Reaction of Bromo Alcohol 3b with Zinc.—The bromohydrin **3b** (1.04 g, 4.75 mmol) was dissolved in 30 ml of methanol, and 10 g of activated zinc was added. The solution was stirred overnight and filtered through sintered glass, and the residue was washed with pentane and water. After the filtrate and washings were shaken, the pentane was removed and the aqueous layer was extracted with 2 × 25 ml of pentane. The combined pentane layers were dried over magnesium sulfate, and the pentane was evaporated at 1 atm, giving 0.52 g (89%) of 1,2-dimethyl-4-methylene-1-cyclohexane (**4b**). Evaporative distillation gave 0.36 g: ir (neat) 3080, 1670, and 885 cm^{-1}; nmr ($CDCl_3$) δ 4.68 (2 H, br s, $=CH_2$), 2.65 (2 H, br, $=CH_2C=$), 2.25 (4 H, m, $=CCH_2$), and 1.62 (6 H, s, CH_3).

Anal. Calcd for C_9H_{14}: mol wt, 122.1095. Found: mol wt, 122.1092.

Reaction of Bromo Alcohol 3c with Zinc.—The bromohydrin **3c** (0.407 g, 1.14 mmol) in 10 ml of methanol was treated with 1.5 g of activated zinc. After 2 hr the solution was filtered with suction and the filtrate was evaporated to dryness. The residue was taken up in 2% hydrochloric acid which was then extracted with 3 × 15 ml of pentane, which was dried over magnesium sulfate and evaporated to give 245 mg (86%) of 3,6-diphenyl-4-methylenecyclohexene (**4c**), pure by tlc and gc: ir (neat) 1650 and 870 cm^{-1}; nmr ($CDCl_3$) δ 7.36 (10 H, s, C_6H_5), 6.03 (2 H, s, $CH=$), 4.83 and 4.90 (2 H, 2 s, $=CH_2$), 4.16 (1 H, br, CH), 3.62 (1 H, m, CH), and 2.42 (2 H, m, CH_2).

Anal. Calcd for $C_{19}H_{18}$: mol wt, 246.1408. Found: mol wt, 246.1407.

Reaction of Bromo Alcohol 3d with Zinc.—The bromohydrin **3d** (200 mg, 0.53 mmol) was dissolved in 10 ml of methanol, and 1 g of activated zinc was added. After 2 hr the reaction was worked up as described previously for **3c** to give 125 mg (83%) of **4d** as colorless crystals which were recrystallized from hexane: mp 100–101°;[10] ir ($CHCl_3$) 1640 and 880 cm^{-1}; nmr ($CDCl_3$) δ 7.2 (8 H, m, C_6H_4), 5.07 (1 H, br s, CH), 4.68 (2 H, s, $=CH_2$), 4.27 (1 H, t, $J = 3$ Hz, CH), and 2.36 (2 H, m, CH_2).

Anal. Calcd for $C_{17}H_{14}$: C, 93.54, H, 6.46; mol wt, 218.1095. Found: C, 93.20; H, 6.55; mol wt, 218.1092.

Acknowledgment.—The author is grateful to the National Science Foundation for financial support and to Professor E. J. Corey for his support and encouragement of this work.

Registry No.—1, 14925-39-4; *exo*-**2a**, 28738-84-3; *endo*-**2a**, 28738-83-2; **2b**, 41894-54-6; **2c**, 41894-55-7; **2d**, 41894-56-8; *exo*-**3a**, 41915-51-9; *endo*-**3a**, 41915-52-0; **3b**, 41894-57-9; **3c**, 41894-58-0; **3d**, 42434-74-2; **4a**, 694-91-7; **4b**, 41894-60-4; **4c**, 41894-61-5; **4d**, 19978-14-4; cyclopentadiene, 542-92-7; 2,3-dimethylbutadiene, 513-81-5; *trans,trans*-1,4-diphenylbutadiene, 538-81-8; anthracene, 120-12-7.

---

[10] The olefin **4d** has previously been prepared as a 9:1 mixture of exo-endo double-bond isomers: S. J. Cristol and G. O. Mayo, *J. Org. Chem.*, **34**, 2363 (1969).

