

Table I. Exo/Endo Conformer Ratios at 0°

Ligand	Reactant CH ₃ CN	Initial product (CD ₃) ₂ CO	Final product (CD ₃) ₂ CO
1,2 Allyl	4.7	0.15	5.2
3,4 2-Methylallyl	0.38	2.4	0.35

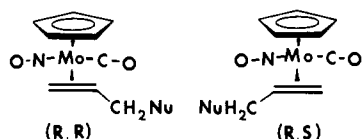
(Scheme I) The NO⁺ cation reacts with **1** endo faster than with **1** exo and the endo configuration is retained. Excess **2** endo is observed because exo–endo interconversion in **1** is rapid compared to reaction with NO⁺. This is consistent with $k_{1xn}[1x] > k_{nn}[\text{NO}^+][1n]$. (Scheme II) The NO⁺ cation reacts rapidly compared with endo–exo interconversion in **1**, but stereoselectively interconverts configuration, e.g., **1x** → **2n**. This is consistent with $k_{xn}[\text{NO}^+] \sim k_{nx}[\text{NO}^+] \gg k_{1nx} \sim k_{1xn}$ or the formation of a common intermediate with stereoselectively decays to product.

A choice may be made between these alternatives on the basis of observations with the 2-methylallyl derivative. The endo conformer of the dicarbonyl complex, **3n**, is thermodynamically preferred due to steric interactions between the ring and the 2-methyl group ($K_{\text{exo/endo}} = 0.38, 0^\circ, \text{CD}_3\text{CN}$). The reaction with NO⁺ proceeds to yield a conformer excess in the initial product opposite to that observed in the reaction with **1**. This product distribution slowly reverses to yield a final equilibrium for the nitrosyl derivative, **4**, of $K_{\text{exo/endo}} = 0.35$. Thus opposite conformations to the allyl system predominate in the 2-methylallyl system at all stages—reactant equilibrium, initial product distribution, and final equilibrium (see Table I).

If the rate constants for reaction with NO⁺ are not significantly perturbed by the methyl group, Scheme I is untenable. Since the endo conformer already predominates in the reactant in **3**, there should be a predominance of endo isomer in the initial product distribution if Scheme I were to be operative. Thus, Scheme II, which implies inversion of conformation in the major isomer upon reaction with NO⁺, appears to be operative.

Since the reaction with NO⁺ occurs so rapidly, it probably does not involve attack on a coordinatively unsaturated species such as $\eta^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{-}\eta^1\text{-C}_3\text{H}_5$ or $\eta^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})\text{-}\eta^3\text{-C}_3\text{H}_5$. Thus it appears that a concerted SE2 attack displaces CO and interconverts allyl conformation, perhaps via a η^1 -allyl. The η^1 -allyl, which might be accessible from either **1x** or **1n**, might produce a product determined by the kinetic preference for re-formation of the two η^3 -allyl conformers.¹²

These chiral cationic allyl complexes react with nucleophiles to produce mixtures of diastereomeric olefin derivatives. Weak stereoselectivity is shown in the addition of hydride or cyanide; however, reactions of **2** with methanol/Na₂CO₃ or sterically hindered enamines produce a single diastereoisomer.¹³



We have observed high stereoselectivity in the formation and reaction of 1-substituted and 1,3-disubstituted analogues of **2**; furthermore, it appears that asymmetric induction in olefin substituents is related to endo–exo isomer ratio. This stereoselectivity of the nucleophilic reactions may be attributed to the asymmetry in charge distribution introduced by the nitrosyl ligand. Thus, in addition to the novel “inversion” of conformation in their formation, these nitrosyls provide a system wherein asymmetric induction in nucleophilic attack

