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The reaction of 5-(3,4-dimethoxyphenyl)pyrazine-2,3-dicarbonitrile (Ib) with alkyl radicals gives addition products at the C(6)-position of the pyrazine ring as the intermediates which collapse into substitution products, 6-alkyl-5-(3,4-dimethoxyphenyl)pyrazine-2,3-dicarbonitrile (II), under oxidative conditions. Under non-oxidative conditions the intermediate is converted into dihydropyrazine derivatives, 6-alkyl-(3,4-dimethoxyphenyl)-5,6-dihydropyrazine-2,3-dicarbonitrile (III), and 3,6-disubstituted pyrazine derivatives, 3,6-dialkyl-5-(3,4-dimethoxyphenyl)pyrazine-2-carbonitrile (IV) and 3-acyl-6-alkyl-5-(3,4-dimethoxyphenyl)pyrazine-2-carbonitrile (V).

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We have been studying photochemical [1a-d] and thermal reactions [2] of 5-substituted pyrazine-2,3-dicarbonitriles which have both electron donating and electron withdrawing groups. 5-((Benzo-*m*-crown-*n*)-4'-yl)pyrazine-2,3-dicarbonitrile (Ia) ( $m = 15$  or  $18$ ;  $n = 5$  or  $6$ ) arose our interest as a biomimetic system having both binding site (crown ether moiety) and redox system (pyrazinedicarbonitrile). 5-(3,4-Dimethoxyphenyl)pyrazine-2,3-dicarbonitrile (Ib) has been used as a reference compound of the benzo-crown ether derivatives cited above, and it has been established that the reaction with some nucleophiles give substitution products on the pyrazine ring or addition products at the nitrile group. Substitution with nucleophiles such as water, an alcohol, ammonia and an amine occurs only at C(2) or C(3)-position of the pyrazine ring where the nitrile group locates [2].

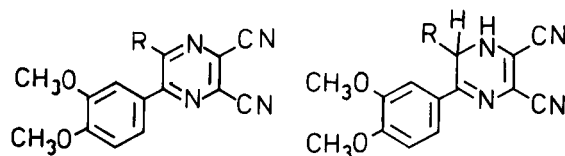
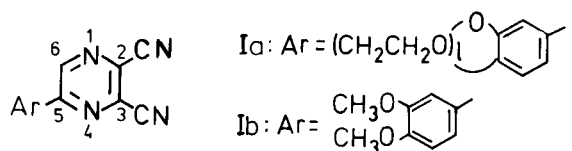
In this paper we report the reaction of Ib with alkyl radicals which has been recognized to be nucleophilic in aromatic substitution reactions [3].

Reaction with Alkyl Radicals Derived from a Carboxylic Acid.

Silver ion mediated oxidation of aliphatic carboxylic acids by peroxy sulfate gives radicals [3]. The alkyl radicals thus formed have nucleophilic properties in the reaction with  $\pi$ -deficient heteroaromatics [4a,b]. The reaction of Ib with isobutyric acid under these oxidative conditions gave 5-(3,4-dimethoxyphenyl)-6-isopropylpyrazine-2,3-dicarbonitrile (IIa) in 60% yield. The structure of IIa was deduced by the displacement of <sup>1</sup>H-nmr signal due to the hydrogen on the original pyrazine ring with the signals at  $\delta = 1.33$  (d, 6H) and 3.69 (septet, 1H) due to isopropyl group. This reaction can be understood by considering the first addition of isopropyl radical at the sterically feasible C(6)-position of Ib to give the radical intermediate which is oxidized to IIa under the reaction conditions (Eq. 1).

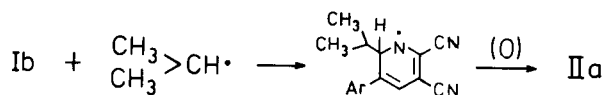
We could not get the methyl substituted product from the reaction Ib and acetic acid under similar conditions.

This fact suggests that the radical substitution of Ib takes place with more stable and nucleophilic isopropyl radical than methyl radical.



