vidual chemical systems, and their interconversion is interpreted as the allylic "rearrangement".

Second, consider the π,σ-routes to the 2-norbornyl cation (Scheme VII). The most probable transformations according to the ratings in the Table I are the routes E_1, E_2, F_1, F_2, and I_1. It is interesting that monocyclic cation **38** can be a precursor of **36** both in the one-stage transformation (route B, Scheme V) and in the two-stage one (route E_1, Scheme VII): if the carbocationic center in **38** attacks the nearest end of the double bond the two-stage process should occur, while the one-stage pathway is possible if the remote end is attacked. The other π,σ-routes of Scheme VII include the anti-Markovnikov electrophilic addition and, hence, are less probable.

Route J_1 is a second example of the two-component electrophilic addition: the precursor **46** in this process is the product of intermolecular addition to bicyclopentenyl cation (cf. route A_1, Scheme VI).

All σ,π-routes, found by FLAMINGOES are depicted in Scheme VIII. These pathways include the σ-shift in the presence of the more nucleophilic double bond which extremely decreases the probability of these processes. Nevertheless the presented σ,π-routes can be of interest for systematic description of "norbornyl cation land" as well as for particular studies under conditions that impede the electrophilic addition in comparison with the σ-shift of a C-C bond.

V. Conclusion

The computer search for the strategic synthetic pathways to selected structures, which was carried out by the FLAMINGOES program system, demonstrates the possibility of finding rather interesting and promising results, based exlusively on a nonempirical approach to organic reactions. Moreover, the proposed strategies of syntheses might be particularly useful for the synthesis of heterocyclic analogues of those carbocyclic structures.

The computer search of the pathways to the 2-norbornyl cation demonstrates the variety of the skeletal rearrangements leading to this well-investigated system. During this search FLAMINGOES (i) reproduced the known routes to the 2-norbornyl cation and (ii) suggested many new precursors of different types. In our opinion, double π routes are of particular interest.

The present version of FLAMINGOES generates only the strategies of synthesis; generation of more detailed predictions probably needs an interaction with some empirical data base. We are planning to supplement our program system by a set of additional empirical selection criteria to make its predictions more precise. It should be mentioned that the FLAMINGOES is multipurpose system and it can be applied in solution of various problems, e.g., for mechanistic problems in organic chemistry.[47] The work presented in this report is only the first step in a long way to the creation of a highly developed apparatus of "artificial intellect" for the solution of synthesis and mechanistic problems in organic chemistry.

Acknowledgment. We are very grateful to Professor R. Caple for improving our manuscript and for stimulating discussions.

Registry No. **1**, 311-75-1; **2**, 35434-64-1; **3**, 52674-19-8; **4**, 24321-81-1.

(47) Zefirov, N. S.; Gordeeva, E. V.; Kuznetsova, T. S.; Kozhushkov, S. I. *Zh. Org. Khim.* **1988**, *24*, 36.

Tetra-*n*-butylammonium Oxone. Oxidations under Anhydrous Conditions

Barry M. Trost* and Rebecca Braslau

Department of Chemistry, University of Wisconsin—Madison, Madison, Wisconsin 53706

Received May 8, 1987

Tetra-*n*-butylammonium Oxone, readily prepared as a white solid from commercially available Oxone, performs oxidations in anhydrous methylene chloride. Under these conditions, sulfides are oxidized to sulfones in the presence of amines, ketones, esters, carbamates, olefins, and hydroxyl functionalities. Very acid-labile groups such as dimethyl ketals and THP ethers require buffering with anhydrous sodium carbonate. Reactions may be worked up either by direct chromatography of the reaction mixture or by two-phase aqueous extraction. Sulfur-containing amino acid derivatives are also oxidized under these conditions.

Our interest in the chemistry of acyl sulfones[1] led us to consider the possibility of their availability by oxidation of thio esters. The anticipated acylating activity of the product requires an oxidizing agent wherein neither the reagent itself nor its reduction products would be nucleophiles. The chemoselectivity of sulfide oxidations with Oxone (Du Pont), a ternary mixture of potassium hydrogen persulfate, potassium bisulfate, and potassium sulfate, turned our attention to this reagent;[2,3] however, the requirement of aqueous or alcoholic solvents had to be overcome. We have found that Tetra-*n*-butylammonium Oxone (TBA-OX) is a readily prepared white solid that may be used for oxidations under totally anhydrous conditions.

(1) Cf. Trost, B. M.; Quayle, P. *J. Am. Chem. Soc.* **1984**, *106*, 2469. Also see: Barton, D. H. R.; Manly, D. P.; Widdowson, D. A. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1568. Schank, K.; Werner, F. *Liebigs Ann. Chem.* **1979**, 1977.

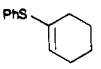
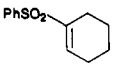
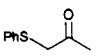
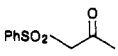
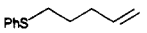
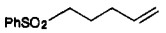
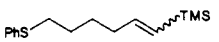
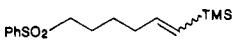
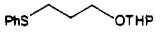
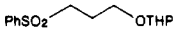
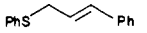
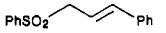
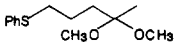
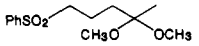
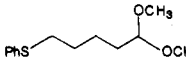
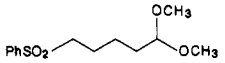
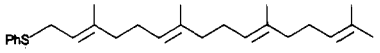
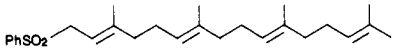
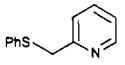
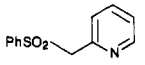
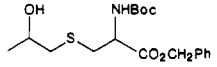
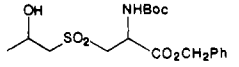
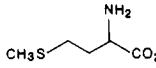
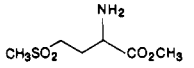
(2) Trost, B. M.; Curran, D. P. *Tetrahedron Lett.* **1981**, *22*, 1287.

(3) For some recent work using Oxone as an oxidant, see: (a) Evans, T. L.; Grade, M. M. *Synth. Commun.* **1986**, *16*, 1207. (b) De Poorter, B.; Ricci, M.; Meunier, B. *Tetrahedron Lett.* **1985**, *26*, 4459. Dehmlow, E. V.; Vehre, B.; Makrandi, J. K. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1985**, *40B*, 1583. (d) Murray, R. W.; Jeyaraman, R. *J. Org. Chem.* **1985**, *50*, 2847. (e) Bloch, R.; Abecassis, J.; Hassan, D. *J. Org. Chem.* **1985**, *50*, 1544. (f) Jeyaraman, R.; Murray, R. W. *J. Am. Chem. Soc.* **1984**, *106*, 2462. (g) Suryawanshi, S. N.; Fuchs, P. L. *Tetrahedron Lett.* **1981**, *22*, 4201.

