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10276-14-9; $PhSCH_2CH_2CH_2C(OCH_3)_2CH_3$, 111087-00-4; $PhSCH_2CH_2CH_2CH_2CH(OCH_3)_2$, 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.

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

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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

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Table I. Equilibrium Constants for Complexes of Ethers and Toluene with Tetrafluoro-*p*-benzoquinone and Tetrachloro-*p*-benzoquinone in Carbon Tetrachloride at 25.0 °C

donor	fluoranil complexes:[a] K_F, L mol^{-1}	chloranil, complexes:[a] L mol^{-1}	ICl complexes:[b] K_{ICl}, L mol^{-1}	I_2 complexes:[b] K_{I_2}, mol^{-1}
	Nonaromatic Donors			
diethyl ether	0.12 ± 0.02	very small		
di-*n*-butyl ether	0.12 ± 0.01	very small	13.3	0.44
1,4-dioxane	0.56 ± 0.05	0.25 ± 0.03	273	0.98
1,1-dimethoxyethane	0.62 ± 0.03	0.30 ± 0.02	15.3	0.63
1,3,5-trioxane	0.68 ± 0.07	very small	2.4	0.35
tetrahydrofuran	0.81 ± 0.02	0.40 ± 0.05	72.3	1.4
diethylene glycol dimethyl ether	1.34 ± 0.05	0.56 ± 0.01	44.5	1.18
1,2-dimethoxyethane	1.86 ± 0.01[c]	0.59 ± 0.03	29.	0.95
triethyl orthoformate	3.1 ± 0.2[c]	0.84 ± 0.02		0.66 ± 0.02[d]
trimethyl orthoformate	4.27 ± 0.24[c]	1.23 ± 0.08	11.5	0.50
18-crown-6	4.3 ± 0.07	1.28 ± 0.01	125.	2.8
12-crown-4	5.82 ± 0.41[c]	1.16 ± 0.11		2.3
15-crown-5	5.86 ± 0.33[c]	1.27 ± 0.05	106.	2.18
	Toluene and Aromatic Ether Donors			
toluene	0.56 ± 0.03[e]	0.41 ± 0.04[f]	0.83	0.18
diphenyl ether	0.45 ± 0.03	0.44 ± 0.03	0.92	0.30
anisole	0.73 ± 0.03	0.50 ± 0.03[f]	1.9	0.34
dibenzyl ether	0.91 ± 0.04	0.64 ± 0.01	7.6	0.48
benzyl methyl ether	1.55 ± 0.07	0.48 ± 0.02	11.0	0.51
1,4-dimethoxybenzene	1.36 ± 0.04	1.05 ± 0.05[f]	3.0	0.54
1,3-dimethoxybenzene	1.83 ± 0.07[c]	1.14 ± 0.07[f]		0.285
1,2-dimethoxybenzene	3.40 ± 0.07[c]	1.37 ± 0.11	5.9	0.61

[a] The values of K_F and K_{Ch} are averages of values obtained through measurement at several different wavelengths at which the absorption of the complexes is substantially greater than that of the uncomplexed acceptor. The values reported for complexes of the nonaromatic donor ethers are based on measurements in the 272–340-nm region; those for aromatic ethers in which oxygens are not bound directly to aromatic rings are based on measurements in the 320–420-nm region; those for ethers in which oxygens are directly bound to aromatic rings and also for toluene are based on measurements in the region of 340–600-nm. [b] Reference 1. [c] Based on slopes of Ketelaar plots of data obtained in the region of relatively low donor concentrations. At higher donor concentrations, the plots deviated from linearity. See Figure 4. [d] Based on measurements at 560, 540, and 520 nm, which were made during the course of the present investigation. [e] A K_F value for toluene of 0.56 L mol^{-1} (CCl_4, 33.3 °C) was reported previously; ref 10d. [f] Values of K_{Ch} for toluene, anisole, 1,3-, and 1,4-dimethoxybenzene (CCl_4, 25 °C) of 0.35, 1.0, 2.0, and 2.0 L mol^{-1}, respectively, have been reported previously. See: Fukuzumi, S.; Kochi, J. K. *J. Org. Chem.* **1981**, *46*, 4116.

coplanar arrangement is maintained in the complexes in solution.[8] While no information appears to exist concerning the orientation of donors and acceptors in complexes of ethers with π acceptors such as *p*-chloranil and *p*-fluoranil, it seems reasonable to assume that the ether oxygens lie above the plane of the acceptor ring. Conceivably, when the ether donors contain more than one oxygen, two or more of those oxygen atoms, in contrast to the ether oxygens in the halogen complexes, may be simultaneously associated with the acceptor in a 1:1 complex. If such is the case, the relative stabilities of iodine and iodine monochloride complexes with various ether donors may be significantly different from the stability orders for the complexes of those same ethers with *p*-chloranil and *p*-fluoranil.

