PART I
STEREOCHEMISTRY AND MOLECULAR REARRANGEMENTS OF BIS(β-DIKETONATO) DIOXOMOLYBDENUM(VI) COMPLEXES

PART II
A TEST OF THE ROLE OF INCIPIENT EXTRACOORDINATION OF SILICON IN SILYLATION REACTIONS

PART III
SYNTHESIS AND STEREOCHEMISTRY OF TRIMETHYLSILYL β-KETOAMINES

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WILLIAM R. CLEMENTS

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T J Pinnavaia
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ABSTRACT

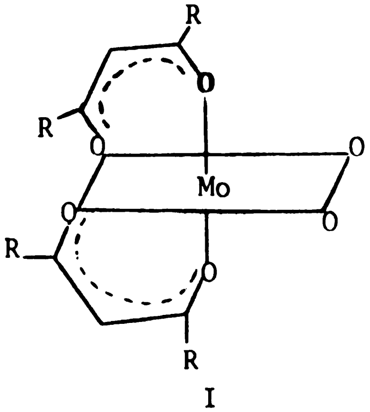
PART I

STEREOCHEMISTRY AND MOLECULAR REARRANGEMENTS OF BIS(β-DIKETONATO)DIOXOMOLYBDENUM(VI) COMPLEXES

by

William R. Clements

A series of octahedral dioxomolybdenum(VI) β-diketonate complexes of the type $MoO_2(dik)_2$ have been prepared by reaction of the free diketone and MoO_4^{2-} in acidic aqueous solution. Proton magnetic resonance studies show that the MoO_2 moiety adopts exclusively a cis configuration as illustrated by isomers I and II-IV for the symmetric (a-c) and asymmetric (d-e) diketonate derivatives, respectively.

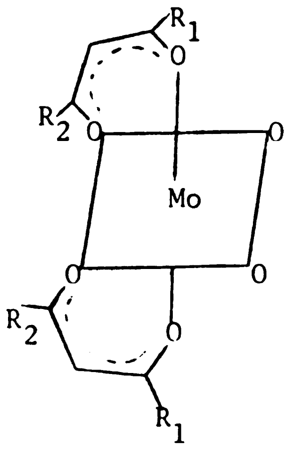


I

a. R = CH_3; dik = acetylacetonate

b. R = tert-C_4H_9; dik = dipivaloylmethanate

c. R = $CD(CH_3)_2$; dik = diisobutylmethanate-d^3



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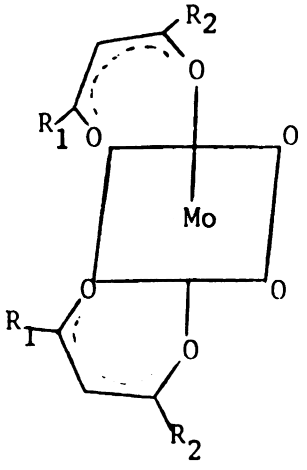
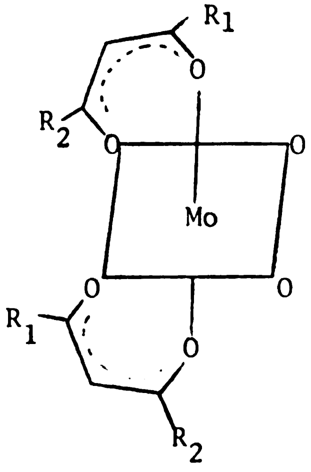


III



IV

d. $R_1 = CH_3$, R_3 = tert-C_4H_9; dik = pivaloylacetonate
e. R_1 = tert-C_4H_9, $R_2 = CH(CH_3)_2$; dik = pivaloylisobutylmethanate
f. $R_1 = CH_3$, $R_2 = CH(CH_3)_2$; dik = acetylisobutylmethanate
g. $R_1 = C_6H_5$; $R_2 = CH(CH_3)_2$; dik = benzoylisobutyrylmethanate

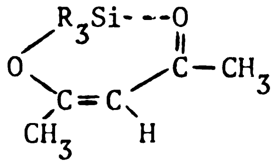
The complexes are stereochemically non-rigid and undergo rapid intramolecular rearrangements which lead to interchange of non-equivalent R group environments in I and isomerization and inversion of II, III, and IV. First order rate constants for the rearrangement of Ib in dichloromethane were determined by full pmr line shape analysis. The values of the Arrhenius activation energy and frequency factor are 17.0 ± 1.0 kcal/mole and exp (12.56 ± 0.57), respectively. The kinetics data indicate that the size of the central metal ion is the principal factor influencing the lability of the coordinate metal-oxygen bonds in this and related nonrigid d^0 and d^{10} metal complexes.

Temperature dependent pmr studies of the benzoylisobutyrylmethanate and deuterated diisobutyrylmethanate derivatives indicate that while a twist mechanism is likely for the rearrangement process it does not occur about one specific axis in the molecules.

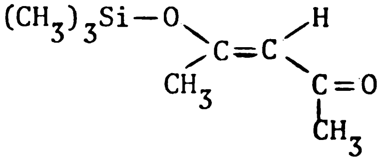
PART II

A TEST OF THE ROLE OF INCIPIENT EXTRACOORDINATION OF SILICON IN SILYLATION REACTIONS

The silylation of methanol by the *seqcis*(V) and *seqtrans*(VI) isomers of trimethylacetylacetone has been investigated in order to

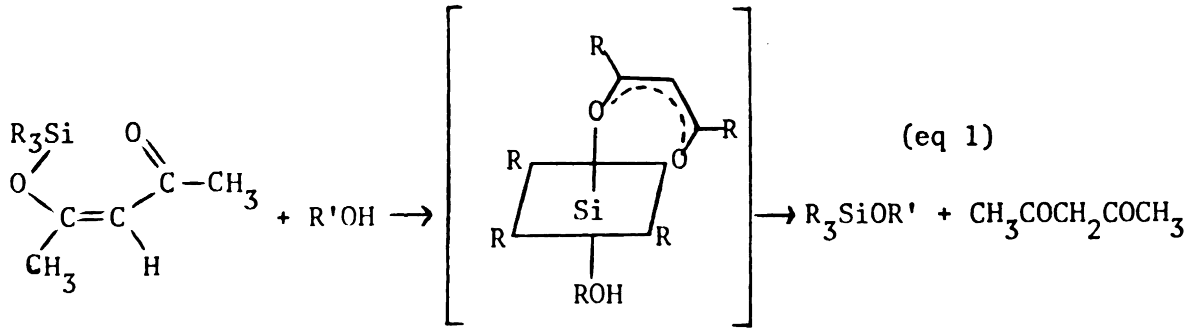


V



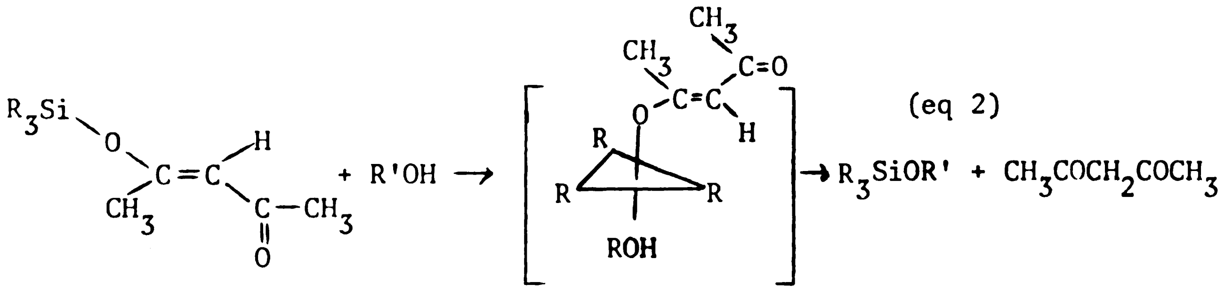
VI

test Klebe's hypothesis (*Accts. Chem. Res.*, **3**, 299(1970)) that incipient extracoordination in the ground state of certain triorganosilicon compounds may facilitate their ability to undergo proton transfer reactions via formation of six-coordinate transition states that are more stable than the five-coordinate transition states that can be achieved by organosilicon compounds which are not incipiently extracoordinated. Compounds V and VI are ideally suited for a test of this hypothesis. As the former isomer may achieve six-coordination in a silylation reaction whereas the latter cannot (eq 2).



(eq 1)

V



(eq 2)

VI

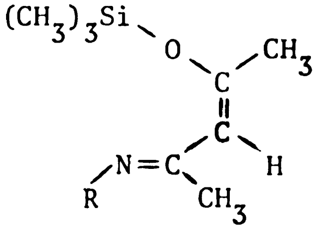
The reaction of methanol with a mixture of V and VI has been monitored by pmr spectroscopy and the ratio of [cis/trans] followed. The seqcis to seqtrans ratio remains constant when the silylation reaction is carried out in methylene chloride and chlorobenzene. Thus, both isomers react with methanol at the same rate and the ability of the seqcis form to expand its coordination does not facilitate the proton transfer reaction It is concluded that expansion of the coordination sphere of silicon from four to five or from four to six is not the rate determining step in the silylation reaction.

William Clements

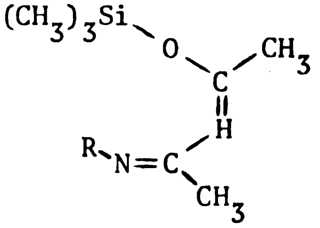
PART III

SYNTHESIS AND STEREOCHEMISTRY OF TRIMETHYLSILYL β-KETOAMINES

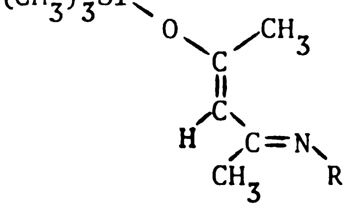
The first examples of silyl β-ketoamines have been prepared by reaction of the potassium salts of three different anilinopentenones and trimethylchlorosilane in hexane. Pmr and ir spectroscopic studies indicate that the compounds are 0-silylated and exist as four diastereomers (VII-X) due to *seqcis*-*seqtrans* isomerization about the C=C bond and *syn*-*anti* isomerization about the C=NR bond (R = C_6H_5, *m*-C_6H_4Cl and *p*-C_6H_4F:



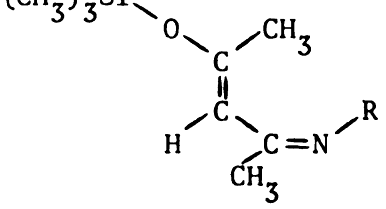
seqcis-*anti* (VII)



seqcis-*syn* (VIII)

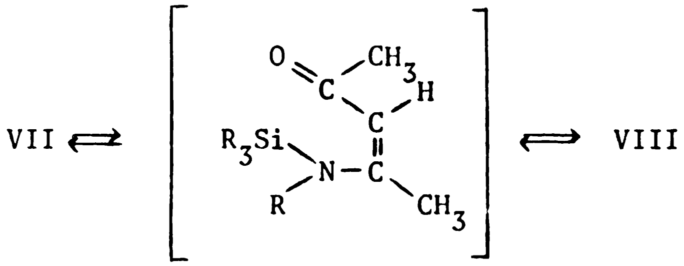


seqtrans-*anti* (IX)



seqtrans-*syn* (X)

Rapid *syn*-*anti* isomerization is observed for both the *seqcis* and *seqtrans* isomeric pairs. Based on tentative chemical shift assignments, the interchange of *syn*-*anti* forms appears to be appreciably faster for the *seqcis* pair due to steric effects and, possibly, a 1, 5 silyl group migration to give a N-silylated intermediate (XI):



XI

Syn-*anti* isomerization of the *seqtrans* pair undoubtedly involves a conventional tortional or lateral shift mechanism.

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By

William R. Clements

A THESIS

Submitted to
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1974

To

Karen

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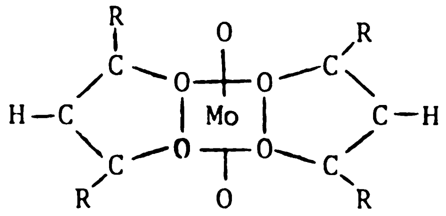
PART I

I. INTRODUCTION

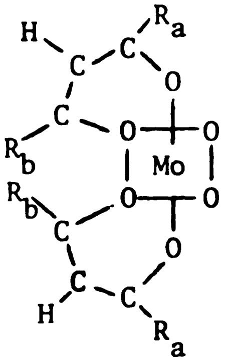
Metal complexes, especially those of d^0 and d^{10} metals, frequently do not possess a static structure in solution, but rather they rapidly alter the coordination about the central atom. Determination of the rates and mechanisms of intramolecular rearrangement reactions of metal chelate complexes has been a long-standing problem of considerable importance in coordination chemistry.[1-3] There are two types of rearrangement mechanisms, twist and bond rupture. The twist mechanism involves a rotation of the bonds in the ground state configuration to give a transition state or intermediate of different symmetry but of the same coordination number. In the bond rupture mechanism a metal ligand bond breaks giving an activated species of reduced coordination. It is difficult in most cases to determine which of these mechanisms is operating.

The β-diketonate complexes of dioxomolybdenum(VI) represent an important class of d^0 metal compounds, about which there was virtually no dynamic stereochemical information available. The earliest known complex of this type was prepared by F. Gach in 1900,[4] but the compound was incorrectly formulated as $Mo(acac)_2$, where acac = acetylacetonate ion. Morgan and Castell[5] in 1928 demonstrated that the compound prepared by Gach was the same as that prepared and correctly formulated as $MoO_2(acac)_2$ by Rosenheim and Bertheim[6] in 1903. It has only been in the last seven years that the structure of these complexes has been elucidated.[7-11]

In principle, two possible isomers might exist for these complexes when the ligand is symmetric. The molybdenyl oxygens may be opposite or trans(I) to one another or they may be adjacent or cis(II) to each other.



(I)



(II)

As late as 1966, Larson and Moore[12] proposed that the oxygens of the MoO_2^{2+} moiety in $MoO_2(acac)_2$ possessed a trans (linear) configuration. This proposal was based on infrared data which showed that the molybdenum to oxygen absorption was 70-100 cm^{-1} lower than that found for many other molybdenyl compounds possessing a cis configuration. They reasoned that this low energy shift in the absorption was a result of a "trans effect" similar to that observed for the trans ReO_2^{+} group. This proposal by Larson and Moore stirred the interests of other workers, including ourselves. Atovmyan and Sokolova performed an x-ray crystal structure determination of dioxobis(8-hydroxyquinolinato)molybdenum(VI)[9] and found that the molybdenyl oxygens were cis. Additional work by Moore[7,8] soon demonstrated that his original proposal was wrong. In fact, the results of all subsequent studies of octahedral dioxomolybdenum(VI) complexes indicates that to date they all contain a cis-MoO_2^{2+} moiety.

The fact that these complexes adopt a cis configuration has important stereochemical implications. It means, for example, that with symmetric ligands these complexes have C_2 symmetry and that the R groups exist in two different environments (cf. R_a and R_b in II). As a result of some dynamic change in the coordination sphere of the central metal atom the process of site exchange may occur, wherein R_a is interchanged with R_b. When these R groups contain hydrogen atoms as in methyl, isopropyl, tertiary butyl, etc., then proton magnetic resonance spectroscopy is an ideal tool for observing site exchange. The shapes of the pmr lines arising from the nonequivalent environments are a function of the rate of site interchange. Thus, from the dependence of line-shape on exchange rate, it is possible to determine the rate of molecular rearrangement.[13-19]

The significance of studying the dynamic stereochemistry of β-diketonate complexes of dioxomolybdenum(VI) is more than simply filling an important information void or determining whether they are cis and/or trans isomers in solution, or even whether they rearrange at all. Although these are certainly meaningful questions, their real significance lies in the fact that they provide a unique opportunity to determine the relative importance of metal ion size and charge on the lability of bis and tris diketonate complexes of d^0 and d^{10} metal ions. These were the principal questions addressed in this research.

At the time this research was initiated, several dynamic stereochemical studies of d^0 and d^{10} metal diketonate complexes had been reported. Their relative labilities depend on the nature of the metal ion as follows: Ge^{4+}(0.50 Å)[20] < Al^{3+}(0.53 Å)[21-23] < Ga^{3+}(0.62 Å)[21-23] < Ti^{4+}(0.68 Å)[24,25] < Zr^{4+}(0.80 Å),[26] Sc^{3+}(0.81 Å),[23] In^{3+}(0.81 Å),[22] where the numbers in parentheses are the Pauling crystal radii. Regardless of the coordination number of the central ion, the labilities spanned a rather remarkable range, from Ge^{4+} which rearranges with a half life on the order of several minutes to Zr^{4+}, Sc^{3+} and In^{3+} which rearrange with a half life of 10^{-5} seconds or less. Based on the above lability sequence, it appears that ionic radius is an important factor determining the rates of molecular rearrangement. At the onset of this work the relationship between lability and ionic radius had not been recognized. It is interesting to note that the ionic charge, in particular the charge to radius ratio, does not appear to play a significant role. This is important because if a bond rupture mechanism operated in the rearrangements, then one would expect the energy needed to open a M-O bond to increase and the rates to decrease with increasing metal ion charge.

The dioxomolybdenum(VI) diketonate complexes offer the opportunity to probe the relative importance of size versus ionic charge better than any of the previously known d^0 or d^{10} metal complexes. Molybdenum(VI) has a Pauling radius of 0.62 Å, the same as that of Ga^{3+} while having a charge to radius ratio twice that of Ga^{3+}. If the charge on the central metal atom is going to exert its influence, it certainly should do so in the case of Mo^{6+}. Thus a study of the dynamic stereochemistry of dioxomolybdenum(VI) diketonates was not only expected to answer important questions about the nature of dioxomolybdenum(VI) complexes, but also to improve our understanding of the dynamic stereochemistry of all d^0 and d^{10} metal complexes.

II. EXPERIMENTAL

A. Reagents and Solvents

Sodium molybdate and acetylacetone were obtained from Matheson, Coleman and Bell, and were used without further purification. Dipivaloylmethane was obtained from Aldrich Chemical Company and used without further purification. Pivaloylacetone was prepared in our laboratory by Jerry Howe, using the method of Adams and Hauser.[27] Alan Schwartz prepared pivaloylisobutyrylmethane, acelylisobutyrylmethane and deuterated disobutyrylmethane by the method of Adams and Hauser. Benzoylisobutyrylmethane was also prepared by this method. The purity of the β-diketones, including those purchased, was checked by nmr spectroscopy.

Methylene chloride, carbon tetrachloride and chlorobenzene were dried over calcium hydride for at least 24 hours and freshly distilled before use. Benzene and hexane were dried over lithium aluminum hydride for at least 24 hours and freshly distilled before use.

B. General Techniques

All glassware was dried at least 24 hours at 180°C and cooled in a desiccator whenever possible. Hygroscopic reagents and products were handled and transfers effected in a polyethylene glove bag under an atmosphere of dry nitrogen. The β-diketones synthesized in our laboratory were purified by vacuum distillation.

Proton magnetic resonance spectra were obtained on a Varian A 56/60 D analytical spectrometer operated at a frequency of 60.000MHz or a Varian HA-100 analytical spectrometer at 100.000MHz. The probe temperature was maintained at ± 0.5°C with a Varian Model V-6040 temperature controller. Temperatures were determined by measuring the chemical shift differences between proton resonances of methanol (low temperatures) or ethylene glycol (high temperatures) and substituting them into the equations of Van Geet.[28] Magnetic field sweep widths were calibrated by the audio-frequency side-band technique. All spectra were recorded at field strengths well below the level required to produce saturation. Chemical shifts were measured using tetramethylsilane as an internal standard.

Theoretical pmr line-shapes for two site exchange were calculated using the Gutowsky-Holm equation[13] as modified by Rogers and Woodbrey[14] (see appendix C ref. 29). Multisite exchange spectra were generated using a modification of the Whitesides-Lisle EXCNMR computer program[30] developed by Pinnavaia and Teets (see appendix). Calculations were performed on a CDC 3600 or CDC 6500 computer at Michigan State University.

C. Syntheses

cis-Dioxobis(acetylacetonato molybdenum(VI)

cis-Dioxobis(acetylacetonato)molybdenum(VI) was prepared according to the method of Gehrke and Veal.[31] Sodium molybdate dihydrate (4.85 g, 0.02 moles) was dissolved in 50 ml of distilled water. The solution was adjusted to a pH of ∼1 with 6 N hydrochloric acid and placed in a 100 ml beaker. The beaker was placed on a stir plate in a darkened hood, as the product was reported to be light sensitive.[31] Acetylacetone (6.0 g, 0.006 moles) was added to the beaker with vigorous stirring. A pale yellow precipitate of $MoO_2(acac)_2$ formed almost immediately. The mixture was allowed to stir for approximately 15 minutes, and then it was filtered through a glass frit and washed with cold ethanol (0°C). The pale yellow solid was dried in vacuo at room temperature for several hours (yield, 49%). Identity of the complex was confirmed by its IR spectrum, which matched exactly the published IR data for $MoO_2(acac)_2$.[31,32] The complex was used without further purification. It can,however, be recrystallized from hot acetylacetone.[33]

cis-Dioxobis(dipivaloylmethanato)molybdenum(VI)

Attempts to prepare cis-dioxobis(dipivaloylmethanato)molybdenum(VI) by the same procedure used for the acetylacetonato complex were unsuccessful. Similar attempts to prepare it by ligand exchange were also unsuccessful.

$$MoO_2(acac)_2 + 2\ Hdpm \not\longrightarrow MoO_2(dpm)_2 + Hacac \tag{1}$$

The dipivaloylmethanate derivative was finally prepared using a modification of M. Jones procedure for making the acetylacetone complex.[34] Sodium molybdate dihydrate (2.42 g, 0.01 moles) was dissolved in 25 ml of water in a beaker and the solution made very acidic with the addition of 1.3 ml of 90% nitric acid. Dipivaloylmethane (5.53 g, 0.03 moles) was added to the molybdate solution with vigorous stirring. Pale yellow $MoO_2(dpm)_2$ precipitated within 3-4 hours. After approximately 24 hours of stirring the mixture was filtered through a glass frit, and the complex was washed several times with cold (0°C) hexane. The complex was dried in vacuo and purified by vacuum sublimation at 110°C.

cis-Dioxobis(dipivaloylmethanato)molybdenum(VI) has not been previously reported in the literature. Its melting point was determined as 131.5°C using a Thomas-Hoover model 6406-H Capillary Melting Point Apparatus. The complex behaved as a nonelectrolyte in nitrobenzene ($\Lambda = 3.62 \times 10^{-2}$ cm^{2}ohm^{-1}mole^{-1} at a concentration of 9.92×10^{-3} M) and was found to be monomeric by a cryoscopic molecular weight determination in purified benzene. Recrystallized benzil was used as the calibrating solute in the determination of the molal freezing point depression constant of benzene (5.87 deg/molal). Freezing point depressions were measured with a Beckman differential thermometer graduated at 0.01° internals and estimated to ± 0.001° using a magnifying thermometer reader. The experimental molecular weight was 475 g/mole, which is within 5% of the actual value of 494 for a monomeric species. Chemical analysis was performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. Anal. Calculated for $MoC_{22}H_{38}O_6$: Mo, 19.42; C, 53.47; H, 7.75. Found: Mo, 19.62; C, 53.26; H, 7.96.

