E1cB mechanism. The catalytic constants are 60 M^{-1} s^{-1} for ethoxide ion and 3.3×10^{-4} M^{-1} s^{-1} for acetate ion, assuming $pK_w = 16.94$. The only irregularity in the plots of k vs. buffer concentration, occurring at pcH 10.35, cannot yet be construed as evidence for the E1cB mechanism.

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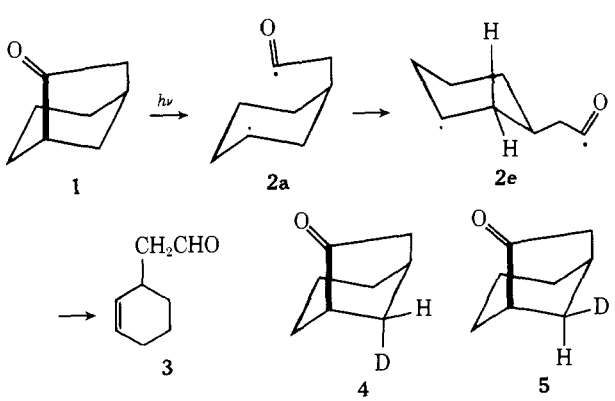
Received April 8, 1976

Stereoselectivity of Hydrogen Transfer in the Photochemical Isomerization of Bicyclo[3.2.1]octan-6-one. Evidence for a Stereoelectronic Effect

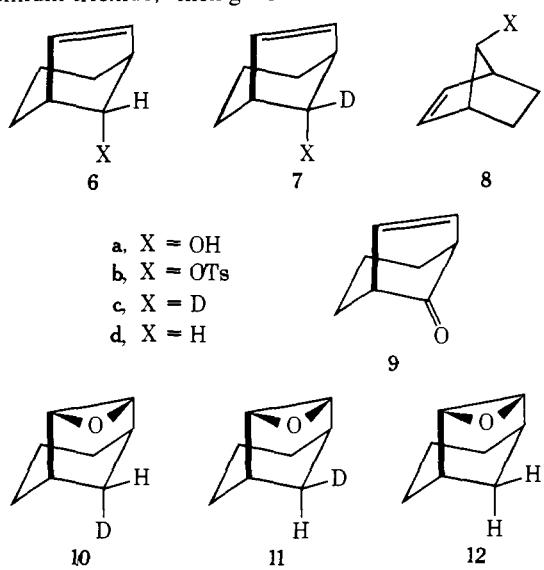
Sir:

Photochemical isomerization of bicyclo[3.2.1]octan-6-one (**1**) yields 2-cyclohexene-1-acetaldehyde (**3**, 93%) with <0.5% of any other volatile product, and there is good evidence that this involves α-cleavage to biradical **2a**, inversion to equatorially substituted **2e**, and finally disproportionation to **3**.[1] In **2e** both an axial and an equatorial hydrogen atom are accessible for transfer to the side chain, and there is the possibility of stereoselectivity in this process. We describe here preparation and photolysis of deuterated ketones **4** and **5**, and report results which answer this stereochemical problem. More importantly, these results furnish evidence of stereoelectronic control in the homolytic cleavage of a carbon-hydrogen bond adjacent to a radical center, and thus touch upon a matter of general theoretical and mechanistic interest.



1 2a 2e 3 4 5

Starting material for synthesis of **4** and **5** was alcohol **6a**, which was prepared as previously described.[2] The derived tosylate **6b** undergoes solvolysis with retention of configuration due to participation of the double bond,[2] and this fact permitted us to introduce deuterium stereospecifically. The reaction conditions employed were those developed for trapping of carbonium ions with sodium borohydride[3] and previously used in conversion of *anti*-7-norbornenyl tosylate (**8b**) to norbornene-*anti*-7-*d* (**8c**).[4] Thus **6b** reacted with excess sodium borodeuteride in 65% diglyme–35% D_2O containing NaOD at 50° to furnish labeled olefin **6c**. In order to introduce deuterium into the epimeric position alcohol **6a** was oxidized to ketone **9**[2] using chromium trioxide–pyridine complex[5] and then reduced back with lithium aluminum deuteride at −78° to form **7a**. The reduction was stereospecific, and only alcohol **7a** (or **6a** with lithium aluminum hydride as reducing agent) was obtained.[6] The derived tosylate **7b** was now reduced as above, but with sodium borohydride, to furnish labeled olefin **7d**. Similar treatment of tosylate **6b** with sodium borohydride gave unlabeled bicyclooctene **6d**, previously prepared by other routes.[7] The deuterium content of the olefins was determined by mass spectrometry to be 92% d_1, 8% d_0 for **6c**, and 98% d_1, 2% d_0 for **7d**; this result is taken into account in subsequent calculations. The stereospecificity of deuteration was verified through NMR measurements on derived epoxides **10** and **11**. These compounds, along with **12**, were available upon oxidation of the olefins with *m*-chloroperbenzoic acid. In **12** the signal for the axial proton at C(8), anti to the epoxide ring, is shifted upfield to δ 0.92 ppm, and may be integrated without difficulty.[8] Integration of the spectra of **10** and **11** therefore permitted determination of the stereospecificity of deuteration at C(8); in each case there was no evidence of scrambling, and within experimental error the labeling of **6c** and **7d** is stereospecific. Hydroboration and peroxide oxidation[9] of these olefins, followed by treatment of the intermediate alcohols with chromium trioxide,[5] then gave deuterated ketones **4** and **5**.



