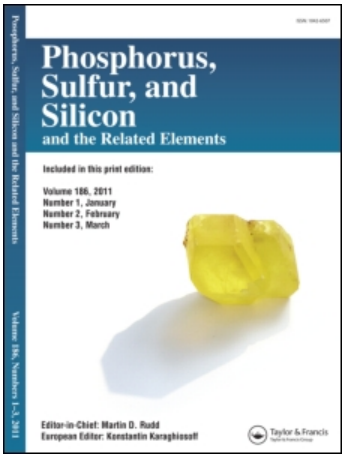

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B. H. Patwardhan[a]; E. J. Parker[a]; D. C. Dittmer[a]
[a] Department of Chemistry, Syracuse University, Syracuse, New York

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SYNTHESIS AND PROPERTIES OF SOME STABLE, NEW THIETES (THIACYLOBUTENES)

B. H. PATWARDHAN, E. J. PARKER and D. C. DITTMER†

†*Department of Chemistry, Syracuse University, Syracuse, New York 13210*

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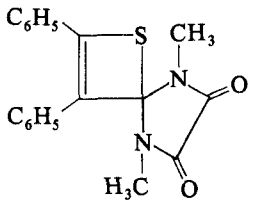
3-Phenyl-, 3-β-naphthyl-, 3-α-thienyl- and 3-α-furylthietes have been prepared. They are considerably more stable than simple, alkyl-substituted thietes. Cobalt cyclopentadienyl complexes of 2-phenylpropenethial and its *S*-methyl derivative have been obtained, the latter exemplifying a new ligand.

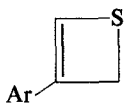
Several simple, alkyl-substituted thietes have been reported.[1] Without exception, they are liquids which decompose rapidly at room temperature to give polymeric material. On the other hand, thietes in which the double bond is part of an aromatic ring system are quite stable,[2] although it may be argued that these are not true thietes since they do not contain a true carbon–carbon double bond. Recently, a highly substituted thiete, (**1**), was reported to be stable.[3] The highly substituted character of (**1**) would appear to disqualify it as a typical representative of thietes as a class, and its reactions may be limited.



(**1**)

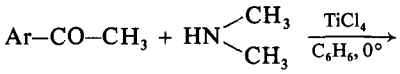
Introduction of an aromatic or heteroaromatic substituent at the 3-position of a thiete, e.g. (**2**), confers considerable stability. The general synthetic procedure is outlined in Scheme 1. (The titanium tetrachloride method[4] is highly recommendable for the preparation of enamines involving dimethylamine.) With the exception of the α-furyl derivative, all are solids which, however, do decompose on melting. 3-Phenyl- and 3-β-naphthylthiete have been purified without decomposition by sublimation.

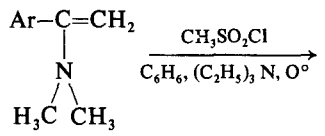
Photolysis of 3-phenylthiete in the presence of cyclopentadienyl cobalt dicarbonyl leads to a complex, (**7**), best formulated, in accordance with the spectroscopic data, as a derivative of 2-phenylpro-



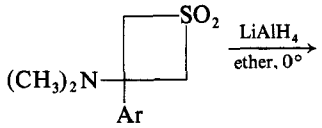
(**2**)

$Ar = C_6H_5, \beta\text{-}C_{10}H_7, \alpha\text{-}C_4H_3S, \alpha\text{-}C_4H_3O$

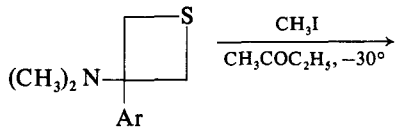




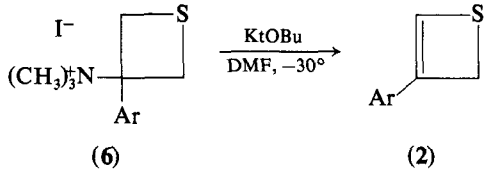
(**3**)



(**4**)



