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Photo-Arylation. IV.[1] Synthesis of 2-Arylpyridines by Photo-Reaction of 2-Iodopyridine with Substituted Benzenes[1]

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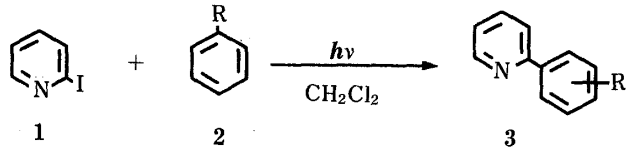
Photolysis of a mixture of 2-iodopyridine and a variety of substituted benzenes in dichloromethane afforded the corresponding 2-arylpyridines as isomeric mixtures. Based on the isomer distributions of the products and the formation of 2-chloropyridine as a by-product, the reactivity of 2-iodopyridine in the present reaction was suggested to be electrophilic in character.

Keywords——arylpyridine; 2-pyridinylation; photo-arylation; photolysis; 2-iodopyridine; homolytic aromatic substitution

Among various reported methods for the synthesis of 2-arylpyridines,[3] the most simple and widely used may be homolytic substitution reactions on pyridine with aryl radicals derived thermolytically from appropriate radical sources.[3a-i] The method, however, results in the formation of a regioisomeric mixture whose isolation is often tedious or difficult. On the other hand, the procedure involving a pyridyl radical obtained by the modified Gomberg reaction was successfully applied only for the synthesis of 3-arylpyridines but not for the 2-isomers.[4,5] Photolysis of halobenzenes in benzene solution has been shown to be a useful method for the synthesis of biphenyls.[6] Application of this photochemical procedure might provide a simple and general synthetic method for biheteroaryl compounds.[7-9] In the preceding paper, we reported the synthesis of phenylpyridines by the photolysis of 2-, 3- and 4-halopyridines (halogen; Cl, Br, I) in benzene, and the photolysis of 2-iodopyridine has been considerably accelerated in dichloromethane solution.[1,7] We wish to report here the preparation of 2-arylpyridines by the photo-reaction of 2-iodopyridine[8] with substituted benzenes in dichloromethane.

A solution of 2-iodopyridine (**1**) (5 mmol) and a substituted benzene (**2**) (10 ml for R= CO_2CH_3, Cl, CH_3, OCH_3, OH; 30 mmol for R=OCH_3)$_2$) in dichloromethane (CH_2Cl_2) (100 ml) was irradiated for 3—10 h with a 60 W low-pressure mercury lamp to afford a 2-arylpyridine (**3**) as a possible regioisomer together with 2-chloropyridine (**4**) (Chart 1). The products thus obtained were isolated by column chromatography on either silica gel or silica gel pretreated with formic acid (for **3b**) or with acetic acid (for **3c—d**)[1] in the solvent systems listed in Table I. The results are summarized in Table II.



1 2 3

Chart 1

TABLE I. Conditions of Column Chromatography for 2-Arylpyridines (3)

Run	R	Silica gel (g)	Solvents	Product (3)
2a	CO_2CH_3	50	Hexane–acetone (10:1)	2-(2-Carbomethoxyphenyl)pyridine (**3a**$_2$) 2-(3-Carbomethoxyphenyl)pyridine (**3a**$_3$)/ 2-(4-carbomethoxyphenyl)pyridine (**3a**$_4$)
2b	Cl	50 (Formic acid)	Hexane–ethyl acetate (10:1)	2-(2-Chlorophenyl)pyridine (**3b**$_2$) 2-(3-Chlorophenyl)pyridine (**3b**$_3$) 2-(4-Chlorophenyl)pyridine (**3b**$_4$)
2c	CH_3	50	Hexane–acetone (20:1)	2-(2-Methylphenyl)pyridine (**3c**$_2$) 2-(3-Methylphenyl)pyridine (**3c**$_3$) 2-(4-Methylphenyl)pyridine (**3c**$_4$)
2d	OCH_3	100 (Acetic acid)	Benzene–acetone (10:1)	2-(2-Methoxyphenyl)pyridine (**3d**$_2$) 2-(3-Methoxyphenyl)pyridine (**3d**$_3$) 2-(4-Methoxyphenyl)pyridine (**3d**$_4$)
2e	OH	60	Benzene–acetone (25:1)	2-(2-Hydroxyphenyl)pyridine (**3e**$_2$) 2-(3-Hydroxyphenyl)pyridine (**3e**$_3$)/ 2-(4-hydroxyphenyl)pyridine (**3e**$_4$)
2f	1,2-$(OCH_3)_2$	60	Hexane–acetone (10:1)	2-(2,3-Dimethoxyphenyl)pyridine (**3f**$_{2,3}$) 2-(3,4-Dimethoxyphenyl)pyridine (**3f**$_{3,4}$)
2g	1,3-$(OCH_3)_2$	60	Hexane–acetone (5:1)	2-(2,4-Dimethoxyphenyl)pyridine (**3g**$_{2,4}$) 2-(2,6-Dimethoxyphenyl)pyridine (**3g**$_{2,6}$)
2h	1,4-$(OCH_3)_2$	Short column	Benzene	2-(2,5-Dimethoxyphenyl)pyridine (**3h**)