Pivaloylacetone, Pivaloylisobutyrylmethane, Acetylisobutyrylmethane, Benzoylisobutyrylmethane and Deuterated Diisobutylrylmethane Derivatives of Dioxomolybdenum(VI).

MoO_2^{2+} complexes of pivaloylacetone, pivaloylisobutyrylmethane, acetylisobutyrylmethane, benzoylisobutyrylmethane and deuterated diisobutyrylmethane were prepared using the method outlined for the preparation of cis-dioxobis(dipivaloylmethanato)molybdenum(VI). All were pale yellow solids. Physical properties of these complexes are given in Table I.

Table I. Properties of Synthesized Dioxobis(β-diketonato)molybdenum(VI) Complexes

Complex[a]	Melting Point	Solubility[b]	Remarks
$MoO_2(acac)_2$	185°	CH_2Cl(sl.sol.); $CHCl_3$(sl.sol.); C_6H_6(sl.sol.) CH_3OH(v.sol.);[c] C_2H_5OH(v.sol.);[c] 1,2-$C_2H_4(OH)_2$(sol.)[c]	Complex is light sensitive and decomposes in aromatic solvents
$MoO_2(dpm)_2$	132°	CH_2Cl_2(sol.); $CHCl_3$(sol.); C_6H_6(sol.); CH_3OH(v.sol.);[c] C_2H_5OH(v.sol.);[c]; 1,2-$C_2H_4(OH)_2$(sol.)	Decomposes rapidly in nitrobenzene
$MoO_2(d^3\text{-dibm})_2$	110°	CH_2Cl_2(sol.); 1,2-$C_2H_4Cl_2$(m.sol.); C_6H_6(sl.sol.)	Deuteriums exchange very slowly
$MoO_2(pvac)_2$	151°	CH_2Cl_2(m.sol.); $CHCl_3$(m.sol.); C_6H_6(sl.sol.); C_6H_5Cl(m.sol.)	No solvents found which give good solubility
$MoO_2(aibm)_2$	81°	CH_2Cl_2(sl.sol.); C_6H_5Cl(sl.sol.); C_6H_6(sl.sol.); CH_3CN(sl.sol.); CCl_4(insol.); C_6H_8(insol.)	Melting point unusually low; may be a result of contamination. No suitable solvent found for recrystallization or nmr

Table I (Cont'd)

Complex[a]	Melting Point	Solubility[b]	Remarks
$MoO_2(bibm)_2$	155°	CH_2Cl_2(sol.); $CHCl_3$(sol.); 1,2-$C_2H_4Cl_2$(sol.); C_6H_5Cl(m.sol.); CCl_4(insol.); C_6H_6(insol.); C_6H_8(insol.)	Decomposes rapidly in nitrobenzene

[a] All the complexes are a pale yellow color.

[b] Very soluble = v.sol.; soluble = sol.; moderately soluble = m.sol.; slightly soluble = sl.sol.; insoluble = insol.

[c] Complexes dissolve very readily in alcohols, but appear to form alkoxides.

III. RESULTS AND DISCUSSION

A. Preparation and Characterization of Dioxobis(dipivaloylmethanato)-molybdenum(VI).

Prior to this work only a few complexes of dioxomolybdenum(VI) had been reported.[8] Furthermore, all of the known molybdenyl β-diketonate complexes are not especially well suited for accurate kinetic studies by nmr line broadening methods due in part to their limited solubility in organic solvents and their tendency to decompose in the presence of light.[8,31] The acetylacetonate derivative, which is the most widely studied and best characterized complex,[4-9,11,12,31-40] is only sparingly soluble in most common organic solvents and decomposes upon standing in solvents such as benzene, methylene chloride and chloroform [8,12,31] to give a molybdenum blue. Furthermore, upon exposure to light the complex gradually turns blue-green.

Thus, the need for a new, more stable and soluble bis diketonate of dioxomolybdenum(VI) was apparent. In the hope of fulfilling this need we attempted the synthesis of $MoO_2(dpm)_2$, where dpm = dipivaloylmethanate, by the method of Gehrke and Veal.[31] This method was unsuccessful with the molybdenum apparently undergoing gradual reduction to a molybdenum blue.[41] A modification of this procedure, wherein concentrated nitric acid was used in place of dilute hydrochloric, was successful. Two possible reasons for this may be that (1) an oxidizing acid is necessary to prevent reduction of the molybdenum(VI) and (2) depolymerization of the isopolymolybdates occurs in very strong acid solutions.[41]

$$Na_2MoO_4 + 2Hdpm + 2HNO_3 \rightarrow MoO_2(dpm)_2 + 2H_2O + 2NaNO_3 \qquad (2)$$

The dioxobis(dipivaloylmethanato)molybdenum(VI) proved to be much better suited for an nmr line broadening study than previously known derivatives. It was relatively soluble (10-20 g per 100 ml solvent) in solvents such as methylene chloride, chloroform and chlorobenzene. In addition, the complex was much more stable in solution, decomposing only after aging for several weeks. However, the compound decomposed in only 3-4 days in benzene and 1-2 hours in nitrobenzene. Furthermore, the dipivaloylmethanate derivative was not sensitive to light, and only slightly sensitive to atmospheric moisture, gradually turning blue-green.

Infrared vibrational frequencies agree very well with those of the analogous acetylacetonate complex.[32] The molybdenyl stretch, ν_{Mo-O} (904 cm^{-1}) is identical, while the ligand oxygen to metal stretches, ν_{Mo-O} (512, 481 cm^{-1}) are shifted slightly to lower energy. The ligand ring stretches, $\nu_{C\overset{\cdots}{=}O}$ (1584 cm^{-1} and $\nu_{C\overset{\cdots}{-}C}$ (1500 cm^{-1}) are also in exact agreement with the assignments for acetylacetonate complex. Figure 1 shows the infrared spectrum of dioxobis(dipivaloylmethanato)-molybdenum(VI) in the region 1650-450 cm^{-1} and table II gives some of the important assignments based on comparisons with the analogous acetylacetonate complex, for which Soptrayanov, Nikolovski and Petrov[32] have made spectral assignments.

Proton magnetic resonance spectroscopy clearly shows that $MoO_2(dpm)_2$ exists solely in the cis configuration. The pmr spectrum exhibits only one ligand -CH= line indicating that only one of the two possible isomers is present; while, the ligand tertiary butyl region exhibits two lines of equal intensity, consistent with the C_2 symmetry of the cis isomer. The relative intensities of the lines are 1:9:9 thus, confirming a cis dioxo structure. This pmr spectrum was observed in both aromatic and

Figure 1. Infrared spectrum of $MoO_2(dpm)_2$ as a nujol mull between CsI salt plates. The 1601.8 and the 1028.3 cm^{-1} absorptions of polystyrene were used as references.

Figure 1

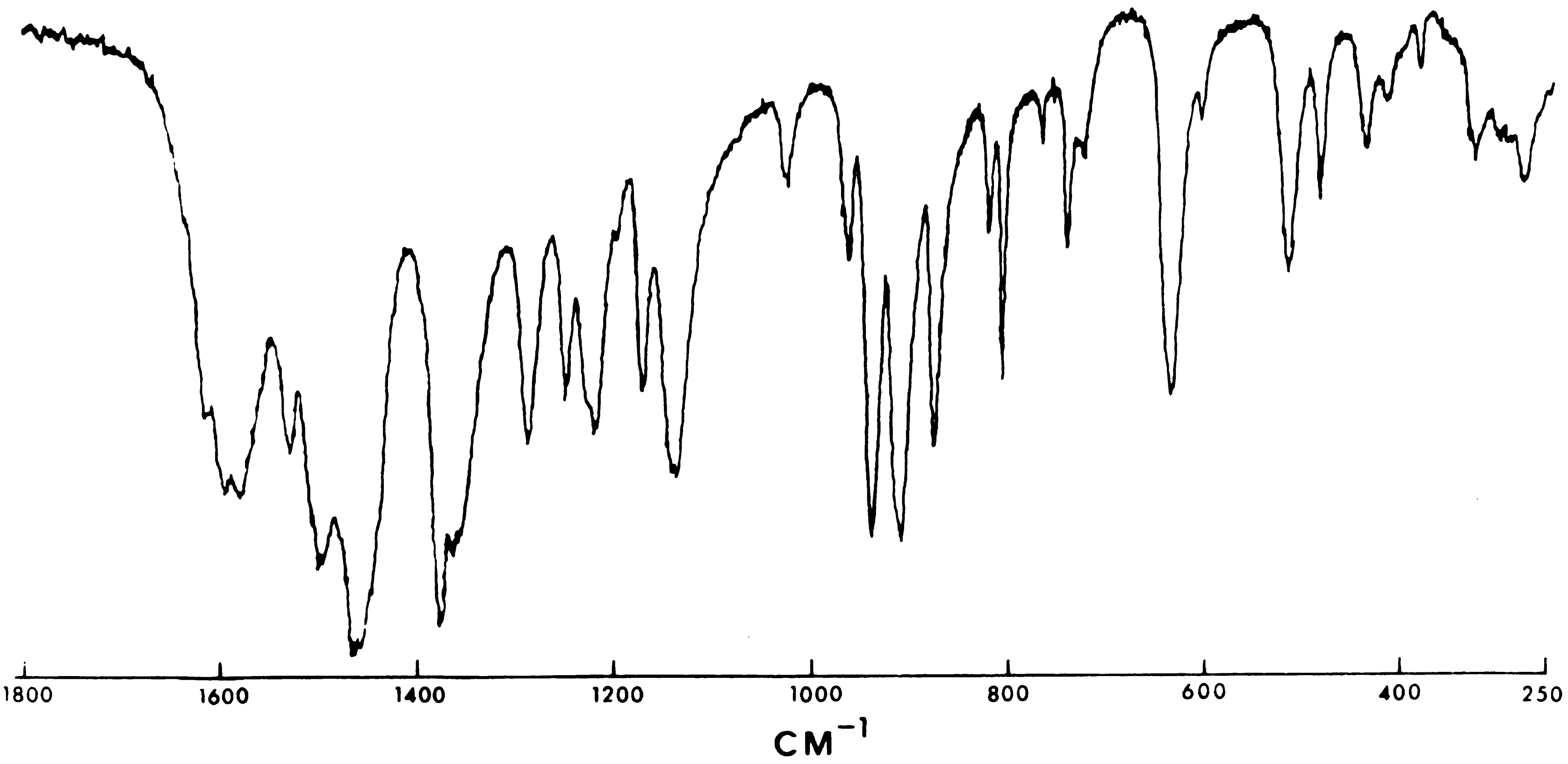


Table II. Infrared Assignments for $MoO_2(dpm)_2$

$\bar{\nu}$ (cm^{-1})	I	Approximate Description
1584	VS	$\mathrm{C}\overset{\cdots}{-}\mathrm{O}$ stretch
1500	VS	$\mathrm{C}\overset{\cdots}{-}\mathrm{C}$ stretch
1024	m	Mo = 0 stretch
938	VS	$\mathrm{C{-}CH_3}$ stretch + $\mathrm{C}\overset{\cdots}{-}\mathrm{O}$ stretch
904	VS	Mo = 0 stretch
806	S	C—H deformation (out-of-plane)
512	S	Mo—O stretch
481	m	

I = intensity; m, medium; S, strong; VS, very strong.

non-aromatic solvents. Figure 2 shows the pmr spectrum for $MoO_2(dpm)_2$ in chlorobenzene.

B. Kinetics Study of Dioxobis(dipivaloylmethanato)molybdenum(VI) Rearrangement.

In methylene chloride solution below 35°C, the interchange of the nonequivalent dipivaloylmethanate *tert*- C_4H_9 groups is sufficiently slow to observe two well resolved *tert*- C_4H_9 proton resonance lines in the pmr. Above 35°C the two lines broaden and coalesce into a very broad line (ca. 50°C), which then sharpens above the coalescence temperature (see Figure 3). The *tert*- C_4H_9 resonances did not exhibit temperature dependent chemical shifts and the separation of the two lines in the absence of exchange (low temperature) was 6.84 Hz. The natural line width at half maximum amplitude was 0.55 Hz for both lines.

The weak central peak in Figure 3 corresponds to an approximately 1% impurity of free ligand. The amount of free ligand impurity could be reduced to this level by recrystallization or sublimation, but it was never completely removed. This small impurity did not interfere with the line shape analysis and, in fact, served a useful purpose. It proves that the rearrangement process is an intramolecular process and not intermolecular (*i.e.*, complete ligand dissociation does not operate) because the free ligand line remains unchanged throughout the exchange region. If ligand dissociation were responsible for the observed site exchange then we would expect to see the free ligand line become averaged (coalesce) with the complex lines. This is not observed. Further, evidence that the exchange process was exclusively intramolecular

Figure 2. Proton nmr spectrum (60MHz) of $MoO_2(dpm)_2$ in chlorobenzene at ambient machine temperature (*ca*. 40°C); concentration 10g/100ml of solvent.

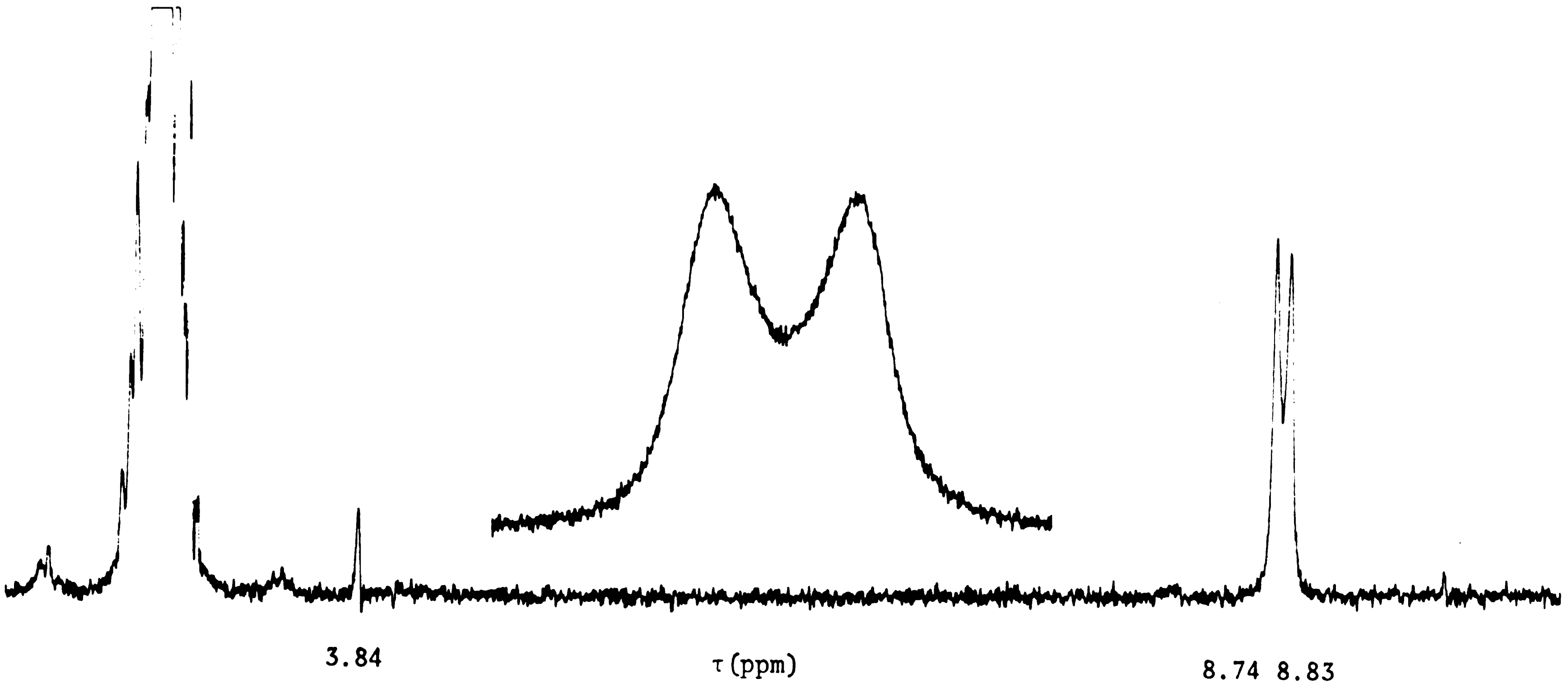


Figure 2

Figure 3. Temperature dependence of tert-C_4H_9 resonance lines of $MoO_2(dpm)_2$ in methylene chloride; concentration is 10g/100ml solvent.

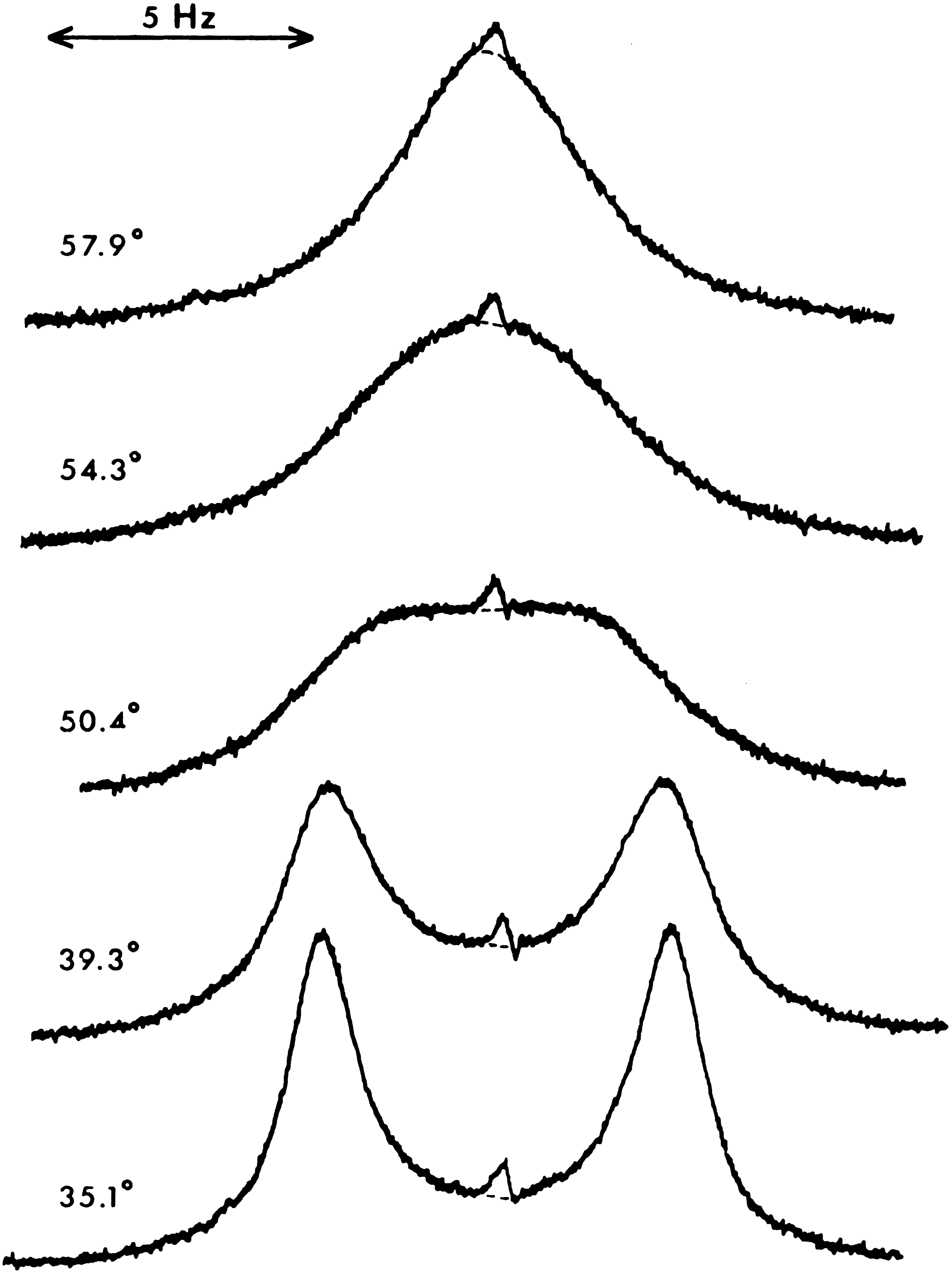


Figure 3

was the fact that adding free ligand had no effect on the rate of interchange and that the rates were independent of complex concentration.