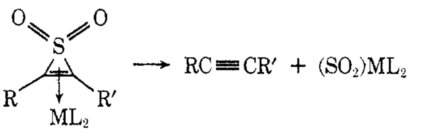
Synthesis and Thermolysis of Thiete 1,1-Dioxide Iron Tetracarbonyl[1,2]

John E. McCaskie, Peter L. Chang, Thomas R. Nelsen, and Donald C. Dittmer*

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

Received July 3, 1973

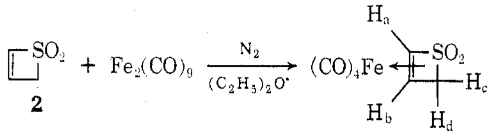
Thermolysis of thiete sulfones (thiete 1,1-dioxides) has been suggested to proceed *via* vinylsulfenes as reactive intermediates.[3] We have observed that thiete sulfone yields sulfur dioxide at elevated temperatures, indicating the possible formation of three-carbon intermediates such as vinylcarbene, cyclopropene, methylacetylene, or allene. Since a number of reactive intermediates have been obtained as stable complexes of transition metals,[4] we investigated the synthesis and properties of thiete sulfone iron tetracarbonyl in which the iron atom conceivably could trap vinylsulfene and reactive intermediates formed during the extrusion of sulfur dioxide. Thermolysis of palladium and platinum complexes (**1**) of thiirene 1,1-dioxides yields an



1, M = Pt, Pd; L = Ph_3P

acetylene and a complex of sulfur dioxide.[5] Uncomplexed thiirene 1,1-dioxides also yield an acetylene and sulfur dioxide;[6] thus thermolysis of **1** is not fundamentally different from the thermolysis of the uncomplexed sulfone.

Pale yellow crystals of thiete sulfone iron tetracarbonyl (**3**) were obtained (50% yield) either by refluxing a solution of the sulfone **2** in ether with diiron nonacarbonyl or by irradiation of **2** and iron pentacarbonyl in benzene.[7] Under the same conditions no iron complexes could be obtained from 2-sulfolene, 4-phenyl-2*H*-thiete 1,1-dioxide, or 7-thiabicyclo[4.2.0]-1(8)-octene 7,7-dioxide.



2

3

The pmr spectrum of **3** shows all protons shifted to higher field relative to the protons of **2**. The chemical shifts of the protons of the double bond show the greatest displacement: $\Delta\delta_{H_a}$ 1.70, $\Delta\delta_{H_b}$ 2.20, $\Delta\delta_{H_c}$ 0.93, $\Delta\delta_{H_d}$ 0.68 ppm.[8] Sulfone absorption in the infrared is essentially unaltered, as is observed in other sulfone complexes,[8b] and C–H stretching vibrations occur in

---

[1] Taken in part from the Ph.D. Thesis of P. L. Chang, Syracuse University, 1970.

[2] Reported at the Northeast Regional Meeting of the American Chemical Society, Buffalo, N. Y., Oct 1971, Abstract 166.

[3] J. F. King, P. de Mayo, C. L. McIntosh, K. Piers, and D. J. H. Smith, *Can. J. Chem.*, **48**, 3704 (1970); D. C. Dittmer, R. S. Henion, and N. Takashina, *J. Org. Chem.*, **34**, 1310 (1969).

[4] The following examples are illustrative: Carbenes, E. O. Fischer, *Pure Appl. Chem.*, **24**, 407 (1970); vinyl alcohols, C. H. de Puy, R. N. Greene, and T. E. Schroer, *Chem. Commun.*, 1225 (1968); H. Thyret, *Angew. Chem., Int. Ed. Engl.*, **11**, 520 (1972); cyclobutadienes, G. F. Emerson, L. Watts, and R. Pettit, *J. Amer. Chem. Soc.*, **87**, 131 (1965); cyclohexyne, M. A. Bennett, G. B. Robertson, P. O. Whimp, and T. Yoshida, *ibid.*, **93**, 3797 (1971); trimethylene, G. F. Emerson, K. Ehrlich, W. P. Giering, and P. C. Lauterbur, *ibid.*, **88**, 3172 (1966); vinyl ketenes, A. E. Hill and H. M. R. Hoffmann, *J. Chem. Soc., Chem. Commun.*, 574 (1972).

[5] J. P. Visser, C. G. Leliveld, and D. N. Reinhoudt, *J. Chem. Soc., Chem. Commun.*, 178 (1972).

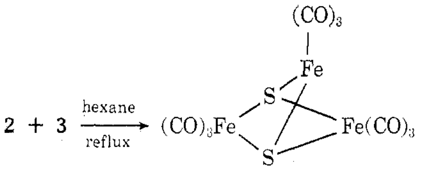
[6] L. A. Carpino and L. V. McAdams, III, *J. Amer. Chem. Soc.*, **87**, 5804 (1965); L. A. Carpino and R. H. Rynbrandt, *ibid.*, **88**, 5682 (1966); L. A. Carpino, L. V. McAdams, III, R. H. Rynbrandt, and J. W. Spiewak, *ibid.*, **93**, 476 (1971).