TABLE II. Synthesis of 2-Arylpyridines (3)

2	Reaction time (h)	3					Recovery of 1 (%)	4 (%)
		Yield (%)		Isomer ratio				
				o	*m*	*p*		
a	3	2.1	(10)[b]	65	16	20	80	8
	10	3.3	(10)	42	24	33	67	14
	3[a]	3.5	(12)	18	39	42	70	5.5
b	15	10	(26)	35	27	38[c]	62	12
c	15	10.5	(37)	40	26	34[c]	72	19
d	6	64	(67)	51	13	36	5	4.7
e	10	25	(48)	81	2	17	48	—[d]
f	3	2	(33)		25 (2′, 3′)	75 (3′, 4′)	94	3.2
	12	6.7	(13)		25	75	48	18
	3[a]	10.5	(45.5)		40	60	77	3
g	3	3.3	(24)		75 (2′, 6′)	25 (2′, 4′)	86	3.8
	3[a]	7.7	(28)		76	24	72	2.3
h	3	3.4	(15)				77	6
	3[a]	11.6	(33)				65	3.4

The yields and the isomer ratios were determined by GLC. *a*) The reactions were carried out in the presence of aq. K_2CO_3 (5 g in 10 ml of water). *b*) ( ); based on **1** consumed. *c*) Isolated. *d*) Not determined.

The structural assignments of the isolated **3** were primarily made on the basis of elemental analysis, mass spectra (MS) and proton nuclear magnetic resonance (^{1}H-NMR) spectra as listed in Tables III and IV, respectively.

In the cases of the chromatographically inisolable **3a**$_3$ and **3a**$_4$ and **3e**, the structures were confirmed by the following procedures. Isolation of **3a**$_4$ (R = 4′-CO_2CH_3) was achieved by fractional recrystallization of the mixture with **3a**$_3$ from hexane, and the structure was

TABLE III. Physical Data for 2-Arylpyridines (3)

Compd.	mp (°C)	Crystn. solvent	Physical form	Formula	Analysis (%) Calcd (Found)		
					C	H	N
3a$_2$[a]	171—178 (dec.)	Ethanol	Yellow needles	$C_{19}H_{14}N_4O_9$	51.59 (51.74	3.19 3.17	12.67 12.69)
3a$_4$	98	Hexane	Colorless needles	$C_{13}H_{11}NO_2$	73.22 (73.12	5.20 5.03	6.57 6.47)
3b$_2$[a]	136.5—138	Ethanol	Yellow needles	$C_{17}H_{11}ClN_4O_7$	48.76 (48.81	2.65 2.59	13.38 13.21)
3b$_3$[a]	140.5—142	Ethanol	Yellow needles	**3b**$_3$ + picric acid (1 : 1.2)[b]	46.95 (46.73	2.51 2.48	13.84 13.76)
3b$_4$[a]	162—165	Ethanol	Yellow feathers	$C_{17}H_{11}ClN_4O_7$	48.76 (48.81	2.65 2.58	13.38 13.39)
3c$_2$[a]	141—142.5	Ethanol	Yellow crystals	[10]			
3c$_3$[a]	178—182	Ethanol	Yellow needles	[11]			
3c$_4$[a]	175.5—177	Acetone	Yellow plates	[11]			
3d$_2$[a]	155.5—156	Acetone	Yellow needles	[12]			
3d$_3$[a]	158.5—159.5	Ethanol	Yellow needles	$C_{18}H_{14}N_4O_8$	52.18 (52.25	3.41 3.37	13.52 13.52)
3d$_4$	53.5—54.5	Benzene–petroleum ether	Colorless leaflets	[12,13]			
3e$_2$[a]	177—179	Ethanol	Yellow needles	**3e**$_2$ + picric acid + H_2O (1 : 0.85 : 0.5)[b]	51.75 (51.80	3.37 3.20	13.52 13.24)
3e$_4$	164—165	$CHCl_3$–hexane	Colorless needles	[13]			
3f$_{2,3}$[a]	156—159.5	Ethanol	Yellow needles	$C_{19}H_{16}N_4O_9$	51.35 (51.25	3.63 3.53	12.61 12.27)
3f$_{3,4}$[a]	174—176	Acetone	Yellow needles	$C_{19}H_{16}N_4O_9$	(51.25	3.61	12.74)
3g$_{2,6}$[a]	141—142	Ethanol	Yellow needles	$C_{19}H_{16}N_4O_9$	(51.37	3.58	12.61)
3g$_{2,4}$[a]	147.5—148.5	Ethanol	Yellow needles	$C_{19}H_{16}N_4O_9$	(51.39	3.56	12.69)
3h[a]	156—158.5	Ethanol	Yellow columns	$C_{19}H_{16}N_4O_9$	(51.43	3.63	12.49)
3i$_2$[a]	127—128	Acetone	Yellow prisms	$C_{18}H_{14}N_4O_8$	52.18 (51.94	3.41 3.30	13.45 13.45)
3i$_4$[a]	200	Ethanol	Yellow plates	$C_{18}H_{14}N_4O_8$	(51.96	3.39	13.28)

