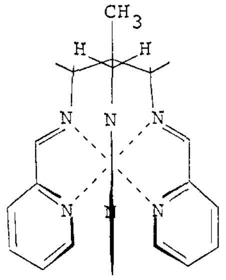
of 4°)[3b] and reflects the greater rigidity of the capping group (a cyclohexane ring) present in py$_3$tach.

If the donors of py$_3$TPN were arranged in a trigonal-prismatic manner, the methylene protons of the capping group would be expected to be equivalent (see II).



II, M(py$_3$TPN)

A distortion from this configuration would lead to a "twist" in the capping group and a resulting nonequivalence of the methylene protons. In the ^{1}H nmr spectrum of [Zn(py$_3$TPN)]$^{2+}$, the methylene protons appear as two signals (τ 5.93 and 5.92, CD$_3$CN solution). For [Fe(py$_3$TPN)]$^{2+}$, the difference in chemical shifts of the methylene signals is larger (τ 6.12 and 6.08) and suggests a greater octahedral twist for this complex. The nmr spectra of the two complexes are different in other respects; the pyridyl protons of the zinc complex give rise to a resonance pattern similar to that observed for many 2-substituted pyridines,[8] whereas the iron complex gives rise to an entirely different pattern, and the position of the resonance arising from the imine proton differs for the complexes (τ 1.42, Fe(II) and 1.06, Zn(II)). These differences may also arise in part from an increased octahedral twist in the iron complex. Such distortion for a low-spin d^6 system has been proposed for [Fe(PccBF)]$^{+}$ [1] and [Fe(py$_3$tach)]$^{2+}$,[3a] and has been found for [Co(dmg)$_3$(BF)$_2$]$^+$.[9]

The absorption envelope for [Ni(py$_3$TPN)]$^{2+}$ (11,230 cm^{-1} (sh), ϵ 21; 12,440 cm^{-1}, ϵ 28) in the 11,000–13,000-cm^{-1} region is similar in position and shape to that found for octahedral tris(α-diimine) complexes.[10,11] However, the extinction coefficients are considerably higher than those generally observed for these octahedral complexes and more closely parallel those found for [Ni(py$_3$tach)]$^{2+}$ (11,100 cm^{-1}, ϵ 27.0; 12,100 cm^{-1}, ϵ 26.6)[12] and [Ni(PccBF)]$^+$ (9430 cm^{-1}, ϵ 28; 11,000 cm^{-1}, ϵ 27).[1] Although the abnormal extinction coefficients reflect the considerable distortion from octahedral geometry for [Ni(py$_3$TPN)]$^{2+}$, the trigonal component of the ligand field is not dominant and trigonal splitting, found for [Ni(py$_3$tach)]$^{2+}$ and [Ni(PccBF)]$^+$, is not observed.

The infrared spectra of the Zn(II), Ni(II), Co(II), and Mn(II) complexes are quite similar and different from that of the Fe(II) complex. An imine stretch, occurring in the 1650–1660-cm^{-1} region for the other complexes, is either absent or has shifted under the pyridine bands for the iron complex; similar behavior has been reported for [M(py$_3$tach)]$^{2+}$ [3a] and has been attributed to rotation about the imine bond to yield octahedral coordination for Fe(II). Differences in the pyridine bands and in the 1200–1400-cm^{-1} region may also be the result of octahedral coordination for [Fe(py$_3$TPN)]$^{2+}$.

In the case of metal complexes of py$_3$TPN, two distinct types of complexes are found. Since the sexadentate ligand py$_3$TPN is less rigid than py$_3$tach and the clathro chelate ligands, it is probable that octahedral coordination is attained for the iron complex, [Fe(py$_3$TPN)] (ClO$_4$)$_2$.

