Table I. Rates of Transport of Amino Acids and Other Molecules through a Liquid Membrane[a]

Entry	Substrate	Rate of transport, 10^8 mol/(hr cm^2)	Entry	Substrate	Rate of transport, 10^8 mol/(hr cm^2)
1	Phenylalanine	500	9	Glycyltyrosine	52
2	Tryptophan	475	10	Glycylphenylalanine	190
3	Leucine	250	11	Phenylalanylglycine	250
4	Tyrosine	200	12[b]	Tyrosine	370
5	Valine	37	13[b]	Tryptophan	220
6	Alanine	18	14[c]	Tyrosine	100
7	Glycine	14	15[d]	Acetylcholine	3000
8	Serine	8	16[e]	OH^-	200

[a] Except when otherwise stated the experiments follow Figure 1a, with 10^{-2} *M* N^+ = Aliquat 336 (methyltricaprylylammonium chloride) in toluene and a starting concentration of amino acid in L of 5×10^{-2} *M*. Reproducibility is within 5%. [b] Experiment following Figure 1b, with 10^{-2} *M* $DNNS^-$ (dinonylnaphthalenesulfonate) in toluene and 5×10^{-2} *M* starting concentration of amino acid in L. [c] L = 3×10^{-2} *M* Tyr in 0.1 *N* HCl; M = 10^{-2} *M* $DNNS^-$ in toluene; R = 3×10^{-2} *M* Tyr and 1 *M* KCl in 0.1 *N* HCl. [d] L = 0.87 *M* acetylcholine bromide in water; R = 1 *M* KBr; M = $DNNS^-$ 0.1 *M* in toluene. [e] L = 5×10^{-2} *N* KOH; R = 5×10^{-3} *N* HCl; M = 10^{-2} *M* Aliquat 336 in toluene.

Measurement of distribution coefficients of AA^- between 0.1 *N* KOH (L) and toluene containing N^+ (M) showed that the relative rates of AA^- transport from L to R follow the order of the distribution coefficients. Thus, the specificity of the process is controlled by the thermodynamic interphase equilibrium between L and M phases. The kinetically important steps, *i.e.*, L → M and M → R transfer, seem to be sufficiently similar for the various amino acids so that only the concentration of (AA^-,N^+) in M appears to differentiate the various substrates. The same result holds for T^- transport (Table I, entries 12, 13, and 15). A case which may lead to interesting further development is the transport of acetylcholine against K^+ (Table I, entry 15).

It has also been found that transport of OH^- itself is competing with AA^- transport (Figure 2; Table I, entry 16). Finally, three dipeptides have been included in our study. Interestingly, about a 20% difference in transport rate is observed between phenylalanylglycine and glycylphenylalanine (Table I; entries 10 and 11).[15]

The present results lead to certain conclusions as well as to prospects for further investigations. (1) Transport of amino acids against Cl^- or K^+ has been demonstrated. (2) Transport against the concentration gradient, pumped by chemical energy, has been observed. (3) With the present carriers the specificity of the process is thermodynamically controlled by the distribution equilibrium between the starting aqueous phase and the membrane. (4) Steric effects in the substrate–carrier species on transport specificity should be observable. (5) Carrier design *via* organic synthesis may allow controlling transport specificity. (6) Kinetic effects on transport specificity should be observable as is the case in cation transport.[4] (7) *Chirospecific* transport, allowing separation of racemic mixtures, may be envisaged using either an optically active membrane phase or a chiral carrier. (8) Similar experiments may be performed on various types of molecules. A deeper understanding of transport processes of organic molecules as well as applications in separation science may result from such studies. Research along these lines is being actively pursued.[16]

Acknowledgment. J. P. Behr thanks the Délégation Générale à la Recherche Scientifique et Technique for a research fellowship. We thank the Schering Co., Bloomfield, N. J., for the supply of some chemicals.