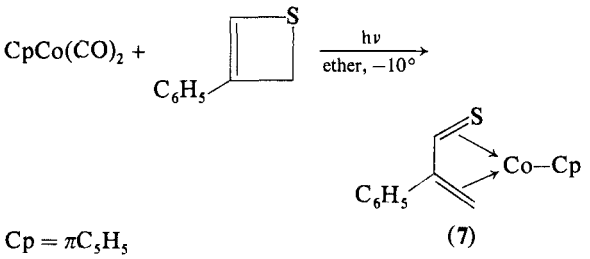
(**5**)



(**6**) (**2**)

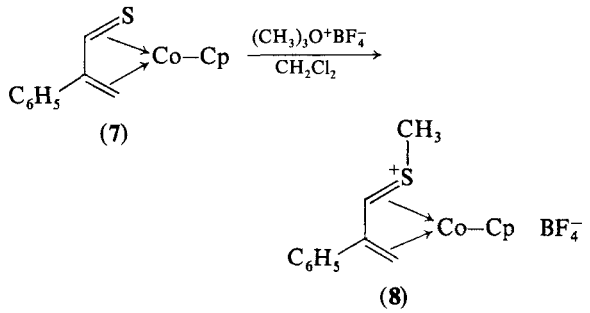
SCHEME 1

penethial. The alkyl-substituted thietes give similar complexes.[5]



$Cp = \pi C_5H_5$ (7)

Complex (7) is a nucleophile and can be alkylated with trimethyloxonium tetrafluoroborate. The sulfur-containing ligand in (8) exemplifies the hitherto unknown salts of *S*-alkyl α,β-unsaturated thioaldehydes.



EXPERIMENTAL SECTION

Microanalysis done by Microanalysis Inc., Wilmington, Del. Melting points are uncorrected. Nmr spectra were obtained on a Varian T-60 spectrometer. Cmr spectra were obtained on a Varian CFT-20 spectrometer and chemical shifts are referenced to internal tetramethylsilane.

N,N-Dimethyl-N-(1-phenylvinyl)amine (α-N,N-Dimethylaminostyrene) (**3**, Ar = C_6H_5) Anhydrous dimethylamine (135 g, 3 mol) was dissolved in dry benzene (1000 ml). The resulting solution was placed in a 3-liter, 3-necked, round-bottomed flask, fitted with an overhead stirrer, a nitrogen inlet and exit, and a pressure-equalizing dropping funnel. Acetophenone (60 g, 0.5 mol) was added to the amine solution. The reaction flask was flushed with dry nitrogen. Titanium tetrachloride (31 ml, 0.278 mol) was dissolved in dry, degassed benzene (100 ml) and the solution was placed in the dropping funnel. The reaction flask was surrounded with an ice-bath and the titanium tetrachloride solution was added dropwise during 90 min. After the addition was completed, the reaction mixture was stirred at 0° for 3 h and then allowed to stand overnight. The next day, the reaction mixture was filtered under nitrogen. The precipitated titanium dioxide was washed with benzene and the combined filtrates evaporated *in vacuo*. The resulting yellow oil (57 g, 77%), bp (1.5 mm) 83° (Lit.[6] bp (1.5 mm) 82°) was quite pure by nmr analysis and was used for the next step without further purification: nmr ($CDCl_3$) δ 2.56 (s, 6H), 4.26 (d, 2H), 7.39 (m, 5H).

