Acknowledgments. The authors are indebted to Miss Paula Glose for the bioassays done under the direction of Dr. L. Nangeroni, New York State Veterinary College, Cornell University.

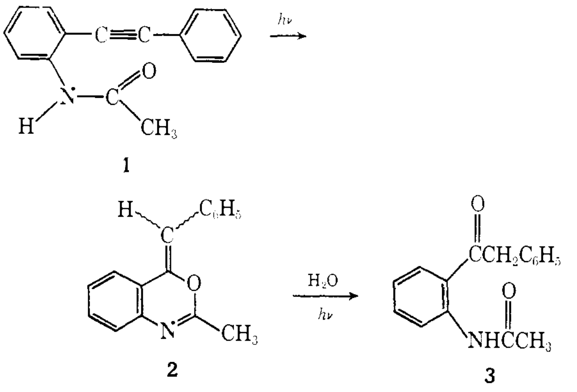
Communications to the Editor

New Photochemical Addition Reactions of Acetylenes. Neighboring Group Participation in Photolytic Hydration of Acetylenes

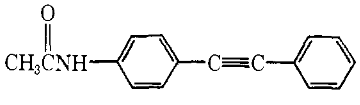
Sir:

The photochemistry of diphenylacetylene has been previously limited to cycloaddition[1a,b] and to oxidation.[1c] We wish to describe three new photolytic reactions of diarylacetylenes: (1) hydration to arylcarbinyl aryl ketones involving accelerative intramolecular participation of amido groups, (2) addition of methanol to give methyl *cis*- and *trans*-1,2-diarylvinyl ethers, and (3) reduction by methanol resulting in *cis*- and *trans*-diarylethylenes.

It has been found that *o*-acetamidophenyl(phenyl)-acetylene (**1**) photolyzes[2] rapidly in wet hexane in the absence of oxygen to give *o*-acetamidophenyl benzyl ketone (**3**, mp 98.5–99.5°, lit.[3] 97–98°). Irradiation of **1** (0.005–0.01 *M*) under nitrogen in dry hexane in quartz for 8 hr, removal of solvent, and crystallization of the resulting yellow oil from acetone–water afforded **3** in 85% yield. Photolysis of *p*-acetamidophenyl phenyl ketone (**4**) under conditions identical with that for **1** did not result in detectable reaction. To account for the rapid photochemical response of **1** and the unidirectional hydration resulting in **3**, it is proposed that upon excitation (eq 1) there is neighboring group interaction of the *o*-acetamido and the acetylene groups, giving 2-methyl-4-benzylidene-4H-3,1-benzoxazines (**2**); hydrolysis of **2**, apparently photochemically accelerated, thus yields **3**.



(1)



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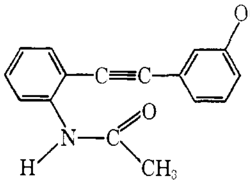
Inquiry as to whether benzoxazine intermediates of the type such as **2** are indeed formed photolytically and can be isolated was made by irradiating *o*-acetamidophenyl-*m*-methoxyphenylacetylene[4] (**5**, 0.005–0.01 *M*; mp 108–109°) in dry hexane containing Linde 3A Molecular Sieve. Photolysis[2] was effected for 25 hr to ensure complete conversion of **5**, the solvent was vacuum evaporated, and the yellow product was rapidly analyzed. The infrared spectrum did *not* show significant NH or C=O stretching. The nmr in $DCCl_3$ shows absorption at τ 7.92 (3 H, s), 6.4 and 6.31 (3 H, s, relative area *ca.* 2:3), 4.11 and 3.85 (1 H, s, relative area *ca.* 3:2), and 2.5–3.4 (8 H, m). Upon adding one drop of water and warming the nmr sample at 50° for several days, the spectrum gradually changed to that of *o*-acetamidophenyl *m*-methoxybenzyl ketone[5] (**7**, mp 100°);



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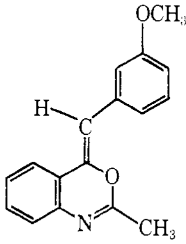
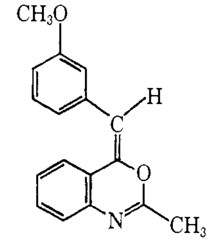
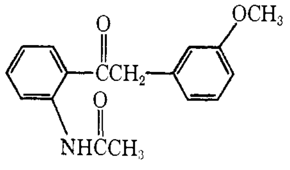


6a



6b



7

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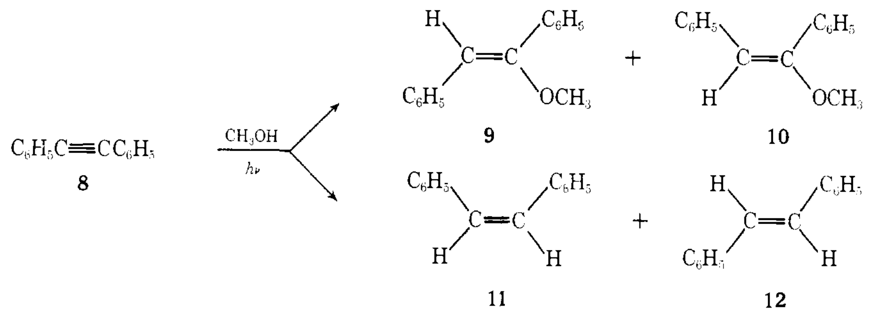
(1) (a) G. Buchi, C. W. Perry, and E. W. Robb, *J. Org. Chem.*, **27**, 4106 (1962); (b) O. L. Chapman and G. Lenz in "Organic Photochemistry," Vol. I, O. L. Chapman, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, p 283 ff; (c) R. C. Henson, J. L. W. Jones, and E. D. Owen, *J. Chem. Soc., A*, 116 (1967), and references therein.

