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NEW PHOTOCHEMICAL ADDITION REACTIONS OF ACETYLENES II. SYNTHETIC POTENTIAL OF NEIGHBORING GROUP PARTICIPATION IN PHOTOLYTIC HYDRATION

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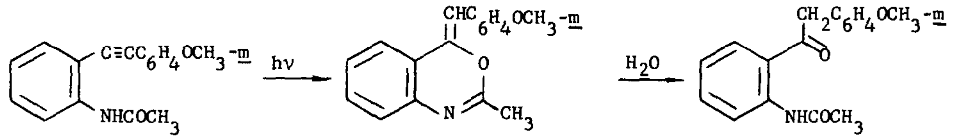
Irradiation of 2-acetamidophenyl(*m*-methoxyphenyl)acetylene, 1, with ultraviolet light results in facile unidirectional hydration to 2-acetamidophenyl *m*-methoxybenzyl ketone, 3.[1]



1 2 3

Neighboring group participation via 2-methyl-4-(*m*-methoxybenzylidene)-4H-3,1-benzoxazine, 2, has been postulated.[1] We now wish to report two new observations which greatly increase the synthetic potential of this new reaction: (1) the hydration step involves addition to the nitrogen-carbon double bond, (2) nitriles undergo facile photolytic hydration when catalyzed by an *o*-amide group, probably from the triplet excited state.

When 1 was irradiated[2] in an nmr tube in dry acetonitrile (0.1 - .2M) under N_2, monitoring showed reduction of N-H absorption at 1.7-1.9 τ while a peak at 4.1 τ (=CH) increased. After significant change ceased (214 hr at 366 nm)[3] a small drop of ^{18}O enriched water (62.8%) was added. A new peak emerged at 5.8 τ (O=C-CH) as =CH absorption disappeared. The solid, 3-^{18}O, obtained upon vacuum evaporation of the solvent was analyzed by mass spectrometry (m.s.) and compared to 3 (Table 1). Dideuterated 3 was synthesized by repeated refluxing of 3 in D_2O-dioxane containing triethylamine. NMR analysis showed that the peak at 5.8 τ (assigned to -C(O)CH_2- in 3) was essentially missing. Table 1 records the pertinent m.s. data for 3-D_2. Low and high resolution m.s. data on 3 also appears in Table 1.[4] Under the conditions of the experiment 3 does not exchange ^{18}O.[5]

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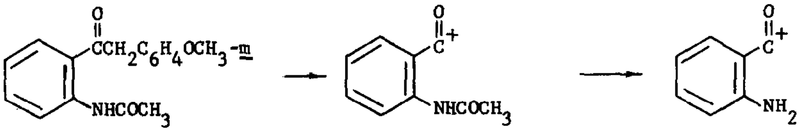
Table 1. Pertinent Mass Spectral Data

m/e	Relative Intensity 3	Relative Intensity 3-^{18}O	Relative Intensity 3-D_2	Measured Mass, 3[4]	Calc. Mass	C,H,N,O Ratio
285	0.14	2.79	4.07			
283	4.29	4.55	0.0	283.1243	283.1208	$C_{17}H_{17}NO_3$
164	1.05	66.30	4.07			
162	100.00	100.00	100.00	162.0565	162.0554	$C_9H_8NO_2$
122	0.65	2.45	2.76			
120	29.74	60.70[a]	33.28	120.0439	120.0449	C_7H_6NO

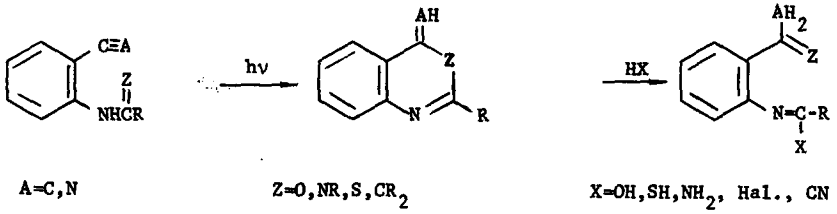
[a] This number appears high. However peaks at m/e=164 and 162 fragment to this ion.

In order to determine the location of ^{18}O in 3 a fragmentation path which separates the oxygen atoms was sought. Two well-documented m.s. fragmentation paths[6] are α cleavage at a carbonyl and elimination of ketene from acetanilides. Applied to 3 these paths provide a method of separation of the O atoms and suitably explain major peaks in the low resolution m.s.

