

range  $-30$  to  $-100^\circ$  (in isopentane as solvent) showed that the intensity of the color decreased very much less on cooling the sample than did the radical concentration. We have been informed by Professor Nelsen that he has observed purple colors during the decomposition of tetraalkyltetrazenes and we must therefore suppose that our color also arises from the tetrazene.

We are currently investigating the decay kinetics for these radicals.

V. Malatesta, K. U. Ingold\*

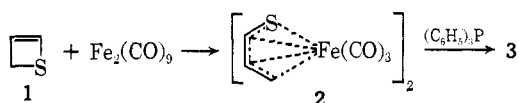
Division of Chemistry, National Research Council of Canada  
Ottawa, Ontario, Canada, K1A 0R9

Received May 5, 1973

## Iron Complexes of Thioacroleins Derived from Thietes

Sir:

Thietes (thiacyclobutenes) are a new class of highly reactive heterocyclic compounds whose preparation and chemical reactions have been discussed.<sup>1</sup> Treatment of thiete, **1**, either with diiron nonacarbonyl (thermal) or with iron pentacarbonyl (photochemical) yields a volatile orange solid (dimeric in hexane by osmometry) (30% yield, mp  $28^\circ$ ), **2**, which was converted to the monomeric, red iron dicarbonyl triphenylphosphine complex, **3**, of thioacrolein, a hitherto un-



known thioaldehyde:<sup>2</sup>  $^1\text{H}$  nmr ( $\text{CDCl}_3$ )  $\delta$  6.10 (d, 1, =CHS), 5.60 (m, 1, -CH=CS), 1.95 (d, 1, exo or endo proton of  $\text{CH}_2$ ), 0.90 (doublet of doublets, 1, exo or endo proton of  $\text{CH}_2$  coupled to phosphorus); mass spectrum (70 eV)  $m/e$  446 (parent), 418 (-CO), 390 (-2CO), 128 ( $\text{C}_3\text{H}_4\text{SFe}$ ), 72 ( $\text{C}_3\text{H}_4\text{S}$ ). *Anal.* Calcd for  $\text{C}_{23}\text{H}_{19}\text{FeO}_2\text{PS}$  (**3**): C, 61.90; H, 4.29. Found: C, 62.11; H, 4.14.

X-Ray analysis of **3** established the structure as a thioacrolein complex.<sup>3</sup> The thioacrolein ligand (a four-electron donor) is essentially planar with the iron atom above the plane. Figure 1 indicates the principal bond distances. Thioacrolein was suggested as a possible decomposition product of thiete a number of years ago<sup>4</sup> and evidence for the formation of thioacroleins from thietes has been obtained recently.<sup>1</sup>

Oxidation of the iron tricarbonyl complex yields the yellow *S*-oxide complex, a reasonable structure for which is **4**, mp  $112-114^\circ$ : ir (KBr)  $1030\text{ cm}^{-1}$  ( $\text{S}=\text{O}$ ); mass spectrum (70 eV)  $m/e$  228 (parent), 212 (-O), 200 (-CO), 172 (-2CO). *Anal.* Calcd for  $\text{C}_6\text{H}_4\text{S}$ -

(1) D. C. Dittmer, P. L. Chang, F. A. Davis, M. Iwanami, I. K. Stamos, and K. Takahashi, *J. Org. Chem.*, **37**, 1111 (1972); D. C. Dittmer, P. L. Chang, F. A. Davis, I. K. Stamos and K. Takahashi, *ibid.*, **37**, 1116 (1972).

(2) A patent claims the preparation of thioacrolein from sulfur and glycerine at 20 psi and  $260-450^\circ\text{F}$ , but the compound was not characterized. The substance was said to be "highly germicidal" and useful "in the bath for treatment of skin diseases and rheumatism," J. Delson, U. S. Pat. 2,067,261, Jan 12, 1937.

