of DMSO at 115° and thence through the gas train. For a mixture of 55 mmol of N_2 and 47.1 mmol of CO, 53.2 mmol (97%) of N_2 and 42.2 mmol (89.6%) were recovered. In all cases, the DMSO was an orange-brown color upon terminating the experiment. Attempts to isolate possible reaction products from the mixture were unsuccessful.

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(17) The results of some preliminary studies involving the photolysis of ABFA suspended in cumene provide additional support for homolysis as a decomposition path for *cis*-ABFA. When a stirred suspension of ABFA in cumene was irradiated in an immersion-type reactor with a 200-W mercury arc using a Pyrex filter for 6 days at room temperature, TFH and N_2 were the major decomposition products. TFH accounted for >30% of the starting ABFA while N_2 accounted for most of the remaining azo nitrogen of ABFA. Carbon monoxide, biurea, urea, biuret, and bicumyl were minor reaction products.
(18) The justification for the latter assumption is found in our photolysis study,[13] in which we found the half-life of *cis*-ABFA to be approximately 5 min at 25°. At 115°, ABFA has a half-life of 100 min. The lifetime of *cis*-ABFA is estimated to be at least three orders of magnitude shorter at this temperature.
(19) P. D. Bartlett, E. P. Benzig, and R. E. Pincock, *J. Amer. Chem. Soc.*, **82**, 1762 (1960).
(20) Over the course of a given experiment at 115°, the maximum temperature variation was 0.05°, while 0.02° was typical.
(21) In practice, reaction temperatures were reached after *ca.* 15 min.
(22) The gas train is of the standard type and was assembled to detect and measure, in the following order, basic volatiles, carbon dioxide, carbon monoxide, and nitrogen.
(23) Final nitrogen volume was corrected for hydrostatic pressure, vapor pressure of water, and STP.
(24) The amount of nitrogen and all other reaction products as entered in Table III have been normalized for 1 mol of ABFA.
(25) Relatively slight modifications in the work-up procedure were employed in several cases where solvents other than DMSO and/or additives were present.
(26) The composition of the dried residues was determined by nmr from a comparison with spectra of authentic samples. The amounts (per cent by weight) of the various components were subsequently calculated from the integrated area.
(27) W. Y. Youden, "Statistical Methods for Chemists," Wiley, New York, N. Y., 1951.
(28) A. Streitweiser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, p 8.
(29) The amounts of TMABFA and **3** were determined from the integrated area of each component. Chemical shifts attributed to **3** at δ 2.84 (d, 18 H) and 8.67 (s, 1 H).

Photochemical Alkylation of s-Triazolo[4,3-b]pyridazine and Imidazo[1,2-b]pyridazine

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s-Triazolo[4,3-b]pyridazine (I), when irradiated in methanol and the reaction mixture was heated to 250°, gave nearly a 50:50 mixture of 7-methyl- and 8-methyl-s-triazolo[4,3-b]pyridazines (Va and VIa). There was no reaction when I was irradiated in tetradeuteriomethanol. Similar products were isolated in ethanol. The intermediate mixture when I reacted with isopropyl alcohol decomposed on heating to 7-isopropyl- and 8-isopropyl-s-triazolo[4,3-f]pyridazines (Vc and VIc) and 7,8-dihydro-s-triazolo[4,3-b]pyridazine (VII). Product VII resulted from a reverse aldol-type condensation reaction. Imidazo[1,2-b]pyridazine (II) did not react when irradiated in methanol. In acidified methanol and in the presence of benzophenone, II reacted to give 8-hydroxymethylimidazo[1,2-b]pyridazine (X) and a trace of the 8-methyl product (XI).

