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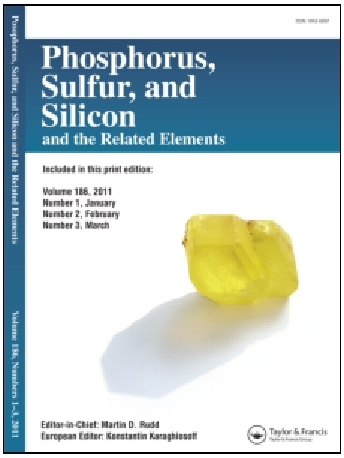

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STERICALLY HINDERED 4-HYDROXYBENZENESULFENYL CHLORIDE: REACTIVITY WITH TRIVALENT PHOSPHORUS ESTERS

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STERICALLY HINDERED 4-HYDROXYBENZENESULFENYL CHLORIDE: REACTIVITY WITH TRIVALENT PHOSPHORUS ESTERS

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The reaction of 3,5-di-*tert*-butyl-4-hydroxybenzenesulfenyl chloride, **1**, with the trialkyl phosphites **5a–d** gave the corresponding *S*-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-*O*,*O*-dialkyl phosphorothiolates **6a–d**. The formation of **6a–d** constitutes chemical evidence for the intermediacy of **1** which was previously inferred from spectroscopic evidence.

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The chemistry of the sulfur-chlorine bond continues to be an active area of research from both a mechanistic and synthetic point of view.[1] The synthetic methodology for the preparation of both sulfenate esters and sulfenamides by the reaction of sulfenyl halides with alcohols and amines, respectively, is well documented in the literature.[2] Sulfenyl derivatives have been used to protect amines, alcohols, and thiols in organic synthesis and have, for example, been used in the synthesis of peptides, penicillins, and nucleosides.[3]

Little is known about the chemistry of hydroxyarenesulfenyl halides which is no doubt due to their propensity for rapid self-condensation.[4] Hydroxyarenesulfenyl halides are proposed intermediates in the reaction of phenols with sulfur dichloride leading to the formation of bis(hydroxyphenyl) sulfides.[4]

The kinetic stabilization of both reactive intermediates and strained molecules is a well-known tool[5] which recently has been used effectively to study the chemistry of phosphorus doubly bonded to itself and other elements.[6] Quite recently, we reported the first observation of a 4-hydroxybenzenesulfenyl chloride (**1**) which was stabilized towards self-condensation by two *tert*-butyl substitutes *ortho* to the hydroxyl group.[7]

The reaction of **1** with amines led to the formation of the diphenoquinone **2** for which **3** was a suggested intermediate formed by the 1,6-elimination of hydrogen chloride from **1**. The existence of **1** was inferred from both the IR and ^{1}H NMR spectral data. In this paper we report chemical evidence for the existence of **1**.

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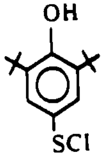

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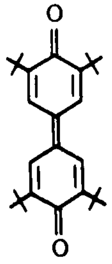

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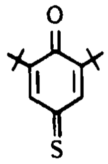
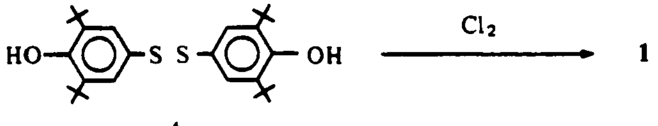


3

RESULTS AND DISCUSSION

The reaction of sulfenyl chlorides with phosphites is well-known in the literature. Denney *et al.* have studied the mechanism of the reaction of trisubstituted phosphites with benzenesulfenyl chloride for which stereochemical results were consistent with nucleophilic attack of phosphorus on sulfur to give a phosphonium ion intermediate.[8]

The reaction of **1**, prepared *in situ* from the disulfide **4** and chlorine, with **5a** gave the *O,O,S*-trisubstituted phosphorothiolate **6a** (50% recrystallized). The spectral and elemental data were fully in accord with the proposed structure **6a**. Similarly, **6b**–**c** were prepared by the reaction of **1** with the corresponding phosphites **5b**–**c**.



