Tetrahedron. Vol. 27, pp. 513–522 Pergamon Press 1971. Printed in Great Britain

NITROGEN PHOTOCHEMISTRY—VI

THE PHOTOREDUCTION OF HYDROXYMETHYLPYRIDINES

V. I. STENBERG and E. F. TRAVLOEDO
Department of Chemistry, University of North Dakota, Grand Forks, North Dakota 58201

(*Received in the USA* 23 *June* 1970; *Received in the UK for publication* 13 *August* 1970)

Abstract—The irradiation of 2- and 4-(hydroxymethyl)pyridines in aqueous acid-2-propanol solutions provides the corresponding methylpyridines and 1,2-dipyridylethanes. Only retarded formation of 3-methylpyridine with low yields resulted from the irradiation of 3-(hydroxymethyl)pyridine. Neither the methylpyridines nor the 1,2-(dipyridyl)-1,2-ethanediols serve as precursors for the dipyridylethane products. It has also been demonstrated that the 1,2-dipyridylethanes do not generate the methylpyridines in the reaction solution. Evidence is presented for an excited singlet state mechanism for the reactions.

INTRODUCTION

As a consequence of our interest in the photochemistry of hydroxymethylquinolines,[1] we have become involved in the study of the corresponding pyridine photochemistry. The pyridine photochemical studies are interesting because of myriad of reactions which are now known.

One feature of pyridine and 2-methylpyridine photochemistry is their ability to dimerize to 2,2'-dipyridyl and 6,6'-dimethyl-2,2'-dipyridyl, respectively, in low yields, *ca* 1%, on UV irradiation.[2] The irradiations were done on the pure compounds under a nitrogen atmosphere and in quartz glass. On the other hand, variously substituted 2-aminopyridines and 2-pyridones provide 1,4-dimers on irradiation in acid solution.[3] A third type of dimerization occurs during the irradiation of 4-nitropyridine in alcoholic acid solution to produce 4,4'-azopyridine.[4] However, this last reaction may be attributed to the nitro group because nitrobenzene undergoes analogous photochemical reactions.

On irradiation of pyridine in aqueous solutions, glutaconaldehyde and its derivatives are produced.[5–8] Joussot-Dubien and Houdard[9] postulated reversible formation of the aminoaldehydes as the first-formed intermediates in this reaction on the basis of UV analysis of the reaction solutions. Recently, Dewar pyridine has been proven to be an intermediate in this reaction.[10]

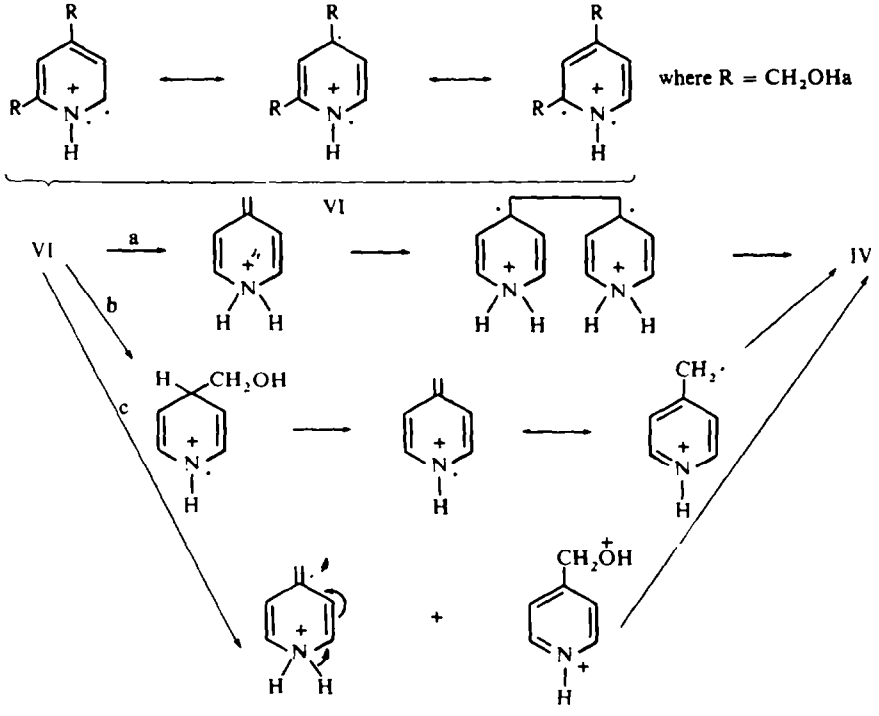
Linnell and Noyes[11] reported that pyridine in the vapor phase at 240°C is stable when it is irradiated with wavelengths longer than 200 nm. Similar results have been found by Lemaire.[12]

