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Photochemical Studies. XXII.* Photochemical Ring-opening of Pyridine *N*-Oxide to 5-Oxo-2-pentenenitrile and/or 5-Oxo-3-pentenenitrile. A Reassignment of Structure

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Irradiation of pyridine *N*-oxide results in the generation of unstable primary products, which polymerize even at low concentrations. When the irradiation is performed in the presence of strong base, the anion of 5-hydroxy-2,4-pentadienenitrile is formed, whereas if the irradiation is performed in the presence of secondary amines, derivatives of 5-amino-2,4-pentadienenitrile are generated. The light-induced ring-opening appears to be general for 2-unsubstituted pyridine *N*-oxides, but no counterpart was observed for a number of other aromatic amine *N*-oxide systems examined.

Vapor phase irradiation of pyridine *N*-oxide mainly results in deoxygenation,[3] whereas irradiation of solutions leads to complicated mixtures, the composition of which is solvent dependent; the material balance was poor in all these experiments (Table 1). The observation that one of the photoprocesses consisted of deoxygenation prompted a series of papers examining the transfer of oxygen to various substrates, but again the material balance was poor, and deoxygenation only took place as a minor process upon irradiation. However, the deoxygenation could be drastically increased by adding strong Lewis acids (Table 1).

Irradiation of simple alkyl and alkoxy substituted pyridine *N*-oxides likewise gives complicated mixtures of the same type of products as found above, but the material balance is better.[4,7,12,15,16] By introducing bulkier groups like benzyl or phenylethyl in the 2-position, a good material balance is obtained for complex reaction mixtures.[13,14]

The result of irradiation is changed with highly arylated pyridine *N*-oxides. Thus 2,4,6-triphenylpyridine *N*-oxide gave a good chemical yield of a mixture of three products,[17] and tetra- and pentaarylpyridine *N*-oxides led to the corresponding 1,3-oxazepines in high yields.[18] Also 2,6-dicyanopyridine *N*-oxides have a good material balance of relatively simple mixtures of products.[19]

A series of *N*-oxides of pyridinecarboxylic acids and carboxamides was irradiated, resulting in generation of complicated mixtures, from which a product, the corresponding *N*-formylpyrrole, was isolated only in one case in rather low yield.[20] Irradiation of 2-(phenyldiazomethyl)pyridine *N*-oxide led to loss of nitrogen and oxygen transfer to generate 2-benzoylpyridine in almost quantitative yield,[21] and photolysis of pentachloropyridine *N*-oxide resulted in a complicated mixture from which were isolated pentachloropyridine and 1,2,3,4,4-pentachloro-1,3-butadienyl isocyanate.[22]

Some nitropyridine *N*-oxides have also been irradiated; however, their behavior clearly sets them apart from the other pyridine *N*-oxides.[23] Upon γ-irradiation of pyridine *N*-oxide the 2- and 4-azacyclohexadienyl *N*-oxide radicals were the only reaction products observed,[24] whereas the

* For two previous papers in this series, see Refs. 1 and 2. Ref. 1 is a short communication of some of the results that are given together with experimental details in this paper.

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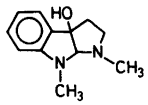
Table 1. Product distribution from the irradiation of pyridine *N*-oxide (*1*) under various conditions taken from the literature.



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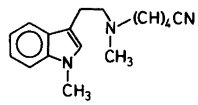

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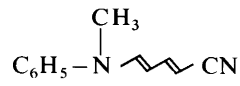

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Solvent and added reagents, *etc.*	Products, yields when given in the literature	Ref.
"Inert"	2-Formylpyrrol (*3*), 10 %	4
Benzene	Pyridine (*2*) + phenol, 15 %	5
ROH, R = CH_3 or C_2H_5, Pyrex filter	*1*, 50 % + *2*, 6.8 % + *3*, 1.3 % + *N*-dimethoxymethylpyrrol, 2.7 % + RCHO, 2.6 %	6
Quartz filter	*1*, 10 % + *2*, 6.9 % + *3*, 5 % + *N*-diethoxymethylpyrrol, 3.6 % + RCHO, 4.2 %	
Ether	*2*, 30 % + *3*, 2 %	7
10^{-2} M *1*, $Cu(NO_3)_2$ in H_2O, Vycor, 100 h	*3*, 32 %	
2×10^{-2} M *1* + 2×10^{-1} M $Cu(ClO_4)_2$ in H_2O, Vycor, 6 h	*3*, 40 %	8
CH_2Cl_2 + *N*,*N*'-dimethyltryptamine, 254 nm	*4*, 10 %	10
CH_2Cl_2 + *N*,*N*'-dimethyltryptamine, visible light	*4*, trace + *5*	
CH_2Cl_2 + *N*-methylaniline, visible light	*6*, 25 %	
H_2O	*3*, 2 % + *2*, 11 %	
as $Co(1)_6(ClO_4)_2$ in H_2O	*3*, 2 %	
as $Ni(1)_6(ClO_4)_2$ in H_2O	*3*, 2 %	12
as $Zn(1)_2Cl$ in H_2O	*3*, 2 %	
as $Cu(1)_2(NO_3)_2$ in H_2O	*3*, 26 %	
with $CuSO_4$ present in H_2O	*3*, 42 %	
CH_2Cl_2 – benzene (1:1)	Phenol, 1 % + *3* + 2-pyridone	13
CH_2Cl_2 – benzene (1:1), 0.04 M *1*,BF_3	Phenol, 7 %	
CH_2Cl_2 – benzene (1:0.75), 0.018 M *1*,BF_3	Phenol, 7 %	
CH_2Cl_2 – toluene, 0.018 M *1*, BF_3	Benzyl alcohol, 10.5 % + *o*-cresol, 1.7 % + *m*- and *p*-cresol, 1.7 %	14
CH_2Cl_2 – anisol	*o*-Methoxyphenol, 7 % + phenol, 0.5 %	

