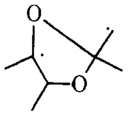
3:1.2:1.[12] The low values of the quantum yields for formation of photo-Cope products ($\Phi_{5\rightarrow 8} = 0.04$, $\Phi_{8\rightarrow 5} = 0.05$) make it clear that the bulk of the inefficiency in intramolecular photocycloaddition of these β-oxa-γ,δ-enones is *not* due to β-cleavage of 1,4-biradical intermediate **6**. Since kinetic studies indicate that the intramolecular oxetane formation is an S_1 reaction and that trapping of the ketone $^1n,\pi^*$ state of **5** or **8** by the internal olefin is efficient,[13] the low quantum yields for oxetane formation must result from inefficient reaction from some intermediate on the pathway to **7** other than the γ,δ-enone $^1n,\pi^*$ state or biradical **6**. The obvious candidate is an exciplex formed by interaction of the electrophilic half vacant oxygen atom of the n,π^* state and the electron-rich γ,δ-double bond. Analogous exciplexes have been postulated as intermediates in intermolecular and intramolecular photocycloaddition reactions of ketones and electron-rich olefins.[1l,2b,14] Our quantum yield measurements indicate that the efficiency of formation of biradical **6** from both exciplexes is at most 20%.[15] The inefficiency in proceeding from the exciplex to **6** could result from direct decay of the exciplexes to the ground state of the starting γ,δ-enone and/or from competitive formation from the exciplexes of 1,4-biradicals in which oxygen is bonded to the γ-carbon, e.g., **9**. Since our mass balances are high (>70%), formation of biradicals such as **9** followed by closure to a 2,5-dioxabicyclo[2.1.1]hexane cannot be a major pathway for decay of the exciplexes.[16] Thus if biradicals with oxygen bonded to the γ-carbon are formed they must primarily undergo cleavage to regenerate starting γ,δ-enones.



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In summary, we have shown that acyclic β-oxa-γ,δ-enones **5** and **8** undergo photo-Cope reactions in competition with inefficient intramolecular photocycloaddition to form dioxabicyclo[2.2.0]hexanes. Both photoreactions most likely proceed through a common 1,4-biradical intermediate, **6**. The bulk of the inefficiency in production of 1,4,6-trimethyl-2,5-dioxabicyclo[2.2.0]hexane is attributed to inefficient formation of biradical **6** from an exciplex initially generated by interaction of the carbonyl $^1n,\pi^*$ state with the internal olefin.

Acknowledgment. We wish to acknowledge the National Science Foundation, the Hoffmann-La Roche Foundation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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(2) 1,4-Biradicals analogous to **4** have also been postulated as intermediates in the intermolecular photocycloaddition of carbonyl compounds to electron-rich olefins. See, for example, (a) N. J. Turro and P. A. Wriede, *J. Am. Chem. Soc.*, **92,** 320 (1970); (b) N. C. Yang and W. Eisenhardt, *ibid.*, **93,** 1277 (1971); (c) D. R. Arnold, *Adv. Photochem.*, **6,** 301 (1968).

(3) Although it is a priori possible that the γ,δ-enone analogous to **8**, but with the methyl groups trans, could also be formed, only **8** is observed (vide infra).

(4) See ref 1g for an earlier example of a photo-Cope reaction of a γ,δ-enone in which the γ,δ-double bond is allenic.

(5) We observed formation of 2,5-dioxabicyclo[2.2.0]hexanes but no photo-Cope product on irradiation of 3-methyl-4-oxa-5-hexen-2-one. In this case, however, the photo-Cope product would be an aldehyde which might not be stable under the reaction conditions. See ref 1o.

(6) γ,δ-Enone **5** was prepared in 15% yield by a transetherification reaction between 3-hydroxy-2-butanone and isopropenyl methyl ether using mercuric acetate as the catalyst. See H. Yuki, K. Hatacha, K. Nagata, and K. Jajiyama, *Bull. Chem. Soc. Jpn.*, **42,** 3546 (1969).

(7) γ,δ-Enone **8** was obtained by dehydrohalogenation of *erythro*-6-iodo-5-methyl-4-oxahexan-2-one or the corresponding bromo compound. The erythro iodo was prepared by reaction of *trans*-2-butene, acetol, mercuric oxide, and iodine while the erythro bromo compound was prepared by reaction of acetol, *N*-bromoacetamide, and *trans*-2-butene. See (a) M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, E. A. Smith, and W. E. Vaughn, *J. Am. Chem. Soc.*, **60,** 440 (1938); (b) P. J. Stang and M. G. Mangum, *ibid.*, **97,** 1459 (1975).

