has been interpreted as indicating that rotation is a slower process than inversion for simple acyclic hydrazines,[54b] and that the barrier to nitrogen inversion is 6.8–8.0 kcal/mol in these compounds.[54] This result is in excellent agreement with the present calculations (7.4 kcal/mol, **19**). For acyclic hydroxylamines, however, the interpretation of small steric effects within a related series of compounds has resulted in conflicting claims as to which is the rate-limiting process (inversion or rotation) in the isomerization.[60] The calculated barrier for nitrogen inversion in trimethylhydroxylamine (**18**, 11.8 kcal/mol) is near the observed barriers[60] of 12.3–12.9 kcal/mol, but *ab initio* calculations indicate a rotational barrier of similar magnitude (12.0 kcal/mol[58]). Perhaps only a single "coupled" barrier separates isomers,[61] and further attempts to assign the barrier to either rotation or to inversion may be bootless.

The success with which the present method duplicates known barriers to pyramidal inversion for a variety of chemical structures permits its application to the prediction of as yet unreported barriers (Table II) with a considerable degree of confidence. One such application, the prediction of barriers to pyramidal inversion in various thiophene *S*-oxides and S-alkylated thiophenium ions, has been recently reported.[62] Additionally, barriers to pyramidal inversion are predicted for an acylphosphine (**55**, 22.3 kcal/mol), for an acyl sulfoxide (**99**, 28.6 kcal/mol), and for silyl-substituted phosphorus and sulfur compounds (trimethoxysilyldimethylphosphine, **65**, 16.0 kcal/mol; methyldisilylphosphine, **63**, 13.2 kcal/mol; 1-silylphosphole, **84**, 6.0 kcal/mol; 1-silylphosphindole, **85**, 9.3 kcal/mol; methyl silyl sulfoxide, **98**, 18.8 kcal/mol). Finally, phosphorus is anticipated to be planar in phosphorinium ion (**87**), in 1-methyl-2,5-diboraphosphol-3-ene (**88**), and in 1-methyl-2,5-diboraphospholane (**89**). Other compounds listed in Table II with no accompanying reported barriers represent further predictions by this treatment.

Several of our predictions have since been confirmed by experiment. Thus, studies in these laboratories have yielded barriers for an acylphosphine (19.4 kcal/mol),[63] a trimethoxysilylphosphine (17.1 kcal/mol),[64] a disilylphosphine (12.2 kcal/mol),[65] and a phosphonitrile (>26 kcal/mol),[66] all in reasonable agreement with calculated values for **55**, **65**, **63**, and **56**, respectively.

In conclusion, the present method offers a relatively simple and reliable means for obtaining quantitative estimates to barriers of pyramidal inversion in systems comprised of first- and second-row elements, and hopefully will serve both to stimulate and to direct new research efforts in this field.

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[60] (a) See Griffith and Roberts, Table II, footnote *z*; (b) M. Raban and G. W. J. Kenney, Jr., *Tetrahedron Lett.*, 1295 (1969); (c) J. R. Fletcher and I. O. Sutherland, *Chem. Commun.*, 687 (1970).

[61] See section 3.2.4 in ref 3a.

[62] J. D. Andose, A. Rauk, R. Tang, and K. Mislow, *Int. J. Sulfur Chem. A*, **1**, 66 (1971).

[63] Value reported for acetylisopropylphenylphosphine: W. Egan and K. Mislow, *J. Amer. Chem. Soc.*, **93**, 1805 (1971).

[64] Value found for isopropylphenyl(trimethoxysilyl)phosphine; R. D. Baechler and K. Mislow, unpublished results.

[65] Value found for bis(dimethylphenylsilyl)phenylphosphine; G. H. Senkler, Jr., and K. Mislow, unpublished results.

[66] A lower limit to the inversion barrier for isopropylphenylcyanophosphine; W. Egan and K. Mislow, unpublished results.

Hindered Rotation in Some Organometallic Carbamates, Thiocarbamates, and Dithiocarbamates

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Abstract: Hindered rotation in systems of the type $R'YC(=X)NR_2$, where X,Y = O,O; O,S; S,O; S,S; R = CH_3, C_2H_5; R′ = CH_3, $Si(CH_3)_3$, $Sn(CH_3)_3$, has been investigated by variable temperature nmr spectroscopy. Rotational parameters were calculated by the total line shape and intensity ratio methods. Effects of substituent groups X, Y, and R′ on the free energy of activation are discussed in terms of their effect on the relative importance of the contributing resonance structures.

