Preparation and Reaction of Compounds Related to 2,2,4,4-Tetramethylpentane-3-thiol [Di(*tert*-butyl)methanethiol]

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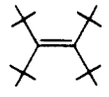
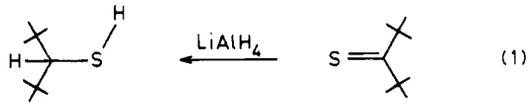
Reduction with lithium aluminum hydride of 2,2,4,4-(tetramethyl)pentane-3-thione (**3**) gives the thiol (**2**). Treatment of **2** with chlorine affords 2,2,4,4-(tetramethyl)pentane-3-sulfenyl chloride (**4**), the reactions of which were investigated. Substitution of **4** on sulfur proceeds normally with diazomethane, phthalimide, and methanol. Hydrolysis of **4** likely provides the corresponding sulfenic acid (**11**), which dimerizes to a thiol sulfoxide (**7**). Reaction of **4** with ozone gives 2,2,4,4-(tetramethyl)pentane-3-sulfinyl chloride (**8**). This compound can be converted to the sulfine (**13**) by treatment with pyridine at −30 °C. Several substitution reactions on sulfinic sulfur were investigated. Alkylation of **2** with benzyl bromide and oxidation of this product gave benzyl[2,2,4,4-(tetramethyl)-3-pentyl] sulfone (**17**) that was converted to a dianion on treatment with excess *n*-butyllithium. Some reactions of this dianion were investigated.

We, and others,[1] have been interested for some time in devising a synthesis of tetra-*tert*-butylethylene (**1**). Although our experiences in this area parallel those of other workers, namely failure to obtain **1**, we have during this effort developed a considerable amount of chemistry centered around the thiol **2**, which we viewed as a possible intermediate in a synthesis of **1**. We now report some of the chemistry of this hindered thiol.



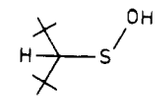
1

Thiol **2** was prepared in excellent yield by reduction (eq 1) of di(*tert*-butyl)thione (**3**), which has recently become available.[1a,2] This thiol proved more susceptible to chemical manipulation than its oxygen analogue, di(*tert*-butyl)carbinol, which enters cleanly into relatively few reactions other than esterification.[3,4]



2 **3** (1)

Reaction of **2** with chlorine[5] proceeded smoothly to give in essentially quantitative yield the sulfenyl chloride (**4**). This compound was not stable enough for analysis and was characterized by spectral data and reactions as outlined in Scheme I. Attempts to add **4** to olefins failed to give characterizable products. However, the reactions with phthalimide[6] and methanol[7] to form respectively the *N*-(alkylthio)phthalimide **5** and the sulfenate ester **6** are characteristic for reasonably stable sulfenyl chlorides. The corresponding sulfoxide and sulfone derivatives of **5** were also prepared. With water **4** reacted cleanly to give the thiosulfinate **7**, which is the expected condensation product of the sulfenic acid **11**.[8] Attempts to trap **11** by addition to conjugated systems were unsuccessful, however. Oxidation of **4** with ozone was extremely clean and gave the sulfinyl chloride **8**; all attempts to force the reaction further failed. The same was true with *m*-chloroperbenzoic acid (MCPBA) as oxidant, which gave again, even under the most forcing conditions, only **8**. We were unable to obtain the sulfonyl chloride. The samples of **8** prepared by oxidation with MCPBA were for unknown reasons not stable and on attempted purification by chromatography on silica gel the product decomposed readily to give chiefly the unsaturated chloride **12**. A mechanism involving the formation of the di(*tert*-butyl) carbonium ion is likely involved in the formation of **12**.[3]