(8) **7**: ^{1}H NMR (CCl_4, δ, 100 MHz) 1.22–1.28 (9 H, includes 1.28 (s), 1.22 (s), and 1.28 (d, $J = 8$ Hz)), 4.7–5.0 (3 H, includes 4.7 (ABq), and 4.96 (q, $J = 8$ Hz)); ν_{max} (CCl_4, cm^{-1}) 955 (oxetane); MS (*m/e*, relative intensity, 20 eV) 128 (M^+, 3), 85 (4), 72 (5), 71 (10), 70 (9), 58 (13), 55 (21), and 43 (100).

(9) Product ratios were determined by GLPC using internal standards. Products were isolated by removal of solvent followed by preparative GLPC.

(10) Quantum yields were measured using the photoreduction of benzophenone by benzhydrol as an actinometer. See W. M. Moore and M. Ketchum, *J. Am. Chem. Soc.*, **84,** 1368 (1962).

(11) Small, but variable, yields of 3-methyl-2,5-hexanedione and 2-butanone are also observed on irradiation of 8. These products most likely arise via acetonyl radicals formed by β-cleavage of **8**.

(12) The photo-Cope products could also be formed by β-cleavage of the β-oxa-γ,δ-enones to acetonyl radicals, followed by recoupling to rearranged β-oxa-γ,δ-enones. This mechanism seems quite unlikely, however, since photolysis in piperylene partially quenches formation of hexanediones, believed to be formed via β-cleavage to acetonyl radicals,[11] but does not quench formation of photo-Cope or 2,5-dioxabicyclo[2.2.0]hexane products. A concerted photo-Cope reaction from **5** or **8** is also unlikely both on the basis of orbital symmetry considerations and because of restrictions placed on the transition state for intramolecular photocycloaddition by the stereoelectronic requirements for electrophilic attack by the carbonyl oxygen on the γ,δ-double bond (see, for example, N. J. Turro, J. C. Dalton, K. Dawes, G. Farrington, R. Hautala, D. Morton, M. Niemczyk, and N. Schore, *Acc. Chem. Res.*, **5,** 92 (1972)). It is also possible that photo-Cope products could be formed by unimolecular decomposition of hot ground state 2,5-dioxabicyclo[2.2.0]hexane (**7**) formed by closure of biradical **6**. Bond energy and ring strain considerations suggest that **7** is formed from **6** with approximately 35 kcal/mol of excess vibrational energy. Vibrational relaxation of vibrationally excited **7**, however, should be much faster than cleavage to γ,δ-enones, a process whose activation energy can be estimated to be on the order of 36 kcal/mol using bicyclo[2.2.0]hexane as a model. See C. Steel, R. Zand, P. Hurwitz, and S. G. Cohen, *J. Am. Chem. Soc.*, **86,** 679 (1964).

(13) Formation of **7** and photo-Cope product upon irradiation of **5** or **8** is not quenched in neat 1,3-pentadiene. Unlike normal alkanones ($\Phi_f \sim 10^{-3}$), but like other acyclic γ,δ-enones,[1l,1o] both **5** and **8** show no measurable fluorescence ($\Phi_f < 10^{-4}$) indicating that the singlet lifetime, τ_1, is much shorter for these γ,δ-enones than for normal alkanones.[1l,1o] This provides strong evidence for efficient trapping of the alkanone $^1n,\pi^*$ state by the γ,δ-double bond.

(14) See, for example, (a) R. A. Caldwell, G. W. Sovocool, and R. P. Gajewski, *J. Am. Chem. Soc.*, **95,** 2549 (1973); (b) I. E. Kochevar and P. J. Wagner, *ibid.*, **94,** 3859 (1972); (c) N. E. Schore and N. J. Turro, *ibid.*, **97,** 2482 (1975); (d) N. C. Yang, M. H. Hui, and S. A. Bellard, *ibid.*, **93,** 4056 (1971).

(15) This requires the reasonable assumption that the only pathways for decay of biradical **6** are β-cleavage or closure.

