Chem. Pharm. Bull. 30(1) 140—151 (1982)

Intramolecular Ring Formation of Phenyl Azide and Furan Moieties[1]

KENICHI YAKUSHIJIN, TOYOHISA TSURUTA, and HIROSHI FURUKAWA*

Faculty of Pharmacy, Meijo University, Yagoto-Urayama, Tempaku-cho, Tempaku-ku, Nagoya 468, Japan

(Received June 15, 1981)

Thermal decompositions of methyl 5-[2-(2-azidophenyl)ethyl]-2-furoate (**3a**), methyl 5-[2-(2-azido-4,5-methylenedioxyphenyl)ethyl]-2-furoate (**3b**) and methyl 5-[2-(2-azido-4,5-dimethoxyphenyl)ethyl]-2-furoate (**3c**) gave methyl pyrrolo[1,2-*a*]quinoline-3-carboxylates (**10a—c**); in the case of **3a**, the 4,5-dihydro product **9** was also obtained. Photochemical decompositions of **3a** and **3b** in ethanol gave methyl 4,5-dihydro-1-ethoxypyrrolo[1,2-*a*]-quinoline-3-carboxylates (**15a, b**). In contrast, the cyclization product was not detected from **3c** under similar conditions.

Methyl 5-(2-azido-4,5-dimethoxybenzyl)-2-furoate (**8**) gave 7,8-dimethoxypyrido-[1,2-*a*]indole-1,2-dione (**22**) on thermolysis, and on photolysis in ethanol, gave methyl 6,7-dimethoxy-9*H*-pyrrolo[1,2-*a*]indole-3-carboxylate (**23**), *trans*-methyl 3-(6,7-dimethoxy-3-hydroxy-2-quinolyl)acrylate (**25**) and **22**. The pathways of these reactions are discussed.

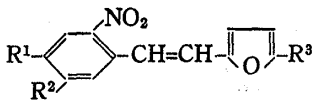
Keywords——2-azidophenylethylfuran; 2-azidobenzylfuran; thermolysis; photolysis; nitrene; pyrrolo[1,2-*a*]quinoline; pyrrolo[1,2-*a*]indole; pyrido[1,2-*a*]indole

We have shown that some reactions of the azido group can be utilized as a valuable step in the preparation of fused furans such as furoindoles,[2] furoisoquinolines[3] and furobenzazepines.[4] One of the advantages of the synthesis of fused furans through azido derivatives is the character of their regiospecific cyclizations. In the course of these studies, thermal and photochemical reactions of *o*-azidobiaryl systems separated by one or two methylenes between the phenyl azide moiety and the furan ring were carried out. It is known that phenyl azides bearing dipolarophile groups such as alkenyl, alkynyl and nitrile, or butyl groups undergo intramolecular 1,3-dipolar cycloadditions[5] or nitrene insertion reactions.[6] Furthermore, intramolecular cyclization of the 2-(2-azidobenzyl)-substituted benzene[7] or thiophene[8] system is also reported. We report here some novel results on the thermolysis and/or photolysis of 2-azidophenylethyl furans **3a—c** and 2-azidobenzyl furan **8**.

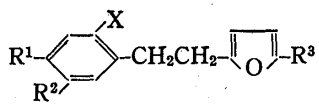
Preparation of the Azides 3a—c and 8

The three phenylethyl azides **3a—c** were prepared by the condensation of the appropriate *o*-nitrobenzaldehydes with 5-methoxycarbonyl-2-furfuryl triphenylphosphonium chloride,[9] followed by catalytic hydrogenation, and treatment of the diazotized 2-aminophenyl derivatives with azide ion. On the other hand, diazotization of the amines **2d** and **2e** lacking the methoxycarbonyl group in the furan ring, which were obtained from the condensation of the appropriate furfurals with *o*-nitrobenzyl triphenylphosphonium bromide[10] followed by catalytic reduction, failed and the corresponding azides were not obtained.

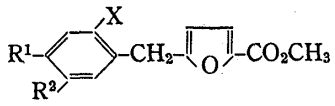
The benzyl azide **8** was prepared by the Friedel–Crafts reaction of veratrole with methyl 5-chloromethyl-2-furoate,[9] then nitration of the 3,4-dimethoxyl compound **4a** which was separated from the isomer **5a** by column chromatography, followed by treatments similar to those described above. Mndzhoian *et al.*[11] have reported that the Friedel–Crafts reaction of toluene with chloromethylfuran gave only the 4-methylbenzylfuran **4b**. However, the formation of the isomer **5b** substituted by a furfuryl group at the *ortho* position of toluene was also observed in a ratio of 1 : 1 in this reaction. In the similar reaction of *o*-xylene, a mixture (1 : 1) of the 3,4-dimethyl compound **4c** and the isomer **5c** was also obtained. Thus, the Friedel–Crafts reaction of toluene and *o*-xylene was not suitable for the synthesis of **4b** and **4c** because the separation of the two isomers, even after nitration, was difficult.[12]



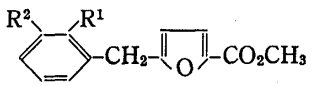
1a: $R^1=R^2=H$, $R^3=CO_2CH_3$
1b: $R^1R^2=OCH_2O$, $R^3=CO_2CH_3$
1c: $R^1=R^2=OCH_3$, $R^3=CO_2CH_3$
1d: $R^1=R^2=R^3=H$
1e: $R^1=R^2=H$, $R^3=CH_3$



2a: $R^1=R^2=H$, $R^3=CO_2CH_3$, $X=NH_2$
2b: $R^1R^2=OCH_2O$, $R^3=CO_2CH_3$, $X=NH_2$
2c: $R^1=R^2=OCH_3$, $R^3=CO_2CH_3$, $X=NH_2$
2d: $R^1=R^2=R^3=H$, $X=NH_2$
2e: $R^1=R^2=H$, $R^3=CH_3$, $X=NH_2$
3a: $R^1=R^2=H$, $R^3=CO_2CH_3$, $X=N_3$
3b: $R^1R^2=OCH_2O$, $R^3=CO_2CH_3$, $X=N_3$
3c: $R^1=R^2=OCH_3$, $R^3=CO_2CH_3$, $X=N_3$



4a: $R^1=R^2=OCH_3$, $X=H$
4b: $R^1=CH_3$, $R^2=X=H$
4c: $R^1=R^2=CH_3$, $X=H$
6: $R^1=R^2=OCH_3$, $X=NO_2$
7: $R^1=R^2=OCH_3$, $X=NH_2$
8: $R^1=R^2=OCH_3$, $X=N_3$



5a: $R^1=R^2=OCH_3$
5b: $R^1=CH_3$, $R^2=H$
5c: $R^1=R^2=CH_3$

Chart 1

Thermolysis of Methyl 5-[2-(2-Azidophenyl)ethyl]-2-furoates (3a—c)

Decomposition of the azide **3a** in *o*-dichlorobenzene solution at 170—180°C gave four products, though the total isolated yield was less than 50%. On the basis of elemental analyses and molecular weights, the molecular formulae of the first product (8%) and the second product (8%) were found to be $C_{14}H_{13}NO_2$ and $C_{14}H_{11}NO_2$, respectively, corresponding to the loss of oxygen together with N_2 from the starting azide **3a**. The second product showed a characteristic peak at 1685 cm^{-1} attributable to a conjugated carbonyl group in its infrared (IR) spectrum. Its nuclear magnetic resonance (NMR) spectrum indicated the presence of eight aromatic protons, of which four appeared at δ 8.14 (J=9.5 Hz) and 7.32 (J=9.5 Hz), and δ 7.76 (J=3 Hz) and 7.22 (J=3 Hz) as two AB systems, and an *O*-methyl singlet at δ 3.91. The ultraviolet (UV) spectrum was characteristic of the pyrrolo[1,2-*a*]quinoline chromophore.[13] Consideration of these data led to the structure methyl pyrrolo[1,2-*a*]quinoline-3-carboxylate (**10a**) for the second product. This structure of **10a** was confirmed by direct comparisons (IR, NMR and mixed mp) with the sample prepared by Acheson *et al.*[13] On the other hand, the first product exhibited, instead of an AB system as seen in **10a**, two methylene multiplets at δ 3.33 and 2.90, and the other signals in the NMR spectrum were similar to those of **10a**. Thus, the structure of the first product was assigned as the 4,5-dihydro derivative **9** of **10a**. This assignment was further supported by the identification of **10a** with the dehydrogenation product of **9** with dichlorodicyanobenzoquinone (DDQ).

The other two products were concluded to be the 2-(2-furyl)indoline **12** (18%) and the 2-(2-furyl)indole **11a** (11%) by consideration of their UV, IR and NMR spectra. The formation of the indole **11a** seems to occur by the abstraction of hydrogen by nitrene from the indoline **12**.[6] The indole **11a** was also obtained in good yield in the decomposition of *trans*-methyl 5-[2-(2-azidophenyl)vinyl]-2-furoate (**14**) prepared from **1a**, and by the dehydrogenation of the indoline **12** with palladium charcoal in xylene.

