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Registry No.—3, 63096-02-6; 4, 58521-45-2.

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Communications

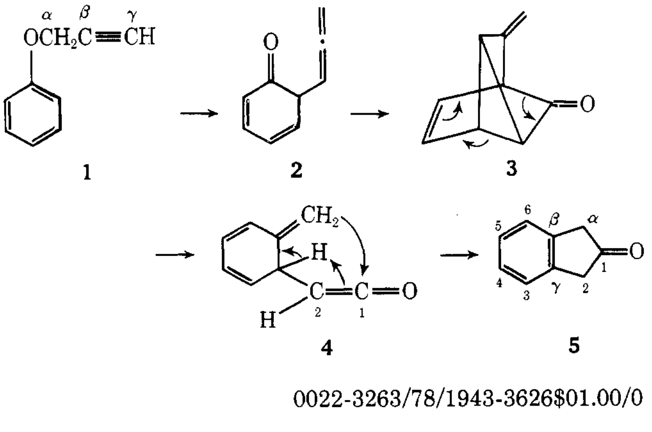
On the Mechanism of Flash Vacuum Pyrolysis of Phenyl Propargyl Ether. Intramolecular Deuterium Kinetic Isotope Effect on Claisen Rearrangement[1]

Summary: We wish to report the first intramolecular deuterium kinetic isotope effect observed in the Claisen type rearrangement of 2-deuteriophenyl propargyl ether (**8**), which is interpreted in terms of a nonsynchronous mechanism.

Sir: It has been reported by Trahanovsky and Mullen[2] that flash vacuum pyrolysis (FVP) of phenyl propargyl ether (**1**) gives rise to benzocyclobutene and 2-indanone (**5**). Based on their mechanistic studies, they proposed[2] the mechanism shown in Scheme I for the formation of **5**. Kinetic studies on the thermal rearrangement of **1** indicated that the step **1** to **2** is rate determining.[3] Furthermore, rearrangement of **1** to **2** has been classified as a [3,3] sigmatropic process.[3] Very recently, Dewar[4] has presented results of MINDO calculations on some pericyclic reactions and has concluded that two-bond ractions are never synchronous, with the exception of a number of ene reactions, but are two-stage or two-step processes which involve unsymmetrical transition states. Furthermore, it has been indicated that the Cope rearrangement of 1,5-hexadienes, a [3,3] sigmatropic process according to Woodward–Hoffmann rules,[5] is not a pericyclic reaction but follows a different mechanism which involves reaction intermediates.[4]

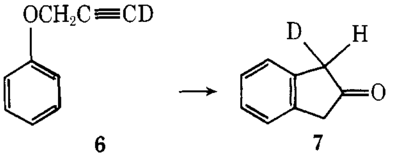
The study of secondary deuterium kinetic isotope effects provides a useful method to estimate the degree of force constant changes at the isotopic position between the ground and transition states,[6] and consequently is a powerful tool in determining the degree of bond cleavage–bond formation that occurs at the transition states of two-bond reactions.

Scheme I



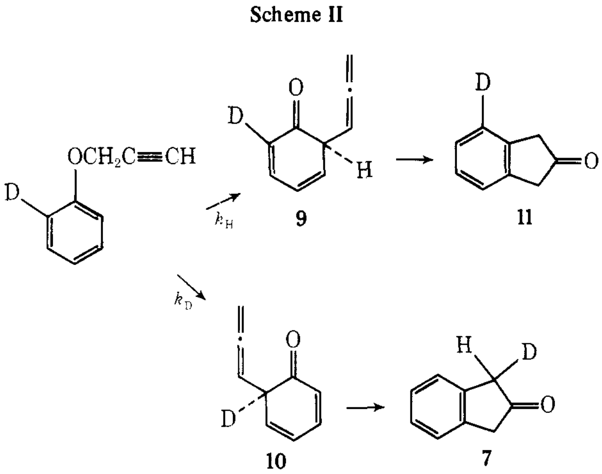
It is the purpose of this work to further test the mechanism outlined in Scheme I, and to determine the relative timing of bond cleavage–bond formation at the transition state for the rearrangement of **1** to **2**.

