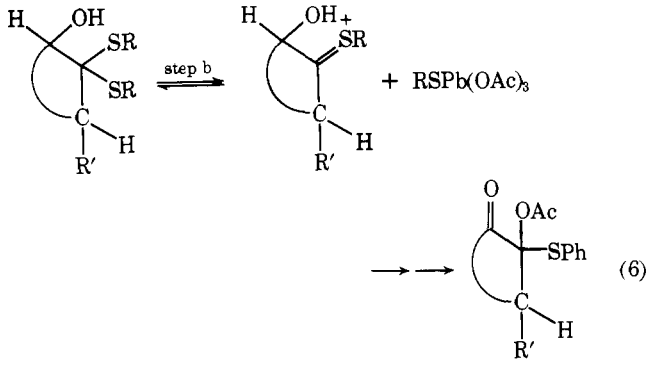

to serve its normal useful role as a key group for structural elaboration by addition of nucleophiles. (3) It selectively sulfenylates (oxidizes) C(3) of the original cycloalkanone. Sulfenylated carbonyl systems have proved to be versatile directing groups for structural elaboration.[3,6a,11] (4) It selectively dehydrogenates C(3)-C(4) of the original ketone. Thus, this method allows selective oxidation at C(1) and C(2), or C(1), C(2), and C(3), or C(1), C(2), C(3), and C(4). The structural flexibility provided by this new ring cleavage reaction should prove useful in synthetic elaborations.

Acknowledgment. We wish to thank the National Science Foundation and the National Institutes of Health for their generous support of our programs.

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(8) (a) Addition of methyllithium to the dithianes derived from cyclononanone and cyclododecanone led to recovered starting material—presumably because of enolization. (b) In the cyclononanone case, reduction of the keto dithiane with diisobutylaluminum hydride ($PhCH_3$, −78°, 90% yield) was preferred.
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Acid–Base Catalysis and Autocatalysis of a Dehydrochlorination

Sir:

Interest in the concertedness of base-catalyzed elimination reactions continues to be very strong.[1] The dependence of rate on pH and base concentration in buffer solutions is an essential criterion for multistep mechanisms, though more thorough comparison of compounds and standardization of the properties of the non-aqueous buffers are needed than our single published example furnishes.[2] Investigating the elimination of HCl from β-chloro-β-phenylpropiophenone in methanol at 25°, we found the reaction to be catalyzed not only by base, as expected, but also by acid.

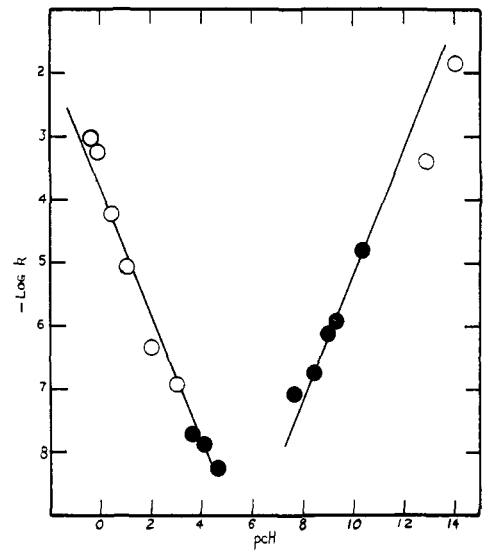

Figure 1. pcH-rate profile for the elimination of HCl from β-chloro-β-phenylpropiophenone in methanol. Lines drawn with slopes ±1, k in s^{-1}: dark circles, buffer solutions extrapolated to zero concentration; open circles, HCl or CH_3ONa.

$$C_6H_5COCH_2CHClC_6H_5 \rightarrow C_6H_5COCH{=}CHC_6H_5 + HCl \quad (1)$$

Since the most comprehensive reviews[2b] mention no acid-catalyzed dehydrochlorinations (we know of no others except that of camphene hydrochloride in ether[3]) and since the substrate is a type used in studies of E1cB reactions, it seems timely to show the pcH-rate profile for reaction 1.