Gutowsky and Holm[13] have shown that the mean lifetime, τ_A and τ_B, of protons exchanging between two nonequivalent sites can be determined from the nmr line shapes if the frequency separation between the resonance lines in the absence of exchange, $\delta\nu$, and the transverse relaxation time T_2, are known. This is done by matching the theoretical spectra calculated using the Gutowsky-Holm equation as modified by Rogers and Woodbrey[14] (3) for different values of τ ($\tau = \tau_A\tau_B/(\tau_A+\tau_B)$ with experimental spectra.

$$v = \frac{-\omega, Mo \left\{P\left[1+\tau\left(\frac{P_B}{T_{2A}} + \frac{P_A}{T_{2B}}\right)\right] + QR\right\}}{P^2 + R^2} \tag{3}$$

where $P \equiv \tau\left[\frac{1}{T_{2A}\,T_{2B}} - \Delta\omega^2 + \left(\frac{\delta\omega}{2}\right)^2\right] + \frac{P_B}{T_{2B}} + \frac{P_A}{T_{2A}}$

$$Q \equiv \tau\left[\Delta\omega - \frac{\delta\omega}{2}(P_A-P_B)\right]$$

$$R \equiv \Delta\omega\left[1 + \tau\left(\frac{1}{T_{2A}} + \frac{1}{T_{2B}}\right)\right] + \tau\,\frac{\delta\omega}{2}\left(\frac{1}{T_{2B}} - \frac{1}{T_{2A}}\right) + \frac{\delta\omega}{2}(P_A-P_B)$$

v describes the proton absorption line shape (amplitude)

ω_1 describes the applied radiofrequency field

M_o is the static nuclear magnetization at thermal equilibrium

P_A, P_B are the proton fractions contributing to each component

T_{2A}, T_{2B} are the transverse relaxation times

$\Delta\omega$ represents different values between the applied radiofrequency and the frequency at the center of the two resonances

$\delta\omega$ is the separation of the components assuming no exchange and no overlap of the components

Values of τ for $MoO_2(dpm)_2$ in the region of exchange were determined by a trial and error method. Theoretical spectra calculated for different values of τ were plotted and compared to the experimental spectra of $MoO_2(dpm)_2$ at different temperatures. This process of comparison was repeated until the best possible match of total line shape was obtained for each experimental spectrum. Figure 4 shows the experimental spectra with their matching theoretical spectra and τ values. Table III shows the nmr line shape parameters and kinetics data for $MoO_2(dpm)_2$, where $k = 1/2\tau$.

Activation parameters were calculated using the first-order rate constants determined from the nmr line shape analysis. A plot of ln k vs. 1/T is shown in Figure 5. A linear least squares analysis (see ref. 29 appendix B) was used to determine the slope and intercept, which gave an Arrhenius activation energy and frequency factor of 17.0 ± 1.0 kcal/mole and exp (12.56 ± 0.57), respectively. The errors in the activation parameters are estimated to the 95% confidence level. An activation entropy of -3.0 ± 2.6 eu at 25°C was calculated from the frequency factor assuming that the Eyring equation (4) holds.

$$\Delta S^* = R \ln A - R[1 + \ln \frac{kT}{h}] \quad (4)$$

R = gas constant = 1.9872 defined cal/°K mole

A = frequency factor

T = temperature (°K)

k = Boltzmann constant = 1.3805×10^{-16} erg/°K

h = Planck constant = 6.6254×10^{-27} erg sec

Figure 4. (A) Temperature dependence of tert-C_4H_9 resonance lines of $MoO_2(dpm)_2$ in methylene chloride; concentration is 10g/100ml solvent; 60MHz spectra. The weak central peak corresponds to a 1% impurity of free ligand. (B) Calculated pmr spectra for the mean lifetimes indicated. The values of the frequency separation in absence of exchange ($\delta\nu$) and the transverse relaxation time (T_2) used in the calculations were 6.84Hz and 0.58 sec, respectively.

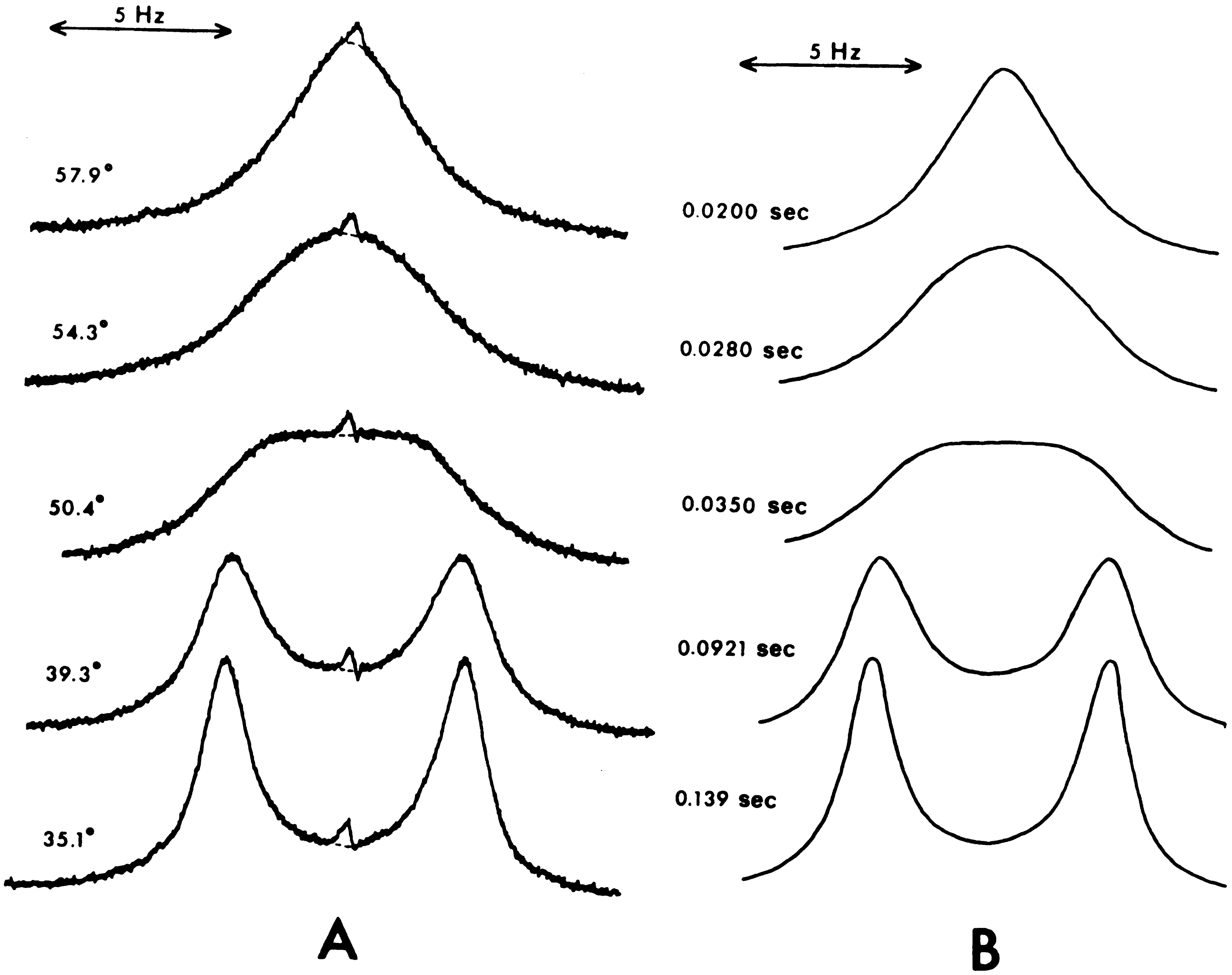

5 Hz
57.9°
54.3°
50.4°
39.3°
35.1°
A
5 Hz
0.0200 sec
0.0280 sec
0.0350 sec
0.0921 sec
0.139 sec
B

Figure 4

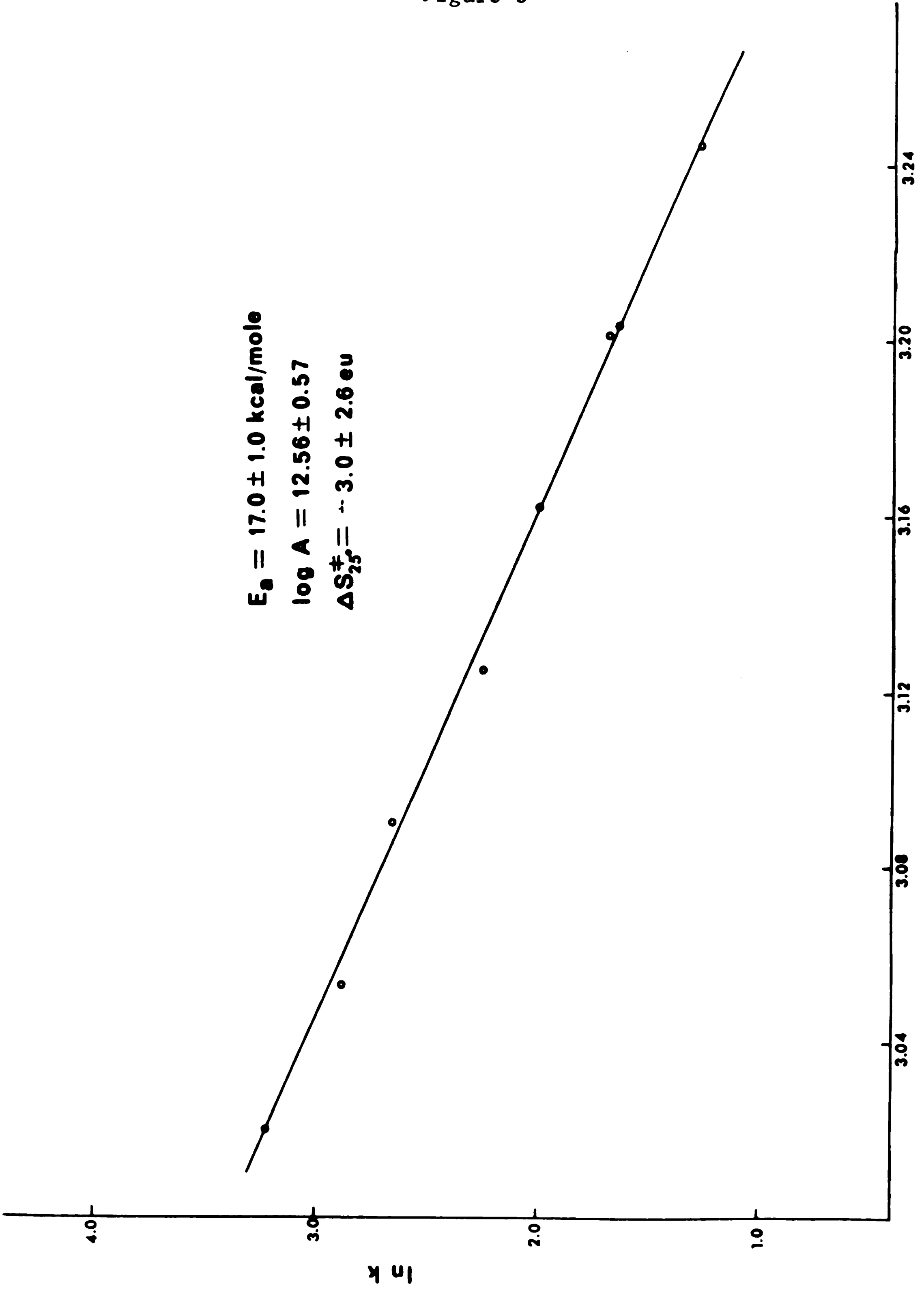
Table III. *tert* - C_4H_9 PMR Line Shape Parameters and Kinetic Data for $MoO_2(dpm)_2$ in Methylene Chloride

Temp, °C	r[a]	W*[b], Hz	k, sec^{-1}
35.1	5.25		3.60
39.0	3.12		5.20
39.3	2.92		5.43
43.1	1.92		7.43
46.9	1.37		9.56
50.4	∿1.00	7.40	14.3
54.3		5.80	17.9
57.9		4.10	25.0

[a] Ratio of maximum to central minimum amplitude below coalescence.
[b] Full line width at half maximum amplitude above coalescence.

Figure 5. Ln k vs. 1/T plot for $MoO_2(dpm)_2$ in methylene chloride solution.

Figure 5


$E_a = 17.0 \pm 1.0$ kcal/mole
$\log A = 12.56 \pm 0.57$
$\Delta S^{\ddagger}_{25°} = -3.0 \pm 2.6$ eu
ln k
4.0
3.0
2.0
1.0
1/T × 10^3
3.04
3.08
3.12
3.16
3.20
3.24

These results are in accord with those of Wise, et al.,[11] for the $MoO_2(acac)_2$ complex. Their results are summarized in Table IV which is a reproduction of Table III of reference 11.

The results of our study are extremely interesting because they show that this Mo^{6+} complex rearranges at approximately the same rate as analogous Ga^{3+} complexes.[21,22,23] Thus, the fact that Mo^{6+} has twice the charge to radius ratio of Ga^{3+} does not have any appreciable effect on its relative lability. Quite clearly, this illustrates that ionic radius is an important factor in determining the relative rates of rearrangement for d^0 and d^{10} metal β-diketonate complexes, and that it is much more influencial than ionic charge. Since ionic charge would be expected to have an important effect in bond rupture mechanisms, whereas, ionic size should have the major effect in twist mechanisms, it would appear that a twist mechanism may be the principal method of rearrangement for the known d^0 and d^{10} metal β-diketonates.

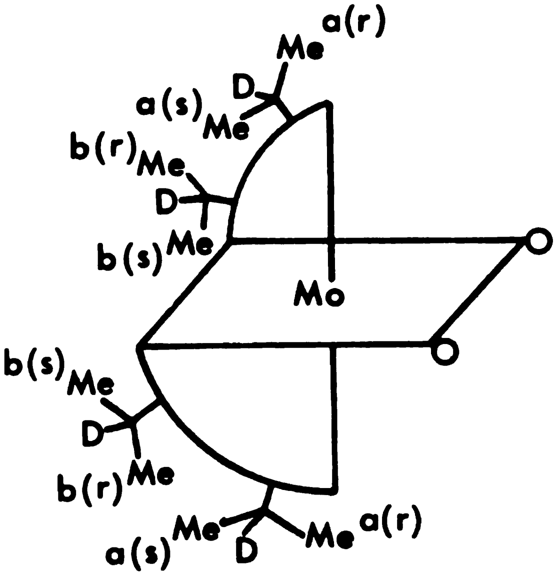
C. Preparation and Study of Dioxobis(d^3-diisobutyrylmethanato)-molybdenum(VI).

Dixoxbis(d^3-diisobutyrylmethanato)molybdenum(VI) was prepared by a modification of Gehrke and Veal's method described earlier for dioxobis(dipivaloylmethanato)molybdenum(VI). The reaction was carried out in deuterium oxide in place of water as a solvent. Although hydrogen ions were available as a result of the nitric acid used, this did not constitute a problem since deuterium exchange is very slow. Proton magnetic resonance spectroscopy confirmed that almost no deuterium exchange occurred during the course of the reaction.

Table IV. Activation Parameters for $MoO_2(acac)_2$[11]

Benzene soln	Chloroform soln
E_A = 17.0 kcal/mol	E_A = 13.0 kcal/mol
$\Delta H^\ddagger$ = 16.4 kcal/mol	$\Delta H^\ddagger$ = 12.4 kcal/mol
$\Delta S^\ddagger$ = 4.4 cal/deg mol	$\Delta S^\ddagger$ = 14 cal/deg mol
$\sigma(E_A, \Delta H^\ddagger)$ = 2.4 kcal/mol	$\sigma(E_A, \Delta^\circ H^\ddagger)$ = 1.0 kcal/mol
$\sigma(\Delta S^\ddagger)$ = 8 cal/deg mol	$\sigma(\Delta S^\ddagger)$ = 4 cal/deg mol

The $MoO_2(d^3\text{-dibm})_2$ complex has some interesting properties. As in the case of the dpm derivative the isopropyl groups of $MoO_2(d^3\text{-dibm})_2$ should exist in two different environments because of the C_2 symmetry of the complex. In addition, as a result of the dissymmetry (no mirror plane) the methyls on each isopropyl group are diastereotopic (labeled r and s in III) and as such should give separate lines in the pmr spectrum. It should be noted that observation of diastereotopic effects in chiral metal chelates was, until very recently, relatively rare.[42-46] This means that for this deuterated complex in the absence of exchange there should be four isopropyl methyl lines in the pmr. This is, in fact, what is observed. Since inversion of configuration is the only way for the diastereotopic methyls to interchange environments, it means that this is a complex in which one can compare the relative rates of inversion and site exchange. This has important mechanistic implications because for twist mechanisms inversion always accompanies site exchange (same rate), whereas, for bond rupture mechanisms inversion



III

may or may not accompany site exchange. Thus, if the rate of inversion and the rate of site exchange are different then a bond rupture mechanism must operate at least to some extent.

In 1,2-dichloroethane solution below 20°C the interchange of the nonequivalent isopropyl methyl groups is sufficiently slow to observe four well resolved methyl proton resonance lines in the pmr. Above 20°C the two low field lines coalesce and as the temperature is raised to 47°C the two high field lines broaden and merge. These two lines, which are already exchange broadened, then coalesce (ca. 60°C) into a single line which becomes sharper as the temperature is raised (see Figure 6).

An approximate determination of the rates of inversion and site exchange was made by applying the simplified Gutowsky-Holm equation (5) to the coalescence of the two high field lines and then to the coalescence of the high field pair with the low field pair of lines. The errors associated with the simplified equation and its region of

$$k = \frac{1}{2\tau} = (\pi/\sqrt{2})(\delta\nu^2 - \delta\nu e^2)^{1/2} \qquad (5)$$

$\delta\nu$ = frequency separation (Hz) of the lines in the absence of exchange

$\delta\nu e$ = experimentally determined frequency separation of the lines in the region of exchange

applicability have been determined by comparison with complete nmr line shape analysis.[13,47,48] It has been shown that, in general, the error introduced by using equation (5) does not exceed 10% for systems for which $\delta\nu\ 2\tau \leq 5$.[47] In the $MoO_2\ (d^3\text{-dibm})_2$ system $\delta\nu\ 2\tau$ did not exceed 1.5. No attempt was made to determine which coalescence

Figure 6. Temperature dependence of isopropyl methyl lines of $MoO_2(d^3\text{-dibm})_2$ in 1,2-dichloroethane; concentration is 10g/100ml solvent; 100MHz spectra.

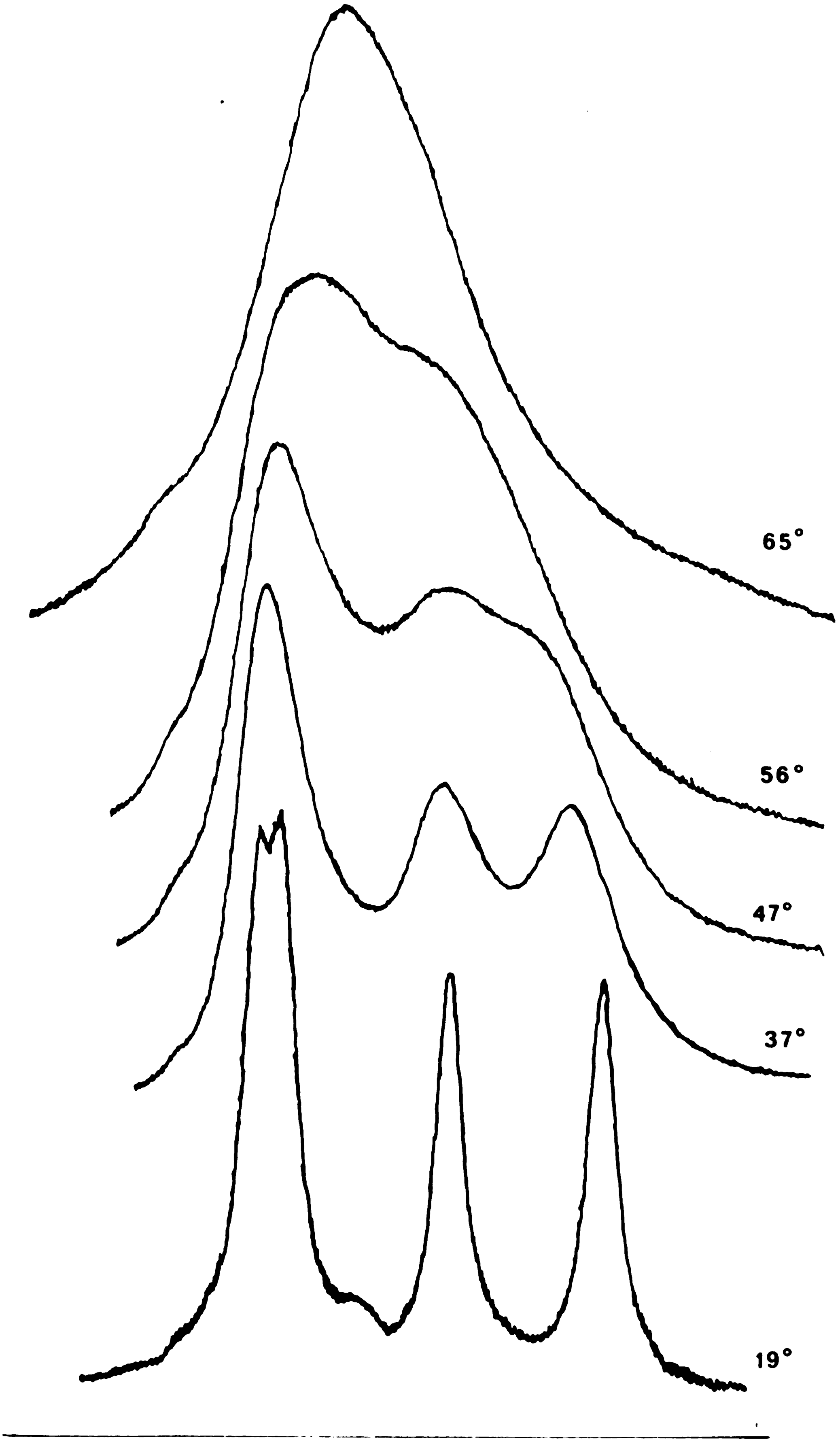
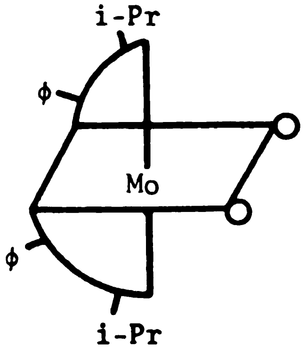


Figure 6

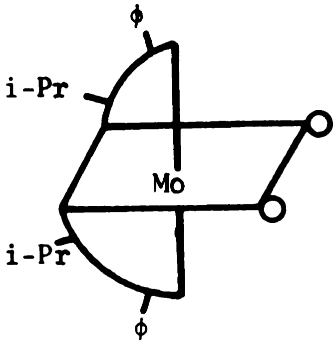
represented lines being averaged by site exchange and which represented the inversion process. Application of equation (5) gave a first order rate constant at 25°C for the averaging of the two high field lines of 8.58 sec^{-1}, and for the averaging of the high field pair with the low field pair of 8.33 sec^{-1}. This means that within the accuracy of the determination the rate of inversion is equal to the rate of site exchange. These results strongly suggest that a twist mechanism is operating since inversion always accompanies site-exchange for a twist, but in the case of bond rupture site exchange may occur without inversion of configuration.

