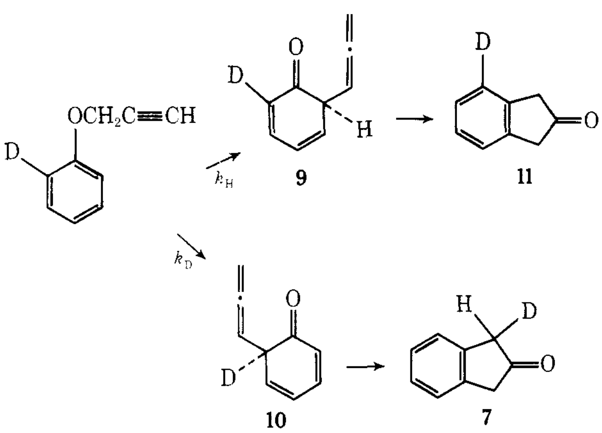
Scheme II



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 ± 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

(1) Based on work by D. M. Al-Fekri in partial fulfilment of the requirements for the M. S. degree at the University of Baghdad, May 1977.

(2) W. S. Trahanovsky and P. W. Mullen, *J. Am. Chem. Soc.*, **94**, 5911 (1972).

(3) (a) J. Zsindely and H. Schmid, *Helv. Chim. Acta*, **51**, 1510 (1968); (b) H. J. Hansen and H. Schmid, *Chem. Br.*, **6**, 111 (1969).

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(5) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Verlag Chemie GmbH, Wienheim, Germany, 1971.

(6) (a) B. H. Al-Sader, *Bull. Coll. Sci., Univ. Baghdad*, **15**, 91 (1974); (b) M. Wolfsberg and M. J. Stern, *Pure Appl. Chem.*, **8**, 225, 325 (1964).

(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.

(10) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances", Prentice-Hall, New York, N.Y., 1954, pp 1013–1045; F. Challenger and S. A., Miller, *J. Chem. Soc.*, 894 (1938).

(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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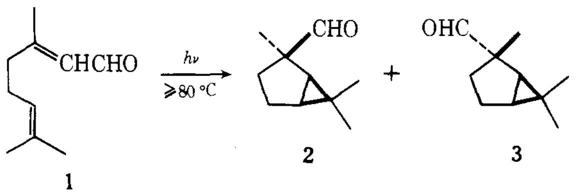
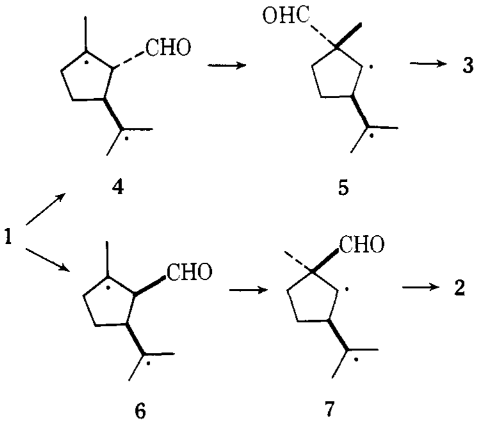
Triplet-Sensitized Photochemical Rearrangement of Geranonitrile at Elevated Temperature

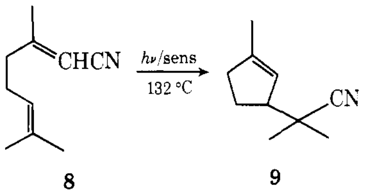
Summary: Photolysis of geranonitrile (8) at 132 °C furnishes 9 in a rearrangement that is not observed at 30 or 80 °C. This novel transformation can be rationalized through 1,3 shift of the cyano group in a biradical intermediate as shown in Scheme II.

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.

