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N-Substituted 3-methoxy-4-pyridones **Ia-e** rearrange to the corresponding *N*-substituted 3-hydroxymethyl-4-pyridones **IIa-e** when irradiated at 254 or 300 nm in benzene or toluene solution.

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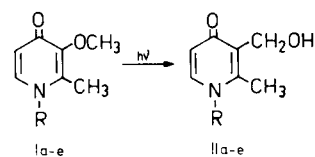
In contrast to the well documented photochemistry of pyridines [1] there are few reports concerning the photochemically induced reactions of structurally related pyridones. Pyridones might be expected to exhibit some photochemical resemblance to pyrones [2]. However, as far as we know, beside the photochemical rearrangement of some dihydro-4-pyridones [4], the only careful photochemical study documented was the photoisomerization of 4-pyridones to 2-pyridones [5].

β -Hydroxy-4-pyridones would be of particular interest in this regard. Since the hydroxyl group is proximate to the carbonyl unit it should be effective (in a fashion similar to that in β -hydroxy-4-pyrone rearrangements [6]) in stabilizing the zwitterion proposed as a key-intermediate in the reaction pathway. The effect in a sense has been illustrated in the photorearrangement of 3-hydroxy-4-pyrones giving the ring contracted cyclopentenone derivatives [7]. Our steady interest in 4-pyridone chemistry [8] was therefore extended to the photochemistry of some *N*-substituted 3-hydroxy-2-methyl-4-pyridones [8a,b]. Preliminary experiments demonstrated that 3-hydroxy-derivatives were too unreactive under irradiation (1-300 hours) either with pyrex filtered or unfiltered high pressure mercury arc uv light. Even after prolonged irradiation only the starting compound, accompanied by a small amount of resinous material could be detected.

In contrast, *O*-methylated compounds *i.e.* 3-methoxy-2-methyl-4-pyridones, were photoreactive yielding new material after several hours of irradiation. There was no sign however, of the expected photo isomerization to 2-pyridone nor to the ring contracted products, similar to those obtained by irradiations of some 4-pyrones [7]. What was observed and what we wish to report here is the first methoxy/hydroxymethyl photorearrangement within methoxy-substituted heterocycles.

Irradiation of **Ia** ($4 \times 10^{-2}M$) in toluene with short wave length or pyrex filtered uv light gave, beside recovered starting material and traces of some unidentified polymere-

Scheme I



R = C₆H₅, *p*-CH₃-C₆H₄, *p*-CH₃O-C₆H₄, *p*-NO₂-C₆H₄, CH₃

rized material, a colourless crystalline product that was identified as *N*-phenyl-3-hydroxymethyl-2-methyl-4-pyridone (**IIa**). Similarly, irradiation of methoxypyridones **Ib-e** gave the corresponding hydroxymethyl derivatives **IIb-e**. Irradiations were monitored by tlc and nmr techniques and were carried out to approximately 50% consumption of **Ia-e** (10-18 hours). Yields of the isolated rearranged product varied from 15-50%. Prolonged irradiation increased the amount of polymerized materials. Results in benzene and toluene solution were comparable. Polar solvent (methanol) did not influence the outcome of the irradiation significantly. Relative rates were evaluated from comparative irradiation experiments conducted in nmr tubes on $2 \times 10^{-2}M$ solutions (hexadeuteriobenzene). It was found that irradiation time and substituent on the nitrogen atom influenced the ratio of hydroxymethyl and methoxy compound in the reaction mixture.

Spectral characteristics of the main isolable photoproduct showed preservation of the 4-pyridone ring system and indicated that the 3-methoxy group was no longer present [9].

Structural assignment of the hydroxymethyl pyridone product were made by spectral analysis. The mass spectra of the products showed the same *m/z* for the M⁺ ion as the starting methoxy compound thus ruling out the possibility of any dimerization. In addition, the fragmentation pattern pointed out a high degree of structural similarities between the starting compounds and the corresponding pho-

Table I
Summary of 3-Methoxy-2-methyl-*N*-substituted-4-pyridones **Ia-e** and 3-Hydroxymethyl-2-methyl-*N*-substituted-4-pyridone Products **IIa-e**