There have been numerous studies of the photochemical alkylation reactions of N-heterocyclic aromatic compounds. Stermitz and coworkers[2] first reported that, when N-heterocyclic aromatic compounds were photolyzed in acidified ethanol, ethyl-substituted compounds were formed. They showed that the reaction proceeded through an n,π^* triplet state much like the photoreduction of benzophenone.[3] The ethyl group was attached to carbon 2 (next to nitrogen) or carbon 4.[2] In the absence of acid, the corresponding hydroxyethyl products formed.[4] Other workers have shown that photoalkylation also takes place in ethers[5] and amines.[6,7]

We have irradiated s-triazolo[4,3-b]pyridazine (I) in methanol and have found that the reaction mixture yielded 7-methyl- and 8-methyl-s-triazolo[4,3-b]pyridazines (Va and VIa) in nearly equal amounts upon heating to 250°. No reaction took place when I was irradiated in tetradeuteriomethanol. When I was irradiated in ethanol and the reaction mixture heated, 7-ethyl- and 8-ethyl-s-triazolo[4,3-b]pyridazines (Vb and VIb) were isolated with a ratio of 1:2. The reaction mixture of the irradiation of I in isopropyl alcohol gave 7-isopropyl- and 8-isopropyl-s-triazolo[4,3-b]pyridazines (Vc and VIc) and 7,8-dihydro-s-triazolo[4,3-b]pyridazine (VII) in a ratio of 2:3:5, respectively, when heated. In each of these reactions, analysis of the crude reaction mixture indicated that the corresponding 7- and 8-hydroxyalkyl-7,8-dihydro-s-triazolo[4,3-b]pyridazines (IIIa-c and IVa-c) were the initial products (see Scheme I). 7,8-Dimethyl-s-triazolo[4,3-b]pyridazine (VIII) was the only product when the reaction mixture from the irradiation of Va in methanol was heated to 250°.

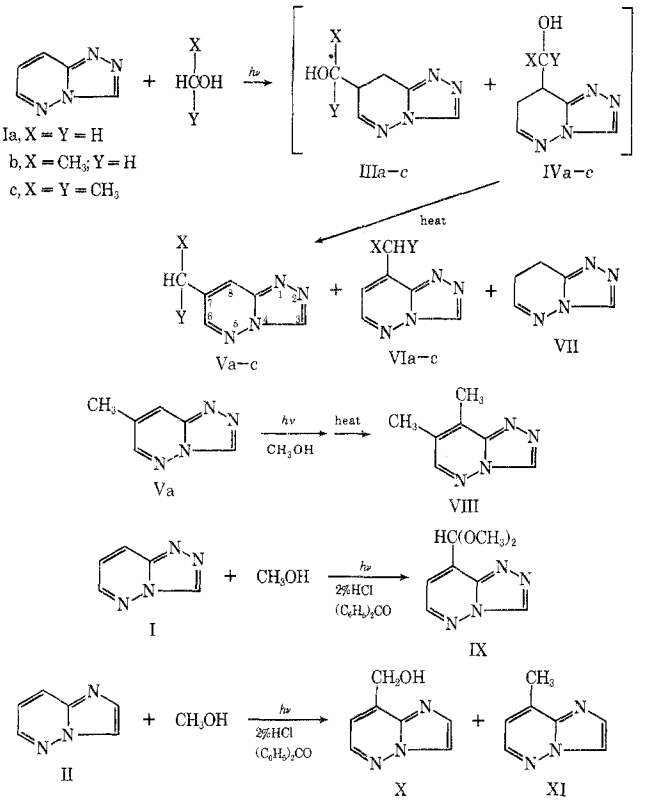
When irradiated in acidified methanol and in the presence of benzophenone, I did not give Va or VIa but gave the dimethyl acetal of 8-formyl-s-triazolo[4,3-b]pyridazine (IX). Imidazo[1,2-b]pyridazine (II) reacted with methanol in the presence of acid and benzophenone to give a good yield of 8-hydroxymethylimidazo[1,2-b]pyridazine (X) and a trace of the 8-methyl product (XI). In the absence of acid and benzophenone, II did not react.