(16) This requires the reasonable assumption that 2,5-dioxabicyclo[2.1.1]hexanes do not decompose to the starting β-oxa-γ,δ-enone. Careful examination by NMR and GLPC yields no evidence for the presence of 2,5-dioxabicyclo[2.1.1]hexanes in the photolysis mixtures.

(17) Shell Fellow, 1974–1975.

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Synthesis and Characterization of a New Series of First Row Element Tetrahedral Mercaptide Complexes

Sir:

Tetrahedral, monomeric complexes of halide and pseudohalide ions with first row transition elements are well docu-

Table I. Physical Properties of the Mercaptide Complexes

					Solution Spectra in CH_3CN	
Complex	Color	% C Calcd (Found)	% H Calcd (Found)	μ_{eff}^{corr} $(\mu_B)^a$	Band position (cm^{-1}) (ϵ)	Assignment
$(Ph_4P)_2Mn(SPh)_2dts$	Yellow	70.12	4.60	5.84		
		(70.93)	(4.69)			
$(Ph_4P)_2Mn(Sph)_4$	Yellow	73.89	5.17	5.79		
		(73.85)	(5.20)			
$(Ph_4P)_2Fe(SPh)_2dts$	Red-brown	70.06	4.59	5.04	5 880 (95)^b	$^5E \rightarrow {}^5T_2$
		(69.28)	(4.88)			
$(Ph_4P)_2Fe(SPh)_4$	Red-brown	73.83	5.16	5.02	5 880 (98)^b	$^5E \rightarrow {}^5T_2$
		(73.70)	(5.07)			
$(Ph_4P)_2Co(SPh)_2dts$	Green	69.87	4.58	4.42	8 200 (154)	$^4A_2 \rightarrow {}^4T_1$ (F)
		(70.45)	(4.73)		14 180 sh (1080)	
					15 040 (1214)	$^4A_2 \rightarrow {}^4T_1$ (P)
					17 240 sh (846)	
$(Ph_4P)_2Co(SPh)_4$	Green	73.64	5.15	4.75	6 900 (211)	$^4A_2 \rightarrow {}^4T_1$ (F)
		(73.65)	(5.19)		13 800 sh (675)	
					14 700 (820)	$^4A_2 \rightarrow {}^4T_1$ (P)
					16 000 sh (590)	
$(Ph_4P)_2Ni(SPh)_2dts$	Dark green	69.88	4.58	Dia		
		(71.25)	(4.69)			
$(Ph_4P)_2Ni(SPh)_4$	Red	73.65	5.15	3.20	5 710 (83)^c	$^3T_1 \rightarrow {}^3A_2$
		(73.47)	(5.03)		13 800 14 800 (327)	$^3T_1 \rightarrow {}^3T_1$ (P)
$(Ph_4P)_2Zn(SPh)_2dts$	White	69.46	4.55			
		(70.09)	(4.71)			
$(Ph_4P)_2Zn(SPh)_4$	White	73.24	5.12			
		(73.39)	(5.12)			

[a] Measurements at ambient temperature using a Faraday technique. [b] Broad band, the shape of which is complicated by solvent overtones. [c] Spectrum recorded using the red solution obtained after reaction of $(Ph_4P)_2Ni(dts)_2$ and excess KSPh and filtration of K_2dts. ϵ values are estimated based on the original weight of $Nidts_2^{2-}$.

mented and extensively studied molecules.[1] By contrast, simple mercaptido complexes of these elements are not known. Usually mercaptide ligands are found in multinuclear coordination compounds where they are bonded to more than one metal ion utilizing two[2] or three[3] pairs of electrons. Terminal mercaptide coordination is not common and invariably is found in mixed ligand complexes.[4] The implication of mercaptide coordination in copper metalloenzymes[5] and the demonstration of this type of coordination in the structures of several non-heme iron proteins[6] prompted us to explore metal-complex-mercaptide ion reactions as an approach to the synthesis of simple mercaptide complexes. In this communication we wish to report on the synthesis and characterization of the hitherto unknown series of simple tetrahedral thiophenolato complexes with first row elements.

