61558-90-5; 2,2-dimethyl-1,3-dithiolane, 6008-78-2; 2,2-dimethyl-d_6-1,3-dithiolane 61558-91-6; 2,2-dimethyl-1,3-dithiane, 6007-22-3; 1,4-dithiaspiro[4.4]nonane, 176-39-6; 1,4-dithiaspiro[4.5]decane, 177-16-2; hydrogen peroxide, 7722-84-1.

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Conformational Analysis. 36. Preferred Conformations of 5-Substituted 1,3-Dioxanes with Sulfur-Containing and Ether Functions in the Side Chain[1,2]

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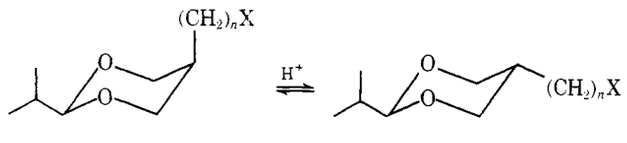
The conformational preferences of 2-isopropyl 5-substituted 1,3-dioxanes in which the 5 substituent is $-(CH_2)_nSCH_3$, $-(CH_2)_nSOCH_3$, $-(CH_2)_nSO_2CH_3$, $-(CH_2)_nS(CH_3)_2^+$, or $-(CH_2)_nOCH_3$ and n = 0, 1, 2 have been determined. The results may be interpreted in terms of the amount of positive charge on the atom attached to C(5) of the ring: the greater the positive charge, the higher the axial preference.

In a previous publication[3] we have reported the conformational preference of compounds of the type shown in Scheme I where n = 0 and X is a polar substituent, such as

Scheme I



SCH_3, $SOCH_3$, SO_2CH_3, or NO_2, or a charged species, such as SMe_2^+, NH_3^+, NMe_2H^+, or NMe_3^+. We have now extended these measurements to the cases where n = 1 or 2 and X is SCH_3, $SOCH_3$, SO_2CH_3, or $S(CH_3)_2^+$. For comparison, the cases where X = OCH_3 are reported also. The results contribute to our as yet meager knowledge of *intra*molecular polar effects.

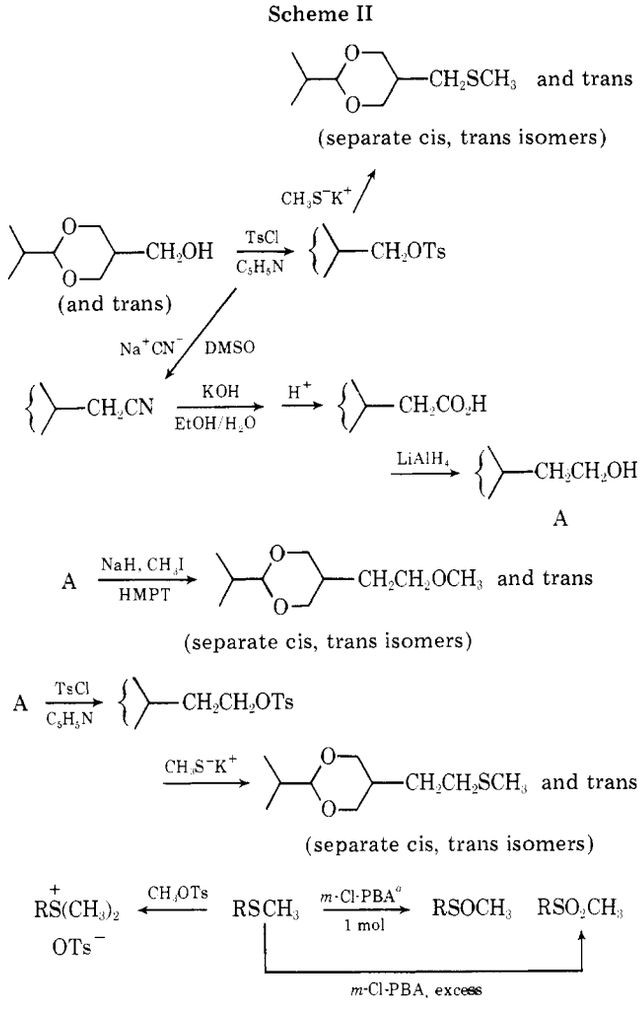
Synthesis, Configurational Assignment, Analysis, and Results. The synthesis of the required compounds from *cis*- and *trans*-5-hydroxymethyl-1,3-dioxane[4] is shown in Scheme II. It was found convenient to start with a mixture of diastereomeric 2-isopropyl-5-hydroxymethyl-1,3-dioxanes and separate the final cis–trans mixtures of ethers or thioethers by gas chromatography. Configurational assignments of the ethers and thioethers rest on the ^1H NMR signals of $H(4)_e$ and $H(4)_a$. In the trans (equatorial) isomers, these protons appeared as a nearly first-order AA'BB'X system, with $H(4)_a$ the upfield, slightly distorted triplet and $H(4)_e$ the downfield, narrow doublet of broad doublets. In the cis (axial) isomers

Table I. Diastereomer Equilibria (Scheme I)[a]