Next, similar decomposition of the azides **3b** and **3c** having oxygen functions in the benzene ring gave the corresponding pyrroloquinolines **10b** (3%) and **10c** (3.5%), and indoles **11b** (32%) and **11c** (41%), but dihydro compounds such as that seen in the reaction of **3a** were not obtained. In the case of **3b** and **3c**, the failure to obtain dihydro derivatives is probably due to the electron-donating effect of the substituents in the benzene ring.[14]

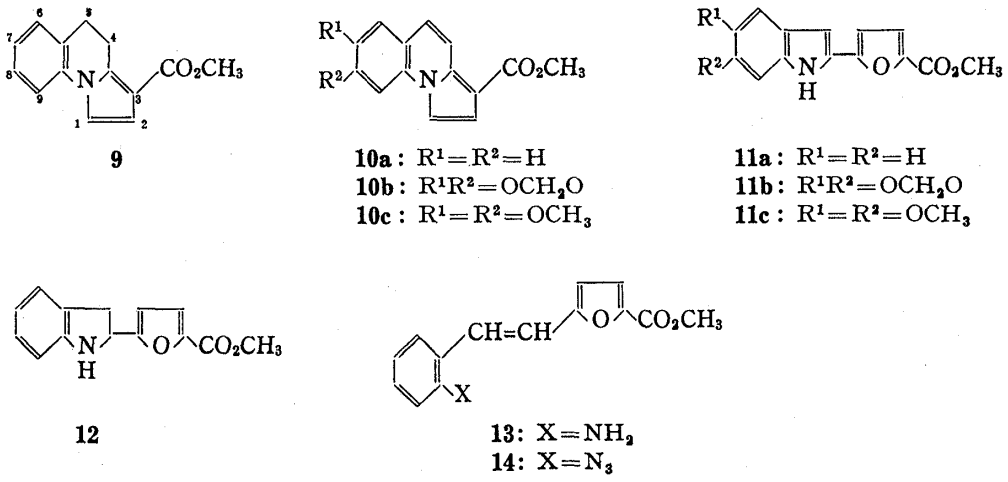


Chart 2

A probable mechanism for the formation of the pyrroloquinolines **9** and **10a** by decomposition of the azide **3a** is proposed in Chart 3. Addition of nitrene to the double bond gives the azanorcaradiene intermediate **A**.[15] Cleavage of a C-C bond in **A** forms the pyrroloquinoline ring system **B**, which leads to **9** through the loss of oxygen. Subsequent dehydrogenation of **9** (possibly by the action of nitrene)[10] gives **10a**.

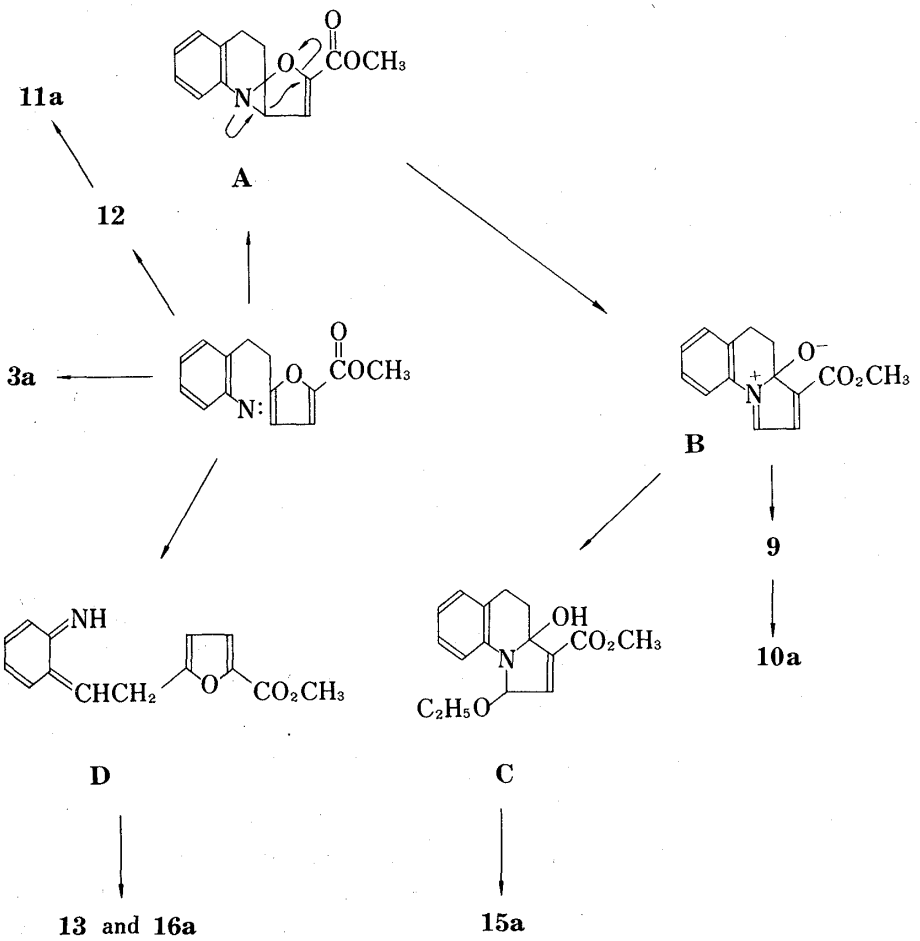


Chart 3

Photolysis of the Azide 3a in Benzene

Irradiation of the azide **3a** with a 100W high pressure mercury lamp gave the amines **2a** and **13** along with the pyrroloquinoline **10a**, the dihydropyrroloquinoline **9**, the indole **11a** and the indoline **12**, the same products as in the thermolysis described above. These structures were easily confirmed by comparisons with samples prepared by known methods.

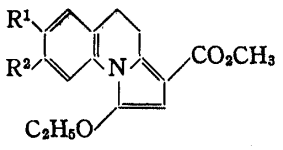
Photolysis of the Azides 3a—c in Ethanol

Irradiation of the azide **3a** in ethanol instead of benzene gave two new products together with the indole **11a** (2.7%), the indoline **12** (16.7%), and amines **2a** (3.1%) and **13** (1.6%). The main product (24.6%) was found to have an O-ethyl group linked to the dihydropyrroloquinoline **9** from the spectral data. Its NMR spectrum showed five aromatic protons, of which two appeared at δ 8.02 as a multiplet and 5.75 as a singlet attributable to the C-9 and C-2 protons of a 4,5-dihydropyrroloquinoline ring system, respectively. The low-field shift of the C-9 proton and the up-field shift of the C-2 proton compared with those of **9** suggested the position of the O-ethyl group to be at C-1, and the structure was considered to be methyl 4,5-dihydro-1-ethoxypyrrolo[1,2-*a*]quinoline-3-carboxylate (**15a**). Dehydrogenation of **15a** with DDQ afforded methyl 1-ethoxypyrrolo[1,2-*a*]quinoline-3-carboxylate (**17**) which exhibited a new AB type signal at δ 8.08 (J=9.5 Hz) and 7.15 (J=9.5 Hz) attributable to C-4 and C-5 protons in its NMR spectrum. Treatment of **15a** with 5% hydrogen chloride–methanol afforded an amide, which was characterized as methyl 1-oxo-1,2,4,5-tetrahydropyrrolo-[1,2-*a*]quinoline-3-carboxylate (**18**). These results also supported the structure of **15a**.

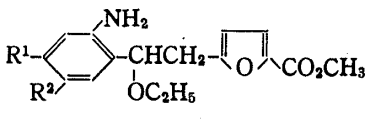
Another product (10.1%) was also found to have an O-ethyl group, and showed amino group absorption in its IR spectrum. Its NMR spectrum exhibited, instead of $-CH_2CH_2-$ group signals as seen in **2a**, new ABC type signals attributable to a $-CH(OC_2H_5)CH_2-$ moiety. These spectral data led to the structure methyl 5-[2-(2-aminophenyl)-2-ethoxyethyl]-2-furoate (**16a**).

Photolysis of the azide **3b** proceeded in the same way as in the case of **3a**, giving rise to the dihydropyrroloquinoline **15b** (3%), amines **16b** (18%) and **2b** (11.6%), and the indole **11b** (3%).

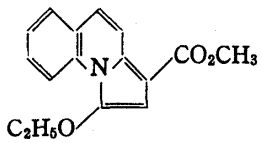
The 1-ethoxypyrroloquinoline **15a** is considered to be produced through the ethanol adduct **C** *via* the intermediate **B**. Furthermore, we assume that the intermediate **D** derived *via* the transfer of a benzylic proton gives the amines **13** and **16a** (Chart 3).



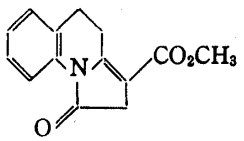
15a: $R^1=R^2=H$
15b: $R^1R^2=OCH_2O$



16a: $R^1=R^2=H$
16b: $R^1R^2=OCH_2O$



17



18

Chart 4

On the other hand, the photochemical reaction of the azide **3c** afforded the indole **11c** (5.6%), the amine **2c** (2.6%) and two new products, and no pyrroloquinoline was detected, in contrast to the case of **3a** and **3b**. The molecular formulae of the new products were found to be the same, $C_{18}H_{23}NO_6$, on the basis of elemental analyses and molecular weights. From

comparisons of the IR and NMR spectra with those of **2c**, addition of an O-ethyl group to the benzene ring of **3c** was confirmed in each molecule. One product (13.7%) had an upfield-shifted O-methyl group at δ 3.20 (at δ 3.15 in the other product) and two olefinic protons as singlets at δ 5.58 and 6.24 in its NMR spectrum. From these data, the structure was assigned as methyl 5-[2-(3,4-dimethoxy-3-ethoxy-6-imino-1,4-cyclohexadien-1-yl)ethyl]-2-furoate (**19**); this structure was supported by the hydrolysis to the *p*-benzoquinone imine **21** with water.

The NMR spectrum of the other product (10.6%) exhibited two olefinic protons as singlets at δ 5.94 and 5.54, and the other signals were similar to those of **19**. Thus, the structure was assigned as methyl 5-[2-(4,5-dimethoxy-4-ethoxy-3-imino-1,5-cyclohexadien-1-yl)ethyl]-2-furoate (**20**).

Scriven *et al.*[17] reported that the product of 1,2-nitrogen migration was often observed in the reaction of an aryl azide with a nucleophile. We propose the intermediates **E** and **F** for the formation of the cyclohexadienes **19** and **20** by decomposition of the azide **3c**. Addition of ethanol to the intermediates **E** and **F** produces the cyclohexadienes **19** and **20**, respectively.