γ-irradiation of 2,3,5,6-tetraphenylpyridine *N*-oxide led exclusively to deoxygenation.[25]

The exact nature of the excited states involved in pyridine *N*-oxide photochemistry and *N*-oxide photochemistry in general has been the subject of a number of speculations.[16,26] It is now firmly established by spectroscopic studies that the low-energy absorption, corresponding to the reactive singlet species, is a $\pi - \pi^*$ transition,[27] and although no firm proof has been presented, it is in correspondence with all available evidence that in the absence of complexing agents the lowest excited singlet state is responsible for the rearrangements, whereas the lowest triplet state leads to deoxygenation.[16,18]

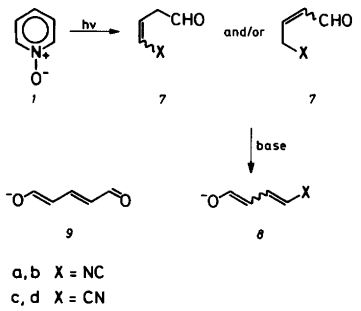
Excepting the most exotic substituted pyridine *N*-oxides, and the nitro substituted ones, there is sufficient similarity between the various irradiation

results to indicate that a common mechanism might be in operation.[16] However, it was annoying that the major part of the products from pyridine *N*-oxide itself were unaccounted for or led to polymeric material of unknown structure,[12] since the results from pyridine *N*-oxide irradiation should be integrated in such a common mechanistic model. Consequently, we decided to attack this problem.

RESULTS

Irradiation of 10^{-3} M or more concentrated solutions of pyridine *N*-oxide in water, alcohol or a variety of non-protic solvents led to the formation of brown material, which often partially separated in non-crystalline form during the irradiation.

In more dilute solutions ($10^{-4}-10^{-5}$ M pyridine *N*-oxide) irradiation led to rapid disappearance of the UV absorption characteristic of pyridine *N*-oxide, without the appearance of any distinctive new absorption. By irradiating in matrices, at cryogenic temperatures, and analyzing by IR spectroscopy, the appearance of new absorptions at 2156, 1705 and 1740 cm^{-1} was observed. This was regarded as indicative of the formation of isocyanide and aldehyde functions and led us to suggest that the product responsible for the new absorp-

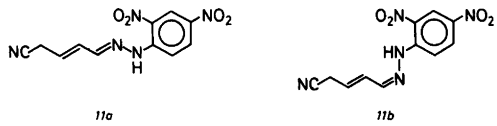


tions had structure *7a* or *b*, and it was found that irradiation of pyridine *N*-oxide in the presence of strong base led to the generation of a relatively stable species with a UV absorption band at 323 nm (in aqueous NaOH).[1] The presence of an IR absorption at 2145 cm^{-1}, likewise in aqueous NaOH, and comparison of the UV absorption band with that of the anion of glutaconaldehyde (*9*), which shows UV absorption at 362 nm under similar conditions,[28] was regarded as good evidence for the anion being *8a*. Upon repetition, we have not been able to confirm that the ion absorbs at 2145 cm^{-1}. Instead, an absorption at 2188 cm^{-1} is observed, which upon prolonged irradiation disappears, while a new absorption at 2145 cm^{-1} appears. Thus the IR spectroscopic evidence for isocyanide appears to be due to the occurrence of a secondary photochemical reaction. We can now conclude that the primary products are not isocyanides but that they have structures *7c* and/or *7d* and *8c*.

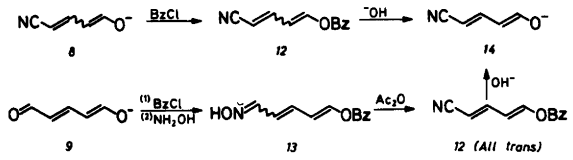
Since *7*, also in the form of the anion *8*, would appear to be a valuable synthon, a series of experiments were undertaken in order to make the molecule preparatively useful, albeit so far with limited success. It was found that the maximum useful concentration of pyridine *N*-oxide was 10^{-2} M and that the base concentration should be greater than 10^{-1} M. In water or alcohol, attempts to concentrate the solutions further led to polymerization, whereas the anion (*8*) could be obtained in more concentrated form by treatment with tetrabutylammonium ion, extraction of $Bu_4N^+ - 8$ with chloroform, and partial evaporation of the extract. It was also found that the anion could be isolated on an ion exchange resin.