Although the synthetic aspects of the insertion of unsaturated species into the organometallic–nitrogen bond have been widely explored,[1] the structural details of the products have received little attention. Most of the insertion adducts contain the grouping $C(=X)NR_2$ and might therefore be expected to exhibit hindered rotation about the C–N bond.

In order to explore hindered rotation in these systems we have prepared a number of trimethylsilyl carbamates and thiocarbamates of the type $R'YC(=X)NR_2$ where X,Y = O,S; R = CH_3, C_2H_5; R′ = $(CH_3)_3Si$, and have measured their nmr spectra at various temperatures. The temperature dependence of the shape of the *N*-alkyl resonances can be used to determine the rotational energy and free energy of activation by what are now standard methods.[2,3]

The primary objectives of the study were: (a) to investigate the existence of hindered rotation about

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[1] M. F. Lappert and B. Prokai, *Advan. Organometal. Chem.*, **5**, 225 (1965).

[2] H. Kessler, *Angew. Chem., Int. Ed. Engl.*, **9**, 219 (1970).

[3] W. E. Stewart and T. H. Siddall, *Chem. Rev.*, **70**, 517 (1970).

the C–N bond in these organometallics, (b) to determine the effect of oxygen and sulfur on the rotational activation parameters in compounds containing the groups $XC(=O)NR_2$ and $XC(=S)NR_2$, where $X = O$ and S, and (c) to determine the effect of the organometallic group, $(CH_3)_3Si$, on these parameters. In order to accomplish the latter objective a series of compounds where $R = CH_3$ and $R' = CH_3$ were also investigated.

Experimental Section

Syntheses. All starting materials except dimethylaminotrimethylsilane and dimethylaminotrimethylstannane were commercial products. Dimethylaminotrimethylsilane was obtained by amination of trimethylchlorosilane with excess dimethylamine, bp 84–86° (lit.[4] 85°). Dimethylaminotrimethylstannane was prepared by lithioamination of trimethylchlorostannane, bp 125–127° (lit.[5] 126°). Carbonoxysulfide was obtained from the reaction of thioacetamide with ethyl chloroformate [6]

Trimethylsilyl insertion products were prepared by addition of the appropriate unsaturated reagent (CO_2, CS_2, or COS) to dimethylaminotrimethylsilane and to diethylaminotrimethylsilane: trimethylsilyl dimethylcarbamate (I), yield 60%, bp 56–58° (13 mm), $n^{20}D$ 1.4157 (*Anal.* Calcd for $C_6H_{15}O_2NSi$: C, 44.68; H, 9.37; N, 8.69. Found: C, 44.59; H, 9.34; N, 7.24); trimethylsilyl dimethyldithiocarbamate (II), bp 102–105° (2.5 mm), $n^{20}D$ 1.5635 (lit.[7] bp 105° (2.5 mm), $n^{20}D$ 1.5640); *O*-trimethylsilyl dimethylthiocarbamate (III), yield 63%, bp 56–57.5° (3 mm), $n^{20}D$ 1.4907 (*Anal.* Calcd for $C_6H_{15}NSi$: C, 40.63; H, 8.53; N, 7.90; Si, 15.84. Found: C, 40.54; H, 8.70; N, 8.08; Si, 15.74); trimethylsilyl diethylcarbamate (IV), bp 77–79° (17 mm), $n^{20}D$ 1.4183 (lit.[7] bp 74° (15 mm), $n^{20}D$ 1.4193); trimethylsilyl diethyldithiocarbamate (V), bp 111.5° (4 mm), $n^{20}D$ 1.5431 (lit.[7] bp 92–97° (0.7 mm), $n^{20}D$ 1.5481); *O*-trimethylsilyl diethylthiocarbamate (VI); yield 70%, bp 71.5–73° (4 mm), $n^{20}D$ 1.4805 (*Anal.* Calcd for $C_8H_{19}NSi$: C, 46.79; H, 9.32; N, 6.82; Si, 13.68. Found: C, 46.99; H, 9.25; N, 6.99; Si, 13.68).

S-Trimethylstannyl dimethylthiocarbamate (VII) was prepared by reaction of COS with dimethylaminotrimethylstannane; mp 40–43° (lit.[8] 40°).

Methyl dimethylcarbamate (VIII) was obtained from the reaction of dimethylcarbamyl chloride with methanol and pyridine in ether; bp 130–132° (lit.[9] 131°).