(3) Complete details of the X-ray investigation will be published elsewhere (R. L. Harlow and C. E. Pfluger, *Acta Crystallogr.*, in press). The conventional *R* factor for 1935 reflections was 0.076.

(4) D. C. Dittmer and M. E. Christy, *J. Amer. Chem. Soc.*, **84**, 399 (1962).

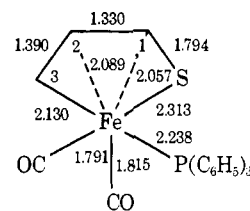
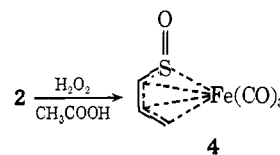
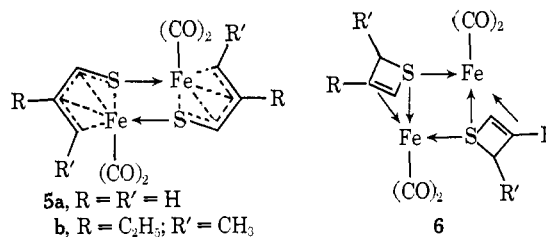


Figure 1. Some bond lengths ( $\text{\AA}$ ) in thioacrolein iron tricarbonyl complex (**3**) ( $\text{C}_3\text{-S} = 2.313\text{ \AA}$ ).



$\text{FeO}_4\text{S}$ : C, 31.58; H, 1.75. Found: C, 31.77; H, 1.62.<sup>5</sup> This complex may be considered a derivative of the unknown vinylsulfine ( $\text{CH}_2=\text{CHCH}=\text{S}=\text{O}$ ).<sup>6</sup>

The iron tricarbonyl complex **2** and an analogous complex derived from 2-methyl-3-ethyl-2*H*-thiete<sup>1</sup> lose carbon monoxide readily on heating to yield orange-brown dimers whose structures may be formulated as **5a** and **5b**, respectively, based on analytical and spectroscopic (ir, nmr, uv, mass) data. The Mössbauer spectrum of **5a** indicates that the two iron atoms are equivalent, there being only one absorption (IS,  $0.058\text{ mm sec}^{-1}$ ; QS,  $1.358\text{ mm sec}^{-1}$ ). Oxidation of **5b** with *m*-chloroperbenzoic acid yields a monosulfide complex of the dimer which rules out structure **6** in which



there are no available free valence electrons on the sulfur atoms. However, dissociation of one of the sulfur ligands in **6**, reducing the number of valence electrons for one iron atom from 18 to 16, could permit formation of an *S*-oxide.

These iron complexes thus show some similarities to iron complexes of the dithiolenes which tend to be dimeric except when a phosphine or other Lewis base ligand is introduced.<sup>7</sup> The iron tricarbonyl complex of thioacrolein differs from the iron complex of acrolein in that the latter forms only an iron tetracarbonyl complex

(5) The *S*-oxide complex also may be formed (ir) when the oxidation is done with ceric ammonium nitrate, ferric chloride, or *tert*-butyl hypochlorite. An *S*-oxide complex entirely analogous to **4** is obtained also from **3**.

(6) For a review of sulfines and their isomerism see B. Zwanenburg and J. Strating, *Quart. Rep. Sulfur Chem.*, **5**, 79 (1970). We have some evidence (nmr) that **4** may exist in two isomeric forms.

(7) The chemistry of the dithiolenes has been reviewed: H. B. Gray, R. Eisenberg, and E. I. Stiefel, *Advan. Chem. Ser.*, No. 62, 641 (1967); G. N. Schrauzer in "Transition Metal Chemistry," R. L. Carlin, Ed., Vol. 4, Marcel Dekker, New York, N. Y., 1968, p 299; J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1968); A. Davison and R. H. Holm, *Inorg. Syn.*, **10**, 8 (1968); L. F. Lindoy, *Coord. Chem. Rev.*, **4**, 41 (1969); G. N. Schrauzer, *Advan. Chem. Ser.*, No. 110, 73 (1972). For recent reports about dithiolene iron tricarbonyl monomers and dimers see J. Miller and A. L. Balch, *Inorg. Chem.*, **10**, 1410 (1971); C. J. Jones, J. A. McCleverty, and D. G. Orchard, *J. Chem. Soc., Dalton Trans.*, 1109 (1972).

