20 °C. All of the titrations were carried out so that the solution was 0.01 N at the equivalence point. The pK_a was calculated as the pH of the solution at half the equivalence point volume. All titrations were carried out three times, and the theoretical equivalence point was within 0.25% of the experimental value. In each case, only a single inflection point was observed. For a discussion on the effect of ethanol on the apparent strength of organic amine bases and for a method for the extrapolation of the pK_a from solutions which are progressively less alcoholic, see the paper of Hall et al.[23]

Acknowledgment is made to the National Science Foundation for partial support of this research.

Registry No. 1, 2809-93-0; 2, 3234-64-8; 3, 74986-44-0; 4, 1571-51-3; 5, 3234-65-9; 6, 74986-45-1; 7, 74986-46-2; 8, 74986-47-3; 9, 74986-48-4; 10, 74986-49-5; 11, 74986-50-8; 12, 74986-51-9; 14, 30389-18-5; acetylene, 74-86-2; 3-pentanone, 96-22-0; 3-ethyl-1-pentyn-3-ol, 6285-06-9; 2,4-dimethyl-3-pentanone, 565-80-0; 4-methyl-3-isopropyl-1-pentyn-3-ol, 5333-87-9; 3-chloro-3-ethyl-1-pentyne, 6080-79-1; 3-chloro-3-methyl-1-pentyne, 14179-94-3; 3-methyl-1-pentyn-3-ol, 77-75-8; 3-chloro-3-methyl-1-butyne, 1111-97-3; 2-methyl-3-butyn-2-ol, 115-19-5; 3-chloro-4-methyl-3-isopropyl-1-pentyne, 74986-52-0; 3-amino-3-methyl-1-butyne, 2978-58-7; 3-amino-3-methyl-1-pentyne, 18369-96-5; 3-amino-4-methyl-3-isopropyl-1-pentyne, 74986-53-1; (1'-ethyl-1'-methyl-2-propynyl)(1,1-dimethyl-2-propynyl)amine, 74986-54-2; bis(1-ethyl-1-methyl-2-propynyl)amine, 74986-55-3; (1-ethyl-1-methyl-2-propynyl)(1,1'-diethyl-2-propynyl)-amine, 74986-56-4; bis(cyclohexylethynyl)amine, 74986-57-5; 1-chloro-1-ethynylcyclohexane, 6209-75-2; bis(1,1-diethylallyl)(1,1-diethyl-2-propynyl)amine, 74986-58-6; bis(1,1-diethylallyl)amine, 74986-59-7; bis(1,1-diethylallyl)(1,1,1-triethylcarbinyl)amine, 74998-56-4; bis(1,1-dimethylpropyl)amine, 2978-47-4; (1'-ethyl-1'-methylpropyl)(1,1-dimethylpropyl)amine, 74986-60-0; bis(1-ethyl-1-methylpropyl)amine, 74986-61-1; (1-ethyl-1-methylpropyl)(1',1'-diethylpropyl)amine, 74986-62-2; bis(1-ethylcyclohexyl)amine trifluoroboron salt, 74986-63-3; 3-ethyl-2-pentene, 816-79-5; 1-ethynyl-1-cyclohexanol, 78-27-3; diisopropylamine HCl, 819-79-4; 2,2,6,6-tetramethylpiperidine HCl, 935-22-8; bis(1,1-dimethylpropyl)amine HCl, 3374-96-7; (1'-ethyl-1'-methylpropyl)(1,1-dimethylpropyl)amine HCl, 74986-64-4; bis(1-ethyl-1-methylpropyl)-amine HCl, 74986-65-5; (1-ethyl-1-methylpropyl)(1',1'-diethylpropyl)amine HCl, 74986-66-6; bis(1,1-diethylpropyl)amine HCl, 74986-67-7; bis(1-ethylcyclohexyl)amine HCl, 74986-68-8.

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Preparation and Stereochemistry of Some Substituted 4-Selenanones and 4-Selenanols

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The preparation of a number of substituted 4-selenanones and four epimeric pairs of 4-selenanols has been described. The configuration and conformation of the 4-selenanones and 4-selenanols were assigned on the basis of IR, ^1H NMR, and ^{13}C NMR spectral data, and the selenane ring was shown to be predominantly in the chair form. The dissociation constants of cyanohydrins from six substituted 4-selenanones were measured in 80% dioxane at 25 °C, and the results were analyzed in terms of steric parameters in the flattened ring systems.

Simple six-membered heterocyclic ketones and the corresponding alcohols containing sulfur,[2-4] oxygen,[2,5,6] nitrogen,[6,7] and phosphorus[8-10] are known to exist mostly in the chair conformation. However, there has been little work on functionalized selenium heterocycles.[6] We report herein general methods of preparation of these systems with spectral and chemical evidence regarding the configuration and conformation for the saturated, six-membered selenium heterocyclics.

Results and Discussion

Lalezari[11a] and co-workers reported the formation of some 2,6-diaryl-4-selenanones during the reaction of symmetrical distyryl ketones with hydrogen selenide in the presence of sodium acetate. In the present investigation, several substituted 4-selenanones were prepared by the condensation of unsymmetrical distyryl ketones with hydrogen selenide. The procedure used for the synthesis of selenanones **2a–d** was similar to that published[11a] but with

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Table I. IR and ^{1}H NMR Data for Substituted 4-Selenanones

