The Acid-catalysed Photodehydration of a Dihydropyran

By A. G. SCHULTZ† and R. H. SCHLESSINGER*‡

(*Department of Chemistry, University of Rochester, Rochester, New York* 14627)

Summary Photolysis of pyran (I) under acidic conditions affords the hydrocarbon 1,2-diphenylacenaphthylene (II): this unusual photodehydration seems to involve the triplet state of (I) and does not occur in the absence of acid.

WE have been studying the photochemical behaviour of *peri*-substituted naphthalene derivatives,[1] and describe here a photoreaction of the *cis*-pyran (I).[2] Photolysis§ (>290 nm light, 6 h) of (I) (1×10^{-2} M) in dry deoxygenated benzene solution saturated with anhydrous HCl gas produced a mixture of 1,2-diphenylacenaphthylene (II)[3] (40% yield) and unchanged (I) (58% yield). Prolonged photolysis of (I) under these conditions did not significantly increase the amount of (II in the reaction mixture. No other products such as ketone (III),[4] *trans*-pyran (IV),[5] or the *cis*- and *trans*-alcohols (V) and (VI)[6] were found on careful chromatographic and spectroscopic examination of the reaction mixture. No photoreaction of (I) occurs either in benzene with HCl gas absent or in methanol with and without HCl gas present. Also, pyran (I) was found to be indefinitely stable in all of these solutions in the dark.

Sensitized irradiation of (I) (366 nm light)§ using benzophenone in benzene solution (HCl gas added) gave hydrocarbon (II) together with unchanged pyran. No photoreaction occurred at 366 nm with the sensitizer absent. These data suggest that photodehydration proceeds *via* the

---

† NDEA fellow.

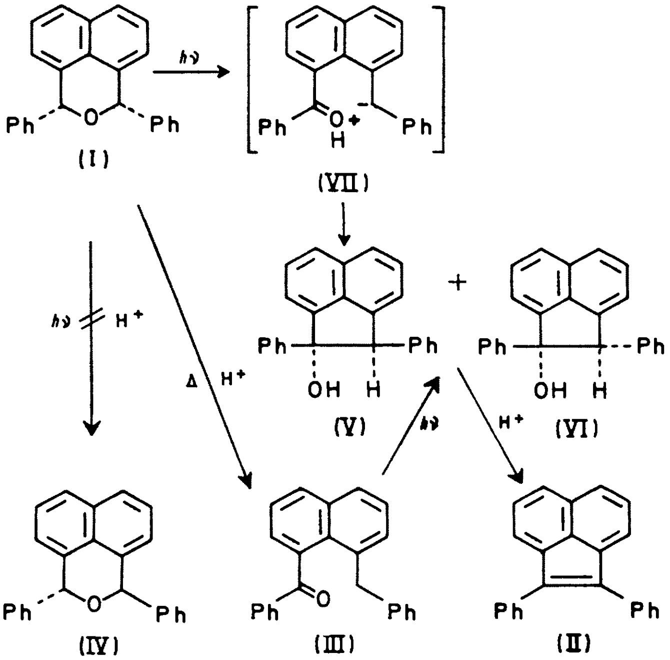
‡ Alfred P. Sloan fellow.

§ A water-cooled Hanovia Type L 450-w medium-pressure lamp fitted with Pyrex filters was used as the light source for the 290 nm experiments. The same lamp fitted with Corning colour filters 0-52 and 7-54 was employed as the 366 nm light source. All photolyses were carried out at 23°.

triplet state of (I). Hence, the observation that (I) is not completely converted into (II) is reasonable since the hydrocarbon, at modest concentrations, should quench the triplet state of the pyran.

Initially, ketone (III) was considered to be a possible intermediate in the photodehydration of (I) into (II). Ketone (III) was known to undergo a ready triplet-state reaction to give the alcohols (V) and (VI),[6] and these alcohols were known to undergo rapid acid-catalysed conversion into hydrocarbon (II).[6] The photoreaction of (III) [formation of (V) and (VI)] was known to be completely inhibited by very low concentrations of quenchers including oxygen.[6] For example, photolysis of (III) in benzene solutions exposed to the atmosphere gave no reaction, whereas, vigorously degassed benzene solutions of (III) efficiently gave the alcohols (V) and (VI).[6] This suggested that the intermediacy of (III) in the reaction (I) → (II) could be examined by photolysis of (I) in the presence of small amounts of dissolved oxygen. Under these conditions a build-up of (III) at the expense of hydrocarbon (II) was anticipated. When irradiation of (I) in HCl-saturated benzene was carried out with oxygen present, hydrocarbon (II) was formed somewhat more slowly than the same reaction run without oxygen, and no detectable amount of ketone (III) was present. The photoreaction of ketone (III) was completely quenched in control experiments run under acidic conditions and exposed to the atmosphere. These data seem to rule out (III) as a viable reaction intermediate and lead us to suggest that the transformation (I) → (II) probably occurs *via* the ionic species (VII) to give alcohols (V) and (VI) which then undergo rapid dehydration into hydrocarbon (II).[7]

It is interesting to contrast the thermal behaviour of pyran (I) in acidic medium with its photobehaviour in acid. Treatment of the pyran with either HCl gas or toluene-*p*-sulphonic acid in xylene solution under reflux slowly gives ketone (III) in nearly quantitative yield. Thus, a marked difference is observed between the ground-state and triplet-state reactivities of (I) with acid.



We thank the Office of Naval Research at the University of Rochester, the Petroleum Research Fund administered by the American Chemical Society, and the National Science Foundation for support of this work.

(*Received, June 22nd,* 1970; *Com.* 977.)

---

[1] A. G. Schultz and R. H. Schlessinger, *Chem. Comm.*, 1969, 1483.

[2] R. L. Letsinger and P. T. Lansbury, *J. Amer. Chem. Soc.*, 1959, **81**, 935.

[3] G. Wittig, M. Leo, and W. Wiemer, *Ber.*, 1931, **64**, 2405.

[4] A. G. Schultz, C. D. DeBoer, and R. H. Schlessinger, *J. Amer. Chem. Soc.*, 1968, **90**, 5314.

[5] A. G. Schultz, unpublished work.

[6] A. G. Schultz and R. H. Schlessinger, in the press.

[7] The absorption spectrum of (I) in benzene solution is the same with or without HCl gas present. Hence, it is not known if (I) undergoes protonation before or after photoexcitation. For other examples of acid-catalysed photoreactions, see D. Bryce-Smith, R. Deshpande, A. Gilbert, and J. Grzonka, *Chem. Comm.*, 1970, 561, and references cited therein.