As a part of the identification procedure, a series of reduction experiments with Raney nickel as catalyst were undertaken. Although the reduction went smoothly, it was difficult to achieve a reproducible method, and the yield of low-molecular weight products was low; varying amounts of pyridine and piperidine were isolated. We were not able to observe *N*-methylpyrrolidine.[1]

As a further part of the identification, as well as in our futile attempts to show the direct use of *8* as a synthon, two derivatives of *7* were synthesized: *i.* Treatment of a solution of *8* with 2,4-dinitrophenylhydrazine gave a precipitate which immediately after its isolation has IR absorption at 2145 cm^{-1}. However, upon purification this band disappeared



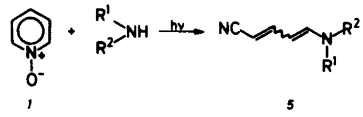
and a new band at 2250 cm^{-1} appeared. The purified product was shown to consist of a mixture of *11a* and *b*. *ii.* By benzoylation of the $Bu_4N^+ - 8$, a mixture of stereoisomers of *12* was produced, the ratio of which depended upon the reaction conditions, a longer reaction time favoring the all-*trans* isomer, *12a*, which was prepared independently from the anion of glutacondialdehyde (*9*).



The oxime, *13*, is generated as a mixture of stereoisomers from which the pure all-*trans* isomer could be obtained upon reflux in acetic anhydride.[9] The mixture of stereoisomeric nitriles, *12*, produced photochemically, as well as the all-*trans* isomer could be hydrolyzed under basic conditions to give the cyanide anion (*14*), corresponding to that produced in the irradiation of pyridine *N*-oxide. Thus *12* gave a product which showed λ_{max} at 329 nm (log ε 4.58) in aqueous solution and at 324 nm (log ε 4.45) in ethanolic solution. The IR spectra contained bands at 2189 cm^{-1} (1 M NaOH in ethanol) or 2188 cm^{-1} (2 M NaOH in water).

In previous work[10] it was reported that irradiation of pyridine *N*-oxide in the presence of *N,N'*-dimethyltryptamine resulted in two wavelength-dependent processes. Using 254 nm light, oxygen transfer was observed resulting in the generation of *4* (Table 1), whereas irradiation with visible light resulted in the generation of *5* (Table 1); similarly the irradiation of a mixture of pyridine *N*-oxide and *N*-methylaniline was reported to give *6*.

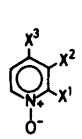
We have reexamined the irradiation of pyridine *N*-oxide in the presence of *N*-methylaniline, and although we cannot confirm that visible light ($\lambda > 400$ nm) causes any reaction, we also observed reactivity at longer wavelengths than in the absence of methylaniline. This effect is presumably only due to the change in solvent. Pyridine *N*-oxide shows a marked solvent assisted hypsochromic shift, from λ_{max} at 254 nm in water to 285 nm in cyclohexane, the high energy transition in polar protic solvents being caused by strong solvation. In methylene chloride, used in the present case, pyridine *N*-oxide has λ_{max} at 280 nm and absorbs considerably above 300 nm. By using a Pyrex filter, we were able to generate *5* in better than 50 % yield. On the contrary, irradiation at 254 nm of a mixture of *N*-methylaniline and pyridine *N*-oxide causes the formation of a dark tarry material. Since *N*-methylaniline absorbs very strongly at this wavelength, the pyridine *N*-oxide is effectively shielded, and mainly photooxidation of *N*-methylaniline is observed. Furthermore, neither IR nor UV spectroscopy of solutions of pyridine *N*-oxide, *N*-methylaniline and mixtures thereof showed any indication of complex formation between pyridine *N*-oxide and the amine; NMR spectroscopy indicated only increased hydrogen bonding of the amine in the presence of pyridine *N*-oxide.



a: $R^1 = C_6H_5$, $R^2 = CH_3$; b: $R^1 = R^2 = CH_3$; c: $R^1 = R^2 = C_2H_5$
d: $R^1 = R^2 = HC(CH_3)_2$; e: R^1, $R^2 = (CH_2)_5$; f: R^1, $R^2 = (CH_2)_2O(CH_2)_2$

The reaction with secondary amines appears to be general. This was shown by undertaking a series of irradiations in UV cuvettes containing mixtures of pyridine *N*-oxide and various secondary amines, and analyzing by UV and IR spectroscopy.[11] The quantum yields for the disappearance of pyridine *N*-oxide in the absence or presence of amine were almost equal. In a flash photolytic examination of pyridine *N*-oxide and perdeuteriopyridine *N*-oxide in aqueous sodium hydroxide, it was shown that the base reacted with an intermediate photoproduct, and the kinetics implied two parallel base catalyzed reactions. However, by keeping the hydroxide ion concentration higher than 10^{-2} M, only the reaction between hydroxide and the intermediate was important. Under these conditions a rate constant of 753 s^{-1} was found for pyridine *N*-oxide, and from the observation that the rate constant for the perdeuteriopyridine *N*-oxide under identical conditions was only 200 s^{-1}, *i.e.*, a primary kinetic isotope effect was operating, we conclude furthermore that the base acts by removing a proton from the photointermediate, thereby giving rise to the formation of *8c*.