compd	mp,[a] °C	% yield	IR C=O stretch, cm^{-1}	δ values H(2)	H(3)	H(6)	other
2a	137-139	64	1691	4.53 (dd, 2 H, H(2), H(6), J = 12.0, 4.0 Hz)	2.92-3.39 (m, 4 H, H(3), H(5))		2.33 (s, 6 H, CH_3), 7.09-7.30 (m, 8 H, ArH)
2b	124-125	65	1694	4.17 (d, J = 11.0 Hz)	3.06-3.55 (m, 3 H, H(3), H(5))	4.56 (dd, J = 12.0, 3.5 Hz)	0.95 (d, 3 H, CH_3), J = 6.0 Hz), 7.20-7.35 (m, 10 H, ArH)
2c	102-103	62	1694	4.25 (d, J = 11.0 Hz)	3.05-3.54 (m, 3 H, H(3), H(5))	4.58 (dd, J = 12.0, 3.0 Hz)	0.79 (t, 3 H, CH_2CH_3, J = 7.0 Hz), 1.16-1.70 (m, 2 H, CH_2CH_3), 7.31 (s, 10 H, ArH)
2d	46	63	1698		2.42-3.24 (m, 4 H, H(3), H(5))	4.42-4.64 (m)	1.42 (s, 3 H, CH_{3a}[b]), 1.56 (s, 3 H, CH_{3e}[b]), 7.12-7.38 (m, 5 H, ArH)
3	106-108	61	1694	4.55 (dd, 2 H, H(2), H(6), J = 12.0, 4.0 Hz)	2.95-3.41 (m, 4 H, H(3), H(5))		7.30 (s, 10 H, Ar H)
4	171-173	68	1690	4.68 (dd, 2 H, H(2), H(6), J = 10.0, 4.0 Hz)	2.59-2.85 (m, 4 H, H(3), H(5))		3.77 (s, 6 H, OCH_3), 6.82 (d, 4 H, Ar H, J = 8.0 Hz), 7.30 (d, 4 H, Ar H, J = 10.0 Hz)

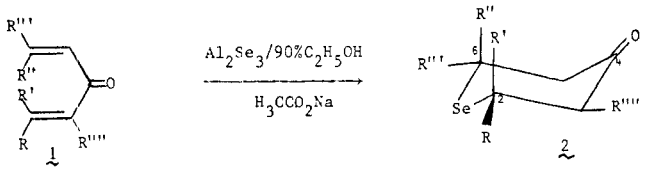
[a] All selenanones were crystallized from petroleum ether (bp 60-80 °C). Abbreviations used are as follows: s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiplet; br s, broad singlet. Elemental analysis data were as follows. Found (2a): C, 66.65; H, 3.31. Calcd: C, 66.47; H, 3.37. Found (2b): C, 65.78; H, 5.59. Calcd: C, 65.65; H, 5.51. Found (2c): C, 66.31; H, 3.90. Calcd: 66.47; H, 3.87. Found (2d): C, 58.19; H, 6.10. Calcd: C, 58.43; H, 6.04. [b] Subscript a and e for axial and equatorial, respectively.

Table II. ^{13}C NMR Chemical Shifts (δ) for Substituted 4-Selenanones[a]

compd	C(2)	C(3)	C(4)	C(5)	C(6)	other
2a	41.20	50.51	208.74			20.98 ($C_6H_4CH_3$), 137.29, 136.98, 129.28, 126.71 (Ar)
2b	51.24	52.11	210.36	48.36	41.99	12.78 (CH_3), 139.89, 139.02, 128.57, 126.81 (Ar)
2c	51.84	59.41	210.21	47.53	42.53	12.12 (CH_2CH_3), 20.24 (CH_2CH_3), 140.00, 139.04, 128.64, 127.59, 126.93 (Ar)
2d	41.65	57.83	208.50	49.75	38.20	31.37 (CH_{3e}), 30.81 (CH_{3a}), 139.66, 128.36, 127.23, 126.91 (Ar)
3	41.46	50.33	208.46			139.83, 128.65, 128.30, 126.84 (Ar)
4	38.71	48.35	209.16			55.06 (OCH_3), 158.44, 133.38, 128.30, 113.80 (Ar)

[a] Given in parts per million downfield from Me_4Si; data were obtained by using 1.5 M $DCCl_3$.

crucial modifications. The details are given in the Experimental Section.



	R	R'	R''	R'''	R''''
a	p-$CH_3C_6H_4$	H	H	p-$CH_3C_6H_4$	H
b	C_6H_5	H	H	C_6H_5	CH_3
c	C_6H_5	H	H	C_6H_5	C_2H_5
d	C_6H_5	H	CH_3	CH_3	H

Stereochemistry of 4-Selenanones. If a chair conformation is accepted for the selenane ring,[11b] the two phenyl groups and the methyl group in **2b** (or the ethyl group in **2c**) may be expected to occupy the stable equatorial position. Much information on the stereochemistry of 4-selenanones **2a–d** can be gathered from their ^{1}H NMR spectral data which are given in Table I. The signals at δ 4.17 (d, J = 11 Hz) and 4.56 (dd, J = 12, 3.5 Hz) for **2b** correspond to the H(2) and H(6) protons, respectively. In selenanone **2b**, $J_{H(2a),H(3a)}$ = 11.00 Hz and is in fairly good agreement for the diaxial arrangement of protons at C(2) and C(3). Hence, the phenyl group and the methyl group in **2b** have been assigned equatorial positions. The coupling constants of 12.0 and 3.5 Hz for $J_{H(6a),H(5a)}$ and $J_{H(6a),H(5e)}$, respectively (which are characteristic of vicinal coupling constants J_{anti} and J_{gauche} in the chair form), suggest that H(6) is in an axial orientation. Likewise, the phenyl group at position 2 and the ethyl group at position 3 in selenanone **2c** have been assigned the equatorial

Table III. Dissociation Constants of Cyanohydrins of Substituted 4-Selenanones at 25 °C in 80% Dioxane

compd	4-selenanone	$10^3K^{25}_D$, mol L^{-1}
2a	r-2,cis-6-di-p-tolyl	9.17 ± 0.02
2b	r-2,cis-6-diphenyl-$trans$-3-methyl	13.15 ± 0.05
2c	r-2,cis-6-diphenyl-$trans$-3-ethyl	23.49 ± 0.01
2d	2,2-dimethyl-6-phenyl	29.97 ± 0.04
3	r-2,cis-6-diphenyl	8.77 ± 0.02
4	r-2,cis-6-di-p-anisyl	9.67 ± 0.03