With that possibility in mind a UV–vis spectrophotometric study of the tetrachloro- and tetrafluoro-1,4-benzoquinone complexes with much the same set of ethers used in studying the iodine and iodine monochloride complexes has now been conducted. Equilibrium constants for complex formation in carbon tetrachloride at 25.0 °C have been evaluated from the experimental data by the method of Ketelaar[9] on the assumption that the donor–acceptor ratios in the association products are 1:1. It appears that a few of the donors form measurable amounts of fluoranil complexes with 2:1 donor–acceptor ratios along with 1:1 complexes when the donor concentrations of the solutions of the components are relatively large.

Experimental Section

Materials. The sources of most of the donor ethers and carbon tetrachloride were the same as those reported in connection with the work on ether–halogen complexes.[1] Triethyl orthoformate was obtained from Kodak. Toluene (A.C.S. Certified Grade) was obtained from Fisher Scientific. Aldrich *p*-chloranil (2,3,5,6-tetrachloro-1,4-benzoquinone) was recrystallized from benzene and dried under vacuum over paraffin before use. Aldrich *p*-fluoranil (2,3,5,6-tetrafluoro-1,4-benzoquinone) was used without further purification.

Determination of Equilibrium Constants. With chloranil or fluoranil as the acceptor, solutions of varying concentrations of the donor and acceptor in carbon tetrachloride were prepared at 25.0 °C. In the measurements on the chloranil complexes, the acceptor concentrations were of the order of 1–2 × 10^{-3} M, and in the case of the fluoranil, complexes the acceptor concentrations were in the range of 1 × 10^{-4}–2 × 10^{-3} M. Where it was feasible to do so, as was usually the case, the donor concentrations of the solutions that were subject to spectrum measurements were varied over an approximately 10-fold range (0.25–2.6 M). For each complex investigated, measurements were made on solutions of at least five or six different donor concentrations. The spectrophotometric equipment that was used and the general method of determining the absorbances of these solutions at various wavelengths were the same as described previously.[1]

Results and Discussion

Equilibrium constants K_c for complex formation, as defined by eq 1, were determined by much the same procedure on the basis of eq 2, which was used in evaluating the equilibrium consxtants for ether–halogen interaction.[1]

$$K_c = [R_2O{\cdot}Ac]/[R_2O][Ac] \qquad (1)$$

$$1/(\epsilon_a - \epsilon_{Ac}) = [1/(\epsilon_c - \epsilon_{Ac})][1/K_c[D]] + 1/(\epsilon_c - \epsilon_{Ac}) \qquad (2)$$

In eq 1 and 2, the term Ac represents the acceptor (chlo-

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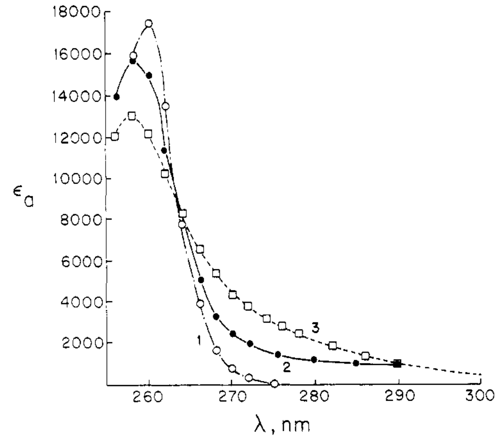

Figure 1. The spectrum of fluoranil in carbon tetrachloride solutions of various nonaromatic donors below 300 nm. Curve 1, fluoranil in CCl_4; curve 2, in 1.34 M diethylene glycol dimethyl ether; curve 3, in 1.33 M triethyl orthoformate.

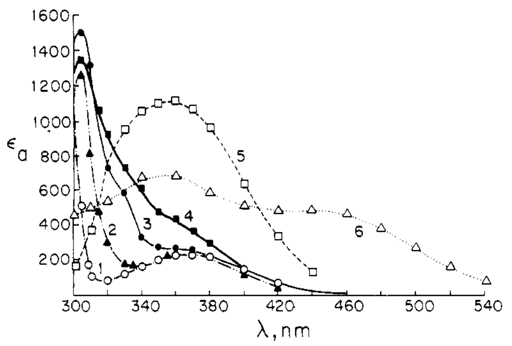

Figure 2. The spectrum of chloranil in carbon tetrachloride solutions of various donors. Curve 1, chloranil in CCl_4; curve 2, in 1.33 M 1,1-dimethoxyethane; curve 3, in 1.33 M 1,2-dimethoxyethane; curve 4, in 0.71 M 18-crown-6; curve 5, in 1.33 M dibenzyl ether; curve 6, in 1.33 M anisole.