In order to examine the scope of this ring-opening reaction, we have irradiated an extended series of substituted pyridine *N*-oxides (*14*) in the presence of strong base, and in each case where the *N*-oxide had a free 2-position, we observed disappearance of the UV absorption corresponding to the starting material, while a new absorption grew up at *ca.*



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a : $X^1 = CH_3$; $X^2 = X^3 = H$
b : $X^1 = CH_2C_6H_5$; $X^2 = X^3 = H$
c : $X^2 = CH_3$; $X^1 = X^3 = H$
d : $X^3 = CH_3$; $X^1 = X^2 = H$
e : $X^3 = CH_2C_6H_5$; $X^1 = X^2 = H$
f : $X^3 = C_6H_5$; $X^1 = X^2 = H$

325–350 nm, in close analogy to the pyridine *N*-oxide results.

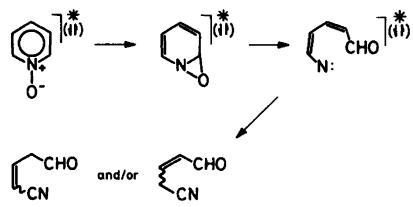
In most of these experiments, no isosbestic points could be observed, presumably due to further photoreaction of the various anions. Irradiation of pyridine *N*-oxides with both the 2- and the 6-position blocked did not lead to ring-opening.

We have also preliminarily examined selected *N*-oxides with a free 2-position in the following series: pyridazine, pyrimidine, quinoline, isoquinoline, cinnoline, 1,5-naphthyridine, quinoxaline, phthalazine, by irradiating *ca.* 10^{-4} M solutions in the presence of 10^{-2} M strong base without observing any similar effect. Thus so far this type of reaction seems to be selective for pyridine *N*-oxides; however, *cf.* Ref. 31.

DISCUSSION

The evidence for our structural assignment of the nitriles *7* and *8* is strongly based on the infrared absorptions. In evaluating these, we came to the conclusion that *7* and *8* were not isocyanides. Similarly, we have concluded that the N≡C absorption at 2156 cm^{-1} of *7* could be caused by a cyanide, and that the shift from 2145 cm^{-1} to 2250 cm^{-1} upon purification of *11* was rather due to a primarily formed α,β-unsaturated cyanide rearranging to the final product.

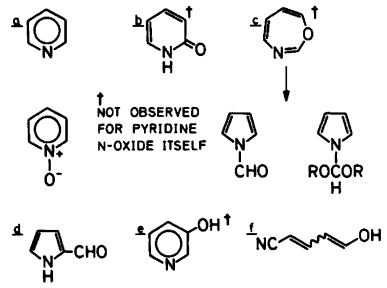
During our occupation with aromatic amine *N*-oxide photochemistry, *cf.* Refs. 1, 2, 16a, 29, we have first attempted to explain the rearrangements as occurring *via* short-lived ground state oxaziridine intermediates,[16a] and later modified this idea in the following way:[2,30] Since all attempts to observe oxaziridines as a result of the irradiation of six-membered aromatic amine *N*-oxides have failed, even down to ns time resolution, and at temperatures down to a few Kelvin, it seems most likely that these are not formed at all,[30] rather the various primary rearrangement products are generated directly from the excited amine *N*-oxide, a view lately shared by other groups.[31] However, the rearrangements all appear to go *via* a configuration on the excited state hypersurface corresponding to



an oxaziridine, and a possibility for the order of events in the formation of the nitrile is shown above.

According to our suggestion, the lowest excited singlet state pyridine *N*-oxide is transformed *via* a series of excited state configurations, to a ring-opened product, possibly a nitrene, which by an intramolecular hydrogen shift is relaxed to the ground-state product *7*.

Until recently, the primary products from almost all aromatic amine *N*-oxides could be classified as *a.* the parent amines, *b.* lactams, *c.* ring-expanded products, *d.* direct ringcontracted products, and possibly *e.*, only for the pyridine series, direct formation of 3-hydroxy derivatives.[16a] We have now added *f.* nitriles. However, isocyano derivatives were recently observed as photoproducts from some quinoxaline *N*-oxides.[31] By looking at pyridine *N*-oxide, the product distribution can be illustrated in the following way (Scheme 1).



Scheme 1.

