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Substituted Macrocyclic Aryl Tetraethers

Everett E. Gilbert

Explosives Division, Feltman Research Laboratories, Picatinny Arsenal, Dover, New Jersey 07801

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Macrocyclic ethers have been prepared by reacting 1,5-dichloro-2,4-dinitrobenzene with various halogenated and alkylated resorcinols and hydroquinones. Electrophilic substitution (nitration, bromination, and sulfonation) of several has been studied, with special emphasis on nitration. Macrocycles derived from the hydroquinones and the 2-substituted resorcinols are more resistant to substitution than those derived from the 4-, 5-, or 6-substituted resorcinols; possible explanations are given.

The high thermal and chemical stability of poly (phenylene oxides) (1) suggested the possible suitability of this basic structure as a substrate for preparing thermally-stable polynitro derivatives. Some years ago, Brown and coworkers (2) reported the incidental isolation of a macrocycle of this type (the unnitrated analogue of I) during the preparation of poly (m-phenoxylene) thermally-stable polymers by the self-condensation of potassium m-bromophenoxide. Their yield was very low, and that method does not appear suitable for synthetic purposes. Later work by Sommer and Staab (3), showing that I could be prepared easily from resorcinol and 1,5dichloro-2,4-dinitrobenzene, prompted us to consider the use of a modification of their method for the synthesis of I (4), II and a number of related macrocycles as a basis for subsequent nitration studies. Following the completion of our study, Lehman F. (5) prepared I, II, and the 25,27dimethyl derivative of I (Im), and studied their conformations. The tetrathio analogues of Land II were recently made by Montaudo and coworkers (6).

Our preparative procedure (heating the dihydric phenol with 1,5-dichloro-2,4-dinitrobenzene and inorganic base for 2 hours at 150° in N,N-dimethylformamide) is faster and gives better yields than previous methods. Use of the difluoro analogue (5), or of high dilution methods, is unnecessary. The method used recently (6) to make the tetrathia analogues of 1 and 11, involving refluxing an ethanol solution of the dichloro compound with the corresponding disodium dithiolates, in our hands did not yield 1 or 11 with resorcinol or hydroquinone. Contrary to a previous report (5), we were able to purify the macrocycles by recrystallization.

Although, as shown in Table I (Procedure A), various halogenated and alkylated resorcinols give fair to good yields of macrocycles, no products could be obtained under similar conditions from the following substituted resorcinols: 2- and 4-acetyl, 4-carboxy, 2- and 4-benzamido, 2,4-dinitroso, 2,4-dinitro, 2,4,6-trinitro, and 2,4,6triiodo. 2,6-Dihydroxypyridine and 4,6-dihydroxypyrimidine likewise failed to react. No macrocycles could be obtained from resorcinol with 2,4-dichloronitrobenzene or with 1,3-dichloro-2,4,6-trinitrobenzene. It therefore appears that ring formation is fairly sensitive to structural factors. The failure of 1,3-dichloro-2,4,6-trinitrobenzene and of 1,3-dihydroxy-2,4,6-trinitrobenzene to yield products was initially attributed to steric hindrance by the nitro group in the 2-position. However, the formation of a macrocycle in fair yield from 2-nitroresorcinol indicates that other factors are involved.

4-Substituted resorcinols would be expected to form two isomeric macrocycles, and such were isolated in approximately equal amounts from the reaction mixtures from 4-bromoresorcinol (Id and e) and 4-chlororesorcinol (If and g). Id and e were also obtained by direct bromina-

