87–90°, which proved to be 18β-cyanocleavamine (IX, R = CN; R_2 = CH_2CH_3; 3,4 double bond). The overall yield was 32% based on starting cleavamine. Hydrolysis and esterification of the latter intermediate gave the known[15] 18β-carbomethoxycleavamine (IX, R = $COOCH_3$; R_2 = CH_2CH_3; 3,4 double bond). The transannular cyclization of this compound to provide catharanthine[14] now completes the total synthesis of this alkaloid.

In summary, the above work describes a versatile synthetic pathway to essentially all the indole units necessary for the synthesis of dimeric Vinca alkaloids. Apart from the dimeric systems which are available *via* the chloroindolenine approach mentioned above, the C_{18}-hydroxy derivatives can also provide dimers from the reaction sequence established by Buchi[16] and more recently applied by Harley-Mason.[17] We hope to present results in these various directions in future publications.

Finally, we wish to mention that the syntheses of velbanamine[18,19] and catharanthine[19,20] have also been reported from other laboratories in which completely different routes have been employed.

Acknowledgment. Financial aid from the National Research Council of Canada and the National Cancer Institute of Canada is gratefully acknowledged.

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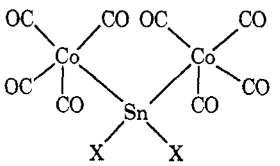
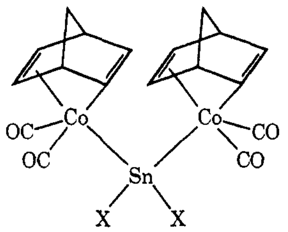
Structure and Activity in a Multicenter π-Complex Reaction

Sir:

We report the isolation and structure of model intermediates in a π-complex multicenter reaction,[1,2] and propose a relationship between the electronic structure and the selectivity of the catalytic species.



Ia, X = Cl Ib, X = Br or I
IIa, X = C_6H_5 IIb, X = CH_3



III, X = Cl
IV, X = C_6H_5

The heterometallic cobalt carbonyls I[3] and II[4] were prepared. These compounds, analogous in structure to catalysts described by Schrauzer and coworkers,[1,2] were also found to catalyze the dimerization of norbornadiene. However, the stereospecificity is markedly sensitive to the substituent X; at 60° Ia gives exclusively the bisnortricyclene known as Binor-S,[1,2,5,6] proved below to be the syn isomer VI, while IIa gives predominantly the exo-trans-exo isomer[2] in addition to three dimers other than Binor-S. From the residues of the respective reaction mixtures we were able to isolate dark-red crystals of the (catalytically active) π-complexes III and IV believed to be intermediates in these reactions.

The structures of III and IV have been determined by X-ray diffraction. Though not isomorphous, both compounds crystallize in space group $P2_1/c$ with four molecules per unit cell. Lattice parameters[7] are: $Cl_2Sn(Co(CO)_2C_7H_8)_2$ (III), a = 18.302 (16), b = 11.838 (13), c = 16.222 (8) Å, β = 143.61 (8)°; and $(C_6H_5)_2Sn(Co(CO)_2C_7H_8)_2$ (IV), a = 9.310 (11), b = 17.279 (27), c = 20.229 (30) Å, and β = 123.06 (5)°. The intensities of 4741 (III) and 2971 (IV) unique reflections were measured on a four-circle diffractometer with Mo Kα radiation. Patterson and Fourier methods were used to solve the structures, and refinement by full-matrix least squares gave conventional R factors of 0.048 (III) and 0.078 (IV) for the 2977 (III) and 1965 (IV) reflections, respectively, above background. Hydrogens were not located; the refinement of III assumed anisotropic thermal motion for all atoms, but for IV the carbon and oxygen atoms were restricted to isotropic temperature factors.

