Arylcyclopropane Photochemistry. Hydroxide Ion as a Leaving Group in the Photochemistry of Certain Arylcyclopropylcarbinyl Alcohols.

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Summary Arylcyclopropylcarbinyl alcohols (**1**) and (**2**) rearrange to the homoallyl alcohols (**3**) and (**4**) when irradiated in cyclohexane and form homoallyl ethers (**8**) and (**9**) in addition to (**3**) and (**4**) when irradiated in methanol.

WE have found that 2-arylcyclopropylcarbinyl acetates rearrange photochemically to homoallyl acetates in cyclohexane and form homoallylic solvolysis products, in addition to the rearranged acetates, when irradiated in methanol.[1] All evidence points to ionic mechanisms for the rearrangements and solvolyses.[1,2]

We now report that analogous rearrangements and solvolyses occur upon photolysis of certain arylcyclopropylcarbinyl alcohols. These processes are much more striking than the acetate rearrangements in that they appear to involve elimination of hydroxide ion, a notably poor leaving group.

Irradiation† of a N_2-purged cyclohexane solution of the *endo*-alcohol (**1**) resulted in rapid isomerization to the *exo*-alcohol (**2**) and less efficient conversion into a 2:1 mixture of two other major products (at low conversion) (**3**) and (**4**).[3] Products (**3**) and (**4**) were identified by reducing their mixture to a 2:1 mixture of alcohols (**5**) and (**6**); the latter

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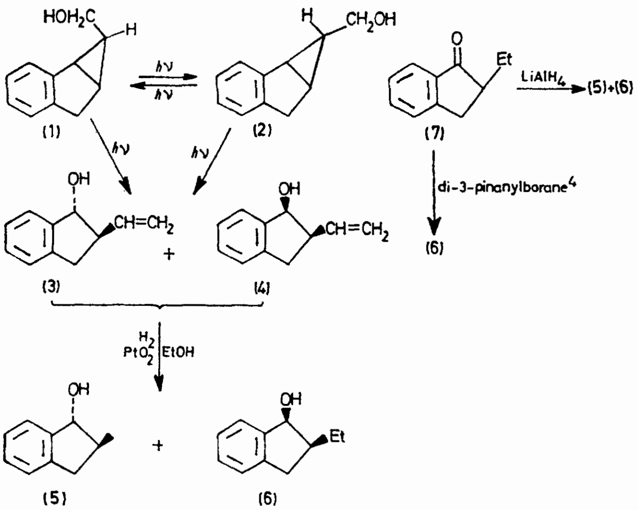
† Vycor-filtered light from a Hanovia 450-W medium pressure Hg arc was used.

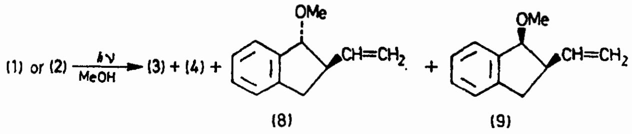
were, in turn, prepared from 2-ethylindanone (**7**). (Scheme 1.) The rearrangement of (**1**) to (**3**) and (**4**) likewise proceeds in the presence of $NaHCO_3$. We are therefore not dealing with an acid-catalysed thermal process.[5] The efficiency of rearrangement is the same at 0·017 and 0·072 M of (**1**).



SCHEME 1

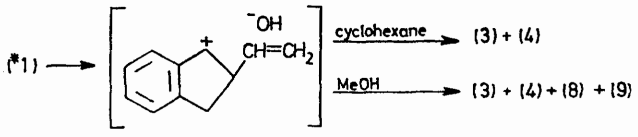
The *exo*-alcohol (**2**) also forms (**3**) and (**4**) upon irradiation. However, the efficiency of rearrangement is much less than that of (**1**): $\phi\ [(\mathbf{1}) \rightarrow (\mathbf{3}) + (\mathbf{4})]/\phi\ [(\mathbf{2}) \rightarrow (\mathbf{3}) + (\mathbf{4})] \geqslant 7$. We find no evidence for a corresponding photochemical cyclopropylcarbinyl–homoallyl rearrangement with 2-phenylcyclopropylcarbinyl alcohol. Acetone sensitization of both (**1**) and (**2**) resulted in *exo* ⇌ *endo* isomerization but no rearrangement to (**3**) or (**4**).[3]

When the *endo* alcohol (**1**) was irradiated in methanol solution, the ethers (**8**) and (**9**) were isolated in a 5 : 4 ratio, in addition to (**3**) and (**4**). Repetition of the photolysis in the presence of 0·1 M NaOMe gave similar results (the solution was still basic after photolysis). The *exo*-alcohol (**2**) likewise forms (**3**), (**4**), (**8**), and (**9**) when irradiated in methanol (Scheme 2).



SCHEME 2

The fact that a mixture of (**3**) and (**4**) is produced at low conversion from both (**1**) and (**2**) means that a concerted 1,3 migration of –OH cannot be the only mechanism for rearrangement that is operative. The production of solvolysis products (**8**) and (**9**) from (**1**) and (**2**) in methanol provides strong evidence for the formation of a carbonium ion. Our results seem best rationalized by Scheme **3** involving initial formation of the ion pair (**10**) from photoexcited (**1**) or (**2**) followed by collapse of (**10**) to (**3**) and (**4**) in cyclohexane. In methanol, attack by solvent on the ion pair occurs to give (**8**) and (**9**). It is clear that the loss of excitation energy which must be occurring upon conversion of the singlet (^1S) state of (**1**) or (**2**) into (**10**) provides considerable driving force for a normally very unfavourable process.



(10)

SCHEME 3

We thank the donors of the Petroleum Research Fund administered by the American Chemical Society for financial support.

(*Received*, 28*th April* 1975; *Com.* 483.)

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[1] S. S. Hixson, *J.C.S. Chem. Comm.*, 1974, 681.

[2] S. S. Hixson and R. E. Factor, unpublished results.

[3] S. S. Hixson and J. Borovsky, *J. Amer. Chem. Soc.*, in the press.

[4] H. C. Brown and V. Varma, *J. Org. Chem.*, 1974, **39**, 1631.

[5] R. Beugelmans and H. C. deMarcheville, *Chem. Comm.*, 1969, 241; S. J. Cristol, G. A. Lee, and A. L. Noreen, *Tetrahedron Letters*, 1971, 4175.