IIa~c

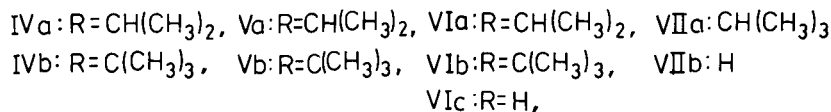
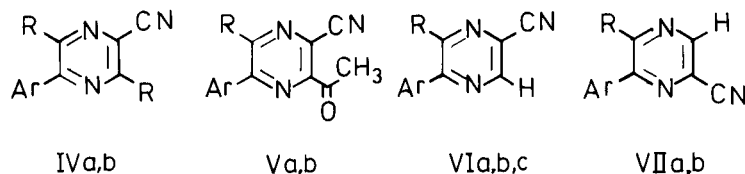
IIIa~c

IIa, IIIa: R = CH(CH<sub>3</sub>)<sub>2</sub>IIb, IIIb: R = C(CH<sub>3</sub>)<sub>3</sub>IIc, IIIc: R = CH(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>

Eq. 1

Photochemical Reaction with Aldehydes or Ketones.

Photolysis of simple aldehydes or ketones gives alkyl radical and acyl radical [5]. In the condensed phase this process is usually not an efficient one with the carbonyl compound having a primary alkyl residue, mostly due to rapid recombination of an alkyl radical and an acyl radical. The aldehyde or ketone having a secondary or a tertiary alkyl group, however, is easily photolyzed to give the radical species [6].



A mixture of Ib and 2-methylpropanal (1:30) in ethanenitrile was photolyzed and the addition product IIIa was obtained in 47% yield (64% based on consumed Ib). The structure of IIIa was deduced by an ir-absorption at 3330 cm<sup>-1</sup> (NH) and the displacement of the <sup>1</sup>H-nmr signal due to the original hydrogen on the pyrazine ring with the signals at 0.78 (d, 3H), 0.96 (d, 3H), and 1.44-1.95 (m, 1H) due to isopropyl group and 4.68 (d, 1H) due to the methine hydrogen on dihydropyrazine ring. The dihydropyrazine derivative IIIa was oxidized by dichlorodicyanobenzoquinone (DDQ) in benzene to give IIa which was formed by the attack of an isopropyl radical under oxidative conditions.

The photolyses of the mixture containing propanal or hexanal did not give the addition product and recovered the starting material. A primary alkyl radical is considered to not generate efficiently by photolysis and also it is not strongly nucleophilic [7a,b]. The situation is similar to the methyl radical generated by the silver mediated oxidation of acetic acid mentioned earlier.

Table

Photoproducts by the Irradiation of Ib and Carbonyl Compounds

Substrate	Product (Yield %)			
(CH <sub>3</sub> ) <sub>2</sub> CHCHO	IIIa (47) [a]			
(CH <sub>3</sub> ) <sub>3</sub> CCHO	IIIb (52) [a]			
(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> CHCHO	IIIc (12) [a]			
(CH <sub>3</sub> ) <sub>2</sub> CHCOCH(CH <sub>3</sub> ) <sub>2</sub>	IIIa (33) [a]	IVa (34)		
(CH <sub>3</sub> ) <sub>2</sub> CHCOCH <sub>3</sub>	IIIa (18) [a]	IVa (6)	Va (30)	
(CH <sub>3</sub> ) <sub>3</sub> CCOCH <sub>3</sub>	IIIb (20) [a]	IVb (1)	Vb (31)	VIb (6)

[a] The yields were calculated after DDQ oxidation to IIa-c.

