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$_6$H$_5$ICl$_2$ (**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–Cl–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.

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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$_3$)$_3$SiBr, (C$_6$H$_5$)$_3$GeBr, (CH$_3$)$_3$SnBr (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$_6$H$_5$)$_3$P=C-HCO$_2$C$_2$H$_5$ 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$_6$H$_5$ICl$_2$ 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$_6$H$_5$)$_3$P=(CI)(COC$_6$H$_5$) (**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 Cl–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–Cl distance of 1.210 (13) Å is the same as that found in **6**.

Supplementary Material Available: Tables of positional parameters, temperature factors, and observed and calculated structure factors for C$_6$H$_5$C$_6$H$_4$COC[P(C$_6$H$_5$)$_3$]IC$_6$H$_4$CH$_3$ BF$_4$ (13 pages). Ordering information is given on any current masthead page.

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(12) Gray, G. A. *J. Am. Chem. Soc.* **1973**, *95*, 7736. Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972; pp 279–309.

(13) Duncan, M.; Gallagher, M. J. *Org. Magn. Reson.* **1981**, *15*, 37.

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

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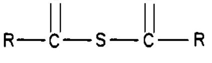
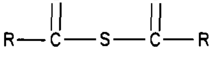
Received May 14, 1984

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]



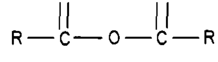
$$\mathrm{R{-}\overset{S}{\overset{\|}{C}}{-}S{-}\overset{S}{\overset{\|}{C}}{-}R}$$

1



$$\mathrm{R{-}\overset{S}{\overset{\|}{C}}{-}S{-}\overset{O}{\overset{\|}{C}}{-}R}$$

2

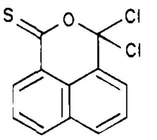


$$\mathrm{R{-}\overset{S}{\overset{\|}{C}}{-}O{-}\overset{S}{\overset{\|}{C}}{-}R}$$

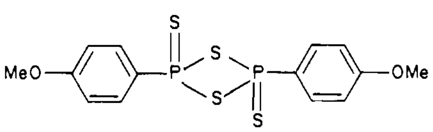
3

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.

(3) Kato, S.; Shibahashi, H.; Katada, T.; Takagi, T.; Noda, I.; Mizuta, M.; Goto, M. *Liebigs Ann. Chem.* **1982**, 1229.

(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: $\lambda_{\max}^{\mathrm{C_2H_4Cl_2}}$ 258 nm (log ϵ 4.33), 330 sh (3.93), 414 (4.26), 556 sh (2.63).

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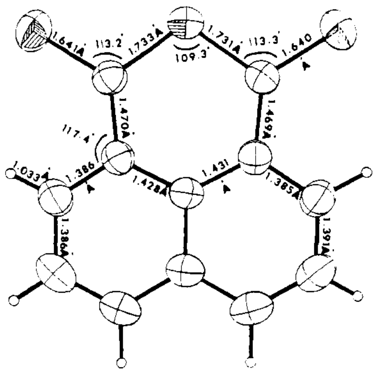


Figure 1. X-ray crystal structure of thioanhydride **8**.

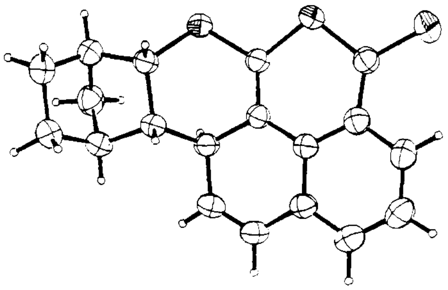
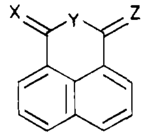
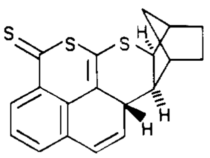


Figure 2. X-ray crystal structure of cycloadduct **9**.

showed no carbonyl absorption; attempts to introduce a third sulfur into **6** using reagent **5** failed. Dithione **6** was rearranged rapidly



6, X = Z = S, Y = O
7, X = Y = S, Z = O
8, X = Y = Z = S



9

(90%) by a catalytic amount of triethylamine in cold DMF to the isomeric thionothioanhydride **7**, which formed green needles, mp 205 °C dec.[6] Thionation of isomer **7** by reagent **5** in boiling chlorobenzene (40 min, N_2) occurred smoothly to give (65%) the trithioanhydride **8** as black irridescent needles, mp 225 °C[7] dec, which were extremely stable, both in the solid state and in refluxing neutral organic solvents like ethanol, benzene, acetonitrile, and chlorobenzene. A single-crystal X-ray analysis of trithioanhydride **8** was carried out[7] (Figure 1).

