Bond Cleavage–Geminate Pair Recombination in a Photochemical 1,3-Allylic Rearrangement

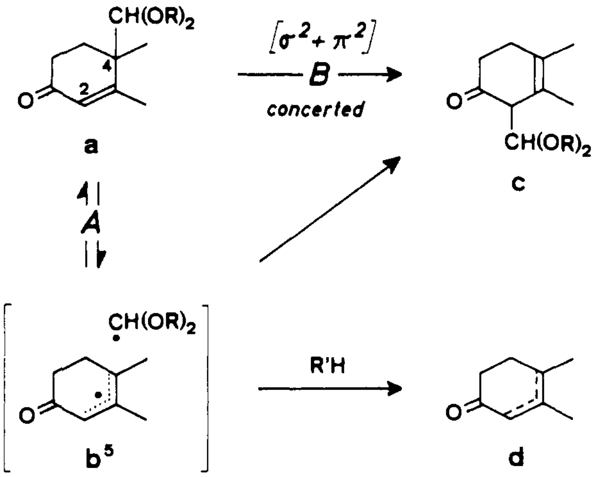
Sir:

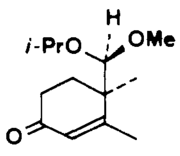
Configurational analysis of the migrating carbon has proved a useful diagnostic tool in distinguishing between concerted and stepwise reactions in 1,3-allylic rearrangements. We report such a study of a nonconcerted substituent (dialkoxymethyl) shift on a ring which thus complements the list of varied results on thermal[1,2] and photochemical[2,3] 1,3-allylic migrations.

We have found previously[4] that 4-dimethoxymethyl-2-cyclohexen-1-ones such as a (R = CH_3) undergo several specifically $\pi \rightarrow \pi^*$ induced—hence, presumably upper excited $^1(\pi,\pi^*)$ state—photoreactions including, inter alia, a shift of the dimethoxymethyl group (a → c), and elimination of this substituent and uptake of a hydrogen to form the isomeric cyclohexenones d (Scheme I). The transformation a → c has been shown to be fully intramolecular and therefore results from either an allylic bond cleavage-geminate pair recombination process (path A)[5] or a concerted 1,3-allylic shift (path B), or even both of them. Retention of configuration of the diastereotopic methoxyl groups is expected for the latter path,[7] whereas such stereospecificity is likely to be lost in the former mechanism via an intermediate b. We have now been able to demonstrate that path A is the predominant, and possibly exclusive, contributor to the rearrangement.

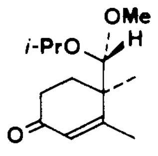
The obvious approach was to use an asymmetrical acetal function as a stereochemical probe in both the photoproduct(s) and the starting material recovered after incomplete conversion.[6] The diastereoisomeric *racemic* compounds (*R**)-**1** and (*S**)-**1** accommodate this structural prerequisite.[8] A mixture enriched with (*R**)-**1**[10,11] (~90%) was dissolved in t-BuOD and irradiated with 254 nm. Compound (*R**)-**1** was found to epimerize progressively during the course of the photolysis, and the rearrangement afforded a ca. 1.4:1 ratio of (*R**)- and (*S**)-**2**[11] when extrapolated to zero conversion. Similar irradiation of a mixture enriched with (*S**)-**1**[11] (~90%) gave a similar but *inverse* ratio of products (*R**)- and (*S**)-**2** (Figure 1). The analysis of the photomixtures was performed by NMR integration[12] of the singlets at δ 3.11/3.08 and 4.05/4.07 for the methoxy and acetal protons, respectively, of (*R**)- and (*S**)-**1**, and the doublets at δ 4.73/4.77 for the acetal protons of (*R**)- and (*S**)-**2**.