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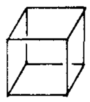
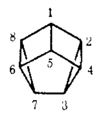
Silver(I)- and Palladium(II)-Catalyzed Isomerizations of Cubane. Synthesis and Characterization of Cuneane

Sir:

We have found that silver(I) and palladium(II) effect quantitative, catalytic isomerization of cubane (**1**) to cuneane (**2**), the parent of an important carbon ring system.[1] Cuneane is the second of the three possible saturated (CH)$_8$ isomers to be synthesized; the first being cubane itself.[2] The rearrangement of cubane to cuneane parallels closely the Ag(I)-catalyzed isomerizations of the homocubyl and 1,1′-bishomocubyl systems reported recently by Dauben[3] and by Paquette.[4]



1



2

Cuneane is a volatile, mobile liquid: fp −1–0°; ir (gas, 10 cm) ν 3056 (s), 1252 (m), 1158 (w), 1044 (w), 927 (m), 883 (w), 845 (w), 804 (m), and 750 (m) cm^{-1}; nmr (CDCl$_3$, 100 MHz) δ 2.7 (2 H, m, H-1,5), 2.3 (2 H, m, H-3,7), 2.1 ppm (4 H, m, H-2,4,6,8).[5] Confirmation of the structure assigned cuneane from its origins comes principally from the ^{13}C nmr spectrum: δ (in parts per million upfield from ^{13}CS$_2$) 152.3 (2 C, d, J = 153 Hz, C-1,5), 161.0 (4 C, d, J = 175 Hz, C-2,4,6,8), 163.2 (2 C, d, J = 162 Hz, C-3,7).[6] Thus, cu-

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(1) Pentacyclo[3.3.0.0^{2,4}.0^{3,7}.0^{6,8}]octane. The name "cuneane" has been adopted for simplicity and is derived from the Latin *cuneus*, a wedge; *cf.*, for example, cuneate, wedge-shaped. Only the octamethyl compound, prepared by way of a diene photoisomerization, has been reported previously [R. Criegee and R. Askani, *Angew. Chem., Int. Ed. Engl.*, 7, 537 (1968)].

(2) P. E. Eaton and T. W. Cole, Jr., *J. Amer. Chem. Soc.*, **86**, 962, 3157 (1964). Cuneane should be ~30–40 kcal/mol less strained than cubane. The as yet unknown third isomer in the set, 2,2′:4,4′-bis(bicyclobutyl), should be intermediate in strain energy.

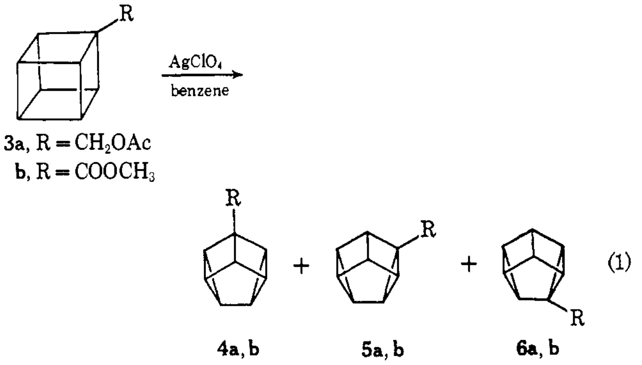
(3) W. G. Dauben, M. G. Buzzolini, C. H. Schallhorn, and D. L. Whalen, *Tetrahedron Lett.*, 787 (1970).

(4) L. A. Paquette and J. C. Stowell, *J. Amer. Chem. Soc.*, **92**, 2584 (1970).

(5) Appropriate analytical and mass spectroscopic data have been obtained.

neane is shown to contain, in the called for ratio, three different types of carbon atoms each bearing a single hydrogen substituent. The observed ^{13}C–H coupling constants are fully appropriate to the assigned structure.

