Table III. 1:1 Association Constants β_L (with Confidence Limits) for Polyamines with Carboxylates at 25 °C and $I = 0.2$ M[a]

	ligand				
	L^1	L^2	L^3	L^4	L^5
carboxylate (A)					
citrate[b]	$(5.5 \pm 0.6) \times 10^1$	$(2.5 \pm 0.3) \times 10^2$	$(1.0 \pm 0.1) \times 10^3$	$(2.4 \pm 0.2) \times 10^2$	$(3 \pm 0.3) \times 10$
succinate[c]	negligible[d]	$(1.2 \pm 0.1) \times 10^2$	$(9.2 \pm 1.0) \times 10$	$(1.8 \pm 0.2) \times 10$	negligible[d]
malonate[c]	negligible[d]	$(6.6 \pm 0.7) \times 10$	$(2.5 \pm 0.3) \times 10$	$(3.3 \pm 0.3) \times 10$	negligible[d]
malate[c]	slightly[e]	$(5.0 \pm 0.5) \times 10$	$(2.6 \pm 0.3) \times 10$	$(1.5 \pm 0.2) \times 10$	negligible[d]
maleate[c]		$(7.6 \pm 0.8) \times 10$		$(2.9 \pm 0.3) \times 10$	
fumalate		slightly[e]		negligible[d]	

[a] At least three separate experiments were performed for each association. [b] $\beta_L = [H_3L^{3+}\text{-}A^{3-}]/[H_3L^{3+}][A^{3-}]$ (M^{-1}). [c] $\beta_L = [H_3L^{3+}\text{-}A^{2-}]/[H_3L^{3+}][A^{2-}]$ (M^{-1}). [d] $\Delta E_{1/2}$ is less than 1 mV. [e] $\Delta E_{1/2}$ is too small (2~3 mV) to permit calculation of β_L.

These biological facts about the anion specificities may suggest a positive charge accumulated environment at the binding site similar to those in our model. A citrate carrier may possess a similar recognition site. Our simplified system, however, is not a good model for a transporter of fumarate, one of the intermediates of tricarboxylate cycle.

In biological anion-transport systems, the dicarboxylate anions are often exchanged for phosphate anions.[20,21] The common structural features of polyoxyanions favoring hydrogen bondings with N^+–H might operate in the biological recognition. A phosphate-transport protein in red blood cells is considered to contain three positive charges (by protonated amino group) at the anion-binding site.[40] Our preliminary experiment by the polarography indicated that the dicarboxylate carrier model indeed interacts with phosphate anions to form 1:1 complexes. We are currently investigating the uptake of phosphate anions (and its derivatives) by using our system.[41]

Further structural modification of fundamental structures of the present macrocyclic polyamine molecules will provide strategies for the rational design of organic anion receptors and carriers. Such results should be of interest in biology as well as in chemistry in view of the active current research on anion binding and transport in biological membranes.

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Isomer Distribution Ratios of Phenols in Aromatic Hydroxylation with the Hydroxyl Radical Generated from α-Azohydroperoxide in Anhydrous Organic Media.[1] Comparison with Fenton's Reagent[2,3]

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Abstract: New isomer distribution ratios of phenols in aromatic hydroxylation with the hydroxyl radical generated from α-azohydroperoxide (**1**) in anhydrous organic media are reported. Photodecomposition of **1** (10^{-2} M) in anisole, toluene, chlorobenzene, and nitrobenzene under argon or oxygen gas gave methoxyphenol, cresol, chlorophenol, and nitrophenol, respectively, in yields and isomer ratios listed in Table I. Photodecomposition of **1** (10^{-2} M) in acetonitrile containing toluene or nitrobenzene with various molar ratios under argon gas or under degassed conditions revealed that the isomer ratios under argon gas presented in Table I were reproducible as long as the reactions were conducted in an excess of the substrate. On the other hand, isomer ratios were varied when the reactions were caried out in an excess of **1** compared with the amount of substrate. The isomer ratios were also varied when oxygen was present in the reactants. On the basis of the isomer ratios found by this study, the degree of electrophilicity of the hydroxyl radical generated from **1** under anhydrous conditions and the mechanism of the aromatic hydroxylation are discussed in comparison with the aromatic hydroxylation with Fenton's reagent and others and with the aromatic phenylation, methylation, and trimethylsilylation reported in the literature.