X	n	Solvent	Temp, °C	K	ΔG°[b]
SCH_3	0[3]	C_6H_{12}	26.5	21.3 ± 0.03	−1.82 ± 0.01
		CCl_4	26.5	18.6 ± 0.6	−1.74 ± 0.02
		Ether	26.5	18.3 ± 0.6	−1.73 ± 0.02
		C_6H_6	26.5	13.5 ± 0.5	−1.55 ± 0.02
		CH_3CN	26.5	6.68 ± 0.2	−1.13 ± 0.02
		DCA[c]	25	7.59	−1.20
		TFA[d]	25	4.81	−0.93
SCH_3	1	C_6H_{12}	41	1.08 ± 0.02	−0.05 ± 0.01
		CCl_4	50	1.08 ± 0.02	−0.05 ± 0.01
		C_6H_6	50	1.24 ± 0.02	−0.14 ± 0.01
		$CHCl_3$	50	1.22 ± 0.02	−0.13 ± 0.01
		CH_3CN	50	1.28 ± 0.02	−0.16 ± 0.01
SCH_3	2	C_6H_{12}	41	1.89	−0.40
		CCl_4	41	1.79	−0.36
		C_6H_6	41	2.23 ± 0.03	−0.50 ± 0.01
		$CHCl_3$	41	2.19 ± 0.02	−0.48 ± 0.01
		CH_3CN	41	2.74 ± 0.04	−0.63 ± 0.01
OCH_3	0[6]	C_6H_{12}	25	5.69	−1.03
		CCl_4	25	4.57	−0.90
		Ether	25	4.06	−0.83
		C_6H_6	25	2.71	−0.59
		$CHCl_3$	25	1.31	−0.16
		CH_3CN	25	0.98	+0.01
OCH_3	1	C_6H_{12}	41	0.92 ± 0.01	+0.05 ± 0.01
		Ether	30	1.08 ± 0.01	−0.05 ± 0.01[3]
		C_6H_6	41	0.985 ± 0.015	+0.01 ± 0.01
		$CHCl_3$	41	0.94 ± 0.01	+0.04 ± 0.01
		CH_3CN	41	1.12 ± 0.01	−0.07 ± 0.01
OCH_3	2	C_6H_{12}	41	2.33	−0.53
		C_6H_6	41	2.53 ± 0.03	−0.58 ± 0.01
		$CHCl_3$	41	2.53 ± 0.03	−0.58 ± 0.01
		CH_3CN	41	3.06 ± 0.06	−0.70 ± 0.01
$SOCH_3$	0[3]	CCl_4	54	0.40	~+0.6[e]
		C_6H_6	54	0.32 ± 0.04	+0.74 ± 0.07[e]
		$CHCl_3$	54	0.28 ± 0.05	+0.82 ± 0.11[e]
		CH_3CN	54	0.26 ± 0.04	+0.86 ± 0.09[e]
$SOCH_3$	1	C_6H_6	50	0.80 ± 0.07	+0.14 ± 0.05[f]
		$CHCl_3$	50	0.47 ± 0.04	+0.49 ± 0.05[f]
		CH_3CN	50	1.10 ± 0.09	−0.06 ± 0.05[f]
$SOCH_3$	2	C_6H_6	50	1.86 ± 0.09	−0.40 ± 0.03[f]
		$CHCl_3$	50	1.47 ± 0.07	−0.25 ± 0.03[f]
		CH_3CN	50	2.14 ± 0.06	−0.49 ± 0.02[f]
SO_2CH_3	0[3]	C_6H_{12}	50	0.165 ± 0.025	+1.16 ± 0.10[e]
		C_6H_6	50	0.19 ± 0.03	+1.07 ± 0.10[e]
		$CHCl_3$	50	0.16 ± 0.03	+1.19 ± 0.10[e]
		CH_3CN	50	0.25	~+0.9[e]
SO_2CH_3	1	C_6H_6	50	0.63 ± 0.02	+0.30 ± 0.02[f]
		$CHCl_3$	50	0.44 ± 0.02	+0.53 ± 0.03[f]
		CH_3CN	50	0.84 ± 0.04	+0.11 ± 0.03[f]
SO_2CH_3	2	C_6H_6	50	1.22 ± 0.07	−0.12 ± 0.03[f]
		$CHCl_3$	50	1.08 ± 0.03	−0.05 ± 0.02[f]
		CH_3CN	50	1.68 ± 0.08	−0.33 ± 0.03[f]
$^+S(CH_3)_2$ OTs^-	0	TFA[d]	25	0.034	2.0[e,g,3]
PF_6^-		CD_3CN	25	0.034 ± 0.004	2.00 ± 0.07[e,g]
$^+S(CH_3)_2$ PF_6^-	1	CD_3CN	25	0.34 ± 0.02; 0.31	0.63 ± 0.03;[f,g] 0.69[e,g]
$^+S(CH_3)_2$ PF_6^-	2	CD_3CN	25	1.27 ± 0.02	−0.14 ± 0.01[f,g]

[a] Catalyst Amberlyst-15 unless otherwise noted. [b] kcal/mol. Analysis by gas–liquid partition chromatography unless otherwise noted. [c] Dichloroacetic acid. [d] Trifluoroacetic acid. [e] Analysis by ^1H NMR. [f] Analysis by ^{13}C NMR. [g] Equilibrated with trifluoroacetic acid.

Scheme II



[a] *m*-Chloroperbenzoic acid.

$H(4)_e$ and $H(4)_a$ were nearly coincident and appeared as a narrow, highly distorted doublet. The sulfoxides, sulfones, and sulfonium salts were prepared from the corresponding sulfides; their configurations follow accordingly and were corroborated by their ^1H NMR coupling constants.

The equilibrium positions are summarized in Table I. Equilibration was brought about either by means of beaded polystyrenesulfonic acid (Amberlyt-15[5]) or by means of trifluoroacetic acid, as shown in Table I. Analysis for the volatile methyl sulfides and methyl ethers was by gas chromatography whereas the involatile sulfoxides, sulfones, and sulfonium salts were analyzed by peak integration of ^1H or ^{13}C NMR spectra (Table II, Experimental Section). It is of interest that the ^{13}C NMR signals of the axial methylene groups attached to C(5) (cis isomers) are, in all cases, *downfield* of the corresponding equatorial methylene group in the trans isomers. Included in

Table II. ^{13}C NMR Chemical Shift Data of 5-Substituted 2-Isopropyl-1,3-dioxanes (Scheme I)[a]

X	Registry no.	n		C_2	$C_{4,6}$	C_5	$CH(CH_3)_2$	$(CH_3)_2CH$	CH_2S	SCH_3	Others
SCH_3	40245-27-0	0	Cis	106.13	70.10	42.18	32.62	(16.99)		14.98	
	40245-28-1		Trans	105.43	70.55	39.63	32.47	16.99		13.26	
$S^+(CH_3)_2$	61543-14-4	0	Cis[a]	107.06	66.25	52.01	33.33	16.87		24.54	
PF_6^-	61522-97-2		Trans[a]	106.62	65.59	46.35	32.79	17.24		23.33	
SCH_3	61522-98-3	1	Cis	106.01	69.09	34.03	32.78	16.78	34.70	15.69	
	61522-99-4		Trans	105.30	70.85	(33.23)	(32.13)	16.64	32.13	15.45	
$SOCH_3$	61523-00-0	1	Cis	106.45	71.11 68.10	29.72	32.73	16.70	55.74	39.29	
	61523-01-1		Trans	105.85	70.84 70.57	30.75	32.53	16.94	53.63	39.50	
SO_2CH_3	61523-02-2	1	Cis	106.36	70.14	29.41	32.70	16.71	54.65	42.20	
	61523-03-3		Trans	105.90	70.47	29.71	32.52	16.94	53.31	41.46	
$S^+(CH_3)_2$	61523-05-5	1	Cis[a]	107.10	69.34	31.70	33.35	16.92	46.39	26.52	
PF_6^-	61523-07-7		Trans[a]	106.61	70.12	31.43	33.15	17.20	42.67	26.16	
SCH_3	61523-08-8	2	Cis	105.96	69.82	33.21	32.76	16.79	32.13	15.23	28.48 ($-CH_2-$)
	61523-09-9		Trans	105.66	71.60	33.79	32.59	17.05	31.15	15.31	27.86 ($-CH_2-$)
$SOCH_3$	61523-10-2	2	Cis	105.93	69.54	33.42	32.66	16.74	52.43	38.47	22.60 ($-CH_2-$)
	61523-11-3		Trans	105.62	71.31 71.20	33.70	32.47	17.01	51.09	38.47	20.95 ($-CH_2-$)
SO_2CH_3	61523-12-4	2	Cis	106.11	69.53	(32.93)	(32.71)	16.77	52.79	40.38	22.81 ($-CH_2-$)
	61523-13-5		Trans	105.82	71.12	33.31	32.53	17.03	51.67	40.49	20.69 ($-CH_2-$)
$S^+(CH_3)_2$	61523-15-7	2	Cis[a]	106.63	69.97	33.97	33.58	17.25	42.42	25.12	24.89 ($-CH_2-$)
PF_6^-	61523-17-9		Trans[a]	106.51	71.37	34.41	33.45	17.62	41.22	25.18	22.96 ($-CH_2-$)
OCH_3	28808-25-5	1	Cis	106.07	67.57	35.18	32.90	16.83	71.80[b]	58.82[c]	
	58619-95-7		Trans	105.81	69.50	35.27	32.76	17.10	71.25[b]	58.87[c]	
OCH_3	61523-18-0	2	Cis	106.13	70.20	31.45	32.91	16.85	70.64[b]	58.43[c]	29.57 ($-CH_2-$)
	61523-19-1		Trans	105.81	72.09	32.74	32.74	17.09	70.39[b]	58.52[c]	28.50 ($-CH_2-$)