3-Phenyl-3-N,N-dimethylaminothietane 1,1-Dioxide (**4**, Ar = C_6H_5) α-*N,N*-Dimethylaminostyrene (**3**, Ar = C_6H_5) (56 g, 0.38 mol) was dissolved in dry benzene (300 ml). Triethylamine (115 g, 1.14 mol) was added to the enamine solution and the mixture was placed in a 2-liter, three-necked, round-bottomed flask, fitted with a pressure-equalizing dropping funnel, an overhead stirrer, and a nitrogen inlet and exit. Methanesulfonyl chloride (43.5 g, 0.38 mol) was dissolved in dry benzene (100 ml) and the solution was placed in the dropping funnel. The reaction assembly was flushed with dry nitrogen and the reaction flask was surrounded by an ice-bath. The methanesulfonyl chloride solution was added dropwise during 60 min. After the addition was completed, the reaction mixture was allowed to stand overnight under nitrogen. It was diluted with diethyl ether (200 ml) and water (200 ml). The reaction mixture was stirred vigorously for 10 min and transferred to a separatory funnel. The organic layer was separated and the aqueous layer extracted with ether. The combined organic layers were dried (anhydrous sodium sulfate) and evaporated *in vacuo*. The residue was recrystallized from ethanol to give white plates (52 g, 61%) mp 124–125°; nmr ($CDCl_3$) δ 2.1 (s, 6H), 4.5 (s, 4H), 7.3 (m, 5H).

3-Phenyl-3,N,N-dimethylaminothietane (**5**, Ar = C_6H_5) 3-Phenyl-3-*N,N*-dimethylaminothietane 1,1-dioxide (**4**, Ar = C_6H_5) (10 g, 0.044 mol) and dry diethyl ether (500 ml) were placed in a 1-liter, three-necked, round-bottomed flask fitted with an overhead stirrer and a nitrogen inlet and exit. The reaction flask was cooled to 0° in an ice-bath and lithium aluminum hydride (4.22 g, 0.11 mol) was slowly added as a solid during 2 h. After the addition was completed, the reaction mixture was stirred for 3 h at 0°C. The lithium aluminum hydride was destroyed by sequential addition of water (5 ml), aqueous sodium hydroxide (20%, 5 ml), and more water (10 ml). The reaction mixture was filtered and the precipitate was repeatedly washed with dichloromethane (total volume 500 ml). The organic filtrate was dried (anhydrous sodium sulfate) and the solvent was evaporated *in vacuo*. A yellow oil (4.6 g, 53%) was obtained: nmr ($CDCl_3$) δ 2.0 (s, 6H), 3.53 (m, 4H), 7.30 (s, 5H).

3-Phenyl-3-trimethylammoniothietane Iodide (**6**, Ar = C_6H_5) 3-Phenyl-3-*N,N*-dimethylaminothietane (**5**, Ar = C_6H_5) (4 g, 0.02 mol) was dissolved in methyl ethyl ketone (10 ml) and the solution was cooled to −20°C. Methyl iodide (2.94 g, 0.02 mol) also was cooled to −20°C. The two reactants were mixed and allowed to stand at −20° for 24 h. The precipitated solid was removed by filtration and the filtrate was diluted with a small quantity of diethyl ether. More product was obtained after 24 h at −20°. It was a yellow solid (5.8 g, 83.5%): mp 92–93° (dec); nmr (DMSO-d_6) δ 3.06 (s, 9H), 4.13 (m, 4H), 7.56 (m, 5H).

3-Phenylthiete (**2**, Ar = C_6H_5) 3-Phenyl-3-trimethylammoniothietane iodide (**6**, Ar = C_6H_5) (4 g, 0.01 mol) in dry dimethylformamide (20 ml) was placed in a 250 ml, three-necked, round-bottomed flask, fitted with a pressure-equalizing dropping funnel, a magnetic stirrer and a nitrogen inlet and exit. The flask was flushed with dry nitrogen and was surrounded with a cold bath at −30°C. Potassium tert-butoxide (2.69 g, 0.023 mol) was dissolved in dry dimethylformamide (25 ml) and the solution was added dropwise during 20 min. After the addition was complete, the reaction mixture was allowed to stir for 45 min at −30°C and then was allowed to warm to 0°C. It was added to a

separatory funnel containing ice-cold water (200 ml) and diethyl ether (200 ml). The organic layer was separated and washed repeatedly with ice-cold water and 5% hydrochloric acid. It was dried over anhydrous sodium sulphate. The solvent was removed *in vacuo*, leaving a pale yellow solid, which was recrystallized from ligroin–diethyl ether (3:1) to give 3-phenylthiete as a white solid (1.5 g, 85%): mp 88–90° (dec); nmr ($CDCl_3$) δ 4.17 (s, 2H), 6.8 (s, 1H), 7.24 (s, 5H); cmr ($CDCl_3$) δ 35.79, 122.36, 126.97, 127.28, 128.50, 134.31, 135.32.

