Table I. Selected Structural Parameters in A, $[Fe_2S_2(o,o'\text{-biphenolate})_2]^{2-}$ (I), B, $[Fe_2S_2(\text{pyrrolate})_4]^{2-}$ (II), C, $[Fe_2S_2(S_2\text{-}o\text{-xylyl})_2]^{2-}$, D, $[Fe_2S_2S(p\text{-tolyl})_4]^{2-}$, and E, $Fe_2S_{12}{}^{2-}$

	A[a]	B[a]	C[b]	D[b]	E[c]
Fe–Fe	2.699 (1)	2.677 (3)	2.698 (1)	2.691 (1)	2.701 (3)
$\overline{\text{Fe–S}_b}$	2.215	2.18	2.21	2.201	2.192
Fe–$O_1(N_1)$	1.895 (2)	1.96 (1)			
Fe–$O_2(N_2)$	1.892 (2)	2.09 (3)			
S_b–S_b	3.512 (2)	3.57 (5)	3.498 (3)	3.483 (3)	3.453 (5)
S_b–Fe–S_b	104.9 (1)[d]	104.3 (4)[e]	104.73 (4)	104.51 (4)	104.0 (2)
O(N)–Fe–(N)O	96.1 (1)	110.6 (6)			
Fe–S_b–Fe	74.1 (1)	75.7 (2)	75.27 (5)	75.39 (4)	76.1 (1)

[a] This work. [b] From ref 1. [c] From ref 2. [d] The other L–Fe–L angles vary from 96.1 (1)° for the O_1–Fe–O_2 angle to 117.8 (1)° for the O_2–Fe–S_1 angle. [e] The other L–Fe–L angles vary from 105.4 (9)° for the N_2–Fe–S_1 angle to 112.4 (6)° for the N_1–Fe–S_1 angle.

II, respectively, are similar to those reported previously[1] for the sulfur terminal ligand analogues and very likely reflect antiferromagnetic coupling between the two high-spin Fe(III) ions in the dimers. As a result of these magnetic moments the NMR spectra of I and II display isotropically shifted proton resonances in CD_3CN solution. The ortho H, meta H, meta H, and para H resonances in I are observed at 2.85, 9.61, 9.31, and 2.69 ppm, and the ortho H and meta H resonances in II are observed at 10.30 and 8.95 ppm. For both I and II irreversible reduction is observed in cyclic voltammetric measurements[15] which show large negative potentials of −1.30 and −1.60 V, respectively. The Mössbauer spectra at 77 K consist of sharp doublets and show isomer shift (IS) values (vs. Fe) and quadrupole splittings (ΔE_Q) of 0.35 (2) and 1.02 (1) mm/s for I and 0.26 (1) and 0.49 (1) mm/s for II. These values are similar to those reported for the $[(PhS)_2Fe_2S_2(SPh)_2]^{2-}$ complex[16] (IS, 0.28 (1); ΔE_Q, 0.32 (2), 77 K) the $[Fe_2S_2(S_2\text{-}o\text{-xyl})_2]^{2-}$ complex,[9] and the oxidized Rieske protein from *Thermus thermophilus*[11] (IS_A, 0.32, IS_B, 0.24; ΔE_{QA}, 0.91, ΔE_{QB}, 0.52; 4.2 K). The Mössbauer data also demonstrate that the Fe(III) IS values in the $[Fe_2S_2L_4]^{2-}$ complexes are relatively insensitive to the nature of the terminal ligands (L) when tetrahedral coordination is maintained.

In the crystal structures[17] of both I and II the dianions are located on crystallographic centers of symmetry. Selected structural parameters for the anions in I and II (Figure 2) are shown in Table I and are compared to corresponding parameters in the structures of the $[Fe_2S_2(S_2\text{-}o\text{-xylyl})_2]^{2-}$, $[Fe_2S_2(S\text{-}p\text{-tolyl})_4]^{2-}$,[1] and $Fe_2S_{12}{}^{2-}$[2] anions. The striking similarities in the Fe_2S_2 units are apparent.