[a] In $CDCl_3$ except for sulfonium salts, which were in CD_3CN. [b] CH_2O. [c] OCH_3.

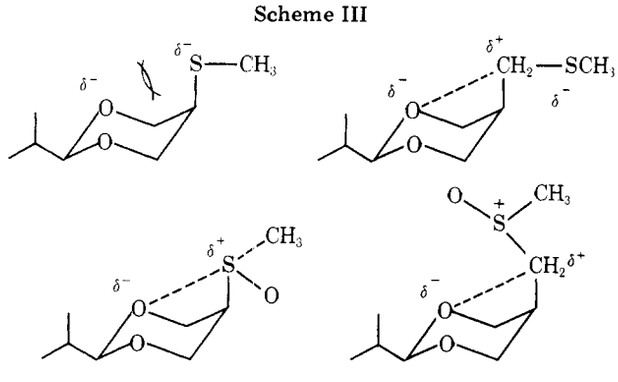
Table I are data for $n = 0$ for the sulfur compounds[3] and for $n = 0$[6] or 1[3] for the ethers, taken from previous papers.[3,6]

Discussion

The following regularities appear to be implied by the data in Table I: (a) When $n = 2$, $\Delta G°$ becomes negative for all X substituents. Presumably $\Delta G°$ converges to the value for an alkane chain (X = H). ($\Delta G°$ is −0.6 kcal/mol for C_2H_5[5] and −0.9 kcal/mol for CH_3.[7]). (b) For the $SOCH_3$ and SO_2CH_3 groups, $\Delta G°$ decreases monotonically as n increases from 0 to 1 to 2. (c) In contrast, for X = SCH_3 and OCH_3 $\Delta G°$ increases substantially as n goes from 0 to 1 and then decreases (presumably converging to the alkyl value) when $n = 2$. (d) The solvent effects for X = SCH_3 and OCH_3 are large when $n = 0$, small or negligible when $n = 1$ or 2. (e) The solvent effects for X = $SOCH_3$ and SO_2CH_3 are small when $n = 0$, if anything slightly larger for $n = 1$, 2. There appears to be a specific preference for the axial position in solvent chloroform.

Scheme III provides the basis for an explanation of these findings.

Scheme III



For SCH_3 and OCH_3 and $n = 0$, the repulsive interaction of the heteroatom with the ring oxygen seems to be dominant. This may alternatively be considered as a repulsive interaction of the dipole of the ring[3] and the XCH_3 dipole. As such, it is subject to a sizable solvent (or solvation[8,9]) effect.[10] (We have previously measured[10] the dipole moments of the stereoisomers with X = OCH_3 and $n = 0$; they are 2.85 D for the axial and 1.30 D for the equatorial isomer.) But when X = SCH_3 or OCH_3 and $n = 1$, the dipole difference between isomers will be small (because of the presence of a number of conformations in each diastereomer) and the dominant effect is now the attraction of the partially positively charged methylene next to O or S and the partially negatively charged ring oxygen. The effect of solvent on this interaction would be largely coulombic,[8] and since the solvent does not effectively penetrate the region, close to the molecules, where the electrostatic interaction is most important, solvent effects are small.[11] For $n = 2$ this (inductive) coulombic effect is dampened by relay through the alkyl chain[12] and $\Delta G°$ approaches the value for that chain.

The situation is otherwise for $SOCH_3$ and SO_2CH_3, $n = 0$. The sulfur atoms in these functions bear a substantial positive charge and are attracted to the ring oxygen. The oxygen atoms are turned toward the outside, even in the sulfone,[3] and are thus more distant from the ring oxygens. Solvent effects on the coulombic attraction are small for the reasons already mentioned and solvation of dipoles is less important than for OCH_3 and SCH_3 because the differences in dipole moment are smaller (e.g., 3.50 D for an axial sulfoxide, 2.46 D for an equatorial one[3]). When $n = 1$ or 2 for the sulfoxide, sulfone, and sulfonium function, the relay of positive charge along the hydrocarbon side chain leads to enough residual charge on the carbon next to the ring to engender substantial attraction (for $n = 1$) or at least to reduce the normal repulsion (for $n = 2$). The fact that solvent effects are appreciable, at least for the sulfoxide and sulfone, when $n = 1$ or 2 suggests some coiling back of the functional group toward the ring (Scheme III). In the conformation shown, some of the coulombic attraction is between side-chain sulfur and ring oxygen, and since the sulfur is now further away from the ring oxygen, solvent penetration into the area of interaction becomes more important so that the effect of the dielectric properties of the

solvent manifests itself. There may, in addition, be a special effect in solvent chloroform which we hope to discuss in more detail in a future publication.

In summary, the data in Table I may all be logically interpreted in terms of charge alternation ($-S^{\delta-}-C^{\delta+}H_2$, $-O^{\delta-}-C^{\delta+}H_2$), attenuation of charge by relay ($O^{-}-S^{+}-C^{\delta+}H_2C^{\delta\delta+}H_2$), coulombic attraction or repulsion and the (generally minor) effect of solvent thereon, and dipole repulsion and dipole solvation. These interpretations are based on the assumption—not absolutely certain—that the ΔG values are dominated by ΔH. They could be vitiated by major differences in ΔS between stereoisomers, either as a result of differences in solvation or as a result of differences in conformational isomerism of the $(CH_2)_nX$ chains (Scheme I).

Experimental Section

Melting points were determined on a Sargent Mel-Temp variable temperature heating block in open capillary tubes. Analytical gas–liquid partition chromatography was carried out with a Hewlett-Packard 5750 research chromatograph, equipped with a thermal conductivity detector, on 0.125-in. columns. Varian Aerograph Series 2700 and Model 960 instruments with matched 0.375-in. aluminum columns were used for preparative GLC. Elemental microanalyses were performed by Galbraith Laboratories, Inc., Knoxville Tenn.