a) Colorless oil; physical data are for the picrate. *b*) Duplicate analyses showed that **3b**$_3$ picrate and **3e**$_2$ picrate contain 1.2 eq of picric acid, and 0.85 eq of picric acid plus 0.5 eq of H_2O, respectively. The latter was identical with the product obtained by hydrolysis of **3d**$_2$ (HI). The structures of these compounds were supported by the spectra.

supported by the MS and ^{1}H-NMR. Further, the mixture of **3a**$_3$ and **3a**$_4$ was derived to an isomeric mixture of 2-hydroxymethylphenylpyridine (**3i**, R = CH_2OH) with lithium aluminum hydride ($LiAlH_4$), and this product was hydrogenated over palladium–charcoal (Pd–C) to give the chromatographically separable **3c** as mentioned above (Chart 2). The mixture of **3e**,

TABLE IV. Mass and ^{1}H-NMR Spectral Data for **3**

Compd.	MS *m/z* (%)	^{1}H-NMR δ ($CDCl_3$) (J=Hz)						
		6-H	2′-H	3′-H	4′-H	5′-H	6′-H	R(CH_3, CH_2)
3a$_2$	182 (M−OCH_3, 100) 154 (12)	8.64^d (5)	—					3.87^s
3a$_3$	213 (M, 30) 155 (100) 154 (53)	8.73^d (5)	8.66^t (2)	—	8.10^{dt} (9, 2)	7.55^d (9)	8.27^{dt} (9, 2)	3.95^s
3a$_4$	213 (M, 56) 182 (100) 154 (25)	8.73^d (5)	8.10 (2′, 3′5′6′-H)		—			
3b$_2$	189 (M, 50) 154 (M−Cl, 100)	8.70^d (5)	—					
3b$_3$	189 (M, 100) 154 (88)	8.69^d (5)	8.00^t (2)	—				
3b$_4$	189 (M, 100) 154 (70)	8.67^d (5)	7.92^d (9)	7.41^d (9)	—	7.41^d (9)	7.92^d (9)	
3c$_2$	169 (M, 38) 168 (100)	8.68^d (5)	—					2.34^s
3c$_3$	169 (M, 100) 168 (64) 154 (M−CH_3, 10)	8.69^d (5)	7.83^s	—				2.44^s
3c$_4$	169 (M, 100) 168 (66)	8.66^d (5)	7.89^d (8)	7.30^d (8)	—	7.30^d (8)	7.89^d (8)	2.40^s
3d$_2$	185 (M, 100) 184 (99) 154 (97)	8.76^d (5)	—					3.87^s
3d$_3$	185 (M, 83) 184 (100) 154 (62)	8.72^d (5)	7.63^d (2)	—	6.95^{dt} (8, 2)	7.34^t (2)	7.55^{dd} (8, 2)	3.88^s
3d$_4$	185 (M, 100) 170 (36) 142 (52)	8.70^d (5)	7.99^d (9)	7.02^d (9)	—	7.02^d (9)	7.99^d (9)	3.85^s
3e$_2$	171 (M, 100) 143 (13)	8.42^d (6)	—					
3e$_3$	171 (M, 100) 143 (20)							
3e$_4$	171 (M, 100)	8.44^d (6)	7.79^d (9)	6.85^d (9)	—	6.85^d (9)	7.79^d (9)	
3f$_{2,3}$	215 (M, 100) 200 (55) 184 (41) 169 (29)	8.70^d (6)	—	—	6.97^{dd} (8, 2)	7.12^t (8)	7.37^{dd} (8, 2)	3.68^s, 3.92^s
3f$_{3,4}$	215 (M, 100) 200 (21) 184 (14)	8.65^d (6)	7.66^d (1)	—	—	6.95^d (8)	7.52^{dd} (8, 1)	3.93^s, 4.00^s
3g$_{2,6}$	215 (M, 100) 214 (99) 185 (46) 169 (36)	8.71^d (5)	—	6.64^d (8)	7.33^t (8)	6.64^d (8)	—	3.70^s
3g$_{2,4}$	215 (M, 72) 214 (100) 184 (29)	8.62^d (5)	—	6.56^s	—	6.62^{dd} (8, 2)	7.79^d (8)	3.84^s, 3.85^s
3h	215 (M, 100) 214 (78) 200 (31) 184 (28)	8.65^d (5)	—	6.90—6.98^m		—	7.40^t (2)	3.77^s, 3.81^s
3i$_2$	185 (M, 13) 167 (M−H_2O, 100)	8.59^d (5)	—					4.43^s
3i$_3$	185 (M, 32) 183 (96) 154 (M−CH_2OH, 100)							
3i$_4$	185 (M, 19) 183 (100) 154 (60)	8.63^d (5)	7.93^d (9)	7.40^d (9)	—	7.40^d (9)	7.93^d (9)	4.73^s