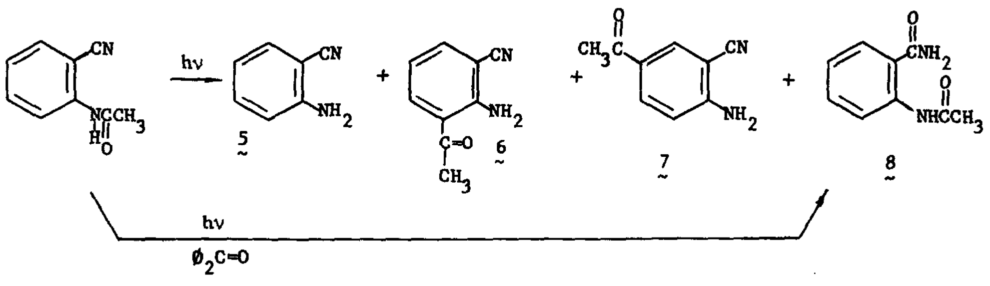


3	m/e = 283	162	120
3-D_2	285	162	120
3-^{18}O	285	164	120

High resolution m.s. analysis confirms this assignment in that the C,H,N,O ratio fits these fragments (See Table 1). When 3-D_2 is subjected to m.s. analysis the parent peak is increased by two units, but as predicted by the above scheme, major peaks at m/e 162 and 120 are still present. The m.s. of 3-^{18}O shows the expected giant increase in the parent+2 peak over that of 3. At m/e=164 another gigantic increase is noted over the same peak in 3 showing that ^{18}O is still retained in the fragment. However the m/e=122 peak remains very small, showing virtually no ^{18}O content. A suitable explanation of this data assigns ^{18}O to the amide group. Thus water adds to the nitrogen-carbon double bond of the benzoxazine. Coupled with experiments described below, one may postulate synthetic routes to a number of new heterocycles and by proper choice of HX provide mild addition reactions for carbon-carbon and carbon-nitrogen triple bonds. Thus elements of synthetic control are clearly evident. Current research involves several of these examples.



Heretofore photolytic hydration of nitriles has not been reported.[7] If neighboring group participation in photolytic hydration has wide application, nitriles should be investigated. Accordingly 2-acetamidobenzonitrile, 4, was irradiated (253.7 nm) in a quartz container under nitrogen in 50% aq. acetonitrile for 97 hr.[3] After vacuum evaporation of the solvent four products were isolated by GLC[8] and column chromatography techniques. They were identified as:[9] 2-aminobenzonitrile, 5 (identical to an authentic sample[10]); 2-amino-3-acetylbenzonitrile, 6 [m.p. 97-8; ir 3470, 3440, 3340, 2180, 1650, 795 cm^{-1}; nmr ($CDCl_3$) τ 7.4(s,3H) 2-3.5 (m,5H); m.s., m/e=160 (parent)]; 2-amino-5-acetylbenzonitrile, 7 [m.p. 156°C; ir 3490, 3400, 3300, 2200, 1635, 825, 770; nmr (acetone-D_6) τ 7.5 (s, 3H), 1.8-3.2 (m,3H), 3.75 (broad s,2H) m.s., m/e=160, (parent)]; and 2-acetamidobenzamide, 8 [m.p. 178;[11] ir (KBr) 3390, 3160 (broad), 1670, 1620, 1590, 1580, 1500, 1390, 1300, 760 (broad) 640 cm^{-1}, nmr (acetone-D_6) τ 7.9 (s,3H), 1.3-3 (m,7H); m.s., m/e=178 (parent)]. Apparently photo-Fries rearrangement[12] competes effectively with hydration. When the experiment was repeated with added benzophenone (4 x 10^{-4}M) and a 366 nm source (4 absorbs less than 1%), 8 was the only product (60% yield in 290 hr.). A possible explanation for this data is that the photo-Fries rearrangement of anilides occurs from singlet excited states[13] and ring-closure to 2-methyl-4-imino-4H-3,1-benzoxazines occurs from triplet excited states.



Thus a mild method of hydration of amides is available for compounds of this type. Experiments designed to extend this reaction type to molecules having C=O, C=S, C=C, and C=N bonds in place of C≡C or C≡N are in progress.

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1. T. D. Roberts, L. Ardemagni, and H. Shechter, *J. Amer. Chem. Soc.*, **91**, 6185 (1969).

2. Either 16 G. E. G25T8 tubes or 16 G. E. F15-T8-B1 tubes mounted in a circular bank served as the light source.

3. Reaction times in nmr tubes are greatly extended over similar reactions in 50 mm quartz tubes.

4. Obtained in cooperation with R. C. Dougherty, Florida State University. Acknowledgment is hereby rendered to Florida State University, National Science Foundation and the National Institutes of Health for support of this work.

5. Determined by mixing **3** with water containing $H_2{}^{18}O$ under the conditions of the experiment. After the designated time period, pyrolysis with mercuric chloride and mass spectral analysis of the resulting CO_2 showed negligible ^{18}O content.

6. H. Budzikiewicz, C. Djerassi, D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, Cal., 1967.

7. The only case reported involving a C≡N system is a cyanamide, Y. L. Chow and K. E. Haque, *Can. J. Chem.*, **46**, 2901 (1968).

8. Loss of water to form 2 methyl-4-hydroxyquinazoline by 2-acetamidobenzamide during GLC analysis was noted.

9. Discussion of differentiation between **6** and **7** will be differed until the full paper.

10. Purchased from Aldrich Chemical Co., Inc.

11. Literature 180°, P. Grammatricakis, *Bull. Soc. Chim. Fr.*, **20**, 207 (1953).

12. Photo-Fries rearrangements involve esters usually, but have been reported with anilides: See V. I. Stenberg in "Organic Photochemistry," Vol. I, O. L. Chapman, Ed., Mercel Dekker, Inc., New York, N. Y., 1967, p. 127 ff.

13. H. Shizuka and I. Tanaka, *Bull. Chem. Soc. Japan*, **41**, 2343 (1968).