Tetrahedron Letters No. 51, pp 4895 - 4898. 0040-4039/79/1215-4895$02.00/0

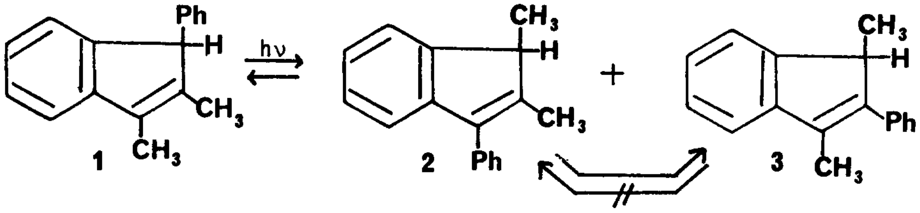
ON THE MECHANISM OF THE PHOTOISOMERIZATION REACTION OF ARYL SUBSTITUTED INDENES

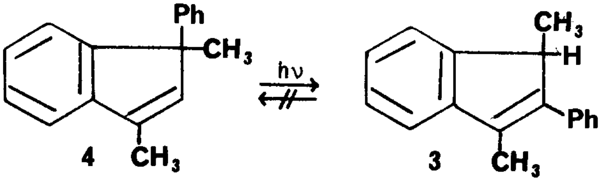
Albert Padwa*, Steven Goldstein, Roman Loza and Mitchell Pulwer
Department of Chemistry, Emory University
Atlanta, Georgia 30322

Abstract: The mechanism of the phototransposition reaction of a number of arylalkyl substituted indenes has been found to be markedly dependent on the nature and location of the substituent groups.

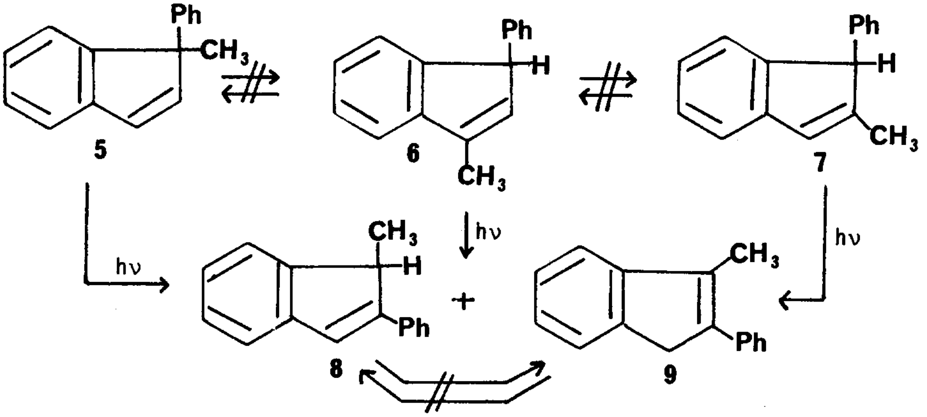
Considerable interest has been focused in recent years on phototransposition reactions which have the net effect of interchanging atoms within a five-membered ring[1]. Examples have been reported for variously substituted heterocycles[2] and cyclopentadiene derivatives[3]. Bicyclo[2.1.0]pent-2-enes and 3-vinylcyclopropene analogs are the most commonly invoked intermediates responsible for these rearrangements; in some instances, such molecules have been detected and characterized.[4] Recently, we described the photochemical rearrangement of indenes in which the sp^3 and adjacent sp^2 atoms were interchanged.[5] Similar skeletal rearrangements had also been reported by Morrison and coworkers.[6] Because of the intriguing nature of this reaction, we wished to explore its generality, its limitations, and structural effects governing the reaction course.[4] This communication summarizes some of our observations in this area with particular reference to the mechanism of the reaction.

Irradiation of 1-phenyl-2,3-dimethylindene (1) in benzene for 1 hr under an argon atmosphere gave a 1:2 mixture of 1,2-dimethyl-3-phenyl (2) and 1,3-dimethyl-2-phenylindene (3). The structures of these indenes were unambiguously confirmed by comparison with authentic samples. Irradiating a sample of indene 2 under similar conditions resulted in the isolation of 3 (95%). The formation of 3 from 2 was due to the conversion of 2 back to 1 which was further transformed to 3 under the reaction conditions.[7] Photolysis of the isomeric indene 4 also gave 3 as the exclusive photoproduct. These reactions proceed exclusively in one direction since the irradiation of indene 3 resulted in recovered starting material, even under lengthy photolytic conditions.