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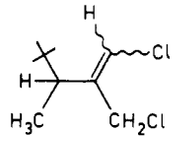
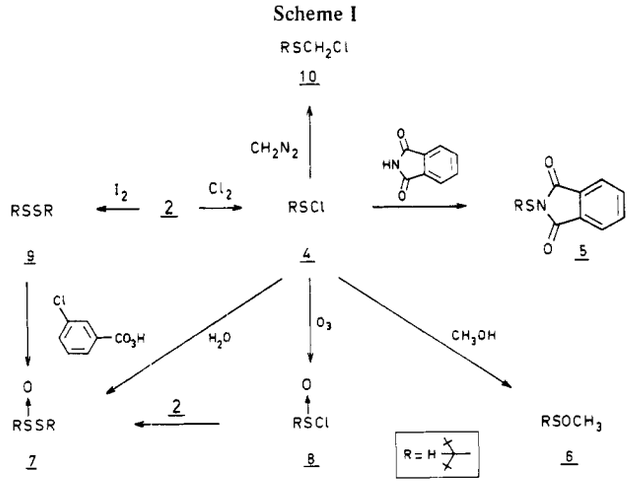


12

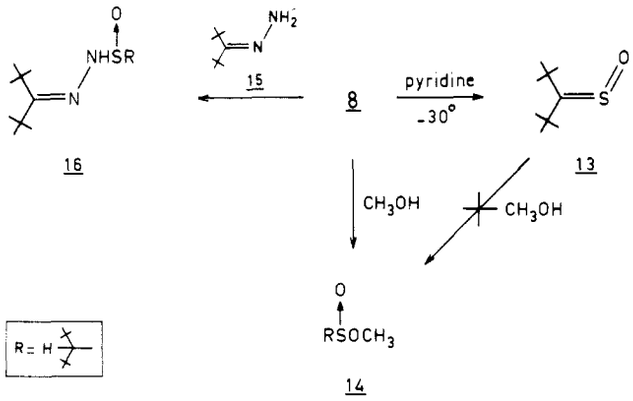
Scheme I



The thiolsulfinate **7** was also obtained by oxidation with MCPBA of disulfide **9**, formed by the (rather sluggish) oxidation of **2**. The combination of **2** with **8** afforded also the thiolsulfinate. Reaction of **2** with diazomethane[9] proceeded normally to give chloromethyl compound **10**.

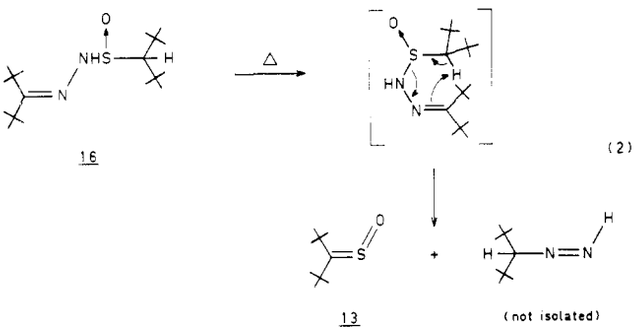
Some additional reactions as shown in Scheme II were carried out on sulfinyl chloride **8**. Dehydrohalogenation with pyridine at −30 °C gave cleanly the sulfine **13**, which has been prepared previously by Barton and co-workers by oxidation of the thione **3**.[10,2] No or only a very poor yield of **13** was obtained on treating **8** with pyridine at temperatures higher than −30 °C, with triethylamine, diisopropylamine, or calcium hydroxide.[11]

Scheme II



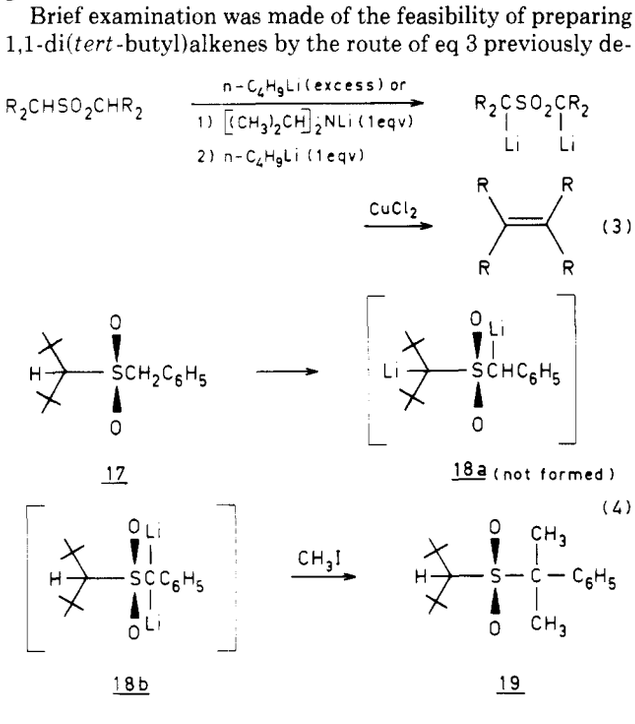
Since reaction with methanol gave the sulfinate ester **14**, whereas sulfine **13** fails to react with methanol, we suspect that there is a competition in the reactions of **8** between catalyzed elimination leading to sulfine formation and attack at sulfur to form sulfinates, which can be isolated when suitable nucleophiles like methanol or **2** are used.

