

VINYL CATIONS AS INTERMEDIATES IN PHOTOHYDRATION OF ACETYLENES

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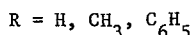
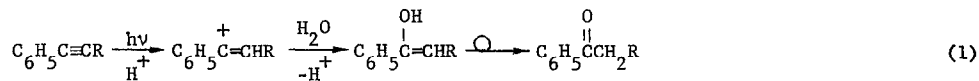
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Vinyl cations are of current interest for their unusual reactivity, novel structure and unknown chemistry.¹ Protonation of acetylenes yields vinyl cations which are rapidly hydrated to ketones.² Unfortunately the acid concentration which is necessary to obtain respectable rates for many acetylenes precludes use of delicate functional groups. Further little use has been made of this method of preparation of vinyl cations. If a method can be devised for rapid protonation of acetylenes to vinyl cations under much milder conditions, the state of the art should be advanced. Three observations in the literature suggest a new experiment concerning irradiation of acetylenes under mild conditions to yield vinyl cations. First, the lowest excited state of acetylenes may have a "bent" trans configuration,³ which closely approximates at least part of the structure of a vinyl cation.¹ Second, since aryls containing α,β unsaturated groups increase their basicity markedly on excitation,⁴ phenylacetylenes should protonate more rapidly in an excited state than in the ground state. Third, since some molecules in the excited state can be protonated intermolecularly prior to fluorescence or intersystem crossing,⁴ phenylacetylenes might also be protonated to vinyl cations upon excitation. Described herein are first experiments designed to test the hypothesis that photoprotonation of acetylenes provides vinyl cations under conditions where acetylenes do not react thermally.

Four available phenylacetylenes were chosen and irradiated at 254 nm in quartz as ca. 0.02 M. solutions in acidic (ca. 0.5 N) aqueous (ca. 25% water) acetonitrile under nitrogen. For example, diphenylacetylene (1.8 g, 0.01 m) was irradiated for 7 hr. Workup yielded a yellow oil which when subjected to GLC gave deoxybenzoin (46%) and starting material (54%). The structure of the product in each case was established by comparing physical and spectral properties to those of authentic samples. In the first three cases the product ketone is that predicted by polar or Markownikoff addition of water to the acetylene bond to yield an enol followed by ketonization (See Equation 1). The fourth case, 1,4-diphenylbutadiyne, also yields the product of polar addition, benzyl phenylethynyl ketone. In each case postulation of the most stable vinyl cation as a precursor of the enol suitably explains orientation of

addition. No other products corresponding to addition of water are found.⁵ These reactions do not progress in the dark under these conditions.



A second piece of evidence is derived from studies of the effect of acid.⁶ Solutions of diphenylacetylene, 0.02 M, in aqueous (25% water by volume) acetonitrile with varying amounts of acid were irradiated for exactly two hours. The amount of deoxybenzoin which was formed was measured by GLC techniques. When the acid concentration was 0.0, reaction was not detectable in two hours. (After irradiation for 27 hrs without acid, 11% deoxybenzoin had formed.) When the acid concentration was 0.05 N, 5% reaction had occurred. An acid concentration of 0.5 N yielded 26% reaction. A 1.0 N acid solution gave 32% in the two hour period. If small amounts of sodium hydroxide are added instead of acid, addition of water does not occur, even after 24 hr of irradiation. This data can also be suitably rationalized by invoking first protonation of the excited acetylene to form a vinyl cation and then addition of water to give an enol (Equation 1).

Finally postulation of an intermediate vinyl cation suitably explains two previous reports concerning photoaddition of methanol and acetic acid to diphenylacetylene.⁷

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1. G. Modena and U. Tonellato in "Advances in Physical Organic Chemistry," Vol. 9, V. Gold, Ed., Academic Press, New York, N.Y., 1971, p 185-274. 2. D. S. Noyce and M. D. Schiavelli, J. Amer. Chem. Soc., 90 1020, 1023 (1968). 3. C. K. Ingold and G. W. King, J. Chem. Soc., 2702 (1953). 4. A. Weller in "Progress in Reaction Kinetics", Vol. 1, G. Porter, Ed., Pergamon Press, New York, N.Y., 1961, Chapter 7. 5. If reaction times are kept short, less than 8 hrs, then only ketones result. As these ketones build up in concentration, products of their photo-reactions begin to appear. Some new chemistry from these latter reactions will be reported in the full paper. 6. Although temperature of the reaction vessel and light intensities were not rigidly monitored, the small variations which are possible should not cause the large effects noted. Thus the trends noted are real. 7. T. D. Roberts, L. Ardemagni, and H. Shechter, J. Amer. Chem. Soc., 91, 6185 (1969); T. D. Roberts, Chem. Commun., 362 (1971).