(4) See reference 3a-c.

0022-3263/88/1953-0532$01.50/0

Table I. Oxidation of Sulfides to Sulfones with Tetra-*n*-butylammonium Oxone

entry	sulfide	sulfone	yield, % method A[a]	yield, % method B[b]
1	$PhSCH_3$	$PhSO_2CH_3$	78	
2			79	
3			83	
4			81	
5			81[c]	78[d]
6			71	85
7			76	
8			24	72
9			64	84
10			49	54
11			76	
12			58	
13			32	

[a] Method A: 3 equiv of TBA-OX, CH_2Cl_2, room temperature; chromatography. [b] Method B: 3 equiv of TBA-OX, 3 equiv of Na_2CO_3, CH_2Cl_2, room temperature; H_2O, ether; chromatography. [c] Starting sulfide, *E*:*Z* 3:1; sulfone, *all E*. [d] Starting sulfide, *E*:*Z* 4:1; sulfone, *E*:*Z* 9:1.

Simply extracting an aqueous solution of Oxone and 5 equiv of tetra-*n*-butylammonium bisulfate obtained from Kodak[5] with methylene chloride, drying, and evaporating gives a white solid which, by iodine titration, corresponds to 37.5 ± 0.6% by weight of tetra-*n*-butylammonium hydrogen persulfate. It is readily soluble in methylene chloride, chloroform, acetone, acetonitrile, and water. NMR experiments show no evidence that any reaction occurred with either acetone or acetonitrile. Only partial solubility can be achieved in benzene, anhydrous THF, or anhydrous dioxane.

Oxidations simply involve stirring a methylene chloride solution of the sulfide with 3 equiv of TBA-OX at room temperature. Direct column chromatography of the reaction mixture then provides the desired product. Table I summarizes our examples and the extraordinary chemoselectivity of this oxidation method. Of special note are the nitrogen-bearing substrates (entries 11–13). The acidity of the TBA-OX provides an in situ protection of the basic nitrogen. The tolerance of olefins is highlighted by entry 10. The vinylsilane substrate of entry 5 is curious. No problem arose from protodesilylation but the olefin geometry appeared to change. Thus, 3–4:1 *E*:*Z* olefin mixtures in the starting material became nearly pure *E* in the olefinic products.

Very acid-labile groups could present problems. For example, acetals or ketals sometimes caused problems (entries 6, 8, and 9) depending upon their acid lability. The very acid-sensitive dimethyl ketal (entry 8) led to only 24% of the ketal sulfone under our standard conditions. Even with carefully controlling reaction time and chromatographing with 2% triethylamine, the keto sulfone was also isolated in 30% yield. Suspending 3 equiv of anhydrous sodium carbonate in the reaction medium and performing a basic aqueous workup prior to chromatography (method B) raised the yield to 72%. The lower sensitivities of the acetals compared to the ketals (entries 6 and 9) led to satisfactory yields under our standard conditions, but these yields did improve under the buffered conditions with basic workup.

Because of the interest in sulfones related to peptides, we examined two amino acid systems (Table I, entries 12 and 13).[6] In the case of entry 12, most of the byproducts derived from TBA-OX could be removed by evaporating the reaction mixture to dryness and triturating the residue with ethyl acetate in which these byproducts were insoluble. The lower yield in the case of entry 13 is, in part, attributable to problems in the chromatographic isolation due to the high polarity of the product.

In short, TBA-OX should prove to be a valuable addition to our approaches for chemoselective oxidations. We have not explored its potential for applications outside of the case of sulfides—an area that should prove fruitful for future endeavors. With respect to sulfide oxidations, it appears to be more chemoselective than some other recently introduced oxidants as exemplified by sodium perborate.[7] While the reactions of TBA-OX are slower than the oxidations in aqueous or alcoholic solvents, the ease of workup and higher chemoselectivity due to the availability of totally anhydrous conditions makes this method a useful approach to these versatile building blocks.

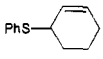
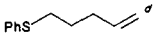
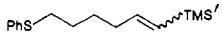
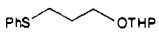
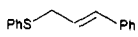
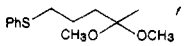
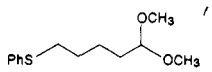
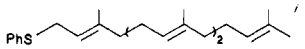
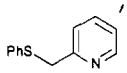
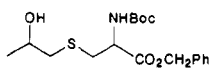
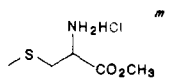
(5) For some inexplicable reason, use of tetra-*n*-butylammonium bisulfate from Aldrich gave a far less potent TBA-OX than use of the ammonium salt obtained from Kodak.

(6) Also see: Girard, Y.; Larue, M.; Jones, T. R.; Rokach, J. *Tetrahedron Lett.* **1982**, *23*, 1023.

(7) McKillop, A.; Tarbin, J. A. *Tetrahedron Lett.* **1983**, *24*, 1505.

(8) Still, W. C.; Kahn, M. N. I.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

Table II. Experimental Details of Oxidation

sulfide		TBA-OX			solvent,	Na_2CO_3		time,		yield	
mg	mmol	g	mmol	method	mL	g	mmol	days	purification	mg	%
$PhSCH_3$											
23.7	0.19	0.635	0.57	A	0.75			4	flash, CH_2Cl_2	23.1	78[a]
											
95.0	0.50	1.42	1.50	A	3.3			1.9	flash, CH_2Cl_2	87.2	79[b]
											
84.5	0.51	1.43	1.51	A	3.3			1.1	flash, CH_2Cl_2	84.1	83.4[c]
											
103.5	0.58	1.65	1.74	A	3.9			0.9	flash, CH_2Cl_2	98.7	81[e]
											
151.7	0.57	1.63	1.72	A	3.8			2	flash, CH_2Cl_2	138	81
138.5	0.52	1.67	1.57	B	3.5	0.166	1.57	1	PLC, CH_2Cl_2	122	78
											
248.1	0.98	2.80	2.95	A	6.5			1.5	flash, 6:4 Et_2O/hexane	201.6	71
86.0	0.34	1.09	1.02	B	2.3	0.108	1.02	2	*h*	82.1	85
											