A rather interesting reaction of **8** was with the hydrazone of di-*tert*-butyl ketone (**15**)[17] as shown in eq 2. The condensation product **16** was isolated in good yield; attempts to couple by pyrolytic means the two di(*tert*-butyl)methyl (or methylene) units resulted in the formation of the sulfine **13** as the only isolated product. A possible sigmatropic rearrangement that could lead to **13** is shown in eq 2. Other paths involving initial homolysis of a bond can, of course, be suggested.



(2)

Brief examination was made of the feasibility of preparing 1,1-di(*tert*-butyl)alkenes by the route of eq 3 previously developed for simple alkenes.[13] Reaction of **2** with benzyl bromide gave the alkylated product, which was oxidized to the sulfone **17**. Treatment of **17** with excess *n*-butyllithium or alternatively first with 1 equiv of diisopropylamide followed by 1 equiv of *n*-butyllithium gave a light yellow solution thought to contain a dicarbanion.[14] Oxidation with $CuCl_2$ gave, however, no isolable amounts of alkene and swamping of the solution with methyl iodide gave in good yield **19**. This suggests that not the α,α' dianion **18a** but rather α,α dianion **18b** is formed (eq 4).



(3)

(4)

Experimental Section

All melting points were determined with a calibrated melting point block or with a Mettler automatic melting point apparatus. UV, IR ^{1}H NMR, and mass spectra were obtained using common laboratory instruments. ^{13}C NMR measurements were made at 25.2 MHz and chemical shifts are relative to Me_4Si.

Chemicals cited without reference were either in stock or were prepared following well-described procedures. Elemental analyses were carried out in the analytical laboratory of this university.

2,2,4,4-Tetramethylpentane-3-thiol (2) was prepared by the reduction of 2,2,4,4-tetramethyl-3-pentanethione (3.0 g, 19 mmol) in dry ether (50 ml) added dropwise to a stirred suspension of $LiAlH_4$ (0.34 g, 10 mmol) in dry ether (70 ml). The solution was let stand for 2 h. After neutralization with dilute H_2SO_4 and workup there was obtained 285 mg (17.8 mmol, 94%) of thiol: bp (43 mm) 96–98 °C; IR (CCl_4) 1150, 1205, 1360, 1395, and 1480 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.10 [s, 18, $(CH_3)_3C$], 1.22 (d, J = 8 Hz, SH), and 2.60 (d, J = 8 Hz, CH).

Anal. Calcd for $C_9H_{20}S$: C, 67.43; H, 12.67; S, 20.00. Found: C, 67.62; H, 12.63; S, 19.75.

2,2,4,4-Tetramethylpentane-3-sulfenyl chloride (4) was prepared by treating a stirred solution of **2** (1.6 g, 10 mmol) in 10 ml of dry CCl_4 with a stream of dry Cl_2 at 0 °C. The reaction was followed by ^{1}H NMR and was stopped once conversion was complete. The material had ^{1}H NMR δ 1.20 [s, 18, $(CH_3)_3C$] and 2.75 (s, 1, CH). The material was only moderately stable and was used without further purification save that excess Cl_2 was blown out of solution with a stream of N_2. Addition of excess Cl_2 gave no evidence for the addition of a second mole of Cl_2 to the sulfur atom. Although the point is not rigorously proven, we believe that exclusively RSCl and not $RSCl_3$ is the compound formed.