(15) The mechanistic details will be discussed in the full account of this work. However, some results may be mentioned here. In the absence of a carrier the rates of transport (leakage) are reduced by a factor of more than 10^5. The transport shows *saturation* kinetics with respect to carrier concentration. The carrier is located in the organic phase (not detected in the aqueous layers; see also ref 6 and 7 and references therein). The chemical nature of the carrier–substrate complex in the membrane phase is thought to be an ion pair in analogy with results on inorganic ions.[6,7] Control experiments confirm the back transport of Cl^- or K^+ ions. Slow changes in pH are observed since (i) amino acid protonation–deprotonation processes occur; (ii) OH^- transport competes with AA^-. The transport of amino acid goes asymptotically to completion in the conditions described here. Finally, the nature of the kinetically important steps, transfer across the interfaces, rests on previous results obtained with inorganic ions (ref 6 and 7 and references therein). We have also shown that changes in surface area at the interfaces lead to proportional changes in transport rates. The formation and dissociation of the ion-pair carrier–substrate complex should be a very fast process.[7] The synthesis of new carriers may shed light on the possible importance of these steps in the overall kinetics. Additional investigations of these mechanistic and kinetic aspects are under way and will be described in detail in the full paper.

(16) Note Added in Proof. In anology to the above results on transport selectivity, it has recently been shown that the permeability of phospholipid vesicles to amino acids is proportional to the hydrophobicity of the latter (P. D. Wilson and K. P. Wheeler, *Biochem. Soc. Trans.*, 1, 369 (1973)).

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The Electron Paramagnetic Resonance Spectra of 1,1-Dialkylhydrazyl Radicals in Solution[1]

Sir:

Although triarylhydrazyl radicals are among the most stable radicals known[2] there is very little information available concerning alkylhydrazyl radicals. The epr spectra of three 1,1-dialkylhydrazyls trapped in an adamantane matrix have been reported very recently.[3] The uv spectra of the radicals formed by reaction of hydroxyl with 1,1- and 1,2-dimethylhydrazines in aqueous solutions have also been reported recently.[4] Since this work was completed data on some trialkylhydrazyls[5] and 1,1-dialkyl-2-benzenesulfonylhydrazyls[6] have appeared.

We wish to report that 1,1-dialkylhydrazyl radicals can be readily produced in solution by photolysis of solutions containing 1,1-dialkylhydrazines and di-*tert*-butyl peroxide. Photolysis in the cavity of a Varian E-3 epr spectrometer yielded strong, well-resolved spectra for a number of 1,1-dialkylhydrazyls (see, *e.g.*,

(1) Issued as NRCC No. 13419.
(2) For a leading review see: A. R. Forrester, J. M. Hay, and R. H. Thomson, "Organic Chemistry of Stable Free Radicals," Academic Press, New York, N. Y., 1968, p 137.
(3) D. E. Wood, C. A. Wood, and W. A. Latham, *J. Amer. Chem. Soc.*, **94**, 9278 (1972).
(4) E. Hayon and M. Simic, *ibid.*, **94**, 42 (1972).
(5) S. F. Nelsen and R. T. Landis, II, *ibid.*, **95**, 2719 (1973); *ibid.*, in press.
(6) A. T. Balaban and R. Istratoiu, *Tetrahedron Lett.*, 1879 (1973).

