Reaction of the Pyrazinium Ion having Aryl and Cyano Groups with Hydride Reagents or Hydroxide Ion

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Reduction of 3-cyano-5-(3,4-dimethoxyphenyl)-1-methylpyrazinium ion by the hydride reagents such as sodium borohydride or Hantzsch ester gave the 1,6-dihydropyrazine derivative, and the 1,4,5,6-tetrahydropyrazine derivative on further reduction. Addition of hydroxide ion to the pyrazinium ion gave mainly a 6-hydroxy-pseudobase, accompanied by the minor formation of a 2-hydroxy-pseudobase. Photoreaction of the pseudobase mixture gave a product from the major pseudobase but thermal transformation gave another product from the minor pseudobase.

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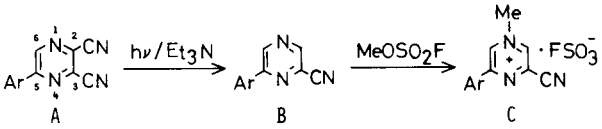
We have studied the photochemistry of dicyanopyrazines (1) and have reported that the photolysis of a dicyanopyrazine derivative (**A**) in the presence of amine provides an efficient method of the synthesis of monocyanopyrazine derivatives (**B**). The monocyanopyrazines (**B**) and the n-alkylpyrazinium salts (C) have an electron donating aryl group (Ar) and an electron withdrawing cyano group, which must provide a versatile nature to the pyrazine ring (2). These pyrazine derivatives may constitute chemical mimicries of NADP(3) and flavin coenzyme (4) due to their redox behavior and electrophilicity. Biochemical functions of these coenzymes are the subject of active research and variety of mechanisms has been proposed, *e.g.*, a single electron transfer, a hydride transfer, an adduct formation with a nucleophile (5).



Here we would like to report the reactions of 3-cyano-5-(3,4-dimethoxyphenyl)-1-methylpyrazinium fluorosulfonate (I) (hereafter Ar denotes the 3,4-dimethoxyphenyl group in all formulae) with hydride reagents or hydroxide ion. The 3, 4-dimethoxyphenyl group was selected due to its strong electron donating property and spectroscopic convenience as described later.

2,3-Dicyano-5-(3,4-dimethoxyphenyl) pyrazine was easily prepared by the condensation of diaminomaleonitrile with (3,4dimethoxyphenyl)ethane-1,2-dione (1,6). 3-Cyano-5-(3,4-dimethoxyphenyl)pyrazine was prepared by the photolysis of the dicyanopyrazine derivative in the presence of triethyl amine (1). The pyrazinium fluorosulfonate I was synthesized by *N*-methylation of the corresponding monocyanopyrazine derivative with methyl fluorosulfonate (7).

Reduction of the pyrazinium ion I with sodium borohydride or an equivalent amount of Hantzsch ester (II) gave 3-cyano-5-(3,4-dimethoxyphenyl)-1-methyl-1,6-dihydropyrazine (III) (83%) and the Hantzsch ester itself was converted into the oxidized from IV (equation 1). Further reduction of the dihydropyrazine III with sodium borohydride gave 3-cyano-5-(3,4-dimethoxyphenyl)-1-methyl-1,4,5,6-tetrahydropyrazine (V), which regenerated III on oxidation with quinones. The tetrahydro-derivative has an NH group (3352 cm^{-1}) and a trisubstituted double bond which shows a singlet olefinic signal in nmr (δ 6.71). These spectral data bring the structures V and VI as possible ones. The selection between V and VI can be made by the existence of β-amino-conjugated cyano group (2199 cm^{-1}) (8) and the nmr signal pattern of 3,4-dimethoxyphenyl group. The nmr signals due to the aromatic hydrogens of V appear as a 3H-signlet in the narrow range of chemical shift (δ 6.60-6.85). When a 3, 4-dimethoxyphenyl group attaches to an sp^2-carbon, the hydrogen at at the C_5-position resonates at higher field giving a 1H-doublet (J = 9 Hz) and the hydrogens at C_2 and C_6-positions resonate at lower field giving a 1H-doublet (J = 2 Hz) and a 1H-double doublet (J = 9 and 2 Hz), or a 2H-multiplet. On the other hand, the 3,4-dimethoxyphenyl group gives a 3H-singlet or a narrow 3H-multiplet on the attachment to an sp^3-carbon (9). Spectral data (ν CN at 2215 cm^{-1} and no ν NH) and the structure of tetrahydro-derivative V defined the structure III for the dihydropyrazine derivative.

