

cessively with water, ethanol, and anhydrous ether and was dried under vacuum [10 hr, 65° (0.05 mm)]. The nitroxide 2,2,5,5-tetramethylpyrrolidin-1-oxyl-3-carboxylic acid was a gift of our colleague, Professor Jerry H. Smith.

(26) Bis(trimethylsilyl)trifluoroacetamide was obtained commercially (Regis Chemical Co.) and was used without further purification.

(27) H. P. Gregor, Guenther K. Hoeschele, J. Potenza, A. G. Tsuk, R. Feinland, M. Shida, and Ph. Teyssie, *J. Am. Chem. Soc.*, **87**, 5525 (1965).

Ortho Neighboring-Group Participation of Amides in Photolytic Hydration of Triple Bonds^{1a,b}

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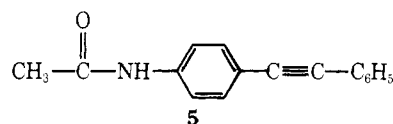
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Abstract: Photolysis of *o*-acetamidophenylacetylenes in hexane or acetonitrile gives 2-methyl-4-methylidene-1,3-4*H*-benzoxazines which add ¹⁸O-labeled water to yield *o*-acetamidophenyl ketones with the label in the amide carbonyl. Proof of the site of the label lies in determination and analysis of the mass spectral fragmentation of the amido ketones. Irradiation of *o*-acetamidobenzonitrile in aqueous acetic acid yields *o*-acetamidobenzamide, 3-acetoanthranilonitrile, 5-acetoanthranilonitrile, and anthranilonitrile. If the photolysis is repeated with added benzophenone and a 366-nm source, only *o*-acetamidobenzamide results. Triplet states are proposed as precursors in photocyclizations of *o*-acetamidobenzonitriles and of *o*-acetamidophenylacetylenes. Irradiation of *p*-acetamidobenzonitrile does not cause photohydration but rather photo Fries-like fragmentation and rearrangement to *p*-aminobenzonitrile and 3-aceto-4-aminobenzonitrile.

Previous reports of the photochemistry of diphenylacetylene have included reduction to stilbene,^{1a} oxidation to benzoic acid,^{2a} addition of protic solvents to give α -substituted stilbenes,^{1a,b} self-cycloaddition to yield dimers, trimers, and tetramers,^{2b} and cyclization of the acetylene moiety with *o*-nitro,^{2c} *o*-ethynyl,^{2d} and *o*-ethynyl groups,^{2e} respectively. A study is presently reported of photochemical hydration of phenylacetylenes and benzonitriles containing amido groups in ortho and para positions. The research investigation illustrates novel examples of photointeraction of amido functions with *o*-ethynyl and cyano groups and reveals the significance of neighboring-group participation in photolytic hydration of triple bonds.

o-Acetamidophenyl(phenyl)acetylene (**1**) photolyzes rapidly (253.7 nm) in wet hexane in the absence of oxygen to give *o*-acetamidophenyl benzyl ketone (**2**, eq 1). The structure of ketone **2** is established by literature melting point comparison,³ analysis of spectral properties, and acid-catalyzed hydrolysis to *o*-aminophenyl benzyl ketone (**3**, eq

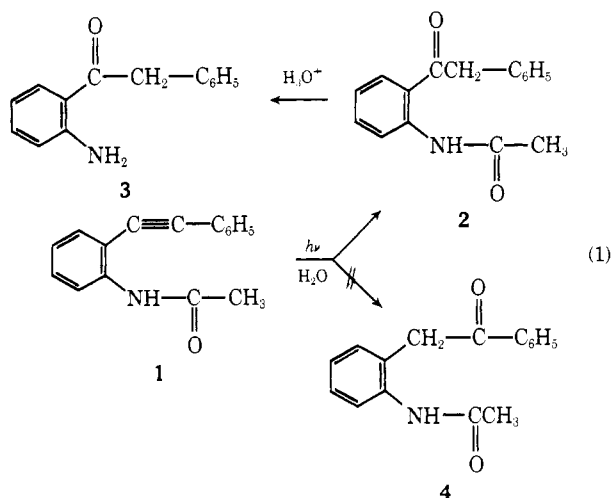
1). Ketone **4** might have been also expected as a product of direct photohydration of the triple bond of **1**. The fact that *p*-acetamidophenyl(phenyl)acetylene (**5**) is *inert* under the above photolysis conditions indi-