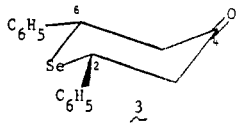
Table IV. Substituted 4-Selenanols and Corresponding Acetates

compd	% yield	mp, °C	formula	anal. % found C	anal. % found H	anal. % calcd C	anal. % calcd H
6a	*d*	210-212[c]	$C_{19}H_{22}OSe$	66.22	6.34	66.08	6.42
6b	*d*	160-161[a]	$C_{18}H_{20}OSe$	65.11	6.16	65.25	6.09
6c	*d*	120-121[b]	$C_{19}H_{22}OSe$	66.22	6.35	66.08	6.42
6d	*d*	133-135[a]	$C_{13}H_{18}OSe$	55.86	6.68	55.99	6.74
7a	*d*	136-137[a]	$C_{19}H_{22}OSe$	66.20	6.36	66.08	6.42
7b	*d*	152-153[a]	$C_{18}H_{20}OSe$	65.12	6.15	65.25	6.09
7c	*d*	106-107[b]	$C_{19}H_{22}OSe$	66.21	6.35	66.08	6.42
7d	*d*	61-62[b]	$C_{13}H_{18}OSe$	57.85	6.68	57.99	6.74
6e	66	120-121[a]	$C_{21}H_{24}O_2Se$	65.02	6.31	65.11	6.25
6f	76	108-109[a]	$C_{20}H_{22}O_2Se$	64.46	5.86	64.34	5.94
6g	73	141-142[b]	$C_{21}H_{24}O_2Se$	65.05	6.29	65.11	6.25
7e	70	114-115[a]	$C_{21}H_{24}O_2Se$	65.04	6.30	65.11	6.25
7f	74	106-107[a]	$C_{20}H_{22}O_2Se$	64.45	5.88	64.34	5.94
7g	71	99-100[a]	$C_{21}H_{24}O_2Se$	65.02	6.33	65.11	6.25

[a] Recrystallized from aqueous ethanol. [b] Recrystallized from petroleum ether (bp 60-80 °C). [c] Recrystallized from ethanol. [d] The yields for the selenanols depend upon the reducing conditions (see Table V).

positions on the basis of similar ^1H NMR data. Since the ^1H NMR shifts and J values for H(2) and H(6) in **2b** and **2c** are quite similar, the two selenanones probably have the same conformation.

Inspection of the ^{13}C chemical shift data in Table II reveals that the resonance signal for the carbonyl carbon C(4) in **2b** is shifted downfield by 1.9 ppm compared to the C(4) signal in **3**. This may be attributed to the 3-alkyl



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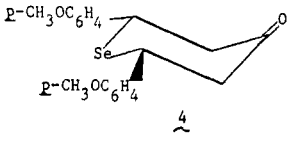

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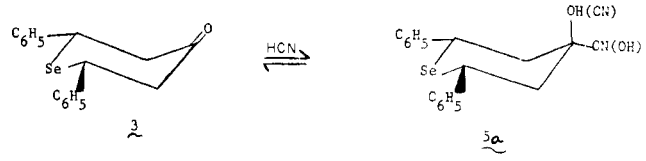
substituent effect on the C(4) resonance. Interestingly, this deshielding effect is close in magnitude to that found[12] for C(4) in *r*-2,*cis*-6-diphenyl-*trans*-3-methyl-4-thianone, which was deshielded by 1.8 ppm compared with the C(4) signal in *r*-2,*cis*-6-diphenyl-4-thianone. Introduction of a methyl group at C(3) causes a large *β effect* (+9.78 ppm) at C(2) in **2b** compared to the corresponding resonance for C(2) in **3**. The effect of methyl substitution on methyl-bearing carbon resonances has been noted in methyl cyclohexanes,[13] in certain piperidine derivatives,[14] and in certain 1-hetera-2,6-diaryl-4-cyclohexanones.[12] A downfield shift of 1.78 ppm is observed for C(3) in **2b** compared to the corresponding signal for C(3) in **3**. The C(3) atom in **2c** is also appreciably deshielded (9.0 ppm), apparently due to ethyl substitution, compared to the corresponding signal found for C(3) in **3**. A similar trend was found in *r*-2,*cis*-6-diphenyl-*trans*-3-ethyl-4-thianone.[12]

Dissociation Constants of Cyanohydrins of 4-Selenanones. The determination of ketone–cyanohydrin equilibria provides a convenient method[15] of studying the ketone reactivity toward nucleophilic addition reactions. The cyanohydrin reaction has been shown[16] to be reversible and to involve a base-catalyzed nucleophilic attack of cyanide ion on the carbonyl carbon. The reaction results in a relief in the bond angle strain in the cyclic system imposed by the ketone and in a reduction of the small steric interference between the keto group and the adjacent hydrogen atoms.[17] This may shift the position of equilibrium toward cyanohydrin. In contrast, molecular crowding around the carbonyl carbon enhances[18,19] the torsional strain and steric interactions with the CN or OH group of the cyanohydrin (in carbocycles) which are relieved when the cyanohydrin dissociates toward the ketone which maybe favored in the equilibrium (**3** ⇌ **5a**). Hence, the magnitude of the dissociation constant can be instructive with regard to a preferred configuration in the 4-selenanones.



3 **5a**

Accordingly, the dissociation constants of variously substituted 4-selenanones were measured in 80% dioxane at 25 °C. The results are recorded in Table III. The dissociation constants of the cyanohydrins of 3-alkyl-4-selenanones **2b** and **2c** have higher values than the cyanohydrin of *r*-2,*cis*-6-diphenyl-4-selenanone (**3**). The dissociation constants increase in the order of H < CH_3 < C_2H_5. The observed differences in K_D are apparently due to differences in steric interactions involving the OH or CN group with the alkyl group in the equatorial position. In the case of the cyanohydrin **5f**, one of the methyl groups will be in an axial position, and, consequently, the compound has a higher dissociation constant, indicating its relative instability due to the axial crowding effect.