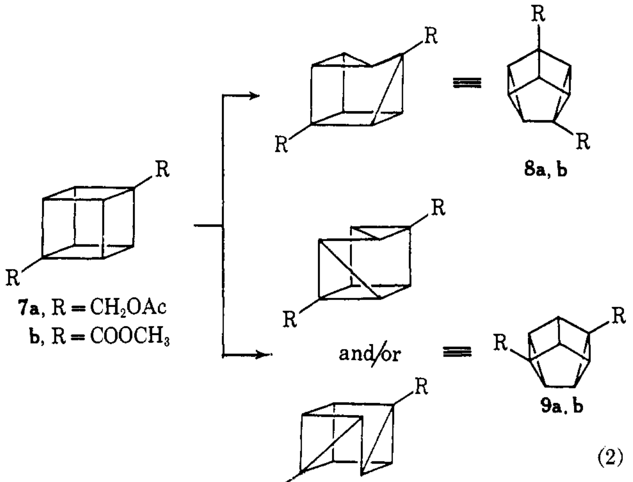
Silver(I)-catalyzed isomerizations of monosubstituted cubanes produce the various possible monosubstituted cuneanes (eq 1).[7] For example, treatment of (acetoxymethyl)cubane (**3a**) with silver perchlorate in benzene at room temperature gives rapidly the cuneanes **4a** [δ 4.33 ppm (2 H, s, −CH_2OAc)], **5a** [δ 4.15, 4.01 ppm (2 H, AB doublet, J = 12 Hz)], and **6a** [δ 4.47 ppm (2 H, s)] in the ratio of approximately 6:2:1, respectively.[8] Similarly, carbomethoxycubane (**3b**) gives the cuneanes **4b** [δ 3.73 (3 H, s, -OCH$_3$), 3.0 (1 H, m, H-5), and 2.5–2.1 ppm (6 H, two multiplets)] and **5b** [δ 3.57 (3 H, s, -OCH$_3$), 3.1–2.6 (4 H, broad, H-1,3,4,5), and 2.5–2.0 (3 H, broad, H-6,7,8)] in the ratio of about 2.5:1; ester **6b** [mp 72–73°; δ 3.68 (3 H, s, -OCH$_3$), 2.9–2.6 (5 H, two multiplets, H-1,2,4,5,7), and 2.3–2.1 ppm (2 H, broad, H-6,8)] is not formed in this reaction, but it has been prepared from **6a**. The assigned structures for these products follow convincingly from the available nmr spectra and chemical interconversion of the a and **b** series.



3a, R = CH$_2$OAc
b, R = COOCH$_3$

4a, b 5a, b 6a, b

If the rearrangements of cubanes to cuneanes proceed in the formal sense *via* the most economic bond-switching path, then isomerization of 1,4-disubstituted cubanes will give rise to only two of the ten possible, nonenantiomeric, disubstituted cuneanes (eq 2). Indeed, silver(I)-catalyzed isomerization of the 1,4-diacetate **7a** gives only (>95%) two products: **8a** [δ 4.50; 4.37 (2 H, AB doublet, J = 12 Hz, -CH_2OAc at C-3), 4.28 (2 H, s, -CH_2OAc at C-1), 2.56 (1 H, m, H-5), 2.45–2.0 (5 H, broad), 2.11 (3 H, s, -CH$_3$CO), and 2.07 ppm (3 H, s, -CH$_3$CO)] and **9a** [δ 4.15, 4.03 (4 H, AB doublet, J = 12 Hz, -CH_2OAc), 2.68 (2 H, m, H-1,5), 2.32 (4 H, m), and 2.03 ppm (6 H, s, -CH$_3$CO)] in the ratio of about 5:1. Similarly, rearrangement of the 1,4-diester **7b** gives in equally high conversion only the two cuneanes **8b** [mp 122–123°; δ 3.74, 3.71 (6 H, two singlets, -OCH$_3$), 3.2–2.8 (4 H, broad, H-2,4,5,7), and 2.6–2.2 ppm (2 H, broad, H-6,8)] and **9b** [mp 116–117°; δ 3.60 (6 H, s, -OCH$_3$) and 3.1 ppm (6 H, m)] in the ratio of about 1:20. The inverse relationship between the major (**8a**, **9b**) and the minor (**8b**, 9a) products from the isomerizations of 7a and **7b** has been established conclusively. Diazomethane esterification of the diacid produced by potassium permanganate oxidation of **8**a in aqueous base gives the dimethyl ester **8b**; acetylation of the diol obtained on lithium aluminum hydride reduction of **9b** gives the diacetate **9**a.



7a, R = CH$_2$OAc
b, R = COOCH$_3$

8a, b

9a, b

Analysis of kinetic measurements made on the AgClO$_4$-catalyzed rearrangements in benzene at 40°, using nmr spectroscopy to follow the reactions, gave the second-order catalytic rate law, $-d[\text{cubane}]/dt = k_{Ag}\cdot[\text{cubane}][\text{AgClO}_4]$. Values of k_{Ag} are listed in Table I.

Table I. Rate Constants at 40° for Silver Perchlorate in Benzene

Cubane	k_{Ag}, M^{-1} sec^{-1}	Relative rate
1	3.0×10^{-1}	17000
3a	2.3×10^{-2}	1300
3b	5.5×10^{-3}	310
7a	1.5×10^{-2}	830
7b	1.8×10^{-5}	1

The isomerizations are fairly sensitive to substituent steric and electronic effects. In general, substituents slow the isomerization; electron-withdrawing groups, the more so. The products from the reactions of both the carbomethoxycubanes **3b** and **7b** can be formulated as arising from bond switching at termini remote from the corner(s) of the cube carrying the electron-withdrawing carbomethoxy group.