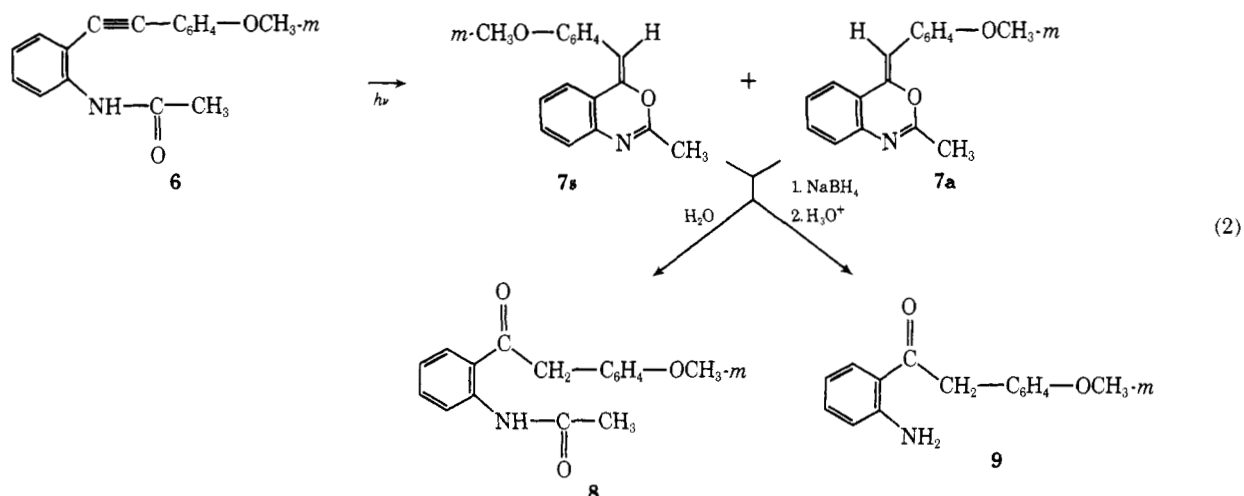
cates that the *o*-acetamido group is playing much more than a simple electronic role in the photochemical hydration of **1** to **2** (eq 1). The collective results of this portion of the study suggest that there is some type of neighboring-group interaction involving the amide and ethynyl groups during photolysis of **1**.

An investigation was then made of the products and mechanisms of photolysis of *o*-amidophenylacetylenes in anhydrous environments. Irradiation of *o*-acetamidophenyl(*m*-methoxyphenyl)acetylene⁴ (**6**) in dry hexane yields a mixture of *syn*- and *anti*-4-(*m*-methoxybenzylidene)-2-methyl-1,3-4*H*-benzoxazines (**7a** and **7s**, eq 2) as a yellow oil which then reacts readily upon addition of water to give *o*-acetamidophenyl *m*-methoxybenzyl ketone (**8**, eq 2). Assignments of structures of the mixture of **7s** and **7a** are based on spectral properties and reduction with sodium borohydride⁵ and then hydrolysis to *o*-aminophenyl *m*-methoxybenzyl ketone (**9**, eq 2). Isomerization and the stereochemistry of **7s** and **7a** are indicated by the benzylic proton absorptions at τ 3.9 and 4.1, respectively, and by the change in the proton magnetic resonance of the mixture of the benzoxazines upon exposure to ultraviolet light and upon storage in darkness. Upon photolysis of **7s-7a** in chloroform at 254 nm, the absorption at τ 3.9 gradually decreases, whereas that at τ 4.1 increases. The proton magnetic resonance changes reverse when irradiated mixtures of **7s** and **7a** are stored in the dark, and thus **7a** is the thermodynamically more stable isomer.⁶

Hydration of benzoxazines **7s** and **7a** could occur by attack of water on their exo carbon-carbon or their endo carbon-nitrogen double bonds to yield **8**. The mechanism path



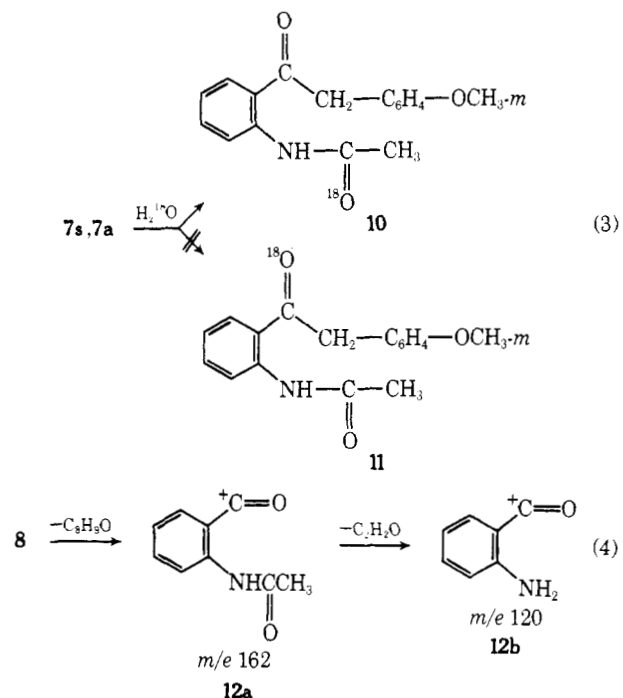
1). This experiment reveals that hydration of the triple bond of **1** occurs upon photolysis to produce only one of two possible benzyl ketones, that is **2** and not *o*-acetamidoben-