The bond angles at cobalt, essentially identical in III and IV, are those of a distorted trigonal bipyramid, if the C=C bonds are regarded formally as single ligands (Figure 1). Both carbonyls are equatorial, tin is axial, and the norbornadienes, which are π bonded to cobalt through the endo lobes of the C=C bonds, each span one equatorial and one axial site. However, the ‖—Co—‖ angles, which range between 71.3 and 72.8° for the four independent cobalt centers, are substantially less than the 90° of an ideal trigonal bipyramid. This orientation permits the olefin–metal bonds, defined by lines drawn from the cobalts to the midpoints of the associated C=C bonds, to be nearly perpendicular (±3°) to the nodal planes of the olefin moieties.

There are, however, significant structural differences between III and IV. These differences can be explained[4,8] by the second-order hybridization effect proposed by Bent,[9] which predicts concentration of p character from the tin atom in bonds to electronegative substituents and the freeing of s character for the metal–metal bonds; in fact, these structures provide some of the most convincing evidence[8] to date for the importance of this hypothesis in compounds with metal–

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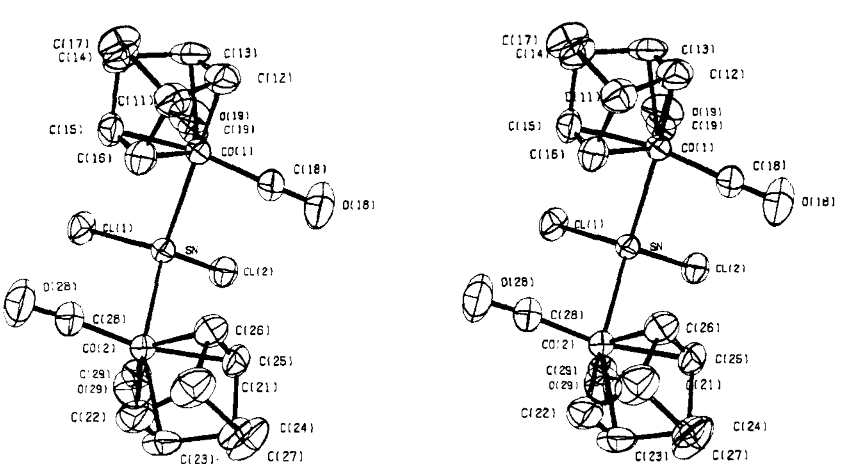


Figure 1. Three-dimensional stereopair view of the dichlorobis(2,3,5,6-*tetrahapto*norbornadienedicarbonylcobalt)tin molecule (III). The ellipsoids represent amplitudes of thermal motion in the crystal at the 50% probability level.

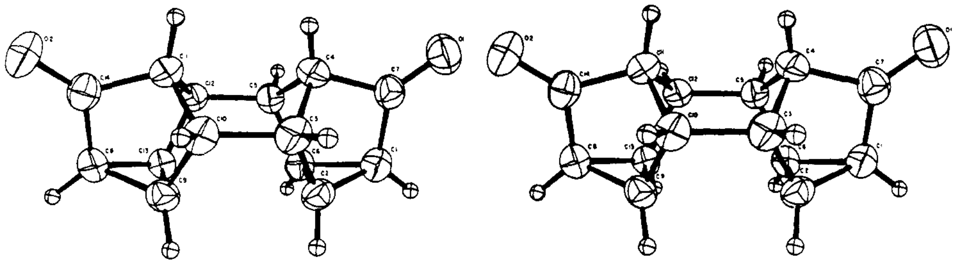
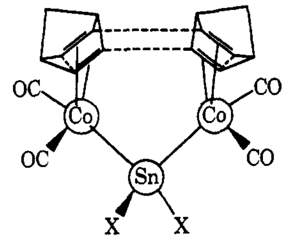


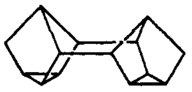
Figure 2. Three-dimensional view of a molecule of decahydro-1,2,4:5,6,8-dimetheno-*s*-indacenedione, the Binor-S dione.