6 7 8 9 10 11 12

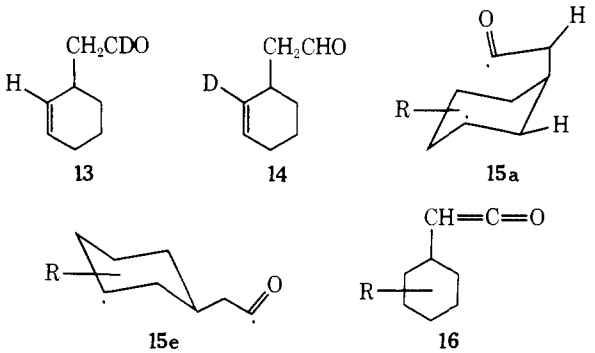
These ketones were irradiated in benzene containing 3% methanol at 30 ± 0.5° and the aldehyde formed was isolated, all as previously described.[1] In each case the aldehyde was a mixture of deuterated species **13** and **14** which could be analyzed by integration of NMR spectra. The results are in Table I, along with the corresponding ratios of the rates of transfer of axial and equatorial hydrogen. These ratios reflect both the inherent stereoselectivity and the deuterium kinetic isotope effect in disproportionation. The magnitude of each of these factors can be calculated from the ratios using the simple formalism of Curtin,[10] with the assumptions that only these two factors are operative, and that the isotope effects for

Table I. Products of Photolysis of Ketones **4** and **5**

Ketone	% aldehyde formed **13**	**14**	k_{ax}/k_{eq}
4	2	90	45
5	88	10	8.8

transfer of axial and equatorial hydrogen in **2e** are identical. This calculation leads to an isotope effect (k_H/k_D) of ~2[11] and an inherent stereoselectivity of ~20:1 favoring transfer of axial hydrogen in intermediate **2e**.

The calculated isotope effect is unexceptional. Quantitative data on intermolecular gas phase radical disproportionations suggest a value of ~1.5,[12] and qualitative agreement comes from observation of small isotope effects in intramolecular disproportionations in solution.[13] The calculated stereoselectivity indicates that in disproportionation of **2e** axial hydrogen is transferred ~95% of the time. In part this selectivity may be steric in origin; although the acyl radical can approach the axial and equatorial hydrogens equally closely, there may well be small energy differences in the favorable geometry for each transfer. We suggest, however, that the most important factor leading to the observed selectivity is stereoelectronic control arising from interaction of the bond being broken with the adjacent p orbital of the unpaired electron. Several investigations indicate that, in homolytic cleavage of a carbon-carbon bond adjacent to a radical center, the bond preferentially broken is the one lying closest to the plane of the p-orbital bearing free spin.[14] Such a requirement applied to cleavage of a carbon-hydrogen bond adjacent to a radical center would lead to preferential transfer of axial hydrogen in **2e**. Stereoelectronic control in radical fragmentations and in the reverse addition of radicals to olefins has been discussed for several years,[14,15] but to our knowledge there is no prior experimental evidence implicating such control in a hydrogen transfer reaction.



We previously showed that in photolysis of substituted bicyclo[3.2.1]octan-6-ones for which **15a** and not **15e** is the stable conformer of the biradical, all disproportionation occurs from **15a** and leads preferentially to ketene **16** through hydrogen transfer from side chain to ring.[1] We established the importance of steric factors in this preferential formation of ketene rather than aldehyde from **15a** and suggested that a stereoelectronic effect might also operate here.[1] The present findings support this suggestion. Disproportionation of **15a** to form aldehyde necessarily involves transfer of equatorial hydrogen to the side chain, and this transfer cannot conform to the stereoelectronic requirement discussed above.[16]

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(16) This research was supported by The National Science Foundation through Grant MPS74-21436.

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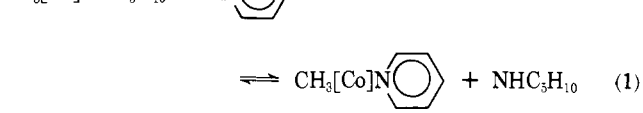
Received March 15, 1976

Kinetic Ambiguity between the I_d and D Mechanisms in Ligand Substitution Reactions. The Intimate Mechanism for Axial Base–Ligand Exchange Reactions in Alkyl(base)cobaloximes and Related Species

Sir:

Recently Jensen and Kiskis have proposed a kinetic differentiation between I_d and D mechanisms for axial base-ligand exchange in alkyl(base)cobaloximes in noncoordinating solvents.[1] These workers concluded that this exchange (eq 1) occurs via a purely dissociative (D) process.



(1)

The proposed mechanism for a dissociative interchange (I_d) ligand substitution proceeding to completion is given below (eq 2, 3, and 4).[2]

$$M(L)_nA + B \overset{K_1}{\rightleftharpoons} M(L)_nA \cdot B \text{ (rapid)} \quad (2)$$

$$M(L)_nA \cdot B \xrightarrow{k_2} M(L)_nB \cdot A \quad (3)$$

$$M(L)_nB \cdot A \xrightarrow{\text{fast}} M(L)_nB + A \quad (4)$$

The rate constant expressions (eq 5 and 6)[3] are:

$$k_{obsd} = \frac{k_2K_1[B]}{1 + K_1[B]} \quad (5)$$

$$\frac{1}{k_{obsd}} = \frac{1}{k_2} + \frac{1}{k_2K_1[B]} \quad (6)$$

On the other hand a purely dissociative (D) mechanism (eq 7 and 8) obeys the rate constant expressions given by eq 9 and 10.[2]

$$M(L)_nA \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M(L)_n + A \quad (7)$$

$$M(L)_n + B \xrightarrow{k_2} M(L)_nB \text{ (rapid)} \quad (8)$$

$$k_{obsd} = \frac{k_1k_2[B]}{k_{-1}[A] + k_2[B]} \quad (9)$$

$$\frac{1}{k_{obsd}} = \frac{1}{k_1} + \frac{k_1[A]}{k_1k_2[B]} \quad (10)$$