(2) In a typical run 16 General Electric G25T8 tubes mounted in a circular bank (shop fashioned) served as the light source for 500-ml solutions (0.01 *M*).

(3) D. W. Ockenden and K. Schofield, *J. Chem. Soc.*, 3440 (1953).

(4) This compound was chosen in order to more conveniently study intermediates of type **2** by nmr techniques.

(5) Mass spectral parent peak 283; nmr ($DCCl_3$) τ 7.96 (s, 3 H), 6.34 (s, 3 H), 5.86 (s, 2 H), 1.30–3.56 (m, 8 H), and −1.3 to −1.52 (s, 1 H); **7** gave proper analysis.



crystallization of the photolysis intermediates from acetone–water also effected their conversion to **7**. The infrared absorption of the photolysis product is not that of **5** or **7**; its molecular weight and nmr spectrum are consistent with that of a mixture of isomers **6a** and **6b**. Hydrolysis of **6a** and **6b** at 40° in aqueous acetonitrile (quartz nmr tubes) is accelerated by irradiation. It is thus apparent that in the unique photochemical hydrations of acetylenes such as **1** and **5**, participation of the *o*-amido group plays a very important role. Work is in progress to characterize more fully and establish the mechanisms of formation and hydrolysis of intermediates such as **2** and **6a,b**. It is also likely that photochemical neighboring group participation will be a most important effect in other electrophilic, nucleophilic, or related addition systems.

Study of the photochemical reactions of acetylenes with other nucleophiles has been initiated. Photolysis of diphenylacetylene (**8**) in pure methanol occurs slowly and results primarily in addition to give methyl *trans*- (major, **9**) and *cis*- (minor, **10**) 1,2-diphenylvinyl ethers (Table I); photochemical reduction of **8** by methanol is a competitive process in that *cis*- (**11**) and *trans*-stilbenes (**12**) are also found. Phenanthrene (**13**) is also obtained, presumably by photolysis of **11**.[6] Irradiation of **8** (0.01 *M*) in methanol–benzene (1:1 v/v) yielded the same products as in Table I. When 2 equiv of 5,5-dimethyl-1,3-cyclohexanedione (**14**) was added to the solvents which had been distilled from these reaction mixtures, formal dimethone (mp 189°, lit.[7] 189, 191°) resulted in high yield. Photolysis of **8** (0.01 *M*) in methanol–mesitylene (1:1 v/v) yields only **11** and **12**; upon addition of **14** to the distilled solvent only traces of formal dimethone are formed. Thus addition of methanol is arrested while transfer of hydrogen from mesitylene is noted. In none of the photochemical experiments was there addition of methanol to **8** resulting in diphenylallyl alcohols. The processes leading to reduction and to addition may be related to either singlet or triplet excited states and/or vibrationally excited ground state. Linear and distorted triplets of different electronic energies may also play a role.[8] Studies now under way are designed to illucidate which of these excited intermediates are involved.

Table I. Photolysis of Diphenylacetylene and Methanol[a]

Time, hr	% reaction	9	10	11	12	13
10	33[b]	62	1	21	10	6
20	35	60	2	19	11	8
40	73	63	3	17	6	10
88	88[c]	62	6	13	6	14

[a] Aliquots were removed at the designated time periods and analyzed by glpc techniques. [b] The unidentified nonvolatile components amount to 8% of the total product. [c] Unidentified nonvolatile components, 15%.

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(6) F. R. Stermitz in ref 1b, p 248 ff.

(7) N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," Interscience Publishers, New York, N. Y., 1957, p 583.

(8) E. F. Ullman and W. A. Henderson, *J. Am. Chem. Soc.*, **89**, 4390 (1967).

(9) National Science Foundation Undergraduate Research Participant, 1968.

T. D. Roberts, L. Ardemagni[9]
Department of Chemistry, University of Arkansas
Fayetteville, Arkansas 72701

H. Shechter
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

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Stereospecific Addition of Alkylcopper Reagents to α,β-Acetylenic Acids. The Nature of the Vinylic Enolate

Sir:

Two communications were published recently on the stereospecific conjugate addition of dimethylcopper–lithium to α,β-acetylenic esters[1,2] at low temperatures and on the fast isomerization (5 min) of the adduct at 0° in ether solution. We obtained similar,[3] although not identical, results when a phenyl was one of the β groups in the product. However, addition of methylcopper[4] to phenylpropiolic acid (Ia) gave an enolate that retained its configuration at room temperature for prolonged periods and yielded on protonation mostly[5] *cis*-

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(1) E. J. Corey and J. A. Katzenellenbogen, *J. Amer. Chem. Soc.*, **91**, 1851 (1969).

(2) J. B. Siddall, M. Biskup, and J. H. Fried, *ibid.*, **91**, 1853 (1969).

(3) N. Aminadav, M.Sc. Thesis, the Hebrew University, 1967; J. Klein and N. Aminadav, submitted for publication.

(4) N. Gilman, R. G. Jones, and L. A. Woods, *J. Org. Chem.*, **17**, 1630 (1952); N. O. House, W. L. Respess, and G. M. Whitesides, *ibid.*, **31**, 3128 (1966).