that the rates and activation parameters for the thermal deazetation of **1** in the solvents CH_3CN and benzene are identical. This suggests that, if the rate-determining steps of the rearrangement and deazetation both pass over the same intermediate, the biradical **4** is the preferred formulation.[15]

The portion of bridged diazene **1** proceeding directly to trappable reactive intermediates and not funneled through fused diazene **2** is given by $100[k_1/(k_1 + k_2)] = 70\%$. Thus, despite the competing rearrangement, most of the **1** and essentially all of the **2** decompose separately.

Bridged diazene **1** can be recovered from 15 runs representing increasing extents of partial photolysis (7–99% reaction, CH_3CN solution, 0 °C, 350 nm), but no rearrangement (<5%) to the fused isomer can be detected. This is in agreement with the quantum yield of 0.95 ± 0.05 for the photodeazetation of **1**.[12] Here also, the deazetations are effectively independent.

Comparisons of the composition of the cycloadduct mixture obtained by thermal or photochemical decompositions of diazene in the presence of an efficient singlet trapping agent (dimethyl fumarate or fumaronitrile)[9b,c] shows the products from **1** and **2** to be identical. Any distinction in structure between the singlet intermediates from proto-planar and proto-bisected precursors either fortuitously fails to result in distinctive reactivities, or, more plausibly, is lost during the lifetime of the intermediate. It is possible that the product equivalences observed here could be attributable to the common intermediacy of the diazenyl biradical **4**. Conceivably, a different method of generating the TMM **3** could still demonstrate independent identities for the planar and bisected forms.

The previously reported[12] low-temperature flash photolysis technique facilitates a further search for intermediates, including the bisected triplet, which might intervene between the proto-bisected diazene **2** and the planar triplet. A sample of **2** in solution is frozen to 4.2 K in the cavity of the ESR spectrometer and exposed to a xenon lamp flash. The ESR signal, monitored at the strong (inside) line of the $\Delta m = 1$ transition with a time resolution of $\sim 5 \times 10^{-2}$ s, rises sharply and without delay to a stable level. A more leisurely scan of the spectrum so generated shows it to be identical with that observed[8,16] upon photolysis of the proto-planar diazene **1**. If ESR-inactive intermediates had been generated from **2**, survived longer than 5×10^{-2} s, and then decayed to the planar triplet, the flash-induced signal either would have passed through a maximum or would have shown a delayed gradual rise.

From the average lifetime of $<5 \times 10^{-2}$ s at 4.2 K in the photodeazetation of proto-bisected diazene **4**, we may conclude that any ESR-inactive intermediates encounter no significant (<190 cal/mol) activation barrier in the pathway leading to the observed triplet. Furthermore, if the bisected triplet lies on this pathway, either its ESR spectrum is very similar to that of the planar triplet,[17] or it is a species of only fleeting existence.

References and Notes

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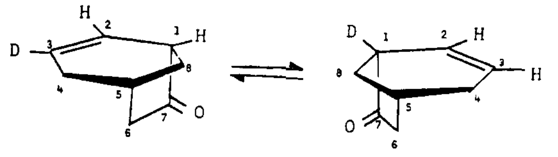
A Thermal [1,3] Sigmatropic Acyl Shift in the Degenerate Rearrangement of Bicyclo[3.2.1]oct-2-en-7-one

Sir:

Thermal [1,3] shifts of acyl or carboalkoxy groups are rare and perhaps unprecedented.[1-6] The difficulty of such reactions might be rationalized plausibly on the grounds that steric factors favor suprafacial migration, and therefore orbital symmetry[7,8] requires a transition state in which the migration origin and terminus are bound to opposite faces of the migrant carbon (C_m). The resulting rehybridization of C_m would change its substituent-binding σ orbitals from approximately sp^2 in the reactant to approximately sp in the transition state, a process that would be unfavorable when the substituents are electronegative.[9] Nevertheless, we now find that bicyclo[3.2.1]oct-2-en-7-one (**1**) undergoes a thermal degenerate rearrangement, which is most readily interpreted as a [1,3] acyl shift.

An optically active, deuterium labeled sample of ketone **1** can be separated by preparative gas chromatography from its isomer **2**. The mixture of **1** and **2** is obtained by application of a known[10,11] ring expansion sequence to optically active norborn-5-en-2-one (**3**), which in turn can be prepared efficiently by the steps shown in Scheme I. The configurations and enantiomeric purities (E.P.) are absolute as shown.[14,15]