appears to be dominated by an electronic rather than a steric effect.¹⁴

References and Notes

- (1) D. A. White, *Organomet. Chem. Rev., Sect. A*, **3**, 497 (1968).
- (2) D. W. Lichtenberg and A. Wojcicki, *J. Am. Chem. Soc.*, **94**, 9271 (1972); A. Rosan, M. Rosenblum, and J. Tancrede, *ibid.*, **95**, 3062 (1973); M. Rosenblum, *Acc. Chem. Res.*, **7**, 122 (1974).
- (3) J. W. Faller, B. V. Johnson, and C. D. Schaeffer, Jr., *J. Am. Chem. Soc.*, **98**, 1395 (1976).
- (4) H. Brunner, *Top. Current Chem.*, **56**, 67 (1975); M. T. Mocella, M. S. Okamoto, and E. K., Barefield, *Synth. React. Inorg. Metal-Org. Chem.*, **4**, 69 (1974); N. G. Connelly, *Inorg. Chim. Acta Rev.*, **6**, 47 (1972).
- (5) B. M. Trost and T. J. Dietsche, *J. Am. Chem. Soc.*, **95**, 8200 (1973).
- (6) J. W. Faller, C. C. Chen, M. J. Mattina, and A. Jakubowski, *J. Organomet. Chem.*, **52**, 361 (1973).
- (7) R. G. Hayter, *J. Organomet. Chem.*, **13**, P1 (1968).
- (8) N. A. Bailey, W. G. Kita, J. A. McCleverty, A. J. Murray, B. E. Mann, and N. W. J. Walker, *J. Chem. Soc., Chem. Commun.*, 592 (1974).
- (9) Some resonances observed in the ¹H Nmr of the initial product mixture decrease with time, while others increase until equilibrium is established. The chemical shifts (in ppm downfield from Me₄Si) are as follows for cyclopentadienyl; two syn protons; and two anti protons: 2 decreasing: 6.52; 5.10, 4.30; 3.80, 3.25. 2 increasing: 6.35; 5.40, 4.90; 3.55, 3.40. 4 decreasing: 6.30; 5.05, 4.90; 3.57, 3.41. 4 increasing: 6.48, 5.00, 4.20; 3.70, 3.05.
- (10) The resonances assigned to endo isomers are characterized by lower field cyclopentadienyl shifts and greater separations between the nonequivalent syn or anti protons. Confirmation of the assignments in the allyl derivative was obtained from the ¹H Nmr of the unstable η^5 -indenyl-Mo(CO)(NO)- η^3 -allyl cation. The major isomer in the initial product had a resonance at δ -0.15 corresponding to an endo isomer with an anti proton proximate to the indenyl ring. The minor isomer had a shift of δ 2.62 for the central proton, an upfield shift of 2.9 ppm as expected for an exo isomer.⁶
- (11) This difference in interconversion rate of a factor of a million in these pseudo-seven-coordinate complexes contrast markedly with the pseudo-six-coordinate [$\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})\text{-}\eta^3\text{C}_3\text{H}_5$] analogue.¹² In the iron system, the carbonyl complex interconverts slightly slower (about a factor of three) than the nitrosyl compound (A. Rosan and J. W. Faller, unpublished). We attribute these differences to the fundamental fluxional characteristics of seven-coordinate vs. six-coordinate complexes. Both the iron and molybdenum complexes can interconvert via a η^3 to η^1 mechanism, but the pseudo-rotation path is of very low energy only for the molybdenum dicarbonyl complex.⁶
- (12) J. W. Faller, B. V. Johnson, and T. P. Dryja, *J. Organomet. Chem.*, **65**, 395 (1974); R. W. Fish, W. P. Giering, D. Marten, and M. Rosenblum, *ibid.*, **105**, 101 (1976).
- (13) Which pair of diastereoisomers is formed is unknown at present. An x-ray structure indicates that under some conditions the dithiocarbamate addition product has the (R,R)-(S,S) configuration;⁹ however, one might anticipate that the chirality produced at the olefin metal center with **2x** might be opposite to that formed with **2n**. We are currently examining the effect of endo–exo isomerism on asymmetric induction, which can be readily studied because the ratio of exo to endo varies slowly from 0.15 to 5.2 as the system approaches equilibrium.
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Chemistry of the Macrocyclic Cobalt(II) Complex, [Co(C₂₂H₂₂N₄)]. Reactions with Halogens, Molecular Oxygen, Alkynes, and Nitriles

Sir:

The multifarious roles of cobalt in the biochemistry of vitamin B₁₂^{1,2} suggest that considerable potential still exists for the development of new chemistry with cobalt in other suitably designed ligand systems. The macrocyclic ligand, derived from the metal-template condensation of *o*-phenylenediamine with 2,4-pentanedione (see Scheme I),^{3,4} is grossly distorted from planarity due to the steric interactions of the methyl groups with the benzenoid rings.^{5,6} These distortions lead to a strained coordination environment for metal ions as well as activated methine carbon atoms of the ligand and may lead to unusual reactivity at either the metal or activated ligand centers, or both. The reactivity of iron(II) complexes derived from this ligand has been recently reported.⁷

Table I. NMR Spectra for the New Macrocyclic Complexes^a

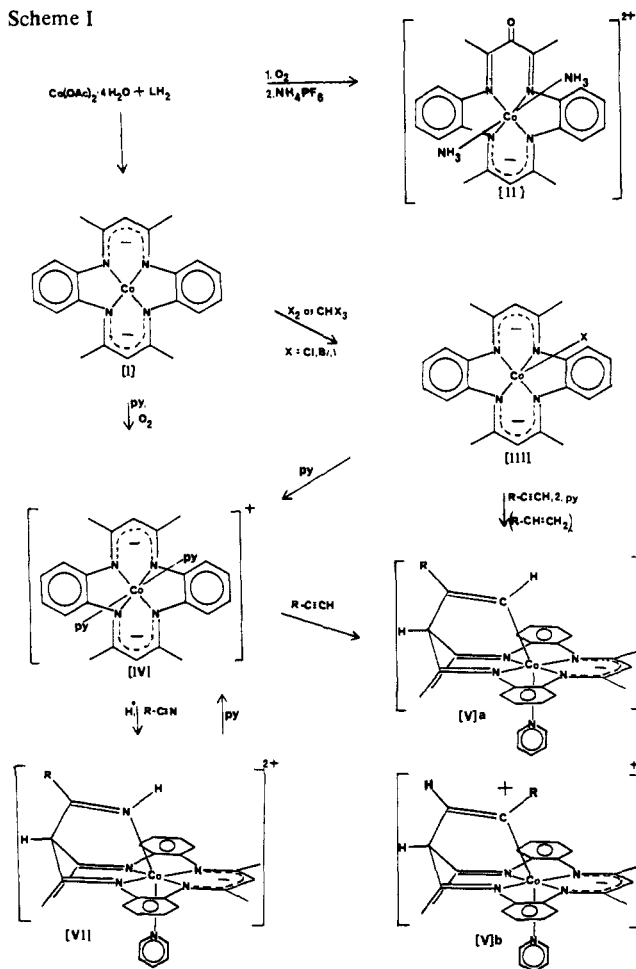
Compound	Solvent	Proton resonances in ppm (δ) ^b		
		Macrocycle (Benzenoid)		Other ligands
II	CD ₃ NO ₂	2.77 (6, s)	7.34 (2, t)	1.94 (6, br)
		3.27 (6, s)	7.61 (2, t)	
		5.54 (1, s)	7.86 (2, d)	
IV	CD ₃ CN	2.13 (12, s)	6.53 (4, m)	7.30 (2, t)
		4.58 (2, s)	6.87 (4, m)	7.56 (2, 6-br)
				7.78 (1, t)
				8.06 (1, t-br)
Va, R = C ₆ H ₅ -	CD ₃ NO ₂	2.44 (6, s)	6.70 (2, t)	8.58 (2, t)
		2.83 (6, s)	6.91 (2, t)	
		5.34 (1, s)		
		6.20 (1, s)	7.08-7.67 (12, m)	
		10.29 (1, s)		
Va, R = CH ₃ -	CD ₃ NO ₂	2.32 (3, s)	6.68 (2, t)	7.16 (2, t)
		2.42 (6, s)	6.90 (2, t)	7.59 (1, t)
		2.78 (6, s)	7.07 (2, d)	8.51 (2, d)
		5.27 (1, s)	7.24 (2, d)	
		5.47 (1, s)		
		9.10 (1, s)		
Va, R = H-	CD ₃ NO ₂	2.53 (6, s)	6.67 (2, t)	7.15 (2, t)
		2.73 (6, s)	6.89 (2, t)	7.60 (1, t)
		5.29 (1, s)	7.08 (2, d)	8.53 (2, d)
		5.68 (1, d)	7.14 (2, d)	
		6.19 (1, t)		
		9.91 (1, d)		
Va, R = HOCH ₂ -	CD ₃ NO ₂	2.35 (6, s)	6.66 (2, t)	7.20 (2, br)
		2.69 (6, s)	6.88 (2, t)	7.67 (1, br)
		4.29 (2, s)	7.01 (2, d)	8.48 (2, br)
		5.21 (1, s)	7.13 (2, d)	
		5.51 (1, s)		
		9.39 (1, s)		
Va, [Co(LCH=CH)CN] R = H	CDCl ₃	2.31 (6, s)	6.82 (2, t)	
		2.59 (6, s)	7.04 (2, t)	
		4.96 (1, s)	7.17 (2, d)	
		5.24 (1, d)	7.24 (2, d)	
		6.14 (1, t)		
		10.70 (1, d)		
VI, R = CH ₃ -	CD ₃ NO ₂	1.55 (3, br)	6.92 (2, t)	7.02 (1, t)
		2.67 (6, s)	7.13 (2, t)	7.24 (1, t)
		2.73 (3, s)	7.37 (2, d)	7.64 (1, t)
		3.18 (6, s)	7.54 (2, d)	7.93 (1, d)
		5.49 (1, s)		8.61 (1, d)
		6.60 (1, s)		
		10.85 (1, s)		
VI, R = CH ₃ CH ₂ -	CD ₃ NO ₂	1.12 (3, br)	6.92 (2, t)	7.02 (1, t)
		1.24 (3, t)	7.13 (2, t)	7.24 (1, t)
		2.68 (6, s)	7.38 (2, d)	7.63 (1, t)
		3.06 (2, q)	7.89 (2, d)	7.94 (1, d)
		3.19 (6, s)		8.60 (1, d)
		5.52 (1, s)		
		6.62 (1, s)		
		10.61 (1, s)		