The photoreaction of Ib with 2,4-dimethyl-3-pentanone under the same conditions as in the case of aldehydes gave dihydropyrazine derivative IIIa and 3,6-diisopropylpyrazine derivative IVa in 33 and 34% yield respectively. The structure of IVa was assigned from the spectroscopic data - two sets of doublets (12H) at 1.27 and 1.38 and the multiplet at 3.28-3.48 (2H) due to the isopropyl groups on the pyrazine ring and the similarity of the uv-spectrum of IVa to 5-(3,4-dimethoxyphenyl)-6-isopropylpyrazine-2-carboni-

trile (VIa), which was obtained together with 5-(3,4-dimethoxyphenyl)-6-isopropylpyrazine-3-carbonitrile (VIIa) by the photo-decyanation of IIa in the presence of triethylamine [1a,b]. The structures of VIa and VIIa were discriminated by the following spectral features. The uv spectrum of VIa has a stronger CT-absorption band than VIIa in the longer wave length region as in the cases of 5-(3,4-dimethoxyphenyl)pyrazine-2-carbonitrile (VIc) and 5-(3,4-dimethoxyphenyl)pyrazine-3-carbonitrile (VIIb) [1a,b].

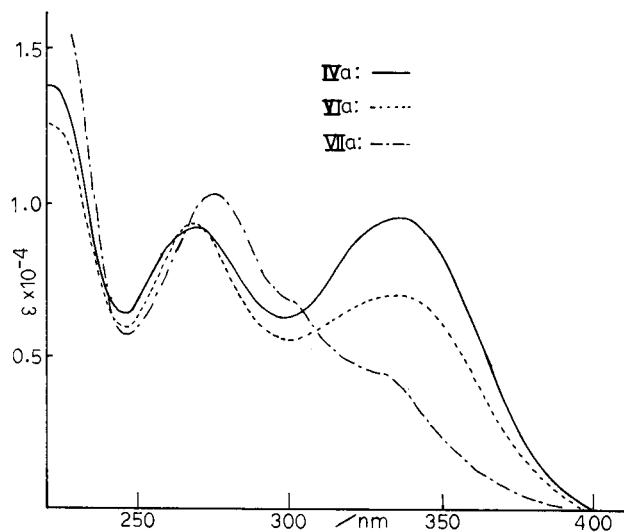
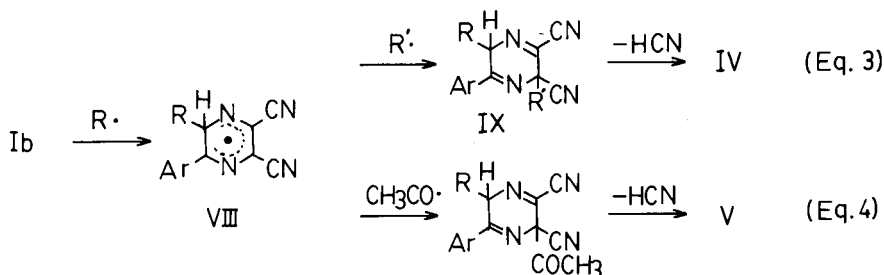
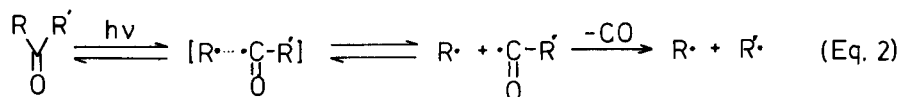


Figure. UV Spectra of IVa, VIa and VIIa in ethanenitrile.

The intensity of ir-absorption of the nitrile group is strong in VIa but weak in VIIa. This is a characteristic feature in all cases in the present and related studies [2a,b]. *para*-Conjugation of the nitrile group with the dimethoxyphenyl group makes the nitrile more polar and hence a stronger ir absorption is observed. The <sup>1</sup>H-nmr signal of the hydrogen on the pyrazine ring is seen at lower field with VIIa (8.75) than with VIa (8.69) due to the *para*-conjugation with the electron donating group.