The catalytic activity of palladium(II) for the isomerization of cubane to cuneane is similar to that of silver(I). On the other hand, as we reported earlier,[9] rhodium(I) effects instead isomerization of cubane to the *syn*-tricyclooctadiene **10** (eq 3). Appropriately, cuneane is isomerized by Rh$_2$(norbornadiene)$_2$Cl$_2$ to semibullvalene (eq 4).

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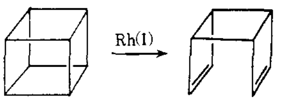
(6) We are grateful to Professor G. L. Closs of this department for making these measurements.

(7) Typical conditions for the isomerization reactions were as follows: 10^{-3}–10^{-2} M AgClO$_4$ in benzene or 10^{-3}–10^{-2} M Pd(benzonitrile)Cl$_2$ in chloroform. The initial cubane concentration was generally 10^{-2}–10^{-1} M.

(8) Interestingly, isomerization of (hydroxymethyl)cubane proceeds about 13 times faster than that of **3a** and gives the parent alcohols corresponding to the (acetoxymethyl)cuneanes **4a**, **5a**, and **6a** in the ratio of ∼1:1:2, respectively. Apparently, the free hydroxyl group can coordinate to Ag(I) and this, in turn, permits close approach of the metal to what is otherwise a sterically shielded area. In line with this picture, inclusion of a small amount of methanol in the reaction medium during the isomerization of (hydroxymethyl)cubane decreases substantially the proportion of reaction proceeding near the substituent; addition of methanol has no effect on the product distribution from isomerization of the acetate **3a**.

(9) L. Cassar, P. E. Eaton, and J. Halpern, *J. Amer. Chem. Soc.*, **92**, 3515 (1970).



(3)

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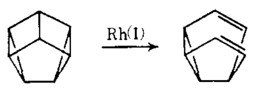

(4)

Our views on the mechanism of the Ag(I)- and Pd(II)-catalyzed rearrangements and on the origin of the difference between the catalytic activity of these metals and that of Rh(I) are still speculative. The fact that Pd(II) ($4d^8$) resembles Ag(I) ($4d^{10}$) rather than the isoelectronic Rh(I) ($4d^8$) in its catalytic properties rules out a simple explanation in terms of a difference of electronic configuration (*i.e.*, d^8 *vs.* d^{10}). A possibly significant distinction is the greater tendency of Rh(I), relative to Ag(I) or Pd(II), to undergo oxidation or oxidative addition. We are continuing to examine mechanistic aspects of these interesting and useful reactions, particularly with a view toward isolation or trapping of intermediates.

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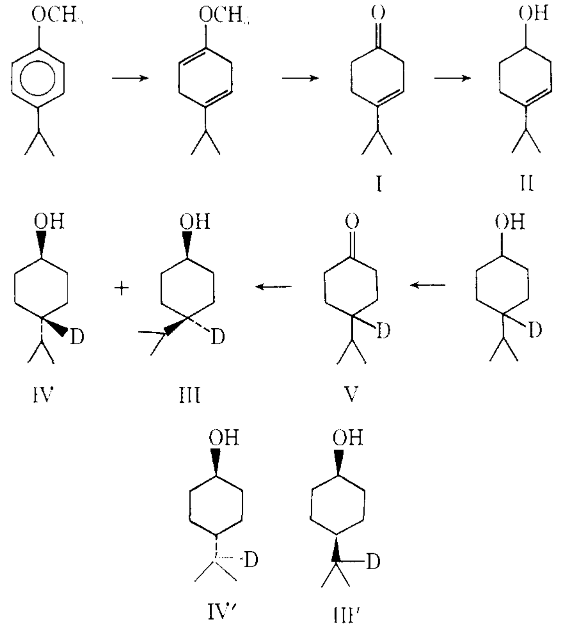
Hidden Stereochemistry in Mass Spectrometry[1,2]

Sir:

Although mass spectrometry has developed into an effective probe of molecular constitution,[3] it has appeared to be an inefficacious technique for stereochemical problems.[4] The fact that this inapplicability derives from the often found apparent whimsical correlation between three-dimensional structure and fragmentation[5] adds special interest to recent investigations of the mass spectrometry of isomeric cyclohexanols. These studies led to the suggestion[5] that stereospecific reactions were hidden in the mass spectra of these compounds even in the absence of apparent rational stereochemical dependence in their fragmentation patterns. We now wish to report that this suggestion is correct, since labeling studies on the loss of water from *cis*- and *trans*-4-isopropylcyclohexanol, molecules which show little stereochemical dependence[5] on their fragmentation, reveal high stereosensibility and specificity for this elimination reaction.

p-Isopropylanisole was converted to 4-isopropyl-3-cyclohexenone by Birch reduction with lithium wire in liquid ammonia.[6] The resulting ketone (I) was shown by gas chromatography to contain no conjugated isomer and was subject to reduction with lithium aluminum hydride to produce the derivative Δ-3 alcohol (II). This material (II) was treated with excess deuterioborane (from boron trifluoride etherate and sodium borodeuteride) followed by refluxing acetic acid. After normal work-up and treatment with lithium aluminum hydride, there resulted a colorless oil which was identical by gas chromatography with an authentic mixture of *cis*- and *trans*-4-isopropylcyclohexanol.[7] These diastereomeric alcohols were oxidized quantitatively by Jones reagent[8] to 4-deuterio-4-isopropylcyclohexanone (V).[9] Reduction of this ketone produced both (III and IV) diastereomeric alcohols in a ratio of 85:15 with *trans*-IV predominating.[10] Vapor-phase chromatog-

Scheme I



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(1) We are grateful to the National Institute of General Medical Sciences for support of this research.

(2) Reported in part at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, Abstract No. ORGN 64.

(3) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967.

(4) The stereochemical potential of mass spectrometry is of high interest, and considerable work on stereoisomers has been reported. See the references in: M. M. Green, *J. Amer. Chem. Soc.*, **90**, 3872 (1968). See also a review by S. Meyerson and A. W. Weitkamp, *Org. Mass Spectrom.*, **1**, 659 (1968). The following recent papers also contain leading references and further stereochemical studies: M. M. Green, R. J. Cook, J. M. Schwab, and R. B. Roy, *J. Amer. Chem. Soc.*, **92**, 3076 (1970); M. L. Gross and C. L. Wilkins, *Tetrahedron Lett.*, 3875 (1969); M. K. Hoffman, M. M. Bursey, and R. E. K. Winter, *J. Amer. Chem. Soc.*, **92**, 727 (1970); S. Meyerson and A. W. Weitkamp, *Org. Mass Spectrom.*, **2**, 603 (1969); V. L. Sadovskaya, V. I. Zaretskii, N. S. Wulfson, and V. F. Sizoy, *ibid.*, **2**, 347 (1969); M. S. Baird and C. B. Reese, *Tetrahedron Lett.*, 2117 (1969); R. Shapiro and S. Nesnow, *J. Org. Chem.*, **34**, 1695 (1969); W. Benz and H. Dürr, *Tetrahedron*, **24**, 6503 (1968); R. M. Dodson, P. J. Cahill, and V. C. Nelson, *Chem. Commun.*, 620 (1968); J. Deutsch and A. Mandelbaum, *J. Amer. Chem. Soc.*, **92**, 4288 (1970).

(5) M. M. Green, R. J. Cook, W. Rayle, E. Walton, and M. F. Grostic, *Chem. Commun.*, 81 (1969).

(6) A. L. Wilds and N. A. Nelson, *J. Amer. Chem. Soc.*, **75**, 5360 (1953).

(7) Prepared from 4-isopropylphenol by hydrogenation followed by conversion to standard ketone derivatives in agreement with literature melting points: H. Erdtman and J. Gripinberg, *Nature (London)*, **161**, 719 (1945).

(8) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 142.

(9) This oxidation and the subsequent reduction served to assure that the isomeric alcohols III and IV were identical with respect to incorporation and position for deuterium. Following heavy precedent we assign the deuterium to C-4. See: D. J. Pasto and F. M. Klein, *J. Org. Chem.*, **33**, 1468 (1968), and references therein.

(10) Stereochemical assignments were based on relative retention times on gas chromatography. See: E. L. Eliel, N. L. Allinger,