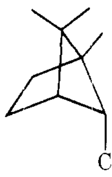


Scheme I

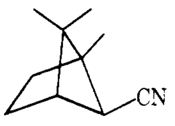




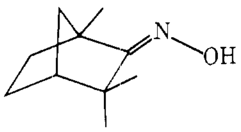
In agreement with earlier observations we found that the triplet-sensitized photolysis of 8 in acetone as solvent at 30 °C gave as the only volatile products a ~4:1 mixture of the [2 + 2] cycloadducts 10 and 11.[2] We obtained similar results with propiophenone as sensitizer in either benzene or chlorobenzene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



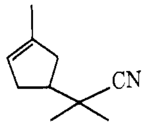
10



11



12

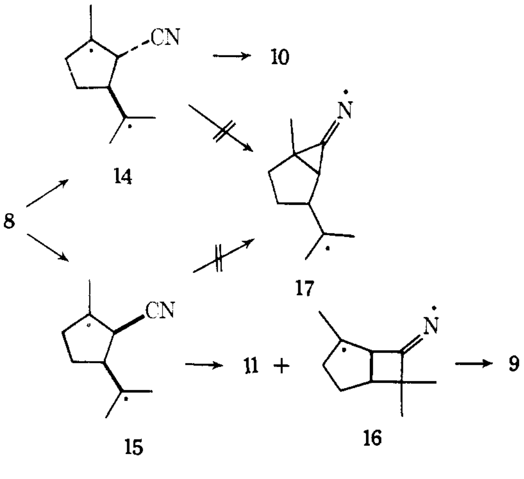


13

°C in refluxing chlorobenzene the propiophenone-sensitized irradiation of 8 furnished a volatile product consisting of 9 (60%), 10 (30%), and 11 (10%). All photolyses in which chlorobenzene was solvent were carried out with solid sodium bicarbonate added to the reaction mixture to prevent the possible accumulation of hydrogen chloride. In all experiments interconversion of the cis and trans isomers of geranonitrile (8) was rapid relative to other reactions, and a considerable amount of polymer was formed. The volatile products were isolated and purified by preparative vapor-phase chromatography, and 9 was tentatively identified on the basis of its spectroscopic properties[3] and the mechanistic considerations discussed below. This assignment was confirmed by comparison of the new photoproduct with an authentic sample of 9 prepared by the known acid-catalyzed Beckmann fragmentation of α-fenchone oxime (12).[4]

A stepwise mechanism for formation of 9, 10, and 11 from 8 is shown in Scheme II. This involves interaction of the double bonds of 8 to furnish biradicals 14 and 15, parallel to the suggested formation of 4 and 6 in Scheme I.[5] Closure of 15 to the bicyclic iminium species 16 and subsequent cleavage of the cyclobutane ring in the opposite sense could then furnish 9. Presumably this cyclization and rearrangement would not be possible in 14 because of the trans stereochemistry of the substituents. The postulated formation of 16 has reasonable precedent in intermediates discussed by other investigators for several 1,4 transfers of a cyano group in radical reactions.[6,7] In one of these earlier cases a labeling study has shown this transfer specifically to be an intramolecular rearrangement.[7] We are unaware, however, of any previous report of the *1,3* transfer of a cyano group in a free-radical process. If the mechanisms of Schemes I and II are valid, irradiation of 1 and 8 leads to analogous biradicals, but in the case of 1 the observed rearrangements entail a 1,2 migration of the formyl group, while in 8 the cyano group undergoes only a 1,3 shift. One possible factor contributing to the observed specificity of rearrangement of the nitrile may be that a 1,2 shift in 14 or 15 would require an intermediate (see 17) with an sp^2-hybridized carbon atom in a strained three-membered ring. A similar intermediate in the rearrangement of 4 to 5, and of 6 to 7, would have only sp^3 carbons in the cyclopropane ring.

Scheme II



The present work then provides a second novel type of photochemical rearrangement that can compete with [2 + 2] cycloaddition at elevated temperature, and that can be rationalized through a biradical intermediate of the sort generally implicated[8] in such cycloadditions. We are continuing our search for additional examples of such processes.[9]

References and Notes

(1) F. Barany, S. Wolff, and W. C. Agosta, *J. Am. Chem. Soc.*, **100**, 1946 (1978).