Compound **8** underwent a novel nonphotochemical addition to norbornene under remarkably mild conditions (15 min in refluxing MeCN or overnight at room temperature). The resulting bright red 1:1 adduct, mp 170 °C, was found to have structure **9**,[11] as determined by X-ray crystallography (Figure 2). The formation of this adduct may be viewed as involving an inverse demand (2 + 4) cycloaddition of the norbornene olefinic bond to an electron-deficient ene-thione moiety of the aromatic thioanhydride system. The closest analogy to this unusual reaction appears to be found in the diene type behavior of the α-dithione function of dimethyl tetrathiooxalate.[12]

Further aspects of the chemistry of cyclic thioanhydrides are currently under investigation in our laboratories.

Acknowledgment. This work was supported by a grant from the National Science Foundation (CHE 83-03897).

Registry No. 4, 91384-89-3; **6**, 91384-90-6; **7**, 91384-91-7; **8**, 91384-92-8; **9**, 91384-93-9; norbornene, 498-66-8.

Supplementary Material Available: Tables of atomic coordinates and thermal parameters (5 pages). Ordering information is given on any current masthead page.

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(6) Mass spectrum of **7**: *m/e* 230 (100%, M^+), 202 (83%, M − 28), 186 (35%, M − 44), 170 (47%, M − 60), 158 (28%, M − 28 − 44), 154 (15%, M − 76), 126 (50%, M − 60 − 44). NMR spectrum: δ 9.02 (dd, *J* = 7.5, 1.25 Hz, 1 H), 8.60 (dd, *J* = 7.5, 1.25 Hz, 1 H), 8.32 (dd, *J* = 6, 1.25 Hz, 1 H), 8.28 (dd, *J* = 6, 1.25 Hz, 1 H) 7.76 (t, *J* = 8.0 Hz, 1 H), 7.72 (*t*, *J* = 8.0 Hz, 1 H). UV-vis: $\lambda_{max}{}^{C_2H_4Cl_2}$ 252 nm (log ε 4.34), 273 sh (4.06), 322 sh (4.00), 335 (4.06), 375 sh (4.08), 410 (4.27); $\lambda_{max}{}^{CS_2}$ 532 sh (1.72), 566 (1.81), 600 (1.81), 640 (1.66). Rearrangement of **6** to **7** appears to also occur readily under electron impact, as evidenced by a strong M − 28 peak in the mass spectra of **6** as well as **7**.

(7) Mass Spectrum of **8**: *m/e* 246 (100%, M^+), 202 (33%, M − 44), 170 (45%, M − 76), 126 (35%, M − 44 − 76). NMR spectrum: δ 8.88 (dd, *J* = 7.5, 1.25 Hz, 2 H), 8.26 (*J* = 7.5, 1.25 Hz, 2 H), 7.68 (t, *J* = 7.5 Hz, 2 H). UV-vis spectrum: $\lambda_{max}{}^{C_2H_4Cl_2}$ 250 nm, sh (log ε 4.11), 265 (4.29), 360 infl (4.04), 375 (4.04), 379 sh (4.01), 443 (4.36), 523 br (2.79), 553 (2.81); $\lambda_{max}{}^{CS_2}$ 533 (2.55), 562 (2.66), 633 br (1.94), 681 (1.92). The planar molecules form stacks parallel to the *c*-axis with the S═C—S—C═S moiety sandwiched between the naphthalene units along the stacks. There are no unusual intermolecular contacts. The distortion of the naphthalene unit is small and not dissimilar to that observed in other 1,8-disubstituted naphthalenes.[8] The C═S bond lengths (1.640 and 1.651 Å) are similar to that reported for thiobenzophenone (1.636 (9) Å).[9] The C-S bond lengths (1.731 and 1.733 Å) are similar to that found for simple diaryl sulfides (1.75 Å),[10] indicating no appreciable mesomeric polarization in the thioanhydride function (Figure 1).