Nelson *et al.*[13] reported the photoreduction of the three isomeric benzoylpyridines in 2-propanol. The two major types of photoproducts are pyridylphenylcarbinols and the 1,2-dipyridyl-1,2-diphenylglycols. The formation of the gycol is hindered by increased acidity.

Kellogg *et al.* have recently reported three novel products resulting from the irradiation of variously substituted 3,5-dialkoxycarbonylpyridines in alcohol solutions.[14] Reduction occurred to produce the 1,4-dihydropyridine structure,

Pathway C is more difficult to eliminate or prove as a possibility. The intermediate glycol, V, is easily characterizable and insoluble in many organic solvents. None of the work-up components showed the presence of V. However, this result is meaningful only if this potential intermediate has a finite lifetime in the reaction solution. To test this, the glycol was irradiated under the reaction conditions and not only was the disappearance slower than that of the corresponding hydroxymethylpyridines, but it produced a new reaction product, presumably 1,2-di(4-pyridyl)ethanol, besides the expected IV. There was no indication at any time that this new product was formed in the hydroxymethylpyridine irradiation solution. By process of elimination pathway D is operating through a presumably transient, as yet unisolatable intermediate.

It is an interesting observation that the irradiation of a mixture of 4- and 3-(hydroxymethyl)pyridines yields only IV. This is additional evidence that the photochemistry of substituents attached to position three on the pyridine ring is quite different from that of substituents on positions two and four. An excited-transition state which places active centers on C_2 and C_4 is required. Thus, an intermediate of the type VI is reasonable. The ethane derivatives could arise *via* the following paths a, b and c of Scheme II.



SCHEME II

Path a is supported by known hydrogen transfer reactions in the presence of radicals.[25] Path b is unlikely since Kellogg *et al.*[14] found that deuterium incorporation occurred at the 4-position of pyridine when carbonyl pyridines are irradiated in O-deuteroethanol. These results show that the initial hydrogen atom abstraction is

done by the nitrogen. If path c were operating, crossover products should have resulted when 3- and 4-(hydroxymethyl)pyridine were irradiated together. Since this did not occur, the latter scheme is unacceptable.

The structure of the dimers may provide a possible clue to the mechanism of formation of the reported dimer of Margerum and Petrusis.[26]

Products resulting from the hydrolysis of the pyridine ring were expected.[5-9]

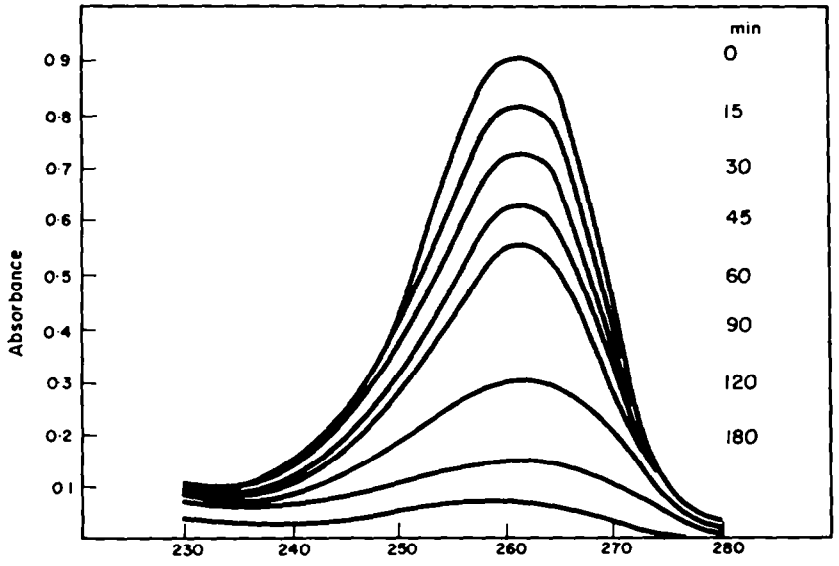


FIG 1. Spectral changes with time during the irradiation of 2-(hydroxymethyl)pyridine.

alkylation proceeded at the two and four positions and ring contraction gave a pyrrole derivative.