The available spectroscopic data on I–III and particularly the Mössbauer and electronic spectral data are very similar to corresponding data for the Rieske proteins. These similarities, however, can only be of limited significance when the pronounced differences in the redox potentials are taken into consideration. In the $[L_2FeS_2FeL_2]^{2-}$ analogue complexes, substitution of the sulfur ligands by either oxygen or nitrogen ligands and maintenance of the tetrahedral coordination for the Fe(III) ions results in complexes with more *negative* redox potentials. A positive shift in the redox potentials of the $[Fe_4S_4(SR)_4]^{2-}$ clusters apparently occurs only when the thiolate ligands are displaced by carboxylate ligands.[18] The possibility that positive shifts in the redox potential of the $[L_2FeS_2FeL_2]^{2-}$ complexes are brought about by carboxylate terminal ligands (and changes in coordination number or geometry) at present is under investigation in our laboratory.

Acknowledgment. This research was supported by a grant from the National Institutes of Health (No. GM-26671). X-ray equipment used in this research was obtained in part by Grant CHE-8109065 from the National Science Foundation.

Supplementary Material Available: Tables of structure factors, positional and thermal parameters, and data reduction and structure solution protocol (20 pages). Ordering information is given on any current masthead page.

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(15) Cyclic voltammetry in CH_3CN on a Pt electrode with Bu_4NClO_4 as supporting electrolyte. Potentials are reported with SCE as a reference electrode.

(16) Gillum, W. O.; Frankel, R. B.; Foner, S.; Holm, R. H. *Inorg. Chem.* **1976**, *15*, 1095.

(17) Crystal and refinement data for $(Et_4N)_2[Fe_2S_2(o,o'\text{-}C_{12}H_8O_2)_2]$ (I): $a = 11.500$ (2) Å, $b = 13.541$ (3) Å, $c = 26.612$ (5) Å, $\beta = 92.25$ (1)°; space group $C2/c$ (No. 15); $Z = 4$; $d_{calcd} = 1.29$ g/cm³, $d_{obsd} = 1.30$ (2) g/cm³; $\mu = 8.07$ cm⁻¹; $2\theta_{max}$ 45° (Mo/Kα,λ 0.71069 Å). Reflections collected 6603; unique reflections used in refinement $F_o{}^2 > 3\sigma(F_o{}^2)$, 2108; parameters 310; final $R = 0.032$. Crystal and refinement data for $(Et_4N)_2[Fe_2S_2(C_4H_4N)_4]$ (II): $a = 9.689$ (3) Å, $b = 16.362$ (2) Å, $c = 11.910$ (5) Å, $\beta = 97.74$ (3)°; space group $P2_1/n$; $Z = 2$; $d_{calcd} = 1.24$ g/cm³; $d_{obsd} = 1.32$ g/cm³; $\mu = 8.84$ cm⁻¹; $2\theta_{max}$ 40° (Mo Kα,λ 0.71069 Å). Reflections collected 2328; unique reflections used in refinement $F_o{}^2 > 3\sigma(F_o{}^2)$, 1197; parameters 173; final $R = 0.069$.

(18) Johnson, R. W.; Holm, R. H. *J. Am. Chem. Soc.* **1978**, *100*, 5338.

Hypervalent Iodine. Mixed Iodonium Ylides

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The relatively unfamiliar aryliodonium ylides owe their stability to delocalization of the carbanionic charge adjacent the onium center in the zwitterionic form:[1]

$$\text{ArI}{=}\text{CR}_2 \leftrightarrow \text{ArI}^+{-}^-\text{CR}_2$$

The first stable iodonium ylide, discovered by Neilands et. al., in 1957, possessed a β-dicarbonyl system ($^-CR_2$ equals $^-C(COR)_2$ in the above expression) and was synthesized via reaction of dimedone with (difluoroiodo)benzene $C_6H_5IF_2$.[2] Most stable iodonium ylides subsequently reported incorporate a β-dicarbonyl carbanionic group,[3a,b] although other stable anionic systems also occur.[4]

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(1) For an excellent review, see: Koser, G. F. "The Chemistry of Functional Groups, Supplement D"; Wiley: 1983; Chapter 18, pp 774–806.

