Tetrahedron Letters No. 4, pp 277 - 280, 1973. Pergamon Press. Printed in Great Britain.

# THE PHOTOCHEMICAL ADDITION OF METHANOL TO ACYCLIC STYRENES

**Stephen S. Hixson**

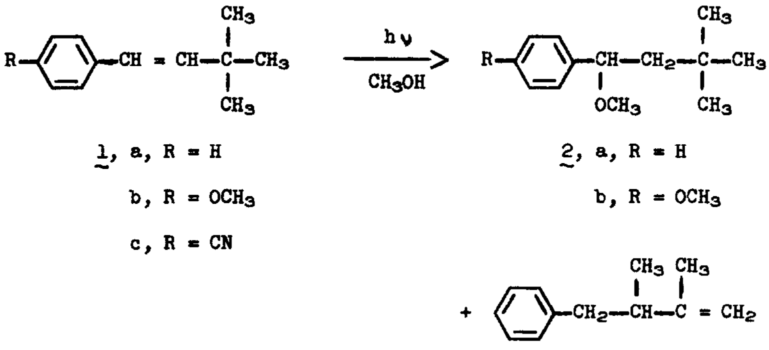
Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01002

(Received in USA 30 October 1972; received in UK for publication 22 December 1972)

Although reported observations of the photochemical addition of alcohols to cyclic olefins are numerous and fairly well understood,[1a-c] cases where the addition occurs to noncyclic olefins have been less frequently noted; these processes are poorly understood. In general the latter additions are found with olefins that are conjugated to highly electron-withdrawing groups which polarize the double bond[2a] or with other olefins conjugated with a polar electron-donating group where added mineral acid is necessary for the reaction to occur.[2b] We recently reported exceptions to these generalities:[3a,b] certain acyclic 1,3-diarylpropenes where the double bond is not directly conjugated to a polar group add methanol photochemically in the absence of added acid. However, even here a polarizing substituent is necessary (and indeed influences the directionality of the reaction) for 1,3-diphenylpropene itself fails to undergo the addition. To probe further the additions to the acyclic styryl system we investigated the photochemistry of the β-t-butylstyrenes 1a-c.

Irradiation[4] of β-t-butylstyrene (1a) in methanol for 9 hrs. gave, in addition to olefin 3[5] and very small amounts of other unidentified products, a 10% yield of ether 2a. This ether was isolated by silica gel chromatography and shown to be identical to a sample of 2a prepared from 3,3-dimethyl-1-phenyl-1-butanol via a Williamson synthesis. Similarly, p-methoxy-β-t-butylstyrene (1b) afforded upon photolysis (6 hrs.) a 60-70% yield of 2b and a small amount of another product, most likely the reduction product 4.[6]

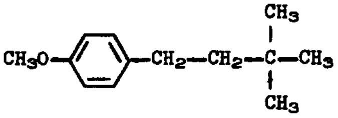
In contrast to the above additions, irradiation of p-cyano-β-t-butylstyrene (1c) afforded no detectable amounts of a methanol addition product. Only products resulting from methyl migration were observed.[7]



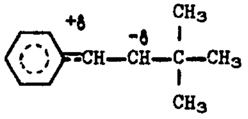
1, a, R = H
b, R = $OCH_3$
c, R = CN

2, a, R = H
b, R = $OCH_3$

3



4



5

The additions to 1a and 1b are truly photochemical since they do not occur in the dark. They do not require added acid nor are they brought about by acid produced photochemically from the methanol, for the additions proceed equally well in the presence of 0.01 *M* sodium methoxide.[8] The triplet states are apparently not involved in the additions since when 1a and 1b are sensitized by xanthone, little, if any, of 2a and 2b can be detected by gas chromatography. That energy transfer did occur is demonstrated by the fact that *trans*-*cis* isomerization was observed in both cases.

The addition of methanol to 1a is unusual in that the olefin undergoing the addition is acyclic and has no polar substituents. Moreover, it is a singlet state reaction not requiring added acid. It would therefore appear to be unique among reported examples of photochemical methanol additions to olefins. The reaction bears a strong resemblance to that of certain non-polar *cyclic* styryl systems which also add methanol via the singlet in the absence of acid.[9] It would appear that this is a reaction of both cyclic and acyclic systems.

Apparently the excited state of 1a is polarized as in 5.[10] Protonation of 5 followed by attack of methoxide gives 2a. That such a polarized state is formed is also indicated by the effects of substituents on the reaction (1b vs. 1c). It is puzzling, though, that the reaction does not appear to be general for styryl systems: 1,3-diphenylpropene does not add;[3b]

*o*-anethole adds only in the presence of added acid.[2b] We feel the most likely explanation is that the addition is basically a slow process, and that in the absence of some additional factor (added acid, the presence of a polarizing group) many styryl systems undergo some other process such as polymerization or rearrangement. **1a** rearranges very slowly and is sterically hindered from polymerization. Thus, the slow, inefficient methanol addition is observed.

*Acknowledgment.* Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We also thank Professor Paul Kropp for providing us with the details of his work.

## References

1. (a) P. J. Kropp and H. J. Kraus, *J. Amer. Chem. Soc.*, **89**, 5199 (1967);
   (b) P. J. Kropp, *Ibid.*, **91**, 5783 (1969);
   (c) J. A. Marshall, *Accounts Chem. Res.*, **2**, 33 (1969).

2. See, for example:
   (a) S. F. Nelsen and P. J. Hintz, *J. Amer. Chem. Soc.*, **91** 6190 (1969), and references therein.
   (b) N. Miyamoto, M. Kawanisi and H. Nozaki, *Tetrahedron Lett.*, 2565 (1971).

3. (a) S. S. Hixson, *Tetrahedron Lett.*, 4211 (1971).
   (b) S. S. Hixson, *J. Amer. Chem. Soc.*, **94**, 2505 (1972).

4. All irradiations were carried out under $N_2$ using Corex-filtered light from a Hanovia 450-W medium-pressure Hg arc and were monitored closely by gas chromatography. Olefin concentrations were 1.2 - 2.5 x $10^{-2}$ *M*.

5. The formation of **3** has been studied by Griffin: H. Kristinnson and G. W. Griffin, *J. Amer. Chem. Soc.*, **88**, 378 (1966).

6. Reduction commonly accompanies methanol addition.[1,3]

7. S. S. Hixson and T. Cutler, manuscript in preparation.

8. Olefin concentrations were $0.6 - 1.2 \times 10^{-2}$ $\underline{M}$. The solutions remained quite basic throughout the irradiation periods.

9. P. J. Kropp, private communication.

10. A similar conclusion has been reached for the cyclic systems.[9]