Scheme I

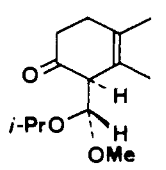




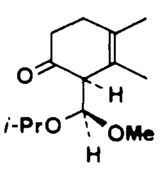
(*R**)-**1**



(*S**)-**1**



(*R**)-**2**



(*S**)-**2**

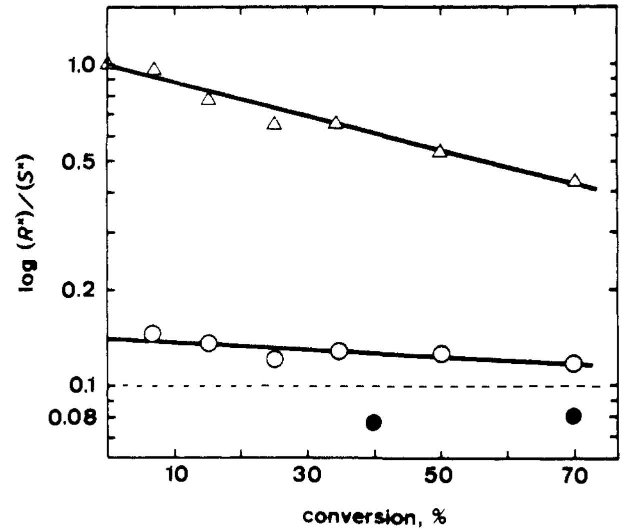


Figure 1. Composition of photomixtures formed from (*R**)-**1** ((*R**)-/(*S**)-**1**, △; (*R**)-/(*S**)-**2**, ○) and (*S**)-**1** ((*R**)-/(*S**)-**2** ●) as a function of photochemical conversion.

An O-deuterated alcohol was used to detect any epimerization which could arise from a proton exchange at C-2 of **2** via reversible enolization subsequent to the photorearrangement. Deuterium incorporation by such a process would cause the appearance of a singlet for the acetal proton and was not observed by NMR. Furthermore, the possibility of photochemical stereomutation unrelated to the specifically $\pi \rightarrow \pi^*$ induced reaction was excluded by direct irradiation of (*R**)-**1** at >300 nm and of (*R**)-**2** at 254 nm and by triplet sensitization of (*R**)-**2** with acetone. In neither case were the corresponding diastereoisomers formed.

The most relevant stereochemical feature of these results is the predominant configurational randomization of the acetal group in product **2** irrespective of the configuration of starting material. *It establishes path A in the 1,3-allylic rearrangement* a → c which involves an intermediate such as b[5] capable of configurational inversion at the migrating carbon prior to recombination to a and c. A stereoselective control of recombination at C-2 would result in the preferential formation of one and the same stereoisomer **2** from the two diastereoisomeric pairs b. Such is not the case. Rather, weak partial retention of configuration is observed in the 1,3-shifts of (*R**)- and (*S**)-**1**. This is attributable to the concerted path B as a minor process and/or to competition between the rates of recombination b → c and epimerization (which requires one geminate-pair component to turn over).

The photoreaction a → c is an unprecedented example of a 1,3-allylic shift which occurs from an upper excited state, involves migration of a saturated acyclic carbon, and proceeds in a nonconcerted fashion. Stepwise mechanisms for photochemical 1,3-allylic shifts have been established previously for cases which involve either the migration of saturated ring carbons in cyclopentenone[3a,b,d,f] and bicyclo[4.1.0]hept-2-ene systems[3c] or the migration of benzoyl through radical recombination.[13] In all these cases excitation to the first singlet state sufficed, and evidence for a reactive triplet is available in most. Other interesting examples, which stand in juxtaposition to our results, are the concerted 1,3-allylic photorearrangements of cyclic and aliphatic 1,1-dicyano-4-phenyl-1-butene systems which occur with retention of configuration at the migrating benzylic carbon.[2,3e,g] They have been attributed to the π,π^* singlet state of the $C{=}C(C{\equiv}N)_2$ system. As shown previously,[4a] the reactive state responsible for a → c + d is not populated by way of the lowest lying singlet state, S_1 (n, π^*), which crosses over to triplet.[14] It is possibly identical with the thermally equilibrated S_2 state which in conjugated ketones has the lowest energy π,π^* configuration. Our present findings together with the literature examples therefore show that spin multiplicity of the reactive state is not the controlling factor for concerted vs. stepwise mechanisms in photochemical 1,3-allylic shifts. Other properties of the chromophore or the migrating group must be involved.

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References and Notes

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(4) (a) J. Gloor and K. Schaffner, *Helv. Chem. Acta*, **57**, 1815 (1974); (b) K. Schaffner, *Pure Appl. Chem.*, **33**, 329 (1973).

(5) The radical nature of intermediate b is not established experimentally.[4a,6] In fact both ion and radical pair forms may be intermediate stages leading from excited to ground state.

(6) A photo-CIDNP study of the reaction, the a priori imperative method to detect the *radical* bond cleavage-pair recombination mechanism a ⇄ b → c (+ d), failed to give conclusive results owing to low quantum yield and insufficient intensity at <260 nm. We thank Professor H. Fischer and A. Henne, University of Zurich, for exploratory experiments.