The exposure of an ethanenitrile solution of the pyrazinium salt I to alkaline condition turns its red color into yellow and the addition of hydrochloric acid to the yellow solution regenerates the red color. The uv-absorption of pyrazinium salt I in alkaline solution is almost identical to that of the dihydropyrazine derivative III (Figure 1). The reversible color change and the uv-

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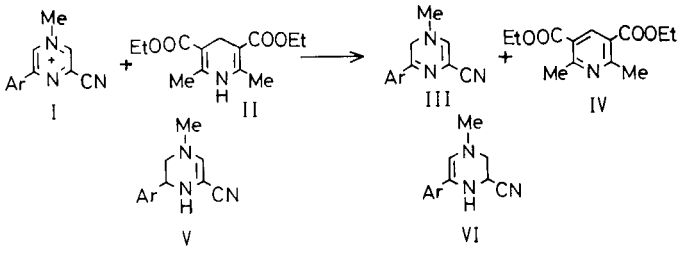


Equation 1

absorption suggest the absence of extensive decay of the chromophore under the basic condition but suggest the reversible addition and elimination of hydroxide ion as formulated in Equation 2. The intensity of the absorption

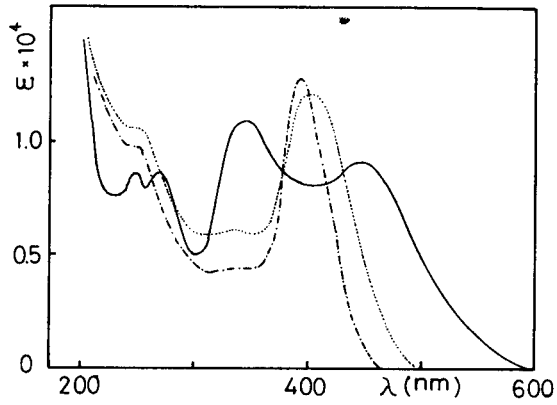
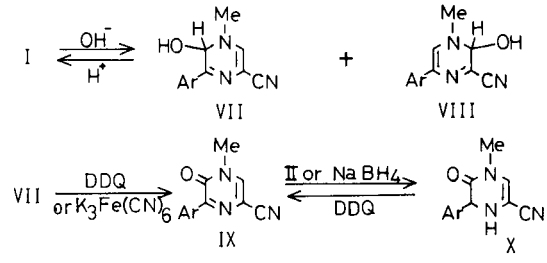


Figure 1. UV-absorption of Pyrazinium salt I (—), Dihydropyrazine III (·····), and Psuedobases VII + VIII (— · —) (a) in Ethanenitrile (a) I in basic ethanenitrile-water (98:2); 1.3*N* sodium hydroxide

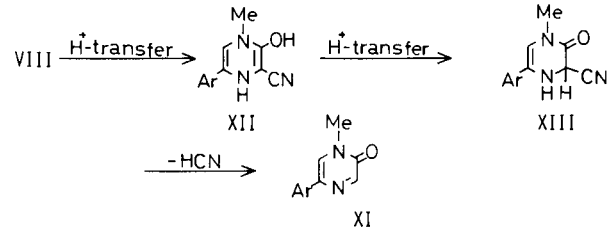
of the alkaline solution of I is similar to that of III and the adduct mixture must consist of mostly the C_6-adduct VII. This sort of reversible process has been reported in a more simple pyridinium (11) and a pyrazinium system (12), though the adducts (pseudobases) are too unstable to isolate (13).

Addition of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) or potassium ferricyanide to the yellow solution of the pseudobases gave 3-cyano-5-(3,4-dimethoxyphenyl)-1-methyl-1,6-dihydropyrazin-6-one (IX, Y = CN), *ca.* 50% by DDQ: 60-70% by potassium ferricyanide. The reduction of IX (Y = CN) by the Hantzsch ester (II) or by sodium borohydride gave 3-cyano-5-(3,4-dimethoxyphenyl)-1-methyl-1,4,5,6-tetrahydropyrazin-6-one (X). The tetrahydropyrazinone derivative X shows a narrow 3H-multiplet signel in the nmr due to the 3,4-dimethoxyphenyl group attached to the sp^3-carbon (9) and ir absorption at 2205 cm^{-1} due to the conjugated cyano group (8). These spectral data eliminate an alternative structure, 3-cyano-5-(3,4-dimethoxyphenyl)1-methyl-1,2,3,4-tetrahydropyrazin-2-one. The oxidation of X by DDQ or potassium ferricyanide regenerated IX and hence the structures IX and X were settled.