102.6	0.45	1.45	1.36	A	3.0			0.875	PLC, CH_2Cl_2	88.4	76[g]
											
91.5	0.38	1.21	1.14	B	2.5	0.12	1.1	0.917	*h*	86.5	72
											
81.3	0.34	1.08	1.02	B	2.25	0.108	1.02	1.25	*h*	76.9	84
											
86.3	0.23	0.64	0.68	A	1.5			1	flash, CH_2Cl_2	45.5	49
35.0	0.09	0.29	0.27	B	0.6	0.029	0.27	4	PLC, CH_2Cl_2	15.7	54
											
81.6	0.41	1.30	1.22	A[j]	2.7			1	PLC, ether	71.5	76[k]
											
59.3	0.16	0.52	0.48	A	1.1			2.67	PLC,[l] 6:4 ethyl acetate/hexane	37.6	58
											
103.9	0.42	1.33	1.36	A	2.8			0.92	flash, 88% ethyl acetate/10% CH_3OH/2% $(C_2H_5)_3N$	26.5	33[n]

[a] Mp 85–87 °C (lit.[18] mp 86–87 °C). [b] Reference 19. [c] Mp 53–55 °C (lit.[20] mp 55–58 °C). [d] Reference 10. [e] Reference 21. [f] Cf. ref 9. [g] Mp 110.0–111.5 °C (lit.[22] mp 114–115 °C). [h] Product isolated pure upon evaporation after aqueous workup. [i] Reference 12. [j] In this case, the workup of method B was followed. [k] Mp 111–112 °C. [l] In this case, the solvent of the reaction mixture was evaporated in a stream of nitrogen and the residue triturated with ethyl acetate. The organic solution was evaporated and purified by PLC. [m] The hydrochloride salt was first dissolved in 0.7 mL of saturated aqueous sodium bicarbonate and extracted with ethyl acetate. After drying and evaporation, the α-amino ester was used directly. See ref 23. [n] Reference 13.

Experimental Section

Preparation of Sulfides. a. 4-Pentenyl Phenyl Sulfide. Following the procedure of Ono,[9] 5-bromo-1-pentene (1.5187 g, 10.2 mmol) was mixed with thiophenol (1.05 mL, 10.2 mmol) and DBU (1.52 mL, 10.2 mmol) in 30 mL of anhydrous benzene with stirring at room temperature under nitrogen. A white precipitate formed immediately (DBU·HBr). After 3.75 h, TLC showed one spot. The solid was removed by filtration and washed with dichloromethane. The methylene chloride solution was backwashed with dilute aqueous sodium chloride solution (emulsion problems). The benzene filtrate was combined with the dichloromethane phase and dried ($MgSO_4$), and the solvents were removed in vacuo to yield a clear oil (1.5637 g, 86.1% yield). The IR and ^1H NMR spectra agree with that reported in the literature.[10] TLC: 7:3 hexane–ether, UV, R_f 0.68.

b. 1-(Trimethylsilyl)-6-(phenylthio)-1-hexene. Following the above procedure, 6-bromo-1-(trimethylsilyl)-1-hexene (1.3603 g, 5.78 mmol), thiophenol (1.6 mL, 5.8 mmol), and DBU (0.86 mL, 5.8 mmol) in 17 mL of anhydrous benzene with a reaction time of 24 h gave 1.48 g (96% yield) of the titled product after Kugelrohr distillation (65–90 °C at 0.008 mm). NMR analysis revealed partial (to 3:1 *Z*:*E* from >95% *Z*) isomerization of the double bond during distillation. TLC: 7:3 hexane/methylene chloride, UV, R_f 0.72. IR ($CDCl_3$): 1605, 1580 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.2 (m, 5 H), 6.22 (dt, J = 14.0 Hz, 7.2 Hz,

(9) Ono, N.; Miyake, H.; Saito, T.; Kaji, A. *Synthesis* **1980**, 952.

(10) Alexakis, A.; Cahiez, G.; Normant, J. F. *J. Organomet. Chem.* **1979**, *177*, 293.

0.75 H), 5.94 (dt, J = 18.5 Hz, 6.1 Hz, 0.25 H), 5.57 (d, J = 18.5 Hz, 0.25 H), 5.44 (d, J = 14.0 Hz, 0.75 H), 2.87 (m, 2 H), 2.05 (m, 2 H), 1.2–1.6 (m, 4 H), 0.05 (s, 6.75 H), –0.02 (s, 2.25 H). ^{13}C NMR (15 MHz, $CDCl_3$): δ 148.2, 146.3, 141.5, 130.2, 129.0, 128.6, 125.6, 36.2, 33.8, 33.1, 29.0, 28.0, 23.9, 16.8, 0.4, –1.0, –1.5.

c. 1-(Phenylthio)-3-[(tetrahydropyranyl)oxy]propane. Following the above procedure, 1-bromo-3-[(tetrahydropyranyl)oxy]propane (1.53 g, 6.86 mmol), thiophenol (0.705 mL, 6.86 mmol), and DBU (1.03 mL, 6.86 mmol) in 21 mL of anhydrous benzene with a reaction time of 4 h gave 1.59 g (92% yield) of the titled product after Kugelrohr distillation (65–90 °C at 0.006 mm). TLC: CH_2Cl_2, UV, R_f 0.41. IR ($CDCl_3$): 1585 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.3 (m, 5 H), 4.57 (m, 1 H), 3.83 (m, 2 H), 3.51 (m, 2 H), 3.04 (t, J = 7.4 Hz, 2 H), 1.95–1.45 (m, 8 H). ^{13}C NMR (15 MHz, $CDCl_3$): δ 136.3, 128.7, 128.5, 125.4, 98.6, 65.5, 62.0, 30.7, 30.4, 29.5, 25.5, 19.5. MS: calcd for $C_{14}H_{20}O_2S$ 252.1184, found 252.1182.

d. 4,4-Dimethoxy-1-(phenylthio)pentane. Following the above procedure, 1-bromo-4,4-dimethoxypentane (1.41 g, 6.66 mmol), thiophenol (0.68 mL, 6.66 mmol), and DBU (1.00 mL, 6.66 mmol) in 20 mL of anhydrous benzene with a reaction time of 4 h gave 1.44 g (90% yield) of the titled compound. TLC: CH_2Cl_2, UV, R_f 0.39. IR ($CDCl_3$): 1585 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.3 (m, 5 H), 3.14 (s, 6 H), 2.92 (t, J = 6.8 Hz, 2 H), 1.72 (m, 4 H), 1.23 (s, 3 H). ^{13}C NMR (15 MHz, $CDCl_3$): δ 136.4, 130.3, 126.9, 123.9, 101.1, 47.9, 35.5, 33.8, 24.0, 20.9. MS: calcd for $C_{13}H_{20}O_2S$ 240.1184, found 240.1179.