metal bonds. Increased s character in the Sn–Co bonds of III is revealed in the remarkable opening of the Co–Sn–Co angle[7] to 128.3 (1)° *vs.* 118.3 (1)° in IV, a change that cannot be explained by steric factors and which is also believed[4] to occur in the parent compounds Ia and IIa, and is also shown by a shortening of about 0.07 Å in the Sn–Co bonds[7] [2.498 (1) and 2.499 (1) in III *vs.* 2.575 (3) and 2.566 (3) in IV]. Similarly, concentration of p character in the Sn–Cl bonds may account, in part, for their increased lengths, 2.410 (2) and 2.412 (2) Å (compare with 2.31 (1) Å in $SnCl_4$),[10] and for the Cl–Sn–Cl angle of 98.1°, which is slightly less than the C–Sn–C angle of 99.6 (7)° in IV and 11.4° below the tetrahedral angle. The inductive effect of the halogen substituent should increase the $3d \rightarrow 5d$ π interaction between the metals.[4] Since Co d electrons will then be less available for back donation to vacant π^* orbitals of the carbonyl and olefin ligands, we expect longer Co—C distances, shorter C$\equiv$O distances, and consequently higher C$\equiv$O stretching frequencies. All three are clearly observed: the average Co–C bond length to a carbonyl is 1.780 Å in III *vs.* 1.714 Å in IV, the average C$\equiv$O distance in III is 1.142 Å *vs.* 1.184 Å in IV, and the C$\equiv$O stretches shift to higher frequencies in Ia[3] and III (2034 s, 2005 m, 1984 s, 1970 sh) when compared to IIa[4] and IV (2011 s, 1991 s, 1960 s, 1951 sh).

We now consider the relationship of these structural effects to the dramatic changes in catalytic selectivity induced by a varied X substituent. Models show that if the cobalt moieties are in the conformation found in the crystal structures, the alignment of the dienes in the transition state is not favorable for forming Binor-S, even allowing free rotation about the Sn–Co bonds.[11] If we assume, however, that in the transition state both diene double bonds are equatorial with respect to the Sn–Co axis, a suitable geometry for obtaining Binor-S by a concerted mechanism[1,2] is readily constructed.



V



VI

Because an electronegative X substituent, such as Cl in III, can weaken π bonds between Co and its ligands, it may serve to reduce the energy required to attain the Binor-S transition state, V, by labilizing these ligands. In accord with this view, we have observed that replacement of Cl by other electronegative ligands, such as Br or I in Ib, did not alter the selectivity, while the activity of the methyl derivative IIb was similar to the phenyl compound IIa. The observations that Lewis acid cocatalysts promote Binor-S formation, and conversely, that Lewis bases such as pyridine alter the product distribution at the expense of Binor-S,[1,2,6]

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(10) R. L. Livingston and C. N. R. Rao, *J. Chem. Phys.*, **30**, 339 (1959).

(11) The assumption of free rotation[1] appears to be valid, since in solution the nmr spectra[12] show no more than two signals, assigned to axial and equatorial positions, for the olefinic protons in the $-Co(CO)_2-C_7H$ fragments. Also, our observation of four different torsion angles about the four independent Sn–Co bonds in the crystal structures of III and IV suggests that these angles are there determined by packing forces.

may originate similarly through the formation of adducts in which the labilities of the ligands are modified by inductive forces.

Nmr data[12] on conformational changes at cobalt also support this picture. At room temperature only one signal associated with olefinic protons is obtained (τ 5.82 for III and 6.16 for IV). The singlet splits into two equal intensity peaks at $-95°$ for III and at $-30°$ for IV. The coalescence phenomenon can be explained by exchange of the diene double bonds between axial and equatorial sites of the cobalt trigonal bipyramid, which can proceed, at least formally, by a pseudorotation mechanism[13] where the C=C bonds act in turn as pivots. This result, which indicates that coalescence temperatures decrease with increasingly electronegative substituents at Sn, is consistent with our hypothesis that electronegative X substituents promote the lability of the ligands at cobalt.

