

## References and Notes

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- (19) We would like to thank Ms. Andrea Stencil and Ms. Louise Hellwig for synthesizing the 3-bromorifamycin S and the 8-O-methyl ether rifamycin S.

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# Novel Polar Photochemical Additions of Acetic Acid to Phenylallenes

Sir:

Photochemical polar addition of a protic solvent to a multiple bond has been one of the most intriguing research subjects.<sup>1</sup> The addition reaction may be divided into two categories (A and B) on the basis of the type of the excited state involved. (A) The reactions of medium size cycloalkenes or strained cycloalkynes seem to proceed through both the triplet excited state<sup>1a-j</sup> and the singlet excited state, although the reaction via the singlet excited state is rather exceptional.<sup>1c</sup> (B) The reactions of acyclic alkenes or acyclic alkynes appear to proceed through the singlet excited state.<sup>1i-w</sup> However, regardless of the multiplicity of the excited state, photochemical polar addition to a multiple bond unconjugated to an electron-withdrawing group occurs generally in the Markownikoff fashion.<sup>2</sup>

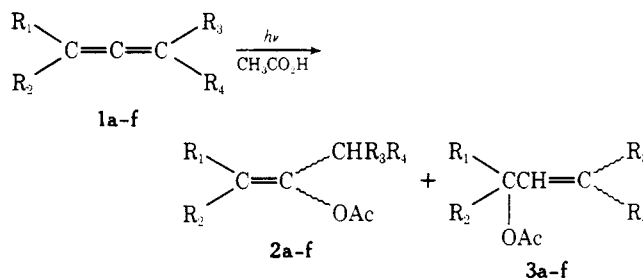
In the present study, we wish to report the first observation of the photochemical polar addition of acetic acid to phenylallenes.

**Table I.** The Product of the Photochemical Addition of Acetic Acid to Allenes

Allene	Irradiation period (hr)	Product <sup>a</sup> (%)	Recovered <sup>a</sup> allene (%)
<b>1a</b>	70	<b>3a</b> (3)	<b>1a</b> (75)
<b>1b</b>	72	<b>2b</b> (2)	<b>1b</b> (74)
<b>1c</b>	48	<b>2c</b> (65)	<b>1c</b> (31)
<b>1d</b>	48	<b>2d</b> (45)	<b>1d</b> (47)
<b>1e</b>	48	<b>2e</b> (40)	<b>1e</b> (51)
<b>1f</b>	96	Trace	<b>1f</b> (nq) <sup>b</sup>

<sup>a</sup> The percentage is based on the amount of the allene initially used. <sup>b</sup> Nearly quantitative.

A solution of an allene (0.5 M) in acetic acid was irradiated with a 15-W low-pressure mercury lamp (mainly 254 nm) to give an enol acetate or an allyl acetate (Table I).<sup>3</sup> The allenes **1a-f** were stable under conditions identical with those of the irradiations except for the absence of light.



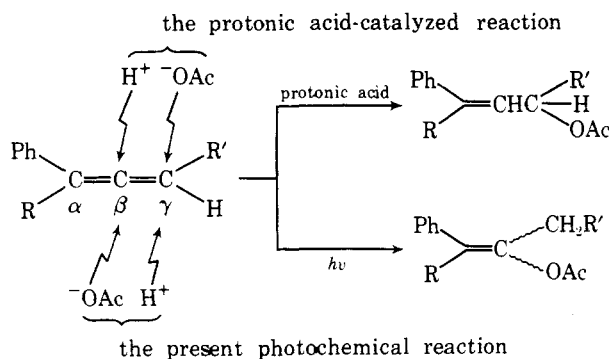
- a,  $\text{R}_1, \text{R}_3 = (\text{CH}_2)_6$ ;  $\text{R}_2 = \text{R}_4 = \text{H}$   
b,  $\text{R}_1 = n\text{-C}_6\text{H}_{13}$ ;  $\text{R}_2 = \text{R}_3 = \text{R}_4 = \text{H}$   
c,  $\text{R}_1 = \text{Ph}$ ;  $\text{R}_2 = \text{Me}$ ;  $\text{R}_3 = \text{R}_4 = \text{H}$   
d,  $\text{R}_1 = \text{Ph}$ ;  $\text{R}_2 = \text{R}_3 = \text{Me}$ ;  $\text{R}_4 = \text{H}$   
e,  $\text{R}_1 = m\text{-MeOPh}$ ;  $\text{R}_2 = \text{Me}$ ;  $\text{R}_3 = \text{R}_4 = \text{H}$   
f,  $\text{R}_1 = m\text{-CF}_3\text{Ph}$ ;  $\text{R}_2 = \text{Me}$ ;  $\text{R}_3 = \text{R}_4 = \text{H}$