The electrophilic property of the hydroxyl radical has been documented by extensive studies on the ortho:meta:para isomer ratios of phenols[1-15] and the reaction rates[16-18] in the aromatic hydroxylation with the hydroxyl radical generated from Fenton's reagent, by radiolysis of water, and by photolysis of hydrogen

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Table I. Isomer Ratios of Phenols in the Reaction of Aromatics with the Hydroxyl Radical Generated from α-Azohydroperoxide (1) in Anhydrous Media under Argon or Oxygen Gas

substrate	product (phenols)	yield,^{a} %	o:m:p^a	yield,^{b} %	o:m:p^b
anisole	methoxyphenol	10	76:0:24	32	64:0:36
toluene	cresol	7	71:9:20	6	44:40:16
chlorobenzene	chlorophenol	7	38:23:39	22	32:33:35
nitrobenzene	nitrophenol	14	27:47:26	21	37:38:25

^{a} Under argon. ^{b} Under oxygen.

Scheme I

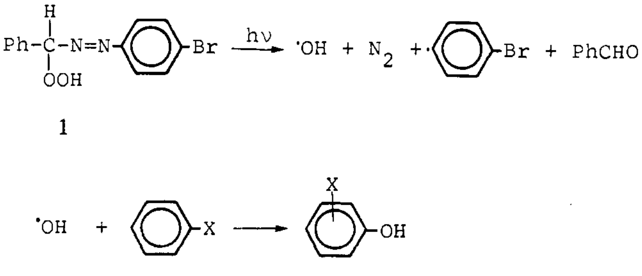


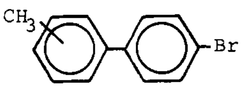
Table II. Isomer Ratios in Photoreaction of 1 (10^{-2} M) with Toluene or Nitrobenzene in Acetonitrile under Argon Gas or Degassed Conditions

run	substrate	molar ratio 1:substrate	gas	isomer ratio o:m:p	phenols
1	toluene	1:100	Ar	70:11:19	cresol
2	toluene	1:10	Ar	74:8:18	cresol
3	toluene	1:1	Ar	73:12:15	cresol
4	toluene	1:0.1	deg	61:20:19	cresol
5	nitrobenzene	1:100	deg	23:44:33	nitrophenol
6	nitrobenzene	1:1	deg	34:17:49	nitrophenol

peroxide. The isomer ratios in the aromatic hydroxylation have been used as a proof for the presence or absence of the hydroxyl radical as a reactive intermediate species in chemical and biological processes.[19,20] However, it appears that there are still many ambiguities concerning the o:m:p isomer ratios and mechanistic paths for the formation of phenols. Walling et al. have reported various isomer ratios of cresols in the hydroxylation of toluene with Fenton's reagent,[22] while the aromatic hydroxylation by radiolysis gives other ratios.[13] It is considered that these variations in the isomer ratios arise from several selective oxidation paths from the intermediate hydroxycyclohexadienyl radical to phenols. Many attempts to clearify the mechanism have been put forward by using Fenton's reagent and radiolysis techniques.[2-15,22] However, several reactive species are produced together with the hydroxyl radical in the reactions by these reagents and techniques, which make the analysis of the reaction mechanism more complicated. Under these circumstances, it is desirable to investigate the aromatic hydroxylation by using a new different hydroxyl radical source. Recently, we have found that α-azohydroperoxide (**1**) generates the hydroxyl radical under anhydrous conditions[1] and investigated the aromatic hydroxylation by using **1**. In this report, we describe the new isomer ratios of phenols in the aromatic hydroxylation with the hydroxyl radical generated from **1** in anhydrous organic media and the comparison of the isomer ratios with those in the reactions with Fenton's reagent and by radiolysis.