[7] *Cf.* the preparation of thiophene 1,1-dioxide iron tricarbonyl: Y. L. Chan, J. Fossey, and R. A. Perry, *J. Chem. Soc., Chem. Commun.*, 501 (1972).

[8] (a) Shifts to high fields are typical of olefin–iron tetracarbonyl complexes, shifts of the olefin protons being the greatest: E. Weiss, K. Stark, J. E. Lancaster, and H. D. Murdoch, *Helv. Chim. Acta*, **46**, 288 (1963). (b) A. N. Nesmeyanov, L. V. Rybin, M. I. Rybinskaya, N. T. Gubenko, I. F. Leshcheva, and Y. A. Ustynyuk, *J. Gen. Chem. USSR*, **38**, 1428 (1968).

both the olefinic (3040 cm^{-1}) and aliphatic (2950 cm^{-1}) region. It is unlikely that the complex involves the ring-opened structure of vinylsulfene ($CH_2{=}CHCH{=}SO_2$) because the infrared and nmr spectra are not consistent with a structure containing three olefinic protons and one proton of an aldehydic type.

Complex **3** and extra thiete sulfone were refluxed under nitrogen for 1.5 hr in olefin-free hexane. (Thiete sulfone is stable under these conditions.) Within 10 min the heterogeneous mixture became dark red. Sulfur dioxide and carbon monoxide were detected in the effluent gas by infrared analysis. The deep purple solution yielded red-black crystals of $Fe_3S_2(CO)_9$ (19% based on 2 mol of thiete sulfone being consumed per mole of product) and a considerable amount of thiete sulfone (91% of the total amount both complexed and uncomplexed). This inorganic iron–sulfur derivative was identical with the complex **4** obtained by Hieber and Gruber from tetracarbonyl iron ferrate and sulfite ion[9] and whose structure has been determined.[10] Attempts to identify the carbon fragment or fragments from thiete sulfone were unsuccessful. Formally, a C_3H_4 fragment must be obtained on extrusion of sulfur dioxide and, in fact, the mass spectra of thiete sulfone and of complex **3** show abundant ions at *m/e* 40 ($C_3H_4^+$) and 39 ($C_3H_3^+$). When complex **3** was subjected to thermolysis in the absence of thiete sulfone, only $^1/_{13}$ of the amount of **4** obtained in the regular thermolysis was isolated. Thiete sulfone was recovered in 90% yield, the result of decomposition of the complex into its components.



4

The reduction of the sulfone group to sulfide (as in **4**) under such relatively mild conditions (69°) is worthy of note. Deoxygenations of nitro, nitroso, and azoxy groups, *N*-oxides, and nitrones by iron pentacarbonyl in refluxing *n*-butyl ether (24 hr) have been observed previously.[11] Equimolar quantities of pure thiete sulfone and complex **3** appear to be required for the formation of **4**. This suggests that a complex containing 2 mol of thiete sulfone may be involved. No **4** was obtained when an equimolar mixture of maleic anhydride iron tetracarbonyl[8a] and thiete sulfone was heated (80–140°, 2 hr); starting materials were recovered.

Experimental Section[12]

Thiete 1,1-Dioxide Iron Tetracarbonyl. A.—Diiron nonacarbonyl (1.82 g, 5 mmol) was added to a solution of thiete sulfone[13] (1.04 g, 10 mmol) in dry ether (50 ml). The reaction mixture was refluxed under nitrogen with stirring for 1.5 hr. The brown reaction mixture was filtered and slowly concentrated. Yellow needles of thiete 1,1-dioxide iron tetracarbonyl (1.30 g, 4.78 mmol, 47.8%) separated: mp 99–100°; ir (KBr) 2100 (s, CO), 2050 (s, CO), 2030 (s, CO), 1970 (s, CO), 1275 (m, SO_2), 1230 (s, SO_2), 1120 cm^{-1} (s, SO_2); nmr ($CDCl_3$) δ 5.10 (d, 1, $={CHSO_2}$), 4.50 (m, 1, $CH{=}CSO_2$), 3.90 (complex d, 1, endo or exo CH_2), 3.65 (complex d, 1, endo or exo CH_2); mass spectrum (70 eV) *m/e* 272 (parent), 244 (− CO), 216 (− 2CO), 188 (− 3CO), 160 (− 4CO), 104 ($C_3H_4O_2S$).

