benzyl alcohol, 100-51-6; *tert*-butyl alcohol, 75-65-0; *tert*-butylammonium chloride, 10017-37-5.

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Preparation of Iminosulfuranes Utilizing the Dimethyl Sulfoxide–Oxalyl Chloride Reagent[1,2]

S. L. Huang and Daniel Swern*

Fels Research Institute and Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122

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In earlier studies,[3,4] we showed that the dimethyl sulfoxide (Me_2SO)–oxalyl chloride (OC) reagent was the most generally useful of a large number of "activated" Me_2SO reagents for the low-temperature (−60 to −10 °C) oxidation of many classes of alcohols to carbonyl compounds in high yields. During those investigations we also examined the reaction of the Me_2SO–OC reagent with selected arylsulfonamides, methanesulfonamide, *p*-toluenesulfonylhydrazide, *p*-nitroaniline, and *p*-nitrobenzamide for the preparation of iminosulfuranes (sulfilimines) at −60, −20, and 0 °C (procedures A, B, and C respectively); the results are reported in this note (Table I).

p-Chlorobenzenesulfonamide was employed as a model; excellent yields (85–94%) of iminosulfuranes were obtained by procedures A, B, and C, although A and C yield products of somewhat higher purity. Since the low temperatures used in procedure A cause solubility problems and require the use of large amounts of solvent to achieve homogeneity, it was abandoned in favor of B and C. On the basis of the melting points of the once-precipitated products and convenience of operation at 0 °C, procedure C was adopted as the preferred procedure. However, it is necessary to use larger quantities of OC as considerable decomposition of the Me_2SO–OC reagent occurs at the relatively high reaction temperature. Operationally, OC is preferably added to the Me_2SO solution of the amino compound to trap as much Me_2SO–OC reagent as possible before it decomposes. With *p*-nitroaniline, aqueous sodium hydroxide is preferred for basification rather than triethylamine (TEA) as product purification seemed easier with the former.

Only one carboximide, *p*-nitrobenzamide, was examined with the Me_2SO–OC reagent (procedure A). The major product (70%) was the nitrile corresponding to the amide; iminosulfurane was the minor product (15%), as determined by LC of the crude reaction mixture. Some unreacted amide was still present. Iminosulfuranes were not isolable from methanesulfonamide and *p*-toluenesulfonylhydrazide upon reaction with the Me_2SO–OC reagent. No further studies were carried out with these amino compounds.

Experimental Section[8]

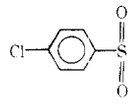
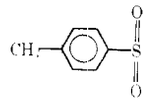
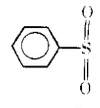
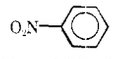
Preparation of Iminosulfuranes (Table I). Procedure C (Preferred Method, 0 °C). To a stirred solution of Me_2SO (5 mL, 71 mmol) and *p*-chlorobenzenesulfonamide (1.92 g, 10 mmol) in CH_2Cl_2 (40 mL) at 0 °C (ice bath) in a 100-mL three-neck flask, OC (1.9 mL, 22 mmol) in CH_2Cl_2 (5 mL) at 0 °C was added in 15 min. After an additional 30 min at 0 °C, TEA (8.5 mL) was added dropwise in ca. 5 min at 0–5 °C. The reaction mixture was allowed to warm to room temperature, diluted with additional CH_2Cl_2 (ca. 120 mL), and washed successively with water (50 mL), sodium chloride solution (50 mL), 2 N NaOH (50 mL), and sodium chloride solution (50 mL). The organic layer was dried over anhydrous $MgSO_4$ and filtered and the solvent was evaporated in a rotary vacuum evaporator at room temperature. The solid residue was dissolved in a minimum quantity of warm CH_2Cl_2 (5–10 mL) and ether (15–20 mL) was added until no further precipitation occurred. After being cooled to 0–5 °C, the precipitate was filtered and dried. IR, NMR, R_f, and melting points were virtually identical with those of an authentic sample.[1,5]

Procedure B (−20 °C). Similar to C except for the higher reaction temperature and the use of a smaller excess of OC (1.3 mL, 15 mmol) and TEA (7.0 mL).