Results

As previously reported,[1] photodecomposition and thermal decomposition of α-azohydroperoxide (**1**) give hydroxyl and aryl radicals; the former reacts with benzene, for example, to give phenol (Scheme I). In order to obtain the o:m:p isomer ratios of phenols, we carried out the photodecomposition of **1** in anisole, toluene, chlorobenzene, and nitrobenzene. The photolysis of **1** in these aromatics with a high-pressure mercurry lamp through a Pyrex filter under argon gas gave methoxyphenol, cresol, chlorophenol, and nitrophenol in yields and isomer ratios listed in Table I, together with benzaldehyde and diphenyl derivatives. For example, products[5] other than cresol in the reaction of toluene with **1** under argon gas were benzyl alcohol (3%), dibenzyl (6%), ditolyl (1%), bromomethyldiphenyl (**2**, 32%), bromobenzene (42%), *p*-bromophenol (trace), and benzaldehyde (111%). It is to be noted that the isomer ratios of phenols indicated in Table I under argon gas were not varied even when the reactions were carried out in acetonitrile as far as the molar ratios of the substrate to **1** were kept sufficiently large. For example, the photolysis of an acetonitrile solution of a 1:100 or 1:10 mixture of **1** and toluene (10^{-2} M) under argon gas gave cresol with the o:m:p isomer ratio of approximately 70:10:20 (Table II, runs 1 and 2) identical with that observed in toluene (see Table I). Similarly, photolysis of an acetonitrile solution (10^{-2} M) of a 1:100 mixture of **1** and nitrobenzene under degassed conditions gave nitrophenol with the isomer ratios listed in Table II (run 5) which is identical with that observed in nitrobenzene within experimental errors (see Table I).



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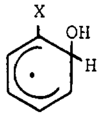

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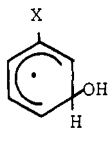

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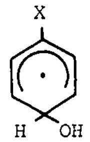

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On the other hand, when relative amounts of the hydroperoxide **1** to the substrate increased, the isomer ratios were varied. The photolysis of a degassed acetonitrile solution (10^{-2} M) of a 1:0.1 mixture of **1** and toluene gave cresol with the o:m:p isomer ratio of 61:20:19 (Table II run 4) in which the ratio of *o*-cresol decreased while the m isomer increased slightly in comparison with the isomer ratio observed in excess toluene such as in a 1:100 mixture of **1** and toluene (Table II run 1) or in the decomposition of **1** in toluene (Table I). The same trend for the isomer ratio was also observed in the reaction of a 1:1 mixture of **1** and toluene (Table II, run 3). Similarly, the photolysis of a degassed acetonitrile solution (10^{-2} M) of a 1:1 mixture of **1** and nitrobenzene

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Table III. Isomer Ratios of Phenols in the Reaction of Anisole, Toluene, Chlorobenzene, and Nitrobenzene with Fenton's Reagent

phenols	isomer ratio o:m:p	ref
methoxyphenol	84:0:16	4
	85:4:11	30
cresol	71:5:24	5
	59:12:29[a]	3
chlorophenol	42:29:29	4
	58:10:32	3
nitrophenol	24:30:46	4
	15:35:50[b]	3

[a] Cu^{2+} added. [b] Fe^{3+} added.

gave nitrophenol with the o:m:p isomer ratio of 34:17:49 (Table II, run 6) in which *m*-nitrophenol decreased, while the o and p isomer ratios increased in comparison with the isomer ratio observed in excess nitrobenzene such as a 1:100 mixture of **1** and nitrobenzene (Table II, run 5) or in the decomposition of **1** in nitrobenzene (Table I). The test for a 1:0.1 mixture of **1** and nitrobenzene could not be made because of analytical difficulty.

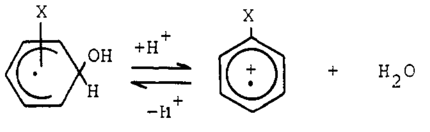
The isomer ratios of phenols were also widely varied when oxygen was present in the reactants. When α-azohydroperoxide (**1**) was decomposed in anisole, toluene, chlorobenzene, and nitrobenzene when bubbling through oxygen gas, methoxyphenol, cresol, chlorophenol, and nitrophenol were formed in yields and isomer ratios listed in Table I. The ratios observed here are considerably different from those observed under argon gas.

Discussion

The general trend of the isomer distribution ratios of phenols in the aromatic hydroxylation with **1** under argon gas indicated in Table I may be consistent with that observed in the reaction with Fenton's reagent except for nitrophenol, some examples of which are listed in Table III. However, the following differences are to be noted.