Pyridine *N*-oxide has previously been shown to give only the parent amine (*2*) and 2-formylpyrrole (*3*) of the possible primary products, and by comparison with other systems[16] it could be argued that the two minor products from irradiation in MeOH or EtOH, *i.e.*, *N*-formylpyrrole and *N*-(dialkoxymethyl)pyrroles, could be derived from the *c*-product, 1,3-oxazepine, which itself has never been observed, but is well-known for more heavily substituted systems. In trying to understand the

photochemistry of pyridine *N*-oxide, we are handicapped by the fact that in none of our experiments have we been able to observe pyridine, thereby placing it as less than 1 % of the products, and 2-formylpyrrole was observed in 1 – 2 % yield only,[1] whereas the nitrile, trapped either in the form of a polymer in acetonitrile solution, or as *8* in various protic solvents, has corresponded to 90 – 98 % of the pyridine *N*-oxide consumed.

We find it most likely that the triplet pyridine *N*-oxide is responsible for the deoxygenation, but wish to point out that the yield of oxygen transfer may be very dependent on the oxygen acceptor, as found for other systems,[32] and that under certain circumstances, the singlet excited state also may lead to oxygen transfer. The rearranged products are believed to be formed directly from the singlet excited state, and the rates and isotope effect, observed in the flash photolysis experiments, are regarded as evidence for the contention that the primary nitrile is in fact *7*.

With these results we have explained why the pyridine *N*-oxide photochemistry previously was regarded as "messy", as well as how this can be remedied. We believe that some of our results can be extrapolated to explain the poor material balance reported in the irradiation of a number of other pyridine *N*-oxides, and we further believe that some of our results have preparative applicability.

EXPERIMENTAL

UV spectra were recorded on a Perkin Elmer 137 spectrophotometer. Except when noted, all spectra were recorded in 96 % EtOH, infrared spectra on a Perkin Elmer 337 spectrophotometer, and NMR spectra on a Varian T60 or a Bruker 270 MHz instrument (see also the description of matrix experiments). Mass spectra were recorded on a Varian MAT CH-7a coupled to a Varian 2700 GS *via* a one stage Watson Biemann separator.

Irradiations. Small scale irradiations for UV spectral observation were undertaken in 1 cm quartz cuvettes with an SP-200 Mercury lamp as light source. Preparative irradiations were undertaken with a Rayonet reactor, type RS (see also description of matrix experiments).

Matrix experiments. Pyridine *N*-oxide was isolated in a nitrogen or argon matrix by deposition onto a CsBr-window held at 14 K in an Air Products A C31 Cryodip. The slow spray-on method[33] was used. Matrix isolated pyridine *N*-oxide was irradiated, and the photolysis was followed by UV or IR spectroscopy. As light source were used either a Phillips low pressure mercury arc mounted in a microwave cavity, or a Phillips HPK-125 W high pressure mercury lamp mounted in a self-made lamp house in combination with a lattice monochromator. Ultraviolet spectra were recorded on a Perkin Elmer 356 Two Wavelength Double-Beam Spectrophotometer. IR spectra were recorded on a Perkin Elmer 521 Grating Infrared Spectrophotometer.

Preparative layer chromatography was done on 40 × 20 cm or 100 × 20 cm plates with a 0.25 mm layer of silica gel (Merck $PF_{254+366}$).

Pyridine *N*-oxide, purchased from Ega-Chemie, was purified by distillation at reduced pressure before use. Perdeuteriopyridine was purchased from Merck and *N*-oxidized by a known procedure.[34] The solvents were reagent grade or for small scale experiments spectrograde quality. The amines were reagent grade, and with the exception of *N*-methylaniline used without prior purification; *N*-methylaniline was distilled before use.

4-Cyano-1,3-butadiene-1-olate (8). Pyridine *N*-oxide (0.931 g ~ 0.01 mol) and sodium hydroxide (4.0 g ~ 0.1 mol) were dissolved in water (1 l) and irradiated with 254 nm light until no more pyridine *N*-oxide could be observed by UV spectroscopy.

To the above solution was added 3.15 g of tetrabutylammonium bromide, and the solution was extracted with chloroform (3 × 200 ml), dried over $MgSO_4$ and concentrated *in vacuo* to yield 2.06 g of a light brown oil, which rapidly darkened, and which should be used immediately after being prepared. The above solution was treated with a number of anion exchange resins (20 g) which all retained *8*.