(2) Gudrinietse, E.; Neilands, O.; Vanag, G. *J. Gen. Chem. USSR (Engl. Transl.)* **1957**, *27*, 2777.

(3) (a) For example, the carbanionic part may be derived from 1,3-indanedione (Neilands O.; Vanag, G. *Dokl. Chem. (Engl. Transl.)* **1961**, *141*, 1232), dibenzoylmethane (Neilands, O. *J. Org. Chem. USSR (Engl. Transl.)* **1965**, *1*, 1888, 5-phenyl-1,3-cyclohexanedione and benzoylacetone (Neilands, O.; Vanag, G. *J. Gen. Chem. USSR (Engl. Transl.)* **1961**, *31*, 137. Neilands, O.; Karele, B. *J. Org. Chem. USSR (Engl. Transl.)* **1966**, *2*, 49, ethyl acetoacetate and dimethyl and diethyl malonate (Neilands, O.; Karele, B. *J. Org. Chem. USSR (Engl. Transl.)* **1965**, *1*, 1884), Meldrum's ester and isopropylidene malonate (Neilands, O.; Karele, B. *J. Org. Chem. USSR (Engl. Transl.)* **1971**, *7*, 1674), and barbituric acid and *N,N*-dimethylbarbituric acid (Neilands, O.; Neiman, D. E. *J. Org. Chem. USSR. (Engl. Transl.)* **1970**, *6*, 2522). (b) Monocarbonyl ylides of the type ArI=CHCOR have not been isolated presumably due to the lack of sufficient stabilization of the carbanionic system (the present authors have proposed the intermediacy of ArI(OH)CH_2COAr in the reaction of ArI=O with $ArCOCH_3$). The final product in this reaction results from I^{III}–C cleavage rather than loss of H_2O (to form the ylide).

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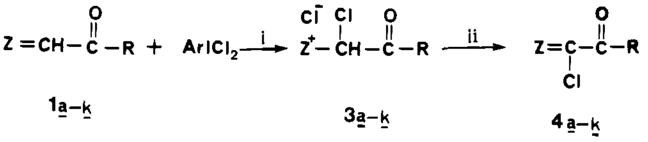
Table I. Mixed Iodonium Ylidse[d]

compd	IR, cm^{-1}[e]	NMR (^{1}H, ^{13}C, ^{31}P)	mp, °C	yield, %
2a[a]	1600	^{1}H, 0.95 (t, 3 H, CH_2CH_3), 4.0 (q, 2 H, CH_2CH_3), 7.53–7.83 (*m*, 20 H, Ar;[f] ^{13}C, 14.44 (CH_3), 62.41 (OCH_2), 190.62 (CO^-);[j] 136.33, 135.04, 134.56, 133.97, 133.01, 132.43, 131.52, 130.76, 130.14; ^{31}P, +28.53 (Z), +20.44 (E)[k]	185–187[i]	70
2b[a]	1580	^{1}H, 7.4–7.61 (m, 25 H, Ar)[f]	145–147[i]	64
2c[c]	1590	^{1}H, 2.35 (s, 3 H, CH_3), 6.93–7.5 (m, 24 H, Ar);[f] ^{13}C, 24.31 (CH_3), 190.51 (CO^-),[j] 134.87, 134.65, 134.06, 133.48, 131.71, 130.94, 130.27,129.49, 128.76.	113–116	64
2d[c]	1605	^{1}H, 2.4 (s, 3 H, CH_3), 7.26–8.85 (m, 24 H, Ar)[f]	131–133	66
2e[c]	1600	^{1}H, 2.4 (s, 3 H, CH[3), 2.42 (s, 3 H, CH_3), 7.34–7.72 (m, 23 H, Ar)[f]	112–114	54
2f[b]	1605	^{1}H, 3.36 (s, 3 H, OCH_3), 6.4–7.56 (m, 24 H, Ar)[g]	131–132	78
2g[b]	1610	^{1}H, 2.7 (s, 3 H, CH_3), 3.8 (s, 3 H, OCH_3), 7.2–8.2 (m, 23, Ar)[g]	103–104	72
2h[c]	1595	^{1}H, 6.8–7.26 (m, 29 H, Ar)[f]	147–150	82
2i[c]	1545	^{1}H, 2.36 (s, 3 H, CH_3), 7.23–8.13 (m, 28 H, Ar);[f] ^{13}C, 24.4 (CH_3), 190.63 (CO^-),[j] 136.02, 135.53, 135.13, 134.86, 134.65, 134.26, 133.56, 132.68, 130.93, 130.27, 130.07, 129.47, 129.18, 128.09, 127.91; ^{31}P, +26.48 (Z), +21.62 (E)[k]	133–134	76
2j[c]	1580	^{1}H, 2.67 (s, 3 H, CH_3), 7.2–8.8 (m, 18 H, Ar)[h]	207–212	55