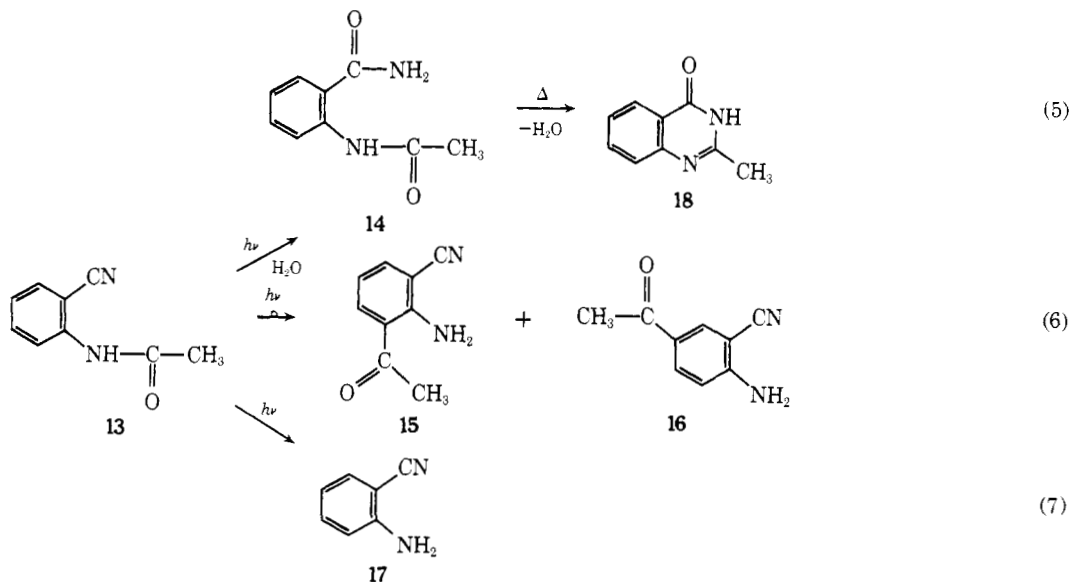
is indicated to involve addition at the imino functions by reaction of **7s** and **7a** with ^{18}O -labeled water (62.8% ^{18}O) to give ketoamide **10** containing ^{18}O in the amide group (eq 3) rather than in the ketone carbonyl (**11**). Dissociation of unlabeled **8** by electron impact involves initial loss of $\text{C}_3\text{H}_5\text{O}$ (*m*-methoxybenzyl) to form ion **12a** which then loses $\text{C}_2\text{H}_2\text{O}$ to give ion **12b** (eq 4). Equation 4 is shown to be the major decomposition pathway for **8** by (1) the atom content of its fragments as determined by high-resolution methods, (2) the mass spectrum (see Table III) of its dideuterio derivative labeled α to ketone carbonyl ($-\text{C}(=\text{O})-\text{CD}_2-\text{C}_6\text{H}_4-\text{OCH}_3$), and (3) the characteristic broad absorption of a metastable ion at m/e 89 revealing that **12a** decomposes to **12b**. Mass spectral analysis of **10** indicates that it and its initial fragment ion (**12a**- ^{18}O) contain ^{18}O , whereas the subsequent ion **12b** does not, and thus **10** has ^{18}O in its amide carbonyl group.

Although nitriles are isoelectronic with acetylenes, there are in fact few photoreactions in which carbon-nitrogen triple bonds are altered.⁸ Since hydration of acetylenes has been found to be accelerated by neighboring-group participation, it is of interest to determine if nitriles respond similarly. A study was thus made of possible photochemical hydration of benzonitriles containing *o*- or *p*-acetamido groups.

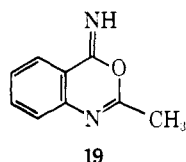
Irradiation of *o*-acetamidobenzonitrile (**13**) in aqueous acetic acid gives *o*-acetamidobenzamide (**14**, eq 5), along with 3-acetoanthranilonitrile (**15**, eq 6), and 5-acetoanthranilonitrile (**16**), and anthranilonitrile (**17**, eq 7).



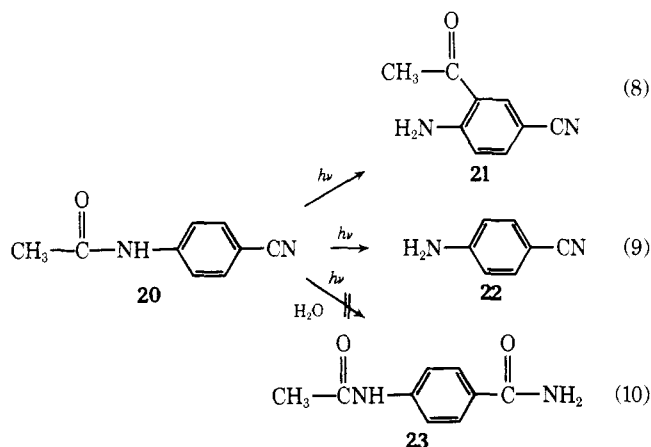
Photoaddition of water to **13** to yield **14** is a new reaction of nitriles; **14** dehydrates during gas-liquid chromatography to form 2-methyl-4-quinazolone (**18**, eq 5). Isomerization of **13** to **15** and **16** and cleavage of **13** to **17** are appar-