Methyl dimethyldithiocarbamate (IX) was obtained by reaction of dimethylamine with methyl iodide and carbon disulfide; bp 110–112° (12 mm), mp 45–47° (lit.[10] bp 243° (760 mm), mp 46–47°).

O-Methyl dimethylthiocarbamate (X) was prepared from dimethylthiocarbamyl chloride, methanol, and pyridine in ether; bp 87–92° (12 mm), $n^{20}D$ 1.5225 (lit.[11] bp 193° (760 mm), $n^{20}D$ 1.5242).

S-Methyl dimethylthiocarbamate (XI) was obtained from the reaction of dimethylcarbamyl chloride with methyl mercaptan in pyridine; bp 184° (lit.[12] 180°).

Nmr and ir spectra of the compounds above were consistent with their proposed structures. The structures of III and VI are discussed below.

Nmr Measurements. Nmr spectra of each compound as a 30% solution in chlorobenzene containing *ca.* 5% TMS were measured on a Varian A-60D spectrometer. Three to five tracings of the *N*-methyl region were obtained at 50- or 100-Hz sweep width and at low rf fields at each temperature. Resolution was carefully optimized at each temperature by tuning on the TMS peak. Temperatures were measured from the peak separations obtained with the standard methanol or ethylene glycol samples and the equation of Van Geet.[13] Peak locations in the *N*-methyl region relative to TMS were obtained by the standard side-banding method using a Hewlett-Packard 200 CD audio oscillator and Model 522B electronic counter.

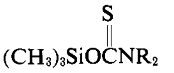
The mean lifetime, τ, at each temperature was obtained from the experimental spectra by both the intensity ratio[14] and total line shape methods. For the total line shape procedure the Gutowsky–Holm equation[15] for the equal population case was programmed in FORTRAN IV. The computer-generated line shape was then fitted to the experimental line shape by varying τ until the sum of the percentage errors (computer generated *vs.* experimental) in intensity ratio, peak separation, and peak width at half-height were minimized. For compounds with $\Delta\nu < 6$ Hz, τ was obtained by minimizing the percentage error in peak separation and peak width at half-height after reducing the percentage error in intensity ratio to 3%.

Since the doublet for each compound was slightly unsymmetrical, two of the parameters—intensity ratio and width—were measured for the most intense peak only. Use of the transverse relaxation time, T_2, obtained from internal TMS produced a better fit than T_2 from the doublet. The peak separation at the slow rotation limit was corrected for overlap[15] and was assumed to be temperature independent (this was verified for several compounds).

The activation energy was obtained from the usual least squares Arrhenius plot (five to nine points for each compound; 20–30° temperature range) while the free energy of activation at 25° was obtained from the Eyring equation (transmission coefficient = 1; τ at 25° taken from the least-squares Arrhenius plot).

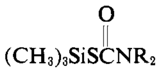
Results

Structure of Insertion Products. The reaction of the unsymmetrical species COS with dialkylaminotrimethylsilanes could lead to two products, **1** and **2**. The



$(CH_3)_3SiO\overset{\overset{S}{\|}}{C}NR_2$

1



$(CH_3)_3SiS\overset{\overset{O}{\|}}{C}NR_2$

2

products of the reaction of COS with dimethylaminotrimethylsilane and diethylaminotrimethylsilane both have ir spectra containing no peaks in the 1550- to 1800-cm^{-1} region. The same is true for the dithiocarbamates, while the ir spectra of the carbamates, I and IV, exhibit an intense peak at 1680 cm^{-1}. The trimethylsilyl chemical shift of the dimethyl COS adduct, III, is also considerably closer to the trimethylsilyl shift in the carbamate derivative, I: I, $\delta(Si(CH_3)_3)$ 0.27; III, $\delta(Si(CH_3)_3)$ 0.31; II, $\delta(Si(CH_3)_3)$ 0.53. Thus, it seems reasonable to assume that the structures of these adducts are of type **1**, and this is substantiated by the similar rotational parameters (*vide infra*) found for the dimethyl derivative, III, and its methyl analog, X. This is in agreement with the structure which has been assigned to the adduct formed from COS and dimethylaminosilane.[16]

Since the isomer $(CH_3)_3SiSC(=O)N(CH_3)_2$ cannot be obtained by the insertion reaction, the organometallic series was completed by the preparation of the trimethylstannyl analog, VII, from COS and dimethylaminotrimethylstannane. The product of this reaction has been assigned a structure of type **2**.[8]