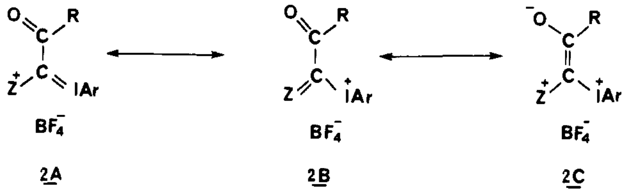
[a] Ylide + $ArIF_2$, HBF_4, MeOH, 0 °C. [b] Ylide + ArI=O, HBF_4, MeOH, 0 °C. [c] Ylide + $ArI(OAc)_2$, HBF_4, MeOH, 0 °C. [d] Correct microanalyses were obtained for all compounds. [e] Measured as KBr pellets. [f] Spectrum measured in CD_3CN. [g] $CDCl_3$. [h] CD_3COCD_3. [i] Reference 7. [j] Reference 12. [k] Reference 13.

Scheme I[a]



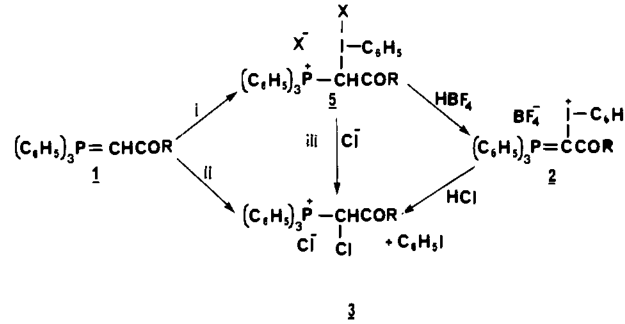
[a] (i) Benzene, 0 °C; (ii) K_2CO_3/H_2O or CH_2Cl_2/Et_3N.

We report now the synthesis of a new series of stable iodonium ylides (**2a–j**) in which one of the stabilizing groups contains an atom Z such as phosphorus which is capable of d-orbital stabilization or nitrogen which serves this stabilizing function via p-orbital delocalization. These compounds are mixed ylides of iodonium–phosphonium and ammonium type and conform to the general formula shown below with various resonance structures (**2A–C**).



2a, Z = $(C_6H_5)_3P$, R = OC_2H_5, Ar = C_6H_5
b, Z = $(C_6H_5)_3P$, R = C_6H_5, Ar = C_6H_5
c, Z = $(C_6H_5)_3P$, R = C_6H_5, Ar = o-$CH_3C_6H_4$
d, Z = $(C_6H_5)_3P$, R = p-$CH_3C_6H_4$, Ar = C_6H_5
e, Z = $(C_6H_5)_3P$, R = p-$CH_3C_6H_4$, Ar = o-$CH_3C_6H_4$
f, Z = $(C_6H_5)_3P$, R = p-$CH_3OC_6H_4$, Ar = C_6H_5
g, Z = $(C_6H_5)_3P$, R = p-$CH_3OC_6H_4$, Ar = o-$CH_3C_6H_4$
h, Z = $(C_6H_5)_3P$, R = p-$C_6H_5C_6H_4$, Ar = C_6H_5
i, Z = $(C_6H_5)_3P$ R = p-$C_6H_5C_6H_4$, Ar = o-$CH_3C_6H_4$
j, Z = (C_5H_5N), R = p-$C_6H_5C_6H_4$, Ar = o-$CII_3C_6H_4$
k, Z = $(C_6H_5)_3As$, R = p-$CH_3OC_6H_4$

Scheme II[a]



[a] (i) $C_6H_5IX_2 \xrightarrow{(HBF_4)} C_6H_5\overset{+}{I}X + BF_4^-$ ($X_2 = F_2, Cl_2, O, OAc_2$); (ii) direct displacement upon $C_6H_5IX_2$; (iii) $ArICl_2$, HBF_4 (to yield fluoroborate).