Both *cis*- and *trans*-1,2-di(4-pyridyl)ethylene undergo photosensitized isomerization.[15] The double bond is photochemically reduced to 1,4-di(4-pyridyl)ethane in the presence of methylcyclohexane on 2-propanol.[16] With prolonged irradiation in benzene, the ethylene compound disproportionates to 1,4-di(4-pyridyl)ethane and diazaphenanthrene.[16] The *trans* isomer of the ethylene dimethiodide is hydrated photochemically to 1,2-di(4-pyridyl)ethanol dimethiodide.[17, 18]

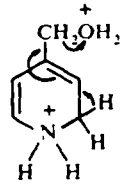
Linschitz and Connolly[19] reported changes in the UV spectrum during the irradiation of alcoholic solutions of pyridine. Although early attempts to photoalkylate pyridine with carboxylic acids were unsuccessful,[20] this has now been accomplished by irradiation of pyridine in aqueous and nonaqueous HCl-methanol solutions.[21] Reduced dimeric products are also formed in the latter reaction.

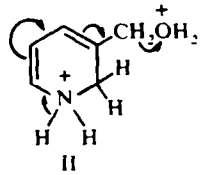
Stermitz and Huang[22] observed that 2-, 3-, and 4-pyridylacetic acids decarboxylate to give the corresponding methylpyridines. This type of photocleavage was extended to 2-(2-pyridyl)-1-ethanol, 3-(2-pyridyl)-1-propanol, and 1-(2-pyridyl)propane.

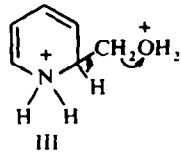
The rearrangements of pyridyl ylids and N-oxides, styrylpyridine cyclizations to azaphenanthrenes, and bromopyridine debrominations though important are probably not mechanistically related to this work and, for this reason, are not cited here.

DISCUSSION

All three isomeric hydroxymethylpyridines provide the corresponding methylpyridines upon irradiation in 2-propanol-aqueous acid solutions, albeit 3-(hydroxymethyl)pyridine provides 3-methylpyridine in only trace quantities (Table 1). In addition, the 2- and 4-(hydroxymethyl)pyridines produced the reduced dimeric products 1,2-di(2-pyridyl)ethane and 1,2-di(4-pyridyl)ethane, respectively. None of the ethane derivative could be detected in the 3-(hydroxymethyl)pyridine reaction solution. Besides the lack of ethane compound and low yields, a further anomaly of the latter reaction was the considerably slower disappearance rate of starting material compared to the other two carbinols. The latter fact can be readily rationalized on the basis of an extension of the postulated mechanism for the quinine reduction.[1] The three postulated intermediates are I–III. The elimination of water least readily occurs from II because of the required participation of a positively charged atom in the conjugated system.