Anal. Calcd for C_9H_8S: C, 72.92; H, 5.44; Found: C, 72.56, H, 5.42; mass spectrum, *M/e* 148 (molecular ion) 147 (base peak). Rast mol. wt. (camphor): Calcd., 148; found, 157.

3-(2-Naphthyl)-, 3-(2-thienyl) and 3-(2-furyl)thietes were prepared in a similar manner.

N,N-Dimethyl-N-[1-(2-naphthyl)vinyl]amine (**3**, Ar = 2-$C_{10}H_7$) Oil: nmr ($CDCl_3$) δ 2.56 (s, 6H), 4.16 (d, 2H), 7.49 (m, 7H).

3-(2-Naphthyl)-3-N,N-dimethylamino-thietane 1,1-Dioxide (**4**, Ar = 2-$C_{10}H_7$) White solid, recrystallized from ethanol: mp 145–146°; nmr ($CDCl_3$) δ 1.93 (s, 6H), 4.43 (s, 4H), 7.43 (m, 7H).

3-(2-Naphthyl)-3-N,N-dimethylaminothietane (**5**, Ar = 2-$C_{10}H_7$) White solid, recrystallized from ether–petroleum ether (1:2): mp 65°; nmr ($CDCl_3$) δ 2.16 (s, 6H), 3.69 (m, 4H), 7.56 (m, 7H).

3-(2-Naphthyl)-3-N,N-trimethylammoniothietane Iodide (**6**, Ar = 2-$C_{10}H_7$) Pale yellow: mp 109–110° (dec); nmr (DMSO-d_6) δ 3.2 (s, 9H), 4.29 (m, 4H), 7.82 (m, 7H).

3-(2-Naphthyl)thiete (**2**, Ar = $C_{10}H_7$) Off-white solid: mp 123–125° (dec); nmr ($CDCl_3$) δ 4.16 (s, 2H), 6.86 (s, 1H), 7.49 (m, 7H), cmr ($CDCl_3$) δ 35.9, 120.5, 120.9, 125.6, 126.4, 127.7, 128.1, 131.7, 132.4, 133.4, 135.0.

Anal. Calcd. for $C_{13}H_{10}S$: C, 78.78; H, 5.05; S, 16.16. Found: C, 78.42; H, 5.17; S, 15.89. Rast mol. wt. (camphor): Calcd., 198; Found, 208.

N,N-Dimethyl-N-[1-(2-thienyl)vinyl]amine (**3**, Ar = 2-C_4H_3S) Oil: nmr ($CDCl_3$) δ 2.54 (s, 6H), 4.31 (d, 2H), 6.97 (m, 3H).

3-(2-Thienyl)-3-N,N-dimethylaminothietane 1,1-Dioxide (**4**, Ar = 2-C_4H_3S) White solid, recrystallized from ethanol: mp 132–133°; nmr ($CDCl_3$) δ 2.19 (s, 6H), 4.46 (s, 4H), 7.09 (m, 3H).

3-(2-Thienyl)-3-N,N-dimethylaminothietane (**5**, Ar = 2-C_4H_3S) Oil: nmr ($CDCl_3$) δ 2.09 (s, 6H), 3.53 (m, 4H), 7.09 (m, 3H).

3-(2-Thienyl)-3-N,N-trimethylammoniothietane Iodide (**6**, Ar = 2-C_4H_3S) Pale yellow solid: mp 85° (dec.).

3-(2-Thienyl)thiete (**2**, Ar = 2-C_4H_3S) Off-white solid: mp 64–65° (dec.); nmr ($CDCl_3$) δ 4.06 (s, 2H), 6.56 (s, 1H), 6.90 (m, 3H).