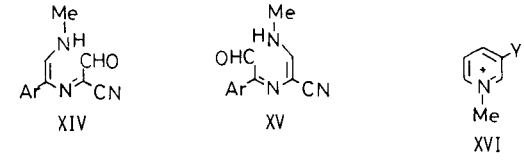
Oxidation of the pseudobase VII by potassium ferricyanide is facile, and the exclusive formation of the pyrazinone IX (Y = CN) indicates that the pseudobase VII is overwhelming another pseudobase VIII in the equilibrium mixture (Equation 2). Minor formation of the pseudobase VIII, however, is indicated by the isolation of 5-(3,4-dimethoxyphenyl)-1-methyl-1,2-dihydropyrazin-2-one (XI) (44%) in addition to IX (Y = CN) (6%) and its hydrolysis product, 3-carbamoyl-5-(3,4-dimethoxyphenyl)-1-methyl-1,6-dihydropyrazin-6-one (IX, Y = $CONH_2$) (37%), after allowing the alkaline solution of the pseudobases to stand for a week. The formation of dihydropyrazinone XI is accounted for by the prototropy



Equation 2



Equation 3



Equation 4

of keto-enol type involving an imino (C=N-) and a carbonyl group followed by dehydrocyanation (Equation 4).

In contrast to the thermal transformation of the pseudobase VIII to XI in the dark, the photolysis of the pseudobase mixture in argon atmosphere gave the tetrahydropyrazinone X as a main product and its oxidation product IX (Y = CN) as a minor product. The

photolysis in open air reversed the product ratio (see Table I). This result suggests that the product IX (Y = CN) is formed, at least partly, from X by autoxidation. The oxidized product IX (Y = CN), however, may partly be formed by the oxidation of X by the starting pyrazinium ion I (11,13), which exists in the reaction mixture as an equilibrating species though the reduced product from I was not successfully isolated under the photolysis condition.

Table I

Transformation of the Pseudobase Mixture (VII and VIII)

		product		
	IX (Y)	(%)	X (%)	XI (%)
Oxidation (DDQ)	(CN)	50	—	—
Thermal (in air)	(CN, $CONH_2$)	43	—	44
Photochemical (in argon)	(CN	19	42	—
Photochemical (in air)	(CN)	33	6	—

The unstable pseudobases VII and VIII, which have an acetal like structure, isomerize to the tetrahydropyrazinone systems X and XIII by proton transfer. The product XIII from the pseudobase VIII looses hydrogencyanide to give the stable dihydroprazinone XI. It is noteworthy that the thermal proton transfer gives the decyano-derivative XI as the final product from the minor pseudobase VIII. This phenomenon can be understood by considering the relative stabilities of the pseudobases VII and VIII. The pseudobase VII is expected to be more stable than the pseudobase VIII, since VII has a wider conjugate system than VIII which has a cross conjugate system. The tetrahydropyrazinone derivative X lacks the intrinsic property to loose hydrogencyanide since the cyano group is attached to the sp^2-carbon. On the other hand, the intermediate XIII is stabilized by loosing hydrogencyanide to give the pyrazinone derivative XI from the minor pseudobase VIII by thermal process. It is conceivable that the photochemical proton transfer is fast and indiscriminate, and the product X from the major pseudobase VII is the only isolable one.

In general, the yields of the products from the pseudobases are not very high and the formation of complex and polar products was accompanied in each reaction. This can be accounted for by the instability of the pseudobases which are assumed to open the ring to afford enamino-aldehydes XIV and XV and to decompose under basic condition (11).