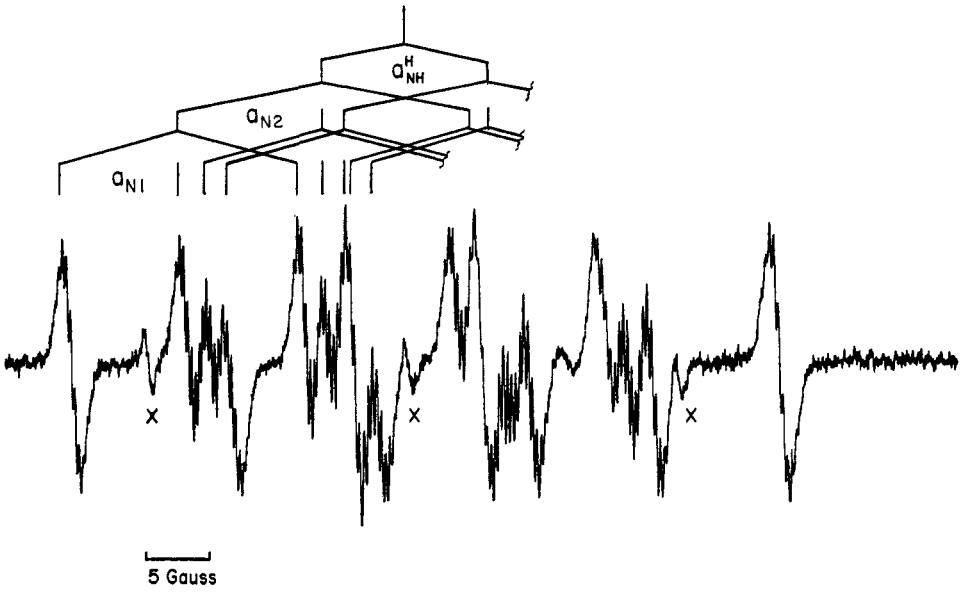


Figure 1. The epr spectrum of $\dot{C}(CH_3)_2(CH_2)_3C(CH_3)_2NNH$ in di-*tert*-butyl peroxide at 24°. The X's result from a small nonreproducible impurity radical.

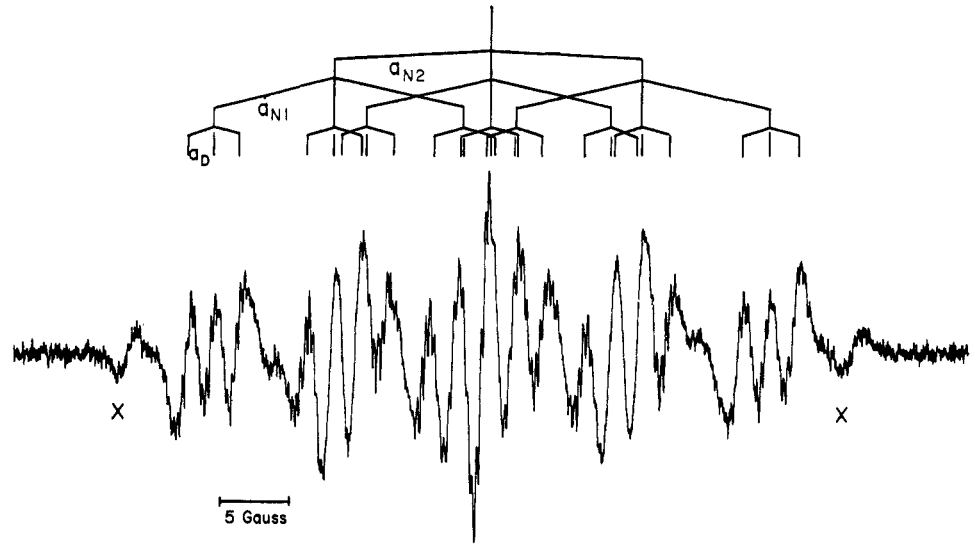


Figure 2. The epr spectrum of $\dot{C}(CH_3)_2(CH_2)_3C(CH_3)_2NND$ in di-*tert*-butyl peroxide at 24°. The X's result from impurity of the undeuterated compound.

Figures 1 and 2). The epr parameters for some representative radicals are recorded in Table I.