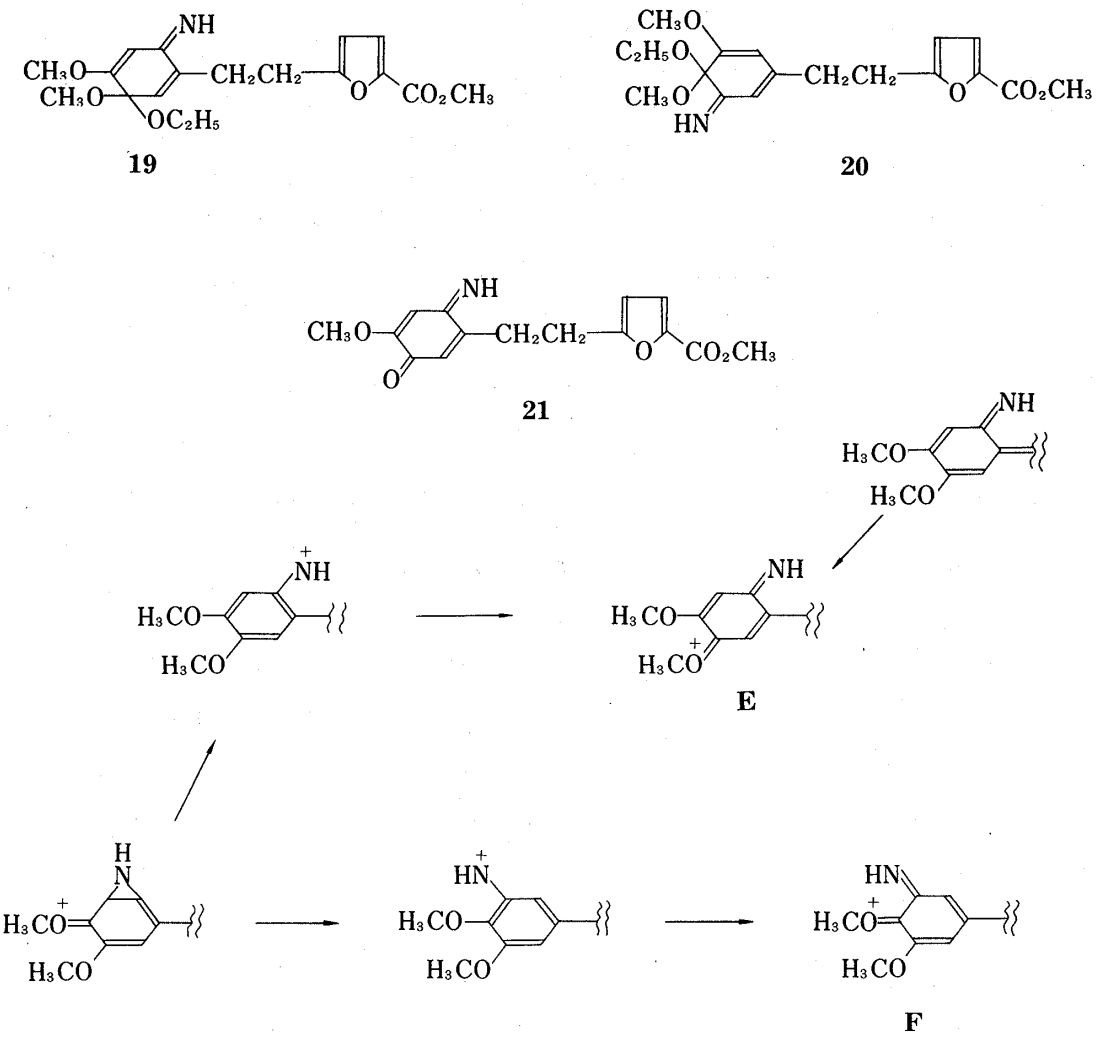


Chart 5

Thermolysis of Methyl 5-(2-Azido-4,5-dimethoxybenzyl)-2-furoate (8)

Decomposition of the azide **8** gave two products in poor yields. One of the products showed the presence of two O-methyls (δ 3.89 and 3.96), three aromatic proton singlets (δ 6.73, 6.94 and 7.91) and an AB system (J=9 Hz) (δ 6.27 and 7.37) in its NMR spectrum. Its IR spectrum indicated the presence of an α-diketone moiety at 1700 and 1655 cm^{-1} instead of

the ester carbonyl group in **8**. The molecular formula was found to be $C_{14}H_{11}NO_4$ by elemental analyses and molecular weight determination. Thus, the structure of this product was assigned as 7,8-dimethoxypyrido[1,2-*a*]indole-1,2-dione (**22**). The other product (1%) was identified as the amine **7** by comparison with an authentic sample.

We explain the formation of the pyridoindole **22** as follows: attack of nitrene on the α-position of the furan moiety gives the dipolar spiro intermediate **G**, as described by Meth-Cohn *et al.*[18] Cleavage of the furan ring in **G** forms the α-ketoester **H**, which leads to **22** through the loss of methanol after cyclization (Chart 6).

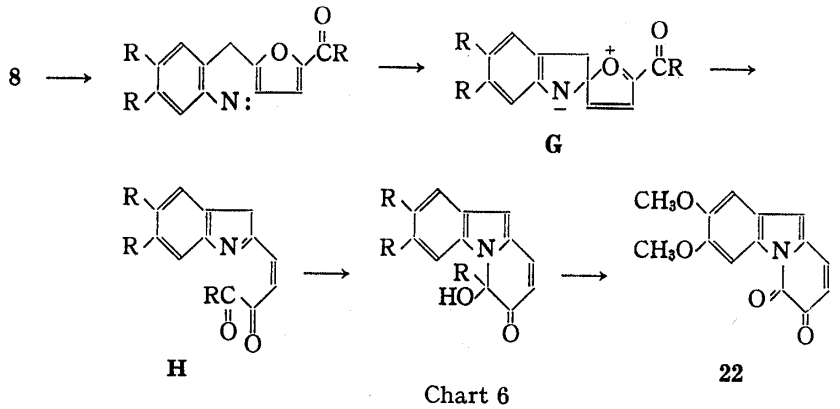


Chart 6

Photolysis of the Azide 8 in Ethanol

Irradiation of the azide **8** gave three new products together with the pyridoindole **22** (2.5%) and the amine **7** (7%). The NMR spectrum of the first product (4.6%) showed two benzene proton singlets at δ 6.89 and 8.38 and an AB system (J=4 Hz) at δ 6.10 and 7.05 together with three O-methyl singlets and a methylene singlet. The low-field signal at δ 8.38 was assigned to the C-5 proton of the 9*H*-pyrrolo[1,2-*a*]indole ring system under the influence of the deshielding effect of the ester group, as described by Franck *et al.*[19] The structure of this product was assigned as methyl 6,7-dimethoxy-9*H*-pyrrolo[1,2-*a*]indole-3-carboxylate (**23**) from the NMR and other spectral data. The second product (5.8%) was found to be methyl 5-(3,4-dimethoxy-3-ethoxy-6-imino-1,4-cyclohexadien-1-yl)methyl-2-furoate (**24**) from comparisons of spectral data with those of **19**. The third product (11%) showed the presence of a hydroxyl and a carbonyl groups at 3460 and 1722 cm^{-1} in its IR spectrum, and the molecular formula was found to be $C_{15}H_{15}NO_5$ on the basis of elemental analyses and molecular weight determination. Its NMR spectrum showed the presence of *trans*-olefinic protons at δ 7.04 and 7.81 (d, J=16 Hz), three aromatic proton singlets and three O-methyl singlets. These spectral data suggested the formation of a quinoline ring, and the structure was considered to be *trans*-methyl 3-(6,7-dimethoxy-3-hydroxy-2-quinolyl)acrylate (**25**).

The pyrroloindole **23** is thought to be formed by loss of oxygen from the bicyclic intermediate **I** which could be derived from the spiro species **G**. On the other hand, we assume that the dihydrofuroquinoline **J**[8] derived from the attack of nitrene on the β-position of furan gives the quinoline **25**.

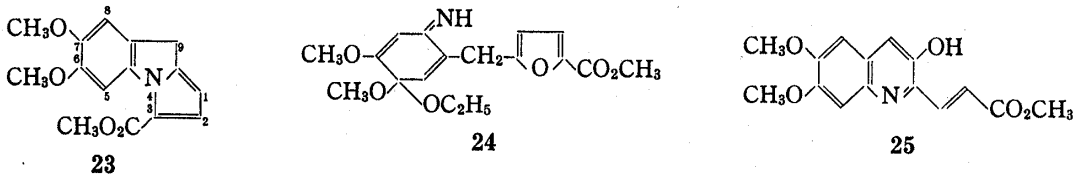


Chart 7

Finally, the intramolecular ring formation between a phenyl azide and a furan separated by two methylene groups gives pyrrolo[1,2-*a*]quinolines having a methoxycarbonyl group

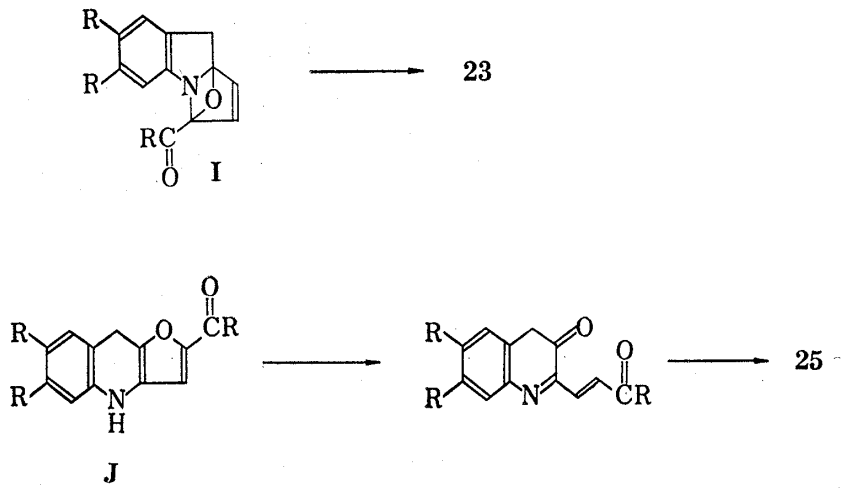


Chart 8

at the 3-position. In contrast, the case of a phenyl azide and a furan separated by a methylene group results in a pyrrolo[1,2-*a*]indole having a methoxycarbonyl group at the 3-position. Thus, mechanisms involving the azanorcaradienes in the former case, and the spiro species in the latter as intermediates were postulated.

Experimental

All melting points were determined on a Yanagimoto micro-melting point apparatus, and are uncorrected. IR spectra were recorded on a Jasco IR-A-1 spectrometer. ^{1}H- and ^{13}C-NMR spectra were taken on JEOL PX-100 and JEOL FX-100 spectrometers with tetramethylsilane as an internal standard. Mass spectra (MS) were obtained with a Hitachi M-52 spectrometer operating at an ionization potential of 70 eV. Irradiation was carried out with a 100W high pressure mercury lamp, Taika HLV-B, with a Pyrex filter.