e. 5,5-Dimethoxy-1-(phenylthio)pentane. Following the above procedure, 1-bromo-5,5-dimethoxypentane (380 mg, 1.8 mmol), thiophenol (0.20 mL, 2.0 mmol), and DBU (0.27 mL, 1.8 mmol) in 5.3 mL of anhydrous benzene with a reaction time of 23 h gave 412 mg (95% yield) of the titled compound after Kugelrohr distillation at 210–230 °C at 0.5 mm. TLC: CH_2Cl_2, UV, R_f 0.47. IR ($CDCl_3$): 1580 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.21 (m, 5 H), 4.25 (t, J = 5.38 Hz, 1 H), 3.21 (s, 6 H), 2.82 (t, J = 7.14 Hz, 2 H), 1.66–1.29 (m, 6 H). ^{13}C NMR (125 MHz, CDCl): δ 136.5, 136.5, 128.5, 128.4, 125.3, 104.0, 52.3, 33.1, 31.7, 28.7, 23.5. MS: calcd for $C_{13}H_{20}O_2S$ 240.1184, found 240.1178.

f. 2-[(Phenylthio)methyl]pyridine. Following the above procedure, 2-picolyl chloride hydrochloride (576 mg, 3.51 mmol), thiophenol (0.36 mL, 3.5 mmol), and DBU (1.05 mL, 7.02 mmol) in 10.3 mL of anhydrous benzene with a reaction time of 24 h gave 674 mg (95% yield) of light brown oil. The hydrochloride was prepared by dissolving the sulfide in ethanolic hydrogen chloride, partioning between ether and water, and removing the water in vacuo to give an off-white solid, mp 135–137 °C (lit.[11] mp 133–135 °C). TLC: ether, UV, R_f 0.82. IR ($CDCl_3$): 1587 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.54 (m, 1 H), 7.58 (m, 1 H), 7.25 (m, 7 H), 4.26 (s, 2 H).

Preparation of *all-E*-Geranylgeranyl Phenyl Sulfide. Following a modified procedure of Castro and Selve,[12] *all-E*-geranylgeraniol (0.8925 g, 3.07 mmol) was dissolved in THF (8 mL) and carbon tetrachloride (0.77 mL, 8.45 mmol, distilled over CaH_2). After cooling to –78 °C, hexamethylphosphorous triamide (0.56 mL, 3.07 mmol) was added under nitrogen and the resultant mixture stirred for 1 h. Predistilled thiophenol (0.32 mL, 3.07 mmol) was added to triethylamine (0.47 mL, 3.38 mmol, distilled over CaH_2) and the mixture was diluted with THF (1 mL), cooled to –78 °C, and cannulated into the geranylgeraniol mixture. A yellow color appeared immediately which faded as the cannulation proceeded. After 20 min, the cooling bath was removed and stirring of the pale yellow suspension was continued for 5 h. Diethyl ether (25 mL) was added, the white precipitate was filtered, and the filtrate was washed with 10% sodium hydroxide (4 × 10 mL), water (1 × 10 mL), and saturated sodium chloride (1 × 5 mL) and dried over magnesium sulfate. The solvent was removed in vacuo to yield a yellow oil (1.2943 g). Purification on a Chromatotron (hexane/ether gradient) yielded a clear oil (0.7393 g, 62.9%) which contained a single aromatic impurity by ^{1}H NMR. TLC: hexane, UV, R_f 0.20. IR ($CDCl_3$): 1660, 1580 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.2 (m, 5 H), 5.24 (t, 1 H, J = 7.4 Hz), 5.03 (m, 3 H), 3.48 (d, 2 H, J = 7.4 Hz), 1.96 (m, 12 H), 1.61 (s, 3 H), 1.42 (m, 12 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.76, 135.21, 134.82, 129.86, 128.64, 128.59, 125.91, 124.38, 124.20, 123.77, 119.28, 39.71, 39.66, 39.57, 32.23, 26.79, 26.65, 26.40, 25.65, 17.65, 16.02, 16.00, 15.99. MS: calcd for $C_{26}H_{38}S$ 382.2694, found 382.2695.

Preparation of Other Sulfides. L-Methionine was esterified in 86% yield according to Rachele to its methyl ester, mp 150.5–151.5 °C, $[\alpha]_D$ +25.3° (c 1.0, H_2O) [lit.[13] mp 147–150 °C, $[\alpha]_D$ +26.8° (c 1.0, H_2O)]. Cystine was converted to its bis-t-boc derivative in 59% yield according to Moroder et al.,[14] mp 144–145 °C, $[\alpha]_D$ –134.4° (c 2.5, CH_3OH) [lit.[15] mp 145–146 °C, $[\alpha]_D$ –138° (c 2.5, CH_3OH)]. *N,N'*-Bis[(*tert*-butyloxy)carbonyl]cystine was converted to its dibenzyl ester as follows.[16] *N,N'*-Bis[(*tert*-butyloxy)carbonyl]cystine was dissolved in 1.8 mL of saturated sodium bicarbonate solution. A mixture of benzyltriethylammonium chloride (0.41 g, 1.8 mmol) and benzyl bromide (0.26 mL, 2.16 mmol) in 1.8 mL of dichloromethane was added and the resulting mixture was stirred vigorously at room temperature for 6 days. The mixture was diluted with water, washed with dichloromethane (2 × 10 mL), washed with saturated sodium chloride (5 mL), and dried over magnesium sulfate. The solvent was removed in vacuo to yield 0.4974 g of a yellow-white solid. Purification on a Chromatotron (4-mm plate, hexane/ether gradient elutant) yielded 226.8 mg of white solid (40.6% yield), mp 99.0–101.5 °C. TLC: 1:1 hexane/ether, UV, R_f 0.45. IR ($CDCl_3$): 3420, 1737, 1708, 1493 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.35 (s, 5 H), 5.39 (m, 1 H), 5.17 (s, 2 H), 4.61 (m, 1 H), 3.12 (m, 2 H), 1.43 (s, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.4, 154.9, 134.9, 128.4, 128.3, 128.2, 80.0, 67.3, 52.9, 41.0, 28.2. MS: m/e (relative intensity) 255 (4.8), 137 (9.0), 92 (13.7), 91 (100). M^+ not observed, but disulfide cleavage and McLafferty fragment on *t*-Boc group observed: $C_{11}H_{13}NO_4S$ calcd 255.0565, found 255.0522. $[\alpha]_D$ +45.2° (c 0.68, $CHCl_3$).