Anal. Calcd for $C_7H_4FeO_6S$: C, 30.96; H, 1.49. Found: C, 31.17; H, 1.70.

B.—Iron pentacarbonyl (3.0 g, 14.4 mmol) and thiete sulfone (1.04 g, 10 mmol) were dissolved in benzene (500 ml, dry, degassed) and the solution was irradiated for 1 hr at room temperature under nitrogen with a high-pressure mercury lamp equipped with a Vycor filter. The orange mixture was filtered, concentrated, and triturated with ether to yield the complex (1.36 g, 5 mmol, 50%), mp 99–100°.

Thermolysis of Thiete 1,1-Dioxide Iron Tetracarbonyl in Presence of Excess Thiete Sulfone.—A suspension of thiete 1,1-dioxide iron tetracarbonyl (0.824 g, 3.03 mmol) and thiete sulfone (0.312 g, 3.00 mmol) in hexane (25 ml, olefin-free) was refluxed under nitrogen with stirring for 3 hr. After *ca.* 1 hr a deep purple solution was obtained. Sulfur dioxide and carbon monoxide were detected in the effluent gas stream by infrared analysis. Continuous extraction of the solid residue with ether yielded thiete sulfone (0.395 g, 3.79 mmol). The hexane solution was chromatographed on Florisil and elution with ether gave additional thiete sulfone (0.175 g, 1.68 mmol).[14] Elution with hexane gave, after removal of solvent, red-black crystals of $Fe_3S_2(CO)_9$ (0.026 g, 0.054 mmol, 19%):[15] mp 109–110° (lit.[9b] mp 114°); ir (KBr) 2047 (s, CO), 2015 (s, CO), 1996 cm^{-1} (s, CO); uv–visible (hexane) λ_{max} 203 nm (ϵ 190,000), 550 (shallow); mass spectrum (70 eV) *m/e* 484 (parent) and ions resulting from the consecutive loss of nine molecules of carbon monoxide; X-ray analysis, triclinic, $b = 9.16$ Å (lit.[10] $b = 9.22$ Å). The compound was identical with a sample of $Fe_3S_2(CO)_9$ prepared according to Hieber and Gruber.[9a] Attempts to trap carbon-containing fragments by passing the effluent gas through bromine in methylene chloride or through cyclopentadiene were not successful. No $Fe_2SO_2(CO)_8$[16] or $Fe_3S_2(CO)_6$[9a] was detected in the reaction mixture.

Acknowledgments.—We are grateful to the National Science Foundation (Grant GP 20729) and the National Cancer Institute of the Public Health Service (Grant CA 08250) for financial support of this work. We are indebted to Professor C. E. Pfluger for the X-ray data.

Registry No.—**2,** 7285-32-7; **3,** 42116-78-9; **4,** 12287-77-3; diiron nonacarbonyl, 15321-51-4; iron pentacarbonyl, 13464-40-6.

---

[9] (a) W. Hieber and J. Gruber, *Z. Anorg. Allg. Chem.*, **296**, 91 (1958); (b) R. Havlin and G. R. Knox, *J. Organometal. Chem.*, **4**, 247 (1965).

[10] L. F. Dahl and P. W. Sutton, *Inorg. Chem.*, **2**, 1067 (1963).

[11] H. Alper and J. T. Edward, *Can. J. Chem.*, **48**, 1543 (1970).

[12] Infrared spectra were recorded on a Perkin-Elmer Model 137 spectrometer. Pmr spectra were obtained on a Varian Associates Model A-60 spectrometer. Mass spectra were recorded on a Hitachi Perkin-Elmer RMU6E spectrometer. Melting points are uncorrected.

[13] D. C. Dittmer and M. E. Christy, *J. Org. Chem.*, **26**, 1324 (1961); D. C. Dittmer, M. E. Christy, N. Takashina, R. S. Henion, and J. M. Balquist, *ibid.*, **36**, 1324 (1971); P. L. Chang and D. C. Dittmer, *ibid.*, **34**, 2791 (1969).

[14] 90.7% of the total amount of thiete sulfone, complexed and uncomplexed, is recovered.

[15] Based on starting material consumed [2 thiete sulfone → $Fe_3S_2(CO)_9$].

[16] D. S. Field and M. J. Newlands, *J. Organometal. Chem.*, **27**, 221 (1971); E. H. Braye and W. Hubel, *Angew. Chem.*, **75**, 345 (1963).