Methyl 5-[2-(2-Nitrophenyl)vinyl]-2-furoate (1a)——**1a** was prepared according to the literature method[9] in 67% yield. *cis*-Form of **1a**: mp 106—107°C as yellow needles (lit.,[9] mp 106—107°C); ν_{max} (KBr) 1725 and 1505 cm^{-1}; δ ($CDCl_3$) 3.83 (3H, s), 5.98 (1H, d, J=3.5 Hz), 6.58 (1H, d, J=12 Hz), 6.99 (1H, d, J=3.5 Hz), 7.02 (1H, d, J=12 Hz), 7.59 (3H, m), 8.18 (1H, m). *trans*-Form of **1a**: mp 120—121°C as yellow scales (lit.,[9] mp 116—118°C); ν_{max} (KBr) 1720 and 1507 cm^{-1}; δ ($CDCl_3$) 3.92 (3H, s), 6.57 (1H, d, J=4 Hz), 6.88 (1H, d, J=16 Hz), 7.18 (1H, d, J=4 Hz), 7.24—7.74 (3H, m), 7.76 (1H, d, J=16 Hz), 7.96 (1H, m).

Methyl 5-[2-(4,5-Methylenedioxy-2-nitrophenyl)vinyl]-2-furoate (1b)——**1b** was prepared from 4,5-methylenedioxy-2-nitrobenzaldehyde in a manner similar to that described for **1a**. The *cis* and *trans* mixtures (1: 1.3) of **1b** (76%) were separated by chromatography on alumina with $CHCl_3$. *cis*-Form of **1b**: mp 176—177°C as yellow needles; ν_{max} (KBr) 1722 and 1510 cm^{-1}; δ ($CDCl_3$) 3.83 (3H, s), 6.06 (1H, d, J=4 Hz), 6.16 (2H, s), 6.51 (1H, d, J=13 Hz), 6.87 (1H, s), 6.98 (1H, d, J=13 Hz), 7.03 (1H, d, J=4 Hz), 7.68 (1H, s). *Anal.* Calcd for $C_{15}H_{11}NO_7$: C, 56.78; H, 3.50; N, 4.42. Found: C, 56.54; H, 3.43; N, 4.40. *trans*-Form of **1b**: mp 175—177°C as orange plates; ν_{max} (KBr) 1720 and 1503 cm^{-1}; δ ($CDCl_3$) 3.93 (3H, s), 6.15 (2H, s), 6.56 (1H, d, J=3.2 Hz), 6.78 (1H, d, J=16 Hz), 7.04 (1H, s), 7.22 (1H, d, J=3.2 Hz), 7.53 (1H, s), 7.74 (1H, d, J=16 Hz). *Anal.* Calcd for $C_{15}H_{11}NO_7$: C, 56.78; H, 3.50; N, 4.42. Found: C, 56.62; H, 3.36; N, 4.38.

Methyl 5-[2-(4,5-Dimethoxy-2-nitrophenyl)vinyl]-2-furoate (1c)——**1c** was prepared from 4,5-dimethoxy-2-nitrobenzaldehyde in a manner similar to that described for **1a**. The *cis* and *trans* mixtures (1: 1.5) of **1c** (68%) were separated by recrystallisation from $CHCl_3$–MeOH. *cis*-Form of **1c**: mp 143—145°C as yellow needles; ν_{max} (KBr) 1720 and 1515 cm^{-1}; δ ($CDCl_3$) 3.82 (3H, s), 3.87 (3H, s), 3.99 (3H, s), 6.05 (1H, d, J=3.5 Hz), 6.53 (1H, d, J=12 Hz), 6.95 (1H, s), 7.02 (1H, d, J=12 Hz), 7.02 (1H, d, J=3.5 Hz), 7.76 (1H, s). *Anal.* Calcd for $C_{16}H_{15}NO_7$: C, 57.66; H, 4.54; N, 4.20. Found: C, 57.45; H, 4.47; N, 3.91. *trans*-Form of **1c**: mp 185—187°C as yellow needles; ν_{max} (KBr) 1720 and 1520 cm^{-1}; δ ($CDCl_3$) 3.91 (3H, s), 3.96 (3H, s), 4.01 (3H, s), 6.59 (1H, d, J=3.5 Hz), 6.84 (1H, d, J=16 Hz), 7.02 (1H, s), 7.21 (1H, d, J=3.5 Hz), 7.61 (1H, s), 7.83 (1H, d, J=16 Hz). *Anal.* Calcd for $C_{16}H_{15}NO_7$: C, 57.66; H, 4.54; N, 4.20. Found: C, 57.41; H, 4.36; N, 4.00.

2-[2-(2-Nitrophenyl)vinyl]furan (1d)——A solution of furfural (40 g, 0.4 mol) and *o*-nitrobenzyl triphenylphosphonium bromide (48 g, 0.1 mol) in ethanol (100 ml) was added dropwise to a stirred solution of 10% sodium carbonate (1600 ml). After 3 h, the mixture was extracted with $CHCl_3$ and the extract was dried

over $MgSO_4$. The solvent was evaporated off, and the residue was chromatographed on silica gel with benzene to give a mixture (1: 1.5) of *cis* and *trans* **1d** (16.6 g, 77%), bp 120—152°C at 1 mmHg (lit.,[21] bp 145—147°C at 2 mmHg). These isomers were separated by preparative TLC on silica gel containing 10% silver nitrate with hexane–ether (9: 1). *cis*-Form of **1d**: yellow oil; δ ($CDCl_3$) 5.98 (1H, d, J=3.5 Hz), 6.19 (1H, dd, J=2 and 3.5 Hz), 6.41 (1H, d, J=12 Hz), 6.68 (1H, d, J=12 Hz), 7.10 (1H, d, J=2 Hz), 7.45 (3H, m), 8.00 (1H, m). *Anal.* Calcd for $C_{12}H_9NO_3$: C, 66.97; H, 4.22; N, 6.51. Found: C, 66.78; H, 4.12; N, 6.39. *trans*-Form of **1d**: yellow oil; δ ($CDCl_3$) 6.42 (2H, bs, furan-β), 6.86 (1H, d, J=16 Hz), 7.40 (1H, bs), 7.48 (1H, d, J=16 Hz), 7.22—7.72 (3H, m), 7.89 (1H, m). *Anal.* Calcd for $C_{12}H_9NO_3$: C, 66.97; H, 4.22; N, 6.51. Found: C, 66.85; H, 4.32; N, 6.70.

2-Methyl-5-[2-(2-nitrophenyl)vinyl]furan (1e)——**1e** was prepared from 5-methylfurfural in a manner similar to that described for **1d**. The resulting *cis* and *trans* mixture (1: 1.4) of **1e** (75%, bp 125—157°C at 1 mmHg) (lit.,[21] bp 175—178°C at 6 mmHg) was separated by preparative TLC on silica gel containing 10% silver nitrate with hexane–ether (9: 1). *cis*-Form of **1e**: yellow oil; δ ($CDCl_3$) 2.08 (3H, s), 5.78 (1H, m), 5.90 (1H, d, J=3 Hz), 6.34 (1H, d, J=12 Hz), 6.58 (1H, d, J=12 Hz), 7.46 (3H, m), 7.99 (1H, m). *Anal.* Calcd for $C_{13}H_{11}NO_3$: C, 68.11; H, 4.84; N, 6.11. Found: C, 67.91; H, 4.66; N, 6.10. *trans*-Form of **1e**: yellow oil; δ ($CDCl_3$) 2.36 (3H, s), 6.00 (1H, m), 6.31 (1H, d, J=3 Hz), 6.79 (1H, d, J=16 Hz), 7.37 (1H, d, J=16 Hz), 7.19—7.69 (3H, m), 7.85 (1H, m). *Anal.* Calcd for $C_{13}H_{11}NO_3$: C, 68.11; H, 4.84; N, 6.11. Found: C, 67.89; H, 4.62; N, 6.30.

Methyl 5-[2-(2-Aminophenyl)ethyl]-2-furoate (2a)——A solution of **1a** (24.5 g, 0.1 mol) in ethanol (300 ml) containing 5% Pd/C (6 g) was hydrogenated at room temperature. The mixture was filtered and the filtrate was evaporated to dryness. The residue was purified by recrystallization from petroleum benzin–benzene to give **2a** (20.2 g, 93%) as colorless needles, mp 58—59°C; ν_{max} (KBr) 3420, 3350 and 1700 cm^{-1}; δ ($CDCl_3$) 2.94 (4H, m), 3.60 (2H, bs, NH_2), 3.86 (3H, s), 6.08 (1H, d, J=3.5 Hz), 6.69 (2H, m), 7.01 (2H, m), 7.04 (1H, d, J=3.5 Hz); *m/e* 245 (M^+), 214, 184, 156, 106. *Anal.* Calcd for $C_{14}H_{15}NO_3$: C, 68.55; H, 6.16; N, 5.71. Found: C, 68.66; H, 6.11; N, 5.58.

Methyl 5-[2-(2-Amino-4,5-methylenedioxyphenyl)ethyl]-2-furoate (2b)——**2b**, **2c**, **2d** and **2e** were prepared in a manner similar to that described for **2a** from **1b**, **1c**, **1d** and **1e**, respectively. **2b**: yield 87%, colorless needles, mp 119—120°C (from ether); ν_{max} (KBr) 3380, 3320 and 1718 cm^{-1}; δ ($CDCl_3$) 2.87 (4H, m), 3.16 (2H, b, NH_2), 3.86 (3H, s), 5.80 (2H, s), 6.10 (1H, d, J=3.5 Hz), 6.24 (1H, s), 6.48 (1H, s), 7.06 (1H, d, J= 3.5 Hz); *m/e* 289 (M^+), 258, 228, 200, 150. *Anal.* Calcd for $C_{16}H_{15}NO_5$: C, 62.28; H, 5.23; N, 4.84. Found: C, 61.18; H, 5.10; N, 4.58.