4-Cyano-2-butene-1-ylidene-2,4-dinitrophenylhydrazones (11). A solution of the sodium salt of *8* prepared from 1.00 g of pyridine *N*-oxide was cooled to 10 °C and 2 M hydrochloric acid was added to a slightly acidic reaction (pH > 4). To this was added a solution of 2.0 g of 2,4-dinitrophenylhydrazine and 2 ml conc. hydrochloric acid in 10 ml of dimethylformamide under vigorous stirring. The precipitated reddish material (a) was isolated and washed with cold water and ethanol. After drying *in vacuo* it was subjected to IR spectroscopy in KBr which showed a C≡N absorption at 2145 cm^{-1}. The filtrate was concentrated *in vacuo* to yield a yellow solid (b). Both fractions were further purified by preparative layer chromatography (elution with ethyl acetate) and recrystallization. Elemental analysis and spectroscopy established that they were stereoisomers of *11*. The combined yield was 1.25 g (45 %).

a. (*E*)-isomer, red, m.p. 150 – 164 °C. Found: C 47.90; H 3.45; N 24.9. Calc. for $C_{11}H_9N_5O_4$:

C 48.0; H 3.26; N 25.4. IR: 2250 cm^{-1}; UV: λ_{max} 360 (log ε 4.51); NMR: ($CDCl_3$) 11.3, b.s., 1H 8.98, d, $J=2.5$ Hz, 1H; 8.4, q, $J_1=2.5$ Hz, $J_2=9$ Hz, 1H; 8.3, d, $J=9$ Hz, 1H; 8.0; d, $J=9$ Hz, 1H; 6.7, q, $J_1=9$ Hz, $J_2=14$ Hz, 1H; 6.3, m, $J_1=2.5$ Hz, $J_2=14$ Hz, 1H; 3.65; d, $J_1=5$ Hz, 2H.

b. (Z)-isomer, m.p. 169–170 °C. Found: C 47.46; H 3.00; N 24.90. Calc. for $C_{11}H_9N_5O_4$: C 48.0; H 3.26; N 25.4. IR: 2250 cm^{-1}; UV: λ_{max} 360 (log ε 4.51); NMR: ($CDCl_3$) 10.9, b.s., 1H; 8.98 d, $J=2.5$ Hz, 1H; 8.36, q, $J_1=2.5$ Hz, $J_2=9$ Hz; 8.3, d, $J=9$ Hz, 1H; 7.95, d, $J=9$ Hz, 1H; 6.7, q, $J_1=9$ Hz, $J_2=14$ Hz, 1H; 6.3, m, $J_1=2.5$ Hz, $J_2=14$ Hz, 1H; 3.65, d, $J=5$ Hz, 2H.

*5-(*N*-Methylanilino)-2,4-pentadiene nitriles. a.* Pyridine *N*-oxide (0.60 g) and *N*-methylaniline (0.68 g) in dichloromethane was irradiated (Pyrex filter) until all pyridine *N*-oxide had disappeared (TLC, *ca.* 3 h). The solvent was evaporated *in vacuo* to yield a brown oil (1.2 g) which was purified by PLC (eluted with ether-light petroleum 1:6) to give 5-(*N*-methylanilino)-2,4-pentadiene nitrile, mixture of stereoisomers, as a yellow oil (0.7 g, 61 %). Anal. Found: C 77.30; H 6.38; N 15.06. Calc. for $C_{12}H_{12}N_2$: C 78.23; H 6.57; N 15.21.

b. The all-*trans* isomer was prepared in the following manner: 5-(*N*-methylanilino)-2,4-pentadienal oxime, mixture of streoisomers, (5.05 g)[35] and *N*,*N*'-carbonyldiimidazole (6.48 g) were refluxed in dry ether (200 ml) for 48 h, which resulted in the formation of a homogeneous solution. This solution was washed with water (2 × 25 ml), dried ($MgSO_4$) and the ether removed by evaporation, which yielded 3.82 g of a red oil. Upon dissolution in ether–pentane a precipitate was formed which upon recrystallization from methylcyclohexane (955 ml) yielded 2.35 g (51 %) of all-*trans*-5-(*N*-methylanilino)-2,4-pentadiene nitrile. M.p. 50–51 °C. Anal. $C_{12}H_{12}N_2$: C, H, N. IR (KBr): 2199 cm^{-1}; UV (in absolute EtOH): λ_{max} 2.32, log ε 3.74, λ_{max} 345, log ε 4.33.

c. Preparation of a mixture of stereoisomers of 5-(*N*-methylanilino)-2,4-pentadiene nitrile by the thermal route: 5-(*N*-methylanilino)-2,4-pentadienal oxime, mixture of stereoisomers (5.0 g),[35] diisopropylcarbodiimide (3.2 ml) and a trace of copper(II) chloride was refluxed in dichloromethane (25 ml) for 12 h. Upon cooling and removal of the precipitate by filtration, evaporation of the solvent yielded an oil. The oil was distilled *in vacuo*, the main fraction was collected and further purified by PLC (elution with ether-light petroleum (1:1)). The main fraction, which by TLC was shown to consist of a mixture of two components, one identical to the all-*trans* isomer, see below, was identical with the mixture isolated from pyridine *N*-oxide, described above, by TLC, IR and UV analyses.

Furthermore, a series of experiments was undertaken where solutions of pyridine *N*-oxide (10^{-4} M) and secondary aliphatic amines (10^{-2} M dimethyl-, diethyl-, diisopropylamine, piperidine and morpholine) in water were irradiated until no more change could be observed by UV spectroscopy. The samples all behaved similarly in the UV, and upon evaporation of the solvent and IR spectroscopy in chloroform solution they all showed characteristic absorptions in the 2200 cm^{-1} region identifying them as nitriles.