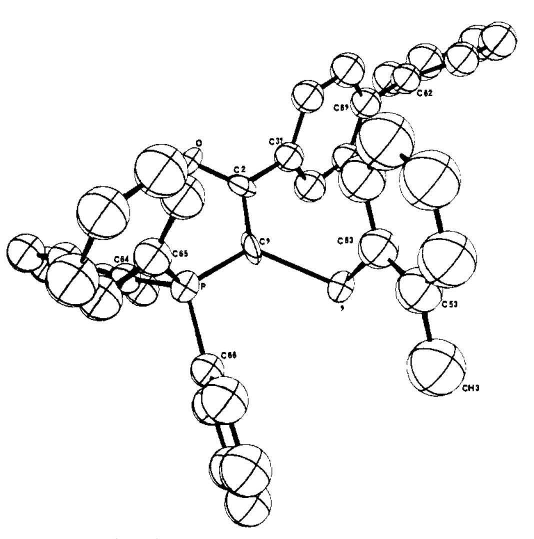
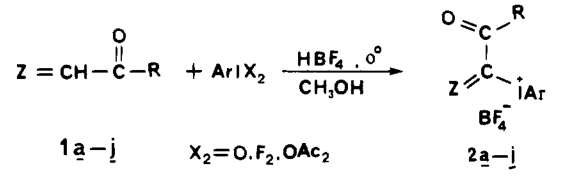


Figure 1. Perspective view (ORTEP) of structure of ion **2i**. All unlabeled atoms are phenyl carbon atoms; H atoms are omitted for clarity.

Ylides **2a–j** were synthesized by the reaction of the appropriate starting ylide Z=CHCOR (**1a–j**) with ArI=O, $ArI(OAc)_2$, or $ArIF_2$ in CH_3OH/HBF_4 (48% HF, H_3BO_3) at 0 °C (Table I).



Reaction of ylides **1a–k** with $ArICl_2$ in C_6H_6 at 0 °C yielded the C-chlorinated derivatives **3a–k** (Scheme I).[5]

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(4) For example: cyclopentadienyl ((a) Fredrich, K.; Amann, W. *Tetrahedron Lett.* **1973**, 3689. (b), (c) Freidrich, K.; Amann, W. *Tetrahedron Lett.* **1977**, 2885. Kreicberge, J.; Kampars, V.; Neilands, D. *Zh. Org. Khim.* **1975**, *11*, 1508, indole (Karele, B.; Treigute, L.; Kalina, S.; Girinberga, J.; Neilands, O. *Khim. Geterotsikl. Soedin.* **1974**, 214; *Chem. Abstr.* **1974**, *81*, 13342*h*, uracil (Karele, B.; Kalina, S.; Girinberga, I.; Neilands, O. *Khim. Geterotsikl. Soedin.* **1973**, 553; *Chem. Abstr.* **1973**, *79*, 32003*a*), pyrazole (Karele, B.; Kalina, S.; Girinberga, I.; Neilands, O. *Khim. Geterotsikl. Soedin.* **1973**, 245; *Chem. Abstr.* **1973**, *79*, 32003*a*), pyrrole (Karele, B.; Kalina, S.; Girinberga, I.; Neilands, O. *Nov. Issled. Obl. Khim. Khim. Tekhnol., Mater. Nauchno-Tekh. Konf. Professorsko-Prepod.* Sostava *Nauchn. Rab. Khim. Fak. RPI 1972* **1973**, 19–20; *Chem. Abstr.* **1975**, *82*, 4204*k*), carbostyril (Kappe, T.; Korbuly, G.; Stadlbauer, W. *Chem. Ber.* **1978**, *111*, 3857), $C_6H_5(CO)\check{C}NO_2$ (Abramovitch, R. A.; Shinkai, I. *J. Chem. Soc., Chem. Commun.* **1973**, 569), $C_6H_5(CO)\check{C}CN$ (Abramovitch, R. A.; Girins, G.; Rogers, R. B.; Shinkai, I. *J. Am. Chem. Soc.* **1976**, *98*, 5671. Seveno, A.; Morel, G.; Foucaud, A.; Marchand, E. *Tetrahedron Lett.* **1977**, 3349), $^-C(SO_2F)_2$ (Maletina, I.; Mironava, A. A.; Savina, T. I.; Yagupol'skii; Yu L. *Zh. Org. Khim.* **1979**, *15*, 2416), and $^-C(NO_2)_2$ (Semenov, V. V.; Shenelev, S. A.; Fainzil'berg, A. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1978**, *10*, 2355) are known.

