Easterly.[13] 6-Methyl-4H-pyran-4-one-2-carboxylic acid (1.50 g) and 10 ml of diphenyl ether were placed in a 25-ml distillation flask to which was attached a small Vigreux column (70 mm), condenser, and receiver. The flask was immersed in an oil bath preheated to 223°. The bath temperature was raised to 230° whereupon ebullition of the mixture began. The bath temperature was maintained between 230 and 245° until the ebullition slackened; about 17 min were required. The bath was lowered and the system was carefully subjected to a vacuum of 220 mm for distillation. Heating of the mixture was resumed and a distillate of 7.63 g was collected at 192–204° (210 mm). The distillate was partitioned between 15 ml of 5 *N* HCl and 50 ml of hexane. The organic layer was extracted with two 15-ml portions of 5 *N* HCl. The acid layers were combined and carefully treated with solid potassium carbonate until the mixture became cloudy. This was extracted with four 40-ml portions of methylene chloride. The dried ($MgSO_4$) and combined extracts were evaporated *in vacuo* leaving a clear oil as residue (1.14 g). Glpc analysis of the residue on a 0.25 in. × 10 ft 410 gum rubber (20% on Chromosorb WAW, 60–80 mesh) column at 150° showed it consists of *ca.* 93% 2-methyl-4H-pyran-4-one, corresponding approximately to a quantitative conversion. Analytical material was obtained by glpc fractionation on a $^3/_8$ in. × 20 ft gum rubber (20% on Chromosorb W HMDS, 30–60 mesh) column at 150°: $n^{25}\mathrm{D}$ 1.5280; $\lambda_{\max}^{\text{hexane}}$ 239 (ϵ 3410); $\lambda_{\max}^{\text{EtOH}}$ 247 (ϵ 1340); $\lambda_{\max}^{\mathrm{CCl_4-CS_2}}$ 5.99 (vs, C=O),[10] 6.15 and 6.29 (s, ring double bonds),[10] 7.04, 7.20, 7.32, 7.96, 11.2 and 12.2 (s), 8.20, 8.50, 9.43 and 9.91 (m), 10.7, and 11.6 μ (vs); nmr ($CDCl_3$), -2.28 (doublet, 2-CH_3, $|J_{2,3}| \leqslant 0.7$ cps), -6.14 (multiplet, 3-H), -6.26 (quartet, 5-H, $|J_{3,5}| = 2.5$, $|J_{5,6}| = 5.7$ cps), and 7.77 ppm (quartet, 6-H), $|J_{3,6}| \leqslant 0.6$ cps) (TMS).

Anal. Calcd for $C_6H_6O_2$: C, 65.4; H, 5.49. Found: C, 65.1; H, 5.46.

Registry No.—I, 14255-36-8; methylenebis(2-methyl-2-[1,3-dioxolanyl]), 14255-37-9; II, 14255-38-0; copper chelate of II, 14495-16-0; IV, 14255-39-1; V, 5848-33-9; VI, 14255-41-5.

Acknowledgment.—Thanks are due Dr. J. P. Heechen and Mr. R. A. Nyquist for determination and interpretation of nmr and infrared spectra, respectively. Appreciation is extended to Professor J. W. Crump of Albion College for helpful discussions and encouragement during the course of this work.

---

[13] J. P. Easterly and H. E. Hennis, U. S. Patent 3,152,148 (1964); *Chem. Abstr.*, **62**, 530 (1965).

Heterocyclic Compounds. VIII.[1] The Reaction of Ethoxyacetylene with 2- and 4-Pyridone

BORIS WEINSTEIN AND DONALD N. BRATTESANI

Department of Chemistry, Stanford University,
Stanford, California 94305

Received June, 6, 1967

Treatment of pyridones with dienophiles leads to variable results. For example, fusion of N-methyl-2-pyridone and maleic anhydride gave a rather unusual derivative,[2] whereas in an autoclave hexafluoro-2-butyne added normally to 2-pyridone.[3] Benzyne and N-methyl-2-pyridone, in contrast, afforded either a Diels–Alder product or a phenylpyridone depending on the exact generation procedure.[4,5] With 2-pyridone the benzyne reagent produced small amounts of 2-phenoxypyridine, 1-phenyl-2-pyridone, and acridone.[4] No related study exists for ethoxyacetylene, although amines do react with the ethynyl function to yield alkoxyvinylamines.[6] Since 2- and 4-pyridone have tautomeric forms, it was felt that a brief investigation into this area would be useful and might provide some interesting N- and O-substitution compounds.[7]