I


II


III

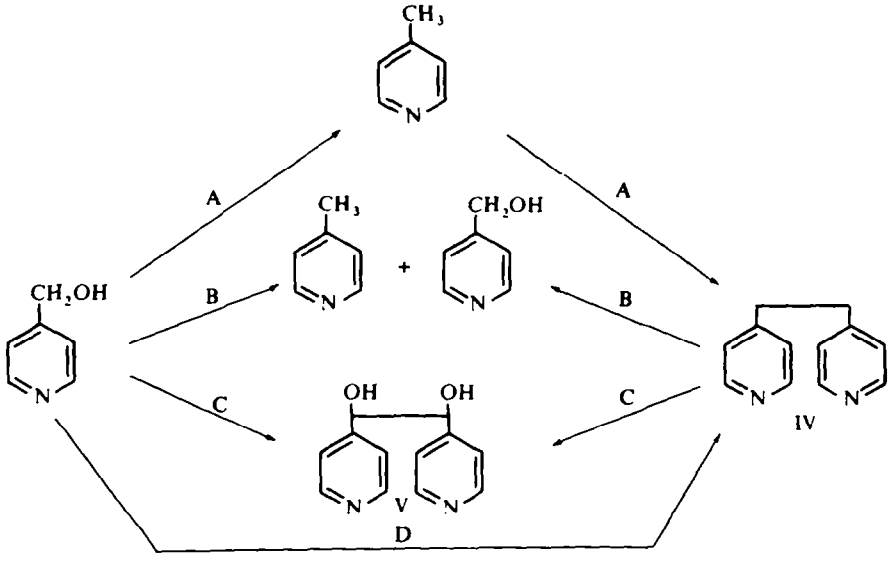
Homolytic cleavage of the C—O bond to generate a hydroxy radical and a pyridylmethyl radical, which upon hydrogen abstraction and coupling could rationalize the products formed, seems unlikely. Since the dissociation energy of the C—O bond exceeds that of the C—C bond by about 8 Kcal/mole,[23, 24] it is expected that the C—C bond would undergo an analogous photochemical cleavage. However irradiation of either 1,2-di(4-pyridyl)ethane or 4-ethylpyridine under the reaction conditions provides no appreciable amount of 4-methylpyridine.

Alcohols are also known to undergo photochemical C—O bond cleavage with 130–150 nm radiation.[23] These wavelengths are unavailable under our conditions.

The formation of the ethane derivatives provides a challenging mechanistic feature of the reaction. Four plausible pathways by which the ethane derivative IV could be formed from 4-(hydroxymethyl)pyridine are illustrated in Scheme I.

Pathway A is not feasible because 4-methylpyridine does not serve as a precursor of IV despite the fact that it is photochemically active. Direct irradiation of 4-methylpyridine gave 15% recovered starting material and no IV.

The validity of pathway B was tested in two ways. A mixture of 4-methylpyridine and 2-(hydroxymethyl)pyridine, when exposed to the reaction conditions, provided only 1,2-di(pyridyl)ethane. If pathway B were operating, crossover products should be present. However, this latter prediction assumes that crossover products are mechanistically allowed. Fortunately, the latter assumption could be tested and found to be correct. When a mixture of 4- and 2-(hydroxymethyl)pyridines was irradiated in aqueous acid-alcoholic solutions, the expected mixture of three ethane compounds resulted: IV, 1,2-di(pyridyl)ethane, and 1-(4-pyridyl)-2-(2-pyridyl)ethane.



SCHEME 1

Ideally, pathway B should be tested with only reactants substituted at the four position. The second experiment closely approximated these requirements. A mixture of 4-ethylpyridine and 4-(hydroxymethyl)pyridine was irradiated. If pathway B were functioning, a 1,2-dipyridylpropane would result. However, only IV actually was obtained. As a consequence of these arguments, pathway B is not functioning in the reaction solution.

However, products like these were not obtained although there is a polymeric fraction of the reaction solutions which proved intractable. The irreversible near disappearance of the pyridine chromphore during the irradiation of the hydroxymethylpyridines (cf. Fig. 1) was not accompanied by the formation of a longer wavelength band in contrast to the work of Joussot-Dubien and Houdard.[9]

Since the isolated products of the hydroxymethylpyridine irradiations retain the pyridine chromophore, it is obvious that photochemical processes are occurring which remain to be characterized. If Dewar pyridine were forming, it should be reversible and 5-amino-2,4-pentadienal should appear.[10]

Nature of the excited state. The hydroxymethylpyridine reactions readily proceed with a Vycor filter ($\lambda > 220$ nm) and fail in Pyrex ($\lambda > 285$ nm). Yields are somewhat enhanced with the Vycor filter as compared to those with quartz (see Table 1). As a consequence, the $^1L_b \leftarrow {}^1A$ transition[27] is the band which is causing the observed reaction.

Similar to the photoreduction of quinine and quinidine,[1] the methylpyridine and ethane products are favored in strong acid solution and are absent when the irradiation is done in neutral, aqueous, 2-propanol solution despite a rapid disappearance of starting material. Consequently, the nonbonding electrons on nitrogen do not play an important part in the reduction and dimerization-reduction reactions, and the responsible excitation must be a $\pi \rightarrow \pi^*$ transition.