Cleavage of the protected cystine to its corresponding cysteine derivative followed a modified procedure of Humphrey.[17] *N,N'*-Bis[(*tert*-butyloxy)carbonyl]cystine dibenzyl ester (328.5 mg, 0.53 mmol), triphenylphosphine (146.0 mg, 0.56 mmol), and sodium acetate (17.2 mg. 0.2 mmol) were suspended in 2 mL of methanol, 1 mL of water, and 17 μL of glacial acetic acid and heated to reflux with stirring for 24 h. The mixture was diluted with 30 mL of dichloromethane, washed with 10 mL of water, back-washed with 5 mL of dichloromethane, washed with 5 mL of saturated sodium chloride solution, back-washed with 5 mL of dichloromethane, and dried over magnesium sulfate and the solvent removed in vacuo to yield 494.1 mg of clear oil. The triphenylphosphine oxide impurity was removed on a Chromatotron (2-mm plate, hexane/ether gradient) to yield 263.8 mg of white solid (80.1% yield), mp 58–60 °C, $[\alpha]_D$ 2.27° (c 1.3, $CHCl_3$). TLC: 1:1 hexane/ether, UV, R_f 0.72. IR ($CDCl_3$): 3415, 1732, 1713, 1491 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.36 (s, 5 H), 5.47 (m, 1 H), 5.24 (AB, J = 12.2 Hz, 1 H), 5.16 (AB, J = 12.2 Hz, 1 H), 4.64 (m, 1 H), 2.97 (m, 2 H), 1.44 (s, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.2, 155.1, 135.1, 128.7, 128.6, 128.4, 80.3, 67.5, 54.8, 28.3, 27.4. MS: calcd for $C_{15}H_{21}NO_4S$ 311.1191, found 311.1178.

For the coupling with propylene oxide, the above-protected cysteine (69.2 mg, 0.22 mmol) was dissolved in 0.45 mL of chloroform. Propylene oxide (50 μL, 0.67 mmol) and triethylamine (31 μL, 0.22 mmol) were added with stirring at room temperature. After 5.5 h and 17 h, additional 50-μL portions of propylene oxide were added. After 18-h total reaction time, the volatiles were removed under a stream of nitrogen. Purification on a Chro-

(11) Haviv, F.; DeNet, R. W.; Michaels, R. J.; Ratajczyk, J. D.; Carter, G. W.; Young, P. R. *J. Med. Chem.* **1983**, *26*, 218.
(12) Cf. Castro, B.; Selve, C. *Bull. Soc. Chim. Fr.* **1971**, *6*, 2296.
(13) Rachele, J. R. *J. Org. Chem.* **1963**, *28*, 2898.
(14) Moroder, L.; Hallett, A.; Wuensch, E.; Keller, O.; Wersin, G. *Hoppe-Seyler's Z. Physiol. Chem.* **1976**, *357*, 1651.
(15) Photaki, I. *J. Am. Chem. Soc.* **1966**, *88*, 2292.
(16) Bocchi, V.; Casnati, G.; Dossena, A.; Marchelli, R. *Synthesis* **1979**, 957.
(17) Humphrey, R. E.; McCrary, A. L.; Webb, R. M. *Talanta* **1965**, *12*, 727.
(18) Otto, R. *Chem. Ber.* **1885**, *18*, 154.
(19) Liu, L. K.; Chi, Y.; Jen, K.-Y. *J. Org. Chem.* **1980**, *45*, 406.
(20) Beck, G.; Gunther, D. *Chem. Ber.* **1973**, *106*, 2758.
(21) Stetter, H.; Lehmann, K.-A. *Liebigs Ann. Chem.* **1973**, *3*, 499.
(22) Baliah, V.; Shanmuganathan, S. *J. Ind. Chem. Soc.* **1958**, *35*, 31.
(23) Eberle, A.; Chang, Y.; Schwyzer, R. *Helv. Chim. Acta* **1978**, *61*, 2360.

matotron (1-mm plate, hexane/ether gradient) yielded 57.1 mg (69.5%) of a clear oil. TLC: 1:1 hexane/ether, UV, R_f 0.11. IR ($CDCl_3$): 3415, 1732, 1700, 1490 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): (6:4 mixture of diastereomers) δ 7.32 (s, 5 H), 5.28 (m, 1 H), 5.13 (m, 2 H), 4.55 (m, 1 H), 3.78 (m, 1 H), 2.93 (m, 2 H), 2.75 (m, 1 H), 2.66 (dd, J = 13.7, 7.5 Hz, 0.6 H), 2.64 (dd, J = 13.6, 7.6 Hz, 0.4 H), 2.41 (dd, J = 13.7, 8.2 Hz, 0.6 H), 2.40 (dd, J = 13.6, 8.5 Hz, 0.4 H), 1.40 (s, 9 H), 1.16 (d, J = 6.2 Hz, 1.8 H), 1.15 (d, J = 6.2 Hz, 1.2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.7, 155.1, 135.0, 128.5, 128.4, 128.3, 80.2, 67.4, 66.0 (65.9), 53.7, (42.4) 42.2, (35.4) 35.0, 28.2, 22.0. MS: m/e (relative intensity) 370 (1.6), 214 (11.1), 269 (6.0), 234 (19.7), 208 (65.8), 91 (100); M + 1 calcd for $C_{18}H_{28}NO_5S$ 370.1688, found 370.1689.