Although about 90% of the photochemical reaction of **1c** (0.5 M) could be quenched by 1,3-pentadiene (0.5 M), about 10% of the reaction remained even though the concentration of the quencher was increased above 0.5 M.<sup>4</sup> Furthermore, sensitization of the reaction by xanthone was observed when the reaction mixture was irradiated with uv light (>300 nm) which is not absorbed by the allene **1c**. These facts indicate that the reaction of **1c** seems to proceed mainly through the excited triplet state.

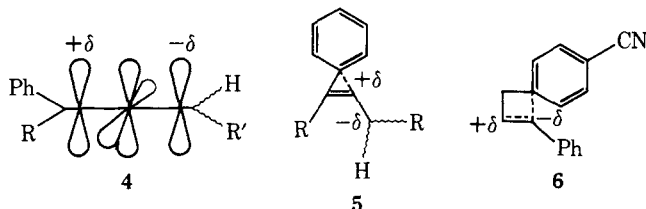
In the reactions of the aliphatic allenes **1a** and **1b**,<sup>5</sup> the products, **3a** and **2b**, were the same as those obtained from the nonphotochemical reaction of the corresponding allenes with acetic acid in the presence of a trace amount of sulfuric acid. In contrast, the results of the photochemical reactions of the phenylallenes **1c**, **1d**, or **1e** were quite different from those of the known protonic acid-catalyzed reactions<sup>6</sup> (Scheme I), in which the initial attack of a proton was reported to occur at the central carbon ( $\beta$ ). On the other hand, in the photochemical addition to **1c-e**, proton attack is observed on the terminal carbon ( $\gamma$ ). It is interesting to note that although styrene type olefins are well known to be far more reactive than simple olefins, the nonconjugated olefinic part ( $\text{C}_\beta=\text{C}_\gamma$ ) was the exclusive reaction site in the present reactions. The marked difference between the yields of the reactions of **1a-b** and those of **1c-e** clearly indicates the remarkable effect of the phenyl group on the reaction.<sup>5</sup> Furthermore, metasubstitution of a strongly electron-withdrawing group ( $\text{CF}_3$ ) on the phenyl ring retarded dramatically the photochemical reaction.

From these observations, it might be suggested that a polarized excited state such as **4** or **5** is involved in the reaction. The tentative species **4** or **5** could rationalize the regioselective addition of acetic acid and the inertness of **1f**.

Scheme 1



Species **4** is similar to that investigated theoretically as a lowest excited state structure of an allene.<sup>7</sup> The tentative structure **5** conceptually resembles the zwitterionic species **6** which was suggested in the anti-Markownikoff photochemical addition of methanol to 3-(*p*-cyanophenyl)-1-phenylpropene<sup>10,p</sup> and resembles the vinylidene phenonium ion which was investigated in the solvolyses of 3-phenyl-2-buten-2-yl triflates.<sup>8</sup>



Thus, the photochemical polar additions of acetic acid to the phenylallenes possess two characteristic aspects. (1) The regioselectivity observed in the photochemical reactions of phenylallenes is quite different from that of the nonphotochemical protonic acid-catalyzed reactions. (2) These photochemical reactions seem to proceed mainly through the triplet excited state even though the structure of the allene is acyclic.