Because of the high energies of the pyridine triplet state (Fig 2),[12, 28, 29] it is not an easy task to determine the multiplicity of the reaction. Good sensitizers with the proper absorption and intersystem crossing rate requirements which are soluble in the reaction medium are virtually unobtainable at the present time. However, a singlet state is indicated since the yields of products are unaffected by the presence of

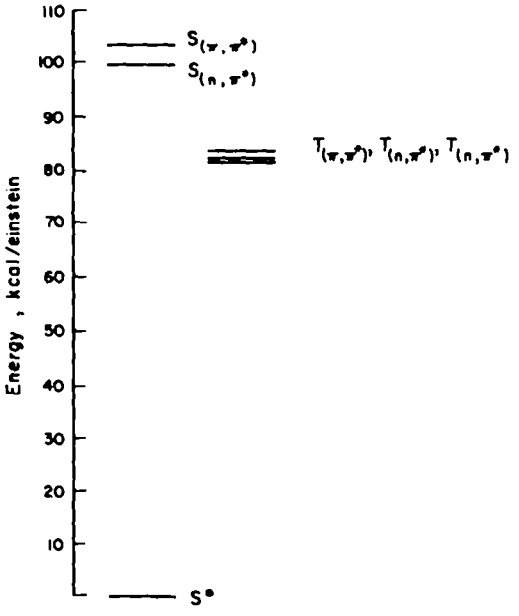


FIG 2. Energy level diagram for pyridine.

oxygen (see Table 1). Furthermore, interchanging HBr for HCl causes a marked decrease in product yield, presumably due to a depopulation of the singlet state *via* the heavy atom effect. Singlet states are also proposed for the conversion of 1,2-di(4-pyridyl)ethylene to 1,2-di(4-pyridyl)ethane ($n \rightarrow \pi^*$)[16] and for the photocarboxylation of pyridinedicarboxylic acids.[30]

To determine if a ground state ketyl radical induced the reduction,[31] benzophenone was placed in the reaction solution and the irradiation done in Pyrex. From consideration of the energy level diagram for pyridine (Fig 2), the 4-(hydroxymethyl)pyridine reaction cannot be sensitized by benzophenone (E_T = 69 Kcal/mole). The lack of reaction with these conditions eliminates the possibility of ketyl radical participation in the reaction.

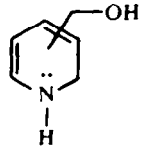
One referee has suggested the possibility that the radical VII is formed in solution by an electron transfer from some identified source. We believe this to be the next logical mechanistic step from VI perhaps not through electron transfer in the 2-propanol solution but rather *via* hydrogen atom transfer to give the protonated form of VII. This intermediate could dimerize to form the products observed by Pfordte and Leuschner[2], explain the deuterium labeling experiment of Kellogg *et al.*[14], and rationalize the photoalkylation of pyridine[32], but does not readily provide much

TABLE 1. QUANTITATIVE RESULTS OF IRRADIATION OF HYDROXYMETHYLPYRIDINES

Compound		Irradiation time (hr)	% Yield[a] methyl-pyridine	% Yield[a] ethane derivative	% Recovered[a] starting material
4-(Hydroxymethyl)-pyridine	2M HCl:22% 2-propanol	1	8	present	
	2M HCl:22% 2-propanol	2·5	13	18	6
	2M HCl:22% 2-propanol	4	16	10	0
	2M HCl:O_2: 22% 2-propanol	2·5	11	15	20
	2M HBr:22% 2-propanol	2·5	2	8	5
	2M HCl:83% 2-propanol	2·5	27	8	28
	2M HCl:83% 2-propanol, benzophenone	2·5	32	2	50
	2M HCl	3·5	5	10	trace
3-(Hydroxymethyl)-pyridine	2M HCl:22% 2-propanol	1	0	0	
	2M HCl:22% 2-propanol	2·5	0·3	0	28
	2M HCl:22% 2-propanol	4	0·3	0	
	2M HCl:22% 2-propanol	24	0·4	0	11
2-(Hydroxymethyl)-pyridine	2M HCl:22% 2-propanol	1	10	present	42
	2M HCl:22% 2-propanol	2	15	19	8
	2M HCl:22% 2-propanol	3·5[b]	18	26	6

[a] Analyses were done on a 90–P Varian Aerograph GLPC equipped with a thermal conductivity detector.
[b] Vycor filter and 450 W medium pressure Hanovia mercury arc lamp.

enlightenment to these studies except that it probably is a bridge between VI and the other intermediates, I–III.