The formation of IVa is supported by the following consideration. The coupling between the radical intermediate VIII and another alkyl radical (R') takes place favorably at



the C(3)-position of pyrazine ring, and dihydropyrazine derivative IX loses hydrogen cyanide to give the substitution product IVa (Eq. 3). Photoreactions of Ib with 3-methyl-2-butanone and 3,3-dimethyl-2-butanone gave the acetylpyrazine derivative Va (30%) and Vb (31%) together with dihydropyrazine derivative IIIa and IIIb. The same mechanistic consideration as for the formation of IVa leads to the structures Va and Vb for the product having an acetylpyrazinecarbonitrile moiety (Eq. 4). In these reactions, however, as 3-methylpyrazine derivative similar to IVa was not obtained since the acetyl radical does not cause decarbonylation with the same ease as 2-methylpropanoyl and 2,2-dimethylpropanoyl radicals (Eq. 2).

The photoreaction of Ib with 3,3-dimethyl-2-butanone gave the third product, 5-(3,4-dimethoxyphenyl)-6-(*t*-butyl)pyrazine-2-carbonitrile (VIb), in minor amount (6%). This product must be formed by the hydrogen abstraction from the *t*-butyl radical by the intermediate VIII. Hydrogen abstraction at the N(1)-position of VIII, which must be intrinsically favorable, is now sterically hindered by the foregoing *t*-butyl group on the adjacent position. In addition, the *t*-butyl radical is too bulky to combine with the intermediate VIII at the C(3)-position and transfers a hydrogen atom to furnish VIb and isobutene.

The photoreactions cited in this paper proceed smoothly on irradiation with a high pressure mercury lamp through a quartz vessel but only sluggishly through a Pyrex vessel, even though Ib has strong absorption over 300 nm;  $\lambda_{\text{max}}(\epsilon)$  in ethanenitrile: 369 (19300). The irradiation by 254 nm radiation also caused a smooth reaction. These results indicate that the photoreaction is caused by the excitation of carbonyl compound.

Some *N*-heterocycles react photochemically with an aldehyde to give an *N*-acyl derivative [8], and this has been attributed to the initial abstraction of a formyl hydrogen from the aldehyde by the excited *N*-heterocycle. In the

present study, however, we could not get an *N*-acyl derivative from any aldehyde. In addition we obtained the same type of the products III from both aldehydes and ketones though no formyl hydrogen exists in the latter. This feature can be accounted for by the lack of  $n\pi^*$  character in the excited Ib due to the intramolecular charge transfer between the phenyl and the pyrazine rings. 2-Ethylbutanal gave the photo-product IIIc in poor yield (12%) compared to 2-methylpropanal (47%) under the same conditions. This feature can be understood by considering a Norrish type II process of the excited 2-ethylbutanal, which is competitive with the Norrish type I fission to give a pair of alkyl and acyl radicals.

Association of Ib and an aldehyde or a ketone could not be detected by uv-absorption and there is no possibility that the ground state perturbation of an aldehyde or a ketone with Ib generates the photo-reactive state of Ib. These discussions support the reaction scheme shown in Eq. 2-4 which involves the initial attack of the alkyl radical generated by the photolysis of an aldehyde or a ketone.

Alkyl radicals, generated by the oxidative decomposition of a carboxylic acid or photolysis of a carbonyl compound, attack the C(6)-position of the pyrazine ring of Ib and this regioselectivity is in marked contrast with the nucleophilic attack of an alcohol or an amine which causes the substitution of the nitrile group at the C(2)- or the C(3)-position of the pyrazine system of Ib [2a,b]. This specificity of radical attack on Ib is accounted for by the formation on the intermediate radical VIII in which the system is stabilized by full conjugation with 3,4-dimethoxyphenyl group.