involving coordination solely with the olefinic double bond.<sup>8</sup>

If it is assumed that the iron atom in **3**, aided by the triphenylphosphine ligand, donates two electrons to the thioacrolein ligand, HMO calculations on dinegative thioacrolein ( $\alpha_S = \alpha_C + 1.5\beta_{OC}$ ,  $\beta_{CS} = 0.5\beta_{CC}$ ) predict bond orders (C-S, 1.09; C<sub>1</sub>-C<sub>2</sub>, 1.72; C<sub>2</sub>-C<sub>3</sub>, 1.68) which are qualitatively in agreement with approximate bond orders derived from the bond distances in **3** (C-S, 1.1; C<sub>1</sub>-C<sub>2</sub>, 2; C<sub>2</sub>-C<sub>3</sub>, 1.7). Essentially a full negative charge is predicted on sulfur, in agreement with its facile oxidation, and the second negative charge is predicted to be distributed principally between C<sub>1</sub> and C<sub>3</sub>. In agreement with the latter prediction, the protons on C<sub>1</sub> and C<sub>3</sub> in **3** are more shielded ( $\delta$  6.10, 1.95, and 0.90, respectively) in the complex than they are in thiethione ( $\delta$  6.50 and 3.80, respectively). The shielding of the proton on C<sub>2</sub> is unchanged ( $\delta$  5.60).

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(8) E. Weiss, K. Stark, J. E. Lancaster, and H. D. Murdoch, *Helv. Chim. Acta*, **46**, 288 (1963). Molybdenum, rhodium, and nickel complexes of acrolein apparently involve coordination also with the carbonyl group: D. P. Tate, A. A. Buss, J. M. Augl, B. L. Ross, J. G. Grasselli, W. M. Ritchey, and F. J. Knoll, *Inorg. Chem.*, **4**, 1323 (1965); M. Hidai, K. Ishimi, M. Iwasa, and Y. Uchida, *Bull. Chem. Soc. Jap.*, **45**, 2935 (1972); G. N. Schrauzer, *Chem. Ber.*, **94**, 642 (1961).

K. Takahashi, M. Iwanami, A. Tsai  
P. L. Chang, R. L. Harlow, L. E. Harris  
J. E. McCaskie, C. E. Pfluger, D. C. Dittmer\*  
Department of Chemistry, Syracuse University  
Syracuse, New York 13210  
Received June 21, 1973

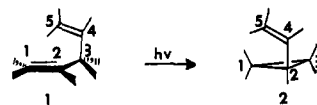
### Di- $\pi$ -methane Stereochemistry. The Effect of Structural Limitations Which Preclude Preferred Modes<sup>1</sup>

Sir:

The photochemical di- $\pi$ -methane rearrangement continues to attract a great deal of attention due to both its general nature and interesting mechanistic variations. Of prime interest to us has been the stereochemistry of this excited-state atom reorganization process which converts di- $\pi$ -methane systems (**1**) to  $\pi$ -substituted cyclopropane products (**2**). Our previous investigations<sup>2</sup> of the photochemistry of 1-phenyl-3-methyl-3-(1-*cis*-propenyl)cyclohexene (**3**) have indicated that the conversion of 1,4-dienes to vinylcyclopropanes by this pathway proceeds with remarkable stereospecificity, accountable for on the basis of a concerted di- $\pi$ -methane rearrangement with preferential three-ring formation by disrotatory motion of the orbitals at C-1 and C-3 anti to the migrating propenyl group.

