5-Methyl-1,3-diisopropyl-1,3-diazolidine-2,4-dione (VI). A liquid: IR 1700 cm^{-1}; NMR (CCl_4) δ 1.05 (d, 6 H), 1.40 (d, 6 H), 1.45 (d, 3 H), 2.8 (m, 2 H), and 4.36 (q, 1 H).

Anal. Calcd for $C_{10}H_{18}N_2O_2$: C, 60.58; H, 9.15; N, 14.13. Found: C, 60.28; H, 9.06; N, 13.95.

3-Isopropyl-2-isopropylimino-4-oxazolidinone (VII). To 0.01 mol of chloro-*N*-chloroacetyl-*N,N'*-diisopropylformamidine in 50 mL of hexane was added 1.4 mL (0.01 mol) of triethylamine at room temperature, followed immediately by the addition of excess water. After a few minutes the amine salt precipitated; the solution was filtered and the solvent evaporated to give 1.6 g (88%) of the 4-oxazolidinone; mp 46–48 °C; IR 1690 and 1750 cm^{-1}; NMR (CCl_4) δ 1.15 (d, 6 H), 1.35 (d, 6 H), 3.59 (s, 2 H), and 4.2 (m, 2 H); mass spectrum parent peak *m/e* 184 (theory 184).

Anal. Calcd for $C_9H_{16}N_2O_2$: C, 58.67; H, 8.75; N, 15.20. Found: C, 58.27; H, 8.48; N, 15.21.

Acknowledgments. The authors wish to express appreciation to the Robert A. Welch Foundation and the North Texas State University Faculty Research Fund for support of this investigation.

Registry No.—I, 63059-02-9; II, 63059-03-0; III, 63059-04-1; IV, 63059-05-2; V, 63059-06-3; VI, 63509-07-4; VII, 57095-80-4; diisopropylcarbodiimide, 693-13-0; chloro-*N*-chloroacetyl-*N,N'*-diisopropylformamidine, 63059-08-5; chloro-*N*-(α-chloropropionyl)-*N,N'*-diisopropylformamidine, 63059-09-6; chloroacetyl chloride, 79-04-9; α-chloropropionyl chloride, 7623-09-8; *N*-chloroacetyl-*N,N'*-diisopropylurea, 63059-10-9; *N*-(α-chloropropionyl)-*N,N'*-diisopropylurea, 63059-11-0; *N*-(α-bromoisobutyryl)-*N,N'*-diisopropylurea, 63059-12-1; α-bromoisobutyryl chloride, 20469-89-0; chloro-*N*-(α-bromosiobutyryl)-*N,N'*-diisopropylformamidine, 63059-13-2.

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Substituent and Geometry Dependence of the Degenerate Ligand Exchange of Dialkoxysulfuranes with Hexafluoro-2-phenyl-2-propanol. Sulfuranes and Sulfilimines Derived from Thianthrene, Phenothiazine, and Phenoxathiin[1]

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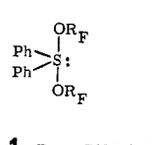
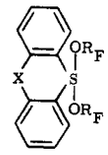
The oxidations of thianthrene, *N*-phenylphenothiazine, and phenoxathiin with bromine in the presence of the potassium salt of 1,1,1,3,3,3-hexafluoro-2-phenyl-2-propanol (R_FOH) lead to the formation of dialkoxysulfuranes. The characterization of sulfuranes is described. All three are very reactive in dehydrating *tert*-butyl alcohol at room temperature. The degenerate alkoxy ligand exchange with R_FOH is determined by NMR to be very fast, with the rates for sulfuranes derived from phenoxathiin, thianthrene, and *N*-phenylphenothiazine increasing in the order listed. The first two of these sulfuranes were shown to react with benzylamine to give the corresponding *N*-benzylsulfilimines.

Over the past few years several types of oxysulfuranes have been isolated and studied.[2] The chemistry of these species, notably that of dialkoxysulfurane **1**,[3] has been shown to derive from rapid ligand exchange reactions involving the weakly bound[2] apical alkoxy ligands. The mechanism for ligand exchange for **1** in solution has been found[4] to very probably be dissociative via the alkoxysulfonium ion. This paper reports the synthesis and some reactions, including a study of the rates of the degenerate ligand exchange with R_FOH, where R_F is $PhC(CF_3)_2$, of cyclic sulfuranes **2**, **3**, and **4**, in which an atom bridge is expected to allow a close approach to coplanarity of the two equatorial aryl ligands.