Methyl 5-[2-(2-Amino-4,5-dimethoxyphenyl)ethyl]-2-furoate (2c)——**2c**: yield 94%, colorless needles, mp 67—68°C (from ether); ν_{max} (KBr) 3360, 3280 and 1717 cm^{-1}; δ ($CDCl_3$) 2.87 (4H, m), 3.40 (2H, bs, NH_2), 3.70 (3H, s), 3.73 (3H, s), 3.83 (3H, s), 6.05 (1H, d, J=3.5 Hz), 6.23 (1H, s), 6.48 (1H, s), 7.02 (1H, d, J= 3.5 Hz); *m/e* 305 (M^+), 274, 255, 244, 230, 216, 166. *Anal.* Calcd for $C_{16}H_{19}NO_5$: C, 57.66; H, 4.54; N, 4.20. Found: C, 57.58; H, 4.49; N, 4.28.

2-[2-(2-Aminophenyl)ethyl]furan (2d)——**2d**: yield 87%, colorless oil; ν_{max} (neat) 3440 and 3360 cm^{-1}; δ ($CDCl_3$) 2.83 (4H, m), 3.48 (2H, bs, NH_2), 5.95 (1H, d, J=3 Hz), 6.23 (1H, dd, J=2 and 3 Hz), 6.52—7.08 (4H, m), 7.28 (1H, d, J=2 Hz). *Anal.* Calcd for $C_{12}H_{13}NO$: C, 76.97; H, 7.00; N, 7.48. Found: C, 76.85; H, 6.93; N, 7.30.

2-Methyl-5-[2-(2-aminophenyl)ethyl]furan (2e)——**2e**: yield 90%, colorless oil; ν_{max} (neat) 3400 and 3310 cm^{-1}; δ ($CDCl_3$) 2.28 (3H, s), 2.86 (4H, bs), 3.53 (2H, b, NH_2), 5.85 (2H, bs, furan-β), 6.58—7.13 (4H, m). *Anal.* Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.45; H, 7.29; N, 6.95.

Methyl 5-[2-(2-Azidophenyl)ethyl]-2-furoate (3a)——A mixture of **2a** (4.9 g, 0.02 mol) in concentrated hydrochloric acid (15 ml) was cooled to 0°C and diazotized with sodium nitrite (1.5 g, 0.022 mol) in water (5 ml). After 30 min, a solution of sodium azide (3.2 g, 0.05 mol) in water (20 ml) was added to the cold diazonium solution. After 30 min, the suspension was extracted with ether and dried over $MgSO_4$. The solvent was evaporated off and the residue was chromatographed on silica gel with $CHCl_3$ to give **3a** (3.7 g, 68%) as a colorless oil, mp 21—22°C; ν_{max} (neat) 2140 and 1720 cm^{-1}; δ ($CDCl_3$) 2.96 (4H, s), 3.87 (3H, s), 6.06 (1H, d, J=3.2 Hz), 7.00—7.34 (5H, m); *m/e* 271 (M^+), 243, 210, 184, 156. *Anal.* Calcd for $C_{14}H_{13}N_3O_3$: C, 61.98; H, 4.83; N, 15.49. Found: C, 61.79; H, 4.77; N, 15.31.

Methyl 5-[2-(2-Azido-4,5-methylenedioxyphenyl)ethyl]-2-furoate (3b)——**3b** and **3c** were prepared in a manner similar to that described for **3a** from **2b** and **2c**, respectively. **3b**: yield 74%, colorless needles, mp 103—104°C (from ether); ν_{max} ($CHCl_3$) 2110 and 1715 cm^{-1}; δ ($CDCl_3$) 2.88 (4H, s), 3.87 (3H, s), 5.92 (2H, s), 6.08 (1H, d, J=3 Hz), 6.54 (1H, s), 6.62 (1H, s), 7.05 (1H, d, J=3 Hz); *m/e* 315 (M^+), 287, 256, 228, 199, 170. *Anal.* Calcd for $C_{15}H_{13}N_3O_5$: C, 57.14; H, 4.16; N, 13.33. Found: C, 57.05; H, 4.05; N, 13.25.

Methyl 5-[2-(2-Azido-4,5-dimethoxyphenyl)ethyl]-2-furoate (3c)——**3c**: yield 72%, colorless needles, mp 70—71°C (from ether); ν_{max} ($CHCl_3$) 2100 and 1715 cm^{-1}; δ ($CDCl_3$) 2.88 (4H, bs), 3.76 (3H, s), 3.83 (6H, s), 6.03 (1H, d, J=3 Hz), 6.52 (1H, s), 6.56 (1H, s), 7.00 (1H, d, J=3 Hz); *m/e* 331 (M^+), 303, 288, 256, 244, 228, 200. *Anal.* Calcd for $C_{16}H_{17}N_3O_5$: C, 58.00; H, 5.17; N, 12.68. Found: C, 57.89; H, 5.07; N, 12.51.

Methyl 5-(3,4-Dimethoxybenzyl)-2-furoate (4a) and Methyl 5-(2,3-Dimethoxybenzyl)-2-furoate (5a)—— Aluminum chloride (56.7 g, 0.43 mol) was added portionwise to a stirred ice-cooled mixture of methyl 5-chloromethyl-2-furoate (99.2 g, 0.58 mol) and veratrole (360 ml). The mixture was stirred for 2 h at room

temperature and further heated at 70°C for 2 h. Ice was added to the mixture and then 15% hydrochloric acid was added until the precipitate dissolved. The oil layer was separated, and the aqueous layer was extracted with ether. The ether extract and the oil layer were combined, washed with water and dried over $MgSO_4$. The solvent was evaporated off and the residual veratrole was removed under a vacuum produced by means of a water pump. The residue was vacuum-distilled to give a mixture (7: 1) (72%) of **4a** and **5a** as a colorless oil, bp 169—170°C at 2 mmHg. These isomers were separated by column chromatography on silica gel with benzene. **4a**: ν_{max} (neat) 1710 cm^{-1}; δ ($CDCl_3$) 3.80 (9H, s), 3.92 (2H, s), 6.05 (1H, d, J=3 Hz), 6.75 (3H, s), 7.05 (1H, d, J=3 Hz); δ (DMSO-d_6) 3.70 (3H, s), 3.78 (3H, s), 3.81 (3H, s), 4.03 (2H, s), 6.08 (1H, d, J=3.8 Hz), 6.77 (1H, dd, J=3 and 7 Hz), 6.97 (1H, d, J=3 Hz), 6.98 (1H, d, J=7 Hz), 7.20 (1H, d, J=3.8 Hz); *m/e* 276 (M^+), 261, 244, 217, 201. *Anal.* Calcd for $C_{15}H_{16}O_5$: C, 65.21; H, 5.84. Found: C, 65.18; H, 5.79. **5a**: ν_{max} (neat) 1710 cm^{-1}; δ ($CDCl_3$) 3.78 (3H, s), 3.84 (6H, s), 4.04 (2H, s), 6.03 (1H, d, J= 3.5 Hz), 6.70—6.98 (3H, m), 7.05 (1H, d, J=3.5 Hz); *m/e* 276 (M^+), 261, 244, 217, 201. *Anal.* Calcd for $C_{15}H_{16}O_5$: C, 65.21; H, 5.84. Found: C, 65.20; H, 5.75.

Methyl 5-(4-Methylbenzyl)-2-furoate (4b) and Methyl 5-(2-Methylbenzyl)-2-furoate (5b)——**4b, c** and **5b, c** were prepared in a manner similar to that described for **4a** from the corresponding materials. A mixture (1: 1) of **4b** and **5b** as a colorless oil, bp 138—139°C at 2 mmHg, was obtained in 77% yield. An attempt to separate these isomers was not successful. δ ($CDCl_3$) 2.26 and 2.30 (each 3H, s), 3.82 (6H, s), 3.94 and 3.96 (each 2H, s), 5.89 and 6.01 (each 1H, d, J=3 Hz), 7.02—7.12 (other H). *Anal.* Calcd for $C_{14}H_{14}O_3$: C, 73.02; H, 6.13. Found: C, 72.98; H, 5.95.

Methyl 5-(3,4-Dimethylbenzyl)-2-furoate (4c) and Methyl 5-(2,3-Dimethylbenzyl)-2-furoate (5c)——A mixture (1: 1) of **4c** and **5c** as a colorless oil, bp 150—151°C at 2 mmHg, was obtained in 76% yield. An attempt to separate these isomers was unsuccessful. δ ($CDCl_3$) 2.15 and 2.26 (each 3H, s), 2.21 (6H, s), 3.81 (6H, s), 3.90 and 3.98 (each 2H, s), 5.86 and 6.02 (each 1H, d, J=3.5 Hz), 6.95—7.05 (other H). *Anal.* Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.56; H, 6.43.

Methyl 5-(4,5-Dimethoxy-2-nitrobenzyl)-2-furoate (6)——A solution of fuming nitric acid (6.8 g) in acetic anhydride (10 ml) was added dropwise to a stirred, ice-cooled solution of **4a** (20 g, 0.07 mol) in acetic anhydride (20 ml), and the whole was stirred for 1 h at room temperature. Then, the mixture was poured into ice-water and extracted with $CHCl_3$ after neutralization with Na_2CO_3. The extract was dried over $MgSO_4$, then the solvent was evaporated off and the residue was chromatographed on silica gel with $CHCl_3$ to give **6** (20 g, 86%) as yellow needles, mp 134—135°C; ν_{max} (KBr) 1715 and 1515 cm^{-1}; δ ($CDCl_3$) 3.84 (3H, s), 3.92 (6H, s), 4.39 (2H, s), 6.15 (1H, d, J=3.6 Hz), 6.76 (1H, s), 7.04 (1H, d, J=3.6 Hz), 7.61 (1H, s); *m/e* 321 (M^+), 304, 290, 276, 244, 153. *Anal.* Calcd for $C_{15}H_{15}NO_7$: C, 56.07; H, 4.71; N, 4.36. Found: C, 55.98; H, 4.69; N, 4.35.