The addition of hydroxide ion to 1-alkyl-3-carbamoylpyridinium ion (XVI, Y = $CONH_2$) takes place indiscriminatively and the adducts give both 1-alkyl-3 carbamoyl-2-pyridone and 1-alkyl-5-carbamoyl-2-pyridone after oxidation with potassium ferricyanide (4). The reaction of 1-alkyl-3-carbamoylpyridinium ion (XVI, Y = $CONH_2$) with sodium borohydride gives 1-alkyl-3-carbamoyl-1,6-dihydropyridine (10). On the other hand, the reduction of 1-alkyl-3-cyanopyridinium ion (XVI, Y = CN) gives both 1,2- and 1,6-dihydropyridines indiscriminatively (10). The present study shows that the attack of nucleophiles on the pyrazinium ion I occurs predominantly on the C_6-position. The attack of hydroxide ion or formal hydride (H^- or $H^+ + 2e^-$) on the pyrazinium ion I is governed by the aryl group rather than the cyano group.

In summary we described the electronic control of nucleophilic (H^- or OH^-) attack on a pyrazinium ion, and the redox properties of pyrazine derivatives.

EXPERIMENTAL

Synthesis of 3-Cyano-5-(3,4-dimethoxyphenyl)-1-methylpyrazinium Fluorosulfonate (I).

To an ice-cooled solution of 261 mg. (1.0 mole) of 3-cyano-5-(3,4-dimethoxyphenyl) pyrazine in 5 ml. of chloroform was added to 5 ml. of chloroform solution of 0.2 ml. of methyl fluorosulfonate during the period of 10 minutes. The reaction mixture was allowed to stand for 24 hours to precipitate a dark solid. After evaporation of the solvent the residue was treated with 3 ml. of ethanol and filtered. the residue on filtration was crystallized from ethanenitrile to give the dark red crystals of I (66%), m.p. 165°; uv (ethanenitril):λ max nm (ε) 249 (8.09 X 10^3), 274 (7.75 X 10^3), 354 (1.11 X 10^4), 450 (7.35 X 10^3); ir (nujol): 2248, 1595, 1500, 1239 1015 cm^{-1}; nmr (DMSO-d_6): δ (DSS reference) 3.88 (S, 6H), 4.53 (S, 3H), 7.26 (d, 1H, J = 8 Hz), 7.82 (diffused singlet, 1H), 8.00 (diffused doublet, 1H, J = 8 Hz), 9.84 (s, 1H), 10.12 (s, 1H).

Anal. Calcd. for $C_{14}H_{14}FN_3O_5S$: C, 47.32; H, 3.97; N, 11.83. Found: C,47.28; H, 4.04; N, 11.70.

Reduction of 3-Cyano-5-(3,4-dimethoxyphenyl)-1-methylpyrazinium Fluorosulfonate (I).

(i).

An equimolar mixture of I and the Hantzsch ester (II) (1.0 mmole) in 70 ml. of ethanenitrile was stirred for 3 hours, and the condensate of the reaction mixture was subjected to preparative tlc (alumina, chloroform-ethanenitrile) to give 3-cyano-5-(3,4-dimethoxyphenyl)-1-methyl-1,6-dihydropyrazine (III) (80%) and the oxidized form of the Hantzsch ester (IV) (85%). Compound III had m.p. 114-116°; (ethanenitrile): uv λ max nm (ε) 400 (1.25 X 10^4); ir (nujol): 2215, 1595, 1504, 1263, 1019 cm^{-1}; nmr (deuteriochloroform): δ 2.86 (s, 3H), 3.84 (s, 8H), 6.75 (d, 1H, J = 9 Hz), 6.85 (s, 1H), 7.13 (d, 1H, J = 2 Hz), 7.51 (double doublet, 1H, J = 9 and 2 Hz).

Anal. Calcd. for $C_{14}H_{15}N_3O_2$: C, 65.35, H, 5.88; N, 16.33. Found: C, 65.58; H, 5.84; N, 16.51.

To an ice-cooled solution of 375 mg. (1.0 mmole) of I in 50 ml. of ethanenitrile, was added 20 mg. (1.8 mmoles) of sodium borohydride in 5 ml. of ethanenitrile and the mixture was stirred for 30 minutes at room temperature. After acidification with dilute aqueous hydrochloric acid the solvent was evaporated. The residue was treated with 40 ml. of chloroform and filtered through celite. The condensate of the filtrate was subjected to chromatography on alumina (1.0 X 10 cm) eluted by chloroform to give III (83%).

(ii).