Reaction of **1a–j** → **2a–j** is an example of the general phenomenon of nucleophilic addition of an anionic systems to hypervalent iodine.[6] In the cases of ArI=O, $ArI(OAc)_2$, and $ArIF_2$, the HBF_4 generates an iodine-based electrophile, $ArI^+{-}X$, which attacks the carbanionic carbon atom (**1** → **5**, Scheme II). Subsequent loss of HX yields the mixed iodonium ylide (**5** → **2**, Scheme II).[7]

The C-chlorination reaction may result from direct anionic attack of the ylides **1a–k** upon undissociated $C_6H_5ICl_2$ (**1** → **3**, Scheme II).[8,9] Alternatively, intermediate **5** may undergo subsequent displacement by chloride anion (**5** → **3**, Scheme II).

The X-ray structure of **2i**[10] is shown in Figure 1. The five atoms I–C1–P–C2–O are essentially coplanar; the largest deviation from the best least-squares plane fitted to them is 0.055 Å; O and I are trans to each other. The X-ray structure indicates that structure **2B** is the principal contributor to the bonding.[11]

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of research.

Supplementary Material Available: Tables of positional parameters, temperature factors, and observed and calculated structure factors for $C_6H_5C_6H_4COC[P(C_6H_5)_3]IC_6H_4CH_3\ BF_4$ (13 pages). Ordering information is given on any current masthead page.

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(5) Yield (%), mp (°C), IR (cm^{-1}): **3a**, 70, hygroscopic, 1730; **4a**, 85, 145–147, 1610; **3b**, 60, 180–183, 1675; **4b**, 58, 155–158, 1600; **3d**, 65, 263–265 dec, 1670; **4d**, 78, 158–161, 1605; **3f**, 62, hygroscopic, 1675; **4f**, 68, 166–175 dec, 1605; **3h**, 71, 186–189, 1665; **4h**, 64, 129–132, 1595; **3k**, 60, hygroscopic, 1670; **4k**, 56, hygroscopic, 1600.

(6) Moriarty, R. M.; Hu, H. *Tetrahedron Lett.* **1981**, *22*, 2747. Moriarty, R. M.; Hu, H.; Gupta, S. C. *Tetrahedron Lett.* **1981**, *22*, 1283. Moriarty, R. M.; Gupta, S. C.; Hu, H.; Berenschot, D. R.; White, K. B. *J. Am. Chem. Soc.* **1981**, *103*, 686. Moriarty, R. M.; John, L. S.; Du, P. C. *J. Chem. Soc., Chem. Commun.* **1981**, 641. Moriarty, R. M.; Hou, K.-C. *Tetrahedron Lett.* **1984**, *25*, 691.