D. Preparation and Study of Dioxobis(benzoylisobutyrylmethanato)-molybdenum(VI).

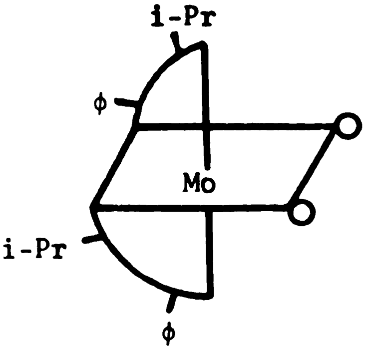
Dioxobis(benzoylisobutyrylmethanato)molybdenum(VI) was prepared by a modification of Gehrke and Veal's synthesis for $MoO_2(acac)_2$, which has been described earlier for dioxobis(dipivaloylmethanato)molybdenum(VI). Benzoylisobutyrylmethanate is an unsymmetrical ligand and as such the complex $MoO_2(bibm)_2$ may exist in three different configurations (isomers) with the molybdenyl oxygens cis. The isopropyl methyls are



IV



V



VI

diastereotopic as they were for the diisobutyrylmethanate derivative, except that in this case the ligand is not deuterated. Assuming that all three isomers exist in solution, the pmr spectrum should be very complicated. Isomer IV should give two isopropyl methyl lines for the diastereotopic isopropyl groups, each of which is split by the proton on the isopropyl group, resulting in a total of four lines. Similarly isomer V should also give four lines in the pmr spectrum. In isomer VI the isopropyl groups exist in two different environments, thus giving rise to two groups of four lines or a total of eight lines. The pmr then should consist of sixteen lines in the isopropyl methyl region, assuming all three isomers are present and all the lines are resolvable. Only twelve lines were resolvable even though the ligand -CH= region indicated that all three isomers were present (see Figure 7).

The pmr studies of $MoO_2(bibm)_2$ were hampered because the complex was not appreciably soluble in many organic solvents. Concentrations of 10g/100ml or higher could be obtained in methylene chloride, chloroform and 1,2-dichloroethane, but solubility was very low in aromatic solvents. The pmr spectrum was essentially the same in all the suitable solvents, and no more than twelve isopropyl methyl lines could be resolved in any solvent at any temperature. The ligand -CH= exhibited only one line at room temperature which would broaden at low temperature indicating three isomers were present, but never splitting out sufficiently to resolve three separate peaks.

The compound was prepared in the hope of analyzing its temperature dependent nmr spectra, using the adaptation of Whitesides-Lisle EXCNMR program for multisite exchange as developed by Pinnavaia and Teets and

Figure 7. Isopropyl methyl lines of $MoO_2(bibm)_2$ in 1,2-dichloroethane; concentration 20g/100ml solvent; 100MHz spectra. The lines marked "x" are due to a small amount of free ligand impurity.

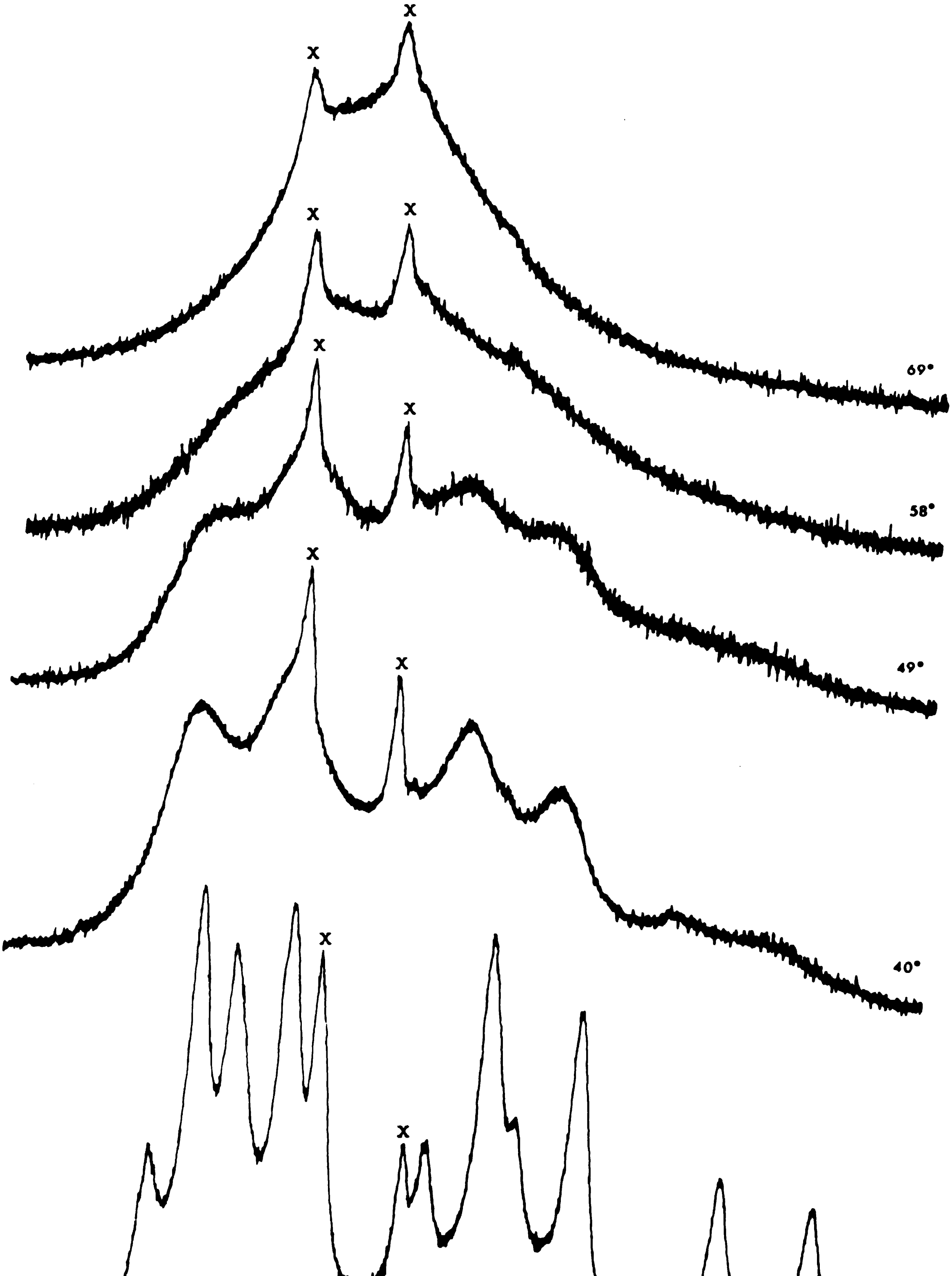


Figure 7

described in the appendix. Unfortunately because of poor solubility in many solvents and lack of resolution it was not possible to make unambiguous line assignments, which are essential to determining the detailed method of rearrangement for these complexes. The pmr shift reagent $Eu(fod)_3$, where fod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione, was used unsuccessfully in an attempt to spread the spectrum out and improve resolution.

The interpretation of the pmr spectrum in terms of a particular mechanism is further complicated by the fact that the coalescence pattern is very complex. It appears that all the isomers are being averaged simultaneously (see Figure 7), which means that no one simple mechanism is operating. This point can be illustrated better by a comparison with the results found for Fe(III)[50] and other metal dithiocarbamates,[51] where the data indicates that intramolecular rearrangement occurs via a trigonal twist mechanism (i.e. rotation about a real or pseudo C_3 axis in the molecule). The dioxomolybdenum(VI) complexes do not possess a real or pseudo C_3 axis, but if rotation were to occur only about that axis which most resembles a pseudo C_3 axis (VII) then we should see a very characteristic coalescence pattern. Figure 8 shows the possible isomers for a dioxomolybdenum(VI) complex with unsymmetrical ligands, such as $MoO_2(bibm)_2$. Although the trans isomers are depicted, there is no evidence to indicate that they exist, except possibly as short lived intermediates. Figure 8 also shows the enantiomeric forms

VII

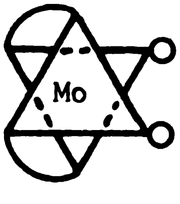
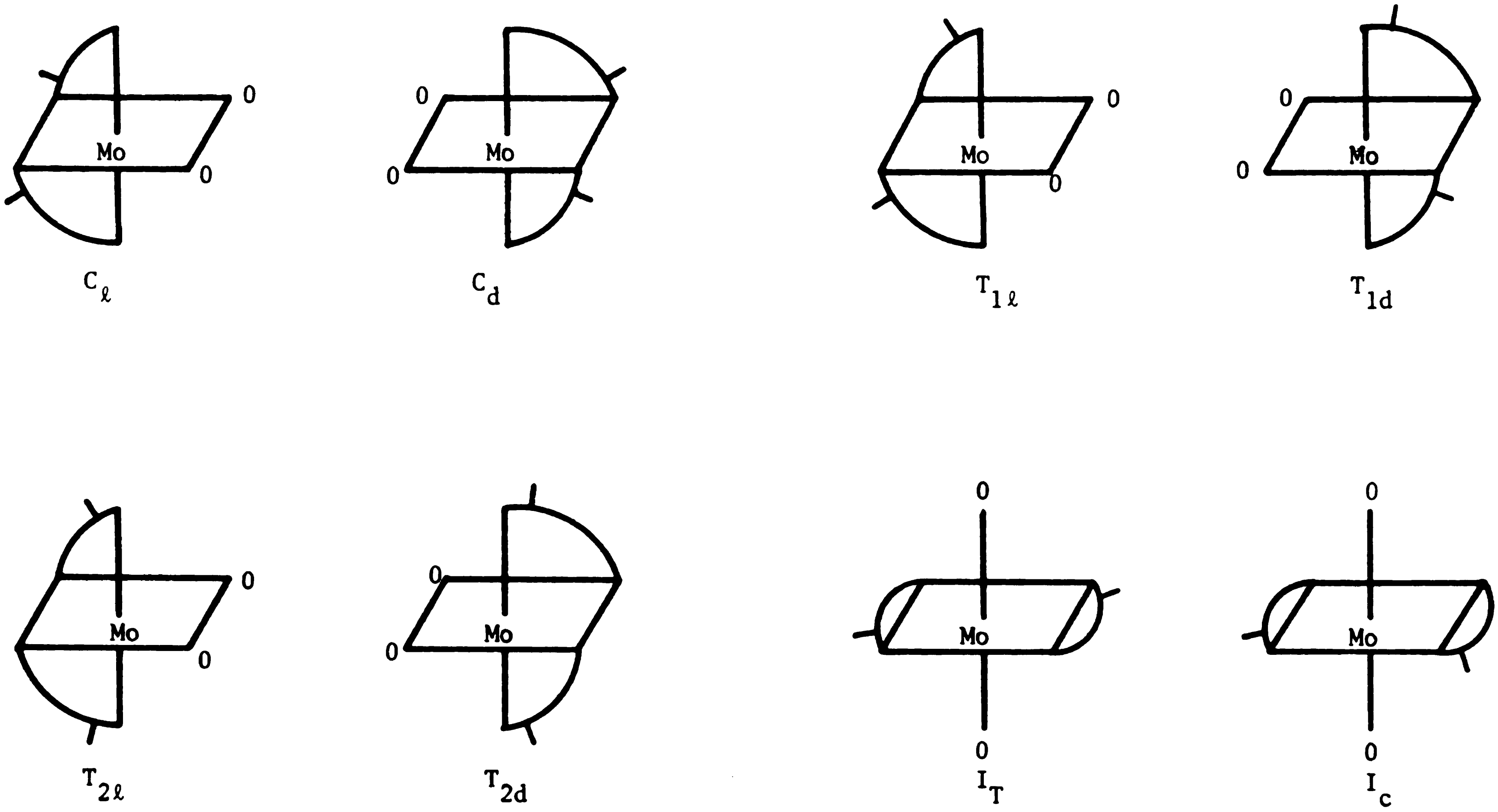


Figure 8. Possible isomers of $MoO_2(bibm)_2$



C_ℓ C_d $T_{1\ell}$ T_{1d}

$T_{2\ell}$ T_{2d} I_T I_c

Figure 8

of each isomer, because, while enantiomers can not be distinguished in the pmr spectrum, nevertheless, interconversion (inversion) leads to averaging of the diastereotopic isopropyl methyls of the $MoO_2(bibm)_2$ complex. Figure 9 shows what happens when "pseudo" trigonal twist (VII) operates in each of the possible isomers. The overall effect then is to interconvert isomers $C_{d,\ell}$ and $T_{2d,\ell}$, and to simply scramble the environments within the $T_{1d,\ell}$ isomers. Thus, if this mechanism alone operated in $MoO_2(bibm)_2$ the four proton resonance lines of isomer IV would coalesce with the four lines of isomer V giving only a spin coupled doublet in the region of rapid exchange. Similarly the eight lines of isomer VI would collapse to a doublet. This is not what is observed (see Figure 7), and so we can rule out a simple Bailar (trigonal) twist as the sole rearrangement pathway. Likewise, rotations solely about other specific axes in the complex can be ruled out. The mechanism of rearrangement of these complexes must then be a nontrivial one, in which rotation about several axes in the complex occurs or in which bond rupture occurs producing several of the possible intermediates.

Figure 9. Results of trigonal twist mechanism operating in $MoO_2(bibm)_2$

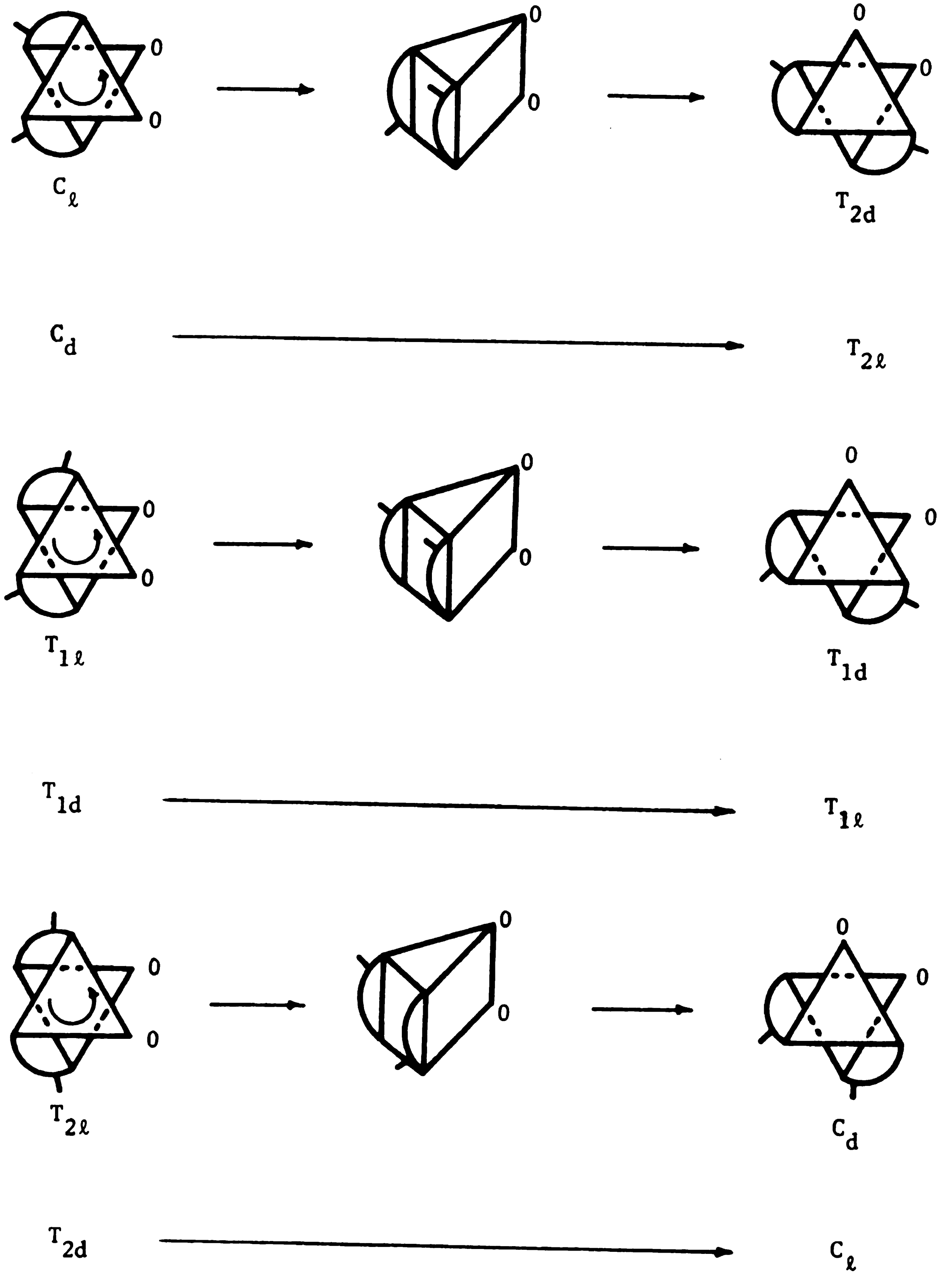

0
0
0
0
0
0
C_ℓ
T_{2d}
C_d
$T_{2\ell}$
0
0
0
0
0
0
$T_{1\ell}$
T_{1d}
T_{1d}
$T_{1\ell}$
0
0
0
0
0
0
$T_{2\ell}$
C_d
T_{2d}
C_ℓ

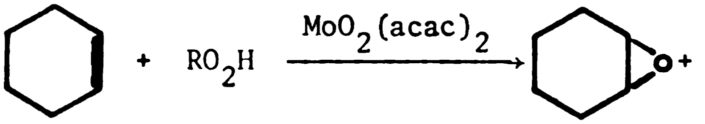
Figure 9

IV. SUMMARY

The relative rates of rearrangement of neutral d^0 and d^{10} bis and tris metal β-diketonate complexes appears to be influenced primarily by the size of the metal ion. With the exception of Sn^{4+} (0.41 Å), the following order of increasing stereochemical lability with increasing Pauling crystal radius of the metal ion is observed for the known neutral, six-coordinated, d^0 and d^{10} metal β-diketonates: Ge^{4+}(0.50 Å) < Al^{3+}(0.53 Å) < Ga^{3+}(0.62 Å), Mo^{6+}(0.62 Å) < Ti^{4+}(0.68 Å) < Zr^{4+}(0.80 Å), Sc^{3+}(0.81 Å), In^{3+}(0.81 Å). Recently Jones and Fay[49] have shown that $Sn(acac)_2X_2$, where X = F, Cl, Br, I, rearranges slower than the $Ti(acac)X_2$ analoges. Nevertheless, the importance of metal ion radius in the above series is clearly evident.

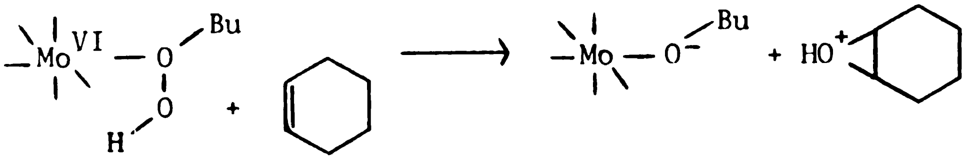
Pinnavaia has interpreted the rearrangements of both aluminum(III) and gallium(III) diketonates in terms of a bond rupture mechanism,[21] whereas Holm,[8] has favored bond rupture for the former complexes and twisting for the latter. The equal rates of inversion and site exchange for the $MoO_2(d^3\text{-dibm})_2$ as well as the similar labilities of molybdenyl and gallium(III) β-diketonates would appear to be explained adequately by twisting mechanisms, because the energy required for the MO_6 core to achieve trigonal prismatic configuration should be about the same in both cases. It should be emphasized, however, that this interpretation does not unequivocally preclude the possibility of bond rupture mechanisms. Although the formal charge to radius ratio of Mo^{6+} is twice that of Ga^{3+}, the large multiple bond order (*ca.* 2.4[8]) for the molybdenum-oxygen bonds of the MoO_2^{2+} moiety should lower the effective charge on the central metal atom and thus decrease the energy needed to open a diketonate oxygen-molybdenum bond.