As is obvious from Table I, the nmr spectra of all the organometallic *N,N*-dimethyl adducts in chlorobenzene contain a doublet in the *N*-methyl region at some temperature. (The *N*-methyl region of I remained a singlet at −50° in $CHCl_3$, while the same was true for II as the neat liquid at −50°.) The nmr spectra of silyl dimethylcarbamate and silyl dimethyldithiocarbamate in CCl_4 measured at 40 Mcps were previously

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[4] E. A. V. Ebsworth and H. J. Emeleus, *J. Chem. Soc.*, 2150 (1958).
[5] K. Jones and M. F. Lappert, *ibid.*, 1944 (1965).
[6] F. H. Suydam, W. E. Greth, and N. R. Langerman, *J. Org. Chem.*, 34, 292 (1969).
[7] H. Breederveld, *Recl. Trav. Chim. Pays-Bas.*, 81, 276 (1962).
[8] R. F. Dalton and K. Jones, *J. Chem. Soc. A*, 590 (1970).
[9] A. P. N. Franchimont and E. A. Klobbie, *Recl. Trav. Chim. Pays-Bas*, **8**, 299 (1889).
[10] R. von Braun, *Chem. Ber.*, **35**, 3371 (1902).
[11] J. Billeter, *ibid.*, 43, 1856 (1910).
[12] M. Delépine and P. Schring, *Bull. Soc. Chim. Fr.*, 7, 902 (1910).
[13] A. L. Van Geet, *Anal. Chem.*, 40, 2227 (1968).
[14] M. T. Rogers and J. C. Woodbrey, *J. Phys. Chem.*, 66, 540 (1962).
[15] H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).
[16] E. A. V. Ebsworth, G. Rocktäschel, and J. C. Thompson, *J. Chem. Soc. A*, 362 (1967).

Table I. Rotational Parameters

Compd	$R'Y\overset{X}{\overset{\|}{C}}NR_2$ R′	Y	X	R	E_a, kcal/mole TLS	IR	Log A TLS	IR	ΔG_a, kcal/mole TLS	IR	Lit.	$\Delta\nu$, Hz	T_c, °C
I	$Si(CH_3)_3$	O	O	CH_3	9.6	2.4	8.2	2.4	15.8	16.5		1.63	5
II		S	S	CH_3	14.3	6.4	13.4	6.4	13.4	15.0		5.21	−7
III		O	S	CH_3	18.6	17.9	12.9	12.5	18.5	18.3		17.88	104
IV[a]		O	O	C_2H_5								2.5	20
V[a]		S	S	C_2H_5								7	−18
VI[a]		O	S	C_2H_5								19	94
VII	$Sn(CH_3)_3$	S	O	CH_3	13.2	12.8	10.4	10.1	16.5	16.4		12.01	43
VIII	CH_3	O	O	CH_3	14.4	7.9	12.5	7.2	14.8	15.5	14.8[b]	3.70	10
IX		S	S	CH_3	13.9	12.6	12.0	11.1	15.0	15.0	15.7[c]	17.05	33
X		O	S	CH_3	16.1	15.2	12.2	11.7	16.9	16.8	17.8[c]	20.10	74
XI		S	O	CH_3	13.0	8.3	12.0	8.1	14.1	14.7		5.36	−3

[a] $\Delta\nu$ and T_c are given for the methylene protons only; VI measured neat; V, 50% CH_2Cl_2; IV, 50% $CHCl_3$. [b] Reference 2; data from E. Lustig, W. R. Benson, and N. Duy, *J. Org. Chem.*, **32**, 851 (1967). [c] J. Sandström, *J. Phys. Chem.*, **71**, 2318 (1967).

found to exhibit sharp singlets even at −40°, an observation which led to the suggestion of rapid intramolecular exchange of SiH_3 groups in these compounds.[16] The nmr spectra of the trimethylsilyl derivatives and the fact that the magnitudes of the calculated rotational parameters for these compounds are similar to the magnitudes of the same parameters for their methyl analogs are best explained by hindered rotation at the C–N bond and no, or slow, exchange of trimethylsilyl groups. The difference in chemical shift between the doublets in I and II at the slow rotation limit is quite small, however. Thus, the low temperature singlets observed for the silyl analogs were likely due to very small differences in chemical shift (another possibility suggested by Ebsworth, *et al.*[16]) and not to rapid exchange of silyl groups.

The nmr spectra of the trimethylsilyl *N*,*N*-diethyl derivatives (IV, V, VI) also showed splitting of the *N*-ethyl resonances at some temperature, with the slow rotation difference in chemical shifts (triplet to triplet, quartet to quartet) again being considerably larger in the COS adduct. Approximate coalescence temperatures and values for $\Delta\nu$ for the methylene resonances are given in Table I. No attempt was made to calculate activation parameters for these derivatives.