Preparation of Tetrabutylammonium Oxone. To a solution of Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, 10.86 g, 18 mmol) in 45 mL of water was added tetrabutylammonium bisulfate (30.0 g, 88 mmol) obtained from Kodak Laboratory and Research Products. After being stirred at room temperature for 0.5 h, the reaction mixture was extracted with dichloromethane (3 × 70 mL), the combined organic phase was dried over magnesium sulfate, and the solvent was removed in vacuo, yielding a white solid (25.64 g). The solid was titrated three times following this representative procedure: to a 0.1859-g sample was added 0.5 mL of glacial acetic acid and 1 mL of 10% aqueous NaI. After dilution to 5 mL of THF, it was titrated with 3.30 mL of a 0.1012 M solution of sodium sulfite to the yellow endpoint. The average of the three trials gave 37.5 ± 0.6% by weight of active oxidizing agent, Bu_4NHSO_5. IR ($CDCl_3$): 3300–3800, 1470, 1380 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 3.2 (br t, 2 H), 1.5 (br s, 2 H), 1.3 (q, 2 H), 0.85 (t, 3 H). ^{13}C NMR (15 MHz, $CDCl_3$): δ 57.7, 23.4, 29.2, 13.3. (**CAUTION**: TBA-OX should be considered a hazardous (potentially explosive) substance. However, we have not experienced any difficulties in handling it and have not seen any indication that it is explosive. Hitting a small sample with a hammer failed to detonate it.)

General Oxidation Procedure. Method A. To an approximately 0.2–0.3 M solution of 1 equiv of the sulfide in methylene chloride is added 3 equiv of TBA-OX. Stirring at room temperature continued until TLC indicated completion of reaction. The very viscous reaction mixture was directly applied to the top of a flash chromatography column and the product eluted with methylene chloride. Evaporation of the solvent gave the pure product.

Method B. Anhydrous sodium carbonate (3 equiv) was suspended in a 0.2–0.3 M methylene chloride solution of 1 equiv of the sulfide, and 3 equiv of TBA-OX was added. After being stirred at room temperature until TLC indicated completion, the reaction mixture was diluted with ether, washed with 2 N aqueous sodium hydroxide, water, and brine, and dried ($MgSO_4$). The solvent was removed in vacuo and the crude product purified chromatographically.

Sulfone Data. a. 5-(Phenylsulfonyl)-1-pentene. TLC: CH_2Cl_2, UV, R_f 0.43. IR ($CDCl_3$): 3060, 1640, 1585, 1445, 1310, 1140, 1085, 990, 790 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.85 (m, 2 H), 7.50 (m, 3 H), 5.60 (m, 1 H, irr. 4.9, br t, J = 6.4 Hz, irr. 2.0, dd, J = 17.7, 9.7 Hz), 4.90 (m, 2 H, irr. 5.6, d, J = 3.3 Hz), 3.00 (m, 2 H, irr. 1.7, s), 2.04 (m, 2 H, irr. 5.6, br t, J = 6.9 Hz, irr. 1.7, br d, J = 6.7 Hz), 1.73 (m, 2 H, irr. 3.0, t, J = 7.1 Hz). ^{13}C NMR (15 MHz, $CDCl_3$): δ 114.3, 112.4, 110.8, 108.2, 107.4, 100.4, 64.0, 49.9, 43.9 ppm. Anal. Calcd for $C_{11}H_{14}O_2S$: C, 62.83; H, 6.71. Found: C, 62.77; H, 6.74.

b. 1-(Trimethylsilyl)-6-(phenylsulfonyl)-(*E*)-1-hexene. TLC: CH_2Cl_2, R_f 0.46. IR ($CDCl_3$): 1615, 1445 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.85 (m, 2 H), 7.50 (m, 3 H), 6.85 (m, 1 H), 6.55 (br d, J = 18.3 Hz, 1 H), 3.00 (m, 2 H), 2.00 (br q, 2 H), 1.65 (m, 2 H), 1.3 (m, 4 H), –0.10 (s, 9 H). ^{13}C NMR (15 MHz, $CDCl_3$): δ 145.1, 139.1, 133.2, 130.8, 128.9, 127.7, 56.1, 35.8, 27.3, 22.2, 1.1 ppm. Anal. Calcd for $C_{15}H_{24}O_2SSi$: C, 60.76; H, 8.16. Found: C, 60.87; H, 8.32.

c. 1-(Phenylsulfonyl)-3-[(tetrahydropyranyl)oxy]propane. TLC: 1:1 hexane/ether, R_f 0.23. IR ($CDCl_3$): 1580, 1440, 1300, 1140, 1070, 1025, 980, 810 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.90 (m, 2 H), 7.60 (m, 3 H), 4.55 (br s, 1 H), 3.74 (m, 2 H), 3.46 (m, 2 H), 3.23 (m, 2 H), 2.01 (m, 2 H), 1.70 (br m, 2 H), 1.55 (m, 4 H). ^{13}C NMR (15 MHz, $CDCl_3$): δ 138.7, 135.2, 130.2, 126.4, 98.6, 64.8, 62.3, 53.4, 30.4, 25.2, 23.4, 19.4. Anal. Calcd for $C_{14}H_{20}O_4S$: C, 59.13; H, 7.09. Found: C, 58.47; H, 6.98.

d. 4,4-Dimethoxy-1-(phenylsulfonyl)pentane. TLC: 4:1 ether/hexane, UV, R_f 0.61. IR ($CDCl_3$): 3055, 2940, 1443, 1300, 1193, 1143, 1081, 1044 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.85–7.92 (m, 2 H), 7.67–7.50 (m, 3 H), 3.15–3.05 (m, 2 H), 3.09 (s, 6 H), 1.82–1.57 (m, 4 H), 1.19 (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.0, 133.5, 129.1, 127.8, 100.8, 56.0, 47.9, 34.9, 20.7, 17.8. MS: m/e (relative intensity) 257 (M – Me, 2.5), 241 (M – OMe, 13.2), 89 (100).

e. 5,5-Dimethoxy-1-(phenylsulfonyl)pentane. TLC: CH_2Cl_2, UV, R_f 0.29. IR ($CDCl_3$): 3050, 2938, 1440, 1300, 1190, 1140, 1080 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.90 (m, 2 H), 7.64 (m, 3 H), 4.30 (t, J = 5.36 Hz, 1 H), 3.28 (s, 6 H), 3.09 (m, 2 H), 1.75 (m, 2 H), 1.57 (m, 2 H), 1.43 (m, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.0, 133.5, 129.2, 127.9, 104.0, 56.1, 52.8, 31.9, 23.2, 22.5. MS: calcd for $C_{13}H_{20}O_4S$ 272.1082, found 272.1092.