The epr hyperfine coupling constants do not vary significantly with temperature (25 to −40°). In the presence of D_2O the hydrazyl H is replaced by a deuterium. The deuterium coupling, $a_{ND}{}^{D}$, is within experimental error of that expected from $a_{NH}{}^{H}$ after allowance for the difference in nuclear magnetic moment and spin. The coupling constant of the β hydrogens in diisopropylhydrazyl is much smaller than for the β hydrogens in dimethyl- and diethylhydrazyl. Such an effect has been observed in many other alkyl-substituted radicals and is usually attributed to hindered rotation of the isopropyl group.[7] This introduces a conformational preference placing the methine hydrogen of the isopropyl group closer to the nodal plane of the orbital containing the unpaired electron than is the case for the β-H's of a freely rotating methyl or ethyl group. The decrease in $a_{\gamma\text{-}H}$ along the series *tert*-alkyl > *sec*-alkyl > alkyl is consistent with that normally observed and is usually accounted for on the basis of a hyperconjugative interaction of these hydrogens with the unpaired electron.[7b]

In hydrazyl itself, $H_2N_{(2)}\dot{N}_{(1)}H$, the hyperfine splitting (hfs) constants have been reported to be 2.3 (H_2), 8.8 ($N_{(2)}$), 11.7 ($N_{(1)}$), and 18.8 G (H).[8] The smaller hfs constant found for the unique proton in 1,1-dialkylhydrazyls (*i.e.*, 13.1–13.8 G) is, we would like to suggest, the result of the inductive (+I) effect of alkyl groups.

(7) See, *e.g.* (a) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **37**, 1326 (1962); (b) G. A. Russell, E. T. Strom, E. R. Talaty, and S. A. Weiner, *J. Amer. Chem. Soc.*, **88**, 1998 (1966); (c) G. D. Mendenhall and K. U. Ingold, *ibid.*, **95**, 2963 (1973).

(8) R. Fantechi and G. A. Helcké, *J. Chem. Soc., Faraday Trans. 2*, **68**, 924 (1972).

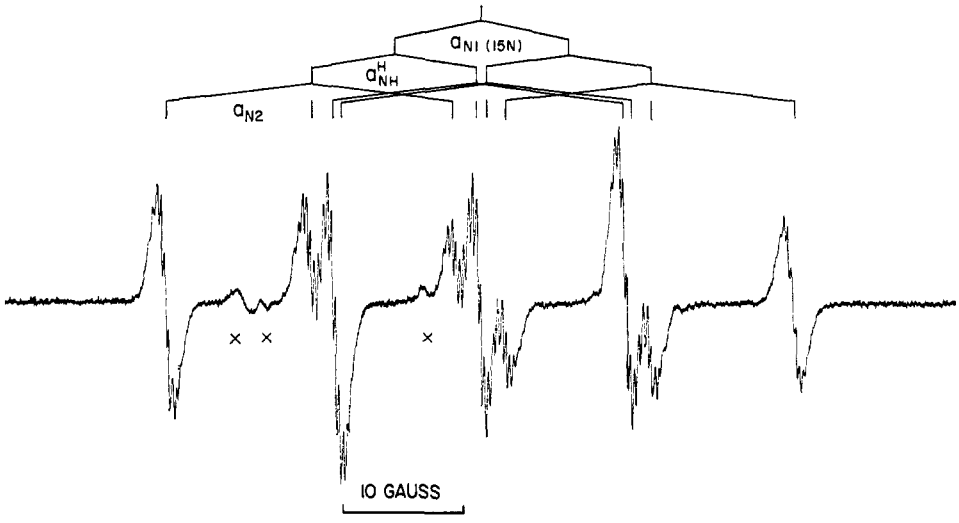
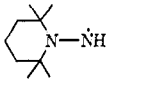
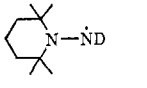
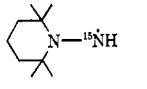


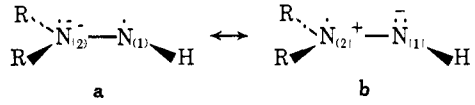
Figure 3. The epr spectrum of $\overline{C(CH_3)_2(CH_2)_3C(CH_3)_2}\dot{N}^{15}NH$ in di-*tert*-butyl peroxide at 24°. The X's result from a small nonreproducible impurity radical.