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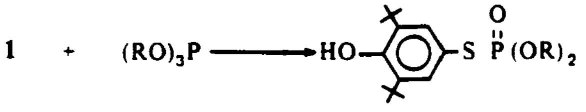

5

a. Ethyl
b. n-Butyl
c. Phenyl
d. Methyl

6

a. Ethyl
b. n-Butyl
c. Phenyl
d. Methyl

The formation of **1** by the reaction of the **4** with sulfuryl chloride was investigated.[9] The course of the reaction was monitored by ^{1}H NMR spectroscopy. One equivalent of sulfuryl chloride was added to a solution of **4** in carbon tetrachloride at −5°C. The ^{1}H NMR spectrum of the reaction mixture showed the formation of new resonances corresponding to those previously reported for **1**.[10]

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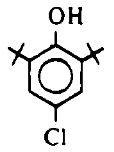

7

The addition of **5d** to **1** prepared from **4** and sulfuryl chloride gave **6d** (68% recrystallized). The examination of the reaction mixture prior to workup by ^{1}H NMR spectroscopy showed only **6d**. No evidence was observed in the ^{1}H NMR spectrum for the diphenoquinone **3**. A reasonable explanation for these observations is that the trivalent phosphites do not promote 1,6-elimination of hydrogen chloride from **1** in comparison to the more-basic amines.[11]

Interestingly, solutions of **1** allowed to stand at room temperature form the diphenoquinone **2** suggesting the slow thermal elimination of hydrogen chloride. The formation of chlorinated phenol **7** was also concurrently observed.[12] The known rearrangement of benzenesulfenyl chlorides to chlorobenzenes provides a reasonable explanation for the formation of **7**.[13]

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EXPERIMENTAL

All melting points were determined in open capillary tubes with a Thomas-Hoover melting point apparatus and are uncorrected. ^{1}H NMR spectra were taken on a Varian Model CFT-20 or XL-200 spectrometer. ^{31}P NMR spectra were taken on a Varian Model CFT-20 or XL-200 spectrometer. ^{31}P NMR spectra were taken on a Varian model XL-200 spectrometer. All ^{1}H chemical shifts are reported in ppm relative to tetramethylsilane. ^{31}P chemical shifts are reported in ppm relative to 85% phosphoric acid (external), where a positive sign is downfield from the standard. ^{31}P NMR spectra were acquired using a 35° flip angle, a 1.4s repetition rate with 0.6s pulse delay and with full proton decoupling. IR spectra (1% solution; sodium chloride cells) were recorded on a Perkin-Elmer Model 1300 spectrometer, and reported peak absorptions are estimated to be accurate to ± 10 cm^{-1}.

Mass spectra were obtained on a Finnigan Model 8200 mass spectrometer. All spectral data were obtained on analytical samples. Solvents were dried prior to use. Reagents were purchased from Aldrich Chemical Company. Reactions were carried out in flame-dried apparatus under a dry nitrogen atmosphere. Elemental analyses were performed by Analytical Research Services, CIBA-GEIGY Corporation.

S-(3,5-Di-tert-butyl-4-hydroxyphenyl)-O,O-diethyl phosphorothiolate, (**6a**). To a stirred solution of 18.96 g (40 mmol) of **4** in 50 mL of toluene at -35 to -45°C was introduced 3.46 g (48 mmol) of chlorine gas through a gas-disparging tube over a 30 m period. The reaction mixture was stirred at -35°C and then to the resultant orange-red solution as added dropwise 13.28 g (80 mmol) of **5a** maintaining the temperature between -35 and -30°C during the addition. The reaction mixture was allowed to warm to rt and it was stirred overnight.