Further reduction of III to 3-cyano-5-(3,4-dimethoxyphenyl)-1-methyl -1,4,5,6-tetrahydropyrazine (V) was carried out in the same manner as for the reduction of I by sodium borohydride (73%) and by the Hantzsch ester (70%). The reduction of III to V is sluggish compared to the reduction of I to III and the reaction time was prolonged to 3 hours for the borohydride reduction and 24 hours for the Hantzsch ester reduction. Compound V was obtained as yellow crystal from benzene-methanol,

m.p. 128-130°; λ max (ethanenitrile): nm (ε) 228 (1.52 X 10^4), 278 (1.41 X 10^4); ir (potassium bromide): 3352, 2843, 2199, 1622, 1598, 1515, 1250 cm^{-1}; nmr (deuteriochloroform): δ 2.58 (s, 3H), 2.96 (m, 1H), 3.83 (s, 6H), 4.04 (m, 1H), 4.75 (m, 1H), 6.60-6.85 (m, 3H), 6.71 (s, 1H), 6.80 (broad singlet, NH, 1H). Compound V regenerated III on oxidation with quinones such as DDQ.

Oxidation of Pseudobase (VIII).

(i).

A suspension of 177 mg. (0.5 mmole) in 20 ml. of ice-cooled ethanenitrile was added with 2 ml. of 1*N* aqueous sodium hydroxide and the mixture turned into yellow from red due to the formation of pseudobases (VII and VIII). To the solution of the pseudobases was added 180 mg. (0.75 mmole) of DDQ in 3 ml. of ethanenitrile. After concentration of the reaction mixture, the condensate was extracted twice with 30 ml. of chloroform. The extract was condensed after washing with water and drying over sodium sulfate to give the crude product. The product was purified by chromatography on alumina (0.5 X 5 cm) eluted by benzene-chloroform (1:1) to give 3-cyano-5-(3,4-dimethoxyphenyl)-1-methyl-1,6-dihydropyrazin-6-one (IX, Y = CN) (50%), m.p. 206-207°; ir (chloroform): 2848, 2235, 1660, 1600, 1570, 1517, 1468, 1146, 1023 cm^{-1}; nmr (deuteriochloroform): δ 3.59(s, 3H), 3.48(s, 6H), 6.75(d, 1H, J = 9 Hz), 7.61(s, 1H, 7,88(d, 1H J = 2 Hz), 8.15(double doublet, 1H, J = 9 and 2 Hz).

Anal. Calcd. for $C_{14}H_{13}N_3O_3$: C, 61.98; H, 4.83; N, 15.49. Found: C, 61.68; H, 4.69; N, 15.22.

The residue left over from the chloroform extraction gave the reduced form of DDQ.

(ii).

A solution of 633 mg. (1.0 mmole) of I in ice-cooled 0.2*N* aqueous sodium hydroxide was added with 633 mg. (1.9 mmoles) of potassium fericyanide and the reaction solution was stirred for 90 minutes in an ice-bath and then for an additional 7 hours at room temperature. Chloroform extraction of the reaction solution gave IX (Y = CN) in 70% yield.

Reduction of 3-Cyano-5-(3,5-dimethoxyphenyl)-1-methyl-1,6-dihydropyrazin-6-one (IX, Y = CN).

(i).

A solution of 135 mg. (0.5 mmole) of IX in 5 ml. of ice-cooled chloroform was treated with 30 mg. (0.81 mole) of sodium borohydride in 5 ml. of ice-cooled methanol and the mixture was allowed to stand for 30 minutes. After evaporation of the solvents the residue was treated with chloroform and the suspension was filtered through celite. The chloroform extract gave 3-cyano-5-(3,4-dimethoxyphenyl)-1-methyl-1,4,5,6-tetrahydropyrazin-6-one (X) (88%) after chromatography on alumina (0.5 X 7 cm) eluted with chloroform, m.p. 166-167°; uv (ethanenitrile): λ max nm (ε) 237 (1.94 X 10^4), 285 (7.51 X 10^3), 305 (6.71 X 10^3); ir (chloroform): 3425, 2830, 2205, 1670, 1635, 1510, 1465, 1135, 1020 cm^{-1}; nmr (deuteriochloroform): δ 3.18 (s, 1H), 3.80 (s, 6H), 4.94 (broad singlet, 2H), 6.80 (s, 4H).