ently photo Fries-like rearrangement and fragmentation processes of anilides which are competitive with photochemical hydration of **13** to **14**. The probable role of the *o*-acetamido group as a participant to form 2-methyl-4-imino-1,3-*4H*-benzoxazine (**19**) as an intermediate in the irradiation



of **13** to **14** is indicated by the photolysis (eq 8 and 9) of *p*-acetamidobenzonitrile (**20**) in aqueous acetonitrile to the Fries-type product, 3-aceto-4-aminobenzonitrile (**21**), and the fragmentation product, *p*-aminobenzonitrile (**22**); 4-acetamidobenzamide (**23**, eq 10) is not pro-



duced. The evidence for the structural assignments of **15**, **16**, and **21** is summarized in the Experimental Section of this manuscript.

In order to begin an exploration of the photochemical hydration of **13**, its irradiation was repeated with added benzophenone and a 366-nm light source. Concentrations were such that the sensitizer absorbed 99% of the light. Under these conditions, only one product, *o*-acetamidobenzamide (**14**, eq 5), was formed. Since the quantum yield of intersystem crossing of singlet to triplet for benzophenone is virtually 100%, any change from the results of direct photolysis of **13** may be ascribed to transfer of energy from triplet benzophenone. These results then suggest that photocyclization of cyanoanilide **13**, possibly to **19**, occurs under these conditions via a triplet process; addition of water then provides the product, diamide **14**. Singlet states have indeed been suggested previously as precursors to photo Fries-like rearrangement and fragmentation of acetanilides.^{9a} Although definitive proof is not yet available, cyclization of ethynylanilides **1** and **6** to benzoxazines (such as **7s** and **7a**) may also occur from triplet states.^{9b}

Work is in progress with other systems in order to determine the scope of the new photoreactions presently reported. Further, the role that neighboring-group participation plays in electrophilic, nucleophilic, or related photoadditions to various unsaturated bonds is under study. Since amido and related functional groups are so prevalent in surfaces of living systems exposed to both visible and ultraviolet irradiation, neighboring-group participation of such moieties may play important roles in nature's various processes.

Experimental Section

A Varian A-60 spectrometer afforded ¹H NMR data which are reported in τ units downfield from tetramethylsilane. Infrared (ir)

spectral data were obtained from either a Perkin-Elmer (a) 337 grating spectrometer or (b) 137 Infracord. A Cary Model 14 recording spectrometer yielded ultraviolet (uv) absorption data. Low-resolution mass spectra (MS) were obtained on a Hitachi RMU-6E mass spectrometer at 70 eV and are recorded as *m/e* values followed by the percent of the base peak in parentheses. MI denotes the molecular ion. A high-resolution mass spectrum of benzyl ketone **8** was recorded at the High Resolution Mass Spectrometry Laboratory of Florida State University. Gas-liquid chromatography (GLC) followed usually by collection of purified compounds from the effluent gases was accomplished by use of a Barber-Coleman No. 5340 unit equipped with a $\frac{3}{8}$ in. \times 20 ft column of 30% SE30 (methyl) at 220°. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn., or Alfred Bernhardt, Mulheim, Germany.

Starting Materials. *o*- and *p*-acetamidophenyl(phenyl)acetylenes (**1** and **5**, respectively) were prepared from copper phenylacetylide and *o*- or *p*-iodoacetanilide.^{10a-c} Acetylene **1** and *o*-acetamidophenyl(*m*-methoxyphenyl)acetylene (**5**) were also obtained from reactions of acetic anhydride with *o*-aminophenyl(phenyl)acetylene and *o*-aminophenyl(*m*-methoxyphenyl)acetylene,^{11a-d} respectively at 20°. *o*- and *p*-acetamidobenzonitriles (**13** and **20**, respectively) were synthesized from acetic anhydride and *o*- or *p*-aminobenzonitrile.¹² The physical constants for these starting materials are in Table I.

Photochemical Methods. Irradiations were carried out under nitrogen either (a) in quartz ¹H NMR tubes so that reaction progress could be monitored, or (b) in 5 \times 60 cm quartz vessels for preparative purposes. Except for sensitization reactions, 16 GE G25T8 germicidal fluorescent tubes mounted in a circular bank served as the light source. When benzophenone was added as a sensitizer, 16 GE F15T8-B1 fluorescent tubes were used. None of these photolytic reactions progress under identical conditions in the dark.

Photolyses. Irradiation of 0.5-l. solutions of ethynylanilide **1** (0.01 *M*) in hexane for 8 hr and evaporation of the solvent affords a yellow oil which upon repeated crystallization (acetone-water) yields benzyl ketone **2** (Table I, 85% purified yield). Hydrolysis of benzyl ketone **2** in aqueous hydrochloric acid (10–20%) gave *o*-aminophenyl benzyl ketone (**3**) as an off-white solid (Table I) as the only organic product. Irradiation of ethynylanilide **5** under the same conditions did not cause detectable reaction.