Table I. Hyperfine Splitting Constants (Gauss)[a] and g Values for 1,1-Dialkylhydrazyl Radicals in Di-*tert*-butyl Peroxide Solutions at 23°

Radical	a_{NH}^{H}	$a_{N(2)}$	$a_{N(1)}$	a_{β}^{H}	a_{γ}^{H}	g
$(CH_3)_2N-\dot{N}H$[b]	13.67	11.49	9.60	6.90		2.00381
$(CH_3CH_2)_2N-\dot{N}H$	13.78	11.14	9.58	6.73	*c*	2.00384
$[(CH_3)_2CH]_2N-\dot{N}H$	13.11	11.66	9.95	2.2	0.25	2.00384
$[(CH_3)_2CH]_2N-\dot{N}D$	2.00[d]	11.14	9.91	2.1	0.2	2.00384
	13.46	12.45	10.01		0.32	2.00383
	2.07[d]	12.04	9.84		0.3	2.00384
	13.48[e]	12.10	14.40[f]		0.32	2.00384

[a] Satisfactory computer simulated spectra were obtained for all radicals. [b] From ref 3, $a_{NH}^{H} = 13.6$, $a_{N(2)} = 11.4$, $a_{N(1)} = 9.6$, and $a_{\beta\text{-H}} = 6.7$ in adamantane at room temperature. [c] Not resolved. [d] Deuterium splitting. [e] Deuterium splitting = 2.1 G. [f] ^{15}N splitting (*i.e.*, a doublet splitting with the expected value of 1.4 for a^{15}_{N}/a^{14}_{N}).

As a consequence, resonance structure **b** will be stabi-



a **b**

lized relative to **a** and the unpaired electron density on $N_{(1)}$ will be decreased and on $N_{(2)}$ increased relative to $H_2N_{(2)}\dot{N}_{(1)}H$.

Theoretical calculations on $H_2N\dot{N}H$[3,8] and on $(CH_3)_2N\dot{N}H$[3] indicate that the divalent nitrogen produces the larger coupling. This assignment receives some support from the slightly larger decrease in $a_{N(2)}$ than in $a_{N(1)}$ on deuteration (see Table I). That is, the amplitude of the out-of-plane bending mode of $N_{(1)}$ should be decreased by deuteration with a consequent decrease in $a_{N(1)}$.[9] However, it is not possible to assign the two nitrogen couplings with certainty without ^{15}N-labeling experiments of the kind used to show that the divalent nitrogen in DPPH has the larger coupling.[10,11] For this reason, we prepared

$$(CH_3)_2\overline{C(CH_2)_3C(CH_3)_2}{}^{14}N^{15}\dot{N}H$$

the epr parameters for which (Table I) leave no doubt that it is the trivalent nitrogen (*i.e.*, the ^{14}N) that is responsible for the larger coupling (see Figure 3). This unexpected result may be a consequence of the +I effect of the alkyl groups referred to above.

At temperatures below *ca.* −35° 1,1-dialkylhydrazyls are relatively stable. They are destroyed irreversibly by warming but their concentration can be reversibly decreased and increased by lowering and raising the temperature between −30 and −70°.

$$2R_2N\dot{N}H \rightleftharpoons R_2NN(H)N(H)NR_2$$

On photolysis of dialkylhydrazine–peroxide mixtures the hydrazyl radical always appears immediately. After 5 min or so of continuous irradiation the dialkylamino radical can also be detected. We suggest that it is produced by photolysis of tetrazene formed by oxidation of the tetrazane. All the amino radicals,

$$R_2NN(H)N(H)NR_2 \xrightarrow[R_2N\dot{N}H]{t\text{-}BuO\cdot \text{ or}} R_2NN{=}NNR_2 \xrightarrow{h\nu} R_2N\cdot$$

including the very stable 2,2,6,6-tetramethylpiperidyl,[12] can be "annealed-out" by storing the sample at −78° for 1 or 2 days. The hydrazyl radicals are unaffected by this treatment.