R	Starting Material	Mp °C	Yield %	UV [i] λ max (log ε)	IR [j] ν C=O	Product	Irradiation hours	Yield % [h]	Mp °C	UV [j] λ max (log ε)	IR [j] ν C=O	IR [j] ν OH
C ₆ H ₅	Ia	132-133 [a]	51 [e]	279 (4.26)	1630	IIa	10	40	218-219	272 (4.35)	3300	1628
<i>p</i> -CH ₃ C ₆ H ₄	Ib	133 [b]	87 [e]	280 (4.30)	1630	IIb	10	80	202-203	272 (4.23)	3450	1630
<i>p</i> -CH ₃ OC ₆ H ₄	Ic	158-159 [c]	66 [e]	279 (4.29)	1625	IIc	10	40	174-175	271 (4.31)	3350	1630
<i>p</i> -NO ₂ C ₆ H ₄	Id	166 [d]	68 [f]	273 (4.18)	1625	IIId	10	20	183-184	272 (4.27)	3350	1630
CH ₃	Ie	85-86	78 [g]	272 (4.17)	1625	IIe	100	35	162-163	263 (4.01)	3210	1635

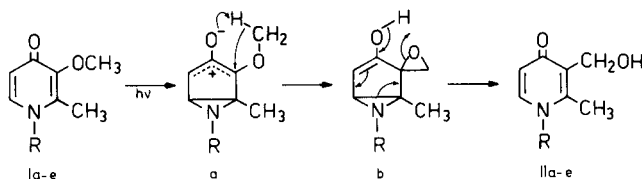
[a] *Anal.* Calcd. for C₁₃H₁₃N₂O₂: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.28; H, 6.23; N, 6.77. Lit. mp 133-135° [8b]. [b] *Anal.* Calcd. for C₁₄H₁₅N₂O₂: C, 73.34; H, 6.60; N, 6.11. Found: C, 73.06; H, 6.32; N, 5.77. Lit. mp 132-135° [8b]. [c] *Anal.* Calcd. for C₁₄H₁₅N₂O₂: C, 68.52; H, 6.17; N, 5.71. Found: C, 68.62; H, 5.90; N, 5.79. Lit. mp 158-159° [8b]. [d] *Anal.* Calcd. for C₁₃H₁₃N₂O₄: C, 59.99; H, 4.65; N, 10.77. Found: C, 59.70; H, 4.70; N, 10.48. Lit. mp 167-168° [8b]. [e] Method A. [f] Method B. [g] Method C. [i] In ethanol. [j] In potassium bromide discs. [h] Calculated on the basis of methoxypyridone converted (50% of I was recovered in each case).

toproducts as would be expected from a simple substituent change. Other data is summarized in Tables I and II. For structural similarity counts almost unchanged uv spectrum showing a hypsochromic shift from 280 nm maxima toward 272 nm for the photoproduct [10]. An intensive infrared band at 1630 cm⁻¹ characteristic of *N*-aryl-4-pyridones, is present in both the starting methoxy compounds **Ia-d** and in the corresponding photoisomers **IIa-d**. The broad band at 3210-3450 cm⁻¹ in the spectra of **IIa-e** suggests a hydrogen bonded hydroxyl group which is absent in the spectra of the corresponding starting compounds [12]. The most significant support for the assignments structures **IIa-e** follows from their ¹H and ¹³C nmr spectra. The ¹H nmr spectra (see Table III) of the corresponding pairs of isomeric compounds, **Ia-e** and **IIa-e**, were almost identical except in one aspect. The singlet for the methoxy group (δ 3.9-4.0 ppm, 3H), present in the spectra of all the starting compounds **Ia-e**, disappeared on irradiation. A new sharp singlet at δ 1.6-4.8 ppm, 2H and a very broad deuteriumoxide exchangeable signal of the hydroxylic proton at δ 2.0-3.0 ppm, 1H, appeared in the spectra of all the photoproducts. Both the above observations strongly corroborate the presence of the hydroxymethyl group in compounds **IIa-e**.

Similarly, the only difference in the ¹³C nmr spectra of the corresponding isomeric compounds, **Ia-e** and **IIa-e**, is caused by the presence or absence of the methoxy and hydroxymethyl groups. Although both the methoxyl and hydroxymethyl pyridones **Ia-e** and **IIa-e**, respectively exhibit signals for the carbon atoms of these groups at almost the same chemical shift *i.e.*, δ 59.0-59.3 ppm, quartet (J = 144.043 Hz) or triplet (J = 144.100 Hz) respectively, is undoubtedly indicative. Chemical shift signals for all other carbon atoms are in full agreement with the proposed structures.

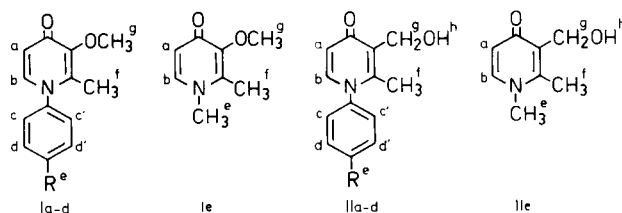
A proposed mechanism to account for the formation of the 3-hydroxymethylpyridones is presented in Scheme II.