Stereochemistry of Reduction with Lithium Aluminum Hydride. The ketones **2a–d** were reduced by lithium aluminum hydride in ether, and the epimeric alcohols obtained were separated by column chromatography over neutral alumina. The results are recorded in Tables IV and V. The less strongly adsorbed axial alcohols were eluted in petroleum ether–benzene fractions, and the more strongly adsorbed equatorial alcohols were eluted in benzene–ether and ether fractions. The reduction of 4-selenanone **2a** by lithium aluminum hydride afforded both the axial and equatorial alcohols. It may, however, be

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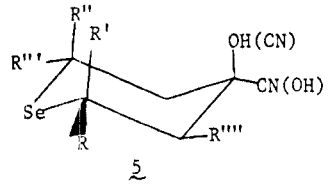
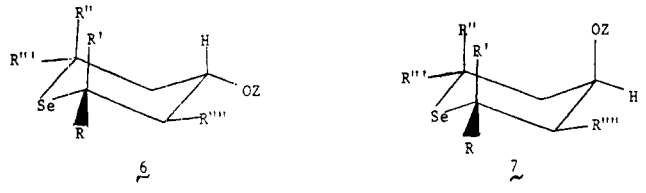


5

	R	R'	R''	R'''	R''''
a	C_6H_5	H	H	C_6H_5	H
b	p-$CH_3C_6H_4$	H	H	p-$CH_3C_6H_4$	H
c	p-$CH_3OC_6H_4$	H	H	p-$CH_3OC_6H_4$	H
d	C_6H_5	H	H	C_6H_5	CH_3
e	C_6H_5	H	H	C_6H_5	C_2H_5
f	C_6H_5	H	CH_3	CH_3	H

noted that the yield of axial alcohol **7a** is only 13% com-



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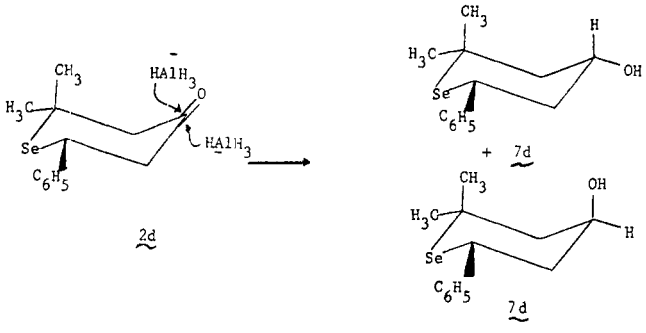
	R	R'	R''	R'''	R''''	Z
a	p-$CH_3C_6H_4$	H	H	p-$CH_3C_6H_4$	H	H
b	C_6H_5	H	H	C_6H_5	CH_3	H
c	C_6H_5	H	H	C_6H_5	C_2H_5	H
d	C_6H_5	H	CH_3	CH_3	H	H
e	p-$CH_3C_6H_4$	H	H	p-$CH_3C_6H_4$	H	$C(O)CH_3$
f	C_6H_5	H	H	C_6H_5	CH_3	$C(O)CH_3$
g	C_6H_5	H	H	C_6H_5	C_6H_5	$C(O)CH_3$

pared with 72% of the equatorial isomer **6a**. However, reduction of **2b** and **2c** with lithium aluminum hydride afforded a mixture of axial and equatorial selenanols. With 2,2-dimethyl-6-phenyl-4-selenanone, of course, the most stable conformation is **2d** in which there is an axial methyl



2d 7d 7d

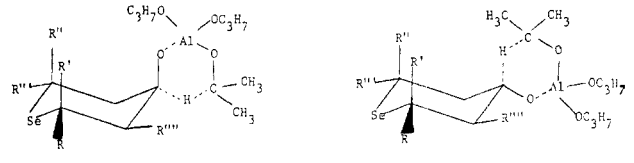
group. When this selenanone is reduced with lithium aluminum hydride, the axial approach of the reducing agent to the carbonyl carbon is hindered by the axial methyl attached at C(2). Consequently, hydride transfer should occur from the equatorial direction, resulting in the formation of axial isomer **7d**. Interestingly, the reduction of 2,2-dimethyl-6-phenyl-4-selenanone (**2d**) afforded isomeric alcohols **6d** (42%) and **7d** (48%). The ratio is very much similar to that for the axial (47%) and equatorial (45%) isomers reported for the lithium aluminum hydride reduction of similarly constituted 2,2-dimethyl-6-phenyl-4-thianone[4] and supports our supposition that the flattened rings result in reduced steric effects by axial 3- or 5-substituents in the attack by small nucleophiles at sp^2-hybridized C(4).

Meerwein–Ponndorf–Verley Reduction of 4-Selenanones. Selenanones **2a–d** were also reduced by using aluminum isopropoxide and isopropyl alcohol. The isomeric alcohols obtained were separated by column chromatography. Upon chromatography, the axial alcohols

Table V. Composition of the Products from the Reduction of 4-Selenanones

selenanones reduced	total crude product, %	unreduced selenanone, %	% yield of epimeric selenanols	
			axial	equatorial
	Reduction with MPV			
2a	90	5	50 (7a)	12 (6a)
2b	95	9	56 (7b)	14 (6b)
2c	93	6	58 (7c)	23 (6c)
2d	94	4	77 (7d)	12 (6d)
	Reduction with $LiAlH_4$			
2a	98	3	13	72
2b	90	8	23	37
2c	94	9	31	48
2d	96	4	48	42

were eluted in the initial fractions. Considering the relative amounts of the two isomers formed in the Meerwein–Ponndorf–Verley reduction, it will be seen from Table V that compounds **2b** and **2c** gave similar isomer ratios, about 56% of the product isolated being the pure axial isomer. In contrast, 2,2-dimethyl-6-phenyl-4-selenanone (**2d**) afforded 77% of the axial isomer. Duplication of the reduction gave similar results. There is a general tendency for the Meerwein–Ponndorf–Verley reduction to afford more of the axial alcohol. This tendency is much greater in the case of hindered ketones **2b–d**. Introduction of an alkyl group α to carbonyl (as in **2b** and **2c**) in the 4-selenanone changes the isomer ratio of 4-selenanones. The presence of an axial methyl in the selenanone **2d** increases the yield of alcohol (axial C–OH) **7d**. With the generally accepted mechanism[20,21] for Meerwein–Ponndorf–Verley reductions, two cyclic transition states, **8a** and **8b**, are



8a 8b

possible for the reduction of 4-selenanones. In **8a**, the hydride transfer occurs from the equatorial side of the developing 4-selenanol, and in **8b** the approach is axial. Transition state **8a** should lead to an axial 4-selenanol and **8b** to an equatorial 4-selenanol. Scale models indicate a greater steric hindrance to the axial approach of the isopropoxy hydrogen. Hence more of axial alcohol may be expected from the hindered 4-selenanones as is observed.