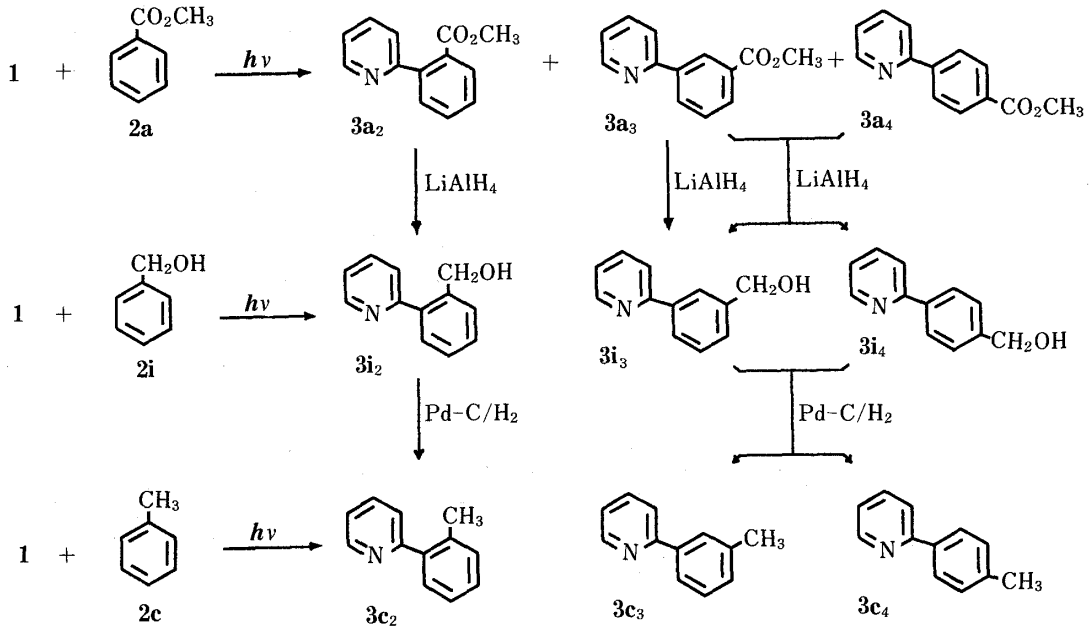


Chart 2

from which the *ortho* isomer (**3e**$_2$) was readily removed by column chromatography, was smoothly converted into a separable mixture of **3d**$_3$ and **3d**$_4$ by methylation with diazomethane; these products were identical with those obtained photochemically. The structure of **3e**$_2$ was deduced on the basis of the spectra.