Recently Gould has reported that dioxobis(acetylacetonato)molybdenum(VI) is a good catalyst in the epoxidation of cycloalkenes.[33] The two possible mechanisms proposed imply that the active metal, in

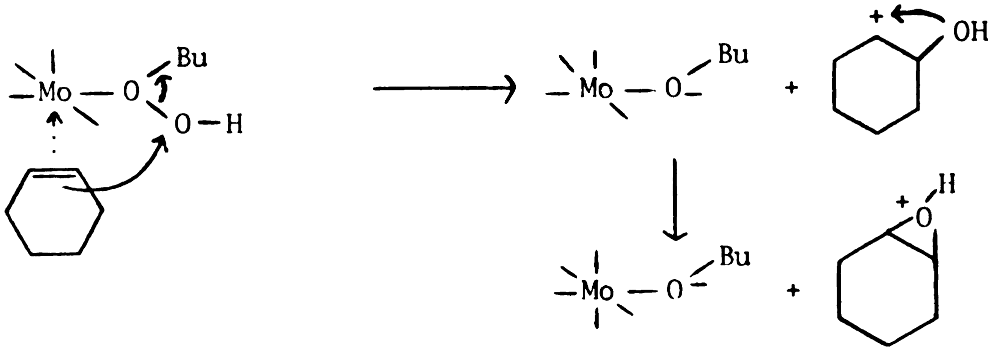


(6)

this case molybdenum, be substitution labile.[33,50] Our studies[10] as well as those of Wise[11] indicate that these complexes are indeed labile,



(7)



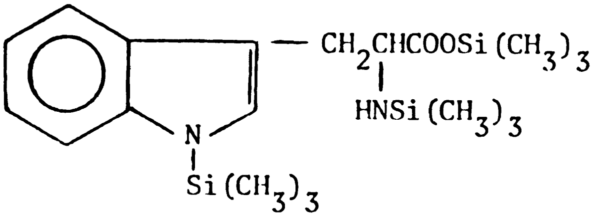
(8)

however, they do not preclude and in fact suggest that a twist mechanism may operate. A twist mechanism would not give the substitution lability required by Gould's mechanisms for the formation of a metal hydroperoxide intermediate. Further, both our work and that of Wise show that a dissociative mechanism clearly does not operate in these complexes for the rearrangement process. It would appear, however, that the intramolecular rearrangement of the molybdenum catalyst probably does not play an important role in its catalytic activity, since the epoxidation reaction is a bimolecular reaction and proceeds at a rate of 10 to 100 times faster than the rearrangement.

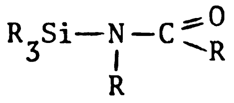
PART II

I. INTRODUCTION

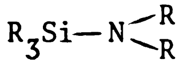
Silylation reactions and the factors affecting them have become increasingly important in recent years. This is largely a result of the fact that a wide variety of organic and biologically significant molecules possessing an acidic hydrogen atom will reversibly form silyl derivatives in which the hydrogen is replaced by an R_3Si group. Silylation has the effect of reducing hydrogen bonding between molecules and consequently increasing the solubility and volatility of the parent molecule. Among the numerous examples which could be cited,[53,54] the amino acid tryptophan which is high melting, insoluble in most organic solvents and has a negligible vapor pressure can be converted to the tris(trimethylsilyl) derivative (VII) which is soluble in organic solvents and capable of being analyzed by glpc.[54] Addition of water will regenerate the tryptophan from the silyl derivative.


VII

The silylamides (VIII) are thermodynamically and kinetically superior to the silylamines (IX) or chlorosilanes (X) as silylating agents for organic and biological molecules. Klebe[55] has suggested


$R_3Si-N(R)-C(=O)R$

VIII

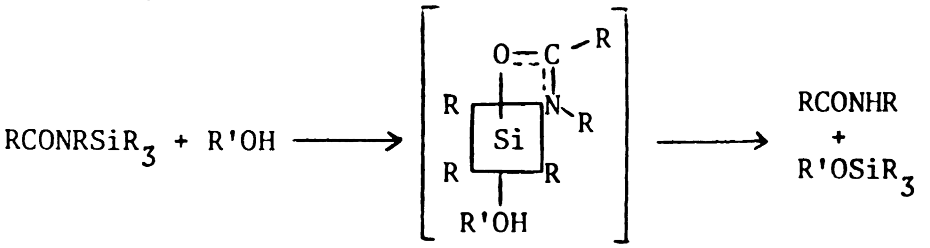

R_3Si-NR_2

IX

R_3SiX

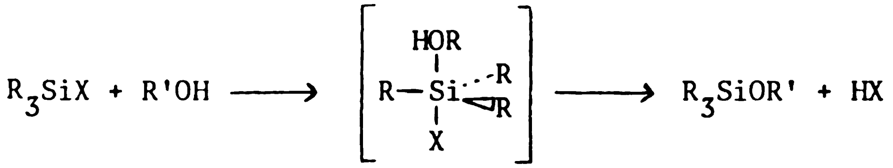
X

that the remarkably high rates of silylation for the amides are intimately related to their ability to expand the coordination sphere of the silicon atom from four to six. As a result of incipient extracoordination of silicon by the amide oxygenation, octahedral transition states or intermediates (XI) are considered likely in the proton transfer reaction:

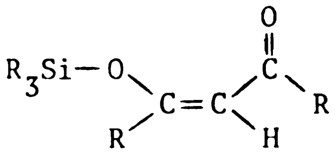

XI

(9)

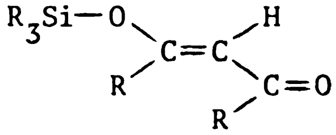
In contradistinction, silylation by silylamines or silylhalides must proceed through higher energy five-coordinate transition states:


(10)

This hypothesis, while reasonable, is in most cases impossible to test. However, silyl enol ethers constitute a group of organosilicon compounds uniquely suited for studying the effects of valence shell expansion on substitution rates. The compounds possess <u>sequence</u> <u>cis</u> (XII) and <u>sequence</u> <u>trans</u> forms (XIII).[56] Incipient extracoordination



XII



XIII

is possible in the *seqcis* isomer, but not in the *seqtrans* form.[57] Thus if the ability of silicon to expand its coordination sphere from four to five or from four to six are important factors in substitution processes of organosilicon, then the rate of silylation of an alcohol should be appreciably more facile for the *seqcis* than *seqtrans* form. The objective of this project, therefore, was to test the importance of incipient extracoordination in the silylation of methanol by the *seqcis* and *seqtrans* forms of trimethylyilylacetylacetonate (R = CH_3 XII and XIII).

NOTE = For an explanation of the terms *seqcis* and *seqtrans* see reference 56.

II. EXPERIMENTAL

A. Reagents and Solvents

Methylene chloride and chlorobenzene were dried over calcium hydride for at least 24 hours and freshly distilled before use. Methanol was dried over calcium sulfate for at least 48 hours and freshly distilled before use.

B. General Techniques

All glassware was dried at least 24 hours at 180°C and cooled in a desiccator whenever possible. Transfers were effected in a polyethylene glove bag under an atmosphere of dry nitrogen.

Proton magnetic resonance techniques have been described already in the experimental section of Part I.

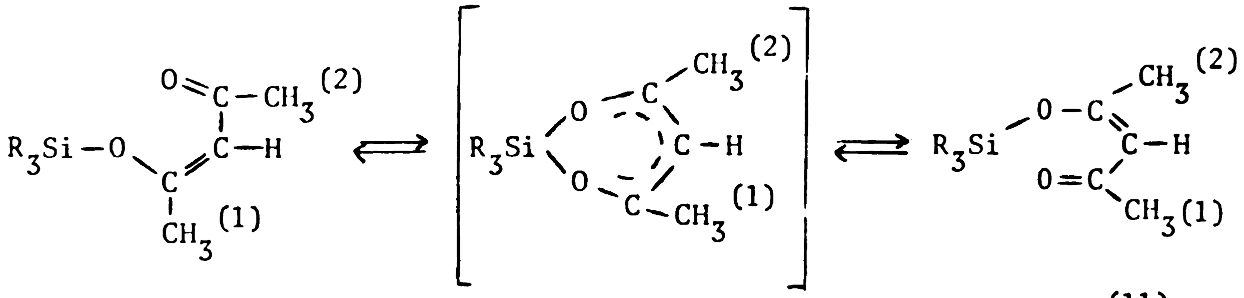
C. Synthesis of Trimethylsilyacetylacetonate

Trimethylsilylacetylacetonate was prepared and purified in our laboratory by Jerry Howe according to the general method described by West.[58] Bp = 66-68° (4 torr), $n_D^{23.6} = 1.4507$, lit.[58] Bp = 66-68°, $n_D^{25} = 1.4546$.

Anal. Calculated for $SiC_8H_{16}O_2$: Si, 16.30; C, 55.77; H, 9.39; Mol wt, 172. Found: Si, 16.51; C, 55.70; H, 9.21; mol wt, 184.

III. RESULTS AND DISCUSSION

Pinnavaia and Howe[59] have confirmed that trimethylsilylacetylacetonate, $(CH_3)_3Si(acac)$, exists in solution as two isomers, a seqcis (XII, R = CH_3) and a *seqtrans* (XIII, R = CH_3). The *seqcis* to *seqtrans* ratio in chlorobenzene is 0.34 ± 0.04.[57] Furthermore, they have shown that the *seqcis* isomer undergoes a rapid degenerate rearrangement which is believed to occur via a pentacoordinated silicon intermediate or transition state. A similar process is not observed for



XII

(11)

the *seqtrans* isomer because of restricted rotation about the carbon-carbon double bond. No broadening of the pmr lines for the *seqtrans* acetylacetonate methyls was observed even at 120°C. This has important implications, because it means that upon substitution the *seqcis* isomer of trimethylsilylacetylacetonate can readily expand its coordination sphere to six, whereas the *seqtrans* isomer can only expand its coordination sphere to five. Figure 10 illustrates the difference in mechanism for the *seqcis* and *seqtrans* isomers reacting with methanol.

Figure 10. Possible mechanism for the reaction of CH_3OH with the *seqcis* isomer (A) and *seqtrans* isomer (B) of $(CH_3)_3Si(acac)$, where R is a methyl group.

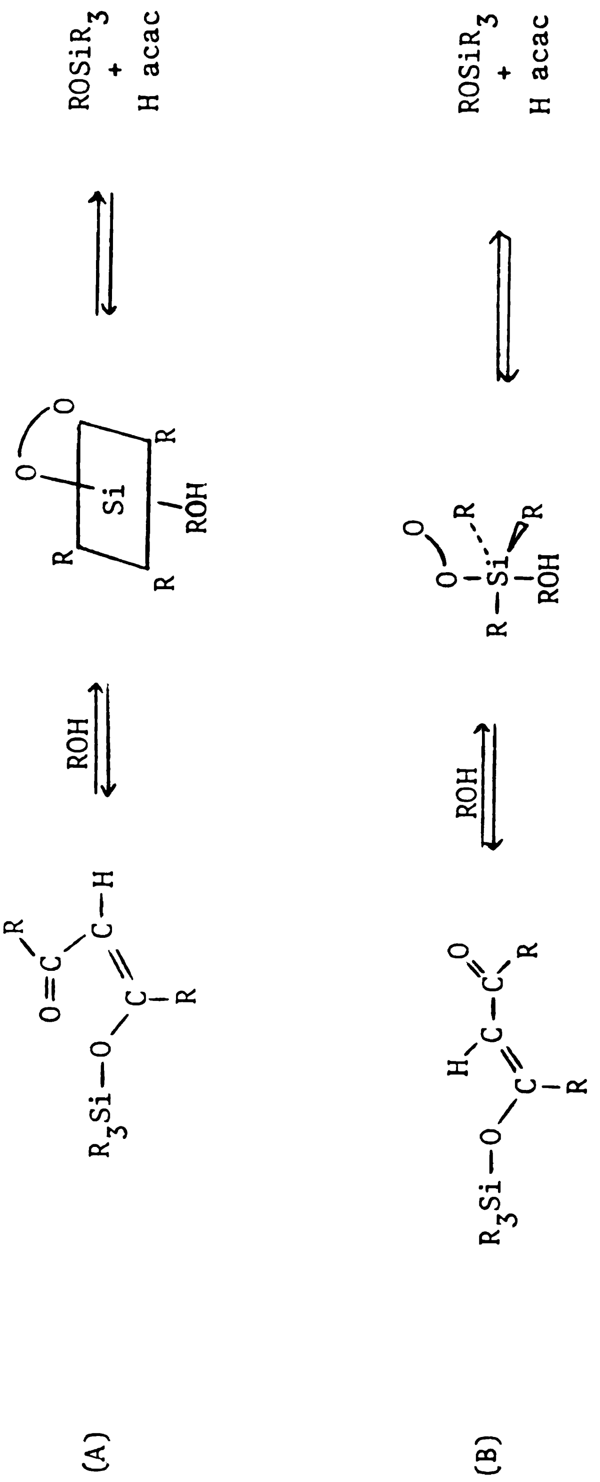

(A)
R_3Si-O
ROH
Si
ROH
$ROSiR_3$
+
H acac
(B)
R_3Si-O
ROH
Si
ROH
$ROSiR_3$
+
H acac

Figure 10

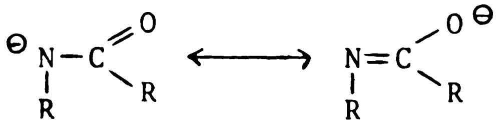
The reaction rates of the seqcis and seqtrans isomers of trimethylsilylacetylacetone with methanol were studied in methylene chloride and chlorobenzene. In a typical kinetics run, 0.16g of $(CH_3)_3Si(acac)$ was dissolved in 0.71g of CH_2Cl_2 in an pmr tube and the solution was allowed to equilibrate at -5.3°C in the probe of the pmr spectrometer. Approximately 60 minutes was allowed for temperature equilibration. A solution of 0.02g of CH_3OH in 0.25g of CH_2Cl_2 was prepared and placed in a vial in an ice bath (∿0°C). To initiate the reaction the methanol solution was extracted from the vial with a pipet and injected into the pmr tube which remained in the probe. The rate of change of the mole fractions of the seqcis and seqtrans isomers was determined by electronic integration of the ligand methyl proton resonance signals. The important variable being measured was the seqcis to seqtrans ratio as a function of time. At -5.3°C the silylation reaction was sufficiently slow that more than one hour was required for complete reaction, and the seqcis to seqtrans ratio could be easily followed. In addition, it should be noted that the rate of silylation is much faster than the rate of seqcis-seqtrans isomerization, which is very slow and permits separation of the isomers.[60] Table IV shows the results obtained in methylene chloride and chlorobenzene.

It is apparent from these results that at least for $(CH_3)_3Si(acac)$ incipient extracoordination does not play an important role in the rate of its silylation reactions. The methanol reacts equally well with both isomers. This would seem to indicate that expansion of the silicon coordination sphere is not the principle factor affecting the activation energy in organosilyl displacement reactions as Klebe has postulated.

Table V. *Seqcis* to *Seqtrans* Ratio of $(CH_3)_3Si(acac)$ During Reaction With CH_3OH -5.3°C.

Methylene Chloride Solvent		Chlorobenzene Solvent	
Time from mixing(min)	[cis]/[trans]	Time from mixing(min)	[cis]/[trans]
0	.64	0	.31
3.0	.60	1.0	.30
5.8	.61	2.0	.32
6.5	.60	5.0	.32
9.4	.62	6.0	.31
10.5	.60	8.7	.31
13.3	.59	10.0	.31
14.3	.61	13.0	.31
16.3	.61	15.0	.30
20.5	.60		
22.5	.58		
26.0	.61		
29.0	.63		

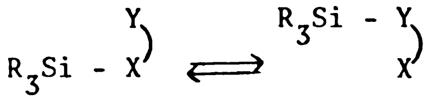
Sommer[61] has pointed out the importance of electronic effects in reactions of this type, whereby the effect on the rate closely parallels the ability of the leaving group to carry a negative charge. This would explain why silylamides are better silylating agents than silylamines or silylhalides, because the leaving anion is resonance stabilized for the amides but not for the amines or halides. Thus, our work suggests that electronic effects rather than incipient extracoordination exert greater influence on rates of organosilyl displacement reactions.



PART III

I. INTRODUCTION

In recent years there has been a good deal of interest in the migration of R_3Si groups between electronegative centers. A general feature of these molecular rearrangements is that they are rapid and reversible. This may be illustrated by the equilibrium between (XIII) and (XIV), where X and Y represent electronegative atoms such as oxygen

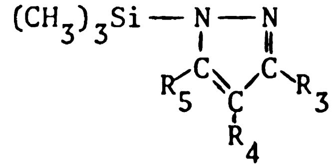


$$\begin{matrix} & Y \\ R_3Si - X & \end{matrix} \rightleftarrows \begin{matrix} R_3Si - Y \\ X \end{matrix} \qquad (12)$$

XIII XIV

or nitrogen. When X and Y are identical, $X\smile Y$ in its unsilylated form is a symmetric, uninegative ligand. The symmetry of the ligand means that the molecular rearrangement is degenerate, but nonetheless observable by temperature dependent nmr spectroscopy. Examples of this growing class of compounds include silyl derivatives of β-diketones,[57,59,62,63] malonates,[64] tropolone,[63] pyrazoles,[65] triazene,[66] benzamidine,[67] and hydrazine anions.[68] In contradistinction, when X and Y are not the same, then X- and Y- silylated constitutional isomers are possible and the intramolecular rearrangement results in their rapid tautomerization. These types of compounds are exemplified by the silyl anilides[55,69] and amides.[70]

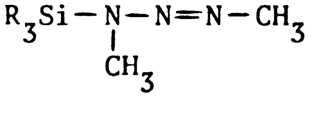
Silyl group 1, 2 migrations have been observed between the two nitrogen atoms in pyrazoles (XV).[65] The rate of rearrangement increases



XV

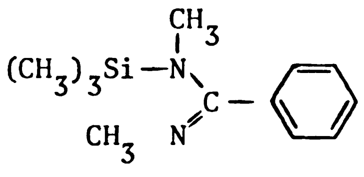
as the substituents R_3, R_4 and R_5 become more electron releasing. This electronic effect has been explained as being due to increased electron density, hence availability, at the free nitrogen.

Nitrogen to nitrogen, nitrogen to oxygen and nitrogen to sulfur 1,3 migrations have been reported. The silyl triazene (XVI)[66] and benzamidene (XVII)[67] exibit facile interchange of the R_3Si group between nitrogen atoms. Rearrangement rates for the triazene derivatives



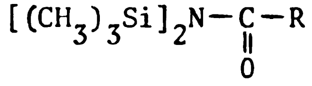
$R_3Si-N(CH_3)-N=N-CH_3$

XVI



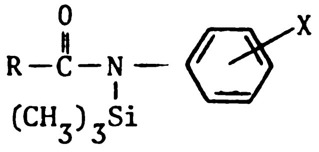
XVII

increase as the electron withdrawing ability of the groups attached to silicon increases. The R_3Si group migrates between oxygen and nitrogen in the silyl amides (XVIII),[70] anilides (XIX),[55,69] and benzimidates (XX).[71]

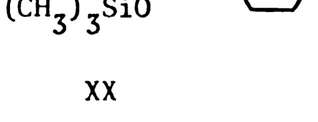


$[(CH_3)_3Si]_2N-C(=O)-R$

XVIII

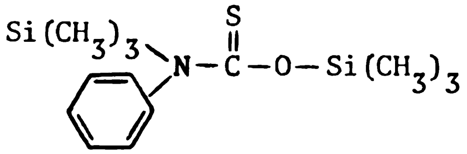


XIX



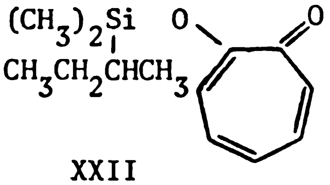
XX

The rate of migration increases in the anilides and benzimidates as electron releasing groups are replaced on the carbonyl carbon.[69,71] This trend parallels that found for substitution on the pyrazole ring. In addition, electron withdrawing substituents increase the equilibrium concentration of the oxygen silylated isomer.[55] Itoh has reported a 1, 3 silyl migration between sulfur and nitrogen in the adduct of bis-trimethylsilyl sulfide with phenyl isocyanate (XXI).[71]



XXI

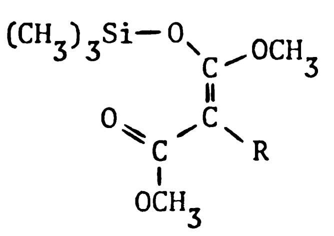
A 1, 4 migration of the SiR_3 group has been observed by Reich in 2-(2-butyldimethylsiloxy)cyclohepta-2,4,6-trienone (XXII).[63] He notes



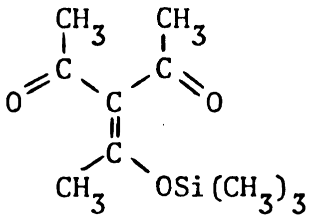
XXII

that while this and other silyl shifts (e.g. XII, XV, XVI) can be considered sigmatropic rearrangements, the facility with which all of these reactions proceed suggests that they are best considered as internal nucleophilic displacements.

Oxygen to oxygen 1, 5 migrations are well documented for the silyl carbomethoxyketene acetals[72] or malonates (XXIII) and silyl enol ethers of triacelylmethane (XXIV)[62] and acetylacetone (XII).[57,59] The



XXIII

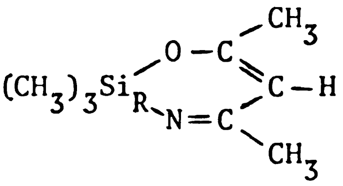


XXIV

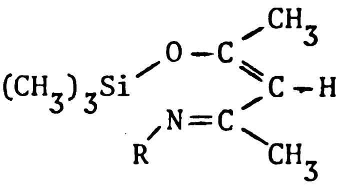
rearrangement is only observed for the *seqcis* form of (XXIII) and (XII) and not for the *seqtrans* forms. Pinnavaia has observed dramatic substituent[57] and angle strain effects[73] on the rate of R_3Si group migrations in enol ethers. Sigmatropic shifts should be relatively insensitive to these effects and, hence, it appears that these 1, 5 shifts are best viewed as internal nucleophilic displacements.