Results and Discussion

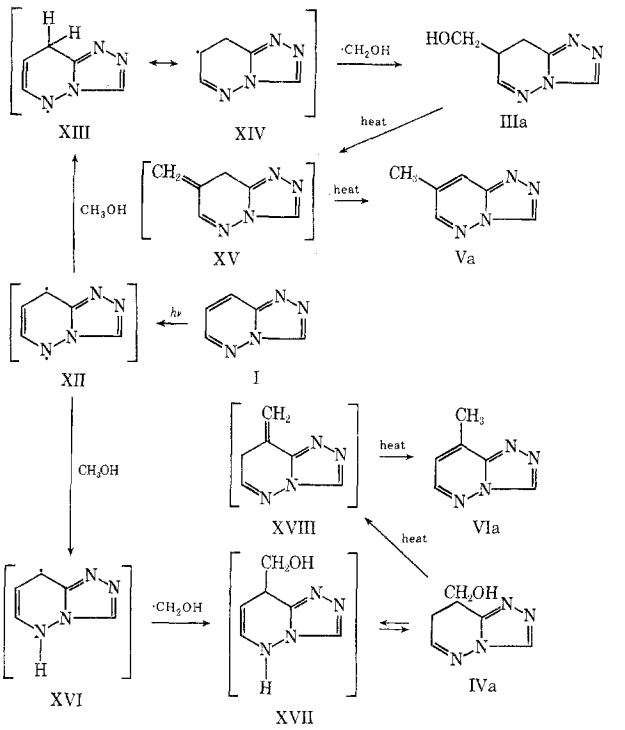
The starting material was dissolved in the appropriate solvent and irradiated until no starting material was left in solution. The solvent was then removed and the gummy material was analyzed by nuclear magnetic resonance (nmr) spectroscopy and separated by vpc (250° inlet temperature) or thin layer chromatography (tlc). The products were compared with authentic samples where possible or analyzed by nmr, infrared (ir), and mass spectrometry. The reactions are shown in Scheme I.

The structures of the products were consistent with their spectra. The nmr spectra for compounds I and II and their derivatives are very distinctive.[8-10] The doubled doublet at δ 7.17 observed for the hydrogen at position 7 in the nmr spectrum of I[8] was not observed in the spectra of compounds Va-c. The nmr spectra of compounds X and XI also did not show the octet at δ 7.95 which was attributed to the hydrogen at position 8 in compound II.[9]

Scheme I

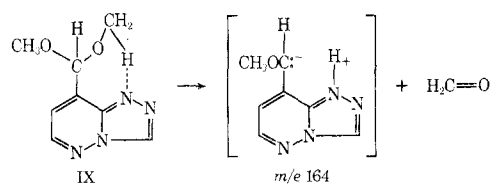


Scheme II



Compound VII was soluble in water and exhibited an nmr spectrum which was the same as that for authentic 7,8-dihydro-*s*-triazolo[4,3-*b*]pyridazine, which we prepared by a different process.

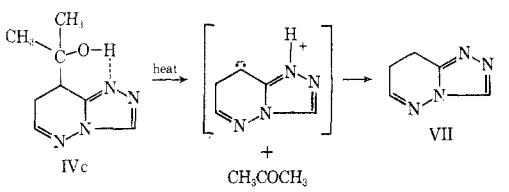
Compound IX exhibited a small parent peak at *m/e* 194 in the mass spectrum. Acetals usually have small parent peaks.[11] A large metastable (M − CH_2O) peak was observed. Generally, dimethyl acetals have large (M − CH_3O)$^+$ peaks.[11] Methyl ethers, on the other hand, have large (M − CH_2O) peaks which have been attributed to the loss of formaldehyde.[12] 8-Dimethylaminoimidazo[1,2-*b*]pyridazine, a structurally similar compound, has been observed to have a large (M − NCH_3)$^+$ peak but no [M − $N(CH_3)_2$]$^+$ peak in the mass spectrum.[13] The second methyl group probably migrated to the nitrogen in position 1. This same type of phenomenon could be taking place with compound IX wherein a hydrogen migrates from a methyl to nitrogen and a neutral formaldehyde molecule is lost.



The initial photochemical reaction of I led to mixtures of what we believe are the 7- and 8-hydroxyalkyl-7,8-dihydro products III and IV. These products were not isolated; however, the nmr spectra of the crude mixtures were very characteristic. Peaks at δ 8.6 and 7.7 are indicative of hydrogens at positions 3 and 6, respectively. The peaks at δ 3.5–2.7 can be attributed to the hydrogens in the 7 and 8 positions and the peak area always equated to three hydrogens. The hydroxy hydrogen peak in the case of the mixture of IIIc and IVc appeared at δ 4.75 and was exchangeable in deuterated water. The remaining alkyl group was also observed in each spectra. The relative amounts of III and IV changed from 50:50 in the methanol reaction to 20:80 in the isopropyl reaction. The two methyls in compound IVc were not equivalent. The separation of the two peaks in hexadeuteriodimethyl sulfoxide was 0.32 Hz at room temperature but decreased to 0.22 Hz at 150°. The nonequivalence of the methyls can be attributed to hindrance in rotation about the alkyl carbon–carbon 8 bond due to hydrogen bonding between the hydroxy group and the nitrogen in position 1. Also at 150° a new peak at δ 2.12 appeared and increased with increasing time. The addition of a trace of acetone increased the size of this peak.