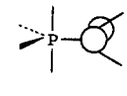
1, $R_F = C(CF_3)_2Ph$



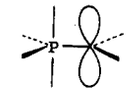
2, X = N-Ph
3, X = O
4, X = S

Results and Discussion

Experimental and theoretical bases exist[5] for the assertion that equatorial π-donor ligands in phosphoranes have a preferred orientation with the donor p orbital in the equatorial plane as in **5** rather than perpendicular to this plane as in **6**.[5k]



5



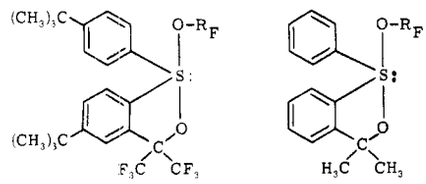
6

The situation is less clear cut in the case of sulfuranes, where calculations[6] suggest that the repulsive interaction of the π donor with the sulfur lone pair may predominate in a con-

formational equilibrium favoring the opposite orientation (8 rather than 7) for a π-donor equatorial ligand.

7 8

It would not be surprising to discover a dependence of sulfurane reactivity on the orientation of π-donor ligands in the equatorial plane. The orientation of the equatorial phenyl rings in 1 has been shown[7] to be skewed (32°22′ and 42°31′ from the plane defined by the sulfur atoms and the two carbon atoms bonded to sulfur) in the crystal, and a number of sulfuranes have been synthesized[8,9,10] in which π orbitals, at least for one of the aromatic equatorial aryl ligands, are expected[11] to be approximately perpendicular to the hypervalent S–O bonds, e.g., 9 and 10. Sulfuranes 2, 3, and 4, having π orbitals

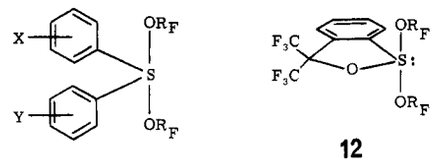


9 10

of the phenyl rings more nearly parallel[12] to the S–O apical bonds than any of the sulfuranes studied[2,4,8] thus far, might be expected to reflect in their patterns of reactivity the result of electronic interactions engendered by this steric constraint.

The syntheses of 2, 3, and 4 were effected by the established procedure[13] in which a carbon tetrachloride solution or suspension of the sulfide is mixed with 2 equiv of KOR_F and 1 equiv of bromine. For sulfurane 2 it was necessary to add ~2 equiv of 1,4-endoxocyclohexane[8] as a cosolvent to dissolve the KOR_F. When the cosolvent was eliminated, no 2 was formed. However, when sulfurane 2 was prepared in ether at 4 °C, no cosolvent was necessary, since all materials were soluble. Attempts to form sulfuranes utilizing phenothiazine, 10-methylphenothiazine, 10-acetylphenothiazine, and thioxanthane by a procedure similar to method A in the Experimental Section did not succeed. Apparently oxidations involving other sites of the molecule predominated over sulfurane formation.

Although sulfuranes 3 and 4 are thermally stable compounds at ambient temperatures, sulfurane 2 is unstable under these conditions and is at least 68% destroyed in carbon tetrachloride solution after 2 days at room temperature to give unidentified products. Attempts to isolate 2 were unsuccessful, but sulfuranes 3 and 4 were easily isolated as crystalline solids (in 71 and 58% yields, respectively). Sulfuranes 3 and 4 show sizable molecular ions (1.5 and 3.5% of the base peak, respectively) in the 70-eV mass spectra and prominent ions at $M^{+\cdot} - 244$ (loss of R_FOH) and $M^{+\cdot} - 243$ (loss of OR_F). Although the assignments of the peaks in the 220 MHz proton NMR (CCl_4) for 2, 3, and 4 were somewhat ambiguous, the chemical shifts of the protons ortho to sulfur are considerably upfield (at higher field than δ 7.6) from those observed for sulfurane 1[3e] (δ 8.0 in $CDCl_3$) and related sulfuranes 11 (δ 7.8–7.9 $CDCL_3$).[4] The downfield shift seen for the ortho protons in these analogues, in which conformations having an equatorial aryl ligand ring coplanar with the apical substituents are either mandated (9 or 10) or allowed (1, 11), can be ascribed to the anisotropy of the apical S–O bond in the conformation which juxtaposes an ortho proton to this bond in a region of space parallel to it. Such a conformation is of course precluded for the sulfuranes (2–4) of this paper. The absence of this downfield shift for the ortho (to S) proton of 12 (δ 7.61,



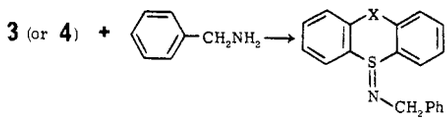
11a X = p-F; Y = H
b X = m-F; Y = H
c X = Y = p-t-Bu
d X = Y = p-OCH_3

12

CCl_4) has been interpreted[14] as evidence for the novel conformation pictured with a diequatorially linked five-membered ring.