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(9) Rindorf, G.; Carlsen, L. *Acta Crystallogr., Sect. B* **1979**, *B35*, 1179.

(10) Tagaki, W. In "Organic Chemistry of Sulfur"; Oae, S., Ed.; Plenum Press: New York, 1977; p 231.

(11) Mass spectrum of adduct **9**: *m/e* 340 (22%, M^+), 246 (100%, M − 94), 202 (30%, M − 94 − 44), 170 (24%, M − 94 − 76). NMR spectrum: δ 8.80 (m, 1 H), 7.50 (m, 2 H), 6.70 (m, 1 H), 6.40 (m, 1 H), 3.15 (m, 1 H), 2.70 (br, 1 H), 2.60 (m, 1 H), 2.35 (m, 1 H), 2.20 (m, 1 H), 1.6–1.8 (m, 3 H), 1.1–1.4 (m, 3 H). Norbornadiene adduct **9** crystallizes in the monoclinic space group $P2_1/c$. Cell dimensions: $a = 10.612$ (1) Å, $b = 14.266$ (1) Å, $c = 11.153$ (2) Å, $\beta = 110.43$ (1)°, $Z = 4$, $d_{calcd} = 1.430$ g cm^{-3}. $R = 0.047$ ($R_w = 0.059$), 263 parameters refined with 2349 reflections ($I > 3\sigma$).

(12) Hartke, K.; Kissel, T.; Quante, J.; Henssen, G. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 953.

Acid-Catalyzed Intramolecular "Diels–Alder" Reactions. The Cycloaddition of Allyl Cations to 1,3-Dienes

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During the last decade, extensive activity has existed in the study of intramolecular Diels–Alder reactions, especially as exploited in the synthesis of natural products.[2] A major limitation of this intramolecular 2 + 4 cycloaddition reaction is that activating groups have to be built into the dienophile in order to achieve the desired reactivity.[3] Because of our extensive interest in carbocations[4] and cation radicals,[5] we were intrigued by the possibility

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(1) National Science Foundation Fellow 1983–1984.

(2) Oppolzer, W. *Angew. Chem.* **1977**, *89*, 10. Mehta, G. *J. Chem. Educ.* **1976**, *53*, 551. Shea, K. J. *Tetrahedron* **1983**, *36*, 1683. Carlson, R. *Annu. Rep. Med. Chem.* **1974**, *9*, 270. Brieger, G.; Bennett, J. N. *Chem. Rev.* **1980**, *80*, 63.

(3) For selected examples, see: (a) House, H. O.; Cronin, T. H. *J. Org. Chem.* **1965**, *30*, 1061. (b) Roush, W. R. *J. Am. Chem. Soc.* **1978**, *100*, 3599. (c) Roush, W. R.; Peseckis, S. M. *Ibid.* **1981**, *103*, 6696. (d) Roush, W. R.; Ko, A. I.; Gillis, H. R. *J. Org. Chem.* **1980**, *45*, 4264. (e) Roush, W. R.; Gillis, H. R. *Ibid.* **1980**, *45*, 4267. (f) Shea, K. J.; Gilman, J. W. *Tetrahedron Lett.* **1983**, *24*, 657.

(4) Gassman, P. G.; Hall, J. B. *J. Am. Chem. Soc.* **1984**, *106*, 4267. Dixon, D. A.; Eades, R. A.; Frey, R.; Gassman, P. G.; Hendewerk, M. L.; Houk, K. N.; Paddon-Row, M. N. *Ibid.* **1984**, *106*, 3885. Gassman, P. G.; Harrington, C. K. *J. Org. Chem.* **1984**, *49*, 2258. Gassman, P. G.; Tidwell, T. T. *Acc. Chem. Res.* **1983**, *16*, 279. Gassman, P. G.; Schaffhausen, J. G.; Starkey, F. D.; Raynolds, P. W. *J. Am. Chem. Soc.* **1982**, *104*, 6411. Gassman, P. G.; Schaffhausen, J. G.; Raynolds, P. W. *Ibid.* **1982**, *104*, 6408.