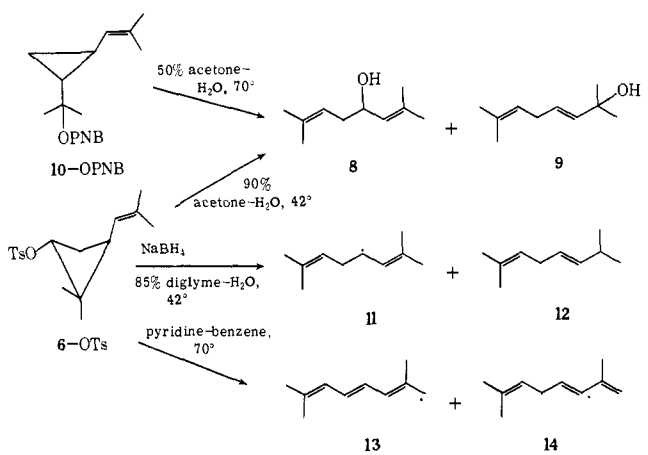
of **1**-OPP[1b,2,3] and the known stereospecificity of cyclopropylcarbinyl rearrangements.[10]

Cycloaddition of dimethylketene (generated *in situ* from dimethylmalonic anhydride)[11] to 4-methyl-1,3-pentadiene at 125° afforded 2,2-dimethyl-3-(2′-methylpropenyl)cyclobutanone (**5**; 60%; ν_{max} 1780 cm^{-1}; δ 5.12 (d, sept, 1 H, J = 1.5, 7 Hz), 1.75, 1.64 (d, 3 H, J = 1.5 Hz), 1.15, 0.99 (s, 3 H)).[12,13] Reduction of **5** with aluminum isopropoxide in isopropyl alcohol gave a 40:60 mixture of **6**-OH (δ 5.13 (d, sept, 1 H, J = 1.5, 7 Hz), ~3.9 (m, 1 H), 1.07, 0.89 (s, 3 H)) and its cis isomer **7**-OH (δ 5.00 (d, sept, 1 H, J = 1.5, 7 Hz), ~3.7 (m, 1 H), 1.04, 0.89 (s, 3 H))[14] which was converted to a mixture of the tosylates since the epimeric alcohols could not be separated.

Hydrolysis of **6**-OTs in 90% acetone–water (sodium acetate buffer) afforded a mixture of the acyclic dienols **8** (27%; δ 5.00 (br t, 2 H, J = 7 Hz), 4.15 (m, 1 H), 2.08 (br t, 2 H, J = 7 Hz), 1.8–1.5 (12 H)) and **9** (55%; δ 5.62 (m, 2 H), 5.03 (br t, 1 H, J = 7 Hz), 2.62 (m, 2 H), 1.71, 1.60 (br s, 3 H), 1.21 (s, 6 H)). The cis tosylate (mp 48–49°) proved to be much less reactive than the trans ($k_{6\text{-OTs}}^{42°}$ = 4.5 × 10^{-4} sec^{-1}, $k_{6\text{-OTs}}^{42°}/k_{7\text{-OTs}}^{42°}$ = 250) as expected[15a] and was efficiently recovered (95%) after complete hydrolysis of **6**-OTs. The same dienol mixture was formed from hydrolysis of the *trans*-cyclopropylcarbinyl ester, **10**-OPNB (mp 64–65°).[16]



(10) (a) K. B. Wiberg and G. Szeimies, *J. Amer. Chem. Soc.*, 92, 571 (1970); (b) Z. Majerski and P. von R. Schleyer, *ibid.*, 93, 665 (1971).

(11) (a) W. E. Hanford and J. C. Sauer, *Org. React.*, 135 (1946); (b) H. Staudinger, *Helv. Chim. Acta*, 8, 306 (1925); (c) H. M. Frey and N. S. Issacs, *J. Chem. Soc. B*, 830 (1970).

(12) H. Bestian and D. Günther, *Angew. Chem., Int. Ed. Engl.*, 2, 608 (1963).