***N*-[(2,2,4,4-Tetramethyl)-3-pentyl]thiophthalimide (5)** was prepared by allowing a freshly prepared solution of **4** (10 mmol) in CCl_4 to react with a stirred slurry of phthalimide (1.47 g, 10 mmol) and triethylamine (1.5 g, 15 mmol) in 20 ml of CCl_4 over a period of one night. Water (25 ml) was added, and the organic layer was separated and dried over $MgSO_4$. The product was recrystallized from CH_3OH affording 3.02 g (10 mmol, 99% yield) of **5** as a white solid: mp 118–120 °C; ^{1}H NMR (CCl_4) δ 1.22 [s, 18, $(CH_3)_3C$], 3.10 (s, 1, CH), and 7.70 (complex, 4, C_6H_4); IR (KBr) 1720, 1700, 1470, 1290, 1050, 870, and 700 cm^{-1}.

Anal. Calcd for $C_{17}H_{23}NO_2S$; C, 66.85; H, 7.59; N, 4.59; S, 10.50. Found: C, 66.89; H, 7.67; N, 4.55; S, 10.53.

Oxidation of **5** to the sulfinamide was carried out by treating **5** (102 mg, 0.35 mmol) dissolved in $CHCl_3$ with *m*-chloroperbenzoic acid (67 mg, 0.33 mmol) at room temperature. Workup gave 103 mg (0.32 mmol, 92% yield) of the sulfinamide: mp 155–160 °C; ^{1}H NMR δ 1.17 [s, 9, $(CH_3)_3C$], 1.40 [s, 9, $(CH_3)_3C$], 4.35 (s, 1, CH), and 7.80 (complex 4, C_6H_4); IR (KBr) 1020 cm^{-1} (S–O).

Anal. Calcd for $C_{17}H_{23}NO_3S$: C, 63.53; H, 7.21; N, 4.35; S, 9.98. Found: C, 63.61; H, 7.12; N, 4.34; S, 9.82.

The sulfonamide of **5** was prepared by treating **5** (102 mg, 0.35 mmol) dissolved in $CHCl_3$ with *m*-chloroperbenzoic acid (134 mg, 0.66 mmol). Workup gave 109 mg (0.32 mmol, 92% yield) of the sulfonamide as a white solid: mp 167–169 °C; IR (KBr) 1300 cm^{-1} (SO_2); ^{1}H NMR (CCl_4) δ 1.42 [s, 18, $(CH_3)_3C$], 3.85 (s, 1, CH), and 7.58 (complex, 4, C_6H_4).

Anal. Calcd for $C_{17}H_{23}NO_4S$: C, 60.51; H, 6.87; N, 4.15; S, 9.50. Found: C, 60.70; H, 6.90; N, 4.13; S, 9.52.

The sulfinamide **5** was also prepared in 73% isolated yield from the reaction of **4** with phthalimide in CCl_4 at −15 °C with added triethylamine.

***O*-Methyl[2,2,4,4-(tetramethyl)-3-pentyl] sulfenate (6)** was prepared by allowing freshly prepared **4** (300 mg, 1.5 mmol) in CCl_4 to react with excess methanol and triethylamine (200 mg, 2 mmol) with stirring at room temperature. After disappearance of the yellow color the precipitated triethylamine hydrochloride was removed by

filtration to give 244 mg (1.28 mmol, 85% yield) of crude **6**: bp (0.2 mm) 48 °C; IR (neat) 1430–1490, 1390, 1365, 1220, and 1000 cm^{-1}; ^1H NMR (CCl_4) δ 1.15 [s, 18, $(CH_3)_3C$], 2.63 (s, 1, CH), and 3.58 (s, 3, CH_3O); mass spectrum *m/e* 190 (parent) (calcd for $C_{10}H_{22}SO$, 190). An acceptable elemental analysis could not be obtained.

2,2,4,4-(Tetramethyl)-3-pentylsulfinyl chloride (8) was best prepared by leading for several hours a stream of ozone through a solution of **4** (5 mmol) dissolved in CCl_4. The course of reaction was followed by ^1H NMR and reaction was stopped once the absorption for **8** had disappeared. As judged by ^1H NMR the sulfinyl chloride was formed in quantitative yield: ^1H NMR (CCl_4) δ 1.27 [s, 9, $(CH_3)_3C$], 1.35 [s, 9, $(CH_3)_3C$], and 3.18 (s, 1, CH); IR (neat) 1300, 1260, 1215, 1150 cm^{-1}. A satisfactory elemental analysis could not be obtained.

