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PHOTOCHEMISTRY OF BENZOTRICYCLO[3.2.0.0^{2,7}]HEPTENE[1]: SINGLET EXCITED STATE REACTIONS DERIVED FROM CYCLOPROPANE RING CLEAVAGE

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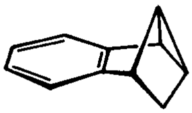
ABSTRACT: *Direct irradiation of the title hydrocarbon in cyclohexane affords 2-vinylindene and benzonorcaradiene as major primary photoproducts. Deuterium labeling is used to determine reaction mechanisms.*

It was recently reported[2] that direct irradiation of the title hydrocarbon (1) at 254 nm in methanol or hexane yields benzonorcaradiene (2), benzonorbornadiene (3) and two unidentified products presumed to be isomeric benzotropilidenes 4 and 5 as primary photoproducts.[3] We describe here our own studies[4] on the photochemistry of 1, which are significantly at variance with these results.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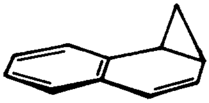
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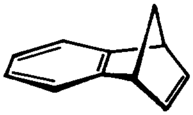
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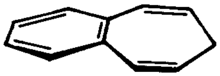
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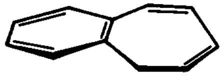
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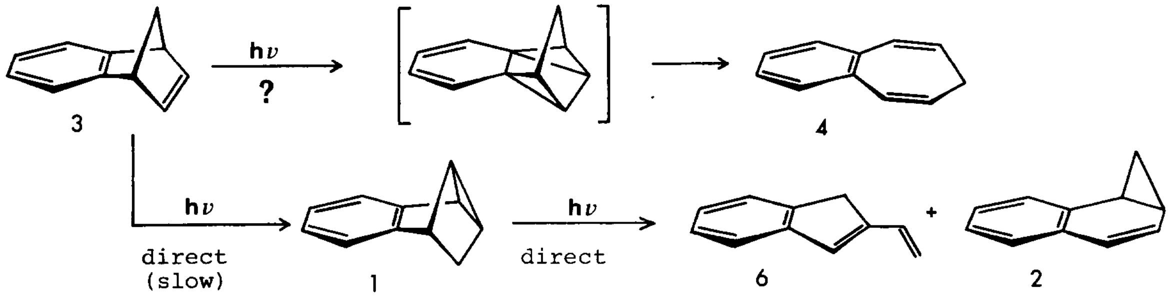
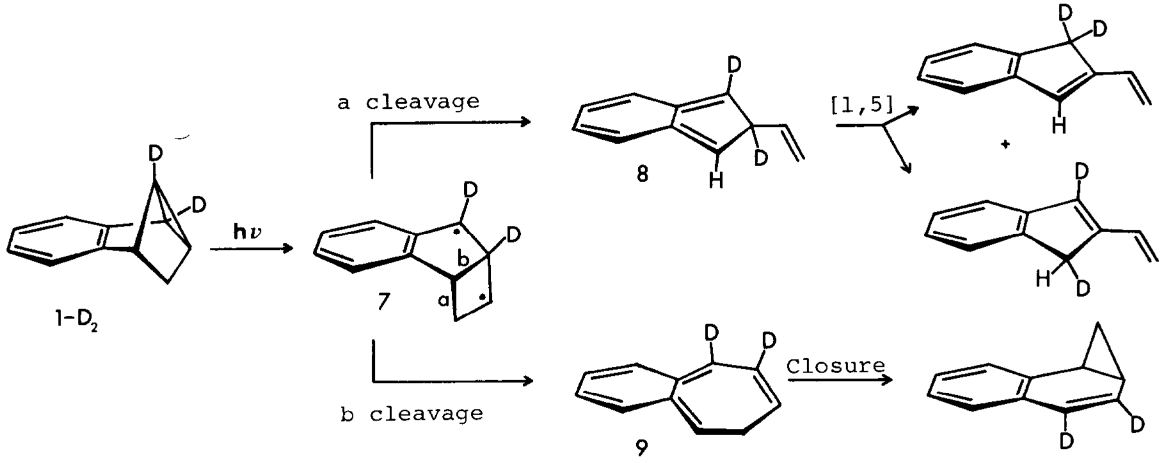
Our interest in the photochemistry of 1 was stimulated by the earlier observation of Edman[5] that prolonged direct irradiation of benzonorbornadiene yielded a long-wavelength absorbing substance, suggested to be 3,4-benzotropilidene (4). In reinvestigating this question, we observed[6] that benzonorbornadiene was slowly converted to 1, which subsequently underwent more rapid secondary and tertiary photoreaction. Direct irradiation of pure 1 in cyclohexane was then investigated; this afforded at low conversion, two major photoproducts (ratio *ca*. 1.5:1) readily characterized as 2-vinylindene (6) and benzonorcaradiene (2), as well as several very minor products.[7] Careful examination of product mixtures and isolated



components at low conversion showed no significant amounts (<1%) of 3, 4 or 5. Vinylindene 6, repeatably the major photoproduct of 1, proved identical with material prepared from 1 *via* flash pyrolysis, a reaction recently reported by Adam and DeLucci[8a] and studied independently by us.[8b] Presence of 6 in low conversion runs (<30%) was clearly established by ^{1}H NMR and through isolation by preparative VPC.[9] This product was not reported by Cerfontain *et al.*[2] for reasons which are not clear to us. Acetone sensitized irradiation of 1 (λ > 300 nm) proved ineffective, leading to the conclusion that we are observing singlet excited state reactions. Irradiation of 1 in methanol gave a product distribution similar to that observed in cyclohexane, except that secondary reactions of 6 (due to methanol photoaddition) led to its rapid disappearance.