Rotational Parameters. Table I presents the energy of activation, E_a, the log of the frequency factor, log A, and the free energy of activation, ΔG_a, as obtained by the total line shape (TLS) and intensity ratio (IR) methods, the limiting chemical shift difference, $\Delta\nu$, and the approximate visual coalescence temperature, T_c, for each of the *N*,*N*-dimethyl derivatives as 30% v/v solutions in chlorobenzene. Literature values for ΔG_a as reported by other workers are also presented. The activation energies obtained by both methods are in good agreement for compounds with $\Delta\nu > 5$ Hz; the intensity ratio method is known to produce rather large errors in τ if the slow rotation widths are not small relative to $\Delta\nu$.[17] The free energies of activation as obtained by both methods are in good agreement for all compounds except II. The discrepancy in ΔG_a for II remains unexplained and the data for this compound must be considered less reliable. The total line shape frequency factors, A, are of a reasonable magnitude for a rotational process.[2,3] The errors in E_a and ΔG_a are estimated to be of the order of ±0.5 to ±1.0 kcal/mole.

Discussion

It is well known that rotational free energies determined by the nmr method are more insensitive to errors than the energy of activation,[2,3] and thus most of the comparisons of the extent of C–N π bonding presented here are based on ΔG_a. This procedure is probably valid for estimates of the relative extents of C–N π bonding among structurally similar species.

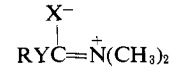
From the data of Table I a number of conclusions concerning the effects of X, Y, and the organometallic group on the extent of C–N π bonding can be extracted:

1. With the exception of compound II (*vide supra*), ΔG_a (and thus the amount of C–N π bonding) for the derivatives where R = $(CH_3)_3Si$ or $(CH_3)_3Sn$ is consistently higher than ΔG_a for the R′ = CH_3 analogs.
2. Comparison of ΔG_a for the pairs $ROC(=O)N(CH_3)_2$ and $ROC(=S)N(CH_3)_2$ and $CH_3SC(=O)N(CH_3)_2$ and $CH_3SC(=S)N(CH_3)_2$ reveals the expected[2] greater C–N π interaction in the RO thiocarbonyl derivative, but in the CH_3S pair the difference in ΔG_a is not outside experimental error.
3. Comparison of ΔG_a for the pairs $ROC(=S)N(CH_3)_2$ and $RSC(=S)N(CH_3)_2$ shows greater C–N π bonding in the RO members. This is in agreement with the observation of Sandström[18] for the pair in which R = CH_3. However, the values of ΔG_a for $CH_3OC(=O)N(CH_3)_2$ and $CH_3SC(=O)N(CH_3)_2$ show only a small difference, contrary to Sandström's[18] interpretation of Valega's qualitative results.[19]

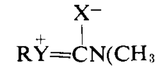
The conclusions above can be rationalized by the following valence bond argument. The electronic structure of these compounds can be approximated by a hybrid of the three resonance structures, A, B, and C.


$RY\overset{X}{\overset{\|}{C}}N(CH_3)_2$

A


$RY\overset{X^-}{\overset{|}{C}}{=}\overset{+}{N}(CH_3)_2$

B


$R\overset{+}{Y}{=}\overset{X^-}{\overset{|}{C}}N(CH_3)_2$

C

The greater the contribution of B, the greater the extent of C–N π bonding.

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(17) A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, *J. Amer. Chem. Soc.*, **88**, 3185 (1966).

(18) J. Sandström, *J. Phys. Chem.*, **71**, 2318 (1967).

(19) T. M. Valega, *J. Org. Chem.*, **31**, 1150 (1966).

The dependence of structure B on the nature of R is probably not due to steric considerations since the greater size of the organometallic groups should result in a decrease of ΔG_a.[2] The percentage contribution of structure C, however, could be affected by the nature of R. For example, the organometallic groups may produce a smaller contribution because of possible (p–d) π bonding from Y to Si or Sn. A decrease in contribution of C would result in an increase in percentage contribution of form B (the percentage contribution of forms A and C could of course change in such a way as to keep their total contribution the same, but this seems less likely).