^{1}H NMR spectra were recorded on a Jeolco C-60HL or a Varian XL-100 spectrometer in cw mode. Samples were 20–30% in $CDCl_3$; shifts are reported in parts per million downfield from internal tetramethylsilane and are accurate to ±0.01 ppm. Coupling constants are in hertz and accurate to ±0.5 Hz. ^{13}C NMR spectra were recorded on the XL-100 instrument in 5- or 10-mm tubes in FT mode at 25.16 MHz. The solvent was $CDCl_3$ and an internal deuterium lock and internal Me_4Si reference (2%) were used except in the case of the sulfonium salts. Assignment of ^{13}C spectra (Table II) was achieved by a combination of off-resonance decoupling and parametric reasoning.

5-(2-Isopropyl-1,3-dioxanyl)methyl *p*-Toluenesulfonates. A cold solution of a mixture of *cis*- and *trans*-5-(2-isopropyl-1,3-dioxanyl)methanol[4] (50 g, 0.31 mol) in 150 mL of pyridine was added to a solution of tosyl chloride (63 g, 0.33 mol) in pyridine (250 mL) and the mixture was allowed to stand in the refrigerator for 48 h. The solution was then poured over ice and placed in the refrigerator overnight. The resulting precipitate was collected, washed several times with water, and dried under vacuum to give 84.5 g (87%) of white solid.

NMR ($CDCl_3$) δ 0.90 [d, J = 7 Hz, 6 H, $(CH_3)_2CH$–], 1.16–2.8 (m, 2 H, –C**H**Me$_2$ and C_5 H). 2.43 (s, 3 H, $-CH_3$), 3.4 (apparent t, 2 H, $C_{4,6}$ H_a), 3.7–4.33 (m, 5 H, $C_{4,6}$ H_e and $-CH_2$ and C_2H_a), 7.3 (AB, J = 9 Hz, 2 H, H_{meta}), 7.73 (AB, J = 9 Hz, H_{ortho}).

***cis*- and *trans*-2-Isopropyl-5-methylthiomethyl-1,3-dioxane.** A solution of the above mixed tosylates (41 g, 0.13 mol) in 700 mL of absolute ethanol was treated with excess CH_3SK [prepared by adding 14.4 g (0.30 mol) of CH_3SH to a solution of 16.8 g (0.30 mol) of KOH in 200 mL of absolute ethanol]. The reaction mixture was stirred at room temperature for 2 h and refluxed for 10 h. The ethanol was removed by distillation, and 400 mL of water was added; the solution was extracted with three 300-mL portions of ether and the combined extracts were dried over $MgSO_4$, filtered, and concentrated (rotary evaporator). Distillation of the residue afforded 18.9 g (75.4%) of clear liquid, bp 53–55 °C (0.01 Torr).

The isomers were separated by preparative GLC techniques employing a 12-ft column packed with 20% Carbowax 20M/10% KOH on 60–80 mesh Chromosorb A at 190 °C.

^{1}H NMR ($CDCl_3$), cis isomer: δ 0.93 [d, J = 7.0 Hz, 6 H, $-CH(CH_3)_2$], 1.3–2.1 [m, 2 H, $-CH(CH_3)_2$, C_5 H_e], 2.06 (s, 3 H, $-SCH_3$), 2.83 (d, J = 7.5 Hz, 2 H, $-CH_2SCH_3$), 2.06 (s, 3 H, $-SCH_3$), 2.83 (d, J = 7.5 Hz, 2 H, $-CH_2SCH_3$), 3.93 (AA′BB′X, J_{gem} = 12 Hz, 4 H, $C_{4,6}$ H), 4.24 (d, J = 4.5 Hz, 1 H, C_2 H_a).

Trans isomer: δ 0.93 [d, J = 6.5 Hz, 6 H, $-CH(CH_3)_2$], 1.4–2.1 [m, 2 H, C_5 H_a, $-CH(CH_3)_2$], 2.08 (s, 3 H, $-SCH_3$), 2.22 (distorted d, 2 H, $-CH_2S$–), 3.34 (apparent t, J = 11 Hz, 2 H, $C_{4,6}$ H_a), 4.14 (d, J = 4.5 Hz, 1 H, C_2 H_a), 4.2 (d of d, J_{gem} = 11–12 Hz, 2 H, $C_{4,6}$ H_e).

***cis*-2-Isopropyl-5-methylsulfinylmethyl-1,3-dioxane.** Preparation from *cis*-2-isopropyl-5-methylthiomethyl-1,3-dioxane by treatment with an equimolar amount of *m*-chloroperoxybenzoic acid proceeded as previously described[3] for the lower homologue. Recrystallization from *n*-hexane afforded white crystals, mp 83.5–86.0 °C, in 70% yield.

^{1}H NMR ($CDCl_3$) δ 0.90 [d, J = 7.0 Hz, 6 H, $-CH(CH_3)_2$], 1.5–2.2 [m, 2 H, C_5 H_e, $-CH(CH_3)_2$], 2.65–2.93 (m, 2 H, $-CH_2SO$), 2.60 (s, 3 H, $-SOCH_3$), 3.93 (m, 4 H, $C_{4,6}$ H), 4.2 (d, J = 4.5 Hz, 1 H, C_2 H_a).

***trans*-2-Isopropyl-5-methylsulfinylmethyl-1,3-dioxane.** This stereoisomer was similarly[3] synthesized from *trans*-2-isopropyl-5-methylthiomethyl-1,3-dioxane in 60% yield, mp 73–75 °C after recrystallization from *n*-hexane.

^{1}H NMR ($CDCl_3$) δ 0.90 [d, J = 7.0 Hz, 6 H, $-CH(CH_3)_2$], 1.0–1.3 [m, 1 H, $-CH(CH_3)_2$], 1.5–2.1 (m, 1 H, C_5 H), 2.46 (distorted d, 2 H, $-CH_2SO$–), 2.60 (s, 3 H, $-SOCH_3$), 3.44 (apparent t, J = 11 Hz, 2 H, $C_{4,6}$ H_a), 4.1–4.4 (m, 3 H, $C_{4,6}$ H_e, C_2 H_a).

***cis*-2-Isopropyl-5-methylsulfonylmethyl-1,3-dioxane.** The sulfone was synthesized, by a procedure analogous to that previously described for the lower homologue,[3] from *cis*-2-isopropyl-5-methylthiomethyl-1,3-dioxane by treatment with 2.5 molar excess *m*-chloroperoxybenzoic acid: yield 91%; mp 87–88 °C after recrystallization from *n*-hexane.