The objective of this work was to prepare and investigate a new class of silyl β-ketoamines with potential for 1, 5 migration of the R_3Si group between oxygen and nitrogen. The silyl β-ketoamines represent a complex system in which six different isomers might be expected (see Figure 11), four oxygen silylated and two nitrogen silylated isomers. The four O- silyl isomers differ by virtue of *seqcis*-*seqtrans* isomerization about the C=C bond and *syn*-*anti* isomerization about the C=NR bond. The N-silyl isomers can exist only as *seqcis* and *seqtrans* forms. The existence of N- and O-silyl tautomers may be anticipated since these tautomers are observed in silyl amides. One or both of the *seqcis* O-silyl isomers (XXV and XXVI) should interchange rapidly with the *seqcis* N-silyl form (XXIX) in presence of 1, 5- R_3Si migration, but the remaining isomers should be stereochemically rigid.

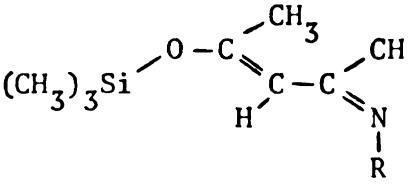
Figure 11. Possible isomers of silyl β-ketoamines.



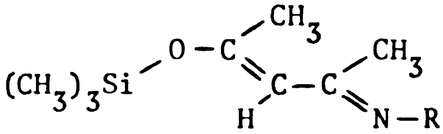
XXV



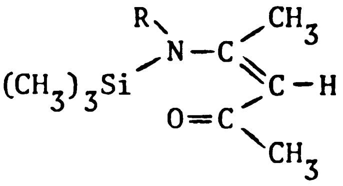
XXVI



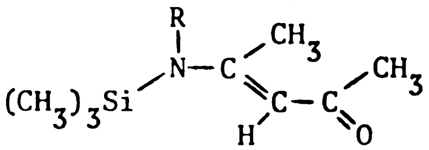
XXVII



XXVIII



XXIX



XXX

Figure 11

II. EXPERIMENTAL

A. General Techniques

All general methods of purifying diketones and solvents and drying of glassware were analogous to those described in Part I and II of this thesis. Aniline was obtained from Fisher Scientific Company, m - chloroaniline from Matheson, Coleman and Bell, and p - fluoroaniline from Aldrich Chemical Company. The aniline and aniline derivatives were used without further purification.

B. Synthesis of 4-Anilino-3-pentene-2-one

4-Anilino-3-pentene-2-one was prepared by using the general method of Everett and Holm.[74] Acetylacetone (30g, 0.30 moles) and aniline (42g, 0.45 moles) were placed in a 100ml round bottom flask and heated to ca. 100°C for 5 hours. The solution was then cooled and extracted with three 50ml portions of ether. The ether solution was dried over anhydrous sodium sulfate and then filtered through a glass frit. Cooling the solution in dry ice produced 4-anilino-3-pentene-2-one. The product was recrystallized three times from ether and then vacuum dried, giving 40.7g (77.5% yield) of off-white crystals with a melting point of 47°-48°C. Literature[75,76] melting point, 47°-48°C.

C. Synthesis of 4-m-Chloroanilino-3-pentene-2-one and 4-p-Fluoroanilino-3-pentene-2-one

4-m-Chloroanilino-3-pentene-2-one and 4-p-fluoroanilino-3-pentene-2-one were prepared by the method described above for 4-anilino-3-pentene-2-one. A 50% mole excess of the primary amine was added directly to the β-diketone, and the mixture was heated to ca. 100°C for several hours. The products were then extracted and crystallized from ether or hexane. The 4-m-chloroanilino-3-pentene-2-one thus prepared had a melting point of 38°-39.5°C and the 4-p-fluoroanilino-3-pentene-2-one melted at 48°-49.5°C. The literature value of the melting point of 4-m-chloroanilino-3-pentene-2-one is 42°.[79] The purity of 4-p-fluoroanilino-3-pentene-2-one was verified by pmr spectroscopy.

D. Synthesis and Characterization of Trimethyl (4-anilino-3-pentene-2-one)silane

There are no previously reported preparations of silyl β-ketoamines. 4-Anilino-3-pentene-2-one (20g, 0.11 moles) was dissolved in ca. 400ml of dry hexane and placed in a 500ml three necked round bottom flask with a gas inlet tube and condenser attached. A gas outlet was attached to the condenser and then to a mineral oil bubbler by means of tygon tubing. The system was purged with dry nitrogen for ca. 15 minutes, and then freshly cut potassium metal (4.4g, 0.11 moles) in small pieces was added to the reaction flask. The mixture was stirred for ca. 12 hours while passing a slow stream of dry nitrogen through the system. At the end of 12 hours a very viscous mixture of hexane and potassium salt of the β-ketoamine had formed. Chlorotrimethylsilane (13.0g, 0.12 moles) was dissolved in 50ml of dry hexane and placed in a dropping funnel (operations performed in dry box), which was then connected to the round bottom flask replacing the glass stopper. The chlorotrimethylsilane was then added dropwise to the hexane-potassium salt mixture. After addition was complete the mixture was heated to ca. 50°C and allowed to stir for 24 hours. The mixture was transferred in a nitrogen filled glove bag into stoppered centrifuge tubes, and the finely divided potassium chloride precipitate was removed by centrifugation. The supernate was then placed in a flask on the spinning band distillation column and the hexane was distilled off. A vacuum of 0.5 torr was applied to the column and the product was vacuum distilled. 4-Anilino-3-pentene-2-one was collected in four fractions boiling from 90° to 97°C at 0.5 torr. The purest fraction as determined by pmr was collected at a temperature of 96°-97°C and was sent to Galbraith Laboratories for chemical analysis.

Anal. Calculated for $SiC_{12}H_{21}NO$: Si, 11.35; C, 67.96; H, 8.56; N, 5.66. Found: Si, 11.14, C, 67.78; H, 8.55; N, 5.47.

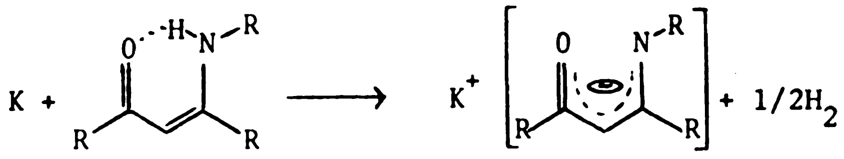
E. Synthesis of Trimethyl(4-m-chloroanilino-3-pentene-2-one)silane and Trimethyl(4-p-fluoroanilino-3-pentene-2-one)silane

Trimethyl(4-*m*-chloroanilino-3-pentene-2-one)silane and trimethyl-(4-*p*-fluoroanilino-3-pentene-2-one)silane were both prepared using the method described above for trimethyl(4-anilino-3-pentene-2-one)silane. They are both pale yellow liquids which boil at 113°C at 0.5 torr and 83°C at 0.1 torr, respectively. Both compounds hydrolyze readily, precluding good chemical analyses. The fraction of hydrolysis products was observed to increase with increasing ageing of the products in sealed nmr tubes.

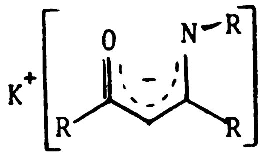
III. RESULTS AND DISCUSSION

A. Preparation and Properties of Silyl β-Ketoamines

The silyl β-ketoamines prepared in this study represent a new class of silicon compounds. While β-ketoamines and their complexes with many metal ions have been widely studied (for a survey see ref. 78) there are no previous reports of silicon β-ketoamine complexes. These compounds were formed quite easily with the aniline derivatives of the β-ketoamines, by simply making the potassium salt with potassium metal (eq. 13) and then allowing this to react with chlorotrimethylsilane (eq. 14). However, when a hydrogen or methyl group was bonded to the nitrogen in place of the phenyl group in the aniline derivatives the reactions would not go.



(13)



+ $(CH_3)_3SiCl \longrightarrow$ KCl + silyl β-ketoamines

(14)

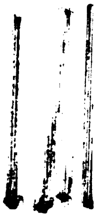
The derivatives of anilino-, m-chloroanilino, and p-fluoroanilino-3-pentene-2-one, abbreviated $(CH_3)_3Si$(papo),[‡] $(CH_3)_3Si$(m-capo) and $(CH_3)_3Si$(p-fapo), respectively, are all high boiling pale yellow liquids.

[‡] For a list of the ligand abbreviations used see Appendix A.

All hydrolyzed easily with the *m*-chloro and *p*-fluoroaniline derivatives being somewhat more susceptible to hydrolysis than the unsubstituted aniline derivative. All the silyl β-ketoamines were stable and miscible in common organic solvents such as methylene chloride and chlorobenzene.

B. Characterization of Silyl β-Ketoamines

Trimethyl(4-anilino-3-pentene-2-one)silane, trimethyl(4-*m*-chloroanilino-3-pentene-2-one)silane and trimethyl(4-*p*-fluoroanilino-3-pentene-2-one)silane all have very similar pmr spectra (see Figure 12). Figure 11 shows the possible isomers that might be expected. Each isomer should give rise to single silyl methyl and ligand C-H lines and two ligand methyl lines as a result of its unsymmetric nature. It is apparent then from the eight ligand methyl lines present that there are present only four of the six possible isomers one might expect. It is interesting to note that even the relative concentrations of isomers appears to be approximately the same for all three compounds. Cooling the solution of $(CH_3)_3Si(papo)$ to -64° did not resolve any new pmr lines or reveal any new isomers. The high temperature spectra of $(CH_3)_3Si(papo)$ and $(CH_3)_3Si(p\text{-}fapo)$ were recorded and they are almost identical. Figures 13 and 14 show the temperature dependent pmr spectra of $(CH_3)_3Si(papo)$. The four isomers have been labeled A, B, C and D. Ligand -CH= assignments were made on the basis of spin decoupling experiments and silyl methyl lines were assigned on the basis of relative intensities (graphical integration). It can be seen that isomers A and B become exchange averaged first and then isomers C and D coalesce, but even at 179°C isomers A and B do not interchange with isomers C and D. Further heating causes irreversible decomposition of the silyl β-ketoamines.



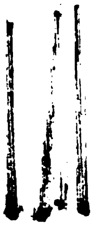


Figure 12. Ambient pmr spectra of: (1), $(CH_3)_3Si$(papo); (2), $(CH_3)_3Si$(m-capo); (3), $(CH_3)_3Si$(p-fapo). Concentrations *ca.* 20g/100ml chlorobenzene.

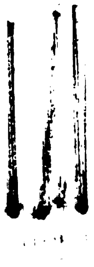


Figure 13. Ligand methyl region of temperature dependent pmr spectra of $(CH_3)_3Si$(papo) in chlorobenzene; concentration is ca. 50g/100ml solvent; 60MHz. The lines marked "x" are due to a small amount of free ligand impurity.

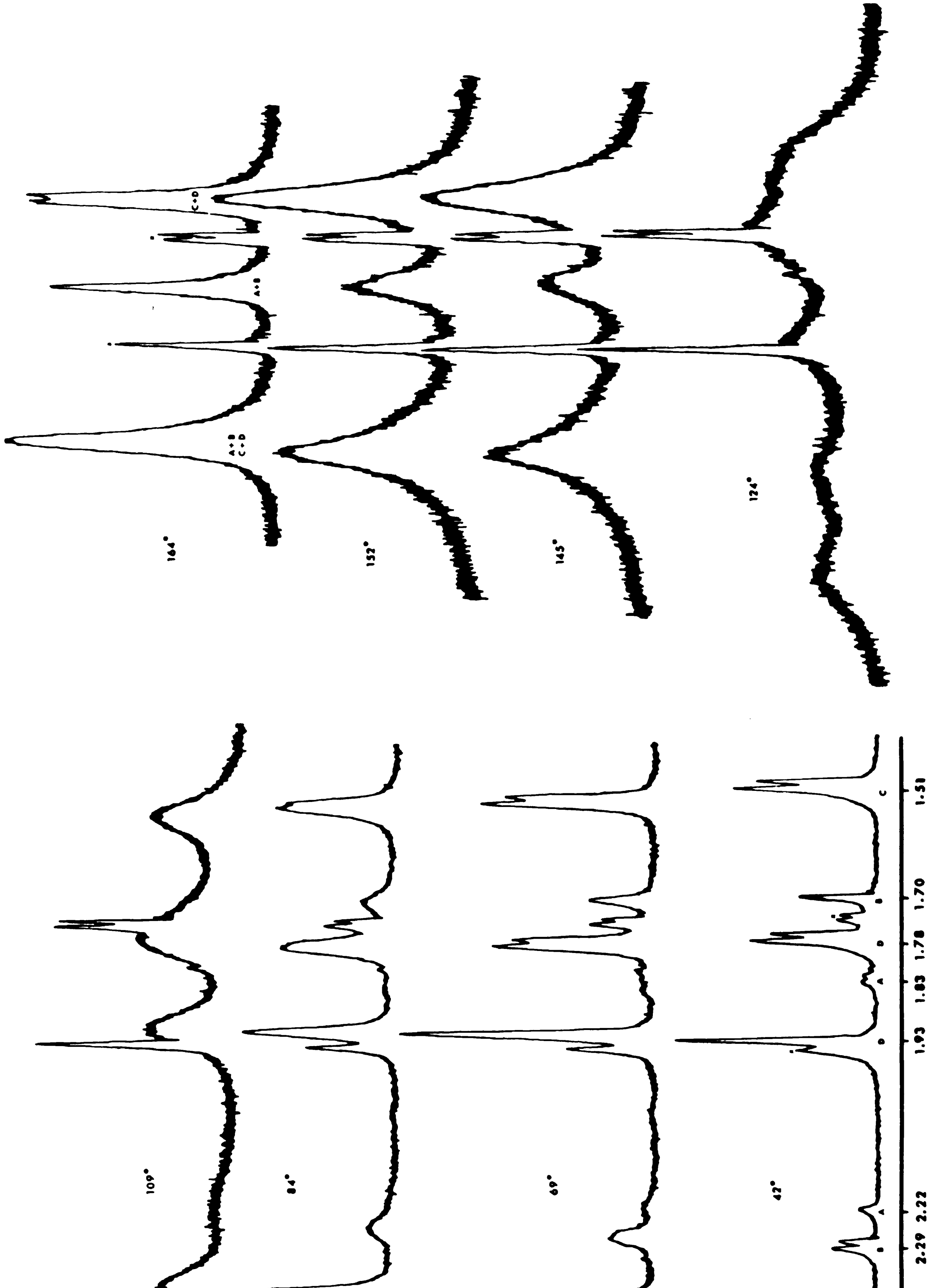

109°
84°
69°
42°
164°
152°
145°
124°
A+B
C+D
A+B
C+D
C
B
A
D
A
D
B
C
2.39
2.29
2.22
δ
1.93
1.83
1.78
1.70
1.51

Figure 13

Figure 14. Silyl methyl and ligand =CH- region of temperature dependent pmr spectra of $(CH_3)_3Si$(papo) in chlorobenzene; concentration is ca. 50g/100ml solvent; 60MHz. The lines marked "x" and "H" are due to a small amount of free ligand and a hydrolysis product, respectively. (Note: The silyl methyl region at 42°C was run at half the sweep width of the other spectra.)

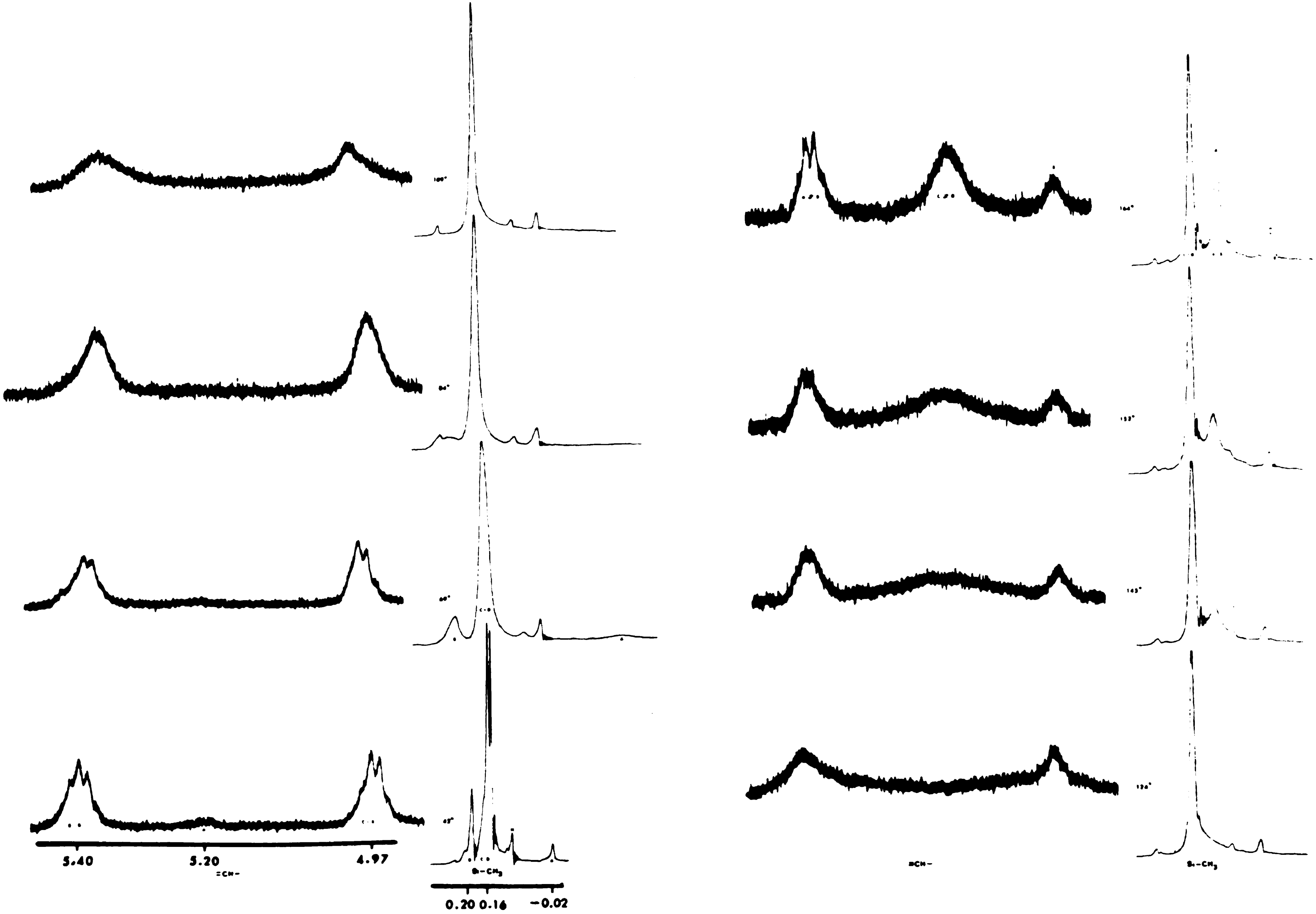
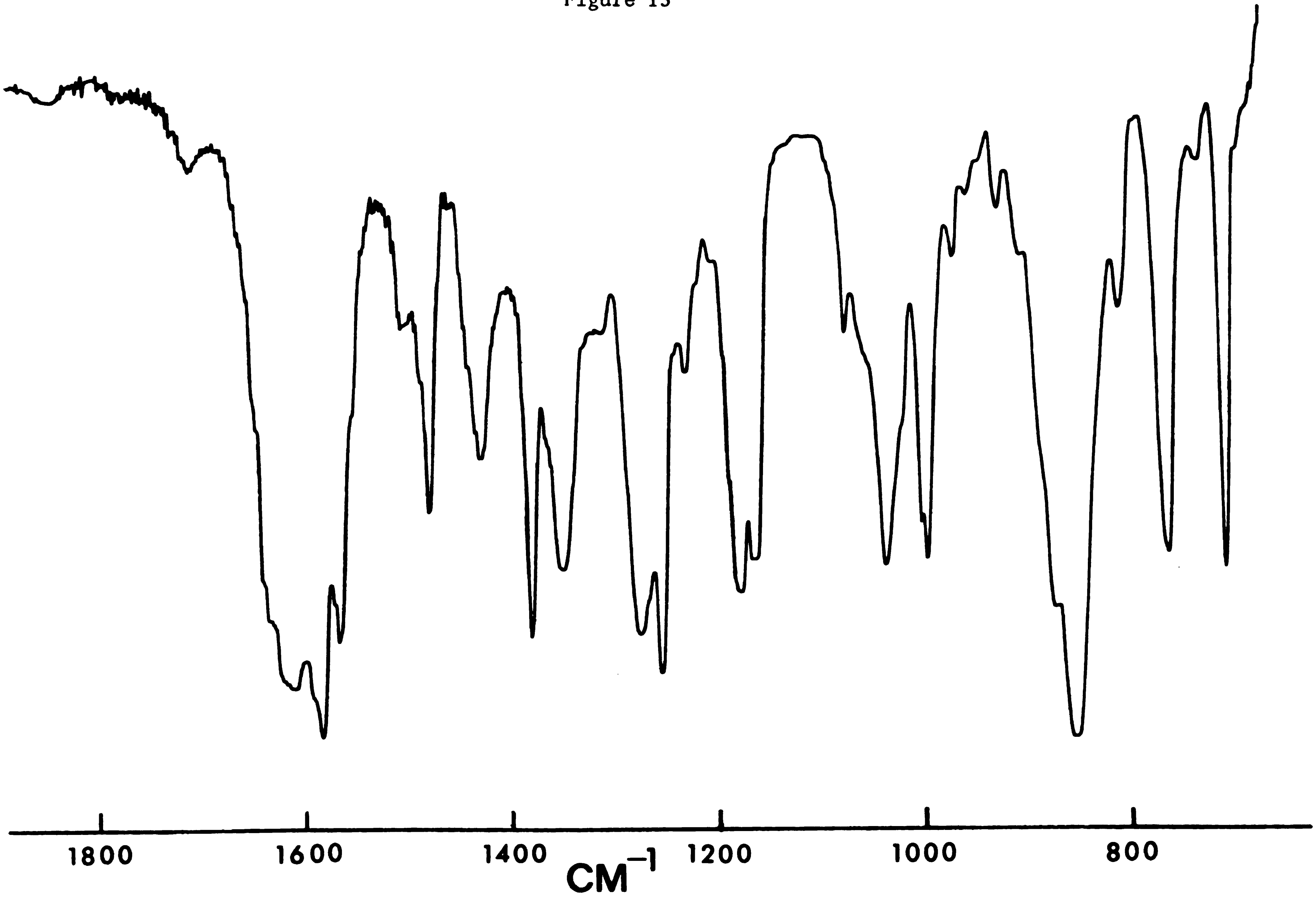


Figure 14

The infrared spectrum of $(CH_3)_3Si$(p-fapo) (see Figure 14) exhibits an intense absorption at 1030 cm^{-1} consistent with the Si-O stretch observed in the silyl enol ethers.[58] In addition a broad intense absorption occurs in the 1570-1630 cm^{-1} which is the region expected for both C=C[58] and C=N[67] stretching vibrations. Furthermore, there is no absorption in the 1700 cm^{-1} region where the stretching frequency of an uncoordinated carbonyl group should be found.[58] All of this indicates that the four isomers present in these compounds are the four oxygen bonded isomers XXV-XXVIII.