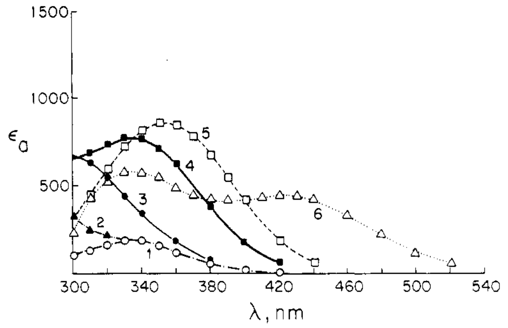

Figure 3. The spectrum of fluoranil in carbon tetrachloride solutions of various donors above 300 nm. Curve 1, fluoranil in CCl_4; curve 2, in 1.34 M 1,1-dimethoxyethane; curve 3, in 1.34 M tetrahydrofuran; curve 4, in 1.33 M benzyl methyl ether; curve 5, in 1.33 M toluene; curve 6, in 1.33 M anisole.

ranil or fluoranil). In eq 2, $\epsilon_a = A/l[\mathrm{Ac}]_t$ where A is the absorbance of the solution in question, l is the light path length in centimeters, and $[\mathrm{Ac}]_t$ is the total acceptor concentration in moles/liter (free and complexed); ϵ_{Ac} and ϵ_c are the absorptivities of free and complexed acceptor, respectively, and [D] is the molar concentration of the donor. The values of K_c, which are reported in Table I for the complexes that have been investigated, were calculated from the slopes and intercepts of the usually straight lines obtained by plotting $1/(\epsilon_a - \epsilon_{\mathrm{Ac}})$ values at a particular wavelength vs the corresponding $1/[\mathrm{D}]$ values. The K_c values for the fluoranil and chloranil complexes are listed in Table I as K_F and K_{Ch}, respectively.

Ideally, to avoid the complication of the formation of 2:1 complexes, D_2Ac, along with 1:1 complexes, the spectrophotometric measurements on which K_c values are based should be made under the condition that the donor and acceptor concentrations are closely similar.[10] Since the solubilities of both chloranil and fluoranil in carbon tetrachloride are very low, it has not been possible to carry out the equilibrium measurements at comparable concentrations of the ether donors and the acceptors and to obtain data useful for calculation of formation constants for the complexes. As observed by Person,[10a] the most accurate values for the formation constants are obtained when the donor concentration in the most concentrated solution is greater than 0.1 $(1/K_c)$. Under these conditions, as was the case in the current investigation, the possibility of obtaining 2:1(D_2Ac) as well as 1:1 complexes cannot be overlooked. While this seems an unlikely possibility when ICl, a significantly polar molecule, is used as the acceptor, there is evidence that it can become a problem with π-type acceptors such as chloranil and fluoranil.[10c,d] As noted in the introduction, evidence suggestive of the formation of some termolecular as well as 1:1 complexes was obtained with some of the strongest donors. As discussed in more detail later, this did not in general appear to be a major complication. The K_c values listed in Table I are considered to be representative of or similar to the equilibrium constants for 1:1 complex formation.

Nonaromatic Ethers as Donors. As shown in Figure 1, fluoranil in carbon tetrachloride has a rather intense absorption peak at about 260 nm, which is somewhat depressed when nonaromatic ether donors are also present in the solutions, the depression becoming generally increasingly apparent as the donor strength of the ether increases. At higher wavelengths, the absorbance drops off sharply but less so when ethers are present than in ether-free solutions. Equilibrium constants for fluoranil complexes were calculated from data recorded above 270 nm, a region in which fluoranil absorbs little or not at all. Solutions of chloranil containing nonaromatic ether donors have absorption peaks in the region of 305 nm, which are much less intense than those which appear at 260 nm when fluoranil is the donor (see curves 1–4 of Figure 2). As the wavelength is increased, the absorption intensities of the chloranil solutions that contain ethers drop off markedly but over a limited region remain significantly greater those that of ether-free chloranil solutions, moreso as the donors become stronger. Chloranil has a low intensity absorption peak in the 360–380-nm region, which is also apparent to varying degrees in the ether containing chloranil solutions. The spectra of fluoranil (low intensity absorption peak in the 330–340-nm region) and its complexes with nonaromatic ethers are similar in this regard (see curves 1, 2, and 3 of Figure 3). Except for the complexes of ethers listed in Table II, the plots of $1/(\epsilon_a - \epsilon_{\mathrm{Ac}})$ values against $1/[\mathrm{D}]$, from which K_F and K_{Ch} values were calculated, remained linear over a relatively wide range of donor concentrations.

