Transition Metal Catalysis of Symmetry Forbidden Reactions; A Linear Free Energy Correlation

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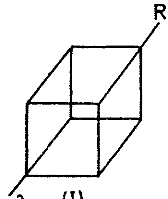
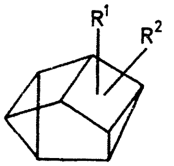
Summary Reported rate constants for the Ag^I catalysed cubane–cuneane rearrangement have been correlated with σ^* constants.

CATALYSIS of thermal, symmetry forbidden, pericyclic reactions by d^8 and d^{10} transition metal ions and complexes is a subject of much current interest.[1a–j] However, systematic investigations of substituent electronic and steric effects are rare, apart from the work of Eaton and his co-workers who report second-order rate constants for silver ion catalysed isomerization of cubane (Ia) and several of its derivatives, (Ib—f), to the corresponding cuneanes, (IIa—f), in benzene solution at 40°.[1j] The uncatalysed reaction which, if concerted, exemplifies a forbidden $[_\sigma 2_a + {_\sigma 2_a}]$ skeletal isomerization, has not yet been reported.



(I)



(II)

	R^1	R^2
a;	H	H
b;	H	CH_2OH
c;	H	CH_2OAc
d;	H	CO_2Me
e;	CH_2OAc	CH_2OAc
f;	CO_2Me	CO_2Me

As part of our study of the mode of metal–σ-bond interaction responsible for catalysis of this and related rearrangements, we have observed a linear free energy relationship between the reported rate constants and the Taft σ^* polar substituent constants. Since substitution in the cubane series was varied exclusively at C-1 and C-4, the correlation is achieved by plotting log *k versus* $\Sigma\sigma^*$ with the summation restricted to those carbon atoms. A more general treatment, designed to accommodate a variety of multiply substituted cubane derivatives, would require that the summation be extended over all eight carbon atoms. Both treatments afford the same ρ^* value for the cubane–cuneane rearrangement. Since we were unaware of a tabulated σ^* value for the acetoxymethyl substituent, this quantity was calculated to be $+1{\cdot}01$ from the reported ionization constant of acetoxyacetic acid (in water at 25°)[2] by application of the Taft equation correlating log K_A values of various carboxylic acids with the appropriate σ^* constants.[3] Least-squares analysis afforded a ρ^* of $-1{\cdot}35$ (correlation coefficient, $-0{\cdot}987$) and a y-intercept of 0·80.

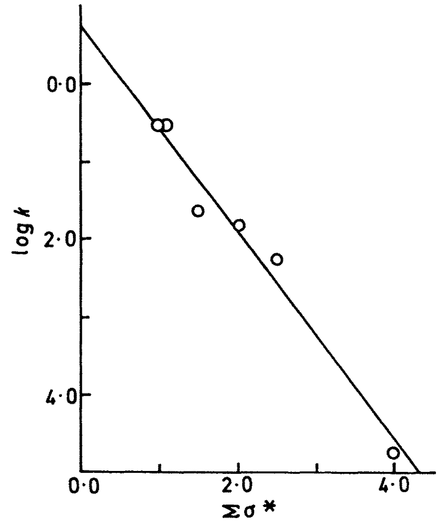


FIGURE. *Isomerization of cubanes to cuneanes in silver perchlorate–benzene solution at* 40°.

From the value of the *y*-intercept, a projected rate constant of 6·3 l mol^{-1} s^{-1} may be calculated for the Ag^{I} catalysed isomerization of 1,4-dimethylcubane which is, therefore, predicted to be 350,000 times more reactive than 1,4-dimethoxycarbonylcubane (If).

The linear correlation is shown in the Figure.†

There has been much speculation concerning the mechanism for metal catalysis of forbidden, pericyclic reactions. It has been suggested that metal–substrate interactions alter orbital symmetry in such fashion that forbidden reactions become allowed.[1b,4a–c] Alternatively, in some instances, the reactions may remain forbidden but the introduction of metal orbitals intermediate in energy between the highest occupied and lowest unoccupied orbitals of the substrate may provide a lower energy pathway for rearrangement.[5] Finally, experimental evidence indicates that some Rh^{I} catalysed reactions may not be concerted but proceed *via* organometallic intermediates formed during rate determining, oxidative addition of the metal to the substrate.[1,6]

Since strained σ-bonds exhibit π-character, it seems reasonable to assume that Ag^{I} catalysis of the cubane–cuneane rearrangement derives from metal–σ-bond interactions analogous to those in silver ion–olefin π-complexes.[7] Electron-withdrawing substituents presumably weaken the "σ-complex" by reducing the capacity of the substrate to function as an electron donor, the diminished interaction being manifested in lowered rate constants for rearrangement. Consistent withth is interpretation is the ability of electron-withdrawing substituents to lower equilibrium constants for complex formation between silver ion and *trans*-3-substituted propenes in water at 25°.[8] Finally, since there are no double bonds in cubane and since C-1 and C-4 are separated by three carbon–carbon single bonds, the relative insignificance of substituent resonance and steric effects is in this case, not surprising.

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† All rate constants were measured by Eaton and his co-workers as discussed in ref. 1j. Although a specific rate constant for (Ib) was not reported, it was stated in a footnote that (Ib) isomerized *ca.* 13 times faster than (Ic). Accordingly, the rate constant for (Ib) was estimated to be $2{\cdot}99 \times 10^{-1}$ l mole^{-1}s^{-1} by multiplying the rate constant of (Ic) by 13.

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