Although some variation was observed in the isomer ratio of **3**, the spread of isomer distributions of **3b—d** seems to follow the characteristic pattern of homolytic aromatic substitutions, where the *meta* isomers are formed in appreciable amounts, in contrast to the *ortho* and *para* isomers, but the observed *o*/*p* ratios are lower than those obtained in the homolytic arylation of monosubstituted benzenes,[6c,14] indicating a distinctive character of the reactive entity of the present reaction.

The existence of some variations in the reaction conditions used for the runs and differences in the side reactions make comparisons unreliable, but the yields of **3** tended to increase as the substituents on the benzene ring became more electron-donating, reflecting electrophilic character of **1** in the present reaction.[15] This conclusion is compatible with the results found by Vernin in homolytic aromatic substitution with the thermally produced 2-pyridyl radical (**5**).[15a]

Interestingly, 2-chloropyridine (**4**) was detected as a by-product in appreciable yields (Table II), and this result is reminiscent of the formation of chlorobenzene by the photolysis of iodobenzene in tetrachloromethane.[16] It is known, however, that the phenyl radial, which abstracts a chlorine atom (Cl) from tetrachloromethane to furnish chlorobenzene,[16,17] does not attack Cl of chloroform but attacks hydrogen (H) to afford benzene.[17b] In contrast, cationic abstraction has been reported to occur at Cl of dichloromethane to give chlorinated compounds.[18] It seems reasonable to assume that the reactive species for the formation of **4** is electron-deficient **5**[19] or the pyridyl cation (**6**), which could be produced from **5** by electron transfer according to the scheme shown in Chart 3.[18,20] However, the latter seems less probable, because the process involving electron transfer from the electron-deficient pyridine moiety is presumed to be energetically unfavorable. Furthermore, when a solution of **1** in dichloromethane was irradiated for 3 h, the reduced product (pyridine) was detected together with **4** and unreacted **1** in the ratio of 1 : 2 : 22. Hence, it seems likely that the reactive species is

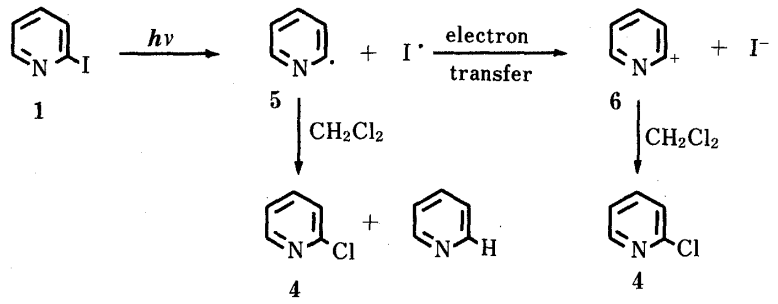


Chart 3

electron-deficient **5** rather than **6**.

The reaction of dimethoxybenzenes (**2f—h**) with **1** could account for the formation of considerable amounts of precipitated salts, composed of pyridine bases and hydrogen chloride, produced in the reaction. In fact, the reaction of **1** with **2f—h** proceeded much more efficiently in the presence of potassium carbonate.

Although the mechanism of the present reaction remains equivocal, this reaction provides a simple method for the synthesis of 2-arylpyridines and should be complementary to the reaction of aryllithiums with pyridine,[3l] particularly when electron-rich substrates are used.

Experimental

All melting points are uncorrected. ^{1}H-NMR spectra were measured with a Hitachi R-40 spectrometer (90 MHz) and chemical shifts are given on the δ (ppm) scale with tetramethylsilane as an internal standard. MS were determined on a Shimadzu LKB-9000 GC-mass spectrometer. Infrared (IR) spectra were recorded on a Shimadzu IR-400 spectrometer. Gas liquid chromatography (GLC) was carried out with a gas chromatograph (Shimadzu GC-6A) equipped with a hydrogen flame-ionization detector using nitrogen as a carrier gas (30 ml/min). Glass columns (1.5 m, 3 mmϕ) of 3% OV-17 on Shimalite W (for **3b—h**) and 2% fluoxylate-K (for **3a** and **3i**) were used. Column chromatography was performed on Kieselgel 60 (Merck) and thin layer chromatography (TLC) was carried out on Kieselgel 60 F_{254} (Merck) TLC plates. Ultraviolet (UV) irradiation was carried out in a Pyrex vessel at room temperature using an Eiko-sha 60 W low-pressure mercury lamp.