With respect to formation of fluoranil and chloranil complexes, the nonaromatic ether donors ranked in strength roughly in the order diethyl and di-*n*-butyl ether $\ll$ 1,4-dioxane $\sim$ 1,1-dimethoxyethane $\sim$ 1,3,5-trioxane $<$ tetrahydrofuran $<$ diethylene glycol dimethyl ether $<$ 1,2-dimethoxyethane $<$ triethyl and trimethyl orthoformate $<$ 18-crown-6 $<$ 12-crown-4 $<$ 15-crown-5. The corresponding order[1] for iodine monochloride and iodine

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[10] See, for example: (a) Person, W. B. *J. Am. Chem. Soc.* **1965**, *87*, 167. (b) Deranleau, D. A. *J. Am. Chem. Soc.* **1969**, *91*, 4044 and 4050. (c) Dodson, B.; Foster, R.; Bright, A. A. S. *J. Chem. Soc. B* **1971**, 1283. (d) Bright, A. A. S.; Chudek, J. A.; Foster, R. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1256.

Table II. Equilibrium Constants for 1:1 (K_1) and 2:1 (K_2) Complexes of Ethers with Fluoranil, CCl_4, 25.0 °C[a]

ether	K_c, L mol^{-1}	K_1, L mol^{-1}	K_2, L mol^{-1}
15-crown-5	5.9 ± 0.3	7.1 ± 0.3	0.59 ± 0.03
12-crown-4	5.8 ± 0.4	6.9 ± 0.5	0.51 ± 0.07
trimethyl orthoformate	4.3 ± 0.2	4.8 ± 0.2	0.32 ± 0.03
1,2-dimethoxybenzene	3.4 ± 0.1	4.30 ± 0.03	0.49 ± 0.06
1,3-dimethoxybenzene	1.8 ± 0.1	2.4 ± 0.1	0.33 ± 0.03
1,2-dimethoxyethane	1.86 ± 0.01	2.5 ± 0.1	0.36 ± 0.03
benzyl methyl ether	1.6 ± 0.1	2.0 ± 0.1	0.18 ± 0.01

[a] Ketelaar plots of data recorded for 18-crown-6 ether and 1,4-dimethoxybenzene were linear over the donor concentrations used; in these cases, because of limited solubility of the donors, the measurements could not be extended to solutions of relatively high donor concentration. There was sufficient scatter of points in the Ketelaar plots of data recorded for triethyl orthoformate that attempts to obtain K_1 and K_2 values for its fluoranil complexes proved to be unsatisfactory.

complexes is trioxane ≪ trimethyl orthoformate ~ 1,1-dimethoxyethane ~ di-*n*-butyl ether < 1,4-dioxane ~ 1,2-dimethoxyethane < diethylene glycol dimethyl ether < tetrahydrofuran < 15-crown-5 < 12-crown-4 < 18-crown-6.

In contrast to what has been observed with respect to halogen complex formation, the polyoxygenated ethers in which more than one oxygen atom is bound to a single carbon atom (trioxane, trimethyl orthoformate, and 1,1-dimethoxyethane) are not markedly weaker donors in their interactions with chloranil and fluoranil than those ethers that lack such a structural feature. The donor oxygen proximity effect that weakens donor strength in halogen complex formation is presumed to relate to the opposition of closely situated oxygens in polarizing the bonds of the carbon to which they are attached (i.e., $O \leftarrow C \rightarrow O$).[1,11]

In halogen complex formation, trioxane falls below *n*-butyl ether in donor strength but significantly above it in complexing with the halobenzoquinones. Except for the crown ethers, trimethyl orthoformate forms the strongest complex with the π acceptors included in the investigation. All three of the donors with O–C–O linkages form stronger complexes with the π acceptors than does 1,4-dioxane, while the opposite is true for the halogen complexes. For a donor with only one oxygen atom, tetrahydrofuran is unusually strong, ranking next to the crown ethers, in halogen complex formation. This unusual donor strength has been ascribed to the eclipsing by the adjacent C–H bonds of the unshared electrons on oxygen.[1,12] In its complexes with the halobenzoquinones, it falls below diethylene glycol dimethyl ether and 1,2-dimethoxyethane in donor strength.