The mechanism suggested for the FVP of **1** implies, among other things, transfer of the acetylenic hydrogen (γ hydrogen) of the reactant, during the rearrangement, to a position which ends up as nonaromatic in the product 2-indanone (**5**, Scheme I). Therefore, by substituting the acetylenic hydrogen in **1** by deuterium, subsequent FVP of the resulting deuterated ether should produce an indanone with all deuterium bonded to the nonaromatic position. Thus, phenyl γ-deuteriopropargyl ether (**6**) was synthesized by five successive exchanges of the γ hydrogen in **1**[7] using D_2O/NaOD in dried diethyl ether. The NMR analysis of **6** revealed that 87% of deuterium is incorporated in the desired position. The FVP[7] of **6** was carried out at 460 °C and 0.02 Torr. The NMR spectrum of the 2-indanone (**5**) in CCl_4 displays peaks at δ 7.15 (singlet, aromatic H's) and 3.25 (singlet, nonaromatic H's) and with an integration ratio of 1.00:1.00. The NMR spectrum of the deuterated 2-indanone derived from **6** gave an aromatic protons/nonaromatic protons ratio of 1.30:1.00, consistent with the prediction and the structure given by **7**. Thus, our observation further substantiates the mechanism proposed[2] for the FVP of **1** (Scheme I).



The problem of gaining an insight into the structure of the transition state for the rearrangement of **1** to **2** could be carried out by examining the magnitude of the intramolecular deuterium kinetic isotope effect involved in the FVP of 2-deuteriophenyl propargyl ether (**8**). Considering Scheme II, if bond formation is taking place at the rate-determining step, then due to the rehybridization change (sp^2 to sp^3) of the ortho C–H and C–D bonds an inverse isotope effect would be expected in the FVP of **8**. If on the other hand, bond formation is occurring in a subsequent fast step, then k_H would be equal to k_D. The FVP of **8** should give rise to dienones **9** and **10**, which subsequently lead to products **11** and **7**, respectively. The proportion of **9** and **10** would depend on the magnitude of the k_H/k_D involved, and would be reflected in the ratio of **11** to **7** as determined by NMR analysis. Synthesis of **8** was accomplished from the reaction of 2-deuteriophenol[9] with

Scheme II



propargyl bromide following the same procedure used for 1.[7] The NMR analysis of 8 revealed 85% deuteration at the desired position. Flash vacuum pyrolysis of 8 was carried out under the same experimental conditions employed for 6. The NMR spectrum of the deuterated 2-indanones derived from 8 gave an integration ratio, obtained from at least ten integrations of aromatic/nonaromatic protons, corresponding to an intramolecular deuterium kinetic isotope effect of $k_H/k_D = 1.00 \pm 0.01$. Such a value of k_H/k_D indicates that the ortho C–H and C–D bonds in 8 are undergoing negligible or no force constant changes in going into the rate-determining transition state. Thus the observed k_H/k_D could be best accommodated by assuming that at the rate-determining transition state the oxygen–propargylic carbon (α carbon) bond in 1 is stretched in advance of any significant bond formation between the terminal acetylenic carbon (γ carbon) and the reacting ortho position. Therefore, the Claisen type rearrangement of 1 could be classified as a nonsynchronous process in accordance with Dewar's conclusion.[4]

Attempts to determine the magnitude of the intramolecular k_H/k_D in the Claisen rearrangement of allyl 2-deuteriophenyl ether, at 200–220 °C in a sealed ampule, leads to some discrepancy in the magnitude of the k_H/k_D. This is due to deuterium exchange[13] caused by the resulting phenol under such experimental conditions.