Sulfurane 1 is a powerful dehydration reagent[3f] and has been shown to dehydrate *tert*-butyl alcohol within seconds, even at temperatures as low as −80 °C, to give isobutylene, Ph_2SO, and R_FOH. Sulfuranes 2, 3, and 4 also show comparable reactivity, giving isobutylene, R_FOH, and the corresponding sulfoxides.

Sulfurane 1 has been shown[15] to give sulfilimines upon reaction with primary amines. The reaction of sulfurane 3 or 4 with benzylamine gives the corresponding sulfilimine 13 or 14. Examples of related sulfilimines have recently been reported.[16]



13 (X = O)
14 (X = S)

Exchange Studies. Solutions of sulfuranes 1–4 and R_FOH in diethyl ether were prepared such that the concentrations of sulfurane and R_FOH were 0.11–0.14 and 0.25–0.27 M, respectively. A series of low-temperature ^{19}F NMR spectra of these solutions, of an ether solution of 10 (0.13 M) with R_FOH (0.25 M), and of sulfurane 9 (0.56 M in dibenzyl ether solvent) with R_FOH (1.2 M) was obtained. In each case the lower temperatures showed widely separated (374–510 Hz at 94.1 MHz) ^{19}F peaks for R_FOH and for the ligand OR_F groups. As the temperature was raised these peaks coalesce toward a single peak (at the high temperature extreme). The approximate coalescence temperatures, the corresponding rates of exchange at the coalescence temperature, and the corresponding free energies of activation are summarized in Table I.

The concentration of R_FOH in a given solution remains constant, of course, since the exchange reaction being observed is a degenerate one, generating one free R_FOH molecule as another is bound to sulfurane sulfur as a ligand. The rate constants of Table I are therefore pseudo-first-order rate constants. The kinetic order in R_FOH is clearly greater than zero, from the observation that exchange rates decrease with decreasing R_FOH concentrations, but the order has not been determined rigorously. The concentration of R_FOH has the same value throughout the series, except for the larger concentration used for the least reactive sulfurane (9) of Table I. The coalescence temperatures are widely enough separated and the pseudo-first-order rate constants similar enough to provide an unambiguous ordering (at a constant temperature) of the rates for these degenerate exchange reactions as follows (fastest to slowest): **10 > 2 > 4 > 3 > 1 > 9.** The degenerate exchange rate can, of course, also be reduced by lowering the concentrations of sulfurane and R_FOH. Dilution of the above

Table I. Approximate Coalescence Temperatures for ^{19}F Peaks Reflecting the Rates of Degenerate Ligand Exchange of Dialkoxysulfuranes with R_FOH

Compd	Registry no.	[Sulfurane], M	[R_FOH], M	Coalescence temp, T_c (±3 °C)	Chemical shift difference, Hz[a]	k_1, s^{-1}	$\Delta G^{\ddagger}$, kcal/mol (at T_c)	[R_FOH], M, to produce coalescence[b]
10	63018-00-8	0.13	0.25	−45	374	830.8	10.2	≪0.031
2	63018-01-9	0.11	0.27	−30	412	915.2	10.8	≤0.034
4	63018-02-0	0.13	0.27	+10	455	1010.8	12.7	0.099
3	63018-03-1	0.11	0.26	+30	454	1008.5	13.6	0.26
1	32133-82-7	0.14	0.26	>30[c]	510	1132.9		
9[d]	52969-48-9	0.56	1.2	148[d]	120[e]	>266.6	>20.3	

[a] Between ^{19}F peaks for sulfurane OR_F ligands and for R_FOH at 94.1 MHz. [b] The concentration of R_FOH at which the coalescence of ^{19}F peaks was observed at 30 °C. [c] Peaks are just beginning to broaden as temperature is raised to 30 °C. [d] In diphenyl ether solvent. [e] Coalescence of ^{19}F quartets for the OR_F ligands only.

samples until the 30 °C spectra showed peak broadening approximating the coalesced spectra gave the same order of exchange rates as that which was deduced from the data reported in Table I.