An examination of molecular models of trioxane and 1,4-tetrahalobenzoquinone reveals that the oxygen atoms or the donor are disposed so that they can all fit over the perimeter of the acceptor ring and contribute simultaneously to formation of a 1:1 complex. Presumably this serves to counter to some degree the unfavorable oxygen proximity effect on donor strength observed for the halogen complexes (at least for the fluoranil complex). Much the same argument can be applied to 1,1-dimethoxyethane. Though the diethylene glycol dimethyl ether molecule has three oxygen atoms, only two of them at a time can fit over the halobenzoquinone ring. As a donor it is, in fact, not quite as effective in complexing with the π acceptors as 1,2-dimethoxyethane. Because it is a more bulky molecule than 1,2-dimethoxyethane, even two of its oxygens may not be able to approach the acceptor ring as closely as those in 1,2-dimethoxyethane. On the other hand, since it offers three potential bonding sites, available only one at a time to a halogen acceptor, its halogen complexes are relatively strong.

1,4-Dioxane is the cyclic analogue of 1,2-dimethoxyethane, and they are both relatively good donors of comparable strength in halogen complex formation. In its interactions with the halobenzoquinones, 1,4-dioxane is much the weaker donor. Presumably, dioxane has a preferred chair conformation, and as a consequence, in this conformation only one of its oxygen atoms at a time, in contrast to those in 1,2-dimethoxyethane, is in position to overlap the acceptor ring. Since, however, it is a considerably stronger donor than di-*n*-butyl ether, it appears to some degree to adjust to an alternate conformation in which both oxygen atoms are in position to associate with the π acceptor at the same time. Tetrahydrofuran retains some of the power as a donor in interacting with the π acceptors that it exhibited in halogen complex formation. It is, for example, a substantially stronger donor than the other monooxygenated ethers, diethyl and dibutyl ether, but as noted above, it yields in strength as a donor to several of the polyoxygenated donors that it outranks when halogens are the acceptors.

The three crown ethers included in this study are all very good donors and are comparable in strength in forming halobenzoquinone complexes. Presumably, three of the oxygen atoms in each one of those donors (in certain of their conformations) are close enough together that they can overlap the acceptor ring simultaneously. Because of the size of the ring, it is doubtful that the additional oxygen atoms in the donor rings are close enough to the acceptor ring to contribute effectively to the interactions. It is noteworthy that the K_F values for the three polyethers are closely similar to each other and so are their K_{Ch} values.[13] In the case of their halogen complexes, there is some indication that their relative donor strengths relate directly to the number of oxygen atoms in the donor molecules.

Aromatic Ethers as Donors. In forming complexes with iodine monochloride and iodine, the donor strengths of toluene, anisole, and di-*n*-butyl ether fall in the order toluene < anisole ≪ di-*n*-butyl ether. Delocalization of the unshared electrons of the ether oxygen in anisole clearly reduces the strength of that oxygen atom as an n donor. Very likely, anisole functions primarily as a π donor in forming halogen complexes. The corresponding order of relative donor strengths with respect to halobenzoquinone complex formation is di-*n*-butyl ether ≪ toluene < anisole. Again anisole is probably functioning primarily as a π donor.[14] The spectrum of the anisole–fluoranil complex resembles that of toluene in that it displays an absorption in the 320–340-nm region, less intense and shifted to a somewhat lower wavelength than that of the corresponding peak in the toluene–fluoranil spectrum (see curves 5 and 6, Figure 3). The absorption of the anisole complex persists considerably further into the visible region than that of the toluene complex in reflection of the delocalization of the unshared electrons of the ether oxygen to the aromatic donor center. The same is true for the

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(13) It should be noted, however, that as the size of the crown ether ring gets very large, as in 24-crown-8, there is a corresponding enhancement of donor strength with respect to fluoranil complex formation in methylene chloride: Jayathirtha, Y.; Krishnan, V. *Z. Naturforsch., A: Phys. Phys. Chem., Kosmophys.* **1978**, *33A*, 243.

(14) On the basis of results obtained in a study of variations of equilibrium constants for complex formation of benzo- and dibenzo-crown ethers with 2,3,5,6-tetracyanopyrazine, it has been concluded that the complexes are largely the products of π–π rather than n–π interaction; Malini, R.; Krishnan, V. *Bull. Soc. Chim. Belg.* **1980**, *89*, 359.