I (a) and Derivatives TABLE I

Halogen	(Found)					22.7 (22.8)		11.5 (11.7)	11.5 (11.3)									
sis Nitrogen	(Found)	10.2 (9.9)	13.2 (13.1)	15.4 (14.7) (j)	15.4 (14.9) (j)	(7.7)		9.1 (9.1)				8.2 (8.2)	9.7 (9.4)	14.8 (14.7)	9.7 (9.9)	1 4.8 (13.8) (j)	9.3 (9.3)	7.8 (8.1)
<u>^</u>	(Found)	2.2 (2.4)	1.6 (1.7)	1.1 (1.3)	1.1 (1.4)	1.4 (1.6)		1.6 (1.9)	1.6 (1.7)			1.2 (1.4)	2.8 (2.9)	1.6 (1.7)	2.8 (3.1)	1.6 (1.7)	3.3	5.0 (5.2)
Carbon	(Found)	52.6 (52.6)	45.2 (45.5)	39.5 (39.7)	39.5 (39.2)	40.8 (40.7)		46.7 (46.8)	46.7 (46.4)	(n)	(u)	42.0 (42.1)	54.1 (54.0)	41.4 (41.7)	54.1 (54.3)	41.4 (41.3)	55.6 (55.7)	60.3 (59.9)
Molecular	Formula	$C_{24}H_{12}N_{4}O_{12}$	C24H10N6O16	$C_{24}H_8N_8O_2O$	$C_{24}H_8N_8O_2O$	$C_{24}H_{10}Br_{2}N_{4}O_{12}$	$C_{24}H_{10}Br_{2}N_{4}O_{12}$	$C_{24}H_{10}CI_{2}N_{4}O_{12}$	$C_{24}H_{10}Cl_2N_4O_{12}$	$\mathrm{C}_{24}\mathrm{H_8}\mathrm{Cl_2N_6}\mathrm{O}_{16}$	$C_{24}H_8Cl_2N_60_{16}$	$C_{24}H_8CI_4N_4O_{12}$	$C_{26}H_{16}N_{4}O_{12}$	$C_{26}H_{12}N_{8}O_{20}$	C26H16N4O12	$C_{26}H_{12}N_{8}O_{20}$	$C_{28}H_{20}N_{4}O_{12}$	C36H36N4O12
Nmr	Ξ	×			×					×	×	×	×	×				
Mol. Wt. (e)	(Found)	548 (548)	638 (638)	728 (728)	728 (728)			616 (m) (616)		706 (m) (706)	706 (m) (706)					756 (756)		
Decomp. Temp. (°C)	(q)	375 (g)	385	355	376	393	382	378	344	358	352	355	320(0)	360	400 (b)	348	282 (o)	
Solvent for Recrystal-	lization	Nitrobenzene	Nitrobenzene	DMF (i)	2-Pentanone	95 (k) Nitrobenzene	90 (1) Nitrobenzene	Nitrobenzene	Nitrobenzene	DMF-H ₂ 0	DMF-H ₂ O	DMF-H ₂ O	DMF-H ₂ 0	DMF-H ₂ 0	DMF	Nitrobenzene	Acetonitrile	
Yield	(c)	09	83	20	95	95 (k)	90 (1)	94 (k)		35	35	06	06	95	62	64	95	92
Prepa- rative Method	(P)	A	¥	B (Ia)	B (I)	А, С	А, С	¥	A	B (If)	B (Ig)	¥	Ą	B(Ik)	¥	B (Im)	¥	∢
	Substituents on I	None	25,27-Dinitro	10,22(24),25,27-Tetranitro (h)	10,12,22,24-Tetranitro	10,22-Dibromo (h)	10,24-Dibromo (h)	10,22-Dichloro (h)	10,24-Dichloro (h)	10,22-Dichloro-12,24-dinitro	10,24-Dichloro-12,22-dinitro	4,6-Dichloro 10,12,22,24-Tetrachloro	11,23-Dimethyl	11,23-Dimethyl-10,12,22,24-tetranitro	25,27-Dimethyl	25,27-Dimethyl-10,12,22,24-tetranitro (h)	10,22-Diethyl (h)	10,22(24)-Di-n-hexyl (h, q)
Substituents	on Resorcinol	None	2-Nitro			4-Bromo	4-Bromo	4-Chloro	4-Chloro			4,6-Dichloro	5-Methyl		2-Methyl		4-Ethyl	4-n-Hexyl
Sm	punod	Ι	Ia	qı	Ic	ΡΙ	le	II	Ig	H	ı	æ	ă	п	m.	'n	임	ď