^a All spectra were recorded at 270 MHz. ^b Key: s = singlet; d = doublet; t = triplet; br = broad; m = multiplet; q = quartet.

The reaction of the free ligand, C₂₂H₂₄N₄, with 1 equiv of Co(OAc)₂·4H₂O in a CH₃OH-CH₃CN solution (1:2, v/v) under N₂ (see Scheme I) yields the low-spin ($\mu_{\text{eff}} = 2.86 \mu_{\text{B}}$) four-coordinate Co(II) complex, I, in high yield (90%). Oxidation of the reaction mixture of I with O₂ leads to a vigorous exothermic reaction and the formation of a Co(III) complex,

II, in which one of the 2,4-pentanediiimino-like rings has been converted into a β -diimine donor function with an adjacent α,β -unsaturated carbonyl. This complex, isolated as the hexafluorophosphate salt, was characterized by elemental analysis and infrared and ¹H NMR (270 MHz) spectroscopy. The carbonyl function was indicated by the presence of a strong

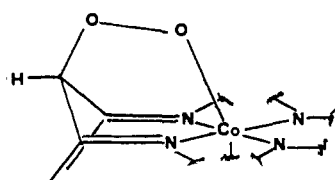
Scheme I



$\text{C}=\text{O}$ stretching frequency in the ir spectrum at 1670 cm^{-1} . Consistent with II, the ^1H NMR spectrum indicates the presence of two types of methyl resonances, 2.77 and 3.27 ppm (δ), and only a single methine proton, 5.54 ppm from the remaining 2,4-pentanediiimato chelate ring (Table I).

