

## Ag<sup>+</sup>-catalysed Rearrangements of Seco-cubane Derivatives

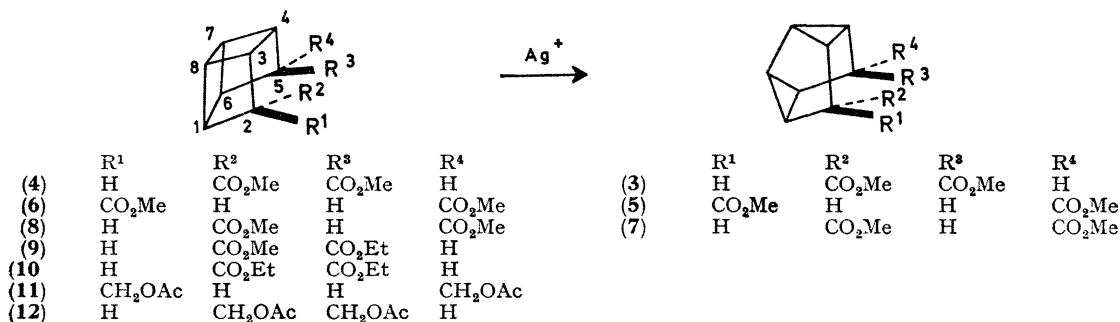
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**Summary** Seco-cubane derivatives are shown to be readily converted into tetracyclo[3,3,0,0,2,8,0<sup>4</sup>,6]octanes on treatment with the silver(I) ion.

METAL-CATALYSED reactions of organic molecules have been receiving current interest.<sup>1-5</sup> We have studied the effect of substituents and ring strain on these reactions and also their stereochemical course using as organic substrates several stereoisomeric seco-cubane derivatives<sup>6</sup> which are readily

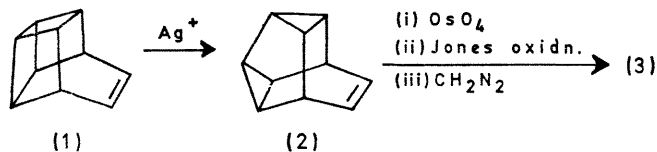
be identical with the product obtained from the isomerization of dimethyl seco-cubane-*endo-endo*-dicarboxylate (4) in the presence of AgBF<sub>4</sub>. The methoxycarbonyl groups of (3) must be oriented *endo-endo*.<sup>6</sup> The product (5) obtained from the *exo-exo* isomer (6) of (4) showed the equivalence of the two methoxycarbonyl groups, whereas the product (7) from the *exo-endo* isomer (8) the non-equivalence. Therefore, we assign to (5) and (7) *exo-exo* and *exo-endo* configuration. Relevant physical data are:



obtainable from basketene (1).<sup>7</sup> We report the structures of products obtained by Ag<sup>+</sup>-catalysed isomerization of these compounds and further correlate the rate of this reaction with the electronic and steric properties of the starting material.

All the seco-cubane derivatives used in this investigation were isomerized quantitatively with AgBF<sub>4</sub>† either in chloroform or acetone at room temperature or 50° to provide tetracyclo[3,3,0,0,2,8,0<sup>4</sup>,6]octane derivatives, a single isomer being obtained in each case. Compound (2)<sup>2,3</sup> was treated with OsO<sub>4</sub> to afford the corresponding dihydroxy-compound, m.p. 124—126°, which in turn was converted into a dicarboxylic acid with an excess of Jones' reagent. The dimethyl ester (3) of this carboxylic acid was shown to

(3), m.p. 84—86° n.m.r.  $\tau$  6.35 (s, 6H), 6.80 (m, 2H), 8.0—8.5 (m, 6H); (5), m.p. 69—71°, n.m.r.  $\tau$  6.30 (s, 6H), 7.28 (s, 2H), 7.95 (m, 2H), 8.25 (m, 4H); (7), b.p. 50°(0.05 mmHg), n.m.r.  $\tau$  6.25 (s, 3H), 6.30 (s, 3H), 6.88 (t, 1H), 6.95 (s, 1H), 8.05 (m, 2H), 8.25 (m, 4H). The stereochemistry of the functional groups of (4), (6), and (8) was maintained during the skeletal rearrangement.



† In the absence of AgBF<sub>4</sub>, these compounds remain unchanged under the described reaction conditions.

Kinetic measurements of the isomerization of the above esters and a few other simple derivatives were performed at  $48.8 \pm 0.10^\circ$  using deuterioacetone as solvent. The concentration range of  $\text{Ag}^+$  and organic substrates was 0.13—0.04 M and 0.4—0.2 M, respectively, and the n.m.r. spectra were taken below  $0^\circ$ . In the cases examined the rate of rearrangement varied directly with the initial  $\text{Ag}^+$  concentration, being given by the expression  $-\text{d}[\text{seco-cubane derivative}]/\text{d}t = k[\text{seco-cubane derivative}][\text{AgBF}_4]_0$ . The results are summarized in the Table.

Compound	$k$ ( $\text{M}^{-1}\text{s}^{-1} \times 10^{-4}$ )	$k_{\text{rel}}$
(4)	2.6	1
(6)	2.5	
(9)	2.3	
(10)	4.7	1.8
(11)	7.7	3.0
(12)	65	25

From our experiments it is evident that the seco-cubyl substrates behave in a manner analogous to homocubyl<sup>3</sup> and 1,1'-bishomocubyl<sup>2,3</sup> derivatives when treated with  $\text{Ag}^+$ . Thus, bridging between positions 2 and 5 is not a

prerequisite for reaction. Since stereochemical integrity is maintained throughout, the bonds (C-1-C-2, C-2-C-3, C-4-C-5, C-5-C-6) immediately adjacent to the substituents are probably not directly involved in the rearrangement. This hypothesis is further supported by the relatively small differences in the observed rate constant on changing substituents at the 2 and 5 positions [*i.e.*, compounds (6) and (11)]. Although the differences are quite small, increasing the strain within the seco-cubyl part of the system does appear to speed up the rearrangement. Thus, compound (12) which possesses more severe *endo-endo* substituent interactions than (11) rearranges about three times faster. A similar trend is observed with (4) and (10). A change from methoxycarbonyl groups as in (6) to the less electron-withdrawing acetoxymethylene substituents as in (11) causes a moderate increase in the rate of reaction.

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