^{1}H NMR ($CDCl_3$) δ 0.93 [d, J = 6.5 Hz, 6 H, $-CH(CH_3)_2$], 1.4–2.4 [m, 2 H, C_5 H, $-CH(CH_3)_2$], 2.95 (s, 3 H, $-SO_2CH_3$), 3.43 (d, J = 6 Hz, 2 H, $-CH_2SO_2$–), 4.00 (AA′BB′X, J_{gem} = 12.5 Hz, 4 H, $C_{4,6}$ H), 4.27 (d, J = 4.5 Hz, 1 H, C_2 H_a).

Anal. Calcd for $C_9H_{18}SO_4$: C, 48.62; H, 8.16. Found: C, 48.40; H, 8.18.

***trans*-2-Isopropyl-5-methylsulfonylmethyl-1,3-dioxane.** The trans sulfone was similarly obtained from *trans*-2-isopropyl-5-methylthiomethyl-1,3-dioxane in 76% yield, mp 108.5–110.0 °C after recrystallization from *n*-hexane.

^{1}H NMR ($CDCl_3$) δ 0.93 [d, J = 7 Hz, 6 H, $-CH(CH_3)_2$], 1.4–2.5 [m, 2 H, C_5 H_e, $-CH(CH_3)_2$], 2.53 (d, J = 8 Hz, 2 H, $-CH_2SO_2$–), 2.80 (s, 3 H, $-SO_2CH_3$), 3.38 (apparent t, J = 11 Hz, 2 H, $C_{4,6}$ H_a), 4.2 (d, J = 5 Hz, 1 H, C_2 H_a), 4.32 (d of d, J_{gem} = 11 Hz, 2 H, $C_{4,6}$ H_e).

Anal. Calcd for $C_9H_{18}SO_4$: C, 48.62; H, 8.16. Found: C, 48.48; H, 8.43.

***cis*- and *trans*-Dimethyl-5-(2-isopropyl-1,3-dioxanyl)sulfonium Hexafluorophosphates.** The appropriate *p*-toluenesulfonate[3] was converted to the hexafluorophosphate by treatment with a slight excess of ammonium hexafluorophosphate in water. The solid separated was collected, washed with water, and recrystallized from water to give white, crystalline material, mp cis, 121.5–123 °C; trans, 182–183 °C.

The isomers were equilibrated in CD_3CN solution by means of a catalytic amount of trifluoroacetic acid (TFA). The equilibrated solution was analyzed by integration of the $-S^+(CH_3)_2$ ^{1}H NMR signals. Attainment of equilibrium was marked by cessation of change in the relative signal areas. The NMR spectra were identical with those of the *p*-toluenesulfonate except for absence of the aromatic signals.

Dimethyl-5-(*cis*-2-isopropyl-1,3-dioxanyl)methylsulfonium *p*-Toluenesulfonate. A mixture of 0.85 g (5 mmol) of *cis*-2-isopropyl-5-methylthiomethyl-1,3-dioxane and 2.79 g (15 mmol) of methyl *p*-toluenesulfonate was heated at 35 °C for 3 days. The solid was triturated with ether and filtered. Crystallization from absolute ethanol gave 1.5 g (80%) of white solid, mp 178–179 °C.

^{1}H NMR (D_2O–DSS) δ 0.93 [d, J = 6.5 Hz, 6 H, $-CH(CH_3)_2$], 1.2–2.2 [m, 2 H, C_5 H_e and $-CH(CH_3)_2$], 2.23 (s, 3 H, $-CH_3$), 2.83 [s, 6 H, $-S^+(CH_3)_2$], 3.53 (d, J = 6 Hz, 2 H, $-CH_2S$), 3.8 (d, J = 2 Hz, 4 H, $C_{4,6}$ H), 4.2 (d, J = 4.5 Hz, 1 H, C_2 H_a), 7.0 and 7.47 (AB, J = 8 Hz, aromatic protons).

The tosylate was converted to the hexafluorophosphate salt as described above, mp 115–117 °C.

Dimethyl-5-(*trans*-2-isopropyl-1,3-dioxanyl)methylsulfonium *p*-Toluenesulfonate. The trans sulfonium salt was similarly obtained from the corresponding sulfide in 85% yield, mp 185–186 °C.

^{1}H NMR (D_2O–DSS) δ 0.88 [d, J = 7 Hz, 6 H, $-CH(CH_3)_2$], 1.33–2.10 [m, 2 H, C_5 H_a and $-CH(CH_3)_2$], 2.23 (s, 3 H, $-CH_3$), 2.87 [s, 6 H, $-S^+(CH_3)_2$], 3.06 (d, J = 7 Hz, 2 H, $-CH_2S$), 3.53 (t, J = 11 Hz, 2 H, $C_{4,6}$ H_a), 4.17 (d of d, J = 5, J_{gem} = 11.5 Hz, 2 H, $C_{4,6}$ H_e), 4.30 (d, J = 5 Hz, 1 H, C_2 H_a), 7.33 and 7.73 (AB, J = 8 Hz, aromatic protons).

The tosylate was converted to the hexafluorophosphate salt as described above, mp 124–125 °C.

Equilibration of the hexafluorophosphates was effected in CD_3CN by means of TFA as described for the lower homologue. Analysis was by ^{1}H NMR [integration of $(CH_3)_2S^+$ signals] and by ^{13}C NMR (integration of all resolved signals).

2-Isopropyl-5-cyanomethyl-1,3-dioxanes. A mixture of 80 g (0.25 mol) of 2-isopropyl-5-hydroxymethyl-1,3-dioxane tosylates and 18.7 g (0.38 mol) of sodium cyanide in 550 mL of Me_2SO was heated to 90 °C for 5 h under nitrogen. The reaction mixture was cooled to room temperature, diluted with 500 mL of water, and extracted with three 300-mL portions of ether. The combined extracts were washed with

water, dried over $MgSO_4$, filtered, and concentrated (rotary evaporator). Distillation of the residue gave 37.0 g (86%) of the cyanomethyl compound, bp 85–87 °C (0.1 Torr).

^1H NMR ($CDCl_3$) δ [d, 6 H, J = 7 Hz, $-CH(CH_3)_2$], 1.46–2.83 [m, 2 H, $-CH(CH_3)_2$, C_5 H], 2.1 (m, 2 H, $-CH_2CN$), 3.4 (apparent t, J = 11–12 Hz, 2 H, $C_{4,6}$ H_a), 3.87–4.3 (m, 3 H, C_5 H, $C_{4,6}$ H_e).

5-(2-Isopropyl-1,3-dioxanyl)acetic Acids. A mixture of 24.2 g (0.14 mol) of the above mixed nitriles and 140 g of NaOH in 600 mL of a 1:1 mixture of water and ethanol was refluxed for 12 h. The reaction mixture was cooled, added to water, and acidified with concentrated HCl. The entire suspension was then extracted with ether, dried over $MgSO_4$, filtered, and evaporated under vacuum to give 25.0 g (93%) of product, mp 65–95 °C.