Methyl 5-(2-Amino-4,5-dimethoxybenzyl)-2-furoate (7)——**7** was obtained in 96% yield from **6** as colorless needles, mp 87—88°C (from ether), in a manner similar to that described for **2a**; ν_{max} ($CHCl_3$) 3440, 3370 and 1720 cm^{-1}; δ ($CDCl_3$) 3.61 (2H, b, NH_2), 3.74 and 3.81 (11H, s), 6.05 (1H, d, J=3.6 Hz), 6.29 (1H, s), 6.61 (1H, s), 7.04 (1H, d, J=3.6 Hz); *m/e* 291 (M^+), 276, 260, 231, 216, 188. *Anal.* Calcd for $C_{15}H_{17}NO_5$: C, 61.85; H, 5.88; N, 4.81. Found: C, 61.82; H, 5.81; N, 4.80.

Methyl 5-(2-Azido-4,5-dimethoxybenzyl)-2-furoate (8)——**8** was obtained in 72% yield from **7** as colorless plates, mp 69—70°C (from ether), in a manner described for **3a**; ν_{max} (KBr) 2085 and 1710 cm^{-1}; δ ($CDCl_3$) 3.84 (3H, s), 3.85 (3H, s), 3.90 (3H, s), 3.93 (2H, s), 6.05 (1H, d, J=3.6 Hz), 6.65 (1H, s), 6.73 (1H, s), 7.06 (1H, d, J=3.6 Hz); δ ($CDCl_3$) 158.67 (s×2), 148.95 (s), 146.37 (s), 143.09 (s), 129.90 (s), 119.65 (s), 118.95 (d), 113.79 (d), 108.45 (d), 102.07 (d), 56.19 (q), 56.07 (q), 51.50 (q), 29.47 (t); *m/e* 317 (M^+), 289, 230, 215, 199, 186. *Anal.* Calcd for $C_{15}H_{15}N_3O_5$: C, 56.78; H, 4.77; N, 13.24. Found: C, 56.75; H, 4.71; N, 13.25.

Thermolysis of 3a——The azide **3a** (1.5 g, 5.5 mmol) in *o*-dichlorobenzene (5 ml) was added dropwise to stirred *o*-dichlorobenzene (15 ml) under reflux. Heating was continued for 2 h, and then the solvent was evaporated off. The residue was chromatographed on silica gel with benzene to give methyl 4,5-dihydropyrrolo[1,2-*a*]quinoline-3-carboxylate (**9**) (100 mg, 8%) and methyl pyrrolo[1,2-*a*]quinoline-3-carboxylate (**10a**) (100 mg, 8%). **9**: colorless needles, mp 65—66°C; ν_{max} ($CHCl_3$) 1690 cm^{-1}: δ ($CDCl_3$) 2.90 (2H, m), 3.33 (2H, m), 3.82 (3H, s), 6.67 (1H, d, J=3.2 Hz), 7.08 (1H, d, J=3.2 Hz) 7.32 (4H, m); δ ($CDCl_3$) 170.89 (s), 135.95 (s), 135.67 (s), 128.94 (d), 128.11 (s), 127.53 (d), 125.04 (d), 115.64 (d), 114.91 (d), 111.79 (s), 111.35 (d), 50.87 (q), 25.73 (t), 21.34 (t); *m/e* 227 (M^+), 212, 196, 194, 168; λ_{max} (EtOH) (ε) 214 (17000), 242 (15100) and 269 (16900) nm. *Anal.* Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 74.01; H, 5.75; N, 6.11. **10a**: colorless needles, mp 132—133°C (lit.,[13] mp 135—136.5°C); ν_{max} (KBr) 1685 cm^{-1}; δ ($CDCl_3$) 3.91 (3H, s), 7.22 (1H, d, J=3 Hz), 7.32 (1H, d, J=9.5 Hz), 7.76 (1H, d, J=3 Hz), 7.31—7.94 (4H, m), 8.14 (1H, d, J=9.5 Hz); *m/e* 225 (M^+), 194, 166, 139; λ_{max} (EtOH) 221, 252, 267, 270, 341, 351, 368 nm. *Anal.* Calcd for $C_{14}H_{11}NO_2$: C, 74.65; H, 4.92; N, 6.22. Found: C, 74.60; H, 4.93; N, 6.19.

Further elution with $CHCl_3$ gave 2-(5-methoxycarbonyl-2-furyl)indole (**11a**) (147 mg, 11%) and 2-(5-methoxycarbonyl-2-furyl)indoline (**12**) (243 mg, 18%). **11a**: colorless needles, mp 165—166°C; ν_{max} (KBr) 3315 and 1692 cm^{-1}; δ ($CDCl_3$) 3.86 (3H, s), 6.60 (1H, d, J=3.5 Hz), 6.78 (1H, m), 6.92—7.30 (3H, m), 7.14 (1H, d, J=3.5 Hz), 7.52 (1H, m), 8.80 (1H, b, NH); *m/e* 241 (M^+), 212, 183, 154; λ_{max} (EtOH) 215, 257, 344 nm. *Anal.* Calcd for $C_{14}H_{11}NO_3$: C, 69.70; H, 4.59; N, 5.80. Found: C, 69.60; H, 4.39; N, 5.70. **12**: colorless prisms, mp 126—127°C; ν_{max} (KBr) 3340 and 1682 cm^{-1}; δ ($CDCl_3$) 3.17 (1H, dd, J=8 and 16 Hz),

3.48 (1H, dd, J=8 and 16 Hz), 3.45 (1H, b, NH), 3.87 (3H, s), 5.02 (1H, t, J=8 Hz), 6.35 (1H, d, J=3 Hz), 6.61—7.05 (4H, m), 7.09 (1H, d, J=3 Hz); *m/e* 243 (M^+), 212, 184, 155; λ_{max} (EtOH) 212, 257 nm. *Anal.* Calcd for $C_{14}H_{13}NO_3$: C, 69.12; H, 5.39; N, 5.76. Found: C, 69.16; H, 5.33; N, 5.67.

Thermolysis of 3b——**3b** was decomposed by a method similar to that described for **3a**. The separation of products was carried out by silica gel column chromatography. Elution with benzene gave methyl 7,8-methylenedioxypyrrolo[1,2-*a*]quinoline-3-carboxylate (**10b**) (38 mg, 3%) as colorless needles, mp 173—174°C; ν_{max} (KBr) 1680 cm^{-1}; δ ($CDCl_3$) 3.89 (3H, s), 6.05 (2H, s), 7.02 (1H, s), 7.15 (1H, d, J=9 Hz), 7.17 (1H, d, J=3.2 Hz), 7.27 (1H, s), 7.51 (1H, d, J=3.2 Hz), 8.00 (1H, d, J=9 Hz); *m/e* 269 (M^+), 255, 248, 210, 180, 152; λ_{max} (EtOH) 218, 231, 249, 256, 271, 290, 316, 330, 346, 362, 381 nm. *Anal.* Calcd for $C_{15}H_{11}NO_4$: C, 66.91; H, 4.12; N, 5.20. Found: C, 66.70; H, 4.01; N, 5.19.

Further elution with $CHCl_3$ gave 2-(5-methoxycarbonyl-2-furyl)-5,6-methylenedioxyindole (**11b**) (439 mg, 32%) as colorless needles, mp 223—224°C; ν_{max} (KBr) 3320 and 1700 cm^{-1}; δ ($CDCl_3$) 3.91 (3H, s), 5.92 (2H, s), 6.57 (1H, d, J=3.6 Hz), 6.75 (1H, m), 6.80 (1H, s), 6.93 (1H, s), 7.21 (1H, d, J=3.6 Hz), 8.74 (1H, b, NH); *m/e* 285 (M^+), 269, 242, 227, 198; λ_{max} (EtOH) 214, 250, 298, 370 nm. *Anal.* Calcd for $C_{15}H_{11}NO_5$: C, 63.16; H, 3 89; N, 4.91. Found: C, 63.11; H, 3.79; N, 4.89.

Thermolysis of 3c——**3c** was also decomposed by the method used in the case of **3a** described above. Elution of the reaction products with benzene from a silica gel column gave methyl 7,8-dimethoxypyrrolo-[1,2-*a*]quinoline-3-carboxylate (**10c**) (45 mg, 3.5%) as pale yellow needles, mp 184—185°C; ν_{max} (KBr) 1682 cm^{-1}; δ ($CDCl_3$) 3.89 (3H, s), 3.96 (3H, s), 4.02 (3H, s), 7.06 (1H, s), 7.20 (1H, d, J=3.2 Hz), 7.22 (1H, s), 7.23 (1H, d, J=9 Hz), 7.59 (1H, d, J=3.2 Hz), 8.04 (1H, d, J=9 Hz); *m/e* 285 (M^+), 254, 227, 210, 183; λ_{max} (EtOH) 215, 232, 268, 278, 286, 327, 342, 358, 377 nm. *Anal.* Calcd for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30; N, 4.91. Found: C, 67.21; H, 5.29; N, 4.90.

Further elution with $CHCl_3$ gave 5,6-dimethoxy-2-(5-methoxycarbonyl-2-furyl)indole (**11c**) (563 mg, 41%) as colorless needles, mp 176—177°C; ν_{max} (KBr) 3330 and 1702 cm^{-1}; δ ($CDCl_3$) 3.90 (9H, s), 6.58 (1H, d, J=3.6 Hz), 6.75 (1H, bs), 6.80 (1H, s), 7.00 (1H, s), 7.19 (1H, d, J=3.6 Hz), 8.84 (1H, b, NH); *m/e* 301 (M^+), 286, 258, 243, 199, 170; λ_{max} (EtOH) 213, 291, 365 nm. *Anal.* Calcd for $C_{16}H_{15}NO_5$: C, 63.78; H, 5.02; N, 4.65. Found: C, 63.66; H, 5.00; N, 4.58.