Scheme II



We believe that the photoisomerization proceeds *via* an oxyallyl zwitterion intermediates as in Scheme II (structure **a**). This could be formed after excitation by 2,6-bonding [13]. Hydrogen transfer from the methoxy group can then follow *via* a six-membered cyclic transition state with the formation of a spirooxiran intermediate **b**. This could then rearrange as shown (*via* a five membered cyclic tran-

Table II

¹H NMR Spectra [a] of Methoxy- and Hydroxymethyl-pyridones

No.	R	a	b	c,c'	d,d'	e	f	g	h [b]
Ia	H	6.45 (d, 1H) J = 7.8			7.2-7.7 (m, 6H) [d]		2.08 (s, 3H)	3.91 (s, 3H)	-
Ib	<i>p</i> -CH ₃	6.41 (d, 1H) J = 7.8			7.1-7.5 (m, 5H) [e]	2.45 (s, 3H)	2.05 (s, 3H)	3.90 (s, 3H)	-
Ic	<i>p</i> -CH ₃ O	6.40 (d, 1H) J = 7.6			6.9-7.5 (m, 5H) [e]	3.96 (s, 3H)	2.08 (s, 3H)	3.97 (s, 3H)	-
Id	<i>p</i> -NO ₂	6.52 (d, 1H) J = 7.2	7.40 (d, 1H) J = 7.2	7.78 (d, 2H) J = 8.8	8.53 (d, 2H) J = 8.8	-	2.21 (s, 3H)	4.00 (s, 3H)	-
Ie	[c]	6.35 (d, 1H) J = 7.3	7.25 (d, 1H) J = 7.3	-	-	3.62 (s, 3H)	2.34 (s, 3H)	3.84 (s, 3H)	-
IIa	H	6.39 (d, 1H) J = 7.6			7.2-7.5 (m, 6H) [d]		2.08 (s, 3H)	4.71 (s, 2H)	3.7 (bs, 1H)
IIb	<i>p</i> -CH ₃	6.39 (d, 1H) J = 7.6			7.2-7.7 (m, 5H) [e]	2.46 (s, 3H)	2.07 (s, 3H)	4.80 (s, 2H)	2.7 (bs, 1H)
IIc	<i>p</i> -CH ₃ O	6.38 (d, 1H) J = 7.5	7.08 (d, 1H) J = 7.5		6.9-7.4 (m, 4H) [f]	3.87 (s, 3H)	2.05 (s, 3H)	4.70 (s, 2H)	3.1 (bs, 1H)
IIId	<i>p</i> -NO ₂	6.39 (d, 1H) J = 7.6			7.1-7.6 (m, 5H) [e]	-	2.08 (s, 3H)	4.66 (s, 2H)	3.7 (bs, 1H)
IIe	[c]	6.27 (d, 1H) J = 7.5	7.24 (d, 1H) J = 7.5	-	-	3.56 (s, 3H)	2.29 (s, 3H)	4.61 (s, 2H)	7.2 (bs, 1H)

[a] In deuteriochloroform. Chemical shifts given in ppm (δ) relative to internal TMS. Coupling constants (J) given in Hz. [b] Exchangeable with deuteriumhydroxide. [c] *N*-Methyl derivative. [d] Protons b,c,c',d,d',e. [e] Protons b,c,c',d,d'. [f] Protons c,c',d,d'.

sition state) to the hydroxymethyl product **IIa-e** [14,15].

In order to confirm the origin of the migrating hydrogen atom, specifically labeled trideuteriomethoxy pyridone **If** [17] was photolized under exactly the same experimental conditions as **Ia**. Deuterium transfer from carbon to oxygen occurred exclusively yielding only deuteriohydroxydideuteriomethyl derivative **IIIf**. None of the protiohydroxy-dideuteriomethyl pyridone could be detected.