Procedure A (−60 °C). Similar to C except that Me_2SO (1.8 mL, 25.5 mmol) in CH_2Cl_2 (5 mL) was added to OC (0.95 mL, 11 mmol) in CH_2Cl_2 (25 mL) at −60 °C. *p*-Chlorobenzenesulfonamide (1.92 g, 10 mmol) in Me_2SO (8 mL)–CH_2Cl_2 (12 mL) was then added and stirring was continued for an additional 75 min at −60 °C. TEA was added at −60 °C. The remainder of the workup paralleled procedure C.

Miscellaneous. The remaining sulfilimines in Table I were prepared by procedures B and C from Me_2SO, OC, and the appropriate amino compound. With *p*-nitroaniline aqueous NaOH was preferred for basification rather than TEA. The preparative procedures were unsatisfactory with *p*-nitrobenzamide, methanesulfonamide, and *p*-toluenesulfonylhydrazide.

Table I. *S,S*-Dimethylsulfilimines,[a] $(CH_3)_2S^+N^-R$

R	registry no.	procedure[b]	yield, %[c]	mp, °C[c]	lit. mp, °C
	52259-84-4	A	85	116–117	116–117[5]
		B	94	113–115	
		C	90	116–117	
	13150-75-9	B	95	153–155	158–159[6]
		C	89	158–159	
	19871-30-8	B	80	126–127	131[7]
		C	73	128–129	
	27691-52-7	B	73	168–170	172–174[5]

[a] IR and NMR spectra and R_f values (TLC) were identical with those of authentic specimens. [b] Procedure A: −60 °C, 1 h; OC, 11 mmol; arylsulfonamide, 10 mmol. Procedure B: −20 °C, 1 h; OC, 15 mmol; amide or amine, 10 mmol. Procedure C: 0 °C, 0.5 h; OC, 22 mmol; amide, 10 mmol. Excess Me_2SO was used in all cases with CH_2Cl_2 as solvent (see Experimental Section). TEA was used for basification except in the reaction of *p*-nitroaniline in which aqueous NaOH was preferred. [c] After one precipitation–purification step.

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Registry No.—*p*-chlorobenzenesulfonamide, 98-64-6; *p*-tolylsulfonamide, 70-55-3; benzene sulfonamide, 98-10-2; *p*-nitroaniline, 100-01-6; dimethyl sulfoxide, 67-68-5; oxalyl chloride, 79-37-8.

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(8) Starting materials and instrumentation used are described in references 1, 3, 4, and 5. *Caution:* Reaction of Me_2SO with OC is highly exothermic.

Synthesis and Molecular Structure of 1,3-Dihydro-1-hydroxy-3-methyl-1,2,3-benziodoxaphosphole 3-Oxide

Terry M. Balthazor,* James A. Miles, and Bailey Ray Stults

Monsanto Agricultural Products Company, Research Department, St. Louis, Missouri 63166

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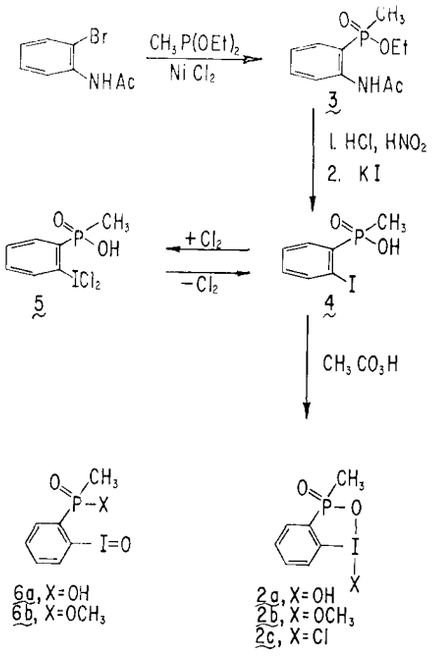
Synthesis of iodosobenzene substituted with phosphorus and sulfur acids in the ortho position has been the subject of several papers[1] since Willgerodt[2] first prepared 2-iodosobenzoic acid (1) in 1893. In all cases, an iodinane (tricoordinate iodine) structure has been proposed based on chemical stability, pK_a measurements, and absorption spectroscopy. This note describes the synthesis and NMR spectra of iodinane **2a.** That **2a** is a tricoordinate iodinane is confirmed by an X-ray structure determination.