Anal. Calcd. for $C_{14}H_{15}N_3O_3$: C, 61.53; H, 5.53; N, 15.38. Found: C, 61.77; H, 5.54; N. 15.44.

(ii).

The mixture of 27 mg. (0.1 mmole) of IX (Y = CN) and 25 mg. (0.1 mmole) of the Hantzsch ester in 5 ml. of ethanenitrile was added with 0.2 ml. of 1*N* hydrochloric acid, and the mixture was allowed to stand for 16 hours. Chromatographic separation of the products by preparative tlc on alumina gave X (85%) and the oxidized form of the Hantzsch ester (85%).

Oxidation of 3-Cyano-5-(3,4-dimethoxyphenyl)-1-methyl-1,4,5,6-tetrahydropyrazin-6-one (X).

An ice-cooled solution of 135 mg. (0.5 mmole) of X in 5 ml. of ethanenitrile was treated dropwise during 20 minutes with 121 mg. (0.6 mmole) of DDQ in 5 ml. of ethanenitrile. Tlc analysis of the reaction mixture showed complete disappearance of X and the formation of IX (Y = CN). Chromatography of the crude product on alumina gave IX (Y = CN) in 76% yield.

Thermal Decomposition of 3-Cyano-5-(3,4-dimethoxyphenyl)-1-methylpyrazinium Fluorosulfate (I) under Basic Condition.

A suspension of 355 mg. (1.0 mmole) of I in 30 ml. of ethanenitrile was added with 3 ml. of 1*N* aqueous sodium hydroxide and the mixture was allowed to stand for 7 days at room temperature in the dark. The condensate of the mixture was separated by preparative tlc on alumina eluted by chloroform to give IX (Y = CN) (6%) as a top fraction, 5-(3,4-dimethoxyphenyl)-1-methyl-1,6-dihydropyrazin-6-one (XI) (44%) as a medium fraction, and 3-carbamoyl-5-(3,4-dimethoxyphenyl)-1-methyl-1,6-dihydropyrazin-6-one (IX, Y = $CONH_2$) (37%). Compound IX (Y = $CONH_2$) had m.p. 222-224°; ir (nujol): 3353, 3173, 1699, 1626, 1602, 1565, 1285, 1150, 1030 cm^{-1}; nmr (deuteriochloroform): δ 3.70 (s, 3H), 3.97 (s, 6H), 7.11 (d, 1H, J = 9 Hz), 7.77 (d, 1H, J = 2 Hz), 8.05 (broad singlet, 1H), 8.28 (double doublet, 1H J = 9 and 2 Hz), 8.41 (broad singlet, 1H).

Anal. Calcd. for $C_{14}H_{15}N_3O_4$: C, 58.12; H, 5.23; N, 14.53. Found: C, 58.10; H, 5.17; N, 14.79.

Compound XI had m.p. 138-140°; ir (chloroform): 2850, 1655, 1510, 1250, 1140, 1025 cm^{-1}; nmr (deuteriochloroform): δ 3.73 (s, 3H), 4.03 (s, 3H), 4.10 (s, 3H), 7.11 (d, 1H, J = 9 Hz), 7.41 (double doublet, 1H, J = 9 and 2 Hz), 7.57 (d, 1H, J = 2 Hz), 7.69 (s, 1H), 8.49 (s, 1H).

Anal. Calcd. for $C_{13}H_{14}N_2O_3$: C, 63.40; H, 5.75; N, 11.38. Found: C, 63.42; H, 5.78; N, 11.72.

Photolysis of 3-Cyano-5-(3,4-dimethoxyphenyl)-1-methlpyraziniumFluorosulfonate (I) under Basic Condition.

A suspension of 426 mg. (1.2 mmoles) of I in 100 ml. of ethanenitrile was added with 5 ml. of 1*N* aqueous sodium hydroxide and the mixture turned to yellow. The solution thus obtained was placed in Pyrex tubes and irradiated in open air with a 450w high pressure mercury lamp, mounted in a rotary irradiation apparatus (the distance between the lamp and the tubes was *ca.* 5 cm). For the irradiation in argon atmosphere the tubes containing the reaction solution were dipped in an ultrasonic bath and purged by bubbling argon before irradiation. After disappearance of the starting material the condensate of the reaction mixture was separated by preparative tlc (alumina/chloroform) to give IX (Y = CN), X, and XI in the yields listed in Table 1.

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