addition of pyridine to the intermediate (eq 2) is *ca.* four times faster than that of CO to the same species.

The kinetic and activation data, summarized in Table I, are in accord with the proposed reaction paths (eq 2). (1) The entropies (ΔS^*) are positive, as expected for a dissociative type mechanism. (2) The rates of CO addition (k_1) increase with decreasing basicity of L, implying that the rate-determining step depends on the removal of the amine (L) from **1**. Furthermore, the activation energies, ΔH_1^* (Table I), are proportional to the squares of the Fe–N stretching frequencies in **1** (ν_{FeN}: *m*-Clpy, 347; py, 350; *p*-CH$_3$py, 368 cm^{-1}, Nujol) which, altogether, relate the dynamics of the substitution to the Fe–L bond properties in **1** (eq 1). The rate constants (k_1) also show a dependence on the electronic excitation energies of the reactant complexes **1** (*E*, Table I), and the latter have been found to increase linearly with the pK_B of the corresponding pyridines. (3) In contrast, the rate and activation parameters for decarbonylation of **2** are nearly invariant, which is compatible with a dissociative mechanism for this reaction in view of the closeness of the spectral data for the three carbonyl complexes, *E* (Table I) and ν_{CO}: *p*-CH$_3$py, 1995; py, 1996; *m*-Clpy, 2000 cm^{-1} (Nujol). It is to be noted that these CO stretching frequencies are somewhat higher than those found in analogous CO–heme–pyridine derivatives (1970–1980 cm^{-1})[9] which appears to reflect a basicity difference between the two types of planar ligand systems, heme > bis-DPGH.

Table I. Electronic Spectral Data and Kinetic and Activation Parameters[a] for the Dissociation of Base (L) and Carbon Monoxide from **1** and **2**, Respectively (Eq 1, 2), in Chlorobenzene at 25°

Reactant			ΔH^*,	
L	*E*, kK[b]	10^5k, sec^{-1}	kcal/mol	ΔS^*, eu
1 $[\text{Fe(DPGH)}_2\text{L}_2] \xrightarrow{k_1} \text{L}$				
p-CH$_3$py	17.8	228	24.7	21
py	18.1	422	23.6	19
m-Clpy	18.7	1810	23.2	20
2 $[\text{Fe(DPGH)}_2\text{L(CO)}] \xrightarrow{k_{-1}} \text{CO}$				
p-CH$_3$py	24.2	2.62	26.3	19
py	24.2	2.50	26.0	17
m-Clpy	24.3	5.33	26.8	21

[a] The first-order kinetic constants were determined spectrophotometrically under these conditions: 20, 25, 30, 35°; 3×10^{-5} *M* solutions in complex; k_1, p_{CO} (constant) = 190–750 mm; k_{-1}, p_{CO} (constant) $\simeq$ 0 mm, [py] = $(1\text{–}6) \times 10^{-2}$ *M*. Maximum standard deviations: k_1, k_{-1}, ±2%; ΔH_1^*, ±0.5, ΔH_{-1}^*, ±1.5 kcal/mol; ΔS_1^*, ±1.7, ΔS_{-1}^*, ±5 eu. [b] The energy corresponding to the longest wavelength absorption band in the visible spectra of the complexes; $a_{\max} = 8110\text{–}17{,}500\ M^{-1}\,\text{cm}^{-1}$.

Acknowledgment. This research was supported by the National Institutes of Health and the Environmental Protection Agency.

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(10) Teijin, Ltd. Predoctoral Fellow; on leave of absence from Teijin, Ltd., Tokyo, Japan.

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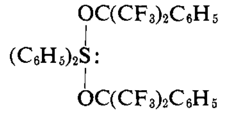
Sulfuranes. IV. The X-Ray Crystal Structure of a Diaryldialkoxysulfurane

Sir:

We report the results of a single-crystal X-ray structure determination on the recently described[1] first example of a tetracoordinate sulfur(IV) compound lacking halogen atom ligands, sulfurane **1**. The ^{19}F nmr evidence that the alkoxy ligands of **1** occupy geometrically equivalent positions in the solution phase is confirmed in the crystal and these positions are identified as the apical positions of a trigonal bipyramid.



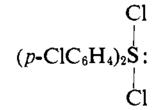
$$(C_6H_5)_2\overset{\displaystyle \overset{|}{OC(CF_3)_2C_6H_5}}{\underset{\displaystyle \underset{|}{} OC(CF_3)_2C_6H_5}{S:}}$$

1

Multiple recrystallizations of moisture-sensitive[1,2] **1** from ether–pentane were carried out using vacuum-line techniques. The transparent, colorless crystals were sealed in thin-walled glass capillaries in a nitrogen atmosphere. The following crystal data were obtained for $C_{30}H_{20}O_2F_{12}S$: mol wt 672.1; triclinic; $a = 10.026$ (3), $b = 14.268$ (3), $c = 10.802$ (3) Å; $\alpha = 109°\ 50'$ (2′), $\beta = 92°\ 52'$ (2′), $\gamma = 95°\ 20'$ (2′); $V = 1447$ Å^3; $Z = 2$; $\rho_{\text{calcd}} = 1.54$ g cm^{-3}; $F(000) = 680$; space group, $P1$ or $P\bar{1}$, the latter choice being established by the results of the analysis.

Two crystals were used to obtain the intensity data on a Picker FACS-1 diffractometer. As the sulfurane reacted with or dissolved in the solvents in every glue that we tried, the crystals had to be wedged between the walls of the capillary, and consequently they frequently moved and had to be realigned (on the order of 20 times). A total of 3364 nonzero reflections was obtained using Cu Kα radiation. The structure was solved by Patterson heavy-atom methods involving sulfur, and at the present stage of refinement (hydrogen atoms located and anisotropic thermal parameters for the nonhydrogen atoms) the crystallographic *R* factor is 0.070. A view of the structure is shown in Figure 1.