(13) All compounds gave nmr, ir, and mass spectra in accord with the indicated structures; only key data are cited. All new compounds except the unstable tosylates, **6**-OTs and **7**-OTs, gave satisfactory combustion analyses.

(14) The stereochemical assignments are based upon the stereoselectivity of lithium aluminum hydride reduction of **5** (**6**-OH/**7**-OH ~ 1/4),[15a-e] the nmr chemical shifts for C*H*OH in **6**-OH and **7**-OH,[15f] and the greater solvolytic reactivity of **6**-OTs.[15a,c,e]

(15) (a) K. B. Wiberg and G. L. Nelson, *Tetrahedron Lett.*, 4385 (1969); (b) G. M. Lampman, G. D. Hager, and G. L. Couchman, *J. Org. Chem.*, 35, 2398 (1970); (c) C. F. Wilcox, Jr., and R. J. Engen, *Tetrahedron Lett.*, 2759 (1966); (d) R. Huisgen and L. A. Feiler, *Chem. Ber.*, 102, 3391 (1969); (e) I. Lllien and L. Handlosser, *J. Amer. Chem. Soc.*, 93, 1682 (1971); (f) I. Lllien and R. A. Doughty, *ibid.*, 89, 155 (1967).

(16) Alcohol **9**-OH was prepared from ethyl diazoacetate and 4-methyl-1,3-pentadiene ($CuSO_4$, 50°, 2:1 trans:cis esters, 40%) followed by reaction with methylmagnesium iodide and column chromatographic separation of the isomers. The stereochemical assignments are based upon the chemical shift of the vinyl protons as compared to *cis*- and *trans*-chrysanthemol and chrysanthemates (A. F. Bramwell, L. Crombie, P. Hemesley, G. Pattenden, M. Elliott, and N. F. Janes, *Tetrahedron*, 25, 1727 (1969)).

Reductive solvolysis of **6**-OTs in the presence of sodium borohydride (1.6 M)[17] gave, in addition to the dienols **8** and **9** (39%), the two known[18] dienes **11** (34%) and **12** (12%), **7**-OTs again being recovered unchanged. The identity of **11** was established by direct comparison with an independently prepared specimen,[18b] while that of **12** relies upon the correspondence of its nmr spectral data with the literature values.[18a] The acyclic trienes **13** (56%; λ_{max} 281 (57,200); δ 6.3–5.5 (m, 4 H), 1.80, 1.73 (s, 6 H)) and **14** (28%; λ_{max} 233 (21,800); δ 6.2–4.8 (m, 3 H), 4.75 (br s, 2 H), 2.73 (br t, 2 H, J = 7 Hz), 1.77 (t, 3 H, J = 1 Hz), 1.70, 1.60 (br s, 3 H)) were obtained when **6**-OTs was heated in pyridine–benzene,[19] a transformation analogous to phytoene biosynthesis.[5]

The facile ring opening reactions of **6**-OTs and **10**-OPNB indicate that the steps subsequent to formation of cyclobutyl intermediate **3** are inherently favorable. Thus, the overt functions of the enzyme(s) in Scheme I would appear to be chiefly avoidance of the thermodynamically favored ring opening of **1**[7] and maintenance of specificity in the final hydride transfer. We suggest that the former function may be accomplished if the plane of the adjacent double bond of **1**-OPP is fixed within the active site so that the π orbitals are aligned perpendicular to the 1,2-cyclopropane bent bond. Since allylic resonance stabilization of the incipient positive charge would not be possible in this conformation, premature ring opening would be avoided. In this same orientation, the π bonds are aligned parallel to the 2,3-cyclopropane bond and may thus assist the ring scission of **3** to **4**.

Acknowledgment. We are grateful to the National Science Foundation and the National Institutes of Health for financial assistance.

(17) H. M. Bell and H. C. Brown, *J. Amer. Chem. Soc.*, 88, 1473 (1966); Z. Majerski, S. Borčič, and D. E. Sunko, *Tetrahedron*, 25, 301 (1969).