General Procedure for the Synthesis of 2-Arylpyridines (3a—h)——A solution of 2-iodopyridine (**1**) (5 mmol) and a substituted benzene (**2a—h**) in dichloromethane (CH_2Cl_2) (100 ml) was irradiated at room temperature for 3—15 h and then 50% aqueous potassium carbonate (K_2CO_3) (2 ml) (in the cases of the reactions with **2f—h**, 50 ml) and a standard material for GLC were added to the reaction mixture. The solution was stirred vigorously for 30 min. After separation of the aqueous layer, the organic layer was dried over anhydrous K_2CO_3. A small portion of the organic layer (1 ml) was passed through a short column of silica gel followed by GLC analysis. The remainder was extracted with 10% hydrochloric acid. The extract was neutralized with K_2CO_3 (in the case of **2e**, sodium bicarbonate was used) followed by extraction with CH_2Cl_2. The extract was dried over anhydrous sodium sulfate (Na_2SO_4) and evaporated, and the residual oil was subjected to column chromatography on silica gel using the solvent system indicated in Table I. The yields of the products (**3**) thus obtained are given in Table II.

2-Hydroxymethylphenylpyridines (3i)——A solution of **1** (5 mmol) in benzyl alcohol (**2**, R=CH_2OH) (100 ml) was irradiated for 6 h. The reaction mixture was worked up according to the general procedure followed by column chromatography on silica gel with benzene–hexane–acetone (5 : 5 : 1) to afford 2-(2-hydroxymethylphenyl)pyridine (**3i**$_2$) (87 mg) and a mixture of 2-(3-hydroxymethylphenyl)pyridine (**3i**$_3$) and 2-(4-hydroxymethylphenyl)pyridine (**3i**$_4$) (86 mg), in a ratio of 1 : 1.8 as determined by GLC (2% fluoxylate-K, 200 °C), together with recovered **1** (400 mg). The physical data are listed in Tables III and IV.

Reduction of 3a——A solution of **3a**$_2$ (29.7 mg) and $LiAlH_4$ (40 mg) in ether (30 ml) was stirred overnight at room temperature. Water was added to the reaction mixture and the precipitates that formed were filtered off. The ethereal layer was washed with water, dried over anhydrous Na_2SO_4 and evaporated *in vacuo*. The residual oil was passed through a short column of silica gel with ether to give **3i**$_2$ (14.2 mg) as a colorless oil, which was identical with photochemically produced **3i**$_2$ on the basis of spectral (MS, IR) and chromatographic (TLC, GLC) comparisons.

Similar treatment of **3a**$_4$ (6.5 mg) with $LiAlH_4$ (13 mg) afforded **3i**$_4$ (5.4 mg) as a viscous oil.

Hydrogenolysis of 3i——**3i**$_2$ obtained above was hydrogenolyzed overnight over 10% Pd on charcoal in ethanol

under atmospheric pressure of hydrogen at room temperature. The reaction mixture was evaporated *in vacuo* to leave **3c**$_2$ (5 mg) as a colorless oil.

Similar treatment of the isomeric mixture of **3i**$_3$ and **3i**$_4$ (5 mg) derived from **3a** with $LiAlH_4$ afforded an oily mixture of **3c**$_3$ and **3c**$_4$, which was separated by column chromatography under the conditions described in Table I to give **3c**$_3$ and **3c**$_4$ in yields of 0.8 mg and 1.3 mg, respectively. These products were identical with photochemically formed **3c** on the basis of MS and chromatographic (TLC, GLC) comparisons and the melting points of their picrates.

Methylation of 3e——An ethereal solution of diazomethane was added to a solution of the mixture of **3e**$_3$ and **3e**$_4$ (7.1 mg) in ether. The reaction mixture was kept standing overnight at room temperature. The insoluble material that formed during the reaction was filtered off and the filtrate was evaporated *in vacuo* to furnish an oily mixture of **3d**$_3$ and **3d**$_4$ (1 : 8) (7.6 mg), which were identical with the products derived photochemically from **2d** on the basis of MS and chromatographic (TLC, GLC) comparisons.

Hydrolysis of 3d$_2$——A solution of **3d**$_2$ (5.3 mg) in 57% hydriodic acid (1 ml) was heated for 1 h at 150 °C, then the reaction mixture was neutralized with sodium bicarbonate and extracted with CH_2Cl_2. The organic layer was washed with sodium thiosulfate ($Na_2S_2O_3$), dried over anhydrous Na_2SO_4 and evaporated *in vacuo* to give an oil (4.5 mg), which was identical with photochemically obtained **3e**$_2$ on the basis of MS and chromatographic (TLC, GLC) comparisons.

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