The percentage contribution of B for those compounds in which X = S is also greater than or equal to the contribution in compounds for which X = O, at least partially because of less effective π overlap between C and S, *i.e.*, smaller (or equal) contribution of structure A when X = S. When X = S, the contribution of resonance structure C apparently increases in going from Y = O to Y = S, presumably due to the greater ability of sulfur to stabilize the positive charge. When X = O, however, a variation of Y from O to S results in little change in the significance of C and thus little change in the contribution of structure B. The insensitivity of form C to a change of Y when X = O (relative to the compounds in which X = S) can be explained by assuming that the greater electronegativity of oxygen causes the C_π orbital to become energetically less compatible with the S_π orbital, thereby making the percentage contribution of form C roughly equal for Y = O and Y = S.

Acknowledgments. The authors are indebted to R. D. Schubert and W. S. Morris for their assistance in some of the synthetic aspects of this work.

Thermal Interconversion of Some (2 + 2) and (2 + 4) Adducts of Cyclopentadiene and Dichloroethylenes. Determination of Erythro and Threo Configurations

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Contribution from the Converse Memorial Laboratory of Harvard University, Cambridge, Massachusetts 02138. *Received February 16, 1971*

Abstract: The C–C bond first formed in the photosensitized biradical cycloaddition of 1,2-dichloroethylene or 1,2-dichloro-1,2-difluoroethylene to cyclopentadiene remains unbroken during thermal rearrangements of the adducts at 400°. Thus only products of the same biradical (erythro or threo) are interconverted, and this makes it possible to complete the assignment of configurations to the bicyclo[3.2.0]heptene adducts. At this temperature the concerted sigmatropic mechanism is overshadowed by stepwise rearrangement *via* biradicals, and by decomposition.

In studies of thermal and photosensitized cycloaddition, the seven possible cycloadducts of 1,2-dichloroethylene[1] and of 1,2-dichloro-1,2-difluoroethylene[2] ("1212") to cyclopentadiene have been isolated and characterized. Evidence for the structures and configurations of these products is unambiguous except for pairs of *trans*-6,7-dichlorobicyclo[3.2.0]heptenes (**1H**, **2H**, **1F**, and **2F**, Scheme I). **1H** and **2H** were called VIIa and VIIb in ref 1, and **1F** and **2F** were called **3** and **4** in ref 2,[3] in each case without final assignment.

If, as there is good reason to believe,[1,2,4] the photosensitized cycloaddition proceeds by way of biradicals, then the cycloadducts are formed in two stereochemical families according to the relative configurations of the two asymmetric centers in the original biradical (**8** and **9**, Scheme I). Except for the trans (1,4) adduct **5**, which is a common product of both series, each product can arise from only one biradical, and may be designated as belonging to the erythro or to the threo series.[5]

If any biradical were to be re-formed from one of the (1,2) cycloadducts it should be, with overwhelming probability, the same biradical from which the adduct was originally formed, for only so can the stabilization belonging to an allylic cyclopentenyl radical and an α-chloroalkyl radical be attained. Because the only remaining question of structural assignment in these

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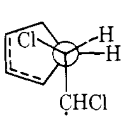
[1] P. D. Bartlett, R. Helgesson, and O. A. Wersel, *Pure Appl. Chem.*, **16**, 187 (1968).

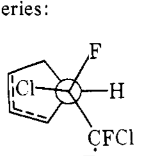
[2] R. Wheland and P. D. Bartlett, *J. Amer. Chem. Soc.*, **92**, 3822 (1970).

[3] VIIa and VIIb are characterized[1] by their yields at 25° when formed by α-acetonaphthone photosensitization from *cis*- and *trans*-dichloroethylenes, respectively. VIIa: 49.4 and 20.9%; VIIb: 13.6 and 17.4%. VIIa is eluted before VIIb in the vpc separation. **3** and **4**[2] are formed from *cis*- and *trans*-1212, respectively, in the following yields: thermal, **3**, 0.9 and 1.2%; **4**, 1% in each case; photosensitized, **3**, 11.5 and 15.7%; **4**, 40.0 and 25.2%. **3** (ref 2) is eluted before **4** (ref 2) in the vpc separation.

[4] P. D. Bartlett, *Science*, **159**, 833 (1968).

[5] Erythro and threo designations are defined by regarding the "free radical" carbon atoms on the two asymmetric centers as corresponding groups, and considering that **F** corresponds to **H** in the 1,2-dichloro-1,2-difluoroethylene series:


8H


8F

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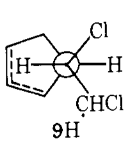
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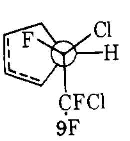
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