^1H NMR ($CDCl_3$) δ 0.93 [d, J = 7 Hz, 6 H, $-CH(CH_3)_2$], 1.47–2.66 [m, 4 H, C_5 H, $-CH(CH_3)_2$, $-CH_2COOH$], 2.7–3.56 (m, 2 H, $C_{4,6}$ H_a), 3.83–4.33 (m, 3 H, C_2 H_a, $C_{4,6}$ H_e).

2-Isopropyl-5-(2-hydroxyethyl)-1,3-dioxanes. Following a procedure similar to that described for 2-isopropyl-5-hydroxymethyl-1,3-dioxane,[4] the 2-isopropyl-5-(2-hydroxyethyl)-1,3-dioxanes were obtained from the acids in 93% yield, bp 85–90 °C (0.5 Torr).

^1H NMR ($CDCl_3$) δ 0.90 [d, J = 7 Hz, 6 H, $-CH(CH_3)_2$], 1.0–2.4 [m, 4 H, C_5 H, $-CH(CH_3)_2$, $-CH_2-$], 3.03–4.3 (m, 8 H, $-CH_2OH$, $C_{4,6}$ H, C_2 H_a).

***cis*- and *trans*-2-Isopropyl-5-methoxymethyl-1,3-dioxane.** These compounds have been previously described.[3]

***cis*- and *trans*-2-Isopropyl-5-(2-methoxyethyl)-1,3-dioxane.** To a well-stirred solution of 2.7 g (15.5 mmol) of the above mixed 2-isopropyl-5-(2-hydroxyethyl)-1,3-dioxanes in 15 mL of dry hexamethylphosphoric triamide (HMPT) at 0 °C was added slowly a 20% excess (0.45 g) of sodium hydride. After 30 min a twofold excess (4.4 g) of methyl iodide was added and the mixture stirred for 3 h at 25 °C.[13] The excess hydride was destroyed by cautious addition of water and the mixture extracted with three 60-mL portions of ether. The combined ether extracts were washed with water, dried over Na_2SO_4, and concentrated to give 1.9 g (66%) of a crude mixture of isomers in approximately 1:1 ratio. The diastereomers were separated by gas chromatography using a 20% Carbowax 20M, 10% KOH on Chromosorb A, 60–80 mesh column at 160 °C.

^1H NMR ($CDCl_3$), cis isomer: δ 0.9 [d, J = 6.8 Hz, 6 H, $(CH_3)_2CH-$], 1.3–1.8 (m, 2 H, C_5 H_e and $-CHMe_2$), 1.97 (q, J = 6.5 Hz, 2 H, $-CH_2-$), 3.27 (s, 3 H, $-OCH_3$), 3.43 (t, J = 6.5 Hz, 2 H, $-CH_2O$), 3.83 (d, with a splitting of 2 Hz, 4 H, $C_{4,6}$ $H_{a,e}$), 4.23 (d, J = 4.5 Hz, 1 H, C_2 H_a).

Trans isomer: δ 0.93 [d, J = 6.8 Hz, 6 H, $(CH_3)_2CH-$], 1.27 (q, J = 6.5 Hz, 2 H, $-CH_2-$), 1.4–2.3 (m, 2 H, C_5 H_a and $-CHMe_2$), 3.27 (s, 3 H, $-OCH_3$), 3.03–3.5 (m, 4 H, $-CH_2O$ and $C_{4,6}$ H_a), 3.9–4.23 (m, i.e., d of d and d overlapped, 3 H, $C_{4,6}$ He and C_2 H_a).

Tosylates of 2-Isopropyl-5-(2-hydroxyethyl)-1,3-dioxanes. The tosylates were prepared from the mixed alcohols in 86% yield as described above for the lower homologues. The mixture solidified with difficulty after extended vacuum drying.

^1H NMR ($CDCl_3$) δ 0.90 [d, J = 6.5 Hz, 6 H, $-CH(CH_3)_2$], 1.1–2.3 [m, 4 H, $-CH_2-$, C_5 H, $-CH(CH_3)_2$], 2.43 (s, 3 H, $-CH_3$), 3.23 (t, 2 H, $C_{4,6}$ H_a), 3.7–4.3 (m, 5 H, $C_{4,6}$ H_e, C_2 H_a, $-CH_2OTs$), 7.26 (d, 2 H, aromatic), 7.66 (d, 2 H, aromatic).

***cis*- and *trans*-2-Isopropyl-5-(2-methylthioethyl)-1,3-dioxane.** Preparation from the above tosylate followed the earlier procedure for the 2-isopropyl-5-methylthiomethyl-1,3-dioxanes. The mixed isomers were obtained in 90% yield, bp 80–88 °C (0.15 Torr). They were separated by GLC on a 12-ft column packed with 20% Carbowax 20M/10% KOH on Chromosorb A, 60–80 mesh at 190 °C.

^1H NMR ($CDCl_3$), cis isomer: δ 0.92 [d, J = 7 Hz, 6 H, $-CH(CH_3)_2$], 1.4–1.95 [m, 2 H, C_5H, $-CH(CH_3)_2$], 2.06 (q, J = 7.5 Hz, 2 H, $-CH_2-$), 2.11 (s, 3 H, $-CH_3$), 2.61 (t, J = 7.5 Hz, 2 H, $-CH_2S-$), 3.9 (d, J = 2 Hz, 4 H, $C_{4,6}$ H), 4.26 (d, J = 4.5 Hz, 1 H, C_2 H_a).

Trans isomer: δ 0.91 [d, J = 7 Hz, 6 H, $-CH(CH_3)_2$], 1.32 (q, J = 7 Hz, 2 H, $-CH_2-$), 1.6–2.2 [m, 2 H, $-CH(CH_3)_2$, C_5 H], 2.09 (s, 3 H, $-SCH_3$), 2.45 (t, J = 7 Hz, 2 H, $-CH_2S-$), 3.30 (apparent t, J = 11.5 Hz, 2 H, $C_{4,6}$ H_a), 4.09 (d of d, J_{gem} = 11.0 Hz, 2 H, $C_{4,6}$ H_e), 4.15 (d, J = 4.5 Hz, 1 H, C_2 H_a).

***cis*-2-Isopropyl-5-(2-methylsulfinylethyl)-1,3-dioxane.** Oxidation of the cis sulfide as described earlier for the lower homologue proceeded in 80% yield, mp 64.5–66.0 °C after recrystallization from n-hexane.

^1H NMR ($CDCl_3$) δ 0.90 [d, J = 7 Hz, 6 H, $-CH(CH_3)_2$], 1.38–1.98 [m, 2 H, $-CH(CH_3)_2$, C_5 H], 2.18 (q, J = 8 Hz, 2 H, $-CH_2-$), 2.62 (s, 3 H, $-SOCH_3$), 2.84 (t, J = 8 Hz, 2 H, $-CH_2SO-$), 3.94 (d, J = 1.5 Hz, 4 H, $C_{4,6}$ H), 4.26 (d, J = 4.5 HZ= [H, C_2 H_a).