A similar solution of ethynylanilide **6** was irradiated for 25 hr in dry hexane containing a few grams of Linde 3A molecular sieve. The solvent was then rapidly evaporated in vacuo to give **7** as a yellow oil in near quantitative yield: ν_{\max} (neat) 1655 (m), 1590, 1500, 1250, 1050, 1035, 860, 755, 690 cm^{-1} ; ¹H NMR (CDCl₃) τ 2.5–3.4 (m, 8 H), 3.9 and 4.1 (2s, relative area 2:3, 1 H), 6.3 and 6.4 (2s, relative area 3:2, 3 H), 7.9 (s, 3 H); MS *m/e* 265 (MI, 70), 223 (*M* – 42 \cong 0), 162 (74), 146 (100), 136 (87), 135 (87). When this reaction is carried out in a ¹H NMR tube, no other peaks are detected. When **7** is dissolved in dry acetonitrile or chloroform in a ¹H NMR tube and irradiated (254 nm), the peak at τ 4.1 increases at the expense of that at τ 3.9. The reverse occurs in the dark. Photolyses in hot aqueous acetone precipitated benzyl ketone **8** as an off-white solid (90% isolated yield).

In a separate experiment, 0.5 g (0.001 mol) of ethynylanilide **6** was irradiated for 58 hr in 25 ml of dry acetonitrile. After the solvent was evaporated, the resulting yellow oil was dissolved in a solution of sodium borohydride (0.08 g, 0.001 mol) in 60 ml of ethanol at –40°. After 2-hr, work-up afforded ethynylanilide **6** (70%) and *o*-aminophenyl *m*-methoxybenzyl ketone (**9**) (30%). When ketone **8** is subjected to only the work-up conditions of this experiment, no reaction occurs.

Addition of H₂¹⁸O to Benzoxazines **7a and **7s**.** A solution of ethynylanilide **6** (0.0002 mol in 1 ml of dry acetonitrile) was irradiated at 254 nm under N₂ in a quartz ¹H NMR tube for 3 days. The ¹H NMR spectrum gradually became that of benzoxazines **7a** and **7s** (see above). Several drops of a 10% solution of 62.8% oxygen-18 enriched water in acetonitrile were then added so that the total weight increased by 20%. The sample was then either maintained in the dark or in the presence of a 254-nm light source until the ¹H NMR spectrum duplicated that of benzyl ketone **8**. Samples maintained in the light hydrolyze approximately twice as fast as those in the dark. A typical MS of benzyl ketone **8** enriched with oxygen-18 is recorded in Table II. Significant peaks from

Table I. Physical Constants

Compd	Mp, °C	IR, α cm ⁻¹			¹ H NMR τ (CDCl ₃)			MS		Uv, λ , nm (log ϵ)		
		NH	C \equiv X	C=O	Aryl H	NH ^b (br, s)	Aryl H (τ , J value, int)	s (int)	MI (int)	Other (int)	Hexane	95% EtOH
1 ^c	120.5–121.5	3280 3200		1650	765, 755 750, 685	2.1	1.6 (dd, 2, 8, 1 H) 2.5–3.1 (m, 8 H)	7.8 (3)				
5 ^d	189.5–190	3300 3250 3310	2200	1650	830, 755 750, 685 870, 775	0.4	2.4–2.8 (m, 9 H)	7.8 (3)	235 (58)	219 (2), 193 (100) 194 (19), 165 (13)	250 (4.2), 267 (4.18) 285 (4.15), 304 (3.93)	245 (4.20) 297 (3.79)
6 ^e	108	3310		1670	750, 685	2.1	1.6 (dd, 1, 8, 1 H) 2.4–3.2 (m, 7 H)	7.8 (3)	265 (100)	223 (99), 180 (9) 162 (62), 120 (29)	286 (4.20), 306 (4.06) 311 (3.77)	286 (4.32) 304 (4.16)
13 ^f	132	3330	2220	1620 1705	755 750	2.0	1.8 (dd, 9, 1.5, 1 H) 2.3–2.6 (m, 2 H)	7.8 (3)	160 (17)	118 (100) 91 (11)	246 (3.83), 295 (3.32) 307 (3.26)	240 (3.91) 291 (3.40)
20 ^{d,g}	205	3310 3260 3220	2220	1670	835	2.8	2.8 (dd, 7, 1.5, 1 H) 2.5 (s, 4 H)	7.8 (3)	160 (26)	118 (100) 91 (6)		265 (4.36)
2 ^h	98.5–99.5			1680 1660	755, 740 725, 700	–1.6	1.3 (dd, 8, 1, 1 H) 2.0 (dd, 8, 1.5, 1 H) 2.3–3.3 (m, 7 H)	7.9 (3) 5.7 (2)	253 (4)	162 (100), 120 (33) 92 (18)		
3 ⁱ	97–98.5	3460 3330 3420 3170		1660	740, 725 690				211 (13) 283	120 (100), 92 (21) 65 (15) 162 (100), 120 (30)		
8	105–105.8			1680 1640	765, 750 700	–1.6	1.1 (dd, 8.5, 1, 1 H) 2.0 (dd, 8, 1.5, 1 H) 2.3–3.3 (m, 6 H) 1.1 (dd, 8.5, 1, 1 H) 2.0 (dd, 8, 1.5, 1 H) 2.3–3.3 (m, 6 H) 1.1 (dd, 8.5, 1, 1 H) 2.0 (dd, 8, 1.5, 1 H) 2.3–3.3 (m, 6 H)	7.9 (3) 6.2 (3) 5.7 (2) 7.9 (3) 6.2 (3) 5.7 (0)	See Table II See Table II			
8- <i>d</i> ₃	93.5–95											
8- <i>d</i> ₂	94					–1.6						
9	76–78	3480 3350 3420 3430 3320 3470 3380 3270 3425 3170		1640	770, 750	4.0 (2) 3.0 (2)	2.3 (dd, 2, 8, 1 H) 2.7–3.7 (m, 7 H) 2.1 (dd, 8, 1.5, 1 H) 2.5 (dd, 8, 1.5, 1 H) 3.4 (t, 8, 1 H)	6.3 (3) 5.9 (2) 7.4 (3)	241 (12) 160 (48)	154 (55), 128 (14) 120 (100), 105 (29) 145 (100), 117 (44) 90 (44)		
16 ^k	149–151.6		2220	1660	925, 825	5.2 (2)	2.1 (d, 2, 1 H) 2.2 (dd, 2, 8, 1 H) 3.4 (d, 8, 1 H) 2.5 (m, \approx 4 H)	7.6 (3)	160 (36)	145 (100), 117 (40) 90 (64)		
18 ^{l,m}	235			1680 1670 1610	770			7.4 (3)	160 (18)	92 (31), 80 (47) 76 (40), 63 (73) 50 (100)		268 (4.06) 298 (3.71) 313 (3.69)
4 ⁿ	174.5–176	3390 3170		1680 1630	760		1.4 (dd, 1.5, 8.5, 1 H) 2.2 (dd, 1.5, 7.5, 1 H) 2.3–3.3 (m, \approx 5 H)	7.9 (3)	178 (15)	160 (11), 136 (33) 119 (70), 43 (100)		248 (4.07) 298 (3.36)