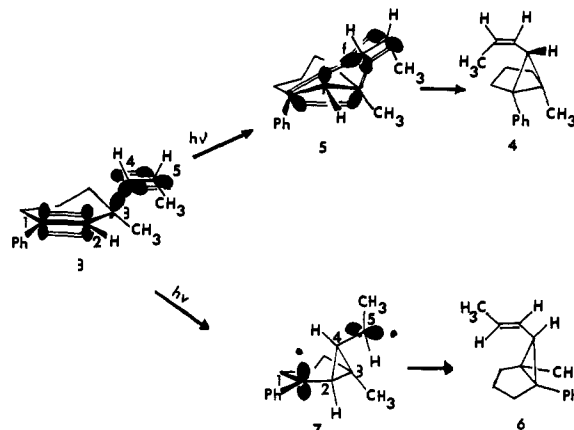
(1) A preliminary report of this work was presented at the 165th National Meeting of the American Chemical Society, Dallas, Texas, 1973. Abstract of Papers No. Orgn-87.

(2) P. S. Mariano and J. K. Ko, *J. Amer. Chem. Soc.*, **94**, 1766 (1972); *ibid.*, in press.



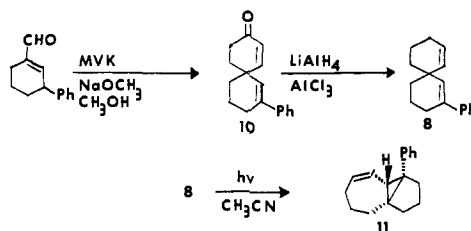
Thus, our rationale for formation of 1-phenyl-5-methyl-*endo*-6-(1-*cis*-propenyl)bicyclo[3.1.0]hexane (**4**) from the singlet excited state of **3** was based on a concerted pathway which proceeded through the low-energy anti-disrotatory transition-state orbital geometry **5**. Similarly, our explanation for formation of the *endo trans* propenyl product **6** was based on a nonconcerted pathway in which diradical **7** was preferentially converted to product by backside displacement of C-4 by C-1 at C-3, as shown in Scheme I. Other observations on the

Scheme I



singlet<sup>3</sup> and triplet<sup>4</sup> di- $\pi$ -methane reactivity have further verified our conclusions. We have continued our initial studies of these intriguing aspects of the di- $\pi$ -methane rearrangement stereochemistry with the hope of gaining more insight into the nature of the factors which control this stereoselectivity and now report our results on the photochemistry of a structurally rigid 1,4-diene, 2-phenylspiro[5.5]undeca-1,7-diene (**8**), which rearranges efficiently on direct irradiation with syn-disrotatory three-ring formation.

Preparation of **8** was by the sequence involving methyl vinyl ketone annelation of the known<sup>3</sup> 3-phenylcyclohexene-1-carboxaldehyde (**9**) followed by lithium aluminum hydride-aluminum chloride reduction of the formed 8-phenylspiro[5.5]undeca-1,7-dien-3-one (**10**).



Irradiation<sup>5</sup> of **8** gave 11-phenyltricyclo[5.4.0.0<sup>7,11</sup>]undec-2-ene (**11**). The structure of photoproduct **11**

(3) H. E. Zimmerman, P. Baekstrom, T. Johnson, and D. W. Kurtz, *ibid.*, **94**, 5504 (1972).

(4) J. S. Swenton, A. R. Crumrine, and T. J. Walker, *ibid.*, **92**, 1411 (1970); H. E. Zimmerman and G. Epling, *ibid.*, **92**, 1411 (1970).

(5) Irradiations were carried out in acetonitrile using a 450-W immersion lamp and a vycor or corex filter on an  $ca. 1 \times 10^{-3}$  M solution of **8**. The photoproduct was separated conveniently from starting material using glc on a 7 ft  $\times$  0.25 in. 5% SE-30 column. Yields were  $ca. 95\%$  at  $ca. 40-60\%$  conversion, based on recovered starting material.