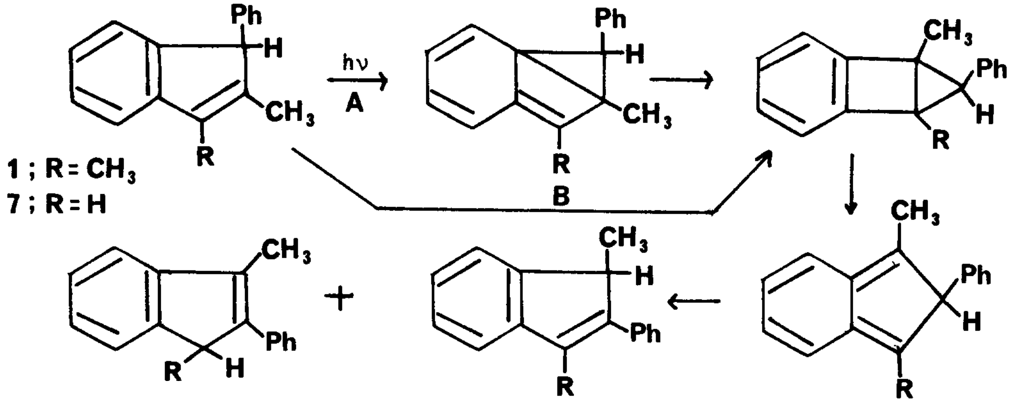




Additional examples of this type of rearrangement were provided by the photolysis of indenes 5, 6 and 7. In all of these cases, the same two rearranged compounds (i.e. 8 and 9) were formed in the same ratio (8:9 = 2:1). Appropriate control experiments established that no photoisomerization of either the starting materials or the products was operative under the reaction conditions.

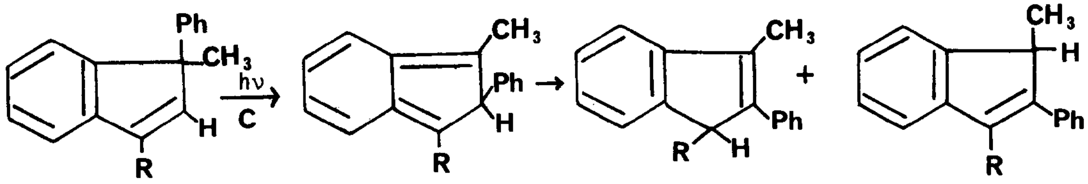


Two possible mechanisms have been suggested to rationalize the interconversions observed on irradiation of alkyl substituted indenes.[6] These consist of a multistep process involving initial $[\Pi^2 + \Pi^2]$ intramolecular cycloaddition (path A) and a "conjugated di-Π-methane" rearrangement (path B). Both of these pathways lead to an isoindene intermediate which undergoes a subsequent 1,5-sigmatropic hydrogen shift. The rearrangement of indenes 1 and 7 can be formulated in exactly parallel fashion using either of the two mechanisms.



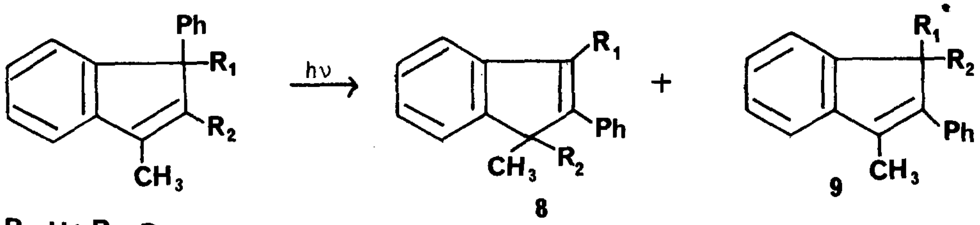
1 ; R = CH$_3$
7 ; R = H

It is particularly interesting to note that the photoisomerization of indenes 4 and 5 do not follow the same reaction mechanism. With these two systems the rearrangement proceeds via 1,2-phenyl migration (path C) as shown below. This process is analogous to that previously described by Miller[8] and McCullough[9] for the thermolysis of 1,1-diaryl substituted indenes.