(a) For nomenclature, see (4). (b) A = by reaction of 1,5-dichloro-2,4-dinitrobenzene with the appropriate resorcinol derivative; B = by nitration of the macrocycle indicated parenthetically; C = by bromination of I. (c) Mole percent crude product, based on either reactant by Method A, and on the macrocycle used by Methods B and C. (d) Uncorrected. (e) By mass spectrometry. (f) An x indicates structural confirmation by nnn; ef. Experimental. (g) Lit. (3) gives "370° dec."; (5) gives ">350° dec.". (h) See text concerning structural assignment. (i) DMF = N,N-dimethyfformamide. (j) High-melting polynitro compounds often give low analyses (7); ef. note (n) below, and Ha in Table II. (k) Combined yield of both isomers by Method C. (m) Basis Cl₃₅. (n) Satisfactory elemental analysis was not obtained with this compound; ef. note (j) above. (o) This compound did not decompose upon melting. (p) Lit. (5) gives ">350°... (q) Obtained only in crude form.

TABLE II
II (a) and Derivatives

				Decomp.		Analysis					
Compound	Substituents on Hydroquinone	Substituents on H	Yield (b)	Temp. (°C)(c)	Molecular Formula	Carbon (Found)	Hydrogen (Found)	Nitrogen (Found)			
11	None	None	44	433 (d)	$C_{24}H_{12}N_4O_{12}$ (e)	52.6 (52.5)	2.2 (2.4)	10.2 (10.5)			
Ha		Tetranitro (f,g)	35	348 (d)	$C_{24}H_{8}N_{8}O_{20}$ (h)	39.5 (39.8)	1.1 (1.4)	15.4 (14.6) (i)			
Hb	2-Methyl	10,21(22)- Dimethyl (g)	45	392	$C_{26}H_{16}N_4O_{12}$	54.2 (54.1)	2.8 (2.9)	9.7 (9.9)			
Hc	2-Bromo	10,21(22)- Dibromo (g)	i 4	428	$C_{24}H_{10}Br_2N_4O_{12}$			8.0 (7.9)			
Hd	2-Chloro	10,21(22)- Dichloro (g)	84	430	$C_{24}H_{10}Cl_{2}N_{4}O_{12}$	46.7 (46.9)	1.6 (1.9)	9.1 (8.9)(j)			
He	2,5-Dichloro	10,21,23,26- Tetrachloro	28	450	$C_{24}H_8Cl_4N_4O_{12}$	42.0 (42.3)	1.2 (1.3)	20.7 (20.7)(k)			

(a) For nomenclature see (4). All compounds were prepared from 1,5-dichloro-2,4-dinitrobenzene and the corresponding hydroquinone (Method A), except as indicated. All were recrystallized from nitrobenzene (except IIa, cf. Experimental). (b) Mole percent crude yield based on either reactant. (c) Uncorrected. (d) Some samples decomposed over a wide range; lit. (5) gives ">350°". (e) Mol. wt. (mass spectrometric) - calcd. 548; found 548. (f) Prepared by nitration of II; nmr data confirm the assigned structure (cf. Experimental). (g) See discussion in text concerning structural assignment. (h) Mol. wt. (mass spectrometric) - calcd. 728; found 728. (i) High-melting polynitro compounds often give low N analyses (cf. Ib, c, and n in Table 1). (j) Calcd. 11.5% chlorine; found 11.6. (k) Calcd. 8.2% chlorine; found 8.0.

tion of L. In both cases, the two pairs had different melting points, and the higher-melting isomer was insoluble in acetone, with the lower-melting one being easily soluble. In each case, the two isomers gave identical infrared, nmr, and mass spectra. The higher-melting isomers are arbitrarily assigned the more symmetrical structures indicated in Table I, but there is no direct evidence for this structure. Only one isomer (le) could be isolated from the product from 4-ethylresorcinol; a low-melting isomer may have been formed, but it could not be obtained in pure form. 4-n-Hexylresorcinol gave a material which could not be satisfactorily purified; the elemental analysis and infrared spectrum of the crude indicate that it is a mixture of macrocyclic isomers.