A notable feature of this order is the placement of sulfuranes **9** and **10** at either extreme. These two molecules have similar geometries, since one aromatic ring is expected to be held[11] rigidly in place by the five-membered ring, essentially coplanar with the apical O–S–O axis. The predominant influence on exchange rates must here be a substituent effect (CH_3 vs. CF_3) in the apical alkoxy ligand trans to the leaving group. Although the base-catalyzed hydrolyses of chlorosulfuranes analogous to **9** and **10** have been shown[9] to proceed by an associative mechanism, the order of rates for the degenerate exchange with R_FOH clearly favor a dissociative mechanism for this reaction.

All of the sulfuranes except **10** have similar trans apical substituents, and α,α-bis(trifluoromethyl)-α-arylalkoxy group. The order **2** > **4** > **3** > **1** > **9** might therefore be reasonably expected to mirror the effects of geometry and of equatorial substitution.

Although **2, 3,** and **4,** with their more nearly coplanar equatorial aryl ligands, are more reactive than sulfuranes **1** and **9** which have sterically enforced noncoplanarity of the equatorial aryl rings, the order seen is also approximately the order of electron density on the aryl rings. An earlier study[4] of meta- and para-substituted analogues of **1** led to the conclusion that the degenerate ligand exchange in that series of sulfuranes was accelerated by electron releasing substituents (an estimated Hammett ρ of −3). The qualitative order of rates in the present series of compounds is roughly in accord with the conclusion. Only the **4** > **3** order is reversed from that based on predictions from Hammett σ values[17] for model substituents for **2, 4,** and **3** (σ_p for the $N(CH_3)_2$, the OCH_3, and the SCH_3 groups, respectively, −0.83, −0.27, and 0.00 lead to the predicted order **2** > **3** > **4**). While faster exchange reactions of **2, 3,** and **4** may reflect an accelerating effect of the enforced geometry of the π-donor equatorial aryl ligands holding the aryl π-bond orbitals roughly parallel with the apical axis, it is not clear that such an effect is demanded.

Experimental Section

NMR spectra were obtained using tetramethylsilane or fluorotrichloromethane as internal standards for ^1H NMR and ^{19}F NMR, respectively. In cases where a dry solvent was necessary, these internal standards were dried over 4A molecular sieves (Linde). Melting points are not corrected. All manipulations of water-sensitive compounds were carried out in an inert atmosphere glove box.

Solvents and Reagents. 10-Phenylphenothiazine,[18] 1,4-endoxocyclohexane,[19] hexafluoro-2-phenyl-2-propanol (R_FOH),[20] and potassium hexafluoro-2-phenyl-2-propoxide (R_FOK)[13] were prepared according to published procedures. Ether was dried by several additions of sodium wire until the wire remained shiny. Carbon tetrachloride was dried by distillation from phosphorus pentoxide.

5-Bis[α,α-bis(trifluoromethyl)benzenemethanolato]-10-phenylphenothiazine (2) (in solution). Method A. A mixture of 0.133 g (0.49 mmol) of 10-phenylphenothiazine and 0.27 g (0.97 mmol) of R_FOK in 3.0 mL of dry CCl_4 was prepared in an inert atmosphere box in a 15-mL centrifuge tube, which was capped by a serum stopper. To this was added 0.100 mL (0.109 g, 1.11 mmol) of 1,4-endoxocyclohexane. The mixture was shaken until nearly all the solids were dissolved. Bromine (25 μL, 0.078 g, 0.49 mmol) was added by syringe and the tube was shaken for several minutes. The resulting mixture was centrifuged and the supernatant solution of **2** was used for NMR analysis and chemical reactions: ^1H NMR (220 MHz, CCl_4 with 1,4-endoxocyclohexane) δ 7.854 (d, 0.6, 4, 6 protons of 10-phenylphenothiazine 5-oxide impurity, J = 8 Hz), 7.632 (d, 2.0, J = 8 Hz), 7.545 (d with fine structure, 2.0, J = 7 Hz), 7.382 and 7.250 (multiplets, 6.3 and 8.0), 7.014 (t, 2.1, J = 7 Hz), 6.673 (m, 3.0); ^{19}F NMR (94.1 MHz, ether) 70.1 ppm upfield from $CFCl_3$.

Upon standing at room temperature for 48 h, 68% (by ^{19}F NMR) of the sulfurane is converted to unidentified ^{19}F-containing products with peaks at δ 70.4, 70.6, and 70.7 ppm upfield from $CFCl_3$.