## EXPERIMENTAL

### The Reaction of Ib with an Isopropyl Radical.

Into a 200 ml two necked flask were placed Ib (532 mg,  $2 \times 10^{-3}$  mole) and silver nitrate (204 mg,  $1.2 \times 10^{-3}$  mole), and the solution of isobutyl-

ic acid (1.056 g,  $1.2 \times 10^{-2}$  mole) in 125 ml of the mixed solvent ethanenitrile-water (4:1). The mixture was treated dropwise with the solution of ammonium peroxy sulfate (1.824 g,  $1.8 \times 10^{-2}$  mole) in 25 ml of water during 10 minutes and then the mixture was warmed to 80° for 3 hours. The mixture was magnetically stirred and kept under nitrogen atmosphere during the entire operation. After cooling the reaction mixture, ethanenitrile was evaporated under reduced pressure and the resulting residue was extracted repeatedly with chloroform (total 200 ml). The extract was washed with water and aqueous sodium hydrogencarbonate, and dried over anhydrous sodium sulfate. Chromatography of the residue on alumina eluted by chloroform-benzene (1:1) gave IIa in 60% yield, mp 143°; ir (chloroform): 2940, 2850, 2250  $\text{cm}^{-1}$ ; uv (ethanenitrile):  $\lambda$  max ( $\epsilon$ ), 222 ( $1.26 \times 10^4$ ), 268 ( $9.35 \times 10^3$ ), 335 nm ( $7.00 \times 10^3$ ); <sup>1</sup>H-nmr (deuteriochloroform):  $\delta$  (J in Hz), 1.33 (d, 6H, J = 7), 3.67 (septet, 1H, J = 7), 3.97 (s, 3H), 3.99 (s, 3H), 6.93-7.35 (m, 3H).

*Anal.* Calcd. for  $\text{C}_{17}\text{H}_{10}\text{N}_4\text{O}_2$ : C, 66.22; H, 5.23; N, 18.17. Found: C, 66.59; H, 5.46; N, 18.18.

#### Photoreaction of Ib with Aldehydes.

A mixture of Ib (133 mg,  $5 \times 10^{-4}$  mole), one of the aldehydes (30 equivalents), and 14 ml of ethanenitrile was placed in a quartz tube with a neoprene serum cap. The mixture was then dipped in an ultrasonic bath and argon was bubbled through with a syringe needle for 10 minutes. The reaction tube was placed in a rotary irradiation apparatus (Rikosha RH-400) equipped with a 400 W high pressure mercury lamp (the distance between the lamp and the reaction tube: ca. 4 cm). After irradiation for 1-4 hours (2,2-dimethylpropanal, 1 hour; 2-methylpropanal, 2 hours; 2-ethylbutanal, 4 hours), the mixture was condensed under reduced pressure and separated by chromatography on alumina eluted by chloroform-methanol (100:2) to give dihydropyrazine derivatives IIIa-c. The <sup>1</sup>H nmr spectra in DMSO are shown by  $\delta$ -value using DSS as an internal reference.

#### Compound IIIa.

This compound had mp 197° dec; ir (potassium bromide): 3330, 2940, 2850, 2225  $\text{cm}^{-1}$ ; uv (ethanenitrile):  $\lambda$  max ( $\epsilon$ ), 291 ( $1.23 \times 10^4$ ), 401 nm ( $1.25 \times 10^4$ ); <sup>1</sup>H-nmr (DMSO-*d*<sub>6</sub>):  $\delta$  (J in Hz), 0.78 (d, 3H, J = 8), 0.96 (d, 3H, J = 8), 1.44-1.95 (m, 1H), 3.82 (s, 6H), 4.68 (d, 1H, J = 10), 6.95 (d, 1H, J = 10), 7.40-7.62 (m, 2H), 8.80 (broad s, NH).

*Anal.* Calcd. for  $\text{C}_{17}\text{H}_{10}\text{N}_4\text{O}_2$ : C, 65.70; H, 5.85; N, 18.05. Found: C, 65.99; H, 5.92; N, 18.03.

#### Compound IIIb.

This compound had mp 167° dec; ir (chloroform): 3305, 2940, 2850, 2235  $\text{cm}^{-1}$ ; <sup>1</sup>H nmr (DMSO-*d*<sub>6</sub>):  $\delta$  (J in Hz), 0.96 (s, 9H), 3.88 (s, 6H), 4.92 (broad s, 1H), 6.93 (d, 1H, J = 10), 7.40-7.65 (m, 2H), 8.92 (broad s, NH).