Alternatively **4** could be oxidized with *m*-chloroperbenzoic acid to give **8** in 65% yield. On attempted purification by chromatography over silica gel a product was isolated to which structure **12** was assigned: bp (45 mm) 120 °C; IR (neat) 1625, 1460, 1365, 1375, and 825 cm^{-1}, ^1H NMR (CCl_4) δ 0.93[s, 9, $CH_3)_3C$], 1.14 (d, J = 7 Hz, 3, CH_3), 2.32 (q, J = 7 Hz, 1, CH_3CH), 3.91 (d, J = 11 Hz, 1, CH_aH_bCl), 4.43 (d, J = 11 Hz, 1. CH_aH_bCl), and 6.02 (s, 1, vinyl H); ^{13}C NMR ($CDCl_3$, δ relative to Me_4Si) δ 15.5 (q, J = 128 Hz, CH_3CH), 27.7 [q, J = 128 Hz, $(CH_3)_3C$], 33.9 [s, $(CH_3)_3C$], 42.5 (t, J = 152 Hz, CH_2Cl), 47.7 ppm (d, J = 120 Hz, CH_3CH), 120.1 ppm (d, J = 192 Hz, CHCl), and 142.2 (s, CCH_2Cl).

Di[2,2,4,4-(tetramethyl)-3-pentyl] disulfide (9) was prepared by dissolving thiol **2** (1.69, 10 mmol) in 3 ml of 15% NaOH solution and allowing this to react with I_2 (1.09 g, 4 mmol) added in portions. The reaction was carried out in an ice bath and the mixture was allowed to stir for 12 h thereafter. The upper layer was separated, the lower layer was extracted three times with ether, and the organic layers were combined and dried over $MgSO_4$. Filtration and removal of the solvent gave 1.65 g (5 mmol, 100% yield) of crude **9**: mp 75.5–76 °C; IR (KBr) 2900–3000, 1475, 1390, 1365, 1250, and 1220 cm^{-1}; ^1H NMR (CCl_4) δ 1.17 [s, 18, $(CH_3)_3C$] and 2.53 (s, 1, CH).

Anal. Calcd for $C_{18}H_{38}S_2$: C, 67.85; H, 12.02; S, 20.13. Found: C, 67.89; H, 11.94; S, 20.04.

The disulfide was also obtained in quantitative yield by allowing **4** (387 mg, 2 mmol) to react with **2** (320 mg, 2 mmol) in pyridine at room temperature.

Hydrolysis of 2,2,4,4-(tetramethyl)-3-pentylsulfenyl chloride (4) was carried out with a solution of **4** (684 mg, 1.75 mmol), which was allowed to react with ice–water. After stirring for 2 h, the solution was extracted with ether and the organic layer was dried over $MgSO_4$. Removal of the solvent gave 438 mg (1.25 mmol, 70% yield) of 2,2,4,4-(tetramethyl)-3-pentylthiol[2,2,4,4-(tetramethyl)-3-pentyl] sulfinate (**7**): mp 113.5–114.5 °C (from CH_3OH); IR (KBr) 1440–1480, 1390, 1370, and 1080 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.17 [s, 8, $(CH_3)_3C$], 1.22 [s, 9, $(CH_3)_3C$], 1.40 [s, 9, $(CH_3)_3C$], 2.97 (s, 2, CH, absorptions overlap).

Anal. Calcd for $C_{18}H_{38}S_2O$: C, 64.61; H, 11.45; S, 19.16. Found: C, 64.95; H, 11.51; S, 19.17.

The thiolsulfinate **7** was also obtained in nearly quantitative yield by oxidation of disulfide **9** with 1 equiv of *m*-chloroperbenzoic acid. All attempts to oxidize this further afforded only uncharacterizable products.

Reaction of sulfinyl chloride **8** with thiol **2** in pyridine gave also thiolsulfinate **7** in 40% yield.