Method B. A solution of 0.158 g (0.574 mmol) of 10-phenylphenothiazine and 0.32 g (1.15 mmol) of KOR_F in 3.0 mL of dry ether was treated in the above described manner with 29.4 μL of bromine (0.574 mmol). After centrifugation, the supernatant solution of **2** was used for subsequent reactions.

5-Bis[α,α-bis(trifluoromethyl)benzenemethanolato]phenoxathiin (3). Phenoxathiin (10.00 g, 0.05 mol) and KOR_F (28.2 g, 0.10 mol), suspended in 100 mL of dry CCl_4, was treated, as above, with 2.56 mL of bromine (0.05 mol). After 30 h of stirring the bromine color had nearly disappeared. Filtration of the mixture in a drybox, washing of the filter cake with CCl_4, and evaporation of the solvent in vacuo gave a cream-white solid which was recrystallized from ether–pentane to give 24.18 g (71%) of sulfurane **3;** mp (sealed tube) 105–107 °C (with decomposition); ^1H NMR (220 MHz, CCl_4) δ 7.545 (d with fine structure, 2.0, J = 8 Hz), 7.418 (m, 4.2), 7.090 (m, 12.4); ^{19}F NMR (94.1 MHz, ether) 70.1 ppm upfield from $CFCl_3$; mass spectrum (70 eV) m/e (rel intensity) 686 (1.5, $M^{+}\cdot$), 459 (1.0, $M^{+}\cdot - R_F$), 443 (21.8, $M^{+}\cdot - OR_F$), 442 (35.6, $M^{+}\cdot - HOR_F$), 244 (24.7, HOR_F^{+}), 227 (4.7, R_F^{+}), 216 (84.7), 215 (100.0), 200 (57.3), 187 (99.1), 175 (48.3), 168 (78.6), 139 (29.4),127 (25.9), 115 (27.2), 105 (78.0), 77 (45.8), 69 (34.2), 63 (27.9), 51 (38.8), 50 (20.5).

Anal.[21] Calcd for $C_{30}H_{18}F_{12}O_3S$: C, 52.49; H, 2.64; S, 4.67. Found: C, 50.87; H, 2.73; S, 4.66.

5-Bis[α,α-bis(trifluromethyl)benzenemethanolato]thianthrene (4). Thianthrene (1.005 g, 4.66 mmol) and KOR_F (2.625 g, 9.31 mmol) suspended in ca. 20 mL of dry CCl_4 were treated with 238.7 μL of bromine (4.66 mmol). After stirring overnight the bromine color was gone. The resulting mixture was filtered in the drybox, the salt cake was washed twice with CCl_4, and the solvent was removed in vacuo to leave an off-white solid. This was recrystallized from ether–pentane to give 1.89 g (58%) of **4** as transparent prisms: mp (sealed tube) 111–113 °C (with decomposition); ^1H NMR (220 MHz, CCl_4) δ 7.511 (d, 3.8, J = 9 Hz), 7.337 (t, 2.0, J = 7.5 Hz), 7.109 (m, 11.3); ^{19}F NMR (94.1 MHz, ether) 70.1 ppm upfield from $CFCl_3$; mass spectrum (70 eV) m/e (rel intensity) 702 (3.5, $M^{+}\cdot$), 475 (0.19, $M^{+}\cdot - R_F$), 458 (16.7, $M^{+}\cdot - HOR_F$), 459 (16.3, $M^{+}\cdot - OR_F$), 244 (27, HOR_F^{+}), 232 (27.3), 231 (28.8), 227 (5.49, R_F^{+}), 216 (81.3), 203 (35.2), 185 (15.8), 184 (100.0), 175 (46.2), 171 (40.9), 105 (70.3), 77 (32.7), 69 (35.3), 51 (16.9), 50 (12.3).

Anal.[21] Calcd for $C_{30}H_{18}F_{12}O_2S_2$: C, 51.29; H, 2.58; S, 9.13. Found: C, 49.47; H, 2.65; S, 9.14.

Reactions of 2, 3, and 4 with *tert*-Butyl Alcohol. To ca. 0.15 M

carbon tetrachloride solutions of each of sulfuranes **2, 3,** and **4** was added 10 μL of *tert*-butyl alcohol at room temperature. Reaction was completed as soon as the NMR spectra could be run. The products isobutylene and R_FOH were detected by ^1H and ^{19}F NMR, respectively. The corresponding sulfoxides were isolated by extraction of the CCl_4 solution with 15% KOH, washing the organic phase with water, drying (Na_2SO_4), and evaporation of the solvent to give the corresponding sulfoxides by comparison with authentic samples (NMR and melting point).