The syn (C_{2v}) structure of Binor-S proposed by Schrauzer and coworkers[1,2,6] is confirmed by an X-ray structure determination of the dione derivative (Figure 2), which was obtained[14] from the catalytic dimer of 7-*tert*-butoxynorbornadiene and can be converted[14] to Binor-S by Wolff–Kishner reduction. The dione, $C_{14}H_{12}O_2$, crystallizes in space group $P2_1/c$ (a = 7.914 (8), b = 12.932 (11), c = 9.614 (9) Å, β = 100° 16 (2)′, Z = 4). Intensities of 1659 reflections were measured on the Picker diffractometer (Cu Kα radiation). The structure was solved by exploiting the σ_2 relationship, and the atomic parameters, including those of the hydrogens, were refined by least squares to R = 0.049 for the 1550 reflections above background.

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Comments on the Barrier to Internal Rotation in Ethane

Sir:

In a recent communication,[1] an explanation of the barrier to internal rotation about the single bond in ethane was given in terms of the behavior of the two occupied pairs of orbitals of e symmetry during the rotation from the staggered to the eclipsed configuration. Since the quantitative aspects of that calculation were derived from the extended Hückel (EHMO) method,[2] we should like to point out here the implications of two accurate self-consistent-field (SCF) calculations on Lowe's explanation for the source of the barrier.

Such qualitative molecular orbital (MO) arguments as that of Lowe must rest very heavily upon symmetry and upon "all other things being equal." In the case of the ethane barrier, the latter phrase must refer at least to the equality of the bond lengths and bond angles in the two forms. The first successful MO calculation of the ethane barrier[3] employed a minimum basis set of Slater orbitals with the same bond lengths for both staggered and eclipsed ethane. As the first column of Table I shows, this calculation obtained a barrier nearly equal to the observed value and found a pattern of orbital differences almost exactly that given by Lowe's arguments. That is, the $1e_u(1e')$ orbitals gave to the barrier a small negative contribution, which was overshadowed by the much larger positive contribution of the $1e_g(1e'')$ orbitals.

In spite of their success in obtaining a good value for the barrier, Pitzer and Lipscomb[3] took care to point out the inherent limitations of this "fixed geometry" approach. It seems unreasonable to ignore the effects of possible changes in the C–C bond length and in the C–C–H angle during rotation. In fact, a simple force constant calculation[4] in which these parameters were allowed to vary gave a barrier within 10% of the experimental value, although large changes were required in the C–C distance and in the C–C–H angle upon rotation. Also, the hyperconjugation model[5] upon which Lowe's argument is based implies that the C–C bond must elongate on rotation to the eclipsed form. When we view ethane as a pseudobutadiene, we see that the C–C bond should be shorter in the trans (staggered) form than in the cis (eclipsed) configuration because of better hyperconjugation in the former.[6]

A more recent SCF calculation,[7] in which exponents and geometry were optimized for both staggered and eclipsed ethane, shows how essential the implicit hypotheses of fixed bond lengths and angles are to Lowe's conclusions. As the second column of Table I shows, in this calculation *both* pairs of e orbitals give near equal positive contributions to the barrier. Also, the $2a_1$ and $2a_2$ orbitals which Lowe dismisses as unimportant make very large positive and significant negative contributions, respectively. The optimized geometries show the increased C–C bond length and C–C–H angle predicted by the hyperconjugation argument[5] and by the force constant calculation.[4] Thus, the orbital changes discussed by Lowe[1] describe the first of two stages: (1) rotation of rigid methyl groups with C–C distance constant and (2) adjustment of the molecular geometry to the new configuration after rotation. In ethane, effect 2 tends to negate (1) as a simple explanation, but in a case where (1) is indeed dominant, an explanation like Lowe's should be useful in a qualitative sense.

Further evidence for the extremely elusive nature of the source of the ethane barrier is provided by the partitioning analysis of Table I. We see that the

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(6) It is hoped that SCF calculations on *cis*- and *trans*-butadiene now in progress in this laboratory will shed further light on this problem.

(7) R. M. Stevens, *J. Chem. Phys.*, **52**, 1397 (1970).