(18) (a) J. E. Baldwin, R. E. Hackler, and D. P. Kelly, *J. Amer. Chem. Soc.*, 90, 4758 (1968); (b) U. T. Bhalerao and H. Rapoport, *ibid.*, 93, 5311 (1971). We are grateful to Professor Rapoport for a copy of the nmr spectrum of 11.

(19) M. Sakai, H. H. Westberg, H. Yamaguchi, and S. Masamune, *ibid.*, 93, 4611 (1971).

(20) A. P. Sloan Foundation Fellow, 1971–1973.

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Model Studies of Terpene Biosynthesis. Cationic Rearrangements Leading to Head-to-Head Terpenes[1]

Sir:

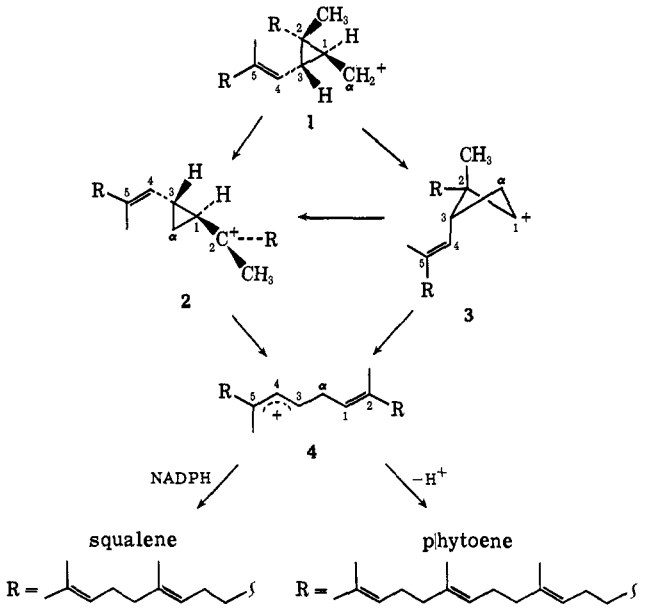
It is now evident that cyclopropylcarbinyl pyrophosphates are key intermediates in the biosyntheses of the symmetric head-to-head terpenes, squalene (C_{30})[2] and

(1) We wish to acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Research Corporation, and the University of Utah Research Fund for support of this work.

(2) (a) H. C. Rilling, C. D. Poulter, W. W. Epstein, and B. Larsen, *J. Amer. Chem. Soc.*, 93, 1783 (1971); (b) L. J. Altman, R. C. Kowerski, and H. C. Rilling, *ibid.*, 93, 1782 (1971); (c) R. M. Coates and W. H. Robinson, *ibid.*, 93, 1785 (1971); (d) J. Edmond, G. Popják, S. M. Wong, and V. P. Williams, *J. Biol. Chem.*, 246, 6254 (1971); (e) R. V. M. Campbell, L. Crombie, and G. Pattenden, *Chem. Commun.*, 218 (1971).

phytoene (C_{40}).[3,4] We,[2a] along with others,[2b,2d,5] have suggested logical mechanisms for the carbon skeletal rearrangements required during the biosynthesis of squalene (Scheme I). Similar proposals suffice to

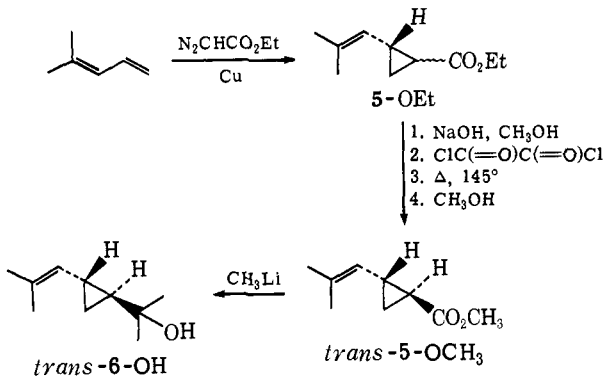
Scheme I



rationalize the formation of phytoene from prephytoene pyrophosphate, where the final step requires elimination of a proton from C_α of allylic cation **4**. Thus far, model studies have shown that, under normal solvolysis conditions, rearrangement of **1** to **2** and **4** is possible[6] but inefficient with respect to cleavage of the C_1–C_3 cyclopropane bond.[4a,4c,6,7] In this communication we report the facile synthesis of head-to-head monoterpenes during solvolysis of appropriate cyclopropylcarbinyl and cyclobutyl precursors of **2** and **3** (R = CH_3).[8,9]