Di(*tert*-butyl)sulfine (13) was obtained by adding slowly to 10 ml of dry pyridine held at −29 to −30 °C sulfinyl chloride **8** (500 mg, 2.38 mmol) with stirring. After standing with stirring at room temperature for 1 h, the pyridinium hydrochloride was removed by filtration, and the solvent removed to give 400 mg (2.37 mmol, 100% yield) of crude sulfine, pure by ^1H NMR spectroscopy and with physical constants identical with those described previously.[10]

2,2,4,4-(Tetramethyl)-3-pentylmethyl sulfinate (14) was obtained by allowing sulfinyl chloride **8** (0.89 g, 5 mmol) to reflux in 15 ml of absolute CH_3OH. Removal of methanol left exclusively **14**: bp (1 mm) 100 °C; IR (neat) 1450–1500, 1400, 1370, 1125, and 1000 cm^{-1}; ^1H NMR (C_6D_6) δ 1.12 [s. 9, $(CH_3)_3C$], 1.28 [s, 9, $(CH_3)_3C$], 2.32 (s, 1, CH), and 3.30 (s, 3, CH_3O).

Anal. Calcd for $C_{10}H_{22}SO_2$: C, 58.21; H, 10.74; S, 15.54. Found: C, 58.48; H, 10.69; S, 15.22.

Di-*tert*-butyl ketone [2,2,4,4-(tetramethyl)-3-pentyl] sulfinylhydrazone (16) was prepared from the reaction of sulfinyl chloride **8** (2.58 g, 12.4 mmol) and 2,2,4,4-(tetramethyl)-3-pentanone ketazine (1.92 g, mmol, 12.3 mmol) at 0 °C in pyridine (30 ml). After 1 h at this temperature followed by 2 h at room temperature pyridine hydrochloride was filtered off, the solvent removed, and the residue recrystallized from *n*-heptane to give 2.42 g (7.38 mmol, 60% yield) of **16** as a white solid: mp 93.5–95 °C; IR (KBr) 3170, 2800–3000 (br), 1460, 1390, 1375, 1370, 1360, 1220, 1190, 1140, 1075, 1040, 995, and 880 cm^{-1}; NMR (CCl_4) δ 1.30 [s, 9, $(CH_3)_3C$], 1.37 [s, 9, $(CH_3)_3C$], 1.42 [s, 18, $(CH_3)_3C$], 2.50 (s, 1, CH), and 7.52 (s, 1, NH).

Anal. Calcd for $C_{18}H_{38}N_2OS$: C, 65.40; H, 11.59; N, 8.47; S, 9.70. Found: C, 65.39; H, 11.63; N, 8.44; S, 9.75.

Pyrolysis of **16** dissolved in toluene in a sealed tube at 150 °C gave a mixture of products from which sulfine **13** was characterized (70% yield).

Benzyl[2,2,4,4-(tetramethyl)-3-pentyl] sulfide was prepared by allowing a mixture of thiol **2** (1.6 g, 10 mmol), benzyl bromide (1.71 g, 10 mmol), and sodium (250 mg, 10.9 mmol) dissolved in ethanol (4 ml) to stir at room temperature overnight. The solution was diluted with saturated NaCl solution and extracted with ether. After drying, removal of the solvent, and distillation there was obtained 2.5 g (10 mmol, 100% yield) of the sulfide: bp (10 mm) 165–167 °C; IR (neat) 1600, 1500, 1475, 1455, 1390, 1360, and 700 cm^{-1}; ^1H NMR (CCl_4) δ 1.12 [s, 18 $(CH_3)_3C$], 1.25 (s, 1, CH), 3.68 (s, 2, CH_2), and 7.21 (complex, 5, C_6H_5).

Anal. Calcd for $C_{16}H_{26}S$: C, 76.73; H, 10.46. Found: C, 76.40; H, 10.42.

An acceptable analysis for sulfur was not obtained.

The sulfoxide of benzyl [2,2,4,4(tetramethyl)-3-pentyl] sulfide was prepared in the usual fashion by oxidation with 1 equiv of *m*-chloroperbenzoic acid: mp 97–98 °C (from CH_3OH); IR (KBr) 1010–1030 cm^{-1} (S–O); ^1H NMR (CCl_4) δ 1.00 [s, 9, $(CH_3)_3C$], 1.35 [s, 9, $(CH_3)_3C$], 2.25 (s, 1, CH), 4.15 (s, 2, CH_2), and 7.28 (complex, 5, C_6H_5).