Reaction of 9 with DDQ——A solution of **9** (200 mg) and DDQ (200 mg) in benzene (10 ml) was boiled for 2 h. The solvent was evaporated off and the residue was chromatographed on silica gel with $CHCl_3$ to give the pyrroloquinoline **10a** as colorless needles, mp 132—133°C. **10a** was identical with the sample prepared from the method of Acheson *et al.*[13]

Synthesis of 11a——A solution of ammonium chloride (0.5 g) in water (2 ml) was added to a solution of the *trans*-nitrophenylvinylfuran **1a** (1 g, 3.7 mmol) in acetone (10 ml).[22] The mixture was boiled then removed from the water bath. Zinc powder (1 g) was added portionwise in order to maintain a moderate reaction. After the addition of Zn, the mixture was refluxed for 30 min. The solution was then filtered hot and the precipitates were washed with acetone. After removal of the solvent by evaporation, the residue was dissolved in ether and washed with water. The ethereal solution was dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography on silica gel with benzene to give *trans*-methyl 5-[2-(2-aminophenyl)ethyl]-2-furoate (**13**) as yellow needles, mp 124—125°C; ν_{max} (KBr) 3400, 3340 and 1719 cm^{-1}; δ ($CDCl_3$) 3.66 (2H, b, NH_2), 3.88 (3H, s), 6.38 (1H, d, J=3.5 Hz), 6.77 (1H, d, J=15 Hz), 7.16 (1H, d, J=3.5 Hz), 7.34 (1H, d, J=15 Hz), 6.63—7.39 (4H, m). *Anal.* Calcd for $C_{14}H_{13}NO_3$: C, 69.12; H, 5.39; N, 5.76. Found: C, 68.88; H, 5.27; N, 5.67.

The amine **13** was diazotized and treated with azide ion to give *trans*-methyl 5-[2-(2-azidophenyl)vinyl]-2-furoate (**14**) as colorless needles, mp 89—90°C; ν_{max} (KBr) 2200 and 1735 cm^{-1}. *Anal.* Calcd for $C_{14}H_{11}N_3O_3$: C, 62.45; H, 4.12; N, 15.61. Found: C, 62.49; H, 3.91; N, 15.59.

Decomposition of the azide **14** in *o*-dichlorobenzene gave **11a** in good yield as colorless needles; this product was identical with the sample obtained from the decomposition of **3a**.

Reaction of 12 with Pd/C——A solution of the indole **12** (200 mg) and 5% Pd/C in xylene (10 ml) was boiled for 2 h. The mixture was filtered and the filtrate was evaporated to dryness. The residue was chromatographed on silica gel with $CHCl_3$ to give the indole **11a** as colorless needles; this product was identical with the sample prepared by the above method.

Photolysis of 3a in Benzene——A solution of the azide **3a** (1 g, 3.7 mmol) in benzene (400 ml) was irradiated for 10 h. After removal of the solvent, the residue was chromatographed on silica gel with benzene to give the dihydropyrroloquinoline **9** (13%) and the pyrroloquinoline **10a** (9%). Further elution with $CHCl_3$ gave the indole **11a** (10%) and the indoline **12** (20%), and amines **2a** (5%) and **13** (2%), respectively. These compounds were identified by comparison with authentic samples.

Photolysis of 3a in Ethanol——A solution of the azide **3a** (0.5 g, 1.8 mmol) in ethanol (400 ml) was irradiated for 10 h under nitrogen. After removal of the solvent, the residue was chromatographed on silica gel with $CHCl_3$ to give methyl 1-ethoxy-4,5-dihydropyrrolo[1,2-*a*]quinoline-3-carboxylate (**15a**) (123 mg, 24.6%), the indole **11a** (12 mg, 2.7%) and the indoline **12** (75 mg, 16.7%). **15a**: colorless needles, mp 126—127°C; ν_{max} (KBr) 1684 cm^{-1}; δ ($CDCl_3$) 1.48 (3H, t), 2.84 (2H, m), 3.27 (2H, m), 3.83 (3H, s), 4.14 (2H, q), 5.75 (1H, s), 7.04—7.37 (3H, m), 8.02 (1H, m); δ ($CDCl_3$) 165.30 (s), 145.99 (s), 135.05 (s), 129.95 (s), 129.07 (s), 128.10 (d), 126.88 (d), 124.50 (d), 118.81 (d), 107.14 (s), 85.45 (d), 66.82 (t), 50.68 (q), 26.94 (t), 21.64

(t), 14.69 (q); *m/e* 271 (M^+), 242, 210, 182, 154; λ_{max} (EtOH) 252 nm. *Anal.* Calcd for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.32; N, 5.16. Found: C, 70.91; H, 6.30; N, 5.08.

Further elution with $CHCl_3$–ether (1: 1) gave the *trans*-aminophenylvinylfuran **13** (7 mg, 1.6%), methyl 5-[2-(2-aminophenyl)-2-ethoxyethyl]-2-furoate (**16a**) (48 mg, 10.1%) and the aminophenylethylfuran **2a** (13 mg, 3.1%). **16a**: a brownish oil; ν_{max} (neat) 3430, 3350 and 1720 cm^{-1}; δ ($CDCl_3$) 1.13 (3H, t), 3.07 (2H, m), 3.45 (2H, m), 3.91 (3H, s), 4.00 (2H, b, NH_2), 4.60 (1H, m), 6.33 (1H, d, J=3.6 Hz), 6.70 (2H, m), 6.98 (2H, m), 7.13 (1H, d, J=3.6 Hz); *m/e* 289 (M^+); λ_{max} (EtOH) 212, 259 nm. *Anal.* Calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84. Found: C, 66.21; H, 6.55; N, 4.70.

Photolysis of 3b in Ethanol——The same procedure as described above was employed. Elution with $CHCl_3$ in the chromatography of the reaction products gave methyl 4,5-dihydro-1-ethoxy-7,8-methylenedioxypyrrolo[1,2-*a*]quinoline-3-carboxylate (**15b**) (15 mg, 3%) and the indole **11b** (14 mg, 3%). **15b**: colorless needles, mp 194—195°C; ν_{max} ($CHCl_3$) 1683 cm^{-1}; δ ($CDCl_3$) 1.45 (3H, t), 2.70 (2H, m), 3.16 (2H, m), 3.75 (3H, s), 4.05 (2H, q), 5.60 (1H, s), 5.85 (2H, s), 6.60 (1H, s), 7.47 (1H, s); *m/e* 315 (M^+), 286, 271, 254, 198; λ_{max} (EtOH) 223, 291, 300 nm. *Anal.* Calcd for $C_{17}H_{17}NO_5$: C, 64.75; H, 5.43; N, 4.44. Found: C, 64.71; H, 5.40; N, 4.41.

Further elution with $CHCl_3$–ether (1: 1) gave methyl 5-[2-(2-amino-4,5-methylenedioxyphenyl)-2-ethoxyethyl]-2-furoate (**16b**) (95 mg, 18%) and the aminophenylethylfuran **2b** (53 mg, 11.6%). **16b**: a brownish oil; ν_{max} (neat) 3410, 3340 and 1720 cm^{-1}; δ ($CDCl_3$) 1.20 (3H, t), 3.01 (2H, m), 3.50 (2H, m), 3.92 (3H, s), 4.56 (1H, m), 5.83 (2H, s), 6.28 (1H, s), 6.34 (1H, d, J=3.6 Hz), 6.48 (1H, s), 7.12 (1H, d, J=3.6 Hz); *m/e* 333 (M^+), 302, 287, 256, 228, 200; λ_{max} (EtOH) 213, 257, 309 nm. *Anal.* Calcd for $C_{17}H_{19}NO_6$: C, 61.25; H, 5.75; N, 4.20. Found: C, 61.15; H, 5.60; N, 3.98.

Photolysis of 3c in Ethanol——The same procedure as described above was employed. Elution with $CHCl_3$ in the chromatography of the reaction products gave methyl 5-[2-(3,4-dimethoxy-3-ethoxy-6-imino-1,4-cyclohexadien-1-yl)ethyl]-2-furoate (**19**) (72 mg, 13.7%) and the indole **11c** (26 mg, 5.6%). **19**: a brownish oil; ν_{max} ($CHCl_3$) 1713, 1662, 1630 and 1610 cm^{-1}; δ ($CDCl_3$) 1.16 (3H, t), 2.84 (4H, m), 3.20 (3H, s), 3.36 (2H, q), 3.77 (3H, s), 3.84 (3H, s), 5.58 (1H, s), 6.10 (1H, d, J=3.6 Hz), 6.24 (1H, s), 7.02 (1H, d, J=3.6 Hz); *m/e* 318 (M^+-31), 304, 289, 273, 259, 231, 217, 203, 181; λ_{max} (EtOH) 240, 263 nm. *Anal.* Calcd for $C_{18}H_{23}NO_6$: C, 61.88; H, 6.64; N, 4.01. Found: C, 61.72; H, 6.51; N, 3.92.

Further elution with $CHCl_3$–ether (1: 1) gave methyl 5-[2-(4,5-dimethoxy-4-ethoxy-3-imino-1,5-cyclohexadien-1-yl)ethyl]-2-furoate (**20**) (56 mg, 10.6%) and the aminophenylethyl furan **2c** (12 mg, 2.6%). **20**: a brownish oil; ν_{max} ($CHCl_3$) 1715 and 1622 cm^{-1}; δ ($CDCl_3$) 1.16 (3H, t), 2.95 (4H, m), 3.15 (3H, s), 3.30 (2H, q), 3.73 (3H, s), 3.84 (3H, s), 5.54 (1H, s), 5.94 (1H, s), 6.13 (1H, d, J=3.6 Hz), 7.04 (1H, d, J=3.6 Hz); δ ($CDCl_3$) 165.17 (s), 160.42 (s), 159.54 (s), 158.73 (s), 142.91 (s), 136.93 (s), 132.19 (d), 118.83 (d), 108.16 (d), 103.36 (d), 95.21 (s), 59.12 (t), 55.31 (q), 51.56 (q), 50.98 (t), 28.48 (t), 27.54 (t), 15.35 (q); *m/e* 349 (M^+), 318, 304, 286, 272, 258, 244, 230, 216; λ_{max} (EtOH) 241, 264 nm. *Anal.* Calcd for $C_{18}H_{23}NO_6$: C, 61.88; H, 6.64; N, 4.01. Found: C, 61.66; H, 6.39; N, 3.87.