Stereochemistry of the 4-Selenanols. The configuration and conformation of the 4-selenanols are assigned on the basis of IR, ^1H NMR, and ^{13}C spectral data which are summarized in Tables VI and VII. It has been shown that the C–O stretching frequency for an equatorial hydroxyl group (near 1040 cm^{-1}) is greater than that for an axial hydroxyl group (near 1000 cm^{-1}).[4,22-24] Examination of Table VI reveals that 4-selenanols with an equatorial hydroxy group give an absorption band at a higher frequency compared to that of their epimers with an axial

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Table VI. IR and ^{1}H NMR[a] Data for Substituted 4-Selenanols and the Corresponding Acetates

compd	IR C-O stretch, cm^{-1}	^{1}H NMR					
		H(2)	H(3)	H(4)	H(5)	H(6)	other
6a	1039	4.37 (dd, 2 H, H(2), H(6), J = 12.0, 3.5 Hz)	1.64-2.68 (m, 10 H, H(3), H(5) CH_3)	3.56-3.94 (m, $w_{1/2}$ = 20.0 Hz)	overlapped with H(3)	overlapped with H(2)	1.58 (s, 1 H, OH), 2.34 (s, 6 H, CH_3), overlapped with H(3) and H(5), 7.01-7.40 (m, 8 H, Ar H)
6b	1020	3.98 (d, J = 10.5 Hz)	2.40-2.72 (m, 2 H, H(3), OH)	3.18-3.52 (m, $w_{1/2}$ = 20.0 Hz)	2.06-2.38 (m)	4.32 (dd, J = 10.0, 3.0 Hz)	0.94 (d, 3 H, CH_3, J = 7.0 Hz), OH overlapped with H(3), 7.10-7.42 (m, 10 H, Ar H)
6c	1042	4.56 (d, J = 3.0 Hz)	2.22-2.43 (m)	3.66-3.94 (m, $w_{1/2}$ = 19.5 Hz)	1.90-2.21 (m, 3 H, H(5), OH)	4.19 (dd, J = 10.25, 5.0 Hz)	0.49 (t, 3 H, CH_2CH_3, J = 7.75 Hz), 1.52-1.82 (m, 2 H, CH_2CH_3), OH overlapped with H(5), 7.06-7.44 (m, 10 H, Ar H)
6d	1038		1.82-2.21 (m)	3.68-4.04 (m, $w_{1/2}$ = 20.5 Hz)	2.13-2.26 (m), 2.34-2.60 (m)	4.12-4.32 (dd, J = 10.0, 3.0 Hz)	1.40 (s, 3 H, CH_3(e)), 1.60 (s, 3 H, CH_3(a)), 1.74 (s, 1 H, OH), 7.12-7.38 (m, 5 H, Ar H)
6e	1030	4.38 (dd, 2 H, H(2), H(6), J = 12.0, 3.5 Hz)	2.12-2.68 (m, 4 H, H(3), H(5))	4.74-5.08 (m, $w_{1/2}$ = 20.0 Hz)	overlapped with H(3)	overlapped with H(2)	2.04 (s, 3 H, $COCH_3$), 2.30 (s, 6 H, CH_3), 7.00-7.31 (m, 8 H, Ar H)
6f	1028	4.06 (d, J = 11.5 Hz)	2.21-2.76 (m, 3 H, H(3), H(5))	4.75 (br s, $w_{1/2}$ = 20.0 Hz)	overlapped with H(3)	4.51 (dd merged into d, J = 12.0 Hz)	0.83 (d, 3 H, CH_3, J = 7.5 Hz), 1.97 (s, 3 H, $C(O)CH_3$), 6.98-7.52 (m, 10 H, Ar H)
6g	1029	4.30 (d, J = 13.0 Hz)	2.32-2.47 (m)	4.82-5.14 (m, $w_{1/2}$ = 18.0 Hz)	2.48-2.70 (m, overlapped with H(3)	4.45 (dd, J = 12.0, 3.0 Hz, partly merged with d of H(2))	0.70 (t, 3 H, CH_2CH_3, J = 8.0 Hz), 1.17-1.72 (m, 2 H, CH_2CH_3), 2.06 (s, 3 H, $C(O)CH_3$), 7.06-7.46 (m, 10 H, Ar H)
7a	1031	4.73 (m, 2 H, H(2), H(6))	2.21-2.4 (m, 10 H, H(3), H(5), CH_3)	4.43 (br s, $w_{1/2}$ = 8.0 Hz)	overlapped with H(3)	overlapped with H(2)	1.89 (s, 1 H, OH), 2.80 (s, 6 H, CH_3) overlapped with H(3) and H(5), 6.96-7.28 (m, 8 H, Ar H)
7b	994	4.46 (d, J = 12.0 Hz)	2.27-2.60 (m, 3 H, H(3), H(5), CH_3)	4.16 (br s, $w_{1/2}$ = 9.0 Hz)	overlapped with H(3)	4.82 (t, J = 8.0 Hz)	0.87 (d, 3 H, CH_3, J = 7.0 Hz), 1.8 (d, 1 H, OH, J = 3.5 Hz), 7.10-7.42 (m, 10 H, Ar H)

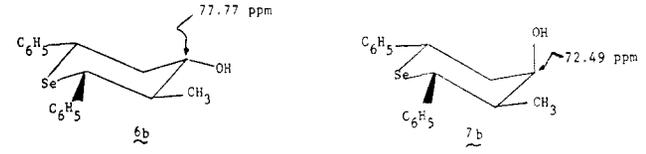
7c	1018	4.5 (d, J = 11.0 Hz)	1.95–2.28 (m)	4.37 (br s, $w_{1/2}$ = 10.0 Hz)	2.38–2.62 (m)	4.81 (dd, J = 10.0, 4.5 Hz)	0.76 (t, 3 H, CH_2CH_3), J = 3.25 Hz), 1.07–1.45 (m, 2 H, CH_2CH_3), 1.73 (d, 1 H, OH, J = 4.0 Hz), 7.08–7.44 (m, 10 H, Ar H)
7d	1030		1.93 (d, J = 4.0 Hz)	4.37 (br s, $w_{1/2}$ = 12.0 Hz)	2.20–2.35 (m)	4.48–4.68 (t, J = 7.5 Hz)	1.32 (s, 3 H, CH_3(e)), 1.68 (s, 3 H, CH_3(a)), 1.74 (s, 1 H, OH), 7.12–7.42 (m, 5 H, Ar H)
7e	1021	4.62 (dd, 2 H, H(2), H(6), J = 11.25, 3.50 Hz)	2.38–2.51 (m, 4 H, H(3), H(5))	5.51 (br s, $w_{1/2}$ = 9.0 Hz)	overlapped with H(3)	overlapped with H(2)	2.10 (s, 3 H, $C(O)CH_3$), 2.27 (s, 6 H, CH_3), 7.00–7.30 (m, 8 H, Ar H)
7f	1018	4.41 (d, J = 11.0 Hz)	2.28–2.74 (m, 2 H, H(3), H(5))	5.39 (br s, $w_{1/2}$ = 8.0 Hz)	overlapped with H(3)	4.63 (dd, J = 11.5, 4.0 Hz)	0.77 (d, 3 H, CH_3, J = 7.0 Hz), 2.08 (s, 3 H, $C(O)CH_3$), 7.00–7.48 (m, 10 H, Ar H)
7g	1022	4.47 (d, J = 11.0 Hz)	2.27–2.50 (m)	5.60 (br s, $w_{1/2}$ = 9.0 Hz)	2.54–2.92 (m)	4.60 (dd, J = 14.0, 3.5 Hz, partly merged with d of H(2))	0.80 (t, 3 H, CH_2CH_3, J = 7.0 Hz), 0.96–1.60 (m, 2 H, CH_2CH_3), 2.17 (s, 3 H, $C(O)CH_3$), 7.12–7.44 (m, 10 H, Ar H)