Anal. Calcd for $C_{16}H_{26}SO$: C, 72.13; H, 9.84; S, 12.03. Found: C, 61.68; H, 9.70; S, 11.76.

The sulfone **17** was prepared by oxidation of the sulfide with 2 equiv of *m*-chloroperbenzoic acid: mp 71.5–73.5 °C (from CH_3OH); IR (KBr) 700, 1120, and 1300 cm^{-1}; ^1H NMR (CCl_4) δ 1.28 [s, 18, $(CH_3)_3C$], 2.63 (s, 1, CH), 4.19 (s, 2, CH_2), and 7.36 (complex, 5, C_6H_5). The sulfone was characterized as a derivative (see below).

Reaction of Benzyl[2,2,4,4-tetramethyl)-3-pentyl] sulfone (17) with Strong Base. To **17** (213 mg, 0.755 mmol) dissolved in 20 ml of pure, dry dimethoxyethane under dry nitrogen at 0 to −5 °C was added *n*-butyllithium (4.4 mmol). A light brown color developed rapidly; the resulting solution was stirred for 1 h. Methyl iodide (426 mg, 3 mmol) was added rapidly and the solution was stirred for 1 h more at 0 °C and kept overnight at room temperature. Quenching with water and straightforward workup gave 308 mg of crude material that was recrystallized from CH_3OH to give 97 mg (0.313 mmol, 41% yield) of **19**: mp 110–111 °C; IR (KBr) 1470, 1370, 1270, 1110, 1090, 780, and 650 cm^{-1}; ^1H NMR (CCl_4) δ 1.09 [s, 18, $(CH_3)_3C$], 1.77 (s, 6, CH_3), 2.82 (s, 1, CH), and 7.25 (complex, 5, C_6H_5).

Anal. Calcd for $C_{18}H_{30}SO_2$: C, 69.63; H, 9.74; S, 10.33. Found: C, 69.63; H, 9.84; S, 10.24.

Various attempts to oxidize a dianion from **17** following procedures described in ref 13 gave only recovered starting material and/or uncharacterized products.

Chloromethyl[2,2,4,4-(tetramethyl)-3-pentyl] sulfide (10) was prepared by allowing **4** (200 mg, 1.02 mmol) dissolved in ether to react with a slight excess of a diazomethane solution in ether. Stirring was continued for 15 h at room temperature. Any remaining diazomethane was destroyed and the solution was concentrated under reduced pressure. Distillation gave 149 mg (0.717 mmol, 70% yield) of **10**: bp (0.1 mm) 50 °C; IR (neat) 1475, 1395, 1370, 1260, 1230, 1080, 1020, 800 (br), and 725 cm^{-1}; ^1H NMR (CCl_4) δ 1.18 [s, 18, $(CH_3)_3C$], 2.49 (s, 1, CH), and 2.76 (s, 2, CH_2).

Anal. Calcd for $C_{10}H_{21}SCl$: C, 57.53; H, 10.14; S, 15.35; Cl, 16.98. Found: C, 57.43; H, 10.17; S, 15.05.

An acceptable analysis for chlorine was not obtained.

Registry No.—**2**, 57602-97-8; **3**, 54396-69-9; **4**, 61258-91-1; **5**, 61258-92-2; **5** sulfinamide analogue, 61258-93-3; **5** sulfonamide analogue, 61258-94-4; **6**, 61258-95-5; **7**, 61258-96-6; **8**, 61258-97-7; **9**, 58712-15-5; **10**, 61258-98-8; **12**, 61258-99-9; **14**, 61259-00-5; **15**, 33420-22-3; **16**, 61259-01-6; **17**, 61259-02-7; **19**, 61259-03-8; phthalimide, 85-41-6; *m*-chloroperbenzoic acid, 937-14-4; methanol, 67-56-1; ozone, 10028-15-6; benzyl bromide, 100-39-0; benzyl[2,2,4,4-(tetramethyl)-3-pentyl] sulfide, 61259-04-9; benzyl[2,2,4,4-(tetramethyl)-3-pentyl] sulfoxide, 61259-05-0; diazomethane, 334-88-3.