Reactions of potassium thiophenolate, KSPh, with tetraphenyl phosphonium salts of the first row dithiosquarato complexes,[7] $(Ph_4P)_2M(Dts)_2$, in hot acetonitrile under rigorously oxygen free conditions, are rapid as evidenced by color changes and the precipitation of K_2Dts. Crystalline tetraphenyl phosphonium salts of the mixed ligand complexes, $[M(Dts)(SPh)_2]^{2-}$ are obtained with M = Fe(II), Co(II), Zn(II), Mn(II), and Ni(II). The properties of these complexes, which, with the exception of the nickel(II) complex, are x ray isomorphous, are shown in Table I. The electronic spectra and magnetic properties of the Fe(II), Co(II), and Mn(II) complexes are very similar to those expected[8] for tetrahedrally coordinated ions. The diamagnetic nickel(II) complex is quite likely planar. The mixed ligand complexes react further, under nitrogen, with KSPh according to the reaction:

$$(Ph_4P)_2M(Dts)(SPh)_2 \xrightarrow[\text{XS KSPh}]{CH_3CN} (Ph_4P)_2M(SPh)_4 + K_2Dts$$

The x ray isomorphous, crystalline, tetrathiophenolato complexes thus obtained appear to be stable at least for short periods of time, but their solutions decompose very rapidly when exposed to air.

The iron(II) complexes show the $^5E \rightarrow {}^5T_2$ transition as a broad band centered at 5900 cm^{-1}. The energy of this transition is similar to the ν_2 band reported[9] for reduced rubredoxin (6000 cm^{-1}). A preliminary voltammetric study[10] on the $(Ph_4P)_2Fe(SPh)_4$ complex[11] reveals a reversible oxidation wave at a potential ~0.9 V more positive than that observed for $Ni(MNT)_2^{2-}$ and is in accord with the extreme sensitivity of this complex toward air oxidation. The low magnetic moment observed for the $(Ph_4P)_2Ni(SPh)_4$ complex in the solid state (3.2 μ_B) may reflect a distortion from ideal tetrahedral geometry. Preliminary solution measurements show the magnetic moment to vary as a function of concentration, solvent, and time. The visible spectrum characteristic of tetrahedral Ni(II) (Table I) can be obtained on a freshly prepared sample and only in the presence of excess mercaptide. Apart from the bis(imidodithiophosphino)nickel(II)[12] for which an x-ray crystallographic study shows[13] tetrahedrally coordinated nickel(II), there exists no other tetrahedral nickel(II) complex having a NiS_4 core. The magnetic moments of the imidodithiophosphinonickel complexes in solution also are low and attributed[11] to a tetrahedral ($S = 1$) $\rightleftarrows$ planar ($S = 0$) equilibrium. The electronic spectra of the $(Ph_4P)_2Co(SPh)_2Dts$ and $(Ph_4P)_2Co(SPh)_4$ complexes (Table I) when compared to those of the $(Ph_4P)_2Co(Dts)_2$ complex[7b] ($^4A_2 \rightarrow {}^4T_1$ (F), 8300 cm^{-1}, and $^4A_2 \rightarrow {}^4T_1$(P), 15100 cm^{-1}) indicate the weak ligand field nature of the mercaptide ligand. The isomorphism of the Mn(II) and Zn(II) complexes to the analogous Fe(II), Co(II), and Ni(II) tetrahedral species is taken as sufficient indication of tetrahedral coordination for these complexes. The reaction of the thiophenolate ion with weakly bound sulfur chelates appears to be a general one.[14]

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(10) Voltammetric studies were conducted in acetonitrile with $(Pr_4N)_4PF_6$ as the supporting electrolyte. A detailed electrochemical study of these complexes is currently in progress.

(11) A crystal structure determination of this complex is currently under way.

(12) A. Davison and E. S. Switkes, *Inorg. Chem.*, **10,** 837 (1971).

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(14) Preliminary studies show that various 1,1-dithio complexes undergo metathesis reactions with the thiophenolate ion. An interesting metathetical reaction is observed with the $(Ph_4P)_4Cu_8(Dts)_6$ cluster. Analytical data on the crystalline product indicates the stoichiometry $(Ph_4P)_4Cu_6(SPh)_{12}{}^{4-}$.

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Photosensitized Decomposition of Diazopropene. Intermolecular Reactions of Vinylmethylene

Sir:

We have studied the triplet-photosensitized decomposition of diazopropene (**1**) and have observed intermolecular abstraction reactions. These results are compatible with triplet vinylmethylene (**2**-*T*) as reactive intermediate. This species may abstract chlorine or hydrogen atoms but apparently prefers hydrogen abstraction over either chlorine abstraction or addition to olefinic double bonds. These reactions are the first examples of intermolecular reactions of a simple vinylmethylene and provide a systematic approach to its reactivity in the triplet state.