***trans*-2-Isopropyl-5-(2-methylsulfinylethyl)-1,3-dioxane.** Similar oxidation of the trans sulfide proceeded in 83% yield, mp 71.0–72.0 °C after recrystallization from n-hexane.

^1H NMR ($CDCl_3$) δ [d, J = 7 Hz, 6 H, $-CH(CH_3)_2$], 1.53 (q, J = 7.5 Hz, 2 H, $-CH_2-$), 1.65–2.4 [m, 2 H, C_5 H_a, $-CH(CH_3)_2$], 2.59 (s, 3 H, $-SOCH_3$), 2.68 (t, J = 8 Hz, 2 H, $-CH_2SO-$), 3.38 (t, J_{gem} = 11 Hz, 2 H, $C_{4,5}$ H_a), 4.04 (d, J_{gem} = 11 Hz, 2 H, $C_{4,6}$ H_e), 4.18 (d, J = 4.5 Hz, 1 H, C_2 H_a).

***cis*-2-Isopropyl-5-(2-methylsulfonylethyl)-1,3-dioxane.** The compound was prepared from the corresponding sulfide as described for the lower homologue in 79% yield, mp 98.5–100.0 °C after recrystallization from n-hexane.

^1H NMR ($CDCl_3$) δ 0.91 [d, J = 7 Hz, 6 H, $-CH(CH_3)_2$], 1.5–1.95 [m, 2 H, C_5 H, $-CH(CH_3)_2$], 2.28 (apparent q, J = 7–8 Hz, 2 H, $-CH_2-$), 2.95 (s, 3 H, $-SO_2CH_3$), 3.19 (t, J = 8 Hz, 2 H, $-CH_2S-$), 3.95 (d, J = 2 Hz, 4 H, $C_{4,6}$ H), 4.29 (d, J = 4.5 Hz, 1 H, C_2 H_a).

Anal. Calcd for $C_{10}H_{20}SO_4$: C, 50.82; H, 8.53. Found: C, 50.53; H, 8.41.

***trans*-2-Isopropyl-5-(2-methylsulfonylethyl)-1,3-dioxane.** Similar oxidation of *trans*-2-isopropyl-5-(2-methylthioethyl)-1,3-dioxane proceeded in 86% yield, mp 121.5–122.5 °C after recrystallization from n-hexane.

^1H NMR ($CDCl_3$) δ 0.90 [d, J = 7 Hz, 6 H, $-CH(CH_3)_2$], 1.45–2.2 [m, 4 H, C_5 H, $-CH(CH_3)_2$, $-CH_2SO_2-$), 2.92 (s, 3 H, $-SO_2CH_3$), 2.9–3.1 (m, 2 H, $-CH_2-$), 3.35 (t, J_{gem} = 11.5 Hz, 2 H, $C_{4,6}$ H_a), 4.11 (two d, J_{gem} = 11.5 Hz, 2 H, $C_{4,6}$ H_e), 4.17 (d, J = 4.5 Hz, 1 H, C_2 H_a).

Anal. Calcd for $C_{10}H_{20}SO_4$: C, 50.82; H, 8.53. Found: C, 50.91; H, 8.46.

Dimethyl-5-(*cis*-2-isopropyl-1,3-dioxanyl)-2-ethylsulfonium *p*-Toluenesulfonate. From 1.02 g (5 mmol) of *cis*-2-isopropyl-5-(2-methylthioethyl)-1,3-dioxane, using the procedure described earlier for the lower homologue, 1.6 g (82%) of sulfonium salt was obtained after recrystallization from ethanol–ether, mp 170–171 °C.

The tosylate was converted to the slightly impure hexafluorophosphate salt by treatment with NH_4PF_6, mp ca. 134–136 °C.

^1H NMR (CD_3CN) δ 0.87 [d, J = 6.5 Hz, 6 H, $-CH(CH_3)_2$], 1.3–2.3 (m, 4 H, $-CH_2-$, C_5 H_e, and $-CH(CH_3)_2$0, 2.8 [s, 6 H, $-S^+(CH_3)_2$], 3.2 (m or apparent q, J = 8 Hz, 2 H, $-CH_2S$), 3.87 (d, J = 2 Hz, 4 H, $C_{4,6}$ H), 4.26 (d, J = 4.5 Hz, 1 H, C_2 H_a).

Dimethyl-5-*trans*-2-isopropyl-1,3-dioxanyl)-2-ethylsulfonium *p*-Toluenesulfonate. This isomer was similarly obtained from the trans sulfide in 85% yield after recrystallization from ethanol–ether, mp 180.5–181.5 °C.

The hexafluorophosphate was prepared from the tosylate, mp 175–176 °C.

^1H NMR (CD_3CN) δ 0.85 [d, J = 6.8 Hz, 6 H, $-CH(CH_3)_2$], 1.30–2.0 [m, 4 H, $-CH_2-$, C_5 H_a, and $-CH(CH_3)_2$], 2.74 [s, 6 H, $-S^+(CH_3)_2$], 3.0–3.4 (m, 4 H, $-CH_2S$ and $C_{4,6}$ H_a), 4.0 (two d, J = 4.5, J_{gem} = 12 Hz, 2 H, $C_{4,6}$ H_e), 4.10 (d, J = 4.5 Hz, 1 H, C_2 H_a).

Equilibration of the diastereomeric sulfonium salts was brought about as described for the lower homologues; analysis was by ^{13}C NMR.

Equilibrations. Unless indicated otherwise, the compound or mixture to be equilibrated was dissolved in the appropriate solvent, the solution was placed in a thermostat, and a few beads of Amberlyst-15 (beaded polystyrenesulfonic acid) were added. After equilibrium was reached (equal composition starting from cis-rich and trans-rich mixtures) the solutions were decanted, shaken with solid potassium carbonate, filtered, and analyzed by GLC.

Sulfonium salts were equilibrated by adding a few drops of TFA to their solution in CD_3CN in an NMR tube, allowing the tube to stand, and recording the NMR spectrum at intervals. Equilibrium was deemed to be reached when the signal ratio of the diastereomers became constant.