When the above-mentioned reaction mixtures were heated at 250°, the 7- and 8-alkyl products were formed. In the case of the 2-propanol reaction, compound VII was also formed as the major product. This product had to be formed from IVc, which was the major intermediate. Acetone was also a product of the thermal reaction, as shown by its presence in the hot dimethyl sulfoxide solution.

The photoreaction probably involves an excited state wherein the 5 and 8 positions of I are activated toward radical reactions (may be like XII in Scheme II). The excited intermediate then abstracts a hydrogen atom from the alcohol either in position 8 to give XIII or in position 5 to give XVI. Resonance form XIV reacts with the hydroxy methyl radical to give IIIa, while XVI leads to IVa. Each of these hydroxyalkyl intermediates dehydrates and rearomatizes in heat to give the observed alkyl products Va and VIa. When the hydroxyalkyl compound IVc is heated, a reverse aldol-type condensation reaction competes with dehydration to give VII and acetone. The reverse aldo-type condensation reaction is most pronounced in the case of IVc (a trace of VII may have formed from IVb) because tertiary alcohols undergo this reaction more readily than do secondary or primary alcohols.[14]



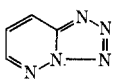
The change in the ratio of III to IV as the alcohol is changed from methanol (50:50 ratio) to 2-propanol (20:80 ratio) is interesting. The reactive intermediate (XII) should not be different in the two cases. Since the first step is probably hydrogen abstraction by XII, this could indicate that the pair of electrons on nitrogen 1 create more steric hindrance than the hydrogen on carbon 3.

Failure of compound I to react in tetradeuteriomethanol is surprising. To the best of our knowledge, this is the first example of an isotope effect in a photoalkylation reaction.

The reactions in acidified methanol were expected to yield methyl-substituted products as previously observed for this reaction with other N-heterocyclic compounds.[2] The dimethyl acetal (product IX) probably derived from the corresponding hydroxymethyl compound. The aldehyde could have formed by oxidation of the hydroxymethyl compound. Formation of the acetal would then be expected in acidified methanol.

We expected at least some 6-substituted products. None was detected. These results closely parallel radical addition to these compounds. Both I and II reacted with radicals to give mainly 8-substituted products with some in position 7 but very little in position 6.[8-10]

The fact that neither II nor the structurally similar tetrazolo[1,5-*b*]pyridazine XIX reacted with methanol in the absence of sensitizer is consistent with other studies of these compounds. We have previously reported that I reacted readily with cyclohexene to form photocycloaddition products wherein the alkene added to the 1,8 positions of I with a concurrent opening of the N_4–N_5 bond.[15,16] Neither II nor XIX reacted to form those products.[15,16] It is also known that II and XIX are not as reactive toward radical reactions as I.[10]



XIX

Experimental Section

Materials and Apparatus. All starting materials, compounds I,[8] II,[17] and VIa,[8] were prepared in this laboratory. All infrared (ir) spectra were obtained on a Perkin-Elmer Model 137 spectrophotometer. A JOEL JNM C60-HL spectrometer was used to obtain the nuclear magnetic resonance (nmr) spectra. A Varian Model 1800 temperature-programming vapor phase chromatograph (vpc) using a 5 ft × 0.25 in. stainless steel column packed with 10% SE-30 on 80/100 mesh Chromosorb G/AW was employed for all separations. The mass spectra were obtained on a CEC-20-110 C high-resolution mass spectrometer. A Rayonet photochemical reactor with 3600-Å lamps was used for all irradiations.