#### Compound IIIc.

This compound was obtained as an oil; ir (chloroform): 3305, 2940, 2850, 2225  $\text{cm}^{-1}$ ; <sup>1</sup>H nmr (DMSO-*d*<sub>6</sub>):  $\delta$  (J in Hz), 0.88 (t, 6H, J = 6.5), 1.10-1.18 (m, 5H), 3.78 (s, 6H), 4.79-4.95 (m, 1H), 6.90 (d, 1H, J = 10), 7.28-7.48 (m, 2H), 8.74 (broad s, NH).

The purification of IIIa-c was tedious and in most of the cases the crude products were oxidized to IIa-c by DDQ in benzene (2 hours) before chromatographic purification.

#### Compound IIb.

This compound had mp 152°; ir (chloroform): 2965, 2850, 2250  $\text{cm}^{-1}$ ; uv (ethanenitrile):  $\lambda$  max ( $\epsilon$ ) 237 ( $1.64 \times 10^4$ ), 275 ( $9.25 \times 10^3$ ), 340 nm ( $4.10 \times 10^3$ ); <sup>1</sup>H nmr (deuteriochloroform):  $\delta$  (J in Hz), 1.28 (s, 9H), 3.88 (s, 3H), 3.93 (s, 3H), 6.91 (diffused s, 3H).

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_{18}\text{N}_4\text{O}_2$ : C, 67.06; H, 5.63; N, 17.38. Found: C, 67.31; H, 5.72; N, 17.27.

#### Compound IIc.

This compound had mp 135°; ir (chloroform): 2965, 2850, 2255  $\text{cm}^{-1}$ ; <sup>1</sup>H nmr (deuteriochloroform):  $\delta$  (J in Hz), 0.77 (t, 6H, J = 7), 1.70 (m, 4H),

3.24 (m, 1H), 3.89 (s, 3H), 3.96 (s, 3H), 6.83-7.18 (m, 3H); ms: Calcd. for  $\text{C}_{19}\text{H}_{20}\text{N}_4\text{O}_2$ :  $m/z$  = 336.1586. Found  $m/z$  = 336.1595.

*Anal.* Calcd. for  $\text{C}_{19}\text{H}_{20}\text{N}_4\text{O}_2$ : C, 67.84; H, 5.99; N, 16.66. Found: C, 67.84; H, 6.05; N, 16.76.

#### Photoreaction of Ib with Ketones.

Irradiation was carried out for 3 hours essentially by the same procedure and on the same scale as in the case of the aldehydes. The condensate of the reaction mixture was subjected to preparative tlc on alumina developed by chloroform-benzene (1:1). This separation procedure gave product IVa from 2,4-dimethyl-3-pentanone, IVa and Va from 3-methyl-2-butanone, and IVb, Vb and VIb from 3,3-dimethyl-2-butanone. Dihydropyrazine derivatives IIIa and IIIb were not separated by this procedure and the crude products from another experiment were subjected to DDQ oxidation in benzene and the oxidation products IIa and IIb were separated in the same manner (see Table for the yields).

#### Compound IVa.

This compound had mp 105°; ir (chloroform): 2975, 2855, 2250  $\text{cm}^{-1}$ ; uv (ethanenitrile):  $\lambda$  max ( $\epsilon$ ), 222 ( $1.38 \times 10^4$ ), 268 ( $9.35 \times 10^3$ ), 337 nm ( $9.58 \times 10^3$ ); <sup>1</sup>H-nmr (deuteriochloroform):  $\delta$  (J in Hz), 1.27 (d, 6H, J = 7), 1.38 (d, 6H, J = 7), 3.28-3.48 (m, 2H), 3.91 (s, 3H), 3.95 (s, 3H), 6.84-7.18 (m, 3H); ms: Calcd. for  $\text{C}_{19}\text{H}_{23}\text{N}_3\text{O}_2$ :  $m/z$  = 325.1790. Found:  $m/z$  = 325.1773.