General base catalysis was observed in acetate buffers (pcH 7.6-10.4) and general catalysis at pcH 3.6 in trichloroacetate buffers. Pseudo-first-order rate constants from the buffered runs were extrapolated to zero concentration to give the dark circles in Figure 1. The open circles represent pcH values controlled by anhydrous hydrogen chloride or sodium methoxide. The product is *trans*-chalcone above pcH 8 but contains 12% cis below pcH 4. The elimination is immeasurably slow in the pcH range 5-7. Unfortunately another, very slow acid-forming reaction, presumably displacement, complicates attempts to complete this portion of Figure 1.

The reaction is obviously catalyzed by $CH_3OH_2^+$; the rate constant, 1.3×10^{-4} M^{-1} s^{-1}, is insensitive to ionic strength. Acid catalysis implies that this elimination should be autocatalytic and in fact Vorlander[4] noted that the product accelerated the reaction, though he attributed it to a solvent effect. However, an unbuffered reaction mixture containing 0.015 M substrate and 0.001 M hydrogen chloride shows the initial acceleration and long period of nearly constant rate characteristic of reactions with rate equation $dx/dt = k(a + x)(s - x)$.

A mechanism consistent with these observations is rate-controlling, acid-catalyzed enolization followed by loss of chloride ion from the enol or its anion. Noyce and Reed[5] assigned an enolization mechanism to the acid-catalyzed dehydration of a β-ketol, $CH_3COCH_2CHOHC_6H_5$, structurally analogous to our β-chloroketone.

At high pcH the kinetics are consistent with an E2 or an

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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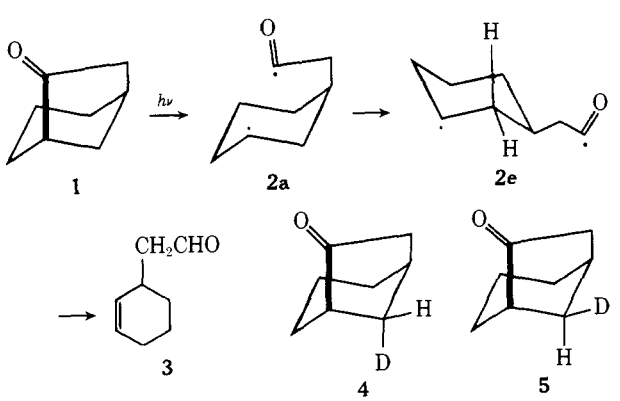
Received April 8, 1976

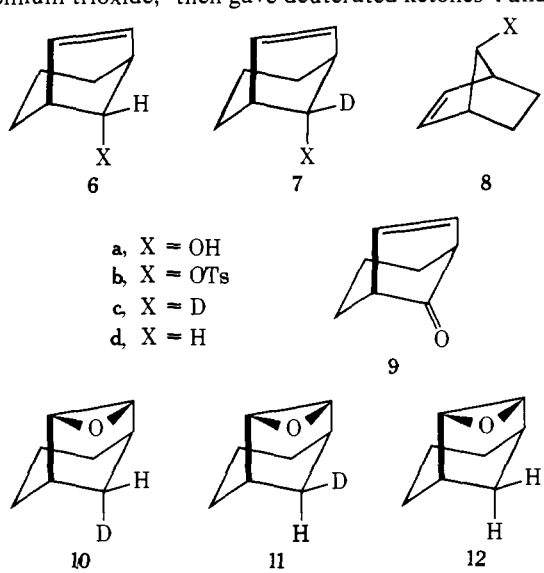
Stereoselectivity of Hydrogen Transfer in the Photochemical Isomerization of Bicyclo[3.2.1]octan-6-one. Evidence for a Stereoelectronic Effect

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.



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**.



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