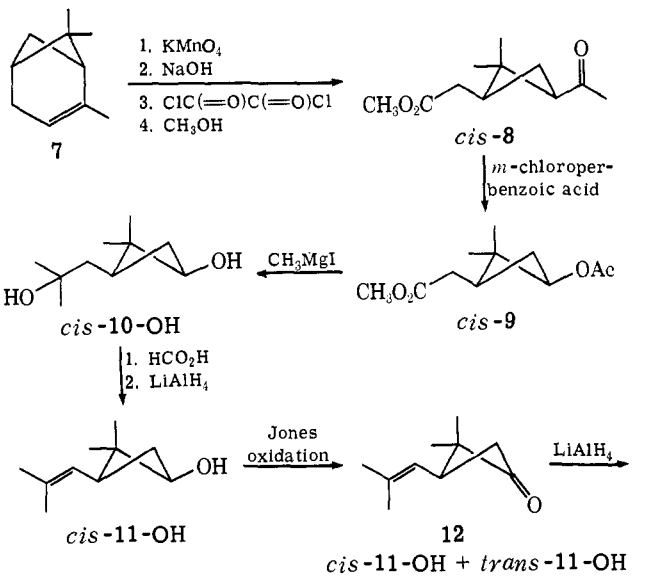
Copper-catalyzed decomposition of ethyl diazoacetate in the presence of 4-methyl-1,3-pentadiene gave an inseparable mixture of *cis*- and *trans*-**5**-OEt (41:59) which was converted to *trans*-**5**-OCH_3 by the procedure of Šmejkal and Farkaš[10] (Scheme II). 2-[*trans*-2′-(2″-

Scheme II



Methylpropenyl)cyclopropyl]propan-2-ol (*trans*-**6**-OH) was obtained by treating *trans*-**5**-OCH_3 with methyllithium. The stereochemistry of *trans*-**6**-OH is consistent with the expected direction of the thermal isomerization[10] and comparisons of chemical shifts for the olefinic protons of *cis*- and *trans*-**6**-OH[11] with those of *cis*- and *trans*-chrysanthemol.[2d,12] *trans*-2,2-Dimethyl-(2′-methylpropenyl)cyclobutanol (*trans*-**11**-OH) was prepared from α-pinene (Scheme III). The cis isomer[13]

Scheme III



was obtained directly; however, hydride reduction of **12** gave an inseparable mixture of *cis*- and *trans*-**11**-OH.

Hydrolysis of *trans*-**6**-OpNB proceeded smoothly in 80% aqueous acetone, $k_{25°} = (4.97 \pm 0.1) \times 10^{-4}$ sec^{-1}. In the presence of a threefold molar excess of 2,6-lutidine, *trans*-**6**-OH[14] (2%) 2,7-dimethyl-2,6-octa-

(3) L. J. Altman, L. Ash, R. C. Kowerski, W. W. Epstein, B. R. Larsen, H. C. Rilling, F. Muscio, and D. E. Gregonis, *J. Amer. Chem. Soc.*, **94**, 3257 (1972).

(4) A similar intermediate may be important in the biosynthesis of non-head-to-tail monoterpenes: (a) C. D. Poulter, S. G. Moesinger, and W. W. Epstein, *Tetrahedron Lett.*, 67 (1972); (b) C. D. Poulter, R. G. Goodfellow, and W. W. Epstein, *ibid.*, 71 (1972); (c) R. B. Bates and S. K. Paknikar, *ibid.*, 1453 (1965).

(5) E. E. van Tamelen and M. A. Schwartz, *J. Amer. Chem. Soc.*, **93**, 1780 (1971).