^a All data from a mixture with KBr pressed into a disk. ^b This peak decreases in intensity when D₂O is added to the sample. ^c Lit.^{10c} mp 117–118°, τ , 1.6, 2.0, 2.9 (1 H each), 7.8 (3 H). ^d Both 5 and 20 have weaker bands in the 3200 and the 3100 cm^{-1} areas of their spectra; for 5, γ_{max} (CHCl₃) 3430, 3290, 2220, 1690 cm^{-1} ; γ_{max} (CHCl₃) 3410, 1670 cm^{-1} ; γ_{max} (neat) 3330, 3200, 1670, 870, 780, 760, 750 cm^{-1} . ^f Lit.¹² mp 132.5°; λ_{max} (EtOH)¹³ 291 (3.40) nm. Other data: γ_{max} (CHCl₃) 3420, 2220, 1700 cm^{-1} ; γ_{max} (neat) 3330, 3320, 2220, 1680, 750 cm^{-1} ; λ_{max} (EtOH)¹³ 268 (4.41) nm. ^h Lit.³ mp 97–98°; ⁱ Lit.³ mp 103–104°; ^j γ_{max} (CHCl₃) 3480, 3330, 2220, 1650 cm^{-1} ; ^k γ_{max} (CHCl₃) 3530, 3420, 2210, 1680 cm^{-1} ; ^l Lit.¹³ mp 235°; λ_{max} (EtOH) 263 (3.90), 301 (3.68), 314 (3.65) nm. ^m Low solubility makes quantitative ^1H NMR work difficult; γ_{max} (CHCl₃) 3390, 3180, 1670 cm^{-1} . ⁿ Low solubility makes quantitative ^1H NMR work difficult; lit.¹⁴ mp 186–187°; λ_{max} (EtOH) 252 (4.18), 301 (3.61) nm.

Table II. Major Peaks from the Mass Spectrum of Ketone 8

<i>m/e</i>	Unlabeled 8	8 after ^{18}O incorporation	8- d_3 (8 after D_3 incorporation)	8- d_2 (8 after D_2 incorporation)
286	0	1	3	0
285	0	6	4	2
284	1	2	1	3
283	4	10	0	1
164	1	66	4	2
163	12	16	35	20
162	100	100	100	100
123		1	1	3
122	1	2	3	2
121	5	9	12	7
120	30	56	33	28

Table III. Major Peaks from the High-Resolution Mass Spectrum of Ketone 8

<i>m/e</i>	Obsd	Calcd	C, H, N, O ratio
283	283.1243	283.1208	$\text{C}_{17}\text{H}_{17}\text{NO}_3$
162	162.0565	162.0554	$\text{C}_9\text{H}_9\text{NO}_2$
120	120.0439	120.0449	$\text{C}_7\text{H}_7\text{NO}$

high-resolution mass spectroscopy of benzyl ketone 8 are recorded in Table III.