(7) Similar examples of electrophilic addition to phosphoranes have been reported (for a review, see: Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 907), e.g., ArSeBr, $TeBr_4$ (Petragnini, N.; Campos, M. de M. *Chem. Ind.* (*London*) **1964**, 1461), $(CH_3)_3SiBr$, $(C_6H_5)_3GeBr$, $(CH_3)_3SnBr$ (Seyferth, D.; Grim, S. O. *J. Am. Chem. Soc.* **1961**, *83*, 1610), and $HgCl_2$ (Nesmeyanov, N. A.; Novikov, V. M.; Reutov, O. A. *Izv. Akad. Nauk SSSR* **1964**, 772; *Bull. Acad. Sci. USSR* **1964**, 724). In the case of ArSeBr, excess $(C_6H_5)_3P{=}CHCO_2C_2H_5$ causes dehydrochlorination to a mixed ylide. In a related study Neilands and Vanag found that (diacetoxyiodo)benzene reacted with carboethoxymethylene triphenylphosphorane and benzoylmethylene triphenylphosphorane to yield the phosphonium–iodonium ylide (Neilands, O.; Vanag, G. *Dokl. Akad. Nauk. SSSR* **1964**, *159*, 373; *Chem. Abstr.* **1965**, *62*, 6510*c*).

(8) C-Chlorination has also been observed by: Märkl, G. *Chem. Ber.* **1961**, *94*, 2996.

(9) Since $C_6H_5ICl_2$ is a T-shaped molecule (Archer, E. M.; van Schalkuyk, T. G. D. *Acta Crystallogr.* **1953**, *6*, 88), ligand transfer with overall reductive elimination via a $^-C{-}{-}{-}Cl{-}{-}{-}I{-}{-}{-}Cl$ colinear transition state is stereoelectronically reasonable.

(10) Crystal data for **2i**: monoclinic, space group $P2_1/n$, $a = 11.944$ (4) Å, $b = 13.479$ (3) Å $c = 21.424$ (1) Å, $\beta = 91.07$ (3)°, $Z = 4$; $V = 3448.5$ (1.5) Å^3; $D_c = 1.464$ gcm^{-3}. Data were collected on a Picker FACS-1 diffractometer modified by a Krisel Control update package. A total of 2102 unique reflections with $F > 3.0\sigma(F)$ and in the range $2.0 < 2\theta \leqslant 35.0$ were used in the structure analysis. The data were corrected for absorption and secondary extinction. The structure was solved by the heavy atom method and refined to $R = 0.0683$, $R_w = 0.0672$ using 167 variable parameters (ACSHEL-X, Sheldrick, G., Programs for Crystal Structure Determination, Cambridge, 1975). All ring carbons were refined with isotropic temperature factors and as parts of rigid groups; hydrogens were placed at calculated positions. Other atoms were refined with anisotropic temperature factors. The BF_4^- ion, which was refined as a rigid group, showed evidence of possible disorder in its anisotropic thermal parameters. The iodine in $(C_{39}H_{31}POI)^+$ is only 2.770 Å distant from the carbonyl oxygen in the next neighboring ion generated by the 2-fold screw axis. Thus the positive ions form a secondary-bonded polymer extending along the *b* direction in the crystal. In contrast the I approaches the BF_4^- ion much less closely (closest contact I–F3 = 3.419 Å).

(11) The bond angles (deg) are I–C1–P 122.5 (8), I–C1–C2 120.1 (10), P–C1–C2 117.2 (10), O–C2–C1 117.4 (12). The C1–I–C63 bond angle is 96.7 (4)°. This geometry agrees with that of simpler iodonium ylides and with hypervalent bonding theory for a two-center, four-electron system. The C–O distance of 1.233 (12) Å is close to normal expectation for a C–O double bond (Sutton, L. E., et al. *Spec. Publ.–Chem. Soc.* **1958**, *11* and shorter than the 1.28 Å reported for C–O in $(C_6H_5)_3P{=}(CI)(COC_6H_5)$ (**6**). The C1–C2 bond length of 1.458 (17) Å is longer than the 1.35 Å found in **6** and equals the 1.46 Å expected for $(sp^2)C{-}C(sp)$ (Stephens, F. S. *J. Chem. Soc.* **1965**, 5640). The C1–I distance of 2.053 (13) Å is shorter than the 2.19 Å found in **6** and close to the 2.08 Å observed in simpler iodonium ylides (Page, S. W.; Mazzola, E. P.; Mighell, A. D.; Himes, V. L.; Hubbard, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 5858. Drück, U.; Littke, W. *Acta Crystallogr.* **1978**, *34*, 3092). Finally the P–C1 distance of 1.210 (13) Å is the same as that found in 6.