First, the ratio of *m*-nitrophenol is considerably varied with the reagents and techniques employed. The highest isomer ratio of *m*-nitrophenol was observed in the reaction with **1** (Table I), while the ratio of *o*-nitrophenol is lowest in the reaction with Fenton's reagent (see Table III). The highest ratio of *m*-nitrophenol, on the other hand, was observed in the reaction with Fenton's reagent under strong acidic conditions in the presence of the metal oxidant (Fe^{3+}), but the pattern of distribution of the isomer in this case changes remarkably (o:m:p = 5:55:40).[3] Second, the isomer ratio of cresol observed in this study is in accordance with that reported by Smith and Norman,[5] but Walling et al. have reported several variations in the isomer ratios of cresols in the reaction with Fenton's reagent.[22]

In general, the change of the isomer ratios in different reaction conditions has been ascribed to the presence of different oxidation steps from the intermediate hydroxycyclohexadienyl radicals **3**, **4**, and **5** which are formed by the attack of the hydroxyl radical at the o:m:p aromatic carbons.[2,3,13,22] It is considered that these variations arise from two sources: the selective oxidation of the isomeric radicals **3**, **4**, and **5** to the corresponding phenols and the interconversion of these radicals to the radical cation (**6**) as shown in eq 1.[3] Since the interconversion of the hydroxycyclohexadienyl radicals **3–5** to the radical cation **6** is effective under aqueous acidic media, the formation of the radical cation **6** in the reaction with **1**, which is carried out in anhydrous organic media, is unfavorable.[3] Therefore, we do not take into account the equilibrium between **3–5** and **6** indicated by eq 1 in our discussion.



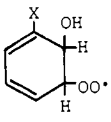
(1)

3–5 6

It is well accepted that suitable oxidants convert the intermediate cyclohexadienyl radicals to the substituted benzenes without causing any secondary isomerization of the radicals. Molecular oxygen has been used as a good oxidant in the aromatic phenylation with the phenyl radical[23] and others. We also have examined the effects of oxygen in the reaction with **1** and found that photodecomposition of **1** in anisole, toluene, chlorobenzene, and nitrobenzene gave the corresponding phenols in higher yields except for cresol, while the isomer ratios were varied widely (Table 1). The isomer ratios observed here are not consistent with those reported in the reaction with Fenton's reagent and by radiolysis in the presence of oxygen except for one case. For example, the following isomer ratios have been reported (o:m:p):39:0:61[8] or 36:–:64[12] for methoxyphenol; 37:42:21[13] or 46:36:18[22] for cresol; 37:22:41[13] for chlorophenol; 46:24:30 or 43:17:22[13,14] for nitrophenol. Among them, the isomer ratio of cresol observed in this study is consistent with that reported by Walling et al. in the reaction with Fenton's reagent in the presence of oxygen[22] within experimental errors. However, it appears that the isomer ratios of phenols under oxygen tend to average in comparison with those of phenols under argon gas. For example, the o:p ratio of methoxyphenol under argon gas is 3.0 (o:m:p = 76:0:24) but changes to 1.8 under oxygen (o:m:p = 64:0:34). Similarly, the o:m:p ratio of chlorophenol shifts to an 1:1:1 ratio under oxygen from the 1.6:1:1.7 ratio under argon gas (see Table 1).

It is important that the effect of oxygen observed in the aromatic hydroxylation with the hydroxyl radical differs considerably from that observed in the aromatic phenylation with the phenyl radical. Morrison et al.[23] have reported that the molecular oxygen present in the reactant affects the yields of the phenylated products, but it does not vary the isomer ratios of the products. The same isomer ratios were obtained regardless of the presence or absence of oxygen for the case of the aromatic phenylation.[23]

In view of Dorfman's mechanism,[17] proposed for the oxidation of the hydroxycyclohexadienyl radical by oxygen, it is expected that molecular oxygen adds with the substituted hydroxycyclohexadienyl radicals,[8] for example, with **3**, to give the peroxy radicals **7** and **8**. From **8**, for example, the m isomer may be derived from the bimolecular decomposition and subsequent hydrogen abstraction followed by the dehydration from **9**. This would bring about the averaging of the isomer ratios of phenols. Of course, we must examine whether or not molecular oxygen enters into phenolic oxygen before we conclude it. Meanwhile, we should consider an alternate possibility: that molecular oxygen abstracts a methine hydrogen from **3**, **4**, and **5** efficiently and hence the isomer ratios of phenols reflect the true extent to which o:m:p aromatic carbons are attacked by the hydroxyl radical. However, as mentioned above, the effects of oxygen in the aromatic hydroxylation with the hydroxyl radical differ considerably from those observed for the aromatic phenylation and others. From these reasons we must leave our discussion on the effects of oxygen



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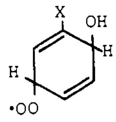

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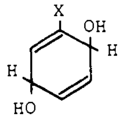

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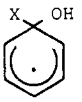

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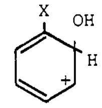

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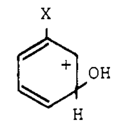

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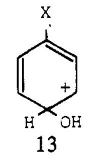

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on the aromatic hydroxylation until our further works are complete.