f. Geranylgeranyl Phenyl Sulfone. TLC: CH_2Cl_2, UV, R_f 0.62. IR ($CDCl_3$): 3045, 2910, 1660, 1442, 1300, 1145, 1080 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.85 (m, 2 H), 7.57 (m, 3 H), 5.17 (m, 1 H), 5.07 (m 3 H), 3.78 (d, J = 7.95 Hz, 2 H), 1.97 (m, 2 H), 1.65 (s, 3 H), 1.57 (s, 9 H), 1.28 (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.3, 138.7, 135.7, 134.9, 133.4, 131.1, 128.9, 128.5, 124.3, 124.0, 123.3, 110.3, 56.1, 39.9, 39.7, 39.6, 26.7, 26.6, 26.2, 25.7, 25.6, 17.7, 16.2, 16.0. MS: calcd for $C_{26}H_{38}O_2S$ 414.2592, found 414.2603.

g. 2-[(Phenylsulfonyl)methyl]pyridine. TLC: Et_2O, UV, R_f 0.43. IR ($CDCl_3$): 3050, 1584, 1431, 1312, 1301, 1145, 1080 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 8.41 (m, 1 H), 7.67 (m, 4 H), 7.46 (m, 3 H), 7.25 (m, 1 H), 4.58 (s, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.5, 148.9, 138.4, 136.5, 133.6, 128.8, 128.3, 125.5, 123.2, 64.6. MS: calcd for $C_{12}H_{12}NO_2S$ 234.0589, found 234.0590.

h. Methyl Methionine *S*,*S*-Dioxide. TLC: ethyl acetate + 10% methanol + 2% triethylamine, Ninhydrin, R_f 0.28. IR ($CDCl_3$): 3380, 1734, 1300, 1135 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 3.73 (s, 3 H), 3.58 (m, 1 H), 3.20 (m, 2 H), 2.91 (s, 3 H), 2.30 (m, 1 H), 2.05 (m, 1 H) (NH_2 very broad: observable only by integration at about 2.0–1.5.). ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.8, 52.7, 52.4, 51.3, 40.8, 27.1. MS: m/e (relative intensity) 196 (1.4), 136 (96.0), 88 (100); M + 1 calcd for $C_6H_{14}NO_4S$ 196.0644, found 196.0653.

i. Benzyl *N*-[(*tert*-Butyloxy)carbonyl]-*S*-(2-hydroxypropyl)cysteine *S*,*S*-Dioxide. TLC: 6:4 ethyl acetate/hexane, UV, R_f 0.34. IR ($CDCl_3$): 3530, 3400, 3030, 1741, 1727, 1495, 1305, 1160, 1043 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): (4:6 mixture of diastereomers) δ 7.34 (s, 5 H), 5.70 (m, 1 H), 5.18 (s, 2 H), 4.68 (m, 1 H), 4.37 (m, 1 H), 3.77 (m, 2 H), 3.16 (m, 1 H), 3.00 (m, 2 H), 1.40 (s, 9 H), 1.26 (s, 1.2 H), 1.23 (s, 1.8 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.3, 155.1, 134.7, 128.6, 128.5, 128.4, 80.9, 68.2 (68.1), 62.6, 62.3, 55.3, 50.0, 28.2, 23.0. MS: m/e (relative intensity) 402 (0.12), 346 (3.3), 302 (2.6), 91 (100); M + 1 calcd for $C_{18}H_{28}NO_7S$ 402.1586, found 402.1582.

Preparation of 3-(Phenylsulfonyl)-1-propanol. Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, 0.89 g, 2.90 mmol of $KHSO_5$) in H_2O (4 mL) was added to 3-[(tetrahydropyranyl)oxy]-1-(phenylthio)propane (0.2442 g, 0.97 mmol) in methanol (4 mL) at 0 °C with stirring. A white precipitate formed immediately. The reaction mixture was allowed to warm to room temperature and was stirred for 24 h. TLC after 20 min, 1 h, 6 h, and 24 h showed only baseline spots. Solvent was reduced in vacuo, the mixture was extracted with chloroform (3 × 10 mL), the organic phase was washed with water (5 mL) and saturated sodium chloride (5 mL) and dried over magnesium sulfate, and solvent was removed in vacuo, yielding 0.1901 g (97.9% yield) of clear oil, identical with the literature compound.[24]

Acknowledgment. We thank the National Institutes of Health, General Medical Sciences Institute, for their generous support of our programs.

Registry No. $PhSCH_3$, 100-68-5; $PhSC{=}CHCH_2CH_2CH_2CH_2$, 4922-47-8; $PhSCH_2C(O)CH_3$, 5042-53-5; $PhSCH_2CH_2CH_2CH{=}CH_2$, 4285-51-2; (*E*)-$PhSCH_2CH_2CH_2CH_2CH{=}CHTMS$, 111086-97-6; (*Z*)-$PhSCH_2CH_2CH_2CH_2CH{=}CHTMS$, 111086-98-7; $PhSCH_2CH_2CH_2OTHP$, 111086-99-8; $PhSCH_2CH{=}CHPh$,

(24) Searles, S. *J. Am. Chem. Soc.* **1951**, *73*, 4515.