References and Notes

(1) See, for example (a) D. H. R. Barton, F. S. Guziec, Jr., and I. Shahak, *J. Chem. Soc., Perkin Trans. 1*, 1794 (1974); (b) D. H. R. Barton in "Organic Sulphur Chemistry, Structure, Mechanism, and Synthesis", C. J. M. Stirling, Ed., Butterworths, London, 1975, pp 229–235; (c) J. A. Boerma, thesis, Groningen, 1972; there has over the years been much interest in the synthesis of *tert*-butyl substituted alkenes. For representative references on

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Reactions of Cation Radicals of EE Systems. 5. Acid–Base Equilibria in Nucleophilic Reactions of Pyridine and Water with Thianthrene Cation Radical[1a]

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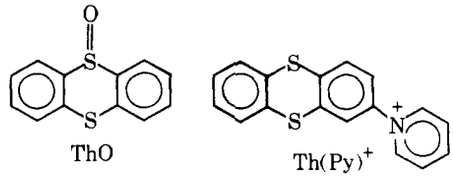
The role of cation radical/nucleophile adduct deprotonation equilibria in the reactions of thianthrene cation radical ($Th^{\cdot+}$) with pyridine and water in acetonitrile solution has been examined using stopped-flow and electrochemical techniques. In both reactions reversible nucleophilic attack and adduct formation at a sulfur site on $Th^{\cdot+}$ is proposed as the first step in a general half-regeneration scheme. Rate-determining electron transfer involves reaction between adduct (oxidant) and deprotonated adduct in the case of a protic nucleophile (e.g., water). In the case of an aprotic nucleophile (e.g., pyridine) the rate-determining encounter is between a nonadducted cation radical and adduct with the adduct functioning here as the reducing agent. The formation of the product of *both* reactions, thianthrene 5-oxide, is discussed in terms of the relative stabilities of the oxidized forms of these cation radical/nucleophile adducts.

Recent studies of the kinetics and mechanisms of the reactions of the 9,10-diphenylanthracene (DPA) cation radical ($DPA^{\cdot+}$) with various nucleophiles and reducing agents[1] suggest that a half-regeneration mechanism[2] predominates in all cases where addition products are observed. Although this scheme is operative in the cases examined thus far, reactions of $DPA^{\cdot+}$ with certain nucleophiles (e.g., chloride)[1d] have exhibited reaction dynamics which are second order in cation radical concentration. These observations are accounted for within the half-regeneration pathway in terms of rapid, reversible cation radical/nucleophile adduct formation which precedes rate-determining electron transfer from this adduct to a second ion radical. By comparison protic nucleophiles (e.g., water) in reaction with $DPA^{\cdot+}$ show a first-order dependence of rate on both nucleophile and cation radical concentration,[3,4] indicative of rate-determining adduct formation. Such observations invite speculation concerning the role of ion radical/nucleophile adduct deprotonation steps and the extent to which processes of this type may influence the observed dynamics of a particular reaction.

An ideal system through which this role can be probed is afforded by the cation radical derived from thianthrene (Th). While the hydrolysis of the thianthrene cation radical ($Th^{\cdot+}$) is known to be second order with respect to radical ion,[5,6] the corresponding anisylation of this species has been accounted for via a half-regeneration mechanism which exhibits concentration-dependent reaction order.[7] This mechanism involves adduction equilibria of the type noted in the chlorination of DPA.[1d]

The reaction of pyridine with $Th^{\cdot+}$ in neat pyridine affords the *ring-substituted* product[8] $Th(Py)^+$ in which charge relief for this two-electron deficient species has occurred via substrate proton loss. Alternatively, the hydrolysis (protic nucleophile) of $Th^{\cdot+}$ affords the addition product, thianthrene 5-oxide (ThO),[5,6] in which charge relief has been attained by



ThO $Th(Py)^+$

discharge of nucleophile protons. The nucleophiles pyridine and water were therefore selected for a comparative evaluation of the mechanistic effects exerted by protic and aprotic nucleophiles upon their respective reactions with the cation radical of thianthrene.