Apart from the arguments on the oxygen effects, we would like to discuss the mechanism of aromatic hydroxylation and the property of the hydroxyl radical generated from **1** under anhydrous conditions and argon gas. We have shown that the isomer ratios of cresol and nitrophenol were varied when a large excess of **1** compared with the amount of the substrate was used for the reaction. We consider that these variations arise from the oxidative effect of the hydroperoxide **1** employed in large excess.[23] It is seen, however, that the isomer ratios in the presence of a large excess of substrate under argon gas converge to constant values (see Table II). Therefore, in the following discussion we use the isomer ratios observed under argon gas listed in Table I.

The fact that fairly good amounts of *p*-bromodiphenyl[1] and bromomethyldiphenyl (**2**) were obtained in the reaction of **1** with benzene and toluene, respectively, suggests that the addition of the *p*-bromophenyl radical generated together with the hydroxyl radical from **1** is sufficiently fast to compete with the abstraction of a hydrogen from **3–5**. In fact, only small amounts of bromobenzene were formed in the reaction of benzene with **1**. In the reaction of toluene, however, fairly good amounts of bromobenzene were formed; this may partially arise from the abstraction of the methyl hydrogens from toluene by the *p*-bromophenyl radical, though it must be confirmed.

Therefore, we consider that an important reaction which converts **3**, **4**, and **5** to phenols in the reaction of **1** under argon gas is the crossover disproportionation. There are two types of crossover disproportionation reactions: the nonselective and selective ones. The former has been observed in the aromatic phenylation,[23a] while the latter is postulated for the aromatic hydroxylation by radiolysis.[13-15] In the nonselective disproportionation, the isomer ratios of phenols arising from **3–5** reflect the extent to which the o:m:p aromatic carbons are attacked by the hydroxyl radical. Though we can not decide whether nonselective or selective disproportionation is operating in the reaction with **1** on the basis of the limited data obtained here, it is worthy to note that we can deduce the degree of the electrophilicity of the hydroxyl radical in connection with its ionization potential or SOMO energy with the assumption that the disproportionation is nonselective.

The m:p value for the hydroxylation of toluene with **1** in anhydrous organic media is now found to be 0.5, while that for nitrobenzene is 1.8 (see Table I). The former is the lowest value in the series of m:p's 2.2, 1.6, and 1.4 for the trimethylsilylation,[25] methylation,[26] and phenylation[27] of toluene, respectively. On the other hand, the latter is the highest value in the series of m:p's 0.2 and 0.4 for the methylation[26] and phenyltion[23,24,27] of nitrobenzene, respectively. These values indicate, as generally accepted, a high degree of electrophilicity of the hydroxyl radical generated even in anhydrous organic media. Since the ionization potential of the hydroxyl radical (−13.2 eV)[28] is the lowest of those of the trimethylsilyl (−7.0),[25] phenyl (−9.2), and methyl (−9.8) radicals,[25,28] it is expected that the SOMO of the hydroxyl radical interacts with the HOMO of aromatics most efficiently.[29] In fact, the isomer ratios of chlorobenzene and nitrobenzene found by this study are fairly consistent with the ratios (%) of the o:m:p MO coefficients for the HOMO of chlorobenzene (42:26:32) and nitrobenzene (36:47:17) calculated by Eberhardt and Yoshida.[13] However, higher o isomer ratios have been observed for cresol and methoxyphenol (see Tables I and III). This may be explained as being due to the ipso attack and subsequent 1,2 OH shift as shown by **10**.[13] Alternatively, it may be explained by the selective disproportionation in **3–5** competing with the nonselective one. If we can assume that the one-electron transfer is involved in the selective disproportionation, then it is expected that the cationic species **11**, **12**, and **13** which are instantly converted to phenols as suggested by Jefcoate et al. are formed as transients.[30] With electron-donating substituents, the cation **11** is most stable among the others (**12** and **13**); therefore we expect that the occurrence of the selective disproportionation of this type in competition with the nonselective one increases the ratios of the o isomer of cresol and methoxyphenol.