7,8-Dihydro-*s*-triazolo[4,3-*b*]pyridazine (VII). A solution of 6-chloro-*s*-triazolo[4,3-*b*]pyridazine[8] (1.56 g) in 70 ml of methanol was treated with 1 ml of concentrated ammonia and 0.15 g of 10% palladium on charcoal. The mixture was stirred in an atmosphere of hydrogen under normal pressure for 6 days. The catalyst was filtered and the filtrate was evaporated under vacuum almost to dryness. The residue was treated with a solution of 20 ml of 5% aqueous sodium hydroxide and extracted five times with chloroform. The combined extracts were washed with water and dried over anhydrous magnesium sulfate. Upon evaporation of the solvent, the residue (0.92 g) was found by nmr analysis to consist of 7,8-dihydro-*s*-triazolo[4,3-*b*]pyridazine (VII, 75%) and *s*-triazolo[4,3-*b*]pyridazine (I, 25%). Several recrystallizations from ethanol gave pure VII: mp 132°; nmr δ 8.60 (s, H_3), 7.70 (t, H_6), 3.20 (m, 8-CH_2), and 2.80 (m, 7-CH_2).

Anal. Calcd for $C_5H_6N_4$: C, 49.17; H, 4.95; N, 45.81. Found: C, 49.30; H, 5.18; N, 45.89.

Irradiation of I in Methanol. Compound I (0.20 g, 1.7 mmol) in 15 ml of methanol was irradiated in a Pyrex tube for 40 hr. Thin layer chromatography (tlc) showed that no starting material remained in the solution. The solvent was removed under vacuum, leaving a yellow gum (0.25 g). The nmr spectrum of this material exhibited peaks at δ 8.65 (s, 1), 7.65 (s, 1), 3.85 (d, 2, J = 5 Hz), and 3.5–2.7 (m, 3). This material could not be further purified. When the material was heated to 250° for 10 min and then sublimed at 250° (1 mm), a mixture (40% overall yield) of 7- and 8-methyl-*s*-triazolo[4,3-*b*]pyridazine (Va and VIa) resulted. The products were isolated by vpc, yielding Va (18%) and VIa (22%). The products exhibited ir and nmr spectra which were identical with those of authentic samples.[8]

Irradiation of I in Ethanol. A mixture of I and 100% ethanol was irradiated as above, yielding 0.27 g of a yellow gum. The nmr of this material contained peaks at δ 8.4 (d, 1), 7.6 (s, 1), 4.3 (m, 1–2), 3.5–2.7 (m, 3), and 1.5–1.0 (m, 4). Peak areas were imprecise. When heated to 250° for 10 min and sublimed at 250° (1 mm), a white semisolid formed (35% overall yield). Three peaks were isolated on the vpc. Peak 1 (9%) proved to be starting material, compound I. Peak 2 (18%, compound VIb) exhibited the following spectra: nmr δ 9.11 (s, 1, H_3), 8.27 (d, 1, J = 7 ± 1 Hz, H_6), 6.90 (d, 1, J = 8 ± 1 Hz, H_7), 3.18 (q, 2, CH_2), 1.47 (t, 3, CH_3); mass spectrum m/e (rel intensity) 148 (M^+, 86), 147 (100), 120 (25), 93 (14), 65 (7); mol wt calcd for $C_7H_8N_4$, 148.07489; found, 148.07588.

Peak 3 (8%) (compound Vb) exhibited the following spectra: nmr δ 9.07 (s, 1, H_3), 8.27 (d, 1, J = 2.5 ± 0.5 Hz, H_6), 7.85 (d, 1, J = 1.5 ± 0.5 Hz, H_8), 3.2 (m, impurity), 2.80 (q, 2, CH_2), 1.38 (t, 3, CH_3); mass spectrum m/e (rel intensity) 148 (M^+, 100), 147 (12), 133 (10), 120 (5); mol wt calcd for $C_7H_8N_4$, 148.07489; found, 148.07559.