4 ; R = CH$_3$
5 ; R = H

With indene 6, both the housene path and the 1,2-phenyl migration route lead to the same set of products. However, a skeletal difference exists. The housene path interchanges C-1 and C-2 of the indene ring while with phenyl migration no such skeletal change occurs. There is good evidence suggesting that the 1,2-phenyl migration route is the predominant path followed with indene 6. Irradiation of 6 labeled with deuterium at C-2 (i.e. 10) gave a mixture of 8 and 9 in good yield. Examination of the NMR spectrum of 8 showed a methyl singlet at δ 1.35 and a less intense (10%) doublet centered at δ 1.35. Similarly, irradiation of deuterium labeled indene 11 also resulted in the formation of 8 and 9. In this case, the methyl doublet for 8 amounted to 90% of the total formed by it and the singlet at δ 1.35. These observations clearly



10 ; R_1= H ; R_2= D
11 ; R_1= D ; R_2= H

demonstrate that the photoisomerization of 6 goes mainly by the phenyl migration route (90%) and to a small but real extent (10%) by the housene mechanism. Our results indicate that the mechanism followed in the photoisomerization of aryl substituted indenes is markedly dependent on the nature and location of the substituent groups present on the ring.

We are continuing to explore the scope and mechanistic details of this novel phototransposition reaction and will report additional findings at a later date.

Acknowledgment: We wish to thank the National Science Foundation for generous support of this work.

References

(1) A. Lablache-Combier, "Photochemistry of Heterocyclic Compounds," O. Buchardt, Ed., J. Wiley and Sons, N.Y., N.Y., 1976, p. 123.
(2) Some examples include (a) P. Beak and W. Messer, Tetrahedron, 25, 3287 (1969); (b) M. Kojima and M. Maeda, Tetrahedron Lett., 2379 (1969); (c) W. M. Williams and W. R. Dolbier, J. Am. Chem. Soc., 94, 3955 (1972); (d) J. A. Barltrop, A. C. Day and R. W. Ward, Chem. Commun., 131 (1978); (e) H. Wynberg, R. M. Kellog, H. van Driel and G. E. Beekhuis, J. Am. Chem. Soc., 89, 3501 (1967); (f) H. Tiefenthaler, W. Dorscheln, H. Goth and H. Schmid, Helv. Chim. Acta, 50, 2244 (1967).
(3) G. D. Andrews and J. E. Baldwin, J. Am. Chem. Soc., 99, 4851 (1977); D. M. Golden and J. I. Brauman, Trans. Faraday Soc., 65, 464 (1969); H. E. Zimmerman and M. C. Hovey, J. Org. Chem., 44, 2331 (1979).
(4) For some examples see (a) E. F. Ullman and B. Singh, J. Am. Chem. Soc., 89, 6911 (1967); (b) G. L. Closs, W. A. Boll, H. Heyn and V. Dev., J. Am. Chem. Soc., 90, 173 (1968); (c) S. T. Reid, Adv. Heterocycl. Chem., 11 1 (1970); (d) E. E. van Tamelen and T. H. Whitesides, J. Am. Chem. Soc., 93, 6129 (1971).
(5) A. Padwa, R. Loza and D. Getman, Tetrahedron Lett., 2847 (1977); J. Org. Chem., 43, 1481 (1978).
(6) F. J. Palensky and H. A. Morrison, J. Am. Chem. Soc., 99, 3507 (1977); D. Giacherio and H. Morrison, ibid, 100, 7109 (1978).
(7) The conversion of 1→2 (and 2→1) could either involve a simple 1,3-H shift or a more complicated mechanism involving a housene intermediate.[5,6] Further work needs to be done in order to establish this point.
(8) L. L. Miller and R. F. Boyer, J. Am. Chem. Soc., 93, 650 (1971).
(9) J. J. McCullough and M. R. McClory, J. Am. Chem. Soc., 96, 1962 (1974).

(Received in USA 6 September 1979)