VII

EXPERIMENTAL

The irradiations were done using a 550 W medium pressure Hanovia lamp, 673A36 and an immersion well. N_2 was flushed for 20–30 min prior to radiation, and a slow bubbling rate maintained during the

irradiation. The reaction soln was stirred by a magnetic bar. Eastman Spectro grade 2-propanol was purified by distillation in a 2 ft Vigreux column. The IR and UV spectra were determined on Beckman IR-12 and a Cary 14 spectrophotometer, respectively. An A-60 Varian Associate spectrometer was employed for the NMR spectra using tetramethylsilane as an internal standard.

Materials. Both 2- and 3-(hydroxymethyl)pyridines were obtained from Aldrich and were distilled under vacuum: b.p. 72·5–73·0° (1·5 mm), 2-(hydroxymethyl)pyridine and 107–108° (1·6 mm), 3-(hydroxymethyl) pyridine. The 4-(hydroxymethyl)pyridine was obtained from Columbia Chemicals and was not further purified. The materials gave one peak on GLPC. The chromatograph used was a Varian Aerograph Model 90-P equipped with a 10 ft × ¼ in Carbowax column on Chromosorb Q. Atmospheric hydrogenation of 1,2-di(2-pyridyl)ethylene (Aldrich) over 10% Pd–C in EtOAc[33] gave 1,2-di(2-pyridyl)ethane: crystals from ethyl acetate–hexane, m.p. 50–51° (lit.[34] 49·5–50·5°).

General procedure for irradiations. The hydroxymethylpyridine (0·02 mole) was dissolved in 2M HCl–22% 2-propanol soln (210 ml) and irradiated for the given length of time (Table 1). The HCl concentration was based on the total volume of solution. At the termination of the irradiation, the pH was raised to approximately 1 by bubbling in NH_3 and the solvents were removed under reduced pressure at 40°. Excess NH_3 was bubbled into the oily residue, and the residue was extracted with CH_2Cl_2 or ether. A brown resin-like insoluble material remained which was soluble in chloroform. The ether extract was dried with $MgSO_4$, filtered, and the solvent removed over a period of 3–4 hr using a 1 ft glass-packed distillation column. With an isomeric methylpyridine as an internal standard and diluting the residue to 10 ml, the soln was analyzed by GLPC using a 7·5 ft × ¼ in Par 1 (Hewlett-Packard) column with mesh size of 40/80 and the column temperature of 190°. In order to analyze for starting material, the column temp was raised to 245°. The quantitative results were obtained using the height × width at half height method.

Further GLPC analysis of the reaction mixture on a 7·5 ft × ¼ in 20% OV-1 (Applied Science Labs) on Chromosorb Q mesh 40/80 column at 215° showed the second main component of the reaction solns. the dipyridylethanes, with 4-methylquinoline as an internal standard. The compounds were collected by GLPC, and the structures proven by comparison of their IR, NMR, and UV spectra with authentic samples (Aldrich). No dipyridylethane compound was detected in the photolysis of 3-(hydroxymethyl)pyridine.

Benzophenone and 2-(hydroxymethyl)pyridine irradiation

Benzophenone (0·1 g–5·5 × 10^{-4} moles) and 2-(hydroxymethyl)pyridine (0·02 mole) were placed in 2M HCL–22% 2-propanol (200 ml) and irradiated for 2 hr with Pyrex-filtered light. The precipitated benzydrol (70%) was filtered off and the filtrate worked up as previously. GLPC analysis on 20% OV-1 at 105° showed 2·5% 2-methylpyridine and greater than 95% of starting material to be present. No. 1,2-di(2-pyridyl)ethane was detected. A control run under the same conditions omitting benzophenone afforded 0·4% 2-methylpyridine and greater than 95% starting material.