anisole–chloranil spectrum (see curve 6, Figure 2). In complexing with fluoranil, at least, diphenyl ether is a weaker donor than anisole, as was also the case for iodine monochloride complex formation. Apparently, the effect of having two rings compete as centers for delocalization of ether oxygen electrons has a slightly debilitating effect on donor strength. The spectra of the diphenyl ether–halobenzoquinone complexes (not shown in Figures 2 and 3) are similar to the spectra of the anisole complexes, as are those of the dimethoxybenzene complexes. In halogen complex formation, dibenzyl ether and benzyl methyl ether, in which the oxygen atoms are not attached to aromatic rings, are considerably stronger donors than anisole and dibenzyl ether. The spectra of their halogen complexes as well as their equilibrium constants suggest strongly that they act primarily as n rather than π donors. Although dibenzyl and benzyl methyl ethers are also somewhat stronger donors than anisole in halobenzoquinone complex formation, particularly when fluoranil is the acceptor, it seems unlikely that their oxygen atoms, acting independently, are the major donor centers. If that were the case, their K_F and K_{Ch} values should be similar to those of the weak donor, di-*n*-butyl ether. The spectra of their halobenzoquinone complexes, which because of strong absorption by the uncomplexed donor unfortunately cannot be examined below 300 nm, give no clear cut indication of a significant contribution of the ether oxygen (functioning as an n donor) to complex formation (see curve 5, Figure 2, and curves 4 and 5, Figure 3). It is conceivable that the geometry of these two ethers is such that an oxygen atom and an aromatic ring may function simultaneously as n- and π-donor centers, respectively, in interacting with a single halobenzoquinone molecule. As donors in fluoranil complex formation 1,2-, 1,3-, and 1,4-dimethoxybenzene are comparable in strength to benzyl methyl ether. The percentage differences in K_{Ch} and K_F values for the complexes of the dimethoxybenzenes as well as of those for other phenolic-type aromatic donors are noticeably less than those for donors in which oxygen is not directly bonded to an aromatic ring. That is, the donors in which the oxygen electrons are delocalized to an aromatic ring are less discriminating in their preference for the acceptors (fluoranil vs chloranil) than other ether donors.

Complication of 2:1 Complex (D_2Ac) Formation. When the complication of 2:1 as well as 1:1 complex formation occurs, it sometimes, but not always, becomes apparent when the Ketelaar equation (eq 2) or related equations are applied in the determination of K_c values from spectrophotometric data as carried out in this investigation.[10b,c] On occasion, the plots of $1/(\epsilon_a - \epsilon_{Ac})$ vs $1/[D]$, from the slopes and intercepts of which K_c values are calculated, deviate from linearity. Such deviations are significant enough to be evident in the plots of data for certain of the fluoranil complexes of relatively strong ether donors, as illustrated in Figure 4. For most of the ether–halobenzoquinone complexes included in this study, those plots appear to be linear over the entire range of donor concentrations. More specifically, when K_c is less than 1.5 L/mol, the plots are linear over a range of donor concentrations up to ca. 1.3 M; the points for 2.6 M solutions are sometimes slightly below that line but still within the range of experimental error in fitting to the line. The plots for the strong crown ether complexes with fluoranil begin to deviate perceptibly from linearity at donor concentrations below 1 M, in probable reflection of a significant contribution of a termolecular complex to donor–acceptor interaction; for complexes of somewhat less strong donors with fluoranil, the deviation becomes obvious at donor concentrations of the order of 2.6 M.

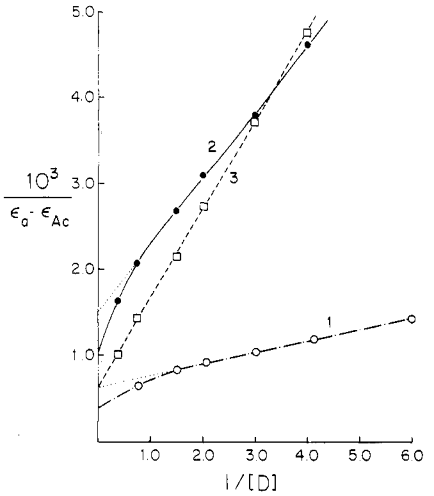

Figure 4. Plots for the determination of the apparent equilibrium constants K_c of several fluoranil complexes from the Ketelaar equation. Curve 1, 5.86×10^{-4} M fluoranil and 12-crown-4 (276 nm); curve 2, 1.17×10^{-3} M fluoranil and 1,3-dimethoxybenzene (500 nm); curve 3, 1.17×10^{-3} M fluoranil and toluene (370 nm).

In cases in which the Ketelaar plots (eq 2) exhibit noticeable deviations from linearity, the procedure outlined by Deranleau[10b] has been used to estimate equilibrium constants K_1 and K_2 for formation of 1:1 (DAc) and 2:1 (D_2Ac) complexes as well as the corresponding absorptivities, ϵ_1 and ϵ_2. The slopes and intercepts of the linear portions of the plots in the region of low donor concentration, L, are respectively

$$\text{slope}_L = 1/(K_1\epsilon_1) \tag{3}$$

$$\text{intercept}_L = (1/\epsilon_1)[1 - (K_2\epsilon_2)/(K_1\epsilon_1)] \tag{4}$$