Prolonged photolysis results in the formation of a purple coloration, λ_{max} 525 nm. Preliminary experiments suggested that this color was due to the hydrazyl radicals (DPPH has λ_{max} 515 nm) since the color was stable below −35° but was destroyed irreversibly on warming the sample to room temperature. However, the apparent extinction coefficient was several times that of DPPH and measurements in the temperature

(9) K. V. S. Rao and M. C. R. Symons, *J. Chem. Soc. A*, 2163 (1971).

(10) M. M. Chen, K. V. Sane, R. I. Walter, and J. A. Weil, *J. Phys. Chem.*, **65**, 713 (1961).

(11) R. W. Holmberg, R. Livingston, and W. T. Smith, Jr., *J. Chem. Phys.*, **33**, 541 (1960).

(12) J. R. Roberts and K. U. Ingold, *J. Amer. Chem. Soc.*, **95**, 3228 (1973).

range −30 to −100° (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.

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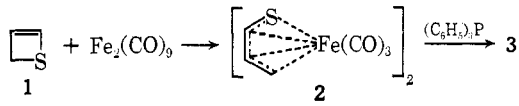
Received May 5, 1973

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.[1] 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°), **2**, which was converted to the monomeric, red iron dicarbonyl triphenylphosphine complex, **3**, of thioacrolein, a hitherto unknown thioaldehyde:[2] ^{1}H nmr ($CDCl_3$) δ 6.10 (d, 1, =CHS), 5.60 (m, 1, -CH=CS), 1.95 (d, 1, exo or endo proton of CH_2), 0.90 (doublet of doublets, 1, exo or endo proton of CH_2 coupled to phosphorus); mass spectrum (70 eV) *m/e* 446 (parent), 418 (−CO), 390 (−2CO), 128 (C_3H_4SFe), 72 (C_3H_4S). *Anal.* Calcd for $C_{23}H_{19}FeO_2PS$ (**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.[3] 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[4] and evidence for the formation of thioacroleins from thietes has been obtained recently.[1]

Oxidation of the iron tricarbonyl complex yields the yellow *S*-oxide complex, a reasonable structure for which is **4**, mp 112–114°: ir (KBr) 1030 cm^{-1} (S=O); mass spectrum (70 eV) *m/e* 228 (parent), 212 (−O), 200 (−CO), 172 (−2CO). *Anal.* Calcd for $C_6H_4FeO_4S$: C, 31.58; H, 1.75. Found: C, 31.77; H, 1.62.[5] This complex may be considered a derivative of the unknown vinylsulfine (CH_2=CHCH=S=O).[6]

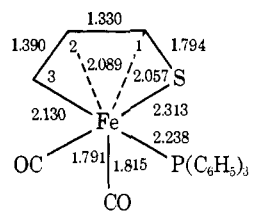
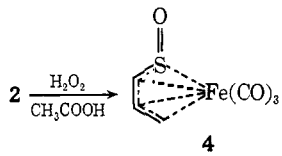
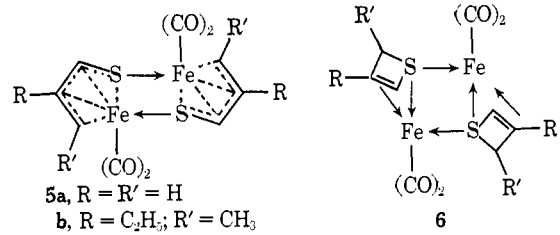


Figure 1. Some bond lengths (Å) in thioacrolein iron triphenylphosphine dicarbonyl (**3**) (C_3-S = 2.837 Å).



The iron tricarbonyl complex **2** and an analogous complex derived from 2-methyl-3-ethyl-2*H*-thiete[1] 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 mm sec^{-1}; QS, 1.358 mm sec^{-1}). Oxidation of **5b** with *m*-chloroperbenzoic acid yields a monosulfoxide 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.[7] The iron tricarbonyl complex of thioacrolein differs from the iron complex of acrolein in that the latter forms only an iron tetracarbonyl complex

(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°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).

(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).