The synthesis of iodinane **2a** is outlined below. Arylphosphinate **3** is prepared in 98% yield via a $NiCl_2$-catalyzed Arbuzov reaction of diethyl methylphosphonite and 2-bromoacetanilide. Without purification, **3** is hydrolyzed, diazotized, and converted to the aryl iodide **4.** Much tar is formed in this preparation, making purification by standard methods difficult. Taking advantage of the ease of oxidation of aryl iodides by chlorine[3] renders this purification trivial. Passing chlorine through a $CHCl_3$ solution of the mixture causes crystallization of iododichloride **5.** Heating **5** in boiling $CHCl_3$ induces reductive elimination of chlorine to give **4** on cooling. Oxidation of **4** to **2a** with peracetic acid completes the sequence.

The field desorption mass spectrum of **2a** exhibits, in addition to a molecular ion at *m/e* 298, peaks for $M^{+\cdot} - O$ and $M^{+\cdot} - OH$. Loss of oxygen probably arises from the radical cation of **6a.** The NMR spectrum of **2a** (Me_2SO-d_6) shows a broad D_2O exchangeable absorption at δ 8.61 for the hydroxyl proton and a poorly defined aromatic multiplet. The methyl group on phosphorus appears as a sharp doublet (J_{PH} = 14 Hz) at δ 1.40. No unique absorptions for an open tautomer, **6a,** are observed. No broadening of the doublet is observed at −45 °C (CD_2Cl_2). If an equilibrium exists (**2a** ⇄ **6a**), it is rapid even at this low temperature (assuming no accidental equivalence). The carbon α to iodine appears at δ 121.06 in the ^{13}C NMR spectrum of **2a,** in contrast to a value of δ 98.24 for the same carbon in **4.** This large downfield shift, resulting from oxidation of iodine, has been observed by us for several iodide–iodinane systems.[4]

When **2a** is allowed to react with hot methanol, **2b** is formed quantitatively. The methoxyiodinane reacts with moist air to give **2a,** and no satisfactory elemental analysis has been obtained. That **2b** exists as the iodinane and not **6b** is clearly shown by its NMR spectrum. The OCH_3 group appears as a singlet (no PH coupling, as would be expected for **6b**) at δ 4.25.

No chloroiodinane **2c** is detected on reaction of **5** with triethylamine, sodium acetate, or hot methanol. Reduction to **4** is found in all cases.

Crystal Structure of 2a. Figure 1 shows the pertinent intramolecular bond distances and bond angles for **2a.** The values are the average of the two unique molecules composing the asymmetric unit in the triclinic cell. Iodinane **2a** is best described as a slightly distorted trigonal bipyramid about iodine. Least-squares mean calculations for both molecules in the asymmetric unit show the five- and six-membered rings to be essentially planar (maximum deviation from planarity is 0.1 Å, with the dihedral angles between the five- and six-membered rings averaging 4.01°). Mean plane calculations for each iodine atom and the three atoms bonded to it show the bonding geometry about each iodine to be planar to within ±0.04 Å. For complete tables of mean plane calculations, see the paragraph at the end of this paper regarding supplementary material.

The O–I–O bond angle is 171.3°. Deviations from 180° comparable to this have been observed for **1** as well as for other hypervalent compounds.[5,6] Strain in the heterocyclic ring and repulsion between the lone pairs and bonding electrons have been advanced to explain these deflections from a linear three center four-electron bond.[5,6]

The exocyclic and endocyclic I–O bond distances are respectively shorter (0.04 Å) and longer (0.30 Å) than the sum of 1.99 Å expected[5] for an I–O single bond. While the elongation of the endocyclic bond may result from steric strain, a significant amount of ionic character in this bond is probably the major factor. Bonding schemes[7] for hypervalent molecules predict high electron densities on the apical ligands. The phosphinate group can more readily accommodate the partial negative charge than can the OH group, and hence dissymmetry in the I–O bond lengths. Iodinane **1** also has an elongated[5] ring I–O bond (2.30 Å). The slight shortening of the exocyclic I–O bond could result from crystal forces or an electrostatic attraction concomitant with increased positive charge character on iodine. Vast size differences between 5d and 2p orbitals make π overlap unlikely at best.[3] Remaining

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