Figure 15. Infrared spectrum of neat $(CH_3)_3Si(papo)$ between CsI salt plates. The 1601.8 and 1028.3 cm^{-1} absorptions of polystyrene were used as references.

Figure 15



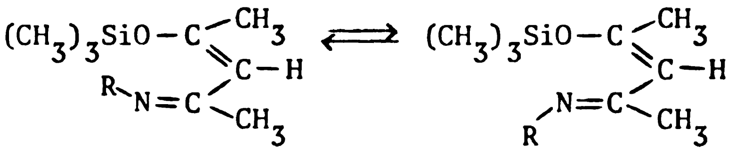
IV. CONCLUSIONS

The pmr data strongly indicate that the silyl β-ketoamines exist exclusively as oxygen silylated isomers XXV-XXVIII. The line broadening observed in the variable temperature pmr spectra is attributed to rapid *syn*-*anti* isomerization about the C=NR bond and occurs in both the *seqcis* and *seqtrans* forms which leads to XXV ⇄ XXVI and XVII ⇄ XXVIII averaging. The only other possible explanation of the variable temperature pmr data must be based on the assumption that both oxygen and nitrogen silyl tautomers are present but that *syn*-*anti* isomerization in the O-bonded forms is fast even at -64°C. This would account for the apparent existence of four isomers. The two high temperature pmr broadening phenomena could then result from *seqcis* ⇄ *seqtrans* isomerization about the C=C bond in the oxygen and nitrogen bonded tautomers. This latter interpretation is improbable, because it requires rotation about the C=C bond to be more facile than a 1, 5 migration of the R_3Si group. In the silyl enol ethers of β-diketones it has been shown that 1, 5 R_3Si group migration is much more facile than *seqcis*-*seqtrans* isomerization.

Using space filling models it is possible to make tentative assignments of some of the pmr lines to specific isomers. The models clearly show that only one isomer, XXV, places the $-Si(CH_3)_3$ group directly over the diamagnetic cone of the phenyl group, thus shifting it well up field of the other silyl methyl lines. This means then that if isomer XXV gives rise to the lines marked A in Figures 13 and 14 then isomer XXVI must be responsible for the lines marked B. The ring current of the phenyl group in isomer XXVII is also responsible for shifting the ligand methyl adjacent to oxygen to higher field and the CH_3-C=NR methyl to lower field relative to the other isomers. Thus, isomer XXVII produces the lines marked C and isomer XXVIII produces the lines marked D in the spectra of Figures 13 and 14. The one area of uncertainty is in the assignment of the C and D silyl methyl lines. The chemical shifts and relative intensities of these lines are too similar to make positive assignments.

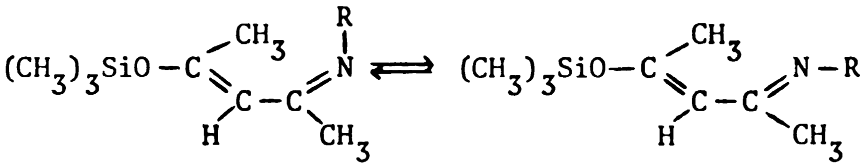
Based on the above pmr line assignments, the lower temperature pmr interchange process is assigned to XXV $\rightleftarrows$ XXVI isomerization and the higher temperature process involves XXVII $\rightleftarrows$ XXVIII interchange:

Lower temperature process



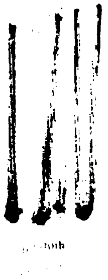
seqcis-syn (XXV) *seqtrans-anti* (XXVI)

Higher temperature process



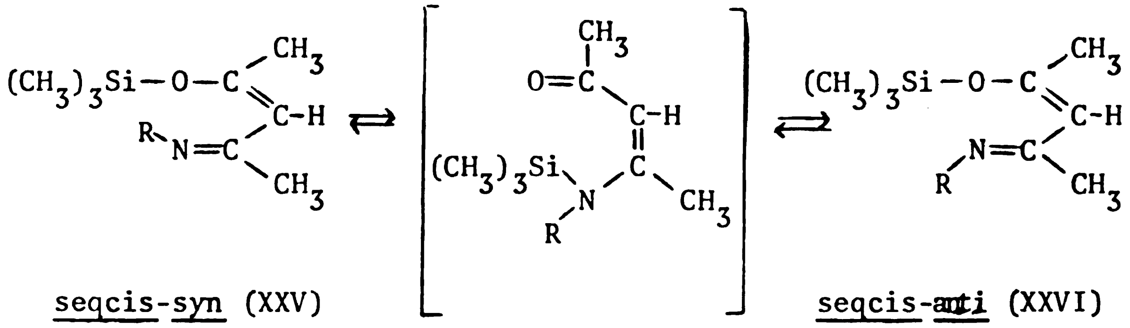
seqtrans-syn (XXVII) *seqtrans-anti* (XXVIII)

The onset of line broadening for the lower temperature process occurs at *ca.* 61°C, whereas for the higher temperature process line broadening begins at *ca.* 92°C. Thus *syn-anti* isomerization is appreciably more facile for the *seqcis* than for the *seqtrans* form. The difference in rates may be due to differences in steric factors. Molecular models


tub

indicate that in the *seqcis* isomers the *syn* conformation should be destabilized by steric factors relative to the *anti* conformation. On the other hand steric factors do not appear to influence the relative stabilities of the *syn*-*anti* conformations in the *seqtrans* form. Thus, whether the mechanism for *syn*-*anti* isomerization involves tortional motion about the C=NR bond or a "lateral shift" analogous to inversion about nitrogen in amines,[79-82] the larger rate for the *seqcis* form could be due to destabilization of the *syn* conformation.

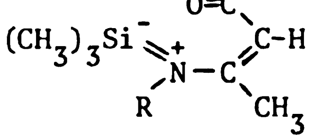
Another possible factor facilitating the *syn*-*anti* interchange in the *seqcis* form is formation of a nitrogen bonded intermediate via a 1, 5 R_3Si group migration:



(15)

seqcis-syn (XXV) *seqcis-anti* (XXVI)

In order for this to be a viable mechanism, the intermediate would have to possess appreciable d_π-p_π Si=N character as illustrated in the resonance form XXIX. This resonance form allows the Si=N-R plane to



XXIX

be perpendicular to the plane of the C=C bond. A 1, 5 migration of the R_3Si group by internalnucleophilic attack of the C=O group would then allow the developing RN=C bond to achieve either a _syn_ or _anti_ configuration.

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APPENDIX

A

Ligand Abbreviations

Abbreviation	Ligand
acac	Acetylacetone
aibm	Acetylisobutyrylmethane
bibm	Benzoylisobutyrylmethane
dibm	Diisobutyrylmethane
dpm	Dipivaloylmethane
pibm	Pivaloylisobutyrylmethane
pvac	Pivaloylacetone
papo	4-Phenylamino-3-pentene-2-one
_m_-capo	4-_m_-Chloroanilino-3-pentene-2-one
_p_-fapo	4-_p_-Fluoroanilino-3-pentene-2-one

APPENDIX

B

Analysis of Multisite Dynamic NMR Spectra

by

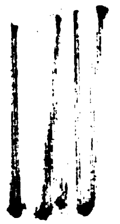
Richard Teets and T. J. Pinnavaia

Anderson-Kubo-Sack Theories

According to the theories of Anderson,[1] Kubo,[2] and Sack,[3] rapid exchange NMR spectra can be calculated in the following manner. Suppose there are N magnetically inequivalent groups which give rise to N lines in a slow exchange NMR spectrum. Let the resonance frequencies and relaxation times for these N groups be designated as W_i and T_{2_i}. Let K_{ij} be the probability per unit time to go from group i to group j. And let K_{ii} be chosen so that

$$\sum_{j=1}^{N} K_{ij} = 0$$

Finally EQ_i is the relative population proportion for group i. This includes both equilibrium concentrations and number of equivalent groups. Suppose, for example, group 1 is a methyl group and group 2 is a methylene group. Then $EQ_1 = 3$ and $EQ_2 = 2$. Suppose further that the isomer containing the methyl group is present at twice the concentration of the isomer containing the methylene group. Then $EQ_1 = 6$ and $EQ_1 = 2$. (Note that for low temperatures, EQ_i will give the relative heights of the N lines in the spectrum). With the definitions given above, the intensity, $I(\omega)$, as a function of frequency, may be calculated by the following equation.



$$I(\omega) = -\text{Real}\left([EQ_1, EQ_2, \ldots EQ_N] \begin{bmatrix} (\omega-\omega_1)i - \frac{1}{T2_1} + K_{11} & K_{12} & & K_{1N} \\ K_{21} & & & K_{2N} \\ K_{31} & & & \\ & & & \\ K_{N1} \cdots & & (\omega-\omega_N)i - \frac{1}{T2_N} + K_{NN} & \end{bmatrix}^{-1} \begin{bmatrix} 1 \\ 1 \\ 1 \\ \cdot \\ \cdot \\ \cdot \\ 1_N \end{bmatrix} \right)$$

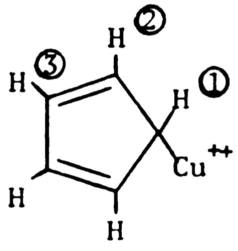
In the above equation, the $i = \sqrt{1-}$ and "Real" means take the real part of the above complex expression.

The above expression may be simplified by the following definitions: Let EQ equal a 1 by N row matrix with elements EQ_J as defined above. Let WR be a diagonal matrix (of order N by N) where the diagonal elements are the W_J defined above. Let T2 be an N by N diagonal matrix with the diagonal elements equal to $1/T2_J$ as defined above. Let K be a matrix with elements equal to the K_{ij} described above. Note that the diagonal elements are fixed so that the rows sum to zero. Finally, let ID be the N by N identity matrix (the diagonal elements are ones) and let [1] be the N by 1 column matrix with each element a 1. With the previous definitions the Intensity can be written as

$$I(\omega) = -\text{Real}\ (EQ\cdot[\omega\cdot ID - WR)i - T2 + K]^{-1}\cdot[1]) \qquad (1)$$

In practice, it is convenient to rewrite K as $(1/\tau)K'$ where K' is the part of the matrix which depends only on the assumed mechanism and τ is a scalar representing the temperature dependence of the rearrangement process. In other words, τ is the mean lifetime before exchange which is temperature dependent.

The above formula can be illustrated by an example due to Whitesides.[4] Consider:



The copper shifts around the ring, thus averaging the signals from the protons in environments 1,2,3. Since environments 2 and 3 have two protons each, while environment 1 has only one proton, the matrix EQ = [1,2,2].

The resonant frequencies for each of the three types of proton environments can be determined from a low temperature spectrum. Call these frequencies $\omega_1,\omega_2,\omega_3$ for groups 1,2, and 3 respectively.

$$\text{Then WR} = \begin{bmatrix} \omega_1 & 0 & 0 \\ 0 & \omega_2 & 0 \\ 0 & 0 & \omega_3 \end{bmatrix}$$

The T2 values were determined from the low temperature line widths. A value of 0.034 seconds was used for each group. So the matrix T2 is

$$T2 = \begin{bmatrix} 1/.034 & 0 & 0 \\ 0 & 1/.034 & 0 \\ 0 & 0 & 1/.034 \end{bmatrix}$$

The kinetic matrix will depend on the mechanism chosen and on the temperature at which the corresponding experimental spectrum was run. Let τ by the mean lifetime before a copper shift. Then $1/\tau$ is the rate of shifting from one environment to another. Now consider a specific mechanism, a 1-3 shift with 1-2 shifts forbidden. Then the probability to go from environment 1 to environment 2 is 0 so $K_{1,2} = 0$. Each time the copper shifts, the environment 1 will go to an environment 3 so $K_{1,3} = 1/\tau$. Since the row must sum to zero, $K_{1,1} = -1/\tau$. Now, half of the time, the copper will shift to one of the "3" environments and the other half of the time, the copper will shift to the other environment. When the 1-3 shift occurs, the other 3 will become a 2. Therefore, $K_{3,2} = 0.5/\tau$ and $K_{3,1} = 0.5/\tau$ so $K_{3,3} = -1/\tau$. Using the same logic we find that

$$K = \begin{bmatrix} 1 & -1/\tau & 0 & 1/\tau \\ 2 & 0 & -0.5/\tau & 0.5/\tau \\ 3 & 0.5/\tau & 0.5/\tau & -1/\tau \end{bmatrix} = 1/\tau \begin{bmatrix} -1 & 0 & 1 \\ 0 & -0.5 & 0.5 \\ 0.5 & 0.5 & -1 \end{bmatrix}$$

Combining all the above matrices according to equation (1) we have:

$$I(\omega) = -\mathrm{Real}\left([1,2,2] \cdot \begin{bmatrix} (\omega-\omega_1)i - \frac{1}{.034} - 1/\tau & 0 & 1/\tau \\ 0 & (\omega-\omega_2)i - \frac{1}{.034} - .5/\tau & 0.5/\tau \\ 0.5/\tau & 0.5/\tau & (\omega-\omega_3)i - \frac{1}{.034} - 1/\tau \end{bmatrix}^{-1} \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} \right)$$

(Note: the above matrix may appear different than that used by Whitesides. The differences is merely one of notation. He used the slightly confusing notations that is indicated on the left below, rather than the more straightforward approach used above and below on the right.)

$$\begin{array}{cc} & \begin{array}{ccc} 2 & 3 & 1 \end{array} \\ \begin{array}{c} 2 \\ 3 \\ 1 \end{array} & \left[\begin{array}{ccc} \quad & \quad & \quad \\ & & \\ & & \end{array}\right] \end{array}$$

Whitesides' matrix

$$\begin{array}{cc} & \begin{array}{ccc} 1 & 2 & 3 \end{array} \\ \begin{array}{c} 1 \\ 2 \\ 3 \end{array} & \left[\begin{array}{ccc} \quad & \quad & \quad \\ & & \\ & & \end{array}\right] \end{array}$$

This paper's matrix

where 1,2,3 indicates nonequivalent environments

Program KINET

Program KINET uses equation (1) to calculate the intensity as a function of frequency. $I(\omega)$ is calculated for evenly spaced frequencies from a specified low frequency to a specified high frequency. These $(I(\omega), \omega)$ pairs are then plotted to give the calculated spectrum. The user must therefore include in his input the parameters in equation (1) plus various plot parameters.

The data must be entered following the format specified in Table 1. In brief, the user must have four sets of data cards. The first set contains only one card, which specifies the low and high frequency limits, the number of $(I(\omega), \omega)$ pairs to calculate, and the number of resonating groups, N. There are N cards in the second card set, one for each group, which specify the resonance frequencies (WR), the equilibrium populations (EQ), and the linewidths which are used to calculate 1/T2 by the relation $1/T2 = \pi \cdot (\text{line width})$. (This assumes a lorentzian line

Table I

Card	Contents and Explanations*	Card Columns
A	Format (12, 2F7.2, 14, F5.2)	
(1 card)	Size of Matrix (N): This is the number of rows in the kinetic matrix. It should be a two place integer less than 20.	1-2
	Low Frequency: This is the frequency which corresponds to the leftmost end of the plot. It is a 7 place decimal number, including the decimal point and an optional + or - sign. Input should be in Hz.	3-9 (Decimal)
	High Frequency: This is the frequency which corresponds to the rightmost end of the plot. Like the low frequency, it is a 7 place decimal number.	10-16 (Decimal)
	Number of calculated points (M): This instructs the computer to calculate the intensity at M evenly spaced frequencies between the low frequency and the high frequency. These M points are then plotted to give the theoretical spectrum. This should be a four place integer less than or equal to 500. Since the computer	17-20 (Integer)

Table I (cont'd.)

Card	Contents and Explanations*	Card Columns
A cont.	calculation time is proportional to the number of calculated points, M should be kept to a minimum, allowing for reasonable resolution on plots.	
	Width of plot in cm: This should be a 5 place decimal number. The maximum width of the plotter is 30 inches so the total width of all plots on one line (including the 1 cm between plots) must be less than 76 cm.	
B	Format (F6.3, 2F7.2)	
(N cards)	Each of the N cards contains the following information for one of the N groups (1 group per card)	
	Equilibrium Population Proportion: This is a 6 place decimal number specifying the relative amount of the group present. It includes both concentration and the number of equivalent absorbing nuclei. This number is only relative to the population of the other groups.	1-6 (Decimal)
	Resonant Frequency: This is a 7 place decimal number specifying the resonant frequency of the group (in Hz)	7-13 (Decimal)

Table I (cont'd.)

Card	Contents and Explanations	Card Columns
B cont.	in the absence of exchange. This may be calculated by extrapolating the chemical shift from the low temperature slow exchange limit into the temperature region of interest. The important thing here is the difference in frequencies between groups. Thus the frequencies entered can be relative to any standard such as TMS. Negative frequencies are therefore acceptable.	
	Line Width: This is the line width at half maximum specified in Hz. It is a 7 place decimal number. This is a relatively uncritical parameter which can be determined from low temperature spectra, and the best fit of the curves to experimental spectra.	14-20 (Decimal)
C	Format (10F8.4)	
2-N Cards	This is the kinetic matrix, not including the mean lifetime parameter (τ)[‡‡] The matrix is read one row per two cards. Each matrix element is read as an 8 place decimal number. After the N elements on the two cards, the rest of the two cards is	1-8, 9-16 17-24 etc. (Decimal)

Table I. (Cont'd.)

Card	Contents and Explanations	Card Columns
C cont.	left blank. Thus a four by four matrix would have 4 numbers on the first half of the first card, the second half of this card would be blank, the second card would be blank, the third card would contain the 4 elements of the second row of the matrix, the fourth card would be blank, and so on. Regardless of the number read in for a diagonal element, the computer will set the diagonal = - (sum of other row elements) so the diagonal may be left blank.	
D	Format (E8.6, F5.2, I1)	
	Tau (τ):	1-8
	This is the mean lifetime before exchange. Each element in the Kinetic Matrix is devided by τ to give the matrix K in equation (1). The value of Tau should decrease with increases in the temperature at which the spectrum was run. Tau is in seconds. This is an 8 place decimal number with an option for a power of ten factor. The number entered must be of the form ± NNN.NNE ± MM. The first part (NNN.NNN)	(Decimal - see text)

Table I (Cont'd.)

Card	Contents and Explanations	Card Columns
D cont.	is multiplied by 10 raised to the ± MM power. Thus 3 x 10^{-4} second could be entered as 0.000300 or as 003.0E-4. The total quantity entered must take 8 spaces, blanks may be used in front of (to the left of the number). If Tau is positive, the computer will proceed to plot the spectrum using the other data read in above. When the plot is finished, the computer will read another value of Tau. If this value is positive, a new plot will be made using this value of Tau and the other data read previously. If Tau is zero (the card is blank) the program will end. If Tau is equal to -1.0, the computer will read in a new set of resonant frequencies (card set B), but use the previous Kinetic matrix. The next card after set B should be a new Tau value. If Tau is -2.0, the computer will read in a new Kinetic matrix (card set C), but not a new set of resonant frequencies. The next card after the matrix should be a new value of Tau.	

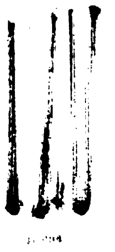


Table I (Cont'd.)

Card	Contents and Explanations	Card Columns
	If Tau is -0.5, the computer will restart completely and read in a new card A, new card set B, new card set C, and then a new value of Tau.	
	Height of Plot in cm: The plot will be scaled so that the highest peak will be the specified height. This should be a 5 place decimal number less than 25 cm.	9-13 (Decimal)
	Plot Option: This controls where the plot is made, with respect to the previous plot. The first plot will be in the lower left corner of the paper. For the rest of the plots, the position of the plot is determined according to the following: Option 0 Start this plot at the left side of the paper, 2cm above the highest previous plot. Option 1 Plot over the previous plot. Option 2 Start plot 1cm to the right of the previous plot. (Make sure that the total length including space between plots is less than 75cm per line.)	14 (Integer)

Table I (Cont'd.)

Card	Contents and Explanations	Card Columns
D cont.	The total height of all plots including the two cm between plots should not exceed about 300cm. Example A-first plot-any option B-second plot-option 2 C-third plot-option 1 D-fourth plot-option 0	

---

*Footnotes for Table I.

1. Blanks are the same as zeros.
2. The entire number including + or - signs (+ sign optional) and the decimal point should fit within the column limits given in Table I.
3. Numbers designated as integers must not contain decimal points. They must be right justified: the rightmost digit should appear in the rightmost column designated for that number. (This is due to the computer interpreting blanks as zeros. For example, the number N on card set A is an integer which occupies columns 1 and 2. If N=3, a 3 should be punched in column 2 and a blank in column 1.)

Table I (Cont'd.)

Card	Contents and Explanations	Card Columns
	4. Numbers designated as decimals should always contain a decimal point.	
	‡‡ Note on Kinetic matrix: the rows of the kinetic matrix should be entered in the same order as the cards for the resonance frequencies.	

shape.)[5] The frequencies and line widths are in Hz. The third card set contains 2 x N cards, 2 for each row of the kinetic matrix K'. The fourth card set contains one card which specifies the mean lifetime before exchange (τ) in seconds. This is used to find $K = 1/\tau\ K'$. After these 4 sets are read in, the computer will plot the spectrum and then read another value of tau.