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- (3) All of the products were characterized by NMR, ir, and mass spectra and identified with the corresponding authentic specimens prepared independently.
- (4)  $\epsilon_{254}$  was estimated to be 50 for *trans*-1,3-pentadiene and 20 for *cis*-1,3-pentadiene in a polar solvent (S. L. Murov, "Handbook of Photochemistry", Marcel Dekker, New York, N.Y., 1973, p 5) while  $\epsilon_{254}$  of **1c** was  $1.3 \times 10^4$  in methanol or  $1.4 \times 10^4$  in *n*-hexane. Under the condition of this quenching experiment, the quencher absorbs at most 1% of the light (254 nm). Therefore the observed quenching of the reaction of **1c** cannot be accounted for by the absorption of the quencher. The preliminary Stern-Volmer plot ( $\Phi_0/\Phi_{\text{quencher}}$  vs. [quencher]) showed a typical pattern suggesting that two excited states are involved in the addition.
- (5) The absorbances of **1a** and **1b** at 254 nm are very weak.  $\epsilon_{254}$  of **1a**: 15 (MeOH), 10 (*n*-hexane).  $\epsilon_{254}$  of **1b**: 8 (MeOH), 4 (*n*-hexane). The differ-

ence of reactivity between **1a-b** and **1c-e** seems to be attributable to the difference in absorption.

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## Acid Dissociation of Chloroform and Phenylacetylene. Solvent Isotope Effects<sup>1</sup>

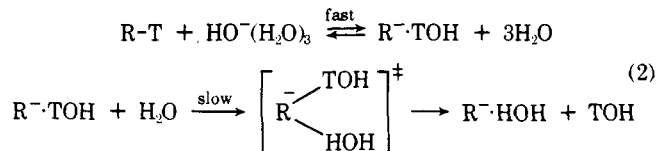
Sir:

Kinetic isotope effects are frequently used to gauge transition state structure, and in particular to estimate the extent of proton transfer at transition states of proton transfer reactions. Use of the solvent isotope effect on proton transfer to the aqueous hydroxide ion, eq 1,



in this way, however, is complicated by the possibility that one of the three water molecules in the primary solvation shell of this ion, which is where most of the isotope effect resides, must be completely removed before proton transfer can begin. However, this complication will play a decreasingly important role as the degree of proton transfer increases, and it should vanish entirely when proton transfer becomes complete, i.e., reactions in which proton transfer is finished by the time the rate-determining transition state is reached should give a full or equilibrium value of this isotope effect.

It is curious, therefore, that the detritiation of phenylacetylene, a seemingly uncomplicated example of this reaction type, has been reported to give an effect which falls considerably short of the expected limiting value. In this reaction, hydrogen ion transfer is believed to be rapid and reversible while subsequent exchange of the transferred hydrogen with the solvent pool is slow (eq 2);<sup>2</sup> proton transfer



is therefore complete at the rate-determining transition state.<sup>3</sup> In an early study of this reaction,<sup>4</sup>  $k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}}$  was found to be 1.60,<sup>5</sup> and yet a limiting value half again as large,  $k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}} = 2.4$ , can be reliably estimated from the measured effect on the autoprotolysis of water and the known fractionation factor of the hydronium ion.<sup>6</sup>

We wish to report that we have corroborated this unexpected behavior and that we have also done further experiments which provide an explanation for the apparent anomaly. We find  $k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}} = 1.36$  for the detritiation of phenylacetylene and also  $k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}} = 1.48$  for the experimentally more accessible detritiation of chloroform, another reaction thought to occur by the same mechanism (eq 2).<sup>7</sup> This value for chloroform is listed in Table I together with three other isotope effects we have measured for the hydrogen exchange of this substance catalyzed by hydroxide ion. In these other experiments (systems II-IV), tritium was