*Anal.* Calcd. for  $\text{C}_{19}\text{H}_{23}\text{N}_3\text{O}_2$ : C, 70.13; H, 7.12; N, 12.91. Found: C, 69.84; H, 7.66; N, 12.68.

#### Compound Va.

This compound had mp 97°; ir (chloroform): 2965, 2850, 2245, 1715  $\text{cm}^{-1}$ ; uv (ethanenitrile):  $\lambda$  max ( $\epsilon$ ), 233 ( $1.44 \times 10^4$ ), 300 ( $8.00 \times 10^3$ ), 351 nm ( $1.04 \times 10^4$ ); <sup>1</sup>H-nmr (deuteriochloroform):  $\delta$  (J in Hz), 1.44 (d, 6H, J = 7), 2.77 (s, 3H), 3.61 (septet, 1H, J = 7), 3.92 (s, 6H), 6.71-7.33 (m, 3H); ms: Calcd. for  $\text{C}_{18}\text{H}_{19}\text{N}_3\text{O}_3$ :  $m/z$  = 325.1426. Found:  $m/z$  = 325.1450.

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_{19}\text{N}_3\text{O}_3$ : C, 66.44; H, 5.89; N, 14.75. Found: C, 66.27; H, 5.57; N, 14.46.

#### Compound IVb.

This compound had mp 128°; ir (chloroform): 2975, 2850, 2250  $\text{cm}^{-1}$ ; <sup>1</sup>H-nmr (deuteriochloroform):  $\delta$  (J in Hz), 1.28 (s, 9H), 1.56 (s, 9H), 3.84 (s, 3H), 3.89 (s, 3H), 6.92 (diffused s, 3H); ms: Calcd. for  $\text{C}_{21}\text{H}_{27}\text{N}_3\text{O}_2$ :  $m/z$  = 353.2103. Found:  $m/z$  = 353.2151.

The sample used for spectroscopic measurement is considered to be homogeneous from chromatographic behavior.

#### Compound Vb.

This compound had mp 125°; ir (chloroform): 2960, 2850, 2245, 1715  $\text{cm}^{-1}$ ; uv (ethanenitrile):  $\lambda$  max ( $\epsilon$ ), 226 ( $1.47 \times 10^4$ ), 240 ( $1.28 \times 10^4$ ), 293 ( $1.18 \times 10^4$ ), 318 nm ( $1.28 \times 10^4$ ); <sup>1</sup>H-nmr (deuteriochloroform):  $\delta$  (J in Hz), 1.63 (s, 9H), 2.68 (s, 3H), 3.95 (diffused s, 6H), 6.76-7.38 (m, 3H).

*Anal.* Calcd. for  $\text{C}_{19}\text{H}_{21}\text{N}_3\text{O}_3$ : C, 67.24; H, 6.24; N, 12.38. Found: C, 67.32; H, 6.21; N, 12.22.

#### Compound VIb.

This compound had mp 137°; ir (chloroform): 2975, 2850, 2250  $\text{cm}^{-1}$ ; uv (ethanenitrile):  $\lambda$  max ( $\epsilon$ ), 238 ( $8.90 \times 10^3$ ), 281 nm ( $1.15 \times 10^4$ ); <sup>1</sup>H-nmr (deuteriochloroform):  $\delta$  (J in Hz), 1.56 (s, 9H), 3.94 (s, 3H), 3.98 (s, 3H), 6.83-7.70 (m, 3H), 8.96 (s, 1H); ms: Calcd. for  $\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_3$ :  $m/z$  = 297.1477. Found:  $m/z$  = 297.1454.

The sample used for spectroscopic measurements is considered to be homogeneous from the chromatographic behavior.

#### Photo-decyanation of IIa in the Presence of Triethylamine.

A mixture of IIa (62 mg,  $2.3 \times 10^{-4}$  mole) and triethylamine (96 mg,  $6.9 \times 10^{-4}$  mole) in 15 ml of ethanenitrile was irradiated for 10 hours in the same manner as the photolysis with aldehydes. The condensate from the reaction mixture was subjected to chromatographic separation by preparative tlc on silica gel eluted with benzene-chloroform-ethyl acetate

(1:1:1). The more polar product was VIa and the less polar product was VIIa.