Reaction of 15a with DDQ——A solution of **15a** (30 mg) and DDQ (30 mg) in benzene (7 ml) was boiled for 2 h. The mixture was filtered and the filtrate was evaporated to dryness. The residue was chromatographed on silica gel with benzene to give methyl 1-ethoxypyrrolo[1,2-*a*]quinoline-3-carboxylate (**17**) as colorless needles, mp 114—116°C; ν_{max} ($CHCl_3$) 1680 cm^{-1}; δ ($CDCl_3$) 1.60 (3H, t), 3.91 (3H, s), 4.30 (2H, q), 6.35 (1H, s), 7.15 (1H, d, J=9.5 Hz), 7.27—7.68 (3H, m), 8.08 (1H, d, J=9.5 Hz), 8.90 (1H, bd, J=9 Hz); *m/e* 269 (M^+), 240, 212, 180, 167, 153; λ_{max} (EtOH) 207, 231, 279, 371, 389 nm. *Anal.* Calcd for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20. Found: C, 71.29; H, 5.60; N, 5.11.

Reaction of 15a with HCl–MeOH——A solution of **15a** (40 mg) in 5% HCl–MeOH was stirred for 5 h at room temperature. The solvent was evaporated off and the residue was dissolved in ether. The ether solution was washed with 10% Na_2CO_3, dried over $MgSO_4$ and evaporated to dryness to give methyl 1-oxo-1,2,4,5-tetrahydropyrrolo[1,2-*a*]quinoline-3-carboxylate (**18**) (94%) as colorless needles, mp 117—118°C; ν_{max} ($CHCl_3$) 1715 and 1685 cm^{-1}; δ ($CDCl_3$) 2.86 (2H, m), 3.31 (2H, m), 3.48 (2H, m), 3.80 (3H, s), 7.07—7.41 (3H, m), 8.34 (1H, bd, J=8 Hz); *m/e* 243 (M^+), 215, 182, 156, 154, 128; λ_{max} (EtOH) 205, 261 nm. *Anal.* Calcd for $C_{14}H_{13}NO_3$: C, 69.12; H, 5.39; N, 5.76. Found: C, 69.05; H, 5.21; N, 5.71.

Hydrolysis of 19 with H_2O——A mixture of **19** (20 mg) in water (7 ml) was heated at 90—95°C for 24 h. The mixture was extracted with $CHCl_3$ and dried over $MgSO_4$. The solvent was evaporated off and the residue was chromatographed on silica gel with $CHCl_3$ to give methyl 5-[2-(6-imino-4-methoxy-3-oxo-1,4-cyclohexadien-1-yl)ethyl]-2-furoate (**21**) (15 mg, 90%) as yellow needles, mp 162—163°C; ν_{max} ($CHCl_3$) 1718, 1675, 1648 and 1603 cm^{-1}; δ ($CDCl_3$) 2.84 (4H, m), 3.77 (3H, s), 3.82 (3H, s), 5.85 (1H, s), 6.06 (1H, d, J=3.6 Hz), 6.36 (1H, s), 6.98 (1H, d, J=3.6 Hz); *m/e* 290 (M^++1), 259, 230, 203, 153; λ_{max} (EtOH) 208, 262 nm. *Anal.* Calcd for $C_{15}H_{15}NO_5$: C, 62.28; H, 5.23; N, 4.84. Found: C, 62.19; H, 5.20; N, 4.81.

Thermolysis of 8——The azide **8** (1 g, 3.2 mmol) in *o*-dichlorobenzene (10 ml) was added dropwise to refluxing *o*-dichlorobenzene (10 ml) with stirring. This solution was then heated for 1.5 h and the solvent was evaporated off. The residue was chromatographed on silica gel with $CHCl_3$ to give 7,8-dimethoxypyrido[1,2-*a*]indole-1,2-dione (**22**) (20 mg, 2.4%) as reddish crystals, mp 183—184°C; ν_{max} ($CHCl_3$) 1700 and 1655 cm^{-1}; δ ($CDCl_3$) 3.89 (3H, s), 3.96 (3H, s), 6.27 (1H, d, J=9 Hz), 6.73 (1H, s), 6.94 (1H, s), 7.37 (1H, d, J=9 Hz), 7.91 (1H, s); *m/e* 257 (M^+), 229, 214, 186, 171, 158; λ_{max} (EtOH) 213, 300, 400 nm. *Anal.* Calcd

for $C_{14}H_{11}NO_4$: C, 65.36; H, 4.31; N, 5.45. Found: C, 65.25; H, 4.11; N, 5.27.

Further elution with $CHCl_3$–ether (1: 1) gave the amine **7** (5 mg, 1%), which was identified by comparison with the authentic sample.

Photolysis of 8 in Ethanol——A solution of the azide **8** (0.5 g, 1.6 mmol) in ethanol (400 ml) was irradiated for 10 h under nitrogen. After removal of the solvent, the residue was chromatographed on silica gel with $CHCl_3$ to give **22** (10 mg, 2.5%) and methyl 6,7-dimethoxy-9H-pyrrolo[1,2-*a*]indole-3-carboxylate (**23**) (20 mg, 4.6%) as colorless needles, mp 86—87°C; ν_{max} ($CHCl_3$) 1692 cm^{-1}; δ ($CDCl_3$) 3.75 (2H, s), 3.84 (3H, s), 3.87 (3H, s), 3.96 (3H, s), 6.10 (1H, d, J=4 Hz), 6.89 (1H, s), 7.05 (1H, d, J=4 Hz), 8.38 (1H, s); *m/e* 273 (M^+), 258, 242, 230, 214, 198, 170; λ_{max} (EtOH) 207, 277, 306 nm. *Anal.* Calcd for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53; N, 5.13. Found: C, 65.90; H, 5.49; N, 5.12.

Further elution with $CHCl_3$–ether (1: 1) gave methyl 5-(3-ethoxy-6-imino-3,4-dimethoxy-1,4-cyclohexadien-1-yl)methyl-2-furoate (**24**) (30 mg, 5.8%), *trans*-methyl 3-(3-hydroxy-6,7-dimethoxy-2-quinolyl)-acrylate (**25**) (50 mg, 11%) and the amine **7** (32 mg, 7%). **24**: a brownish oil; ν_{max} ($CHCl_3$) 1720, 1675, 1640 and 1618 cm^{-1}; δ ($CDCl_3$) 1.22 (3H, t), 3.28 (3H, s), 3.49 (2H, m), 3.77 (2H, s), 3.79 (3H, s), 3.84 (3H, s), 5.60 (1H, s), 6.19 (1H, d, J=3.6 Hz), 6.34 (1H, s), 7.05 (1H, d, J=3.6 Hz); *m/e* 335 (M^+), 305, 291, 245, 231, 217; λ_{max} (EtOH) 242, 262 nm. *Anal.* Calcd for $C_{17}H_{21}NO_6$: C, 60.88; H, 6.31; N, 4.18. Found: C, 60.71; H, 6.18; N, 3.89. **25**: a brownish oil; ν_{max} ($CHCl_3$) 3460, 3340 and 1722 cm^{-1}; δ ($CDCl_3$) 3.90 (9H, s), 6.78 (1H, s), 6.87 (1H, bs), 6.95 (1H, s), 7.04 (1H, d, J=16 Hz), 7.81 (1H, d, J=16 Hz), 8.64 (1H, b, OH); *m/e* 289 (M^+), 257, 230, 214, 202, 186, 171, 158; λ_{max} (EtOH) 213, 445 nm. *Anal.* Calcd for $C_{15}H_{15}NO_5$: C, 62.28; H, 5.23; N, 4.84. Found: C, 62.12; H, 4.99; N, 4.77.

References and Notes

1) Preliminary communication: K. Yakushijin, T. Tsuruta, and H. Furukawa, *Heterocycles*, **12**, 1021 (1979).
2) A. Tanaka, K. Yakushijin, and S. Yoshina, *J. Heterocycl. Chem.*, **14**, 975 (1977).
3) K. Ito, K. Yakushijin, S. Yoshina, A. Tanaka, and K. Yamamoto, *J. Heterocycl. Chem.*, **15**, 301 (1978).
4) K. Yakushijin and S. Yoshina, *Heterocycles*, **6**, 721 (1977).
5) R. Fusco, L. Garanti, and G. Zecchi, *J. Org. Chem.*, **40**, 1906 (1975).
6) G. Smolinsky and B.I. Feuer, *J. Org. Chem.*, **29**, 3097 (1964).
7) P.C. Hayes and G. Jones, *Chem. Commun.*, **1980**, 844, and earlier references.
8) G.R. Cliff, G. Jones, and J.M. Woollard, *J.C.S. Perkin I*, **1974**, 2072.
9) S. Yoshina, A. Tanaka, and K. Izumi, *Yakugaku Zasshi*, **88**, 405 (1968).
10) M. Butcher, R.J. Mathews, and S. Middleton, *Aust. J. Chem.*, **26**, 2067 (1973).
11) A.L. Mndzhoian and E.A. Markarian, *Proc. Acad. Sci. Armenian SSR*, **27**, 305 (1958).
12) The Friedel–Crafts reaction of 1,3-benzodioxole with methyl 5-chloromethyl-2-furoate in the presence of aluminum chloride was unsuccessful.
13) R.M. Acheson and M.S. Verlander, *J. Chem. Soc. (C)*, **1969**, 2311.
14) E.F. Pratt, and T.P. Mcgovern, *J. Org. Chem.*, **29**, 1540 (1964).
15) Intermediate **A** may also possibly be produced by loss of nitrogen after the addition of the azido group; see ref. 5.
16) J.M. Lindley, I.M. McRobbie, O. Meth-Cohn, and H. Suschitzky, *J.C.S. Perkin I*, **1977**, 2194.
17) S.E. Carroll, B. Nay, E.F.V. Scrieven, and H. Suschitzky, *Tetrahedron Lett.*, **1977**, 943.
18) J.M. Lindley, O. Meth-Cohn, and H. Suschitzky, *J.C.S. Perkin I*, **1978**, 1198.
19) R.W. Franck and K.F. Bernady, *J. Org. Chem.*, **33**, 3050 (1968).
20) This intermediate **J** may also be formed directly by an attack of nitrene at the α-position of furan; see ref. 8.
21) S. Yoshina and A. Tanaka, *Yakugaku Zasshi*, **88**, 398 (1968).
22) J.H. Boyer and H. Alul, *J. Am. Chem. Soc.*, **81**, 2136 (1959).