Quantum yields for the disappearance of pyridine *N*-oxide were determined by irradiating 5×10^{-5} M solutions in dichloromethane in 1 cm quartz cells with 300 nm light. The incident light intensity was measured by ferric oxalate actinometry.

5-Benzoyloxy-2,4-pentadiene nitrile (12) from 8. Tetrabutylammonium 4-cyano-1,3-butadiene-1-olate (2.06 g) was dissolved in pyridine (10 ml) whereupon benzoyl chloride (1.14 ml) was added at 0 °C with stirring, which was continued for 15 min. This was followed by addition of ice-water (100 ml), extraction with ether (2 × 100 ml), drying over $MgSO_4$, addition of activated carbon, filtration and evaporation of the ether to give 1.20 g of a yellow oil. The oil was shown by TLC to consist of a mixture of the all-*trans* isomer and a *cis*-isomer besides impurities. The oil was purified by PLC (ether-light petroleum 1:9) to give a mixture of stereoisomers of *12* as a colorless solid (0.35 g) with m.p. 80–85 °C. Anal. $C_{12}H_9NO_2$: C, H, N.

5-Benzoyloxy-trans-*2*-trans-*4-pentadiene nitrile.* 4-Benzoyloxy-2,4-pentadienal oxime (1.2 g) was refluxed in acetic anhydride (10 ml) for 2 h, after which the reaction mixture was concentrated *in vacuo* to give a dark crystalline residue (1.3 g). This was recrystallized from methanol–water to give tan-colored crystals (0.3 g, 27 %), m.p. 118–120 °C. Anal. $C_{12}H_9NO_2$: C, H, N. IR (KBr): 2230 cm^{-1} s, 1750 cm^{-1} s. UV (in abs. ethanol): λ_{max} 271, log ε 4.52; λ_{max} 240 sh, log ε 4.16.

5-Benzoyloxy-2,4-pentadienal oxime. 4-Benzoyloxy-*trans*-2-*trans*-4-pentadienal[28] (5 g) was refluxed for 2 h with a filtered solution of hydroxylamine (hydroxylammonium chloride (3.5 g) and sodium hydroxide (2.0 g)) in methanol (50 ml). The reaction mixture was poured on ice-water (100 ml) to give tan-colored crystals (4.14 g, 77 %). M.p. 122–123 °C. Anal. for $C_{12}H_{11}NO_3$: C, H, N. IR (KBr) 3380 cm^{-1}, 1735 cm^{-1}. UV (in abs. ethanol): λ_{max} 236, log ε 3.98; λ_{max} 268, log ε 3.90.

Preparation of solutions of 4-cyano-trans-*1*-trans-*3-butadiene-1-olate.* The above described benzoates were dissolved in cold aqueous sodium hydroxide or sodium ethoxide solutions which caused an almost instantaneous hydrolysis. The IR and UV spectra are discussed in the previous section.

Hydrogenation of 8. (a) A methanolic solution of the anion prepared from *ca.* 1 g of pyridine *N*-oxide in 1 l of methanol was reduced to 200 ml *in vacuo*, in the cold. This solution was hydrogenated with Raney nickel prepared from 15 g Al–Ni (1:1) for 70 h (5 Atm), after which time the absorption at 327 nm had disappeared. After removal of excess hydrochloric acid the reaction mixture was evaporated to dryness, 100 ml 2M NaOH was added and the solution was extracted with ether. The ether was dried over anhydrous $MgSO_4$, and the ether removed by freeze-drying. The remaining material was analyzed by GLC–MS, to give a fraction corresponding to pyridine.

(b) The yellow solution from 1.00 g of pyridine *N*-oxide in 700 ml of 0.1 M NaOH was hydrogenated (12 h, 80 °C, 42 560 Torr of H_2; 100 mg (10 %) Pd–C Fluka), cooled, filtered and continuously extracted with ether for 24 h. The nearly colorless ether phase was dried (K_2CO_3) and filtered. GCMS (2 m glass column filled with 3 % OV-1 m Diatomite CQ) of this ether solution showed the presence of piperidine and pyridine corresponding to a yield of 0.10 g of piperidine and 0.07 g of pyridine. No *N*-methylpyrrolidine could be seen.

In another experiment, 0.90 g of pyridine *N*-oxide hydrogenated as described above gave 0.17 g of piperidine.