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Thione Analogues of 1,8-Naphthalic Anhydride. The First Cyclic Trithioanhydride

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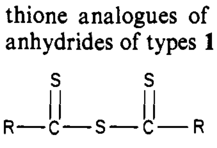
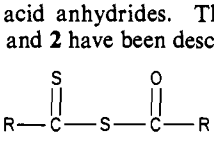
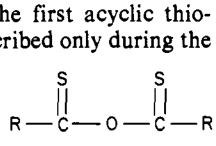
In contrast to the extensive literature on the chemistry of thiocarbonyl (thione) analogues of such carbonyl functions as ketones, acids, esters, and amides,[1] very little is known concerning thione analogues of acid anhydrides. The first acyclic thioanhydrides of types **1** and **2** have been described only during the past few years;[2,3] no example of the dithiono type **3** has yet been reported. Aliphatic compounds of types **1** and **2**, as well as aromatic compounds of type **1**, were found to be highly unstable thermally, whereas several crystalline aromatic examples of type **2** had appreciably greater stability. In both types **1** and **2**, the two C=X systems are believed to be orthogonal in the energetically favored conformations on the basis of MINDO/3 calculations.[2]


$\mathrm{R{-}C({=}S){-}S{-}C({=}S){-}R}$

1


$\mathrm{R{-}C({=}S){-}S{-}C({=}O){-}R}$

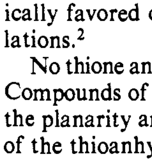
2


$\mathrm{R{-}C({=}S){-}O{-}C({=}S){-}R}$

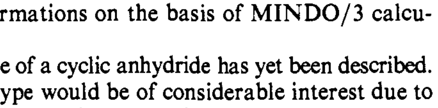
3

No thione analogue of a cyclic anhydride has yet been described. Compounds of this type would be of considerable interest due to the planarity and cisoid configuration forced upon the π-system of the thioanhydride function. We now report the synthesis of the first cyclic anhydrides of types **1**, **2**, and **3**.

1,8-Naphthalic anhydride was converted to the corresponding known acid chloride, which proved to be the pseudo chloride **4**.[4]



4



5

Direct thionation of **4** with Lawesson's reagent (**5**) in refluxing chlorobenzene (3 h, N_2) afforded (57%) red-brown needles of the dithionoanhydride **6**, mp 212 °C dec,[5] the IR spectrum of which

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(1) For leading references on thiocarbonyl compounds, see: Duus, F. "Comprehensive Organic Chemistry"; Jones, D. N., Ed.; Pergamon Press: Oxford, England, 1979; Vol. 3, pp 373–487.

(2) Kato, S.; Sugino, K.; Matsuzawa, Y.; Katada, Y.; Noda, I.; Mizuta, M.; Goto, M.; Ishida, M. *Liebigs Ann. Chem.* **1981**, 1798.

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(4) Arient, J.; Marhen, J. *Collect. Czech. Chem. Commun.* **1963**, *28*, 1292. NMR of **4** δ 8.48 (dd, $J = 7.5$, 2.5 Hz, 1 H), 8.26 (dd, $J = 7.5$, 2.5, Hz, 1 H), 8.19 (d, $J = 7.5$ Hz, 1 H), 8.06 (d, $J = 7.5$ Hz, 1 H), 7.73 (t, $J = 7.5$ Hz, 2 H).

(5) Mass spectrum of 6: *m/e* 230 (100%, M^+), 202 (75%, M − 28), 186 (40%, M − 44), 170 (55%, M − 60), 158 (25%, M − 28 − 44), 154 (15%, M − 76), 126 (58% M − 60 − 44). NMR spectrum: δ 8.8 (dd, $J = 7.5$, 1.25 Hz, 2 H), 8.20 (dd, $J = 7.5$, 1.25 Hz, 2 H), 7.70 (t, $J = 7.5$ Hz, 2 H). UV–vis spectrum: $\lambda_{max}^{C_2H_4Cl_2}$ 258 nm (log ϵ 4.33), 330 sh (3.93), 414 (4.26), 556 sh (2.63).

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