The solvent was removed *in vacuo* and the residue was triturated with 50 mL of hot petroleum ether. The resultant solid was recrystallized from toluene to give 14.8 g (50%) of a white solid: mp 155–157°C; IR (CH_2Cl_2): ν 3635 (OH) cm^{-1}; ^{31}P NMR (benzene $-d_6$): δ 22.4; ^{1}H NMR ($CDCl_3$): δ 1.27 (t, CH_3, 6 H), 1.40 (s, $C(CH_3)_3$, 18 H), 4.15 (dq, CH_2, 4 H), 5.46 (s, OH, 1 H), 7.30 (m, ArH, 2 H). Anal. Calcd. for $C_{18}H_{31}O_4PS$: C, 57.7; H, 8.3; P, 8.3. Found: C, 58,0, H, 7.9; P, 8.3.

S-(3,5-Di-tert-butyl-4-hydroxyphenyl)-O,O-di-n-butyl phosphorothiolate, (**6b**). By the procedure used to prepare compound **6a**, compound **6b** was prepared from 18.96 g (40 mmol) of **4**, 3.64 g (48 mmol) of chlorine gas, and 22.00 g (88 mmol) of **5b**. The residue was recrystallized twice from petroleum ether to give 15.0 g (44%) of a white solid: mp 64–66°C; IR (CCl_4): ν 3640 (OH) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.93 (t, CH_3, 6 H), 1.47 (m, 26 H), 4.23 (dq, OCH_2, 4 H), 5.33 (br s, OH, 1 H), 7.50 (m, ArH, 2 H). Anal. Calcd. for $C_{22}H_{39}O_4PS$: C, 61.4; H, 9.1. Found: C, 61.5; H 9.4.

S-(3,5-Di-tert-butyl-4-hydroxyphenyl)-O,O-diphenyl phosphorothiolate, (**6c**). By the procedure used to prepare compound **6a**, compound **6c** was prepared from 14.20 g (30 mmol) of **4**, 2.6 g (36 mmol) of chlorine gas, and 26.50 g (60 mmol) of triphenyl phosphite. The residue was recrystallized from acetonitrile to give 4.6 g (16%) of a white solid: mp 130–132°C; IR (CH_2Cl_2): ν 3635 (OH) cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.47 (s, $C(CH_3)_3$, 18 H), 5.59 (br s, OH, 1 H), 7.33 (complex m, ArH, 12 H). Anal. Calcd. for $C_{26}H_{31}O_4PS$: C, 66.4; H, 6.6; P, 6.6. Found: C, 66.2; H, 6.8; P, 6.7.

S-(3,5-Di-tert-butyl-4-hydroxyphenyl)-O,O-dimethyl phosphorothiolate, (**6d**). To a stirred solution of 9.5 g (20 mmol) of **4** in 50 mL of carbon tetrachloride at $-5°C$ was added a solution of 2.7 g (20 mmol) of sulfuryl chloride in 10 mL of carbon tetrachloride. The reaction mixture was stirred at 0 to $-5°C$ for 1 hour. The ^1H NMR spectrum of a sample of the reaction mixture [10] was identical to that previously reported.[7] To the reaction mixture at $-20°C$ was added dropwise a solution of 4.96 g (40 mmol) of trimethyl phosphite. After the addition was complete, the reaction mixture was allowed to warm to room temperature. The solvent was removed *in vacuo* and the residue was recrystallized from heptane to give 10.3 g (68%) of a white solid: 128–131°C; IR (CH_2Cl_2): ν 3625 (OH) cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.53 (s, $C(CH_3)_3$, 18 H), 3.85 (d, OCH_3, $^3J_{POCH} = 12.2$ Hz, 6 H), 7.31 (s, ArH, 2 H). Calcd. for $C_{16}H_{27}O_4PS$: C, 55.5; H, 7.9. Found: 55.3; H, 7.8.

