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PHOTOCHEMICAL REDUCTIONS OF NORBORNENES

R. R. Sauers, W. Schinski, and M. M. Mason

Department of Chemistry, Rutgers, The State University

New Brunswick, New Jersey 08903

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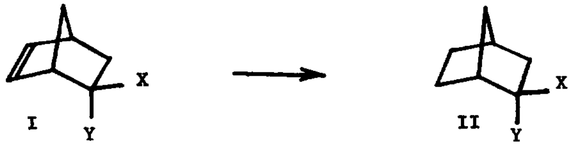
We would like to report some preliminary results involving photochemically-induced reduction of several norbornenes (I) to norbornanes (II) (1). Irradiation (2) of various derivatives of I (X=H, Y=CN; X=CN, Y=H; X=Y=H, X,Y=H,OH; X,Y=H,CO_2CH_3) in dilute (0.1-2 %) solutions of ether, cyclohexane, trimethylpentane, or mixtures of these (3) led to 16-25 % yields of the corresponding norbornanes (4).

The reduction could also be effected by irradiation of acetone solutions of I with pyrex-filtered light. For example, norbornene (I, X,Y=H,H) was converted to norbornane (II, X,Y =H,H) in 25 % yield under these conditions. Other products of this reaction were 2,2'-bi-norbornyl, 2-exo-acetonylnorbornane, norbornene dimers and 2,5-hexanedione (5).

Attempted intramolecular sensitization of the reduction (6) by irradiation of 2-exo-acetyl-5-norbornene in cyclohexane led to high molecular weight products only. Similar treatment of the corresponding endo-isomer produced an oxetane, but no reduction(7).

Free radicals would appear to be the most likely intermediates in these reductions. Very likely, the exited double bonds initiate the reactions by abstraction of hydrogen atoms from the solvents(1). The reductions in acetone probably involve norbornene triplets produced via energy transfer. Abstraction of hdyrogen from acetone would lead to norbornyl radicals and acetonyl radicals. In dilute solution, norbornyl radicals could abstract a second hydrogen atom in competition with the various radical re-combination reactions(8,9).



While photochemically induced reductions of conjugated and homoconjugated double bonds have been reported (10), these results and those of Kropp (1) represent the first examples of reductions of simple olefins. That this novel reaction has not been reported previously is attributable in part to the low concentrations used in this study. In addition, many of the earlier studies with norbornenes have dealt with systems which were able to undergo unimolecular reactions, e.g. intramolecular cycloaddition or rearrangement, in preference to hydrogen abstraction (11). Investigations on the scope of these reactions are continuing.

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REFERENCES

1. During the preparation of this manuscript, P. J. Kropp, J. Am. Chem. Soc., **89**, 3650(1967) reported some closely related results.
2. A 450-w Hanovia immersion lamp was used throughout. Vycor or no filters were used in the direct irradiations.
3. Typically, 6 g. of I (X=H, Y=CN) in 1.2 l of a 1:1 mixture of ether and cyclohexane was consumed in 17 hrs.
4. Numerous higher molecular weight products were formed which were not identified. Norbornene dimers and 2,2'-binorbornyl were identified by comparisons of retention times on two columns (Ucon and Apiezon L) with those of authentic samples. Reduction products were isolated and identified by comparisons of infrared and/or nmr spectra with known samples.
5. D. Scharf and F. Korte, Tetrahedron Letters, No. 13, 821(1963). W. Reusch, J. Org. Chem., **27**, 1882(1962). D. R. Arnold, D. J. Trecker, and E. B. Whipple, J. Am. Chem. Soc., **87**, 2596(1965).
6. H. Morrison, ibid., **87**, 932(1965).
7. The structure of this oxetane will be discussed separately. Dr. P. J. Kropp has informed us that he has also isolated this product.
8. The possibility that ketyl radicals initiate the reductions in acetone cannot be eliminated.
9. Photolyses in diethyl ether led to formation of 2,3-diethoxybutanes. Cf. M. K. N. Ng and G. R. Freeman, ibid., **87**, 1635(1965). A free radical mechanism has been postulated for

some light-catalyzed additions of alcohols to olefins. See W. H. Urry, F. W. Stacey, E. S. Huyser, and O. O. Juveland, *ibid.*, **76**, 450(1954).

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