Unusual high-spin five-coordinate Co(III) complexes of the type $[\text{Co}(\text{C}_{22}\text{H}_{22}\text{N}_4)\text{X}]$, $\text{X} = \text{Cl, Br, I, III}$, were obtained from I by either warming solutions of I in the appropriate halocarbon solvents (e.g., CHCl_3 , CHBr_3 , etc.) or by reaction of I with halogens in noncoordinating solvents. Although diamagnetic five-coordinate organo-cobalt(III) complexes are not uncommon, high-spin, five-coordinate Co(III) complexes have been characterized in only one other instance⁸ with a dianionic open-chain tetraaza ligand. Room temperature magnetic moments for the complexes indicate an $S = 1$ ground state ($\mu_{\text{eff}} = 2.67, 3.15$, and $2.80 \mu_{\text{B}}$ for the Cl, Br, and I complexes, respectively).^{8,9}

Unexpectedly, solutions of the five-coordinate Co(III) complexes were found to react with oxygen irreversibly, even at -60°C . The solutions change color upon warming to room temperature and eventually decompose; however, Co(III) complexes containing the oxygenated form of the ligand, II, have been isolated in small yields from these solutions. The peroxy species depicted below is most likely to be the low



temperature form of the complex, and is a likely intermediate in the formation of II.

Dissolution of either I or III in degassed pyridine, followed by aerial oxidation of I, gave quantitative yields of the diamagnetic six-coordinate species, $[\text{CoL}(\text{py})_2]^+$, IV. ^1H NMR spectra of the complexes in weakly coordinating solvents, (e.g., nitriles) showed that one pyridine exchanges approximately 10^2 times faster than the other; substitution of pyridine for another ligand such as NH_3 is easily accomplished by simply adding an excess of new ligand to solutions of the bispyridine complex. Dilute solutions of $[\text{CoL}(\text{py})_2]^+$ have reactivities similar to those observed for the five-coordinate complexes, although at slower rates, strongly suggesting dissociation of the most labile pyridine to give the reactive five-coordinate intermediate, $[\text{CoLpy}]^+$.

Under acidic conditions complex IV readily adds one molecule of a wide variety of nitriles. The probable four-center interaction (involving the metal center of $[\text{CoLpy}]^+$ with the nitrile nitrogen and the methine carbon of a 2,4-pentanediiimato ring with the nitrile carbon atom) yields a uninegative, pentadentate macrocyclic ligand, VI, containing an imine appendage occupying an axial coordination site, which is similar in form to the iron(II) macrocyclic complex-nitrile adducts studied by Busch and co-workers.¹⁰ The infrared spectrum of the product ($\text{R} = \text{CH}_3$) contains a single N-H absorption at 3250 cm^{-1} . The NMR spectrum indicates only single mirror symmetry for the macrocyclic ligand; two types of methyl resonances (2.31 and 2.59 ppm), and two types of C-H resonances are observed (the 2,4-pentanediiimato C-H at 5.49 ppm and the tertiary C-H appearing at 6.60 ppm). The imine N-H , derived from CH_3CN , appears downfield at 10.85 ppm while the $-\text{CH}_3$ group is at 2.73 ppm. The addition of pyridine to VI regenerates IV and free acetonitrile (NMR).

The unusual reactivity of the Co(III) complexes with oxygen and nitriles suggested that unsaturated hydrocarbons might also participate in similar four-center reactions, especially in view of the exceptional stability of a wide variety of organo- Co(III) complexes. Compounds III and IV react with acetylene and monosubstituted acetylenes ($\text{R} = -\text{Ph}, -\text{CH}_2\text{OH}, -\text{CH}_3$) to give the appendaged, pentadentate macrocyclic ligand containing a vinyl carbanion as one of the axial ligands, V. The ^1H NMR data are listed in Table I.^{11,12} Examination of reaction mixtures and products shows that propyne adds to give Va and Vb, while the more bulky acetylenes add to give only Va. Molecular models of these complexes indicate considerable steric interaction in the framework of the macrocyclic ligand as well as angular strain in the chelate rings involving the acetylene adduct.

The addition of acetylenes across the six-membered chelate ring can be described as a 1,4-addition. Related reactions have been observed between the super dieneophile, hexafluorobutyne, and Pd(II) ^{13,14} and Rh(I) ^{15,16} acetylacetonate complexes, as well as with benzene.¹⁷ Certainly, the "cycloaddition" reactions observed in this work with simple acetylenes are remarkable in light of their lesser reactivity compared to hexafluorobutyne.