Vinylmethylene and many of its derivatives have triplet ground states.[1] However, the pyrolysis or photolysis of their precursors (diazo compounds, diazirines, 3*H*-pyrazoles, or cyclopropenes) yields only intramolecular addition or insertion products,[2] which are most reasonably rationalized via the corresponding singlet states. In an attempt to study intermolecular reactions of vinylmethylene and to test the reactivity pattern of its triplet state, we have studied the benzophenone-sensitized decomposition of diazopropene[3] in the presence of simple chlorinated substrates (CCl_4, $CHCl_3$), saturated hydrocarbons, and olefins.

The benzophenone-sensitized decomposition[5] of **1** in tetrachloromethane produced the geometric isomers, **3** and **4**, in comparable yields totaling >50%.[6] The formation of these products can be rationalized on the basis of a mechanism involving chlorine abstraction by **2**-*T* and coupling of the resulting radicals, chloroallyl and trichloromethyl (pair A). A radical pair mechanism is supported by the strong nuclear spin polarization[7] (Figure 1), which was observed when the irradiation was carried out in an NMR spectrometer. We found enhanced absorption for the allylic and the terminal olefinic protons of products **3** and **4** and emission for the internal olefinic protons. The additional enhanced-absorption signals, three doublets at 4.8, 5.4, and 5.5 ppm, were assigned to a third tetrachlorobutene isomer, **5**. Since we failed to isolate this product, it must either be formed in trace amounts only or it must be unstable under the reaction conditions.

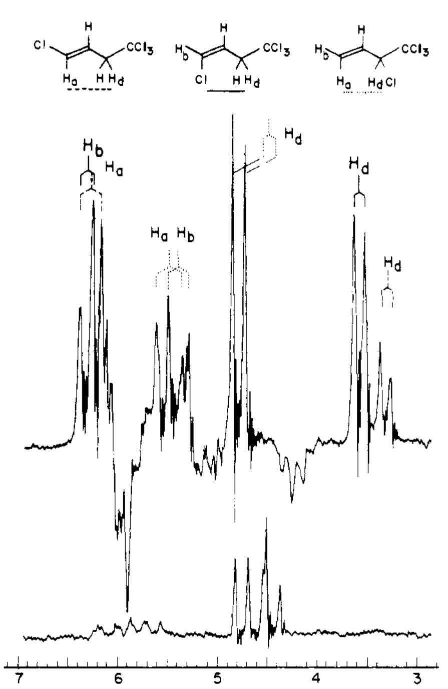
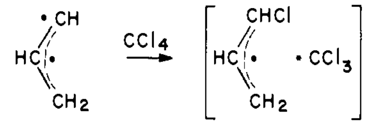


Figure 1. ^1H NMR spectrum (60 MHz) of diazopropene in tetrachloromethane containing benzophenone-d_{10} (bottom) and CIDNP spectrum observed during uv irradiation of this solution (top).



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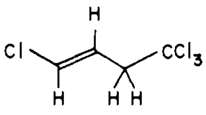

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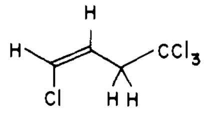

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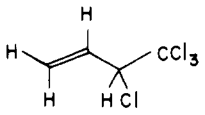

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The signal direction of a CIDNP spectrum is determined by four parameters and may be used to derive the initial spin multiplicity of the intermediate radical pair and its immediate precursor. For the formation of **3**, **4**, and **5** from pair A we assign these parameters as follows. The 1-chloroallyl radical should have a spin density distribution similar to that of the allyl radical ($a_{1,3} < 0 < a_2$). Its *g* factor should be somewhat higher than that of the allyl radical ($g = 2.0026$),[8] but certainly considerably smaller than that of the trichloromethyl radical ($g = 2.0091$),[9] hence, $\Delta g < 0$. Given these parameters and the assumed coupling mechanism ($\epsilon > 0$), the observed signal directions indicate that pair A was generated in the triplet state ($\mu > 0$). The identification of the precursor is somewhat problematic since it is difficult to rule out the participation of the diazo compound in an excited state.[10] Nevertheless, we view the for-