EXPERIMENTAL

Irradiations were carried out in a quartz or pyrex vessel under nitrogen. A "Rayonet" RMR-400 or "Rayonet" RPR-100 photochemical reactor equipped with RPR-253,7 nm or RPR-300 nm lamps was used. Experiments in nmr tubes were carried out with 450 w medium pressure mercury arc lamp. Preparative runs were

carried out in a slow stream of nitrogen (*ca* 1 ml/minute) with water cooled quartz or pyrex immersion well fitted with 125 w "Original Hanau" TQ-150 high pressure mercury arc lamp. For thin layer chromatographic work "Merck" silica GF plates were used. Columns for chromatographic separations and purifications were packed with "Fluka" silicagel and eluted with analytical grade solvents ("Kemika"). Melting points were determined on an Original Kofler Mikroheiztisch apparatus ("Reichert", Wien) and are not corrected. Infrared spectra were taken in potassium bromide pellets with a "Perkin-Elmer" 297 Infracord spectrophotometer. Ultraviolet spectra were recorded on a "Hitachi-Perkin-Elmer" Model 124 double beam spectrophotometer. Proton nmr spectra were obtained using a "Varian" CFT-20 or a "Jeol" FX-100 FF spectrometer. ¹³Carbon nmr spectra were taken on a "Jeol" FX-100 FF instrument at 25.05 MHz. Mass spectra were obtained at 70 eV using a "Varian" Mat CH-7 spectrometer. 3-Methoxy-2-methyl-4-pyrone was prepared by methylation of 3-hydroxy-2-methyl-4-pyrone (Maltol) "Fluka"

with dimethyl sulphate according to a reported procedure [19] and was purified by distillation under reduced pressure (bp 117-119°/17 Torr, (Lit [20] bp 78-79°/4 Torr).

N-Substituted-3-methoxy-2-methyl-4-pyridones **Ia-f**.

Method A (General Procedure) [8a].

N-Aryl-3-methoxy-2-methyl-4-pyridones **Ia-c**.

A mixture of 3-methoxy-2-methyl-4-pyrone (0.05 mole) and the appropriate arylamine (0.005 mole) in water-methanol (1:1, 25 ml) was heated in a thickwalled glass tube at 150-160° for 48 hours. After solvent evaporation under reduced pressure, the product was purified by repeated column chromatography on silica gel with ethyl acetate-acetone (1:1) as an eluent. Recrystallization from ethyl acetate yielded colourless crystals. The yields varied from 50-90% [21].

Method B.

N-(4-Nitrophenyl)-3-methoxy-3-methyl-4-pyridone (**Id**).

A mixture of 3-methoxy-2-methyl-4-pyrone (4.2 g, 0.03 mole) and 4-nitroaniline (4.6 g, 0.034 mole) in water (50 ml) acidified with sulphuric acid (1.5 ml) was heated at reflux for 32 hours. After cooling to -5° unreacted nitroaniline (0.9 g) was filtered off. The product was extracted with chloroform. The solvent from the dried extract was evaporated and the crude product (5.2 g) recrystallized from ethyl acetate.

Method C.

N-Methyl-3-methoxy-2-methyl-4-pyridone (**Ie**).

To a solution of 3-methoxy-2-methyl-4-pyrone (1.4 g, 0.01 mole) in methanol (50 ml) an excess (20 ml) of aqueous methylamine (40%) was added. The mixture was heated in a stainless steel bomb at 90° for 50 hours. After evaporation under reduced pressure the residue (1.2 g) was recrystallized from ethyl acetate-acetone 1:1. Pure **Ie**, (mp 85-86°) was obtained in 50% yield.

N-Phenyl-2-methyl-3-(trideuteriomethoxy)-4-pyridone (**If**).

From a mixture of 2-methyl-3-(trideuteriomethoxy)-4-pyrone [17] (0.66 g, 0.0046 mole) and aniline (0.55 g, 0.0059 mole). Pure compound **If** was obtained in 30% yield according to method A (colourless crystals, mp 131-132°) [22].

Irradiation of *N*-Aryl-3-hydroxy-2-methyl-4-pyridones.

A 4×10^{-2} molar toluene solution of the corresponding *N*-aryl-hydroxypyridone (aryl = phenyl, *p*-tolyl, *p*-methoxyphenyl, *p*-nitrophenyl) [8a] was irradiated ("Rayonet" RPR-100 reactor fitted with 16 RPR-300 nm lamps) under slow stream of nitrogen. The progress of the reaction was monitored by chromatographic (silica gel) and by spectral (uv) methods. There was no change in absorption maxima or R_f value during the irradiation. After 300 hours of irradiation some polymers and 60% of the unchanged starting compound but no photochemical products were isolated.

Similar results were obtained by analogous irradiation with RPR-253.7 nm lamps or by using the unfiltered light of a high pressure mercury arc lamp.

Irradiation of *N*-Substituted 3-Methoxy-2-methyl-4-pyridones.

a) In Benzene.

Aliquots of **Ia** (4×10^{-2} molar) in benzene were divided and simultaneously irradiated in quartz and pyrex vessels with the light

from a water cooled high pressure mercury arc lamp. After 10 hours of irradiation a small amount of polymeric material (less than 10% in quartz and less than 5% in pyrex) were filtered off. After evaporation ¹H nmr spectra of the residue indicated for each case a mixture of roughly 50% of starting methoxy-compound **Ia** and 50% photoisomerized product **IIa**, yield of **IIa**, 40%.