The nature of the reactivity of III with olefins is not as definitive as with acetylenes. A reaction with ethylene does occur and the ^1H NMR spectra of the products have two different types of macrocyclic ligand methyl resonances and two different types of C-H resonances. The electronic spectra of the products are also very similar to those of the organo- Co(III) complexes derived from acetylenes. However, the number of proton resonances in the region expected for the ethylene of the addition compound vary in intensity from preparation to preparation and are too numerous and complex to be attributable to a single product; this may be a consequence of the inherent instability associated with most Co(III) -alkyl complexes containing β -hydrogen atoms.

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References and Notes

- (1) J. M. Pratt, "The Inorganic Chemistry of Vitamin B₁₂", Academic Press, London and New York, 1972.
- (2) H. A. O. Hill, "Inorganic Chemistry", G. Eichorn, Ed., Elsevier Scientific Publishing Company, Amsterdam, Oxford, and New York, 1973, p 1067.
- (3) V. L. Goedken and J. Molin-Case, *J. Chem. Soc., Chem. Commun.*, 337 (1973).
- (4) M. Weiss, Y.-A. Park and V. L. Goedken, to be submitted.
- (5) V. L. Goedken, S.-M. Peng, and Y.-A. Park, *J. Chem. Soc.*, **96**, 284 (1974).
- (6) V. L. Goedken, J. Pluth, S.-M. Peng, and B. Bursten, submitted for publication.
- (7) V. L. Goedken and Y.-A. Park, *J. Chem. Soc., Chem. Commun.*, 214 (1975).
- (8) M. Gerloch, B. M. Higson, and E. D. McKenzie, *Chem. Commun.*, 1149 (1971).
- (9) These magnetic moments are very similar to those reported in ref 8 for which temperature dependent studies suggested an equilibrium between spin singlet and spin triplet states.
- (10) K. Bowman, D. P. Riley, D. H. Busch, and P. W. R. Corfield, *J. Am. Chem. Soc.*, **97**, 5036 (1975); D. P. Riley, J. A. Stone, and D. H. Busch, *ibid.*, **98**, 1752 (1976).
- (11) The ¹H NMR data of the acetylene and nitrile adducts demonstrate the greater trans-labilizing effect of carbon vs. nitrogen donor atoms. Examination of the proton resonances shows that the pyridine trans to the carbon donor exhibits free rotation; distinction can be made only among the α, β, and γ protons. However, the pyridine trans to the nitrogen donor displays five distinct interpretable resonances. For the latter system, the stronger Co-py bond creates sufficient interaction with the macrocyclic ligand to prevent rotation of the pyridine on the NMR time scale. The NMR spectra require the α- and α'-protons of the pyridine ligand to be directed toward the nonequivalent 2,4-pentanediaminato rings rather than toward the equivalent benzenoid rings.
- (12) The x-ray crystal structures of the five-coordinate cobalt(III) iodide complex III and of the acetylene adduct, V, have been completed and are consistent with the conclusions presented in this paper.
- (13) D. M. Barlex, J. A. Evans, R. D. W. Kemmitt, and D. R. Russell, *Chem. Commun.*, 331 (1971).
- (14) D. M. Barlex, A. C. Jarvis, R. D. W. Kemmitt, and B. Y. Kimura, *J. Chem. Soc., Dalton Trans.*, 2549 (1972).
- (15) A. C. Jarvis, R. D. W. Kenneth, B. Y. Kimura, D. R. Russell, and P. A. Tucker, *J. Organomet. Chem.*, **66**, C63 (1974).
- (16) D. R. Russell and P. A. Tucker, *J. Chem. Soc., Dalton Trans.*, 1743 (1975).
- (17) C. G. Krespan, B. C. McKusick, and T. L. Cairns, *J. Am. Chem. Soc.*, **83**, 3428 (1961).