Dealing with Spin-Spin Coupled Systems

Whenever possible, chemical methods (such as use of deuterium) should be used to avoid spin-spin coupling. However, for loosely coupled systems split into doublets where the resonant frequencies and splitting constants can be accurately determined, the following approach can be used.[6] The spectrum for N doublets each with the same value of J can be thought of as a superposition of 2 identical spectra containing N singlets, but with the two spectra offset by J Hz. Due to second order splitting effects, the upfield spectrum should be multiplied by an empirically determined weighting factor so that the doublets have the correct height relative to each other.

Very minor modifications to the program are necessary to allow treatment of the above case. Instructions for making the changes are given in the comments in the program near statement 410 and statement 379.

Error Messages

Inversion of matrices involves many arithmetical operations which can lead to an accumulation of round-off errors. In certain cases these errors can be significant. The algorithm used for inversion of the matrices should minimize the round-off errors. Also the relatively large word of the CDC 3600 (48 bits) should vertually eliminate the chance of round off errors causing erros in the computed spectra. However, the progrm includes two safety checks. After the printout for each Tau value, there will be a message "ERROR INDEX = ..." and the computer will print a number times a power of ten. This number should be less than about 10^{-8}. (See the section "details of the program" for the actual method of calculating the error index.) Also, every fifth calculated point for the spectrum, the computer calculated another error index. If this error is less than 10^{-7}, nothing is printed, if it is greater than 10^{-7}, the computer will print "Error of .... at Freq. ...." It is not anticipated that any of these messages will be printed.

For each plot, the computer wll print the computer calculation time in missiseconds. This is merely for the sake of curiousity.

The computer may also print "Singular ..." and print a number which will either be 2*N or N+1 where N is the order of the matrix. This means that the matrix does not have an inverse. This error probably indicates that there was an error with the input data. If the input data is correct, then there may be a hidden program error. The program has been tested, and no errors have been found, but it is not possible to guarentee that the program is perfect.

Details of the Program

In an attempt to minimize computation time, the NMR spectrum is calculated in a manner slightly different than implied in equation (1) of the general background. Using the definitions of the general background section let $M = (\omega\cdot ID-WR)i-T2 + K$ so that

$$I(\omega) = -\text{Real}\ [EQ\cdot M^{-1}\cdot [1]]$$

since $MM^{-1} = ID$ it follows that $MM^{-1}[1] = ID[1] = [1]$

Let $AR + (AI)i = M^{-1}[1]$ where AR and AI are both real column matrices.

Then $I(\omega) = -\ \text{Real}\ [EQ \cdot (AR + AIi)] = -\ EQ \cdot AR$

Also $M(AR + AIi) = [1]$

Thus to calculate the intensity, we must merely find AR. Write M out completely, and expanding the product we have:

$$M(AR + AIi) = ((\omega \cdot ID-WR)i - T2 + K)\ (AR + AIi) =$$

$$-(\omega \cdot ID\ WR) \cdot AI + (-T2 + K)AR + i[(\omega \cdot ID-WR) \cdot AR + (-T2 + K) \cdot AI] = [1]$$

Thus $-(\omega \cdot ID-WR) \cdot AI + (-T2 + K)AR = [1]$ (2)

and $(\omega \cdot ID-WR) \cdot AR + (-T2 + K) \cdot AI = 0$ (3)

Solving equation (3) for AI we get $AI = -\ (-T2 + K)^{-1}(\omega \cdot ID-WR)AR$. Putting this value for AI in equation 2 we get

$$[(\omega \cdot ID-WR)(-T2 + K)^{-1}(\omega \cdot ID-WR) + (-T2 + K)]Ar = [1] = B \cdot AR \quad (4)$$

The whole problem resolves down to solving equation (4) for the column matrix AR. Despite the apparent complexity of equation 4 it is easier to use than the formula given in equation (1). The matrices $(-T2 + K)$ and $(-T2 + K)^{-1}$ are constant and need be calculated only once for each spectrum. Since $(\omega \cdot ID-WR)$ is a diagonal matrix the product $(\omega \cdot ID-WR)(-T2 + K)^{-1}(\omega \cdot ID-WR)$ can be formed efficiently. It should be noted that AR can be calculated by triangularizing the matrix B in equation 4, thus the matrix does not have to be completely inverted. Finally, this approach uses only real numbers so that time is not wasted in inefficient complex arithmetic. (Note the difference between taking a real product and a complex product: a-c requires one multiplication while $(a+bi)\cdot(c+di) = (ac-bd) + (bc+ad)i$ requires 4 multiplications and 2 additions.)

The quantity $(-T2 + K)^{-1}$ is found by triangularizing (-T2 + K) and then finishing the inversion. Pivotal condensation is used for all triangularization.[8]

Pivotal condensation is explained by S. D. Conte in Elementary Numerical Analysis, McGraw-Hill Inc. 1965 p. 156-163. Essentially, the idea is to use elementary row operations to transform a matrix into upper triangular form. At each step, the rows are interchanged so that division by small numbers is avoided. Subscripted subscripts were used so that row interchange could be accomplished by merely rearranging the subscript matrix rather than actually recopying the rows.

Since the frequencies in equations 1-4 are in angular units, the input frequencies are multiplied by $2\cdot\pi$ to convert them to angular units. The elements of the T2 matrix are 1/T2 values for each group. These are calculated from the line widths by the formula $1/T2 = \pi\cdot$(line width) which assumes a Lorentzion line shape.[5]

If any of the matrices is singular, the computer will print "singular" and also print a number which will be 2*N if the matrix (-T2 + K) is singular and will be N+1 if the matrix B in equation 4 is singular. It is possible that if (-T2 + K) is singular, the spectrum can be calculated using equation 1 and complex arithmetic. However, I imagine that since these equations represent a physical reality, the matrices will never be singular as long as the line widths are nonzero.

The reliability of the inverse $(-T2 + K)^{-1}$ is tested by taking $(-T2 + K)^{-1}(-T2 + K)-ID = E1$ and $(-T2 + K)(-T2 + K)^{-1}-ID = E2$. The Error Index is the square root of the sum of the squares of each of the elements of D1 and E2. Thus, theoretically, the Error Index should be zero. However, due to an accumulation of round-off errors, it will not be zero. If it is on the order of 10^{-8} or less, there should be nothing to worry about, because experimental approximations involved in the kinetic matrix will probably be much larger than 10^{-8}.

For every fifth calculation of the quantity AR in equation (4), an error index is calculated by finding $E3 = EQ\cdot(B\cdot AR-[1])$.

The error index is found by taking the square root of the sum of the squares of the elements of E3. If this error is greater than 10^{-7}, it is reported, otherwise, it is ignored.

The plotting is done using the MSU SUBROUTINE PLOT which plots X, Y pairs on a calcomp plotter. For the first plot, the pen is moved to the left 30 inches to ensure that it is on the left side of the plotter paper.

References

1. Anderson, P. W., J. Phys. Soc. Japan, 9, 316(1954).

2. Kubo, R., J. Phys. Soc. Japan, 9, 935(1954).

3. Sack, Mol. Phys., 1, 163(1958).

4. Whitesides, G. M. and Fleming, JACS, 89, 2855(1967).

5. Emsley, Feeney, Sutcliffe, High Resolution NMR Spectroscopy, Pergamon Press, 1967, p.30.

6. Holm, Inorg. Chem., 10, 1004(1971) uses this approach on spin-spin coupled tris octahedral chelate.

7. Saunders, M., article in:
   A Ehrenburg, B. G. Malstrom, Mag. Resonance in Bio Systems., Pergamon Press, Oxford, 1967.
   This reference contains a concise overview to computer calculation of NMR spectra. It also includes references to work done on closely coupled systems. These systems require about an hour of computer time per plot. Note that Saunders' matrix which corresponds to my equation 1 has a + sign in front of the 1/T2 values instead of a - sign. All other sources use the - sign.

8. Conte, S. D., Elementary Numerical Analysis, McGraw Hill, 1965, p. 156-163.

9. Gutowsky, H. S., Vold, Wells, J. Chem. Phys., 43, 4107(1965).

```
(JOB,212814,515560,2.0,CLEMENTS,BILL
(FOR,L,X
      PROGRAM KINET
      DIMENSION AK(20,20), AKI(20,20),W(20),EQ(20),T2(20),SK(20,20)
      DIMENSION A(20,40),II(20),ANS(500)
      COMMON N,II,A,TEMP,AMAX,IMAX
      TAU=-0.5
      IFLAG=0
C      READ ORDER OF KINETIC MATRIX, LOW FREQUENCY IN HZ, HIGH FREQUENCY IN HZ,
C      AND SIZE OF PLOT IN CM (LESS THAN ABOUT 75)
523   READ 10,N,WLO ,WHI,M,CM
10    FORMAT(I2,2F7.2,I4,F5.2)
      PRINT 503,N,WLO,WHI,M,CM
503   FORMAT(18H ORDER OF MATRIX= ,I3,4X,15H LOW FREQUENCY=,F8.2,4X,16H
     1HIGH FREQUENCY=,F8.2,4X,15HNO. OF POINTS= ,I5,4X,14HSIZE OF PLOT=
     2,F6.2,/)
C     READ RELATIVE POP. IN THE ABSENCE OF EXCHANGE, RESONANT FREQUENCY, AND
C     LINEWIDTH IN HZ.
522   DO 20 K=1,N
      READ 30,EQ(K),W(K),T2(K)
30     FORMAT(F6.3,2F7.2)
20    PRINT 501,EQ(K),W(K),T2(K)
501   FORMAT(24H POPULATION PROPORTION= ,F7.3,1X,20HRESONANT FREQUENCY=
     1,F8.2,4X,12HLINE WIDTH= ,F8.2)
      IF (TAU+1)521,60,521
521   DO 40 K=1,N
C      READ KINETIC MATRIX ONE ROW PER TWO CARDS
      READ 50,(SK(K,I),I=1,10)
40    READ 50,(SK(K,I),I=11,20)
50    FORMAT(10F8.4)
       PRINT510
510   FORMAT(16H0KINETIC MATRIX=,/)
      IF (N-10)506,506,507
506   DO 508 I=1,N
508   PRINT 509,(SK(I,K),K=1,N)
      GO TO 60
507   DO 512 I=1,N
      PRINT 509,(SK(I,K),K=1,10)
512   PRINT 509,(SK(I,K),K=11,N)
509   FORMAT(10(1X,F9.4))
C     READ A PARAMETER TAU AND THE HEIGHT OF THE PLOT IN CM LESS THAN 25
60    READ 70,TAU,HEIGHT,IOPT
70    FORMAT(E8.6,F5.2,I1)
C     IOPT IS THE PLOT OPTION (SEE END OF PROGRAM)
C    TEST TAU TO DECIDE NEXT STEP
C     IF TAU IS POSITIVE THEN USE IT AS PARAMETER TO CALCULATE LINESHAPE
C     IF TAU IS 0 THEN END.  IF TAU IS -1 THEN READ NEW SET OF RESONANCE FREQ
C     IF TAU IS LESS THAN -1 THEN READ IN A NEW KINETIC MATRIX
C      IF TAU IS BETWEEN 0 AND -1 THEN RESTART COMPLETELY
      IF(TAU)520,94,84
520   IF(TAU+1.0)521,522,523
84    TTIM=0.
      TIMEA=TIMEF(TTIM)
      PRINT 504,TAU,HEIGHT
504   FORMAT(5H0TAU=,E11.4,5X,15HHEIGHT OF PLOT=,F6.2)
      DO 80 I=1,N
      DIG=0.
      DO 808 K=1,N
      AK(I,K)=SK(I,K)/TAU
808   DIG=DIG+AK(I,K)
C     SUBTRACT ANGULAR LINE WIDTH FOR DIAGONAL ELEMENTS
C     ALL CALCULATIONS ARE IN ANGULAR UNITS SO MULTIPLY WIDTH TIMES PI
C     ALSO ENSURE THAT THE ROWS SUM TO ZERO BY ADJUSTING DIAGONAL ELEMENTS
80    AK(I,I)=AK(I,I)-T2(I)*3.14159 -DIG
```

```
C      INVERT REAL PART OF MATRIX BY PIVOTAL CONDENSATION
       DO 11 I=1,N
       DO 21 K=1,N
       A(I,K)=AK(I,K)
21     A(I,K+N)=0.
       A(I,I+N)=1.
11     II(I)=I
C     TO IMPLEMENT PIVOTING, USE MATRIX OF SUBSCRIPTS
C      NOW TRIANGULARIZE MATRIX SO IT CAN BE INVERTED
       CALL TRIANG(2*N)
       NNN=N-1
       DO 52 I=1,NNN
C      NOW FINISH INVERSION
       L=N-I+1
       AMAX=A(II(L),L)
       LLL=N+1
       III=2*N
       DO 32 J=LLL,III
32     A(II(L),J)=A(II(L),J)/AMAX
       LLL=L-1
       DO 52 K=1,LLL
       TEMP=A(II(K),L)
       JJJ=N+1
       KKK=2*N
       DO 52 J=JJJ,KKK
52     A(II(K),J)=A(II(K),J)-TEMP*A(II(L),J)
       AMAX=A(II(1),1)
       JJJ=N+1
       KKK=2*N
       DO 62 J=JJJ,KKK
62     A(II(1),J)=A(II(1),J)/AMAX
C     TRANSFER TO SAFE KEEPING
       DO 12 I=1,N
       DO 12 J=1,N
12     AKI(I,J)=A(II(I),J+N)
       ERRO=0.0
        DO 13 I=1,N
        DO 13 J=1,N
       ERR1=0.0
       ERR2=0.0
       DO 313 K=1,N
       ERR1=ERR1+AK(I,K)*AKI(K,J)
313    ERR2=ERR2+AKI(I,K)*AK(K,J)
       IF(I-J)314,315,314
315    ERR1=ERR1-1.
       ERR2=ERR2-1.
314    ERRO=ERRO+ERR1*ERR1+ERR2*ERR2
13     CONTINUE
       ERRO=SQRT(ERRO)
       PRINT 534,ERRO
534    FORMAT(* ERROR INDEX=*,E11.4)
C      ABOVE WAS CALCULATION OF ERROR INVOLVED IN INVERTING REAL PART
C      OF MATRIX.  THE PROCESS USED WAS TO FIND THE PRODUCT OF AK TIMES AKI
C      AND THE PRODUCT OF AKI TIME AK AND TO COMPARE THEM TO THE IDENTITY MATRIX
C       THE NUMBER OUTPUTTED IS THE SUM OF THE SQUARES OF THE DEVIATIONS OF EACH
C      OF THESE PRODUCTS FROM THE IDENTITY MATRIX.  (ACTUALLY THE SQUARE ROOT
C      OF THIS QUANTITY IS OUTPUTTED)
540    DO  4 K=1,M
C       NOW FIND I(W) FOR  M VALUES OF W
         WI=WLO +((WHI-WLO)*K)/M
       DO 24 I=1,N
       DO 24 J=1,N
24      A(I,J)=AKI(I,J)*(WI-W(I))*(WI-W (J))*39.476089+AK(I,J)
C      39.476089 IS (2PI) SQUARED TO CONVERT TO ANGULAR FREQUENCY
       DO 34 I=1,N
       A(I,N+1)=1.
```

```
34     II(I)=I
       CALL TRIANG(N+1)
C      NOW SOLVE THIS SYSTEM OF SIMULTANEOUS EQ. TO GET THE REAL INTENSITY
       A(N,N+2)=A(II(N),N+1)/A(II(N),N)
C      AFTER TRIANGULATING MATRIX, SOLVE BY BACK SUBSTITUTION
       LLL=N-1
       DO 54KK=1,LLL
       J=N-KK
       TEMP=A(II(J),N+1)
       JJJ=J+1
       DO 64 L=JJJ,N
64     TEMP=TEMP-A(L,N+2)*A(II(J),L)
54     A(J,N+2)=TEMP/A(II(J),J)
       ANS(K)=0.
       DO 704 I=1,N
704    ANS(K)=ANS(K)+(EQ(I)*A(I,N+2))
C      THE FOLLOWING ERROR CHECK IS DONE ON EVERY FIFTH POINT
       IF((K/5)*5-K)552,542, 552
C       NOW CHECK FOR ERRORS BY CALCULATING ERROR=SQRT(EQ*EQ*RESIDUAL*RESIDUAL))/
542    TEMP=0.
       DO 550 I=1,N
       TEMP1=-1.
       DO 551 J=1,N
551    TEMP1=TEMP1+A(J,N+2)*(AKI(I,J)*(WI-W(I))*(WI-W(J))*
      139.476089+AK(I,J))
550    TEMP=TEMP+TEMP1*TEMP1*EQ(I)*EQ(I)
       ERROR= SQRT(TEMP)
       IF(ERROR-.0000001)552,552,553
553    PRINT 555,ERROR, WI
555    FORMAT(11H ERROR OF  ,E11.4,10H AT FREQ. ,F8.2)
552    CONTINUE
4      CONTINUE
       TIMEA=TIMEF(TTIM)-TIMFA
       PRINT 99,TIMEA
99     FORMAT(10H TIME     ,F10.2,/)
       IF(IFLAG)410,411,410
411    CALL PLOT (0.,0.,0,200.,6000.)
C      MOVE THE PEN TO THE FAR LEFT OF THE PAPER
       CALL PLOT (0.,-1.,2)
       IFLAG=1
C      FIRST TIME ONLY SET UPPER BOUND TO 240 WHICH IS SUPPOSED TO BE 120 INCHES
       CALL PLOT(240,0.,3,200.,200.)
       HITSAV=HEIGHT
       WITSAV=CM
       IOPT=1
       XPOS=0.
410    TEMP=0.
       DO 414 K=1,M
       Y=ANS(K)
C      TO DEAL WITH COUPLED SYSTEMS, (BUT NOT CLOSELY COUPLED SYSTEMS),
C      CHANGE THE FOLLOWING COMMENTED INSTRUCTIONS TO REAL INSTRUCTIONS BY
C      REMOVING THE C FROM EACH CARD.  ALSO REDEFINE THE VARIABLES IX AND WEIGHT
C      SO THAT IX=(THE NUMBER OF CALCULATED POINTS BETWEEN DOUBLET PEAKS) AND
C      WEIGHT=(THE RELATIVE SIZE OF THE UPFIELD PEAK)
C      SEE ALSO THE COMMENTS AFTER STATEMENT 379
       IX=34
       WEIGHT=0.89
       IF(K-IX)705,705,706
 706   Y=Y+WEIGHT*ANS(K-IX)
705    IF(TEMP+Y)412,413,413
412    TEMP=-Y
413    CONTINUE
414    CONTINUE
       IF(HEIGHT-25.)416,416,417
417    HEIGHT=25.0
416    YSC=200./(TEMP/(HEIGHT/2.54))
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      XSC=200./(M/(CM/2.54))
C     OPTION 0 IS MOVE PEN UP 2 CM ABOVE PREVIOUS HIGHEST POINT AND TO LEFT
C     MARGIN. THEN PLOT.  OPTION 1 IS PLOT FROM PRESENT POSITION.
C     OPTION 2 IS MOVE PEN 2 CM TO RIGHT OF PREVIOUS PLOT AND PLOT FROM THERE
      CALL PLOT (0.,0.,0,200./2.54,200./2.54)
      IF(IOPT-1)601,602,603
603   XPOS=XPOS+WITSAV+1.
      CALL PLOT(0.,WITSAV+1.,2)
      GO TO 607
601   CALL PLOT(HITSAV+2.,-XPOS,2)
      XPOS=0.
      WITSAV=CM
      GO TO 605
602   IF(WITSAV-CM)607,607,608
607   WITSAV=CM
608   IF(HEIGHT-HITSAV)379,379,605
605   HITSAV=HEIGHT
379   CALL PLOT(0.,0.,0,YSC,XSC)
      Y=-ANS(1)
      CALL PLOT(Y,0.,2)
      X=0.
      DO 7 I=2,M
      Y=-ANS(I)
C     FOR COUPLED SYSTEMS, REMOVE THE C FROM THE FOLLOWING 2 CARDS TO MAKE
C     THEM INTO REAL INSTRUCTIONS
      IF(I-IX)707,707,708
 708  Y=Y-WEIGHT*ANS(I-IX)
707   X=X+1.
      CALL PLOT(Y,X,1)
7      CONTINUE
       CALL PLOT(0.,X,2)
       CALL PLOT(0.,0.,1)
       CALL PLOT(0.,0.,-1)
      GO TO 60
94    CONTINUE
      END
      SUBROUTINE TRIANG(MM)
      DIMENSION A(20,40),II(20)
      COMMON N,II,A,TEMP,AMAX,IMAX
C     SUBROUTINE TO CONVERT MATRIX A AND ITS ASSOCIATED CONSTANT
C     MATRIX TO UPPER TRIANGULAR FORM
       NNN=N-1
      DO 71I=1,NNN
      AMAX=ABS(A(II(I),I))
      IMAX=II(I)
      III=I+1
      DO 41 K=III,N
      TEMP=ABS(A(II(K),I))
      IF(TEMP-AMAX)51,51,61
61     AMAX=TEMP
      II(I)=II(K)
       II(K)=IMAX
       IMAX=II(I)
51    CONTINUE
41    CONTINUE
      AMAX=A(IMAX,I)
      IF(AMAX)81,91,81
C      TEST FOR NONSINGULAR OR SINGULAR
81    LLL=I+1
      DO 71 K=LLL,N
      L=II(K)
      TEMP=A(L,I)/AMAX
      IF(TEMP)101,111,101
C     SKIP IF ALREADY 0
101   IJK=I+1
      DO 121  J=IJK,MM
121    A(L,J)=A(L,J)-TEMP*A(IMAX,J)
111   CONTINUE
71    CONTINUE
C     THIS FINISHESHES TRIANGULARIZATION
      IF(A(II(N),N))131,91,131
 91     PRINT 141,MM
141   FORMAT(10H SINGULAR ,I5)
      STOP
131     CONTINUE
      RETURN
      END
```