Experimental Section

Toluene and chlorobenzene were treated with concentrated sulfuric acid, washed with diluted alkali and water, dried over calcium chloride, and then distilled. Anisole and nitrobenzene in reagent grade were distilled before using. α-Azohydroperoxide (**1**) was prepared by the method described in the literature.[1,31] The isomer ratios and yields of phenols were obtained on the average by repeating the same reaction run two or three times.

Photodecomposition of 1 in Anisole under Argon or Oxygen Gas. An anisole solution (30 mL) of **1** (198 mg, 0.65 mmol) in a Pyrex tube was irradiated with a 400-W high-pressure mercury lamp under argon or oxygen gas for 3 h. After removal of excess solvent under reduced pressure, the resulting residue was treated with hexamethyldisilazane to analyze methoxyphenol. After addition of naphthalene as an internal standard, trimethylsilyl ether of methoxyphenol was analyzed by GLC (OV-101 glass capillary column, 20 m; FID).

Photodecomposition of 1 in Toluene under Argon or Oxygen Gas. A toluene solution (40 mL) of 1 (140.5 mg, 0.46 mmol) was photolyzed in the same manner as in the case of anisole. Products were analyzed as follows. (a) To the reaction mixture was added naphthalene as an internal standard, and the mixture was directly analyzed by GLC (4 mm × 3 m glass column, KG-02 on Uniport HP; TCD), by which yields of bromobenzene and benzaldehyde were determined. (b) From the solution utilized above, the solvent was removed under the reduced pressure at room temperature, and the resulting residue was analyzed by GLC (4 mm × 3 m glass column, KG-02 on Uniport HP; TCD with temperature programing for 1 °C/min.), by which yields of cresol, benzyl alcohol, and bromomethyldiphenyl (**2**) were determined. (c) To the above residue was added fluorenone as an internal standard, and the products were analyzed by GLC (4 mm × 2 m glass column, 8% SF-96; FID), by which yields of dibenzyl and ditolyl were determined. (d) To the residue utilized above was added hexamethyldisilazane, and the mixture was analyzed by GLC (KG-02 glass column; FID) by which the o:m:p isomer ratio of cresols was determined.

The structural assignment of these compounds was made by GC/mass and GLC in comparison with the authentic samples. Bromomethyldiphenyl (**2**) was separated from the reaction mixture as a mixture of two components A and B (a mixture of isomers) which have the following spectroscopic properties. A: δ 2.13 (3 H, s, CH_3) and 7.10–7.47 (8 H, m, aromatic); m/e 248, 246 (1:1) (M^+), 167, 152. B: δ 2.35 (3 H, s, CH_3) and 7.20–7.35 (8 H, m; aromatic); m/e 248, 246 (1:1) (M^+), 167, 152.

Photodecomposition of 1 in Chlorobenzene under Argon or Oxygen Gas. A chlorobenzene solution (39 mL) of 1 (98.2 mg, 0.32 mmol) in a Pyrex tube was photolyzed under argon or oxygen gas as in the same manner described. The solvent was removed from the reaction mixture under reduced pressure, and the residue was treated with hexamethyldisilazane to analyze chlorophenol. After addition of diphenyl ether as an internal standard, the mixture was analyzed by GLC (SE-30 glass capillary column, 20 m; FID), by which yield and isomer ratio of chlorophenol were determined.

Photodecomposition of 1 in Nitrobenzene under Argon or Oxygen Gas. A nitrobenzene solution (35 mL) of 1 (96.5 mg, 0.31 mmol) was photolyzed in the same manner described. To the reaction mixture was added hexamethyldisilazane, and the mixture, without removal of the solvent, was analyzed by GLC (4 mm × 3 m glass column, 8% SF-96 on Cellite; FID), by which yield and isomer ratio of nitrophenol were determined.