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Solution Photochemistry of Diazoacetone. Wolff Rearrangement and Acetylmethylene

Sir:

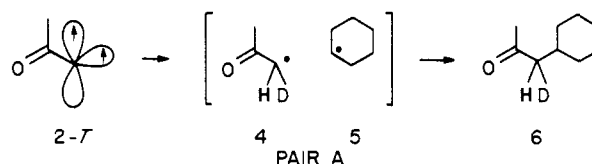
Diazoacetones undergo several interesting reactions: intramolecular insertions and additions,¹ the Wolff rearrangement² and intermolecular additions, which apparently involve triplet ketocarbenes.³ In an attempt to delineate the reactivity pattern of triplet acetylmethylene (2-T), we studied the photosensitized decomposition of diazoacetone (1) in hydrocarbons and chlorinated substrates using chemically induced dynamic nuclear polarization (CIDNP)⁴ as a probe for radical pair derived reaction products. Our results suggest that 2-T may react by hydrogen abstraction or may undergo intersystem crossing to the singlet state (2-S). In partially chlorine substituted solvents chlorine abstraction by 2-S is observed simultaneously with hydrogen abstraction by 2-T. The fact that chlorine abstraction is not observed upon direct photolysis suggests that 2-S is not an intermediate in the Wolff rearrangement of 1.

When solutions of 1 and benzophenone (3) in cyclohexane-*d*₁₂ or cyclohexene-*d*₁₀ were irradiated in the probe of an NMR spectrometer⁵ they displayed broad emission singlets (~2.15 ppm) representing the α-methylene protons of α-cyclohexylacetone (6) and α-(3-cyclohexenyl)acetone (7), respectively. The observation of these effects indicates that the

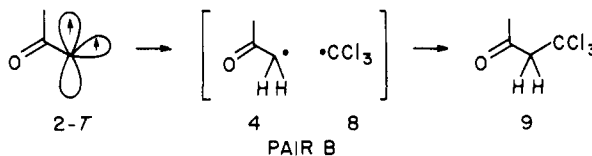


Figure 1. ¹H NMR spectrum (60 MHz) of diazoacetone (1; 0.1 M) in CHCl₃ (bottom) and CIDNP spectrum observed during the photosensitized decomposition (benzophenone, 0.1 M) of 1 in CHCl₃ (top). S denotes the high-field ¹³C satellite of CHCl₃.

products, 6 and 7, are being formed by coupling of radical pairs, e.g., acetylonyl-*d*₁ (4; *g* = 2.0045; *a*_H^α < 0)⁶ cyclohexyl-*d*₁₁ (5; *g* = 2.0026).⁷ The observed signal directions suggest that these pairs are formed either directly from a triplet precursor or by an encounter of free radicals. The second mechanism would imply a chain reaction initiated by the sensitizer via hydrogen abstraction from the solvent and propagated by induced decomposition of the diazo compound (chemical sensitization).⁸ Since similar CIDNP signals were not observed during the radical induced decomposition of 1 in these solvents,⁹ we interpret the observed results as evidence for an energy transfer mechanism with 2-T as key intermediate.



Since triplet carbenes often display a pronounced preference for hydrogen abstraction,¹⁰ we studied the photosensitized decomposition of 1 in trichloromethane. During this reaction we observed indeed a sharp absorption singlet (3.8 ppm) representing the methylene protons of 4,4,4-trichlorobutan-2-one (9). The polarization of this product is consistent with coupling of trichloromethyl (8; *g* = 2.0091)¹¹ with acetylonyl radicals, generated in pairs by hydrogen abstraction of 2-T from the solvent.



However, this reaction also produced two doublets at 4.55 (emission, E) and 6.05 ppm (enhanced absorption, A; Figure 1), which represent the protons in the 3- and 4-positions of 3,4,4-trichlorobutan-2-one (12). This product is most reasonably explained by coupling of pair C, a pair of α-chloroacetylonyl (10; *g* = 2.0070; *a* < 0)¹² and dichloromethyl radicals (11; *g* = 2.0080; *a* = -17 G).¹³ An analysis of the net signal directions and of the superimposed E/A multiplet effects⁴ indicated that this pair is generated from a singlet precursor.¹⁴ This assignment leaves 9 as the only product derived directly from 2-T and asserts that this species is selective.

What is the origin of pair C? Inefficient photosensitization and direct photolysis of 1 to yield 2-S would provide a trivial explanation. However, the irradiation of 1 in the absence of