10276-14-9; $PhSCH_2CH_2CH_2C(OCH_3)_2CH_3$, 111087-00-4; $PhSCH_2CH_2CH_2CH(OCH_3)_2$, 111087-01-5; *all-E*-$PhSCH_2CH{=}C(CH_3)CH_2CH_2CH{=}C(CH_3)CH_2CH_2CH{=}C(CH_3)CH_2CH_2CH{=}C(CH_3)_2$, 57804-27-0; $PhSCH_2\overline{C{=}CHCH{=}CHCH{=}N}$, 71897-63-7; L-(*R*)-$CH_3CH(OH)CH_2SCH_2CH(NHBoc)CO_2CH_2Ph$, 111087-02-6; L-(*S*)-$CH_3CH(OH)CH_2SCH_2CH(NHBoc)CO_2CH_2Ph$, 111087-03-7; $CH_3SCH_2CH_2CH(NH_2)CO_2CH_3$, 10332-17-9; $PhSO_2CH_3$, 3112-85-4; $PhSO_2\overline{C{=}CHCH_2CH_2CH_2CH_2}$, 59059-70-0; $PhSO_2CH_2C(O)CH_3$, 5000-44-2; $PhSO_2CH_2CH_2CH_2CH{=}CH_2$, 41795-36-2; (*E*)-$PhSO_2CH_2CH_2CH_2CH_2CH{=}CHTMS$, 111087-04-8; (*Z*)-$PhSO_2CH_2CH_2CH_2CH_2CH{=}CHTMS$, 111087-05-9; $PhSO_2CH_2CH_2CH_2OTHP$, 95791-15-4; $PhSO_2CH_2CH{=}CHPh$, 20605-46-3; $PhSO_2CH_2CH_2CH_2C(OCH_3)_2CH_3$, 111087-06-0; $PhSO_2CH_2CH_2CH_2CH_2CH(OCH_3)_2$, 111087-07-1; *all-E*-$PhSO_2CH_2CH{=}C(CH_3)CH_2CH_2CH{=}C(CH_3)CH_2CH_2CH{=}C(CH_3)CH_2CH_2CH{=}C(CH_3)_2$, 38818-91-6; $PhSO_2CH_2\overline{C{=}CHCH{=}CHCH{=}\#}$, 1620-50-4; L-(*R*)-$CH_3CH(OH)CH_2SO_2CH_2CH(NHBoc)CO_2CH_2Ph$, 111087-08-2; L-(*S*)-$CH_3CH(OH)CH_2SO_2CH_2CH(NHBoc)CO_2CH_2Ph$, 111087-09-3; $CH_3SO_2CH_2CH_2CH(NH_2)CO_2CH_3$, 111087-10-6; TBA-OX, 104548-30-3; 5-bromo-1-pentene, 1119-51-3; thiophenol, 108-98-5; 6-bromo-1-(trimethylsilyl)-1-hexene, 111087-11-7; 1-bromo-3-[(tetrahydropyranyl)oxy]propane, 33821-94-2; 1-bromo-4,4-dimethoxypentane, 79539-10-9; 1-bromo-5,5-dimethoxypentane, 78643-42-2; 2-picolyl chloride, 6959-47-3; *all-E*-geranylgeraniol, 24034-73-9; *N,N'*-bis[*tert*-butoxycarbonyl]cystine, 10389-65-8; *N,N'*-bis[*tert*-butoxycarbonyl]cystine dibenzyl ester, 92278-77-8; *N*-[*tert*-butoxycarbonyl]cysteine benzyl ester, 92278-78-9; propylene oxide, 75-56-9; oxone, 37222-66-5; 3-(phenylsulfonyl)-1-propanol, 25062-90-2.

Supplementary Material Available: General introduction to Experimental Section (1 page). Ordering information is given on any current masthead page.

p-Chloranil and *p*-Fluoranil Complexes of Certain Mono- and Polyoxygenated Ethers and Ether Aromatic Donors

L. J. Andrews* and R. M. Keefer

Department of Chemistry, University of California, Davis, California 95616

Received July 13, 1987

From the results of a spectrophotometric study of the interactions of *p*-chloranil and *p*-fluoranil as acceptors in carbon tetrachloride with a variety of ether donors, most of which have more than one coordination site, equilibrium constants have been calculated on the assumption that the complexes formed are of the 1:1 type. Both polyoxygenated ethers and ethers that also have aromatic rings have been used. The relative strengths of the ethers as donors in complex formation with these π acceptors, particularly those of the nonaromatic ethers, are at variance with their relative strengths as donors as observed in a recent study of their interactions with iodine monochloride and iodine. The differences are explained on the grounds that halogen acceptors coordinate with only one oxygen of a polyoxygenated donor at a time, while in the coordination of a polyoxygenated donor molecule with a 1,4-tetrahalobenzoquinone molecule, two or more donor oxygen atoms may simultaneously be involved in interacting with the π-acceptor ring. With a few of the stronger donors, there was some positive indication of the formation of 2:1 as well as 1:1 donor–acceptor complexes. In most such cases it proved possible, by using a previously described method, to estimate equilibrium constants for formation of both types of complexes.

The results of a spectrophotometric study of iodine monochloride and iodine complexes of a variety of mono- and polyoxygenated ether donors, including some donors that are also aromatic in character, have been reported recently.[1] The primary objective of this previous investigation was to determine how changes in the number of possible acceptor coordination sites in the donor molecule affected both the equilibrium constants for complex formation (in carbon tetrachloride at 25.0 °C) and the spectra of the complexes.

When iodine or iodine monochloride forms a 1:1 complex with a polyoxygenated donor in solution, it is highly probable that the halogen molecule is associated at any particular instant with only one of the donor oxygen atoms. Crystallographic studies of the iodine and iodine monochloride complexes of dioxane, for example, indicate a linear arrangement, O–I–I or O–I–Cl, for the association of a donor oxygen atom and the halogen molecule. The complexed halogen molecule is directed away from the rest of the donor molecule.[2] Very likely this orientation of donor and acceptor molecules is also characteristic of the complexes in solution. Crystallographic studies have also been conducted to determine the structure of solid benzene–halogen complexes.[3] The results of these investigations and of an investigation of the infrared spectra of benzene–bromine complexes in solid form and in solution[4] indicate that in the solid 1:1 benzene–halogen complex, as well as in the complex in solution, the halogen lies perpendicular to the π-donor ring and on its sixfold symmetry axis.

In crystalline complexes of π acceptors with aromatic substances, such as chloranil–hexamethylbenzene[5] and tetracyanoethylene–naphthalene,[6] the donors and acceptors are stacked in parallel planes,[7] and presumably the

(1) Andrews, L. J.; Keefer, R. M. *J. Org. Chem.* **1987**, *52*, 2690.
(2) (a) Hassel, O.; *Proc. Chem. Soc., London* **1957**, 250. (b) Hassel, O. *Acta Chem. Scand.* **1954**, *8*, 873. (c) Hassel, O.; Hvsolef, J. *Acta Chem. Scand.* **1956**, *10*, 138.
(3) Hassel, O.; Strømme, K. O. *Acta Chem. Scand.* **1958**, *12*, 1146; **1959**, *13*, 1781.
(4) Person, W. R.; Cook, C. F.; Friedrich, H. B. *J. Chem. Phys.* **1967**, *46*, 2521.
(5) (a) Harding, T. T.; Wallwork, S. C., *Acta Crystallogr.* **1955**, *8*, 787. (b) Jones, N. D.; Marsh, R. E. *Acta Crystallogr.* **1962**, *15*, 809. (c) Wallwork, S. C.; Harding, T. T. *Acta Crystallogr.* **1962**, *15*, 810.
(6) For a general review of the structure of such complexes, see: Foster, R. *Organic Charge-Transfer Complexes*; Academic: London, 1974; pp 238–249.
(7) Williams, R. M.; Wallwork, S. C. *Acta Crystallogr.* **1967**, *22*, 899.

0022-3263/88/1953-0537$01.50/0