Irradiation of 1,2-di(4-pyridyl)-1,2-ethanediol. The trihydrate (Aldrich, 0·005 moles) was irradiated in aqueous 2M HCl· 2-propanol through quartz for 3 hr. TLC analysis on silica gel HF_{245} with n-hexane: acetone: diethylamine, 5:3:2, showed the presence of 1,2-di(4-pyridyl)ethane, R_f 0·6, a new component, R_f = 0·4, presumed to be 1,2-di(4-pyridyl)ethanol in an area ratio of 1:1, and traces of starting material, R_f = 0·2.

Irradiation of 4-ethylpyridine and 4-hydroxymethylpyridine

Iradiation of 0·01 mole of each component under the usual conditions for 3 hr afforded 9% of 1,2-di(4-pyridyl)ethane besides 4-methylpyridine. No other component could be detected by GLPC.

Irradiation of 4-methylpyridine. The irradiation of 0·02 mole 4-methylpyridine (Aldrich Chemicals) in 200 ml 2M HCl: 22% 2-propanol was done for 2 hr 15 min. GLPC analysis showed 14% of starting material present and no 1,2-di(4-pyridyl)ethane.

Irradiation of 4-(hydroxymethyl)pyridine in neutral aqueous 2-propanol solution. The irradiation of 4-(hydroxymethyl)pyridine (0·02 mole) through quartz in 200 ml aqueous 22% 2-propanol was done for 2·5 hr. The solvents were removed under reduced pressure after adjusting the pH to 2 by HCl, and the reaction mixture worked up in the usual way. No 4-methylpyridine or 1,2-di(4-pyridyl)ethane was detected by GLPC

Irradiation of 1,2-di(4-pyridyl)ethane. The irradiation of 0·01 mole 1,2-di(4-pyridyl)ethane in 200 ml 2M HCl: 22% 2-propanol through quartz for 2 hr was done. Only trace amounts of 4-methylpyridine were detected by GLPC.

Irridation of 4-methylpyridine and 2-(hydroxymethyl)pyridine

Irradiation of 0·005 mole 4-methylpyridine and 0·015 mole 2-(hydroxymethyl)pyridine in 200 ml 2M HCl:22% 2-propanol through quartz for 2 hr afforded 20% of 2-methylpyridine, 18% of 2-(hydroxymethyl)pyridine, 19% of 1,2-di(2-pyridyl)ethane, and 73% of recovered 4-methylpyridine.

Irradiation of a mixture of 2- and 3-(hydroxymethyl)pyridines

The hydroxymethylpyridines (0·01 mole of each) were irradiated for 2·5 hr under the usual conditions. GLPC analysis on a 15 ft × ¼ in 18% OV-1 column at 245° showed 7·0% 1,2-di(2-pyridyl)ethane, 9·0% of 1-(2-pyridyl)-2-(4-pyridyl)ethane, and 11% of 1,2-di(4-pyridyl)ethane. The crossed product, 1-(2-pyridyl)-2-(4-pyridyl)ethane, was collected by preparative GLPC. Its structure was inferred by IR and NMR spectra comparison with the other two isomeric pyridylethanes.

Irradiation of a mixture of 4-(hydroxymethyl)pyridine and 3-(hydroxymethyl)pyridine. The irradiation was accomplished in 3 hr by dissolving 0·02 mole 4- and 0·02 of 3-(hydroxymethyl)pyridine in 200 ml 2M HCl: 22% 2-propanol and placed in a quartz vessel. GLPC analysis on 20% OV-1 at 215° showed the only dipyridylethane present was 1,2-di(4-pyridyl)ethane.

Acknowledgement—This investigation was supported by a research grant 1-RO1-AI-08138 from the National Institutes of Health, United States Public Health Service and in part by a Public Health Service Research Career Development Award (No. 1 KO4 GM 09888-01) from the National Institute of General Medical Sciences.