Irradiation of I in 2-Propanol. A solution of I in 2-propanol was irradiated as above, yielding 0.21 g of a yellow gum. The gum exhibited nmr peaks ($CDCl_3$) at δ 8.58 (s, 1), 7.80 (m, 1), 4.75 (s, 1, exchanged with D_2O), 3.5–2.8 (m, 3), 1.41 (s, 3), and 1.26 (s, 3). The latter two peaks appeared at δ 1.32 and 1.00 in hexadeuteriodimethyl sulfoxide and changed to 1.34 and 1.12 at 150°. Also at 150°, a new peak appeared in the nmr spectrum at δ 2.12. This peak was increased when a trace of acetone was added. The gum, when heated to 280° for 10 min and sublimed at 250° (1 mm), yielded a white semisolid (29%). The semisolid gave three peaks in the vpc with a ratio of 14:12:74. Peak 1 proved to be starting material, compound I. Peak 2 (compound VIc) exhibited the following spectra: nmr δ 9.01 (s, 1, H_3), 8.19 (d, 1, J = 8 Hz, H_6), 6.82 (d, 1, J = 7 Hz, H_7), 3.63 (m, 1, CH), 1.51 (d, 6, J = 6 Hz, CH_3); mass spectrum m/e (rel intensity) 163 (33), 162 (M^+, 84), 148 (24), 147 (100), 138 (33), 136 (36), 120 (66); mol wt calcd for $C_8H_{10}N_4$, 162.09054; found, 162.09051.

Peak 3 (compounds Vc and VII) exhibited an nmr spectrum as follows: δ 9.21 (s, 1), 8.60 (s, compound VII), 8.42 (d, 1, J = 4 Hz), 7.97 (d, 1, J = 3 Hz), 7.70 (m, compound VII), 3.30–2.80 (m, compound VII), 1.42 (d, 6, J = 6 Hz). The ratio of Vc to VII was 1:3. When the solution was extracted with water, the nmr peaks at δ 8.60 and 7.70 and most of the multiplet at δ 3.30–2.80 were removed from the spectrum. Those peaks were the same as those exhibited by authentic VII as shown above. The new spectrum showed peaks at δ 9.21 (s, 1, H_3), 8.42 (d, 1, J = 4 Hz, H_6), 7.97 (d, 1, J = 3 Hz, H_8), 3.12 (m, 1, CH), 1.42 (d, 6, J = 7 Hz, CH_3). The mass spectrum of purified Vc exhibited peaks at m/e (rel intensity) 162 (M^+, 10), 149 (33), 148 (33), 147 (100); mol wt calcd for $C_8H_{10}N_4$, 162.09054; found, 162.09051.

Irradiation of Va in Methanol. A solution of Va in methanol was irradiated as above. A white solid separated, 0.04 g, mp 200–204°. The solid was insoluble in all normal nmr solvents. Sublimation of the solid at 250° (1 mm) gave a white solid which proved to be compound VIII[8] and some impurity. This material gave only compound VIII when subject to separation on the vpc.

Irradiation of I and Benzophenone in Acidified Methanol. Compound I (0.72 g, 6 mmol), 1.09 g (6 mmol) of benzophenone, and 300 ml of 2% hydrochloric acid in methanol were saturated with nitrogen and irradiated for 65 hr. Nitrogen was sparged through the solution throughout the irradiation. The solvent was then removed under vacuum, 50 ml of water was added, and the resulting aqueous solution was extracted three times with 50-ml portions of ether to yield the neutral fraction. This fraction was found to contain benzophenone and methyl benzoate.[18] The remaining aqueous phase was made basic by adding solid sodium hydroxide and extracted continuously for 24 hr. The ether extract was dried over anhydrous sodium sulfate and evaporated to give 0.35 g of a gummy material. The gummy material was dissolved in methylene chloride and separated on a preparative silica gel thin layer plate using chloroform–methanol (9:1) for development. Two fractions were isolated. Fraction 1 (100 mg) proved to be starting compound I. Fraction 2, 36 mg (5%) (compound IX), was sublimed at 160° (20 mm): nmr δ 9.10 (s, 1, H_3), 8.30 (d, 1, J = 4 Hz, H_6), 7.68 (d, 1, J = 4 Hz, H_7), 5.88 (s, 1, CH), 3.50 (s, 6,

OCH_3); mass spectrum m/e (rel intensity) 164 ($M^+ - 30$, 67), 163 (22), 149 (100); mol wt calcd for $C_8H_{10}N_4O_2$ ($M^+ - 30$), 164.06780; found, 164.06882.