[a] NMR values are in δ units. Abbreviations used are as follows: s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiplet; br s, broad singlet.

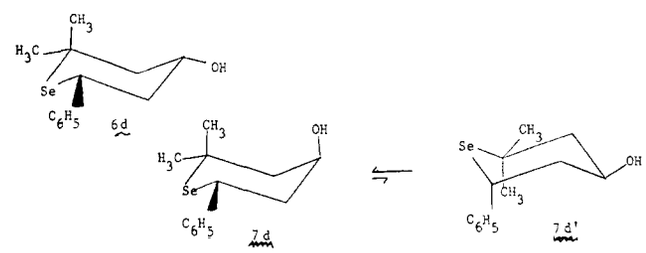
hydroxyl group. The IR spectral data support the suggested configuration of the 4-selenanols along with the method of formation and the degree of adsorption on alumina.

The ^{1}H NMR spectral data of the epimeric 4-selenanols are also summarized in Table VI. In general, in the selenanols an axial proton geminal to an equatorial hydroxyl group gives a signal between δ 4.20 and 4.50. Another interesting feature in the ^{1}H NMR spectra of 4-selenanols that merits mention is the shielding effect of a hydroxyl group on H(2) and H(6). An axial hydroxyl group is found to deshield the diaxial protons H(2) and H(6) by 0.4–0.6 ppm. Such anisotropy effects are manifested in the sulfur analogues too.[4] Information regarding the configuration of the hydroxyl group may be obtained from the chemical shift data of H(4). The interesting aspect of the spectra is the half-width of the carbinol hydrogen H(4) peak.[25] It can be seen from Table VI that the half-width signal for axial selenanols **7a–c** is 8, 9, and 10 Hz, respectively, as compared to 20, 20, and 19.5 Hz, respectively, for the corresponding equatorial 4-selenanols. The $^3J_{HH}$ of 7.5 Hz observed for H(6) in **7d** suggests a possible nonchair conformation.

The configuration of 4-selenanols was also confirmed by the ^{13}C chemical shift data furnished in Table VII. An inspection of the Table VII reveals that the C(4) carbon shielding is influenced by the orientation of the hydroxyl group. An equatorial hydroxyl group deshields the C(4) carbon by about 4–5 ppm as illustrated by structures **6b** and **7b**. Hence, carbon-13 chemical shift differences can



be employed for the successful assignment of the configuration of the hydroxyl function. Such chemical shift differences for epimeric 4-thianols[12] and 4-pyranols[5] have been clearly established. 2,2-Dimethyl-*cis*- (**6d**) and -*trans*-6-phenylselenan-*r*-4-ol (**7d**) were also included in order to determine the influence of axial methyl on the C(4) chemical shift. The results show that the carbon-13 chemical shifts of the C(4) carbon in **6d** and **7d** are almost the same. If 2,2-dimethyl-*trans*-6-phenylselenan-*r*-4-ol (**7d**) exists in a chair conformation, there could be a severe interaction between axial hydroxyl and axial methyl group.



This would lead to the suggestion that there could also be a lower contribution of **7d** to the equilibrium mixture. However, as shown, the syn diaxial CH_3–C_6H_5 interaction in **7d′** should be severe enough to make the chair conformation highly strained, as implied by models. Conceivably, the system may exist in a nonchair conformation in which the nonbonded steric interactions have been relieved to a large extent. Interestingly, similar ^{13}C chemical shift data

(25) R. V. Lemieux, R. K. Kulling, H. J. Bernstein, and W. G. S. Schneider, *J. Am. Chem. Soc.*, **80**, 6098 (1958).

Table VII. ^{13}C Chemical Shifts[a] of Substituted 4-Selenanols and the Corresponding Acetates

