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STEREOCHEMICAL AND RING STRAIN CONSEQUENCES IN THE SILVER(I) ION CATALYZED REARRANGEMENT OF SECO-CUBANE DERIVATIVES[1]

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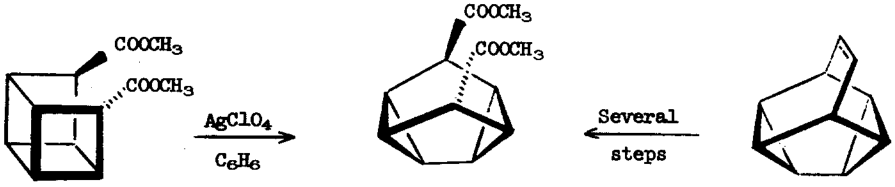
Silver(I) ions are now recognized to catalyze the skeletal bond reorganization of cubyl, homocubyl, and 1,1'-bishomocubyl systems.[3,4] These rearrangements have attracted considerable interest because, in a formal sense, they proceed via thermally disallowed $[_{\sigma}2_a + _{\sigma}2_a]$ pathways. That is to say, excited state behavior (in an orbital symmetry sense) is readily achieved under these conditions. The concerted or stepwise nature of these structural isomerizations remains to be established. Nevertheless, it may be argued that, if the rearrangements proceed in a stepwise fashion, the structural constraints inherent in the above structures do not allow for the incursion of alternative rebonding pathways because of geometrical constraints.

We now describe the Ag^+-catalyzed rearrangement of seco-cubane derivatives, a structural type in which such secondary steric control of reactivity cannot be operative. This study was also particularly concerted with several additional meaningful questions. Initially, it was deemed important to establish whether caged compounds less strained than those previously examined would, in fact, be subject to structural reorganization. Secondly, since the seco-cubane molecule allows for some degree of stereochemical labeling, an analysis of the consequences of the rearrangement at the sp^3-hybridized centers becomes possible. Lastly and perhaps most mechanistically important, the opportunity to evaluate the effect of incremental degrees of ring strain on the rates of rearrangement now presented itself.

Treatment of endo,endo-diester **1**[5] with a solution of anhydrous $AgClO_4$ in dry benzene resulted in quantitative and stereospecific conversion to the endo,endo-tetracyclo$[3.3.0.0^{2,8}$

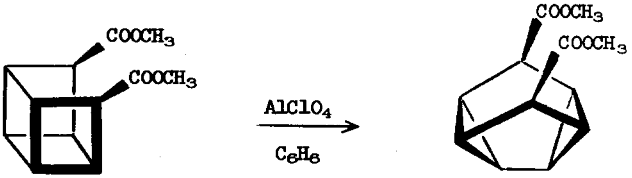
$.0^{4,6}]$octane derivative 2, mp 84-87°; $\delta_{TMS}^{CDCl_3}$ 3.72 (s, 6, $-OCH_3$), 3.17-3.38 (m, 2, $\underline{H}-\overset{|}{\underset{|}{C}}-CO-$),



1 2 3

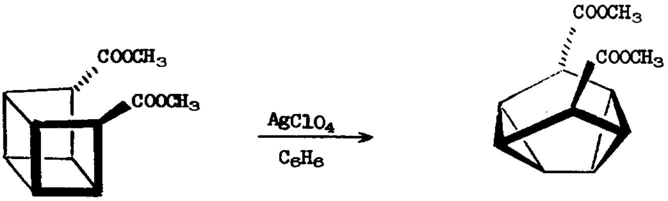
and 1.53-2.13 (m, 6, cyclopropyl). The unmistakable equivalence of the two carbomethoxy groups in 2 and the identity of this diester with the product derived from oxidation and esterification of snoutene (3)[3c,6] serve to confirm the structural assignment.

In like manner, exposure of the related endo,exo isomer (4) to dilute benzene solutions of silver perchlorate led quantitatively to an isomeric liquid shown to be 5; $\delta_{TMS}^{CDCl_3}$ 3.75 and 3.72 (s, 3H each, $-OCH_3$), 3.05-3.27 (m, 2, $\underline{H}-\overset{|}{\underset{|}{C}}-CO-$), and 1.52-2.22 (m, 6, cyclopropyl). The presence of two methoxyl absorptions, together with two α-carbonyl and six cyclopropyl protons, is uniquely consistent with structure 5.



4 5

When 6 was rearranged in this fashion, exo,exo diester 7 was similarly obtained as the sole product, mp 69-72°; $\delta_{TMS}^{CDCl_3}$ 3.75 (s, 6, $-OCH_3$), 2.77 (s, 2, $\underline{H}-\overset{|}{\underset{|}{C}}-CO-$), 2.02-2.27

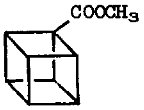
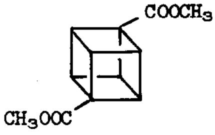


6 7

(m, 2, cyclopropyl), and 1.70-1.92 (m, 4, cyclopropyl). Since each of the three products results exclusively from a *seco*-cubyl precursor of the same stereochemistry, retention of configuration during rearrangement is clearly operative.

Analysis of kinetic measurements performed on the $AgClO_4$-catalyzed rearrangements in anhydrous benzene at 40°, utilizing nmr spectroscopy to follow the reactions, gave the second-order catalytic rate law, $-d[\textit{seco}\text{-cubane}]/d\underline{t} = k_{Ag}[\textit{seco}\text{-cubane}][AgClO_4]$. The values are cited in the table with the rates of two cubyl esters added for comparison.

Table I. Rate Constants at 40° ($AgClO_4$, C_6H_6)

Ester	k_{Ag}, $\underline{M}^{-1}$ sec^{-1}	Relative rate
1	8.0×10^{-5}	4.5
4	4.6×10^{-5}	2.5
6	4.3×10^{-5}	2.4
 8	5.5×10^{-3} [a]	310
 9	1.8×10^{-5} [a]	1

[a] Reference 4c.

Examination of molecular models reveals that substantial steric decompression of the two *endo* substituents occurs during the *seco*-cubane to *seco*-cuneane rearrangement. This steric strain relief is *not* reflected in the rate of rearrangement of 1. In actuality, the three *seco*-cubyl esters and the more strained 1,4-dicarbomethoxycubane (9) all rearrange at comparable rates. We interpret this insensitivity to inherent molecular destabilization to mean that a concerted rearrangement is not operative. Clearly, if alleviation of strain were operative at the individual transition states for these very similar reactions, the rate sequence would be 9 > 1 > 4 > 6, but this is not observed. Rather, the rate-determining step is probably the result of Ag^+-induced rupture of a C-C bond on the cubic surface. According to this mechanism, rate accelerations should be dependent upon the greater availability of electron density at the site of bond cleavage. In accordance with this proposal, the rate constants for Ag^+-induced rearrangement of cubane, 8, and 9 are 17,000:310:1, respectively.[4c] The far greater influence exerted by electronic effects appears reconcilable at this time only with a stepwise mechanism. We plan to elaborate on this point in the future.

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