The slopes and intercepts of the plots in the region of $1/[D] = 0$, H, are respectively

$$\text{slope}_H = [1/(K_2\epsilon_2)](1 - \epsilon_1/\epsilon_2) \tag{5}$$

$$\text{intercept}_H = 1/\epsilon_2 \tag{6}$$

The constant K_2 is defined by eq 7. In the original

$$K_2 = [D_2Ac]/([DAc][D]) \tag{7}$$

Deranleau version of eq 5, K_2 is designated incorrectly as K_1.[10b] The four equations in four unknowns can be solved to obtain the two equilibrium constants and two absorptivities. The values of these constants, as obtained on the assumption that this treatment correctly explains those cases in which significant deviations from linearity in the Ketelaar plots were clearly observed, are listed in Table II. The K_2 values are considered to relate to complexes in which the acceptor molecule is sandwiched between two donor molecules. In all cases K_1 values are somewhat greater than K_c values, but the differences are not marked. The K_1/K_2 ratios range from about 7/1 to 11/1. The K_c and K_1 values generally vary with changes in donor in the same order. It seems safe to say, therefore, that K_c values are representative of the relative strengths of the various donors in 1:1 complex formation. Because of the errors inherent in the measurements of slopes and intercepts (eq 4 and 5), the K_1 and K_2 values that are reported can only be considered to be approximately correct. They are the averages of values calculated from data collected at several wavelengths. The plot for toluene, which is included in Figure 4, is shown to illustrate a case in which no deviation from linearity is observed.

Treatment of those experimental data that do not produce uniformly linear Ketelaar plots (eq 2) by eq 3-6 provides what appear to be reasonable results. The possibility cannot be overlooked, however, that the observed nonlinearities in those plots may be in part the result of deviations of the ether-carbon tetrachloride mixtures from ideal solutions laws.