Prolonged irradiation of 1 led predominantly to isolation of naphthalene and isomeric methylnaphthalenes as volatile components. Literature precedent,[10] reaction monitoring by VPC and ^{1}H NMR, and control experiments with pure 2[11] under the reaction conditions, all clearly showed naphthalene formation to be a secondary reaction proceeding through 2.



Irradiation of pure vinylindene 6 in cyclohexane yielded mostly nonvolatile material.

To elucidate the mechanism of these transformations, we have studied reaction of 1-D_2, prepared by the photochemical di-π-methane rearrangement described by Edman.[5] Low conversion (25-30%) direct irradiation of 1-D_2 afforded 2-vinylindene (6) labeled at the endocyclic vinyl and methylene positions, in proportions indicating essentially statistical transfer of deuterium to either side of the molecule. Benzonorcaradiene proved to be predominantly (*ca*. 80%) vinyl deuterated. Observed label distributions are consistent with a dominant mechanism involving initial cyclopropane ring cleavage to diradical 7, a reaction typical of phenylcyclopropanes.[12] Subsequent homolysis of bonds a or b yields isoindene 8 or isobenzotropilidene 9, which undergo [1,5] hydrogen (deuterium) shift or electrocyclic closure, respectively, to restore aromaticity and give the isolated products. Isobenzotropilidene 9 has been proposed as an intermediate in degenerate thermal isomerization of 2[13] and in its photochemical formation from 2,3-benzotropilidene.[14] Isoindene 8 is almost certainly involved in thermal isomerization of 1, in which case it may arise from concerted intramolecular retro Diels-Alder reaction.[8]

We are continuing to explore photoreactions of 1 and 3 and will report details of these studies in the near future.

ACKNOWLEDGEMENT is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research, and to the National Science Foundation for an NSF-URP fellowship to K.S. Davis.

References and Notes

(1) Current Chemical Abstracts naming for this compound is 1,1a,6,6a-tetrahydro-1,6-methanocycloprop[a]indene. For obvious reasons, we prefer the naming used here. This was named incorrectly as a tricyclohexene by Cerfontain *et al*.[2]

(2) A.P. Kouwenhoven, P.C.M. van Noort and H. Cerfontain, *Tetrahedron Letters*, 1745 (1981).

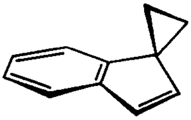
(3) Evidence for formation of 3 consisted solely of its VPC retention time.[2] No evidence was presented for benzotropilidenes 4 and 5 as photoproducts of 1.[2]

(4) Preliminary report: R.P. Johnson and K.S. Davis; Abstracts 16th Midwest Regional Meeting of the American Chemical Society, Lincoln, Nebraska, November 6-7, 1980.

(5) J.R. Edman, *J. Am. Chem. Soc.*, 91, 7103 (1969).

(6) Full details of these and other experiments will be presented in our full paper. This reaction is at least 100 times less efficient than triplet sensitization and thus should not interfere with use of the 3 → 1 reaction as a counter for thermally derived triplets: W. Adam, C.C. Cheng, O. Cueto, K. Sakanishi and K. Zimmer, *J. Am. Chem. Soc* 101, 1345 (1979). In a typical experiment, irradiation of 125 mg of 3 in 15 ml of spectroquality cyclohexane at 254 nm (Rayonet photoreactor) for 4.5 h afforded *ca*. 5% conversion to 1 and its photoproducts.

(7) Minor photoproducts (<2% each) were isolated by preparative VPC and characterized as 10 - 12. Compounds 10 and 11 appear to be secondary products, whereas 12 may arise from conrotatory opening of biradical 7 to a *trans* isobenzotropilidene followed by closure. These questions are under investigation.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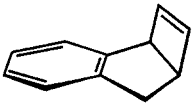
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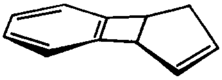
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(8) (a) W. Adam and O. DeLucci, *J. Org. Chem.*, 45, 4167 (1980); (b) W.S. Trahanovsky, K. Swenson and R.P. Johnson, *unpublished results*.

(9) 10% Carbowax 20M on Chromosorb W, 10' x 1/4", at 160 . All photoproducts described here were isolated.

(10) M. Pomerantz and G.W. Gruber, *J. Am. Chem. Soc.*, 89, 6798 (1967); G.W. Gruber and M. Pomerantz *ibid.*, 91, 4004 (1969).

(11) M. Pomerantz and G.W. Gruber, *Org. Photochem. Syn.*, 1, 23 (1971).

(12) For a comprehensive review of phenylcyclopropane photochemistry, see: S.S. Hixson, *Org. Photochem.*, 4, 191 (1979).

(13) E. Vogel, D. Wendisch and W.R. Roth, *Angew. Chem. Int. Ed. Engl.*, 3, 443 (1964).

(14) M. Pomerantz and G.W. Gruber, *J. Org. Chem.*, 33, 4501 (1968).

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