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REFERENCES

1. Buchardt, O., Christensen, J. J., Lohse, C., Turner, J. J. and Dunkin, I. R. *Chem. Commun.* (1977) 837.
2. Tomer, K. B., Harrit, N., Rosenthal, J., Buchardt, O., Kumler, P. L. and Creed, D. *J. Am. Chem. Soc. 95* (1973) 7402.
3. Hata, N. and Tanaka, J. *J. Chem. Phys. 36* (1962) 2072.
4. Streith, J. and Sigwalt, C. *Tetrahedron Lett.* (1966) 1347.
5. Streith, J., Danner, B. and Sigwalt, C. *Chem. Commun.* (1967) 979.
6. Alkaitis, A. and Calvin, M. *Chem. Commun.* (1968) 292.
7. Streith, J. and Sigwalt, C. *Bull. Soc. Chim. Fr.* (1970) 1157.
8. Bellamy, F., Barragan, L. G. R. and Streith, J. *Chem. Commun.* (1971) 456.
9. Becher, J. *et al. Unpublished results.*
10. Nakagawa, M., Kaneko, T. and Yamagushi, J. *Chem. Commun.* (1971) 603; Nakagawa, M., Kaneko, T., Yamagishi, H., Kawashima, T. and Hino, T. *Tetrahedron 30* (1974) 2591.
11. Buchardt, O. *et al. Unpublished results.*
12. Bellamy, F., Martz, P. and Streith, J. *Heterocycles 3* (1975) 395.
13. Serra-Errante, G. and Sammes, P. G. *Chem. Commun.* (1975) 395.
14. Sammes, P. G., Serra-Errante, G. and Tinker, A. C. *J. Chem. Soc. Perkin Trans. 1* (1978) 853.
15. Hata, N. *Bull. Chem. Soc. Jpn. 34* (1961) 1444.
16. For reviews of *N*-oxide photochemistry see: a. Spence, G. G., Taylor, E. C. and Buchardt, O. *Chem. Rev. 70* (1970) 231; b. Kaneko, C. *J. Synth. Org. Chem. 26* (1968) 758; c. Bellamy, F. and Streith, J. *Heterocycles 4* (1976) 1391.
17. Kumler, P. L. and Buchardt, O. *Chem. Commun.* (1968) 1321.
18. Buchardt, O., Pedersen, C. L. and Harrit, N. *J. Org. Chem. 37* (1972) 3592.
19. Ishikawa, M., Kaneko, C., Yokoe, I. and Yamada, S. *Tetrahedron 25* (1969) 295.
20. Caswell, L. R., Lee, F. C. and Creagh, L. T. *J. Heterocyclic Chem. 9* (1972) 551.
21. Güsten, H. and Ullman, E. F. *Z. Naturforsch. Teil B 316* (1976) 1009.
22. Ager, E., Chivers, G. E. and Suchitzky, H. *Chem. Commun.* (1972) 505.
23. Kaneko, C., Yamada, S., Yokoe, I., Hata, N. and Ubukala, Y. *Tetrahedron Lett.* (1966), 4729; Hata, N., Okutsu, E. and Tanaka, I. *Bull. Chem. Soc. Jpn. 41* (1968) 1769; Hata, N., Ono, J. and Tsuchiya, T. *Bull. Chem. Soc. Jpn. 45* (1972) 2386; Ono, I. and Hata, N. *Bull. Chem. Soc. Jpn. 45* (1972) 2951.
24. Quaegebeur, J. P., Perly, B., Surpateanu, G. Lablache-Combier, A. *Can. J. Chem. 55* (1977) 3442.
25. Rosenthal, I. and Buchardt, O. *Acta Chem. Scand. 26* (1972) 2557.
26. Leibovici, C. and Streith, J. *Tetrahedron Lett.* (1971) 387.
27. Ziolkovsky, B. and Dörr, F. *Ber. Bunsenges. 69* (1965) 448; Yamakawa, M., Kubota, T. and Akazawa, H. *Theor. Chim. Acta 15* (1969) 244; Hochstrasser, R. M. and Wiersma, D. A. *J. Chem. Phys. 55* (1971) 5339; Brand, J. C. D. and Tang, K. T. *J. Mol. Spectrosc. 39* (1971) 171; Yamakawa, M., Ezumi, K., Mizuno, Y. and Kubota, T. *Bull. Chem. Soc. Jpn. 47* (1974) 2982.
28. Becher, J. *Acta Chem. Scand. 26* (1972) 3627.
29. Buchardt, O., Tomer, K. B. and Madsen, V. *Tetrahedron Lett.* (1971) 1311.
30. Lohse, C. *J. Chem. Soc. Perkin Trans. 2, 37* (1972) 3592.

31. Albini, A., Colombi, R. and Minoli, G. *J. Chem. Soc. Perkin Trans. 1* (1978) 924.
32. Kaneko, C., Yanamori, M., Yamamoto, A. and Hayashi, T. *Tetrahedron Lett.* (1978) 452.
33. Perutz, R. N. and Turner, J. J. *J. Chem. Soc. Faraday Trans. 2, 69* (1973) 452.
34. Taylor, E. C. and Crovethi, A. J. *Org. Synth. Coll. Vol. 4* (1963) 655.
35. Zincke, T. *Justus Liebigs Ann. Chem. 338* (1905) 131; A full account of the preparation and structure of these oximes will be forthcoming.

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