(6) B. M. Trost, P. Conway, and J. Stanton, *Chem. Commun.*, 1639 (1971).

(7) (a) C. D. Poulter, *J. Amer. Chem. Soc.*, **94**, 5515 (1972); (b) L. Crombie, R. P. Houghton, and D. K. Woods, *Tetrahedron Lett.*, 4553 (1967); (c) R. B. Bates and D. Feld, *ibid.*, 4875 (1967); (d) T. Sasaki, S. Eguchi, M. Ohno, and T. Umemura, *J. Org. Chem.*, **36**, 1968 (1971).

(8) The trans isomers of **6**-OpNB and **11**-OTs were selected because of the known stereospecificity of cyclopropylcarbinyl and cyclobutyl rearrangements in other systems.[2a] A C_{30} cyclobutyl pyrophosphate analogous to **11**-OTs has been proposed as an intermediate in squalene biosynthesis.[2d]

(9) We wish to thank Dr. Coates for informing us of his results of a parallel study prior to publication.

(10) J. Šmejkal and J. Farkaš, *Collect. Czech. Chem. Commun.*, **28**, 481 (1963).

(11) Both isomers were obtained from the mixture of *cis*- and *trans*-**5**-OEt and separated by glpc; *trans*-**6**-OH δ (CCl_4) 0.16–0.84 (3, m, H at $C_{1'}$ and $C_{3'}$), 1.16 (6, s, carbinyl methyls), 1.2–1.6 (1, m, H at $C_{2'}$), 1.6 (1, hydroxyl H), 1.62 (3, d, allylic methyl, J = 2 Hz), 1.67 (3, d, allylic methyl, J = 2 Hz), and 4.50 ppm (1, d of sept, olefinic H, J = 8 Hz); *cis*-**6**-OH δ (CCl_4) 0.37–1.06 (3, m, H at $C_{1'}$ and $C_{3'}$), 1.18 (6, s, carbinyl methyls), 1.14–1.42 (1, m, H at $C_{2'}$), 1.24 (1, hydroxyl H), 1.67 (6, d, allylic methyls, J = 2 Hz), and 5.09 ppm (1, d of sept, olefinic H, J = 8 Hz).

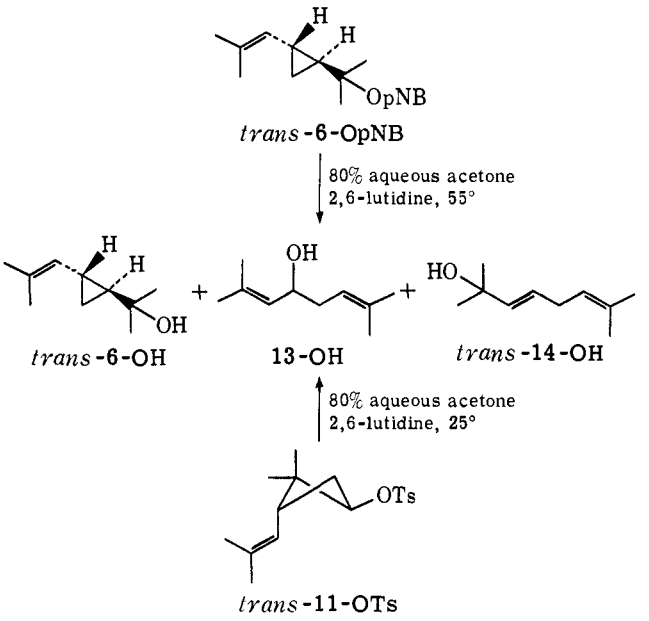
(12) A. F. Bramwell, L. Crombie, P. Hemesley, G. Pattenden, M. Elliott, and N. F. Janes, *Tetrahedron*, **25**, 1727 (1969).