References and Notes

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(7) Prepared from the reaction of phenol with propargyl bromide in the presence of K_2CO_3 according to the published procedure given by: (a) C. D. Hurd and F. L. Cohen, *J. Am. Chem. Soc.*, **53,** 1068 (1931); (b) I. Iwai and J. Ide, *Chem. Pharm. Bull.*, **11,** 1042 (1963).
(8) The apparatus consists of a chair-like tube made of Vycor glass (i.d. 2.2 cm, length 80 cm). The horizontal part is wrapped first with an asbestos tap, then a heating wire made of nickel-chromium, and finally a second asbestos tap giving a heating zone of about 33 cm. Temperature control was carried out by means of a variac. Inside temperature was measured by means of a thermocouple.
(9) 2-Deuteriophenol was prepared from the cleavage[10] of 2-deuterioanisole by ethylmagnesium bromide. 2-Deuterioanisole was prepared from the treatment of the Grignard complex of 2-bromoanisole[11] with deuterium oxide.
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(11) A. I. Vogel "Practical Organic Chemistry", Longmans, Green and Co., New York, N.Y., 1951, p 727.
(12) Corrected for 15% undeuteration.
(13) A. I. Brodskii, G. P. Miklukhin, I. I. Kukhtenko, and I. P. Gragerov, *Dokl. Akad. Nauk SSSR*, **57,** 463–466 (1947); *Chem., Zentr.* II, 828–829 (1948); cited in *Chem. Abstr.*, **44,** 8882f (1950).

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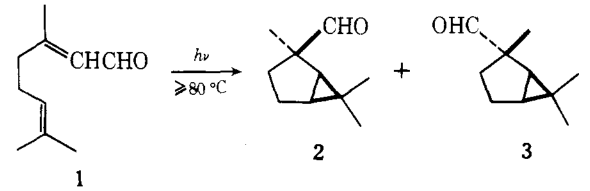
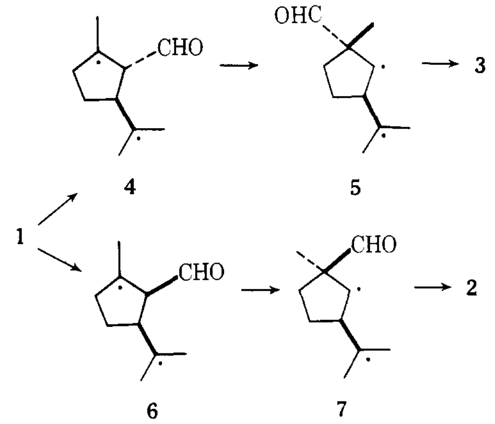
Triplet-Sensitized Photochemical Rearrangement of Geranonitrile at Elevated Temperature

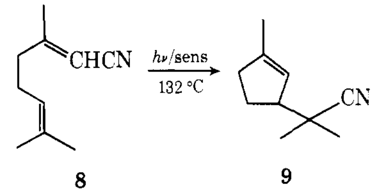
Summary: Photolysis of geranonitrile (8) at 132 °C furnishes 9 in a rearrangement that is not observed at 30 or 80 °C. This novel transformation can be rationalized through 1,3 shift of the cyano group in a biradical intermediate as shown in Scheme II.

Sir: We recently reported the novel photochemical rearrangement of citral (1) at 80–190 °C to form bicyclic aldehydes 2 and 3, products not seen at 30 °C;[1] we noted that these reactions could be accounted for by way of the biradical mechanism of Scheme I, but that other pathways, including concerted [$_\pi 2_s + {}_\pi 2_s + {}_\sigma 2_a$] processes, were possible. In exploring this matter further we have examined the photochemical behavior of the closely related geranonitrile (8) at elevated temperature. We describe here the temperature-dependent photochemical isomerization of 8 to 9 in a process that may be mechanistically related to isomerization of citral to 2 and 3, but that provides an example of a new type of rearrangement requiring overall 1,6 migration of the cyano group.



Scheme I





In agreement with earlier observations we found that the triplet-sensitized photolysis of 8 in acetone as solvent at 30 °C gave as the only volatile products a ~4:1 mixture of the [2 + 2] cycloadducts 10 and 11.[2] We obtained similar results with propiophenone as sensitizer in either benzene or chlorobenzene at 30 °C and in benzene at reflux (80 °C). However, at 132