Registry No. Diethyl ether/fluoranil complex (1:1), 112042-88-3; diethyl ether/chloranil complex (1:1), 112042-89-4; di-*n*-butyl ether/fluoranil complex (1:1), 112042-90-7; di-*n*-butyl ether/chloranil complex (1:1), 112042-91-8; di-*n*-butyl ether/ICl complex (1:1), 106531-92-4; di-*n*-butyl ether/I_2 complex (1:1), 41035-70-5; 1,4-dioxane/fluoranil complex (1:1), 112042-92-9; 1,4-dioxane/chloranil complex (1:1), 24134-39-2; 1,4-dioxane/ICl complex (1:1), 77570-05-9; 1,4-dioxane/I_2 complex (1:1), 2649-24-3; 1,1-dimethoxyethane/fluoranil complex (1:1), 112042-93-0; 1,1-dimethoxyethane/chloranil complex (1:1), 112042-94-1; 1,1-dimethoxyethane/ICl complex (1:1), 108472-77-1; 1,1-dimethoxyethane/I_2 complex (1:1), 108472-78-2; 1,3,5-trioxane/fluoranil complex (1:1), 112042-95-2; 1,3,5-trioxane/chloranil complex (1:1), 112042-96-3; 1,3,5-trioxane/ICl complex (1:1), 16787-68-1; 1,3,5-trioxane/I_2 complex (1:1), 16734-64-8; tetrahydrofuran/fluoranil complex (1:1), 112042-97-4; tetrahydrofuran/chloranil complex (1:1), 22999-73-1; tetrahydrofuran/ICl complex (1:1), 77570-07-1; tetrahydrofuran/I_2 complex (1:1), 2514-43-4; diethylene glycol dimethyl ester/fluoranil complex (1:1), 112042-98-5; diethylene glycol dimethyl ester/chloranil complex (1:1), 112042-99-6; diethylene glycol dimethyl ester/ICl complex (1:1), 106531-93-5; diethylene glycol dimethyl ester/I_2 complex (1:1), 108472-80-6; 1,2-dimethoxyethane/fluoranil complex (1:1), 112043-00-2; 1,2-dimethoxyethane/chloranil complex (1:1), 112043-01-3; 1,2-dimethoxyethane/ICl complex (1:1), 108472-79-3; 1,2-dimethoxyethane/I_2 complex (1:1), 17153-75-2; triethyl orthoformate/fluoranil complex (1:1), 112043-02-4; triethyl orthoformate/chloranil complex (1:1), 112043-03-5; triethyl orthoformate/I_2 complex (1:1), 112043-04-6; trimethyl orthoformate/fluoranil complex (1:1), 112043-05-7; trimethyl orthoformate/chloranil complex (1:1), 112043-06-8; trimethyl orthoformate/ICl complex (1:1), 108472-75-9; trimethyl orthoformate/I_2 complex (1:1), 108472-76-0; 18-crown-6/fluoranil complex (1:1), 66339-22-8; 18-crown-6/chloranil complex (1:1), 112043-07-9; 18-crown-6/ICl complex (1:1), 106532-07-4; 18-crown-6/I_2 complex (1:1), 65324-94-9; 12-crown-4/fluoranil complex (1:1), 112043-08-0; 12-crown-4/chloranil complex (1:1), 112043-09-1; 12-crown-4/I_2 complex (1:1), 65324-92-7; 15-crown-5/fluoranil complex (1:1), 66403-47-2; 15-crown-5/chloranil complex (1:1), 112043-10-4; 15-crown-5/ICl complex (1:1), 106532-02-9; 15-crown-5/I_2 complex (1:1), 65324-93-8; toluene/fluoranil complex (1:1), 17284-54-7; toluene/chloranil complex (1:1), 2473-74-7; toluene/ICl complex (1:1), 6990-47-2; toluene/I_2 complex (1:1), 2605-02-9; diphenyl ether/fluoranil complex (1:1), 112043-11-5; diphenyl ether/chloranil complex (1:1), 112043-12-6; diphenyl ether/ICl complex (1:1), 108472-81-7; diphenyl ether/I_2 complex (1:1), 93119-16-5; anisole/fluoranil complex (1:1), 37437-54-0; anisole/chloranil complex (1:1), 3921-67-3; anisole/ICl complex (1:1), 62094-04-6; anisole/I_2 complex (1:1), 62093-94-1; dibenzyl ether/fluoroanil complex (1:1), 112043-13-7; dibenzyl ether/chloranil complex (1:1), 112043-14-8; dibenzyl ether/ICl complex (1:1), 108472-88-4; dibenzyl ether/I_2 complex (1:1), 108472-89-5; benzyl methyl ether/fluoranil complex (1:1), 112043-15-9; benzyl methyl ether/chloranil complex (1:1), 112043-16-0; benzyl methyl ether/ICl complex (1:1), 108472-90-8; benzyl methyl ether/I_2 complex (1:1), 108472-91-9; 1,4-dimethoxybenzene/fluoranil complex (1:1), 63023-07-4; 1,4-dimethoxybenzene/chloranil complex (1:1), 2200-23-9; 1,4-dimethoxybenzene/ICl complex (1:1), 108472-85-1; 1,4-dimethoxybenzene/I_2 complex (1:1), 62789-30-4; 1,3-dimethoxybenzene/fluoranil complex (1:1), 112043-17-1; 1,3-dimethoxybenzene/chloranil complex (1:1), 3921-68-4; 1,3-dimethoxybenzene/I_2 complex (1:1), 78717-51-8; 1,2-dimethoxybenzene/fluoranil complex (1:1), 63023-06-3; 1,2-dimethoxybenzene/chloranil complex (1:1), 84654-78-4; 1,2-dimethoxybenzene/ICl complex (1:1), 108472-86-2; 1,2-dimethoxybenzene/I_2 complex (1:1), 108472-87-3; 15-crown-5/fluoranil complex (2:1), 112043-18-2; 12-crown-4/fluoranil complex (2:1), 112043-19-3; trimethyl orthoformate/fluoranil complex (2:1), 112043-20-6; 1,2-dimethoxybenzene/fluoranil complex (2:1), 112043-21-7; 1,3-dimethoxybenzene/fluoranil complex (2:1), 112043-22-8; 1,2-dimethoxyethane/fluoranil complex (2:1), 112043-23-9; benzyl methyl ether/fluoranil complex (2:1), 112043-24-0.

Regioselective Acylation of Terpene Hydrocarbons via Allyl- and Benzyltin Derivatives

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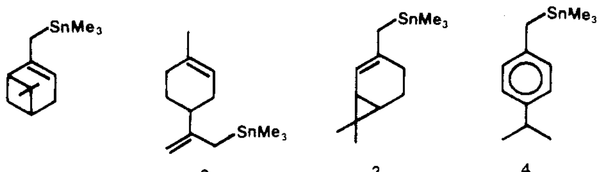
Regioselective acylation of allyl- and benzylstannane derivatives derived from unsaturated terpene hydrocarbons are realized by a rhodium-catalyzed coupling with acyl halides. Mono- and sesquiterpenoid ketones which play an important role in the fragrance industry can be obtained by a three-step process.

Allyl- and benzylstannanes 1-4 (Scheme I) can be readily obtained[1] from terpene hydrocarbons (α-pinene, limonene, 2-carene, *p*-cymene, respectively) by metalation with an *n*-butyllithium-tetramethylethylenediamine complex[2] followed by trapping with trimethyltin chloride. These stannanes are versatile reagents that show high reactivity toward electrophilic species[3] and are useful precursors for the introduction of a variety of functional groups.[4]

Scheme I



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