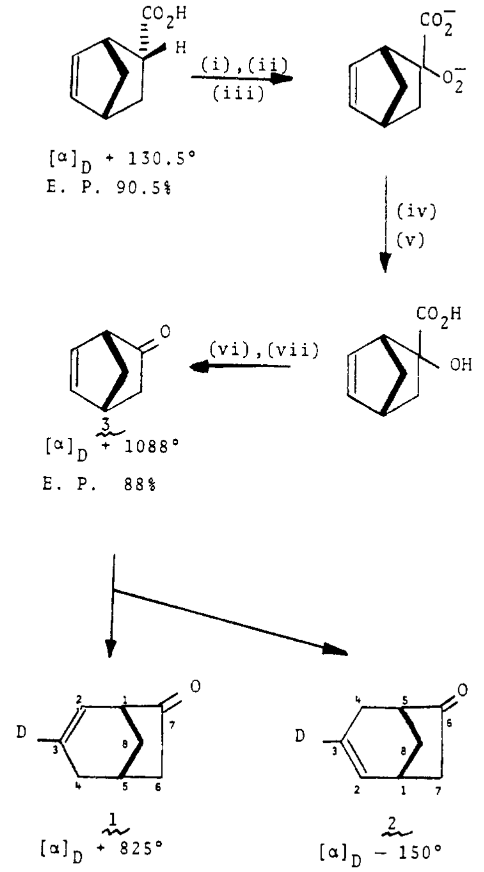
Pyrolysis of (+)-**1**-*3*-*d* in the gas phase above 340 °C results in a degenerate rearrangement to (−)-**1**-*1*-*d* which can be observed by a combination of proton and ^{13}C NMR spectroscopy and polarimetry. The chemical shifts of the olefinic protons (H_2 and H_3) of undeuterated **1** are very similar, even



(+)-1-3-d

(−)-1-1-d

Scheme I[a]



[a] (i) Obtained by resolution of the quinine salt from methanol (For a less efficient resolution see J. A. Berson and D. A. Ben-Efraim, *J. Am. Chem. Soc.*, **81**, 4083 (1959).); (ii) LDA; (iii) O_2;[12] (iv) Na_2SO_3; (v) H_3O^+; (vi) $LiAlH_4$; (vii) $NaIO_4$.[13]

at 270 Mhz, so that the appearance of hydrogen at C_3 in **1**-*1-d* is evidenced in the downfield region only by an increase in intensity of the H_2-H_3 signal at δ 5.5 relative to the remaining protons, which absorb in a complex pattern between δ 1.70 and 2.85. However, the upfield portion of the 270-Mhz spectrum shows a broad, cleanly separated one-proton absorption near δ 2.80 attributable to H_1 in the sample of **1**-*3-d*. The ketone **1** recovered after pyrolysis shows a decrease in this signal and an increase in the H_2-H_3 signal.

The ^{13}C resonances (in parts per million)[16] of **1** can be assigned readily to five of the eight carbons from the broad-band and single-frequency off-resonance proton decoupled spectra on the basis of chemical shift (C_2, 125.03, and C_7, 179.86), chemical shift and observed deuterium coupling in **1**-*3-d* (C_3, 127.33), and chemical shift and off-resonance multiplicity (C_1, 45.84, and C_5, 29.39). That the degenerate rearrangement **1**-*3-d* $\rightleftharpoons$ **1**-*1-d* occurs is confirmed by the proton-decoupled spectrum of ketone recovered from pyrolysis of **1**-*3-d*. The spectrum is run with gated decoupling and 45-s pulse delay Fourier transform acquisition to ensure relaxation of all the carbon transitions. The C_3 signal still shows the characteristic triplet caused by deuterium coupling but now also shows a singlet of greatly increased intensity attributable to the presence of protium. The C_1 signal now shows a deuterium triplet superimposed on the ordinary proton-decoupled singlet.[17]

Since the degenerate rearrangement is also an enantiomerization, (+)-**1**-*3-d* $\rightleftharpoons$ (−)-**1**-*1-d*, the kinetics of the reaction can be followed polarimetrically. Pyrolyses at each of five temperatures between 352.8 and 393.0 °C provide good first-order polarimetric rate constants, defined by $\ln(\alpha_0/\alpha) = k_\alpha t$, the temperature dependence of which leads to the activation parameters $\Delta H^{\ddagger} = 51.0 \pm 2$ kcal/mol, $\Delta S^{\ddagger} = 1.8 \pm 3.4$ eu, $E_a = 52.3 \pm 2$ kcal/mol. The rate is unaffected by packing the pyrolysis sample tube with glass wool. We therefore have no objective reason to suspect a heterogeneous component of the reaction, although a note of caution is appropriate.

It is not clear whether the rearrangement of **1** is a truly concerted [1,3] sigmatropic acyl shift or a stepwise reaction passing over an allylic-acyl biradical intermediate derived by cleavage of the C_1-C_7 bond. In any case, it seems unlikely that this example of thermal [1,3] acyl shift is destined to be unique.[19,20]

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References and Notes

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(20) Dr. S. E. Potter, unpublished work at Yale University, has observed the rearrangement of 7-isopropylidenenorbornane-2,3-dione to 2,2-dimethylbicyclo[3.3.0]oct-8-ene-3,4-dione under flash vacuum pyrolysis conditions.
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