compd	C(2)	C(3)	C(4)	C(5)	C(6)	other
6a	40.63	43.86	72.23			21.04 ($CH_3C_6H_4$), 138.20, 136.80, 129.16, 127.05 (Ar)
6b	47.27	45.60	76.77	44.61	40.05	15.60 (CH_3), 141.20, 140.06, 128.51, 127.81, 127.11 (Ar)
6c	50.12	48.55	76.13	39.79	37.54	16.93 (CH_2CH_3), 15.29 (CH_2CH_3), 141.44, 140.74, 128.54, 128.30, 127.84, 127.29, 127.23, 126.94 (Ar)
6d	44.23	51.67	68.63	40.62	37.82	30.81 (CH_{3a}), 31.95 (CH_{3e}), 141.29, 128.75, 127.16, 126.82 (Ar)
6e	39.93	39.93	73.64			21.00 ($CH_3C_6H_4$), 21.00 ($C(O)CH_3$), 169.57 (C=O), 137.78, 136.64, 129.06, 126.91 (Ar)
6f	46.40	42.83	77.85	41.19	39.50	15.34 (CH_3), 20.85 ($C(O)CH_3$), 169.49 (C=O), 140.65, 139.60, 128.31, 127.60, 126.96 (Ar)
6g	47.13	43.42	74.62	41.50	39.60	8.35 (CH_2CH_3), 21.04 (CH_2CH_3), 20.29 ($C(O)CH_3$), 169.75 (C=O), 140.59, 139.28, 128.42, 128.37, 127.70, 127.00 (Ar)
7a	35.01	39.88	67.19			20.95 ($CH_3C_6H_4$), 138.87, 136.39, 128.98, 127.11 (Ar)
7b	42.22	41.58	72.49	41.20	35.81	17.69 (CH_3), 141.65, 140.77, 128.43, 127.93, 127.46, 126.91 (Ar)
7c	47.97	42.16	67.28	40.82	35.61	22.52 (CH_2CH_3), 11.67 (CH_2CH_3), 141.67, 140.85, 128.42, 127.98, 127.46, 126.88 (Ar)
7d	40.18	46.84	67.73	38.99	37.88	32.60 (CH_{3a}), 33.00 (CH_{3e}), 141.86, 127.93, 127.09, 126.38 (Ar)
7e	35.83	37.28	70.24			21.25 ($CH_3C_6H_4$), 21.04 ($C(O)CH_3$), 169.66 (C=O), 138.49, 136.76, 129.19, 127.15 (Ar)
7f	41.99	40.38	74.32	38.75	36.09	17.00 (CH_3), 20.90 ($C(O)CH_3$), 169 (C=O), 140.83, 140.12, 128.34, 127.64, 127.14, 126.97 (Ar)
7g	46.95	41.49	69.83	38.58	35.89	22.21 (CH_2CH_3), 11.44 (CH_2CH_3), 20.90 ($C(O)CH_3$), 169.55 (C=O), 140.86, 140.25, 128.34, 127.71, 127.17, 126.97 (Ar)

[a] All data are given in parts per million downfield from Me_4Si; solutions used were 0.3 M in $DCCl_3$.

has been reported[12] for structurally related 2,2-dimethyl-*cis*- and -*trans*-6-phenyl-4-thianols.

Experimental Section

Caution: Selenium compounds are highly toxic.

General Data. Melting points were taken on a BOETIUS hot-stage microscope and are uncorrected. ^1H NMR spectra were obtained on a Varian XL-100(15) high-resolution NMR spectrometer (with a time-averaging computer accessory, Model C-1024) operating at 100.00 MHz and are expressed in δ values, relative to Me_4Si. IR spectra were recorded on a Beckman-5A spectrophotometer as KBr pellets. Proton-noise-decoupled ^{13}C NMR spectra were recorded at 25.2 MHz on a Varian XL-100(15) NMR spectrometer equipped with a Nicolet TT-100 Fourier transform accessory. Chemical shift data encompassing 5000- and 6000-Hz spectral regions were collected into 8K data points. Single-frequency, off-resonance spectra were obtained by irradiating with a continuous-wave frequency at about δ −5 compared to Me_4Si in the proton spectrum. The samples were run as 0.3 and 1.5 M solutions in $DCCl_3$ containing tetramethylsilane as an internal reference. The spectra of all samples were recorded at 37 °C. Assignments have been made on the basis of signal multiplicity found in the off-resonance decoupled spectra and from the magnitude of the $^1J_{^{13}C-H}$ couplings.

The selenanones **3** and **4** were prepared by known methods.[11a] All solvents used were reagent grade.

***r*-2,*cis*-6-Diphenyl-*trans*-3-methyl-4-selenanone (2b).** To a boiling mixture of 2-methyl-1,5-diphenyl-1,4-pentadien-3-one (**1b**; 5 g, 0.02 mol) and $CH_3CO_2Na{\cdot}3H_2O$ (5 g, 0.036 mol) in 100 mL of ethanol (90%) was added 5 g of aluminum selenide lumps in one lot. The mixture was boiled for 6 h, and the alcohol was removed on a rotary evaporator. The residue was digested with hot petroleum ether (bp 60–80 °C, 6 × 20 mL). The extracts were combined, and the volume was reduced to about 20 mL under vacuum. The resultant pale yellow solution was refrigerated for 2 h, whereupon the cream-colored solid **2b** separated. The solid was filtered off, dried, and recrystallized (petroleum ether, bp 60–80 °C) to give 4.3 g (65%) of **2b**, mp 124–125 °C.

Other selenanones, **2a–d**, were prepared by following a similar procedure. Relevant details are given in Table I.

General Procedure for Reduction with Lithium Aluminum Hydride. To a well-stirred slurry of lithium aluminum hydride (0.6 g, 0.016 mol) in dry ether was added dropwise a solution of 4-selenanone **2b** (5 g, 0.0152 mol) in dry ether (150 mL). The mixture was stirred under reflux for about 6–8 h and then allowed to stand overnight. Excess hydride was carefully destroyed by the dropwise addition of ethyl acetate, and the resultant mixture was neutralized (1:3 HCl–H_2O, 15 mL) and extracted with ether. The ether layer was washed with water until it was free from acid and dried (Na_2SO_4). The epimeric mixture of 4-selenanols, obtained after evaporation of the ether, was subjected to chromatography over neutral alumina. Details are furnished in Tables IV and V. Similar conditions were used to reduce the other ketones.

Chromatographic Separation of Epimeric 4-Selenanols. This was carried out as described in the literature[4] by employing 30 g of neutral alumina for 1 g of the reduction product. The axial alcohols were obtained from petroleum ether–benzene and benzene eluates and the equatorial alcohols from benzene–ether and ether eluates. The yields, melting points, and solvents of crystallization of the 4-selenanols are recorded in Tables IV and V.

Meerwein–Ponndorf–Verley Reduction. The procedure described in the literature[4] was adopted to carry out the reduction of selenanones. Relevant details about the 4-selenanols prepared are given in Tables IV and V.

Acetates of the 4-Selenanols. A solution of the 4-selenanol **6b** (0.0350 g, 0.0011 mol) in dry pyridine (3 mL) was treated with acetic anhydride (1.5 g, 0.015 mol). The reaction mixture was heated on a steam bath for 5 h and poured over crushed ice. The organic layer was taken up in ether (25 mL), washed with 2% hydrochloric acid and water and dried (Na_2SO_4). Evaporation of the ether layer left an oil which slowly solidified to give 0.300 g (76%) of **6f**, mp 108–109 °C (aqueous ethanol). A similar procedure was adopted to prepare all other acetyl derivatives. Other relevant data are given in Table IV.

