by N_3^- ion occurred at the benzylic site. The relative stereochemistry of the azido and hydroxyl groups in every case was trans. No other regio- or stereoisomer was observed in any of these compounds in the ring-opening step.

Metabolic activation of PAH occurs through conversions of the parent hydrocarbon to "bay region" diol epoxides.[1,2] The resulting activated PAH, that is the electrophilic diol epoxides, bind to nucleophilic sites in DNA, resulting in the formation of PAH–DNA adducts. The major adducts result from a trans ring opening of the oxirane ring with

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