Anal. Calcd. for $C_7H_6S_2$: C, 54.54; H, 3.89; S, 41.55. Found: C, 54.29; H, 4.07; S, 41.22. Rast mol. wt. (camphor): Calcd., 154; Found, 176.

N,N-Dimethyl-N-[1-(2-furyl)vinyl]amine (**3**, Ar = 2-C_4H_3O) Oil: nmr ($CDCl_3$) δ 2.53 (s, 6H), 4.27 (d, 2H), 6.24 (m, 2H), 7.80 (br s, 1H).

3-(2-Furyl)-3-N,N-dimethylaminothietane 1,1-Dioxide (**4**, Ar = 2-C_4H_3O) White solid, recrystallized from ethanol: mp 112–113°; nmr ($CDCl_3$) δ 2.19 (s, 6H), 4.43 (s, 4H), 6.39 (m, 2H), 7.46 (m, 1H).

3-(2-Furyl)-3-N,N-dimethylaminothietane (**5**, Ar = 2-C_4H_3O) Oil: nmr ($CDCl_3$) δ 2.03 (s, 6H), 3.46 (m, 4H), 6.36 (m, 2H), 7.39 (m, 1H).

3-(2-Furyl)-3-N,N-trimethylammoniothietane Iodide (**6**, Ar = 2-C_4H_3O) Pale yellow solid: mp 81–82° (dec.).

3-(2-Furyl)thiete (**2**, Ar = 2-C_4H_3O) Oil: nmr ($CDCl_3$) δ 3.96 (s, 2H), 6.06 (m, 1H), 6.26 (m, 1H), 6.56 (s, 1H), 7.19 (m, 1H).

(η^5-Cyclopentadienyl)(2-phenylpropenethial)cobalt 3-Phenylthiete (**2**, Ar = C_6H_5) (1.30 g, 8.78 mmole) was dissolved in dry ether (500 ml) in a photolysis vessel. The solution was cooled to −10°C and argon was bubbled through it for 1/2 h. (η^5-Cyclopentadienyl) cobalt dicarbonyl (3.20 g, 17.6 mmole) was added and the solution photolyzed (Corex filter, high pressure Hg lamp) for 24 h. The reaction mixture was filtered through a plug of glass wool and concentrated under reduced pressure (water aspirator) below room temperature. The resulting oil was purified by chromatography on an alumina (activity II) column. Elution with pentane gave a red-brown band (unreacted π-$C_5H_5Co(CO)_2$, 1.3–1.5 g). Elution with ether gave a dark brown band (2.0–2.2 g). Ether removal gave the complex (**7**) as a brown solid, mp 58–60°C (83.3–91%).

Anal. Calcd. for $C_{14}H_{13}SCo$: C, 61.76; H, 4.78; Found: C, 62.01, H, 5.42; nmr ($CDCl_3$) δ 7.80–7.17 (m, 6H), 4.87 (s, 5H), 3.23, (s, 1H), 1.10 (s, 1H).

(η^5-Cyclopentadienyl) cobalt (S-methyl-2-phenylpropenethial)-Tetrafluoroborate (**8**) (η^5-Cyclopentadienyl)(2-phenylpropenethial)cobalt (**7**) (200 mg, 0.735 mmole) was dissolved in dry, degassed methylene chloride (15 ml). Trimethyloxonium fluoroborate (108.7 mg, 0.735 mmole) was added and the solution stirred for 90 min at room temperature under nitrogen. The reaction mixture was filtered and the solvent removed under reduced pressure (water aspirator) to give a dark, violet-colored solid (269 mg, 97.5%): mp 128–131°C.

Anal. Calcd. for $C_{15}H_{16}BCoF_4S$: C, 48.15; H, 4.28; Found: C, 48.48; H, 4.54; nmr ($CDCl_3$) δ 7.93–7.17 (m, 6H), 5.37 (s, 5H), 4.23–4.03 (m, 1H), 2.67 (s, 3H), 0.97–0.83 (m, 1H).

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