Irradiation of II and Benzophenone in Acidified Methanol. A mixture of II, benzophenone, and acidified methanol was irradiated as in the preceding experiment. The neutral fraction yielded benzophenone and methyl benzoate[18] as above. The basic fraction yielded 0.55 g of a gummy solid. Most of this dissolved in 5 ml of methylene chloride, leaving 110 mg of a white solid. The solid was sublimed at 170° (20 mm) to give compound X: ir 3200 cm^{-1} (OH); nmr δ 8.22 (d, 1, J = 6 Hz, H_6), 7.88 (s, 1, H_3), 7.62 (s, 1, H_2), 6.98 (d, 1, J = 5 Hz, H_7), 5.09 (s, 2, CH_2OH), 3.05 (s, 1, exchanged with D_2O, OH).

Anal. Calcd for $C_7H_7N_3O$: N, 28.17. Found: N, 27.91.

The remaining gummy material, which was soluble in methylene chloride, was chromatographed on 50 g of alumina using increasing amounts of chloroform in petroleum ether (bp 30–60°) as eluent. Fractions 19–22 contained 95 mg of starting II and 10 mg (>1%) of XI (ir and nmr were the same as those of an authentic sample[10]). Fractions 51–60 were further separated on a preparative silica gel tlc plate to yield 60 mg of X. This gave a total yield of 170 mg (22%) of X.

Miscellaneous Irradiations. No reaction was observed when II or tetrazolo[1,5-*a*]pyridazine (XIX) were irradiated in methanol. No reaction was observed when I was irradiated in tetradeuteriomethanol for over 40 hr or in *tert*-butyl alcohol.

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Registry No.—I, 274-83-9; II, 766-55-2; Vb, 50357-91-0; Vc, 50357-92-1; VIb, 50357-93-2; VIc, 50357-94-3; VII, 50357-95-4; IX, 50357-96-5; X, 50357-97-6; 6-chloro-*s*-triazolo[4,3-*b*]pyridazine, 28593-24-0.

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3-Aryl-1,3,5,5-tetramethylcyclohexanols. Preparation and Stereochemical Characterization by Proton Nuclear Magnetic Resonance[1]

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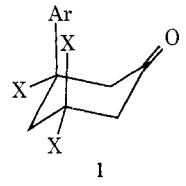
A series of cis and trans isomers of 3-aryl-1,3,5,5-tetramethylcyclohexanols (the 3-aryl substituent being phenyl, *o*-, *m*- or *p*-methoxyphenyl, *p*-chlorophenyl, or α-naphthyl) was prepared; the separated isomers were characterized by detailed proton nmr studies. These studies included an extensive characterization of stereochemistry by means of lanthanide-induced shifts (LIS), primarily using $Eu(FOD)_3$, and by temperature variation. The results of these studies are consistent with the existence of biased mobile equilibria between two chair-like conformers. The extent of biasing is much greater in the cis alcohols than in the trans, with the biasing being toward an axial disposition of the hydroxyl group (with the cis aryl substituent also enjoying an axial oientation). LIS data are used to examine the possible mechanisms involved in aryl ring bond rotation processes in these highly hindered systems. The varying steric requirements and resulting LIS variations (including the observation of numerous *upfield* europium-induced LIS) are investigated using ortho, meta, or para substituents; these studies also provide structurally similar cases for probing shift reagent complexation of two sites of greatly differing basicities. An additional conformational biasing, caused by $Eu(FOD)_3$, was observed in the cis *o*-anisyl alcohol derivative.

For some time now, we have studied a number of 3,3,5,5-tetrasubstituted (and other) cyclohexanones,[3] of the type of structure 1, where X is a substituent other



1

than hydrogen and Ar is an aryl moiety. Also, we have studied various alcohols as well as other compounds[4] derived in turn from these ketones. It was found for the cyclohexanones that, when one of the four substituents is an aryl group, this substituent uniformly exhibits a strong tendency to adopt an axial orientation in preference to a methyl group being in the analogous disposition.[3a] Previous reports have dealt with several consequences of this structural preference, the chemistry, the special nmr spectroscopic observations, and the LIS (lanthanide-induced shifts) in these systems.[3b] In addition to findings previously described, we have noted that, in ketones containing an axial phenyl or axial para-substituted phenyl substituent, the two ortho and the two meta hydrogens appear equivalent on the nmr time scale. It is of interest, then, to obtain an understanding of the process(es) that permits the observed equilibration of these energetically