(7) (a) The possibility of competition by a concerted antarafacial shift with inversion of configuration is discarded in view of the sterically highly unfavorable transition state required; (b) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(8) Compounds (R^*)- and (S^*)-**1** were prepared by HCl-catalyzed treatment of *rac*-1-ethylenedioxy-3,4-dimethyl-4-formylcyclohex-2-ene[9] with methanol and isopropyl alcohol and chromatographic separation into enriched mixtures (~9:1 ratios) of either diastereoisomer.

(9) E. Baggiolini, H. P. Hamlow, and K. Schaffner, *J. Am. Chem. Soc.*, **92**, 4906 (1970).

(10) Satisfactory uv, ir, ^1H NMR, and mass spectral data were obtained for all compounds **1** and **2**.

(11) The relative configurations of **1** and **2** have been chosen arbitrarily and are irrelevant for the evaluation of our results.

(12) For NMR analysis the samples were taken to dryness and redissolved in hexadeuteriobenzene.

(13) H.-U. Gonzenbach, K. Schaffner, B. Blank, and H. Fischer, *Helv. Chim. Acta*, **56**, 1741 (1973).

(14) On n → π^* excitation **1** and 10-dimethoxymethyl-$\Delta^{1(9)}$-octal-2-one, which undergoes rearrangement analogous to a → c,[4] exhibit triplet reactivity, and the bicyclic enone shows the same phosphorescence characteristics as the parent methyloctalone (G. Marsh, D. R. Kearns, and K. Schaffner, *J. Am. Chem. Soc.*, **93**, 3129 (1971)).

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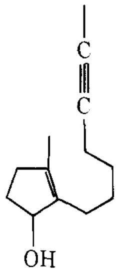
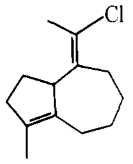
A Novel Synthesis of Longifolene[1]

Sir:

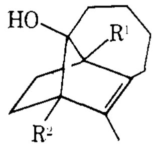
In some exploratory work aimed at developing a new hydroazulene synthesis, we examined the stannic chloride-catalyzed cyclization of the heptynylmethylcyclopentenol (**1**). While the reaction did indeed afford the hydroazulene system (formula **2**) in analogy to the established mode of polyene cyclizations involving the methylacetylenic terminating group,[2] an additional crystalline alcohol was produced, the spectral properties of which were consonant with a tricyclic structure, either **3** or **4**.[3] Recognizing that this presumed bridged-ring structure possessed the basic ring system of longifolene (**14**), our attention was turned to the preparation of the appropriately substituted substrate, namely, the enynol **8** (Chart I), cyclization of which would be expected to give, along with a hydroazulenic substance, the product **9** which is a potential synthon for producing longifolene. The preparation of the tricyclic alcohol **8** and its conversion into longifolene is the subject of the present communication.



1

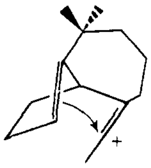


2

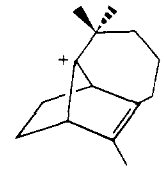


3, $R^2 = H$; $R^1 = CH_3$
4, $R^2 = CH_3$; $R^1 = H$

Although the mechanism of the cyclization of the enynol **1** is open to question,[4] the anticipated cyclization of **8** can be rationalized as follows. It is reasonable to hypothesize that the allylic alcohol **8** would first cyclize to give the vinyl cation A.[5] Reaction of A with an external nucleophile would then yield a hydroazulenic substance. On the other hand, intramolecular nucleophilic attack of the vinyl cation by the olefinic bond in the five-membered ring,[6] as suggested in formula A, would result in further cyclization to yield the interesting cation B which embodies the unusual feature of destabilization due to an apparent violation of Bredt's rule but, on the other hand, the potential stabilizing characteristic of the 7-*anti*-norbornenyl cation.[7] Nucleophilic attack of the cation B by water would yield the 7-*anti*-norbornenyl system **9**. These theoretical considerations, in addition to increasing our optimism about the success of the envisaged synthetic scheme, suggest that the formation of **9** might be favored over the bicyclic product by minimizing the availability of nucleophiles in the cyclization medium. This objective has been realized and the refined version of the total synthesis is set forth below.



A



B

Metalation[8] of 1-iodo-4-hexyne[9] at −78° with 2 mol equiv of *tert*-butyllithium in ether gave 4-hexynyllithium which was treated with 0.5 mol equiv of tetrakis[iodo(tri-*n*-butylphosphine)copper(I)][10] followed by 0.5 mol equiv of 2-isopropylidenecyclopentanone (**5**).[11] This solution, con-