Comparable results were obtained by irradiation in a "Rayonet" RPR-100 reactor in quartz tubes either by RPR-253.7 or RPR-300 nm lamps.

b) In Toluene.

The solutions of **Ia-e** (2×10^{-2} molar) in toluene were partitioned in 6 quartz tubes and were irradiated in a "Rayonet" RPR-100 reactor with 16 RPR-253.7 nm lamps. The progress of the reaction was monitored at regular intervals by chromatographic (tlc) and ¹H nmr spectral analysis of the evaporated samples. After 10 hours the irradiation was interrupted [24]. Solvent was evaporated under reduced pressure and the residue separated by preparative thin layer chromatography on silica (ethyl acetate-methanol 10:1). The corresponding hydroxymethylpyridones **IIa-e** were obtained in yields of 15-50%. (Table I).

Comparable results were obtained in experiments using RPR-300 nm lamps.

c) In Methanol.

The methanolic solution of **Ia** (2×10^{-2} molar) was irradiated under nitrogen in quartz vessel using a "Rayonet" RPR-100 reactor with RPR-253.7 nm lamps for 10 hours. After elaboration as in (a) a product containing roughly a 1:1 mixture of starting **Ia** and photorearranged compound **IIa** was obtained.

Simultaneously irradiated 2×10^{-2} molar solution of **Ia** in toluene (quartz vessel, 253.7 nm) similarly gave a roughly 1:1 mixture of **Ia** and **IIa**.

Comparable results, but with less of resinification, were obtained in experiments performed in pyrex vessels.

Irradiation of **Ia-e** in NMR Tubes.

Solutions of **Ia-e** in hexadeuteriobenzene (2×10^{-2} molar) in standard pyrex nmr tubes were irradiated by a 450 W medium pressure mercury arc lamp. The progress of photorearrangement was monitored by comparison of the nmr signals for the methoxy group, **Ia-e**, and the methylene group **IIa-e**, at regular intervals.

Results.

N-Substituent, content of **IIa-e** (%) after 1, 3 and 10 hours, respectively were: **IIa**, phenyl, 0, 9, 30; **IIb**, *p*-tolyl, 0, 25, 45; **IIc**, *p*-methoxyphenyl, 8, 16, 16; **IId**, *p*-nitrophenyl, 3, 10, 10; **IIe**, methyl, 0, -, 10 (30% after 20 hours).

Irradiation of *N*-Phenyl-3-trideuteriomethoxy-2-methyl-4-pyridone (**If**).

A solution of **If** in toluene (0.2 g, 0.00125 mole in 125 ml) was irradiated in a quartz vessel at 253.7 nm in a "Rayonet" RPR-100 photochemical reactor. After 30 hours the solvent was evaporated and the residue separated by preparative thin layer chromatography ("Merck" alumina 2 mm) using ethyl acetate/methanol (3:1) as eluent. After triple runs 0.1 g of unchanged **If** and 0.03 g of pure *N*-phenyl-3-deuteriohydroxy-dideuteriomethyl-2-methyl-4-pyridone (**IIIf**), mp 218° was isolated; ¹H nmr (deuteriochloroform): δ 6.44 (d, 1H, J = 7.5 Hz) and 7.38 (d, 1H, J = 7.5

Hz) for pyridone H₅ and H₆, respectively, 7.29-7.54 (m, 5H) for *N*-phenyl, 2.1 (s, 3H) for 2-methyl.

Preparative Irradiations.

A typical preparative irradiation of *N*-(*p*-tolyl)-3-methoxy-2-methyl-4-pyridone (**Ib**) follows with the results for the remaining cases summarized in Table I.

A solution containing **Ib** (1.0 g) in toluene (125 ml) was irradiated under nitrogen for 10 hours with an immersion quartz well fitted with 125 W "Original Hanau" TQ-150 high pressure mercury arc lamp. After removal of the solvent *in vacuo* the residue was chromatographed on silica gel with ethyl acetate/methanol (5:1) as the eluent. The early fractions containing polymerized material were discarded. Successive fractions enabled separation of starting compound **Ib** (0.5 g) and photorearranged product **IIb** (0.4 g). Final purification of crude **IIb** by crystallization from acetone yielded *N*-(*p*-tolyl)-3-hydroxymethyl-2-methyl-4-pyridone (**IIb**) (0.25 g, mp 202-203°).

Acknowledgements.

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