Compound I was easily and quantitatively nitrated to Ic, in which each ring contains two "outside" nitro groups, a total of eight. Although each of the four rings in theory has a third position open to nitration (all "inside" - at positions 25, 26, 27, and 28), efforts to introduce more than eight nitro groups were unsuccessful, since only destructive oxidation was noted. Reference to a model of Ic shows that the introduction of two of the four possible additional groups might be sterically allowable, but that further nitration would not. As noted in Table I, several other macrocycles were nitrated, but in no case could more than two nitro groups per ring be introduced. Included is Ia, which already contains two "inside" nitro groups.

The indicated positions of the nitro groups in Ic were established by nmr, and are those to be expected by analogy to the known behavior of other resorcinol derivatives upon dinitration. The positions occuried by the entering nitro groups for the other compounds given in Table I (Ic, h, i, I, and n) could not be similarly established, and are assumed by analogy to Ic. In the case of Ib, the product may be a mixture of isomers containing nitro groups in the 22- or 24-positions.

I was easily converted to a water-soluble disulfonate by heating with concentrated sulfuric acid. The seven other compounds listed in Table I made by Procedure A from 4- or 5-substituted resorcinols could likewise be sulfonated, since they have two or four open positions at 10, 12, 22, or 24. Compound Ij, as expected, did not undergo sulfonation, since these four positions are already chlorine-substituted.

The two macrocycles derived from 2-substituted resorcinols (Ia and m) have markedly different properties from those made from the 4- or 5-substituted resorcinols discussed above. This is shown in a comparison of the isomeric dimethyl derivatives Ik and m. The former, prepared from 5-methylresorcinol, was obtained in high yield, has a comparatively low decomposition temperature, and exhibits fair solubility in several organic solvents at elevated temperatures. It easily undergoes nitration (to II), and sulfonation. Im, in contrast, was prepared from 2-methylresorcinol in lower yield, has a much higher

decomposition temperature, and has lower solubilities. Although it could be tetranitrated (to ln), it resisted sulfonation even at elevated temperatures. Ia, prepared from 2-nitroresorcinol, similarly could not be sulfonated, although two additional nitro groups could be introduced, forming lb.

These results suggest a high degree of steric hindrance in the 10, 12, 22, and 24 positions of the macrocycles prepared from the 2-substituted resorcinols. The fact that nitration occurred, but that sulfonation did not, is consistent with the substantially higher steric requirement of the latter groups compared with the former (8).

In a discussion of the possible conformations of I, Lehmann F. (5) cites its "surprisingly large conformational mobility"---with "relatively free concerted rotation about the four ether links", permitting "not only extensive oscillations, but also complete inversion of the rings relative to the molecular plane". Thus, I can easily exist in a "saddle" or a "basket" conformation. Reference to a model shows that positions 10, 12, 22, and 24 in the "saddle" conformation are sterically unhindered, and that substitution should occur there easily, as was actually observed in all cases where R is a proton (i.e. in the macrocycles prepared from resorcinol or from 4- or 5-substituted resorcinols).

On the other hand, models show that macrocycles derived from 2-substituted resorcinols would not have this mobility because the substituting group is large enough to restrict inversion through the "cavity" (5). Presence of a

substituent in the 2-position might be expected to favor the formation of a macrocycle with "basket" conformation, which is less sterically hindered than the other. That such may have occurred is suggested by the resistance of these macrocycles to further substitution, since models show that the 10, 12, 22, and 24 positions in the "basket" conformation are more sterically hindered than those in the other. The models also show that the formation of a tetranitro derivative from the "basket" conformation of Im is still sterically possible, as was in fact observed in its conversion to In. Since the methyl and nitro groups have similar steric requirements, it was thought possible that la could be similarly tetranitrated. However, only two groups could be introduced, forming lb. Experimental determination of the actual conformation of 1m was precluded by its insolubility in nmr solvents (5).