Among the tetracoordinate sulfur(IV) compounds which have been isolated and characterized are SF$_4$ and a number of its derivatives[3] and several analogous compounds with S–Cl bonds.[4,5] A preliminary X-ray investigation[6] of a compound postulated to have the structure of a spirodiaryldiacyloxysulfurane showed that the molecule had C_2 molecular symmetry in the crystal. This would be consistent with the sulfurane structure, as is the reported chemical evidence.



$$(p\text{-ClC}_6\text{H}_4)_2\overset{\displaystyle \overset{}{Cl}}{\underset{\displaystyle Cl}{S:}}$$

2

Of the halosulfuranes, the unstable adduct of chlorine and 4,4′-dichlorodiphenyl sulfide is perhaps most

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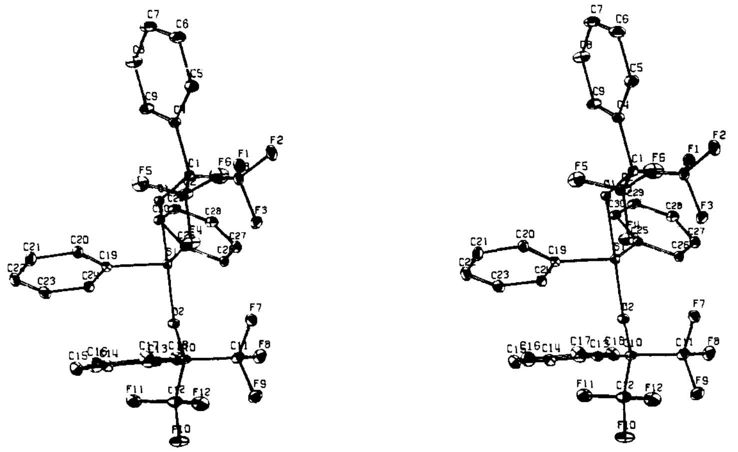
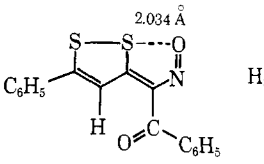


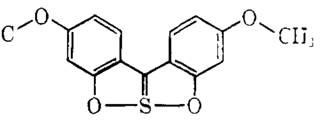
Figure 1. Stereoscopic drawing of **1**. The S–O lengths are 1.889 (4) and 1.916 (4) Å and the S–C lengths are 1.804 (6) and 1.810 (7) Å; the O–S–O angle is 175.1 (2), the C–S–C angle is 104.4 (3), and the O–S–C angles range from 86.4 (2) to 91.2 (2)°.

closely analogous to **1**. Its slightly distorted trigonal-bipyramidal geometry (Cl–S–Cl angle, 174.5 (1)°) is similar to that seen for **1** (O–S–O bond angle, 175.1 (2)°), although the distortion from 180° is away from the lone pair of electrons in **1** and toward the lone pair in **2**. The 0.2-Å elongation of the sulfurane S–Cl bonds, relative to the sum of covalent radii, was interpreted[5] in terms of a bond order for the S–Cl bonds of approximately 0.5, in a three-center, three-orbital, four-electron bond.

The apical S–O bonds of **1** (1.889 (4), 1.916 (4) Å) are unusually long for single bonds when compared to the sum of the covalent radii for sulfur and oxygen (1.70 Å)[7] and the lengths of 1.533–1.616 Å reported in organic sulfates[8,9] and 1.594–1.627 Å found in sulfonates.[10] S–O contacts ranging from 2.034 to 2.65 Å have been reported[11,12] in a number of compounds, *e.g.*, **3**; in many of these cases the oxygen atom lies along an extension of an S–S vector. The sum of the van der Waals radii for sulfur and oxygen is 3.25 Å.[13] Another comparatively short S–O contact (2.81 (1) Å) has been found in 1-acetonyl-1-thionia-5-thiacyclooctane perchlorate,[14] and in that case a distorted trigonal-bipyramidal arrangement, involving a transannular S–S interaction, was found around one of the sulfur atoms. A more pertinent comparison may be made with the structure of the fusion product (**4**) of captan and resorcinol.[15,16] In the essentially coplanar molecule of **4**, the S–O lengths are 1.878 (2) and 1.879 (2) Å. While formally **4** appears as a tricoordinate sulfur(IV) compound, if one considers the equivalent orbital representation, in which the C=S double bond is represented as two equivalent bent bonds,[17,18] the similarity to **1** is apparent. In both **4** and **1** the S–O bonds are elongated by *ca.* 0.2 Å from the usual value for S–O single bonds, as was seen[5] for the S–Cl bonds of **2**. One picture of the bonding which is consistent with this would put two electrons into the three-center (O–S–O) bonding molecular orbital (giving a bond order of 0.5 for the two S–O bonds) and two into the nonbonding molecular orbital (putting negative charge on the electronegative apical substituents). Such an approximation, using no d orbitals on sulfur, has been discussed by Musher[19] for a variety of compounds with what he calls hypervalent bonding.



3



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[20]Annulene[1]

Sir:

All annulenes from [14]annulene to [24]annulene have been obtained as well-characterized crystalline compounds,[2] except for [20]annulene.[3] We now report

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(1) Unsaturated Macrocyclic Compounds. LXXXVI. For part LXXXV, see B. W. Metcalf and F. Sondheimer, *J. Amer. Chem. Soc.*, **93**, 5271 (1971).