Photodecomposition of 1 (10^{-2} M) in Acetonitrile Containing Toluene or Nitrobenzene under Argon Gas or Degassed Conditions. (a) Under Argon Gas. An acetonitrile solution (16 mL) of **1** (50.1 mg, 0.163 mmol)

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and toluene (1.7 mL, 16 mmol; 170 μL, 1.6 mmol; 16 μL, 0.15 mmol) was photolyzed in the same manner as described, and the isomer ratios of cresols were analyzed in the same manner as described.

(b) Under Degassed Conditions. An acetonitrile solution (16 mL) of **1** (46.8 mg, 0.152 mmol) and toluene (1.6 μL, 0.015 mmol) or nitrobenzene (1.6 mL, 16 mmol, or 16 μL, 0.16 mmol) in a Pyrex tube was degassed and sealed. Each solution was photolyzed in the same manner as described. The isomer ratios of cresols and nitrophenols were analyzed in the same manner as described.

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The Permethylcyclosilanes $(Me_2Si)_5$ through $(Me_2Si)_{35}$[1]

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Abstract: The cyclic permethylpolysilanes $(Me_2Si)_n$, where $n = 5$–35, are all formed when dimethyldichlorosilane (Me_2SiCl_2) is added slowly to sodium–potassium (Na/K) alloy in tetrahydrofuran (THF). NMR, UV, and vibrational spectra are reported for compounds $n = 5$–19. The ^{13}C NMR and ^1H NMR spectra are explained in terms of methyl–methyl group interactions. Raman and IR spectra are assigned and partially explained on the basis of a standing wave model.

Until recently the synthesis of cyclopolysilanes was limited to the four-, five-, six-, and seven-membered[2] ring compounds. The medium-ring cyclosilanes $(Me_2Si)_8$ and $(Me_2Si)_9$ were reported in 1978.[3] Recently[4] we communicated the synthesis of the larger cyclics $(Me_2Si)_n$, where $n = 10$–35. These rings apparently form the largest homologous series of cyclic compounds now known, except for the cycloalkanes. Apart from their synthetic interest, these cyclic compounds are of importance because of the unique properties[5] of the five- and six-membered rings, which indicate unusually facile electron delocalization in these molecules. This in turn has generated interest in the study of the permethylated polysilanes in general, as model compounds for the study of eletronic effects in elemental silicon.[10] In this paper we describe the synthesis of the large $(Me_2Si)_n$ rings and present the fundamental spectroscopic properties of all the rings through $(Me_2Si)_{19}$.[11]

Table I. Yield and Mass Spectral Data for Permethylcyclosilanes, $(Me_2Si)_n$

	yield, wt %				
n	a	b	mass calcd	mass obsd	dev, ppm
5	12[a]	17[b]			
6	54	52			
7	3.0	2.6			
8	1.8	1.3	464.1910	464.1908	−0.4
9	1.0	0.76	522.2149	522.2160	2.1
10	0.23	0.15	580.2388	580.2368	−3.4
11	0.26	0.18	638.2626	638.2628	0.3
12	0.23	0.16	696.2865	696.2879	2.0
13	0.21	0.19	754.3104	754.3080	−3.2
14	0.21	0.21	812.3343	812.3332	−1.4
15	0.21	0.22	870.3581	870.3572	−1.1
16	0.18	0.19	928.3820	928.3798	−2.4
17	0.13	0.14	986.4059	986.4077	1.7
18	0.09	0.09	1044.4298	1044.4324	2.5
19	0.05	0.05	1102.4537	1102.4571	3.2
24			1392.5730	1392.5767	2.7

[a] Yields using 10 mol of Me_2SiCl_2. [b] Yields using 2 mol of Me_2SiCl_2.

Experimental Section

Reagent purification and some experimental techniques including safety precautions have been described elsewhere[14,15] and will not be reported here.

Synthesis and Separation of Cyclopolysilanes. Dry THF (1200 mL) and Na/K alloy (185 mL, 4.7 mol) were stirred at reflux in a dried 5-L flask equipped with a high-capacity condenser while Me_2SiCl_2 (244 mL, 2.0 mol) was added dropwise over a period of 8 h. The mixture was then cooled slightly and 1200 mL of hexane was added, after which the excess alloy was gradually destroyed by the *very cautious*, dropwise addition of approximately 100 mL of water. Another 1000 mL of water was then added to dissolve salts. The organic phase was separated, filtered to remove polymer, and washed with small amounts of additional water to

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[1] Paper number 20 in the series "Cyclic Polysilanes". For previous paper in this series see ref 18.

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