Preparation of Dideuterated Ketone 8. *N*-Deuterio-*o*-acetamidophenyl α,α -dideuterio-*m*-methoxybenzyl ketone (8- d_3) was prepared by refluxing a mixture of 0.04 g (0.0001 mol) of benzyl ketone 8 in 10 ml of *p*-dioxane containing 0.5 ml of triethylamine. The solvent was then evaporated and the procedure repeated four times to yield a pale-yellow solid (ca. 100%). Recrystallization of this sample from methanol-water gave *o*-acetamidophenyl α,α -dideuterio-*m*-methoxybenzyl ketone, 8- d_2 (ca. 10%), as a faint-yellow solid.

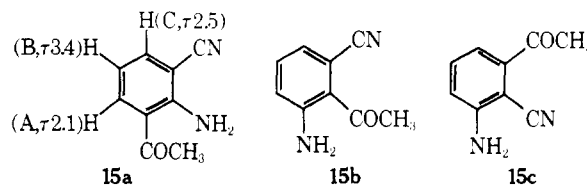
Attempted Incorporation of ^{18}O in Ketone 8. Samples of *o*-acetamidophenyl *m*-methoxybenzyl ketone 8 were stored for up to 168 hr in aqueous acetonitrile (33% water which was 6 atom % H_2^{18}O). Pyrolysis of these samples at 500° with mercuric chloride-mercuric cyanide gave carbon dioxide which was analyzed¹⁵ for excess oxygen-18. Incorporation was negligible.

Irradiation of Nitrile 13. A solution of 8 g (0.05 mol) of *o*-acetamidobenzonitrile (13) in 500 ml of 50% aqueous acetonitrile was degassed and irradiated for 97 hr at 254 nm. After the solvent was evaporated, the resulting sticky, brown solid was analyzed by GLC techniques. The five components collected from the effluent gas stream was identified as follows (Table I): fraction 1, 24%, retention time, ir, and ^1H NMR identical with those of authentic anthranilonitrile; fraction 2, 38%, mp, ir, and ^1H NMR identical with those of starting cyanoanilide 13; fraction 3, 18%, yellow needles, 3-acetoanthranilonitrile (15); fraction 4, 7%, 5-acetoanthranilonitrile (16); fraction 5, 9%, 2-methyl-4-quinazolinone (18) (Table I). When this experiment was repeated with added benzophenone (amide:benzophenone ratio is 166:1) and a 366-nm source, only cyanoanilide 13 and quinazolinone 18 resulted. If the product mixture is separated instead by column chromatography (silica gel: petroleum ether, benzene, then ether), cyanoanilide 13 (42%) and *o*-acetamidobenzamide (14) (58%) result.

Irradiation of *p*-Acetamidobenzonitrile (20). Nitrile 20 (0.32 g, 0.002 mol) in aqueous acetonitrile (1 ml in 20 ml) was photolyzed under N_2 in quartz for 92 hr. The mass spectrum of the solid obtained did not show significant absorption at *m/e* 178. Column chromatography (silica gel: benzene) gave a brown oil. GLC techniques separated *p*-aminobenzonitrile (22), 40% and 3-aceto-4-aminobenzonitrile (21), 60%; mp 132.5–133.5°; ν_{max} (KBr) 3490, 3420, 3370, 3310, 2220, 1670, 827 cm^{-1} ; ^1H NMR (CDCl_3) τ 2.1 (d, J = 2 Hz, 1 H), 2.7 (dd, J = 2, 8 Hz, 1 H), 3.4 (d, J = 8 Hz, 1 H), 3.2 (br, s, 2 H), 3.5 (s, 3 H); MS *m/e* 168 (P).

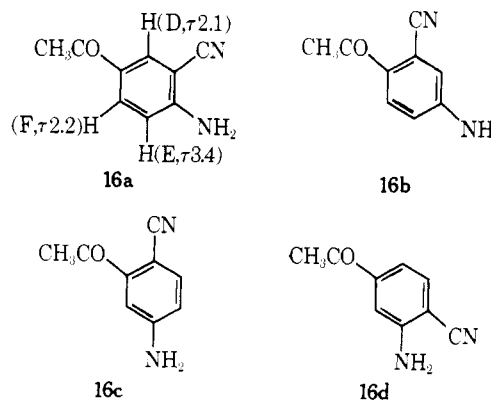
Structural Assignments of 3-Acetoanthranilonitrile (15) and 5-Acetoanthranilonitrile (16). Of the trisubstituted ring structures possible for the two isomeric acetoanthranilonitriles, 1,3,5 trisubstitution can be eliminated by consideration of out-of-plane infrared bending absorptions of aryl hydrogens. The first of these

two isomers to elute from chromatographic columns, acetoaminonitrile 15, exhibits a strong band at 740 and weaker bands at 745 and 790 cm^{-1} . Of the three possible arrangements about the ring, this isomer can only be 1,2,3 trisubstituted. The ^1H NMR coupling constants substantiate this fact. Usually J values range between 6–9 and 1.2–3 Hz for ortho and meta protons, respectively.¹⁶ If the protons of a 1,2,3-trisubstituted aryl are labeled A, B, and C so that the B proton is ortho to protons A and C, proton B should be coupled to both A and C with large J values (see Figure 1, struc-



ture 15a). If coupling of proton B to both A and C is approximately the same, then B should appear as a triplet. The doublet of doublets that will appear for A and C will have one large and one small coupling constant. The ^1H NMR spectrum of acetoaminonitrile 15 exhibits this predicted pattern for the three aryl protons.