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REFERENCES AND NOTES

1. For reviews, see (a) C. R. Russ and I. B. Douglass in *Sulfur in Organic and Inorganic Chemistry*; A. Senning, Ed.; Marcel Dekker: New York, 1971; Vol. 1, Chp. 8; (b) E. Kuhle, *Synthesis*, 563 (1971); (c) E. Kuhle, *Synthesis*, 617 (1971); (d) L. Field, *Synthesis*, 101 (1972); (e) L. Field, *Synthesis*, 713 (1978); (f) W. H. Hardstaff and R. F. Langer in *Sulfur in Organic and Inorganic Chemistry*, A. Senning, Ed.; Marcel Dekker: New York, 1982, Vol. 4, Chp. 5.
2. (a) N. Kharasch, S. J. Potempa and A. Wehrmeister, *Chem. Rev.*, **39**, 269 (1946); (b) R. B. Langford and N. Kharasch, *J. Org. Chem.*, **23**, 1649 (1958); (c) L. L. Chang, D. B. Denney, D. Z. Denney and R. J. Kazior, *J. Am. Chem. Soc.*, **99**, 2293 (1977); (d) D. B. Denney, D. Z. Denney and D. M. Gavrilovic, *Phosphorus Sulfur*, **11**, 1 (1981).
3. For examples, see: T. W. Green, *Protective Groups in Organic Synthesis*; Wiley-Interscience: New York, 1981.
4. (a) C. Y. Meyers and G. Picciola, *Tetrahedron Lett.*, 971 (1962); (b) S. Cabiddu, F. Ciuccatosta, M. T. Cocco, G. Loi and M. Secci, *J. Heterocycl. Chem.*, **14**, 123 (1977).
5. For examples, see: C. Wentrup *Reactive Intermediates*; Wiley-Interscience, 1984, pp. 265–326.
6. (a) M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu and T. Higuchi, *J. Am. Chem. Soc.*, **103**, 4587 (1981); (b) E. Niecke and R. Ruger, *Angew. Chem., Int. Ed. Engl.*, **22**, 155 (1983); (c) A. H. Cowley, J. G. Lasch, N. C. Norman, M. Pakulski and B. R. Whittlesey, *J. Chem. Soc., Chem. Comm.*, 881 (1983); (d) A. H. Cowley, J. E. Kilduff, N. C. Norman and M. Pakulski, *J. Am. Chem. Soc.*, **105**, 4845 (1983); (e) M. Yoshifuji, K. Shibayama, N. Inamoto, T. Matsushita and K. Nishimoto, *J. Am. Chem. Soc.*, **105**, 2495 (1983); (f) M. Yoshifuji, I. Shima, K. Shibayama and N. Inamoto, *Tetrahedron lett.*, **25**, 411 (1984).
7. S. D. Pastor, *J. Org. Chem.*, **49**, 5260 (1984).
8. D. B. Denney and M. A. Moskal, *Phosphorus*, **4**, 77 (1974).
9. H. Brintzinger, K. Pfannstiel, H. Koddebusch and K. E. Kling, *Chem. Ber.*, **83**, 87 (1950).
10. An equal volume of deuteriochloroform was added to provide a deuterium lock for the ^1H NMR spectrometer.
11. (a) J. G. Verkade, *Phosphorus Sulfur*, **2**, 251 (1976); (b) L. J. Vande Griend, J. G. Verkade, J. F. M. Pennings and H. M. Buck, *J. Am. Chem. Soc.*, **99**, 2459 (1977); (c) R. R. Hodges, F. A. Houle, J. L. Beuchamp, R. A. Montag and J. G. Verkade, *J. Am. Chem. Soc.*, **102**, 932 (1980); (d) K. Taira and D. G. Gorenstein, *J. Am. Chem. Soc.*, **106**, 7825 (1984).
12. A quantity of **7** was isolated from the reaction mixture, mp 75–78°C; ^1H NMR ($CDCl_3$): δ 1.51 (s, $C(CH_3)_3$, 18 H), 5.64 (s, OH, 1 H), 7.10 (s, ArH, 2 H); MS: m/z 240 (M^{+}). Calcd. for $C_{14}H_{21}ClO$: C, 69.8; H, 8.8. Found: C, 69.9; H, 8.6
13. R. Mayer and H. J. Frey, *Angew. Chem.*, **76**, 861 (1964).