(13) Nmr δ ($CDCl_3$) 0.92 (3, s, methyl at C_2), 1.05 (3, s, methyl at C_2), 1.59 (3, d, allylic methyl, J = 2 Hz), 1.68 (3, d, allylic methyl, J = 2 Hz), 1.8–2.6 (3, m, H at C_3 and C_4), 2.81 (1 hydroxyl H), 3.75 (1, d of d, H at C_1, J = 7, 9 Hz), and 5.03 ppm (1, d of sept, olefinic H, J = 8 Hz).

(14) Tentatively identified by coinjection with an authentic sample; 500-ft Carbowax 20M and 5 ft × 1/8 in. 3% SE-30.

dien-4-ol (**13**-OH) (38%),[15] and *trans*-2,7-dimethyl-3,6-octadien-2-ol (*trans*-**14**-OH)[16] (60%) (Scheme IV) were formed. The allylic alcohols were also obtained in high yield by acid-catalyzed isomerization of *trans*-**6**-OH (80% aqueous dioxane, 8.8×10^{-3} *N* $HClO_4$, 62°). Although *cis*- and *trans*-**11**-OTs were not separated prior to solvolysis,[16a] the kinetics and products of *trans*-**11**-OTs could be obtained because of the large rate differential between the isomers. Hydrolysis of *trans*-**11**-OTs,[17] $k_{25°} = (3.27 \pm 0.01) \times 10^{-4}$ sec^{-1}, afforded *trans*-**6**-OH (1%), **13**-OH (36%), and *trans*-**14**-OH (63%) (Scheme IV).

Scheme IV



It is apparent that *trans*-**6**-OpNB and *trans*-**11**-OTs give products formally derived from **4** in high yield. The partial double bond between C_3 and C_4 in the allylic cation generated during solvolysis must be trans since *trans*-**14**-OH is obtained to the exclusion of its cis isomer. Parallel behavior is found during hydrolysis of chrysanthemyl derivatives where the disubstituted double bond of yomogi alcohol was found to be trans.[4a] The stereochemistry of **4** undoubtedly is a result of ionization of covalent precursors to **1**, **2**, and **3** from conformations in which the 2-methylpropenyl substituents adopt a relatively unhindered orientation and the protons at C_3 and C_4 are trans.[18] Subsequent rearrangements to the less hindered allylic isomer (*trans*-**4**) would be expected. Similar steric considerations may also be important in the enzyme-catalyzed transformations of presqualene and prephytoene pyrophosphates.[19]

The inefficient rearrangement of **1** to **4** under solvolytic conditions stands in contrast to the high yield of squalene obtained from presqualene pyrophosphate in the presence of an enzyme.[2b] We suspect that the head-to-head monoterpenes are the ultimate thermodynamic products of the rearrangement sequence. However, without a detailed knowledge of the kinetic and thermodynamic profiles of each step, we cannot choose among several possibilities by which an enzyme could assist rearrangement to **4**. Studies in this area are now in progress.

(15) Nmr δ (CCl_4) 1.62 (6, d, allylic methyls, J = 2 Hz), 1.67 (6, d, allylic methyls), 1.98 (1, hydroxyl H), 2.08 (2, t, H at C_5, J = 6.5 Hz), 4.12 (1, d of t, H at C_4, $J_{3,4}$ = 8 Hz, $J_{4,5}$ = 6.5 Hz), and 4.8–5.2 ppm (2, m, H at C_3 and C_6).

(16) Nmr δ (CCl_4) 1.22 (6, s, methyls at C_2), 1.63 (6, d, allylic methyls, J = 2 Hz), 2.00 (1, hydroxyl H), 2.59 (2, m, H at C_5), 5.20 (1, t of sept, H at C_6, J = 7.3 Hz), and 5.43 ppm (2, m, H at C_3 and C_4). The assignment of stereochemistry to the disubstituted double bond was based on a strong ir band at 970 cm^{-1}.

(16a) Note Added in Proof. *trans*-11-OTs has now been obtained in >93% purity. The solvolysis results remain unchanged.

(17) *cis*-11-OTs could be recovered from the solvolysis mixture. Hydrolysis of *cis*-11-OTs in 80% aqueous acetone, $k_{50°} = (4.55 \pm 0.04) \times 10^{-5}$ sec^{-1}, gave *trans*-**6**-OH (1%), **13**-OH (59%), and *trans*-**14**-OH (40%). A rearrangement **4** → **2** could account for *trans*-**6**-OH.