Macrocycles obtained from hydroquinone and its derivatives are listed in Table II. These materials were obtained in lower yields (except for IId) than the analogues from the 4- or 5-substituted resorcinols, have higher decomposition temperatures, and are less soluble in solvents. Although I could be easily brominated or sulfonated, II was recovered unchanged in both cases even after much more drastic treatment. I was easily and quantitatively tetranitrated to one product. II could also be tetranitrated, but the yield was low because of extensive oxidative side reactions, and a mixture of nitro compounds was obtained. Both of these observations are consistent with the known behavior of various other hydroquinone derivatives in nitration (9).

Macrocycles 11b, c, and d are theoretically capable of formation in two isomeric forms. Only one form was noted in each case, however, and (as indicated in Table II) there is no basis for definite structural assignment. Macrocycles could not be obtained from phenyl- or t-butylhydroquinones or from 1,4-dihydroxynaphthalene.

Aryl ethers have a substantial degree of double bond character in the C_{Ar} -O- bond (1). In all the compounds described herein, this tendency is enhanced by mesomerism with the nitro groups placed ortho and para to the ether bridges (5). In the case of II, such tendency to double bonding would be increased even further as the result of the tendency to conjugation of the hydroquinone-based rings; this would not apply to the meta-oriented ether linkages of 1. This may help to explain the high decomposition temperature, low solubility, and reduced reactivity of II compared with I, since such properties would be expected to depend to a considerable degree upon the rigidity of the macrocyclic skeleton, which in turn would correspond to the degree of double bond character in the bridges. Inspection of models suggests that steric factors, on the other hand, may play a comparatively minor role in inhibiting the electrophilic substitution of H.

As indicated above, the properties and low reactivity of the "inside" substituted resorcinol-based macrocycles la and m resemble those of 11 and related hydroquinone compounds more closely than those of the other resorcinol-derived materials. With la and m, the explanation may lie more with steric crowding than with double bond enhancement.

EXPERIMENTAL

Decomposition temperatures are uncorrected and were made in capillary tubes in a Mel-Temp apparatus using a 500° thermometer. Nmr spectra were determined in the stated solvent on a Varian T-60 spectrometer using tetramethylsilane as internal reference. Ir spectra (potassium bromide) were determined on a Perkin-Elmer Model 457 A spectrophotometer. Microanalyses were run by Schwarzkopf Microanalytical Laboratory, Woodside, New York

Typical Preparative Procedure (Method Λ).

A mixture of 4.8 g. (0.02 mole) of 1,5-dichloro-2,4-dinitrobenzene, 0.02 mole of a resorcinol or hydroquinone derivative, 3.4 g. (0.04 mole) of sodium bicarbonate, and 25 ml. of N,Ndimethylformamide was heated with magnetic stirring in an open flask for 2 hours at 150°. The solution was cooled and allowed to stand overnight, since complete precipitation occurs slowly. The solid was filtered and washed with cold solvent. The moist solid was slurried with hot water to remove sodium chloride, and dried to yield the crude macrocycle. Recrystallization was effected from the solvent shown in the tables. Since the macrocycles tend to retain high-boiling solvents, final purification was effected by boiling with 1-propanol, in which they are insoluble.

The above isolation procedure is applicable to all the macrocycles in Tables I and II listed as preparable by Method A, except Id, e, f, g, k, o, and p, which are soluble in cold dimethylformamide. Those compounds were isolated by pouring the reaction mixture into 10 volumes of hot water, followed by refluxing for I hour to coagulate the product, which is otherwise difficult to filter.

Separation of isomers Id-e, and If-g was effected by stirring the crude solids for 1 hour at room temperature with three successive portions of acetone (15 ml. per g. of solid). The acetone extracts were combined and diluted with 40 vol. percent of water to precipitate the crude low-melting isomer. The two isomers were obtained in approximately equal amounts.

Bromination of I (to Id and e).