The second of these isomers to elute, acetoaminonitrile 16, shows only one major aryl hydrogen out-of-plane infrared bending absorption at 825 cm^{-1} . Such a band is usually assigned to out-of-plane bending absorption of two adjacent aryl hydrogens. The much weaker absorption at 925 cm^{-1} is attributed to out-of-plane bending of an isolated aryl hydrogen. Again ^1H NMR coupling constants of the aryl protons confirm that a 1,2,4-trisubstituted ring is present in acetoaminonitrile 16. One aryl proton, proton D (see Figure 2, structure 16a), has a coupling constant of only 2 Hz



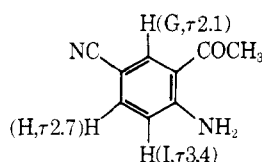
as expected for an isolated proton located between substituents and coupled only to a meta proton. Since another proton, E, exhibits a doublet with a coupling constant of 8 Hz, coupling to an ortho but not a meta proton is indicated. Since the remaining proton, proton F, is coupled to both protons D and E, a doublet of doublets results. Thus acetoaminonitrile 16 is 1,2,4 trisubstituted.

Exact assignments of the structures of isomers 15 and 16 depend upon the NMR chemical shifts of amino and aryl protons. The 1,2,3-trisubstituted isomer 15 may have the structure 15a, 15b, or 15c (Figure 1). The proton magnetic spectrum shows the usual broad peak at τ 3 for the nitrogen protons. Such a low value for the chemical shift of these protons is indicative of *o*-acetylanilines.¹⁷ The nitrogen protons of *o*-cyanoanilines usually absorb near τ 5.7,¹⁷ and thus structure 15c is eliminated. Aryl protons ortho to cyano groups usually absorb near τ 2.8, while aryl protons ortho to amino groups absorb near τ 3.5.¹⁷ Aryl protons ortho to carbonyl groups are usually shifted down to about τ 2.3.¹⁷ Since one of the protons of acetoaminonitrile 15 absorbs at τ 2.1, the product can not be 15b. Thus isomer 15 is 3-acetoanthranilonitrile (15a), and its assigned values for aryl hydrogen absorption (Figure 1) fit that expected for this structure.

Of the six 1,2,4-trisubstituted isomers that are possible structures for acetoaminonitrile 16, two are cyano-*o*-aminoacetophenones. The nitrogen protons of *o*-aminoacetophenones usually absorb near or lower than τ 4.1.¹⁷ (As further proof see the data for 3-acetoanthranilonitrile and 3-aceto-4-aminobenzonitrile of this research.) Since the nitrogen protons of acetoaminonitrile 16 fall at τ 5, the *o*-aminoacetophenones are dismissed. The chemical

shifts of the aryl protons of isomer **16** then allow a decision among the four remaining possible structures (see Figure 2). Since the chemical shifts of two of the aryl protons are so low (τ 2.1 and 2.2), both of these must be ortho to a carbonyl group. Thus structures **16b** and **16c** cannot be correct. Structure **16d** is also eliminated since all three aryl protons are ortho to either a carbonyl or a cyano group and thus should absorb below τ 3. Since the proton which absorbs at τ 2.2 exhibits a doublet of doublets, it must be ortho to one proton and meta to the other proton. Only structure **16a** (5-acetoanthranilonitrile) suitably satisfies these requirements. The assigned values for aryl hydrogen absorption in Figure 2 fit that expected.

Structural Assignment for 3-Aceto-4-aminobenzonitrile (21). The mass spectrum parent peak and infrared spectral data confirm that aceto, nitrile, and amino groups are attached to the ring in a 1,2,4 pattern. The ^1H NMR peak for the N-H is at τ 3.2 as expected for an *o*-aminoacetophenone. One of the three aryl protons, proton G, Figure 3, is shifted downfield to τ 2.1 as expected for a proton



ortho to a carbonyl. The low value of 2 Hz for the coupling constant of this proton confirms a location between two nonproton substituents and coupled only to a meta proton. Protons H and I are ortho protons as shown by a *J* value of 8 Hz. Since proton H is shifted downfield to τ 2.7 and exhibits a doublet of doublets, coupling with proton G is also indicated. Further, such a low chemical shift shows that proton H is ortho to a cyano group. Proton I shows only a doublet as expected. Only 3-aceto-4-aminobenzonitrile fits these data.

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