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Registry No.—*cis*-5-(2-Isopropyl-1,3-dioxanyl)methyl *p*-toluenesulfonate, 61523-20-4; *trans*-5-(2-isopropyl-1,3-dioxanyl)methyl *p*-toluenesulfonate, 61523-21-5; *cis*-5-(2-isopropyl-1,3-dioxanyl) methanol, 28808-24-4; *trans*-5-(2-isopropyl-1,3-dioxanyl)methanol, 35113-53-2; tosyl chloride, 98-59-9; CH_3SK, 26385-24-0; dimethyl-5-(*cis*-2-isopropyl-1,3-dioxanyl)methylsulfonium *p*-toluenesulfonate, 61523-22-6; dimethyl-5-(*trans*-2-isopropyl-1,3-dioxanyl)-methylsulfonium *p*-toluenesulfonate, 61523-23-7; methyl *p*-toluenesulfonate, 80-48-8; *cis*-2-isopropyl-5-cyanomethyl-1,3-dioxane, 61523-24-8; *trans*-2-isopropyl-5-cyanomethyl-1,3-dioxane, 61523-

25-9; *cis*-5-(2-isopropyl-1,3-dioxanyl)acetic acid, 61523-26-0; *trans*-5-(2-isopropyl-1,3-dioxanyl)acetic acid, 61523-27-1; *cis*-2-isopropyl-5-(2-hydroxyethyl)-1,3-dioxane, 61523-28-2; *trans*-2-isopropyl-5-(2-hydroxyethyl)-1,3-dioxane, 61523-29-3; *cis*-2-isopropyl-5-(2-hydroxyethyl)-1,3-dioxane tosylate, 61523-30-6; *trans*-2-isopropyl-5-(2-hydroxyethyl)-1,3-dioxane tosylate, 61523-31-7; dimethyl-5-(*cis*-2-isopropyl-1,3-dioxanyl)-2-ethylsulfonium *p*-toluenesulfonate, 61523-32-8; dimethyl-5-(*trans*-2-isopropyl-1,3-dioxanyl)-2-ethylsulfonium *p*-toluenesulfonate, 61523-33-9; *cis*-2-isopropyl-5-methoxy-1,3-dioxane, 28808-16-4; *trans*-2-isopropyl-5-methoxy-1,3-dioxane, 36094-12-9; *cis*-2-isopropyl-5-(methoxymethyl)-1,3-dioxane, 28808-25-5; *trans*-2-isopropyl-5-(methoxymethyl)-1,3-dioxane, 58619-95-7; *cis*-2-isopropyl-5-(methylsulfinyl)-1,3-dioxane, 40245-31-6; *trans*-2-isopropyl-5-(methylsulfinyl)-1,3-dioxane, 40245-32-7; *cis*-2-isopropyl-5-(methylsulfonyl)-1,3-dioxane, 40245-33-8; *trans*-2-isopropyl-5-(methylsulfonyl)-1,3-dioxane, 40245-34-9; dimethyl-5-(*cis*-2-isopropyl-1,3-dioxanyl)sulfonium *p*-toluenesulfonate, 58620-17-0; dimethyl-5-(*trans*-2-isopropyl-1,3-dioxanyl)sulfonium *p*-toluenesulfonate, 58620-19-2.

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Ion Radicals. 38. Reactions of Phenoxathiin and Thianthrene Cation Radicals with Alkyl- and Dialkylamines[1,2]

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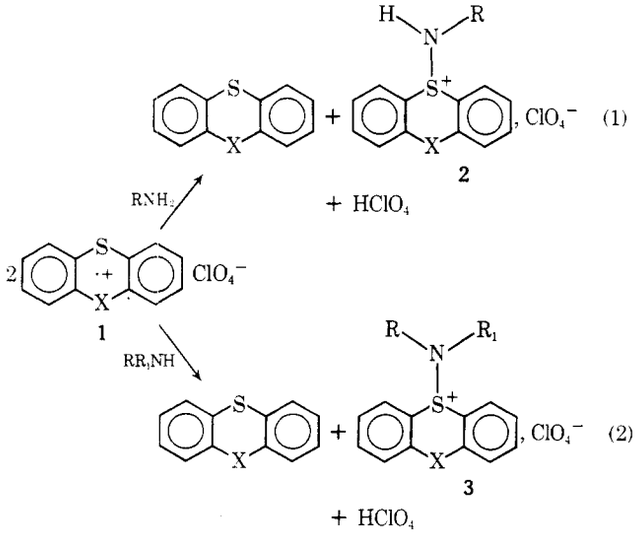
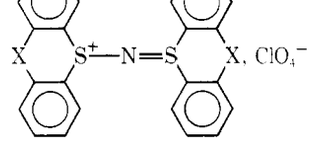
Phenoxathiin cation radical perchlorate (**1c**) reacted with alkylamines to form protonated *N*-alkylsulfilimine perchlorates (**2c**) and with dialkylamines to form *N,N*-dialkylaminosulfonium perchlorates (**3c**). Analogous reactions were obtained with thianthrene cation radical (**1d**), giving products **2d** and **3d**. Reaction of **1d** with alkylamines also gave in every case some 5,5-dihydro-5-(5-thianthreniumylimino)thianthrene perchlorate (**4d**). Only in one case, reaction with propylamine, did **1c** give the analogous **4c**. The salts **2c** were deprotonated to give the *N*-alkylsulfilimines (**5c** and **5d**) and these were methylated with methyl iodide giving *N*-alkyl-*N*-methylaminosulfonium iodides (**6c** and **6d**). Most of the sulfonium salts (**6c** and **6d**) were converted into the corresponding perchlorates (**3c** and **3d**) which were also obtained directly by reactions of **1c** and **1d** with *N*-alkylmethylamines.

It was shown recently that the cation radical perchlorates of 10-methyl-(**1a**, X = *N*-Me) and 10-phenylphenothiazine (**1b**, X = *N*-C_6H_5) react with alkyl- and dialkylamines according to eq 1 and 2.[5] We have found, subsequently, that



phenoxathiin cation radical perchlorate (**1c**, X = O) undergoes analogous reactions. Further, it was reported by Kim and Shine[6] that thianthrene cation radical perchlorate (**1d**, X = S) did not react with alkylamines according to eq 1 except in the case of *tert*-butylamine. That is, reaction of **1d** with ethyl-, propyl-, and cyclohexylamine was reported to give the dimeric product (**4d**, X = S) instead of products **2d** (R = Et, Pr, C_6H_{11}). We have found now that this report is not correct.



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4c, X = O; 4d, X = S

Reaction of alkylamines with **1d** (eq 1) is not as facile as with the analogues **1a–c**, but it does give the sulfilimine salts **2d** (X = S) although in poor yields. At the same time the dimer byproduct **4d** is formed but not exclusively as was reported earlier.[6]

Separation of products **2d** from the other products of reaction is tedious and apparently was not achieved earlier. Thus, the reactions of eq 1 and 2 are general for the series X = S, O, *N*-Me, *N*-C_6H_5, but yields vary from case to case. Data for reactions of **1c** and **1d** are given in Tables I and II. These data show that the dimer **4d** was obtained from all reactions of **1d** with alkylamines, whereas the dimer **4c** was obtained only in reaction of **1c** with propylamine. Small amounts of phenoxathiin 5-oxide and thianthrene 5-oxide were also obtained presumably from reaction of the cation radicals with water in the reagents or solvents.[7]

Deprotonation of the products **2c** and **2d** was carried out