Solvents. Dioxane (E. Merck) was purified as reported in the literature.[26] The dioxane (80 volumes) was mixed with conductivity water (20 volumes), and the resulting solvent had a refractive index of d^{25}_4 1.0350. Triethylamine (AR, BDH) was distilled in an inert atmosphere after being dried over potassium hydroxide pellets; bp 89 °C.

Hydrogen Cyanide Solution. Exactly equal volumes of a 0.1 M solution of KCN and $HClO_4$ in 80% dioxane were mixed and

(26) A. Weissberger and E. S. Proskauer, Eds., "Organic Solvents", Interscience, NY, 1955, p 371.

refrigerated for 4 h. The clear solution was decanted off from the precipitated $KClO_4$ and stored in the refrigerator.

Cyanohydrin Formation. The formation of the cyanohydrin was studied in 80% dioxane. The procedure was essentially that of Lapworth and Manske.[27] The dissociation constant (K_D) was computed by using the eq 1, where a is the initial [selenone], b

$$K_D = (a - x)(b - x)/x \quad (1)$$

is the initial [HCN], and x is the equilibrium [cyanohydrin]. Each experiment was repeated three times, and the consistency of various determinations of K_D is illustrated by the values obtained with *r*-2,*cis*-6-diphenyl-4-selenanone (**3**): 10^3K_D = 8.75, 8.79, and 8.74 (mean 8.77 ± 0.02).

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(27) A. Lapworth and R. H. F. Manske, *J. Chem. Soc.*, 2335 (1928); 1976 (1930).

Registry No. **1a**, 621-98-7; **1b**, 14164-67-1; **1c**, 63114-78-3; **1d**, 55901-61-6; **2a**, 74966-31-7; **2b**, 74966-32-8; **2c**, 74966-33-9; **2d**, 74966-34-0; **3**, 54232-38-1; **4**, 74966-35-1; **6a**, 74966-36-2; **6b**, 74966-37-3; **6c**, 74966-38-4; **6d**, 74966-39-5; **6e**, 74966-40-8; **6f**, 74966-41-9; **6g**, 74966-42-0; **7a**, 74985-55-0; **7b**, 74985-56-1; **7c**, 74985-57-2; **7d**, 74966-43-1; **7e**, 74985-58-3; **7f**, 74985-59-4; **7g**, 74985-60-7.

Pressure Effects on Azocumene Decomposition Rates, Efficiencies of Radical Production, and Semibenzene Dimers[1,2]

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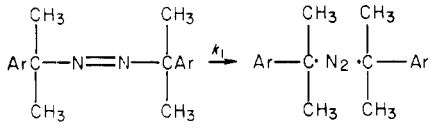
Rates of thermal decomposition of azocumene (**1a**) and *p,p'*-dimethylazocumene (**1b**) in cumene or chlorobenzene are decreased by pressure with decomposition activation volumes of +5 cm^3/mol (**1a**, cumene), +4.3 cm^3/mol (**1a**, chlorobenzene), and +4.6 cm^3/mol (**1b**, cumene). Efficiencies (f) of radical production, with di-*tert*-butyl nitroxide (DBNO) or thiophenol as scavengers, decrease with pressure; however, the pressure dependence of f with DBNO is anomalous. This is explained by the formation of semibenzene dimers as cage products, which subsequently decompose to give cumyl radicals. The corresponding α-ortho semibenzene dimers of cumyl radicals are formed from both **1a** and **1b**. The α-para semibenzene dimer from decomposition of **1a** in chlorobenzene appears to rearrange to give *p*-cumylcumene. No such rearrangement appears to occur from the α-ortho dimers nor is it likely that any α-para dimer is formed from **1b** decomposition. An apparent activation volume for thermal decomposition of the α-ortho semibenzene dimer in cyclohexane at 20 °C is ca. +6 cm^3/mol. Pressure favors disproportionation over coupling for geminate cumyl radicals.

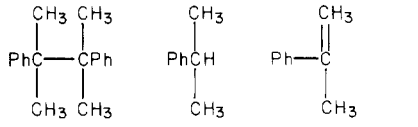
Azocumene (**1a**) thermally decomposes to give two cumyl radicals and a molecule of nitrogen in the primary scission step (eq 1).[5] The resulting radicals combine,



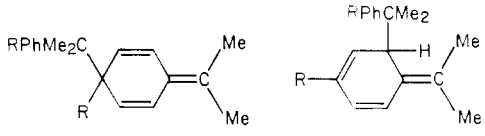
(1)

1a, Ar = phenyl
b, Ar = *p*-methylphenyl

disproportionate, or diffuse apart. It had been thought that the sole reaction products in an inert medium were bicumyl (**2**) from combination and cumene (**3**) and α-methylstyrene (**4**) from disproportionation. However, Bartlett obtained evidence which led him to suggest that the semibenzene **5a** was also a combination product.[5]



2 **3** **4**



5a, R = H
b, R = CH_3

6a, R = H
b, R = CH_3

Subsequently, McBride concluded that both **5a** and **6a** are formed from cumyl radical combination.[6] These semibenzenes are unstable and can revert to cumyl radicals under conditions used to thermally decompose azocumene. However, they have been generated and studied spectrally by photolyzing azocumene at low temperatures.

Several years ago, as part of a continuing study of radical initiators,[7,8] we investigated effects of pressure on the rates,

(1) High-Pressure Studies. 23. Part 22: R. C. Neuman, Jr., and C. T. Berge, *Tetrahedron Lett.*, 1709 (1978).
(2) Support by the National Science Foundation through Grants GP-8670 and GP-23968 is gratefully acknowledged.
(3) To whom correspondence should be addressed.
(4) Taken from the Ph.D. Dissertation of Michael J. Amrich, Jr., University of California, Riverside, CA, Dec 1971.
(5) S. F. Nelsen and P. D. Bartlett, *J. Am. Chem. Soc.*, 88, 137 (1966).
(6) K. J. Skinner, H. S. Hochster, and J. M. McBride, *J. Am. Chem. Soc.*, 96, 4301 (1974).

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