(18) The barrier to rotation about the C_3–C_4 bond of **4** should be too high to compete with solvent collapse in aqueous solvents: P. von R. Schleyer, T. M. Su, M. Saunders, and J. C. Rosenfeld, *J. Amer. Chem. Soc.*, **91**, 5174 (1969).

(19) It is also interesting to note that the orientation about the C_α–C_3 bond is important in determining the geometry of the central double bond in phytoene. However, any simple interpretation is complicated by reports of both double bond isomers: G. Britton, "Aspects of Terpenoid Chemistry and Biochemistry," T. W. Goodwin, Ed., Academic Press, New York, N. Y., 1971, p 259.

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(21) Research Corporation Undergraduate Fellow.

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Nonlinear Coordination of NO in $Mo(NO)_2Cl_2(PPh_3)_2$

Sir:

Nitrosyl complexes are presently under intensive study[1] as potentially useful homogenous catalysts in a variety of reactions. Particularly intriguing is the recent report[2] that $Mo(NO)_2Cl_2(PPh_3)_2$ and related species catalyze the disproportionation of internal and α olefins, as well as the intramolecular disproportionation of α,ω-dienes. The "noninnocence" of the nitrosyl group,[3] manifested by its ability to coordinate either linearly as a Lewis base or in a bent fashion as a Lewis acid, is thought to be responsible for its efficacy in catalysis; tautomerism between base and acid behavior converts a coordinately saturated metal to a more reactive unsaturated species without the usual requirement of dissociation of a ligand. Eisenberg, *et al.*,[4] have recently synthesized $Ru(NO)_2Cl(PPh_3)_2{}^+PF_6{}^-$, which contains one linear and one bent (136°) Ru–N–O group.

In seeking an explanation for the efficiency of $Mo(NO)_2Cl_2(PPh_3)_2$ as a catalyst, we have noted infrared evidence suggestive of noninnocent behavior of the nitrosyl ligands. In particular, the large value of $\Delta\nu = \nu_{sym} - \nu_{asym}$ for $Mo(NO)_2Cl_2(PPh_3)_2$, 120 cm^{-1}, is in marked contrast to the values for a variety of *cis*-dicarbonyl complexes.[5] This anomalously large separation of ν_{sym} and ν_{asym} for $Mo(NO)_2Cl_2(PPh_3)_2$ has led others[6] to discard the original assignment[7] of *cis*-

(1) J. P. Collman, N. W. Hoffman, and D. E. Morris, *J. Amer. Chem. Soc.*, **91**, 5659 (1969); S. T. Wilson and J. A. Osborn, *ibid.*, **93**, 3068 (1971).

(2) E. A. Zuech, W. B. Hughes, D. H. Kubicek, and E. T. Kettleman, *ibid.*, **92**, 528, 532 (1970); G. C. Bailey, *Catal. Rev.*, **3**, 37 (1969).

(3) C. K. Jorgensen, "Oxidation Numbers and Oxidation States," Springer-Verlag, New York, N. Y., 1969.

(4) C. G. Pierpont, D. G. Van Derveer, W. Durland, and R. Eisenberg, *J. Amer. Chem. Soc.*, **92**, 4761 (1970).

(5) $\Delta\nu$ values for *cis*-dicarbonyl complexes range from 65 to 80 cm^{-1}: see ref 10 and J. Chatt and H. R. Watson, *J. Chem. Soc.*, 4980 (1961); L. W. Houk and G. R. Dobson, *Inorg. Chem.*, **5**, 2119 (1966); R. Colton and R. H. Farthing, *Aust. J. Chem.*, 1283 (1967).

(6) W. Beck and K. Lottes, *Chem. Ber.*, **98**, 2657 (1965).

(7) F. A. Cotton and B. F. G. Johnson, *Inorg. Chem.*, **3**, 1609 (1964).