(2) R. F. C. Brown, R. C. Cookson, and J. Hudec, *Chem. Commun.*, 823 (1967); R. C. Cookson, *Q. Rev., Chem. Soc.*, **22**, 423 (1968). As noted in these publications, direct irradiation of **8** leads to products totally different from those discussed here.

(3) Spectroscopic data for **9** and **13** in CCl_4 follow. For **9:** IR 3048 (m), 2977 (s), 2940 (s), 2875 (s), 2850 (s), 2240 (m), 1655 (m), 1467 (s), 1451 (s), 1435 (s), 1382 (s), 1374 (m), 1367 (s), 977 (m) cm^{-1}; NMR (60 MHz) δ 5.24 (m, 1 H), 2.72 (br m, 1 h), 2.57–1.88 (m, 4 H), 1.78 (m, 3 H), 1.28 (s, 6 H). For **13:** IR 3045 (m), 2975 (s), 2930 (s), 2840 (s), 2235 (m), 1658 (w), 1468 (s), 1432 (s), 1380 (s), 1372 (m), 1362 (s), 1010 (m) cm^{-1}; NMR (60 MHz) δ 5.22 (m, 1 H), 2.30 (br s, 5 H), 1.72 (br s, 3 H), 1.33 (s, 6 H).

(4) D. Varech and J. Jacques, *Bull. Soc. Chim. Fr.*, 3505 (1969), and references cited therein. None of these earlier reports gives details allowing ready distinction of **9** from its isomer **13**, which is formed concomitantly on fragmentation of **12**, and we have accordingly recorded the IR and NMR spectra of **9** and **13** in ref 3 above. These data permit the desired assignment without difficulty; for NMR analysis of related cyclopentenes see A. G. Singer, S. Wolff, and W. C. Agosta, *J. Org. Chem.*, **42**, 1327 (1977).

(5) For the original proposals of such biradical intermediates in the formation of **10**, **11**, and the photoproducts from citral at room temperature, see ref 2 and also R. C. Cookson, J. Hudec, S. A. Knight, and B. R. D. Whitear, *Tetrahedron*, **19**, 1995 (1963), and G. Büchi and H. Wüest, *J. Am. Chem. Soc.*, **87**, 1589 (1965).

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(7) J. Kalvoda, *Helv. Chim. Acta*, **51**, 267 (1968).

(8) For references to mechanistic studies of [2 + 2] photocycloaddition see R. O. Loutfy and P. de Mayo, *J. Am. Chem. Soc.*, **99**, 3559 (1977).

(9) This investigation was supported by the National Science Foundation through Grant CHE74-21436. We thank Dr. W. I. Taylor, International Flavors and Fragrances, Inc., for a generous gift of geranonitrile.

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Poitediol, a New Nonisoprenoid Sesquiterpene Diol from the Marine Alga *Laurencia poitei*

Summary: A new sesquiterpenoid diol, poitediol (1), has been isolated from ethanol extracts of the red seaweed *Laurencia poitei* (Lamouroux) Howe. The structure of poitediol, as determined by X-ray crystallography, is composed of an unprecedented and nonisoprenoid bicyclo[6.3.0]undecane skeleton.

Sir: Red seaweeds of the genus *Laurencia* are known to produce regular terpenoids which contain halogens.[1] Brominated compounds are more commonly observed, but many chlorinated examples are known. Structurally these compounds appear to be the products of a bromonium ion induced cyclization of acyclic precursors.[2] We wish to report here the structure of an unusual *Laurencia* metabolite, poitediol (1), which contains neither the expected halogen substituents nor regular sesquiterpenoid structure characteristic of metabolites from this source. Recent investigations indicate that halogen solvolysis and concomitant rearrangement may be the

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