#### Compound VIa.

This compound had mp 118°; ir (chloroform): 2975, 2850, 2250  $\text{cm}^{-1}$ ; uv (ethanenitrile):  $\lambda$  max ( $\epsilon$ ), 222 ( $1.27 \times 10^4$ ), 268 ( $9.30 \times 10^3$ ), 336 nm ( $7.00 \times 10^3$ );  $^1\text{H-nmr}$  (deuteriochloroform):  $\delta$  (J in Hz), 1.29 (d, 6H, J = 7), 3.50 (septet, 1H, J = 7), 3.93 (s, 6H), 6.79-7.25 (m, 3H), 8.69 (s, 1H); ms: Calcd. for  $\text{C}_{16}\text{H}_{17}\text{N}_3\text{O}_2$ : m/z = 283.1321. Found: m/z = 283.1330.

Anal. Calcd. for  $\text{C}_{16}\text{H}_{17}\text{N}_3\text{O}_2$ : C, 67.82; H, 6.05; N, 14.83. Found: C, 68.35; H, 6.13; N, 15.07.

#### Compound VIIa.

This compound had mp 84°; ir (chloroform): 2970, 2850, 2250  $\text{cm}^{-1}$ ; uv (ethanenitrile):  $\lambda$  max ( $\epsilon$ ), 275 ( $1.04 \times 10^4$ ), 305 ( $6.40 \times 10^3$ ), 334 nm ( $4.23 \times 10^3$ );  $^1\text{H-nmr}$  (deuteriochloroform):  $\delta$  (J in Hz), 1.28 (d, 6H, J = 7), 3.48 (septet, 1H, J = 7), 3.92 (broad s, 6H), 6.77-7.19 (m, 3H), 8.75 (s, 1H); ms: Calcd. for  $\text{C}_{16}\text{H}_{17}\text{N}_3\text{O}_2$ : m/z = 283.1321. Found: m/z 283.1308.

Anal. Calcd. for  $\text{C}_{16}\text{H}_{17}\text{N}_3\text{O}_2$ : C, 67.82; H, 6.05; N, 14.83. Found: C, 68.26; H, 6.07; N, 15.26.

#### REFERENCES AND NOTES

- [1a] M. Tada, H. Hamazaki and H. Hirano, *Chem. Letters*, 921 (1980); *Bull. Chem. Soc. Japan*, **55**, 3865 (1982); [b] M. Tada and K. Tsuzuki, *Chem. Letters*, 415 (1984); [c] H. Hamazaki and M. Tada, *Bull. Sci. Eng. Res. Lab. Waseda Univ.*, **103**, 35 (1983); [d] M. Tada, H. Hamazaki and K. Tsuzuki, *J. Heterocyclic Chem.*, **22**, 977 (1985).
- [2] H. Hirano, R. Lee and M. Tada, *J. Heterocyclic Chem.*, **19**, 1409 (1982).
- [3] F. Minisci and A. Citterio, *Acc. Chem. Res.*, **16**, 27 (1983).
- [4a] F. Minisci, *Synthesis*, 1 (1973); [b] A. Citterio, V. Franchi and A. Minisci, *J. Org. Chem.*, **45**, 4252 (1980).
- [5] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", John Wiley and Sons, New York, 1966, Chapter 5.
- [6] N. J. Turro, "Modern Molecular Photochemistry", Benjamin/Cummings, Publishers, Menlo Park, CA, 1978, p 528.
- [7a] T. Corrona, G. Franza, F. Minisci and O. Porta, *J. Chem. Soc., Perkin Trans. II*, 1477 (1972); [b] B. Giese, *Angew. Chem., Int. Ed. Engl.*, **22**, 753 (1983).
- [8] T. Makoto, S. Goto and T. Matsuda, *Bull. Chem. Soc. Japan*, **53**, 1777 (1980).