5-(Benzylimino)phenoxathiin (13). To 0.1568 g (0.229 mmol) of **3** in 0.6 mL of dry $CHCl_3$ was added 25 μL (0.229 mmol) of benzylamine and the solution was shaken. The solution was extracted twice with 1–2 mL of 15% KOH solution, twice with water, and dried (Na_2SO_4). After removal of solvent on the rotary evaporator, 49.3 mg (70.6%) of a white solid remained. This was recrystallized from ether–pentane to give 26.0 mg (37.2%); mp 120–122 °C (some crystal changes noted), 130–145 °C (all melted); ^1H NMR (60 MHz, $CDCl_3$) δ 7.88 (d of d, 2.1, 4, 6 protons of sulfilimine, J_{AB} = 7.5, J_{BC} = 2.0 Hz), 7.36 (m, 11.0, remaining aromatic protons), 3.51 (s, 2.0, $-CH_2C_6H_5$); IR ($CHCl_3$) 3075 (w), 3083 (w), 3018 (m), 2928 (m), 1594 (s), 1497 (m), 1479 (m), 1465 (s), 1438 (s), 1322 (m), 1271 (s), 1130 (m), 1093 (m), 1070 (m), 1030 (m), 888 (m), 858 (m), 791 (m,br), 701 (m), 674 (w), 665 (w) cm^{-1}.

Anal. Calcd for $C_{19}H_{15}NOS$: C, 74.72; H, 4.95; N, 4.58; S, 10.50. Found: C, 74.54; H. 5.06; N, 4.46; S. 10.64.

5-(Benzylimino)thianthrene (14). The above procedure was used in the preparation of sulfilimine **14.** From 0.5462 g (0.778 mmol) of sulfurane **4** was obtained a mixture of 53% of sulfilimine **14** detected by NMR (benzylic protons, δ 4.20 in $CDCl_3$) and 47% of thianthrene *S*-oxide resulting from hydrolysis either of the original sulfurane or of the sulfilimine in the workup. Separation of the materials by recrystallization proved impossible. Hydrolysis of sulfilimine **14** to the sulfoxide was observed when the above mixture dissolved in ca. 5 mL of CCl_4 was treated with gaseous HCl followed by a 15% aqueous KOH extraction. After drying (Na_2SO_4) and evaporation of solvent the NMR ($CDCl_3$) indicated 35% of sulfilimine **14** remaining and new benzylamine peaks at δ 3.82 ($-CH_2-$) and 1.98 (br, $-NH_2$).

Exchange Rate Studies. Solutions of sulfuranes **1–4** and **10** in dry ether were prepared (0.11–0.14 M). Some hydrolysis occurred due to traces of moisture present in the ether. Sufficient R_FOH was added until the molarity of the R_FOH was roughly twice that of the sulfurane (0.25–0.27 M). The temperature dependence of ^{19}F NMR spectra was studied at 94.1 MHz. The results are listed in Table I. Also a number of sulfuranes (**2, 3, 4,** and **10**) were studied at 30 °C. In these studies dilutions of one-half, one-fourth, and one-eighth of original concentrations were used and the NMR behavior recorded. In only two sulfuranes (**3** and **4**) was it possible to slow exchange sufficiently to see two peaks by this dilution procedure (see Table I). For sulfurane **2,** the coalescence point was being approached at one-eighth of original concentration; however, for sulfurane **10** the original sulfurane–R_FOH singlet was only broadening at one-eighth of its original concentration. The exchange rates are calculated in the usual way,[22] and the Eyring equation was used to calculate the activation energies.

For sulfurane **9,** the compound was dissolved in dibenzyl ether and due to the presence of moisture was partially hydrolyzed. The concentrations of **9** and R_FOH were calculated from the ^{19}F NMR integral and the sample was studied over the temperature interval 28–148 °C. A dilute sample in ether (ca. 0.02 M) with a large excess (ca. 0.2 M) of R_FOH showed no exchange nor any broadening at 28 °C.

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Registry No.—**13,** 61558-76-7; **14,** 61558-80-3; 10-phenylphenothiazine, 7152-42-3; R_FOH, 37818-31-8; phenoxathiin, 262-20-4; thianthrene, 92-85-3; benzylamine, 100-46-9.

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