REFERENCES

[1] V. I. Stenberg, E. F. Travecedo, and W. E. Musa, *Tetrahedron Letters* 2031 (1969); E. F. Travececo, V.I. Stenberg, and W. E. Musa, *Proc. N. Dak. Acad. Sci.* **23**, 25 (1969)
[2] K. Pfordte and G. Leuschner, *Liebigs Ann.* **646**, 30 (1961)
[3] E. C. Taylor and R. O. Kan, *J. Am. Chem. Soc.* **85**, 776 (1963)
[4] S. Hashimoto, K. Kano and K. Ueda, *Tetrahedron Letters* 2733 (1969)
[5] H. Freytag, *J. Prakt. Chem.* **139**, 44 (1933)
[6] F. Feigl, *Ibid.* **139**, 343 (1934)
[7] H. Freytag and W. Neudert, *Ibid.* **135**, 15 (1932); H. Freytag and F. Hlucka, *Ibid.* **135**, 288 (1932); H. Freytag, *Ibid.* **139** 343 (1934)
[8] F. Feigl and V. Anger, *Ibid.* **139**, 180 (1934)
[9] J. Joussot-Dubien and J. Houdard, *Tetrahedron Letters* 4389 (1967); *Bull. Soc. Chim. Fr.* 2619 (1969)
[10] K. E. Wilzbach and D. J. Rausch, *J. Am. Chem. Soc.* **92** 2178 (1970)
[11] R. H. Linnell and W. A. Noyes, Jr., *Ibid.* **73**, 3986 (1951)
[12] J. Lemaire, *J. Phys. Chem.* **71**, 612 (1967)
[13] D. A. Nelson, G. D. Norton and W. H. Stanley, *Abstracts, 157th National Meeting of the American Chemical Society* O-146. Minneapolis, Minn., Apr (1969)
[14] R. M. Kellogg, T. J. van Bergen and H. Wynberg, *Tetrahedron Letters* 5211 (1969)
[15] D. G. Whitten and M. T. McCall, *Ibid.* 2755 (1968)
[16] D. G. Whitten and Y. J. Lee, *Ibid.* **92**, 415 (1970)
[17] D. G. Whitten, Y. J. Lee and M. T. McCall, *Abstracts, 158th National Meeting of the American Chemical Society* O-16. New York, N.Y., Sept (1969)
[18] M. T. McCall and D. G. Whitten, *J. Am. Chem. Soc.* **91**, 5681 (1969)
[19] H. Linschitz and J. S. Connolly, *Ibid.* 90, 2979 (1968)
[20] H. Nozaki, M. Kato, R. Noyori and M. Kawansis, *Tetrahedron Letters* 4259 (1967)
[21] E. F. Travecedo and V. I. Stenberg, *J. Chem. Soc.* (D), 609 (1970)
[22] F. R. Stermitz and W. H. Huang, *J. Am. Chem. Soc.* **92**, 1446 (1970)
[23] J. G. Calvert and J. N. Pitts, Jr., *Photochemistry*, pp. 824, 444. Wiley, New York, N.Y. (1967)
[24] M. Szwarc, *Chem. Revs* **47**, 75 (1950)
[25] W. A. Pryor, *Free Radicals*, p. 258. McGraw-Hill, New York, N.Y. (1966)
[26] J. D. Margerum and C. T. Petrusis, *J. Am. Chem. Soc.* **91**, 2467 (1969)
[27] H. H. Jaffe and M. Orchin, *Theory and Application of Ultraviolet Spectroscopy*, p. 375. Wiley, New York, N.Y. (1962)

[28] R. J. Hoover and M. Kasha, *J. Am. Chem. Soc.* **91**, 6508 (1969)
[29] R. N. Narmukhametov, *Russ. Chem. Rev* **36**, 693 (1967)
[30] C. Azuma and A. Sugimori. *Kogyo Kagaku Zasshi* **72**, 239 (1969); *Chem. Abstr.* 70, 96575k (1969)
[31] A. Padwa, W. Bergmark and D. Pashayan, *J. Am. Chem. Soc.* **91**, 2653 (1969)
[32] E. F. Travecedo and V. I. Stenberg, *J. Chem. Soc.* (D) 609 (1970)
[33] M. Yamin and R. M. Fuoss, *Ibid.* **75**, 4860 (1953)
[34] P. G. Campbell and P. C. Teague, *Ibid.* **76**, 1371 (1954)