A mixture of 3.0 g. (5.5 mmoles) of 1, 9.0 g. (55 mmoles) of bromine, and 30 ml. of glacial acetic acid was refluxed for 7 hours (60-70°). The suspension was filtered and the solid dried, yield 3.5 g. (90%). The crude product was separated into isomers Id and e by acetone extraction and recrystallization as described above. They were shown to be identical with those made by Method A by comparison of melting points and ir spectra. Nitration Experiments.

I, If, g, and k were nitrated by heating a suspension of 1.0 g, with 8 g, of 98% nitric acid and 16 g, of 96% sulfuric acid at $80\text{-}90^\circ$ for 2 hours, followed by dilution with ice water. Ia and m were nitrated similarly at $140\text{-}160^\circ$ for 6 hours and at $130\text{-}140^\circ$ for 4 hours, respectively. Compound II was nitrated at $90\text{-}100^\circ$ for 4 hours. The crude product was slurried with cold

acetone to extract Ha from the insoluble H. The solution was diluted to turbidity with 1-butanol, and then boiled briefly to precipitate Ha. (Caution! These polynitro compounds may be explosive.)

Sulfonation of L

A stirred suspension of 1.0 g, of 1 in 10 ml, of 96% sulfuric acid was heated 2 hours at $70\text{-}80^\circ$; a clear solution was gradually formed. The reaction mixture was poured on to 20 g, of crushed ice, and the resulting precipitate was filtered. It was boiled with 50 ml, of saturated sodium chloride solution, forming a clear solution. On cooling to room temperature, a precipitate formed which was filtered and dried at 50° ; the yield 1.3 g. The solid was stirred with hot dimethylformamide and filtered to remove sodium chloride. The filtrate was evaporated to dryness and the solid was triturated three times with boiling 1-propanol to remove residual dimethylformamide.

Anal. Calcd. for $C_{24}H_{10}N_4O_{18}S_2N_{32}\cdot 3\cdot H_2O$: C, 35.8; H, 2.0; S, 8.0. Found: C, 36.1; H, 2.5; S, 7.8.

Spectral Data.

All of the macrocycles gave major ir peaks (potassium bromide pellets) at about 1620-1580 (doublet), 1525 (aromatic nitro), 1475, 1350 (aromatic nitro), 1280 (aromatic ether), 1230, 1050, 920, 830 (para-substituted aromatic), and 680-710 (meta-substituted aromatic) cm⁻¹. The halogenated derivatives of 1 also showed absorption at 1400, 1100-1140, and 860-880 cm⁻¹. Three derivatives of 1 with "outside" alkyl groups (lk, o, and p) also had peaks at 1110, 960, and 870 cm⁻¹, while the one with an "inside" alkyl group (lm) did not.

Nmr spectra confirm the assigned structures as follows: I (DMSO- \mathbf{d}_6), 9.00 (111), 7.30 (4-II), 6.73 ppm (1-II). These data agree with published data for I (5) and its tetrathia analogue (6).

Ic (acetone-d₆), 9.00 (1 H), 7.97 (1 H).

Ih and i (DMSO- d_6), 9.08 (1 II), 8.67 (1 II), 7.67 (1 II), 7.57 (1 II).

lj (acetone-d₆), 8.95 (1 H), 7.92 (1 H), 7.67 (1 H), 7.58 (1 H). lk (DMSO-d₆), 8.93 (1 H), 7.07 (3 H), 6.82 (1 H), 2.37 (3 H). ll (DMSO-d₆), 9.07 (1 H), 7.83 (1 H), 7.77 (1 H), 2.43 (3 H). Ha (acetone-d₆), 9.07 (1 H), 7.08 (1 H), 7.03-8.20 (2 H). Most of the other macrocycles were too insoluble for determination of nmr spectra.

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- 21,23-dodecaene. This name is used in (3). H: 4,6,15,17-Tetranitro-2,8,13,19-tetra o xapenta cyclo[18,2,2,2 9 ,1 2 ,1 3 ,7,1 14 ,1 8] octa cosa-3,5,7(28),9,11,14,16,18(25),20,22,23,26-dodecaene. Lehmann F. (5) has proposed alternative nomenclature.
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