The condensation of 2-pyridone with ethoxyacetylene in refluxing chloroform proceeded sluggishly; the black solution on distillation was readily separated into two liquid fractions. The major, low-boiling material was identified as 2-acetoxypyridine (I), previously formed with difficulty from sodium 2-pyridinolate and acetyl chloride[8,9] or by heating pyridine 1-oxide with acetic anhydride.[10,11] The infrared, nuclear magnetic resonance, and ultraviolet spectral data confirmed this assignment of structure. The minor, high-boiling material analyzed for $C_9H_{11}NO_2$ and was formulated as N-(1-ethoxyvinyl)-2-pyridone (II). The ultraviolet spectrum held two maxima at 227 and 303 mμ that was suggestive of an unchanged chromophoric system, for a similar pair of bands is found in the parent 2-pyridone at 227 and 297 mμ.[12] In the infrared the lack of a strong absorption between 3700–3300 cm^{-1} indicated the masking of the amide hydrogen function; additional correlations were made at 1670 (conjugated ketone) and 1286 cm^{-1} (vinyl ether).[13] The nuclear magnetic resonance spectrum exhibited the expected resonances at δ 1.32 (methyl), 4.00 (aliphatic methylene), 4.40 and 4.47 (vinyl methylene), and 6.27, 6.55, 7.50, and 7.55 (ring hydrogens).[14–16] Such a consequence is interesting, as only a few N-acylpyridones are known at present.[17] It has been mentioned that the rarity of N-acylpyridones may be caused by a rapid rearrangement of these compounds to the corresponding O-acylpyridines.[18] Employing this suggestion, the reaction course here would proceed from II through an unstable N-acetylpyridone to I. The direct formation of I can alternatively occur by formation

---

[1] For the previous paper in this series, see B. Weinstein and D. N. Brattesani, *J. Heterocyclic Chem.*, **4**, 151 (1967).

[2] B S. Thagarajan and K. Rajagopalan, *Tetrahedron*, **19**, 1483 (1963).

[3] L. A. Paquette, *J. Org. Chem.*, **30**, 3107 (1965).

[4] L. Bauer, C. L. Bell, and G. E. Wright, *J. Heterocyclic Chem.*, **3**, 393 (1966).

[5] These results should be considered with caution in view of a recent disclosure concerning the effect of the silver ion on the reactions of benzyne; see L. Friedman, *J. Am. Chem. Soc.*, **89**, 3071 (1967).

[6] For a review on the chemistry of ethynyl ethers, see J. F. Ahrens, "Advances in Organic Chemistry," Vol. 2, R. A. Raphael, E. C. Taylor, and H. Wynberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p 117.

[7] For a brief discussion of N-acetylpyridones and acetoxypyridines, see H. Meislich, "The Chemistry of Heterocyclic Compounds," Vol. 14, E. Klingsberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1962, pp 509 and 643–646.

[8] A. E. Chichibabin and P. G. Szokow, *Ber.*, **58**, 2650 (1925).

[9] Y. Yeno, T. Takaya, and E. Imoto, *Bull. Chem. Soc. Japan*, **37**, 864 (1964)

[10] J. H. Markgraf, H. B. Brown, Jr., S. C. Mohr, and R. G. Peterson, *J. Am. Chem. Soc.*, **85**, 958 (1963).

[11] T. Cohen, I. H. Song, and J. H. Fager, *Tetrahedron Letters*, 237 (1965).

[12] A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorpon Spectroscopy in Organic Chemistry," Edward Arnold Ltd., London, 1957, p 157.

[13] K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p 207.

[14] C. L. Bell, R. S. Egan, and L. Bauer, *J. Heterocyclic Chem.*, **2**, 420 (1965).

[15] W. Brügel, *Z. Elektrochem.*, **66**, 159 (1962).

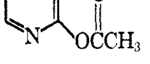
[16] H.-H. Perkampus and U. Krüger, *Chem. Ber.*, **100**, 1165 (1967).

[17] M. Dohrn and P. Diedrich, *Ann.*, **494**, 284 (1932).

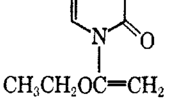
[18] D. Y. Curtin and L. L. Miller, *J. Am. Chem. Soc.*, **89**, 637 (1967), footnote 23.

of a ketene acetal intermediate, followed by a hydrolysis sequence.

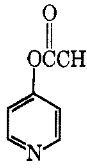
Ethoxyacetylene very slowly combined with 4-pyridone to give a crude liquid, which was fractionated by distillation. The first cut solidified on cooling and was characterized as the known 4-acetoxypyridine (III).[19] This particular compound is very unstable and upon exposure to moisture quickly reverts to 4-pyridone. The second product darkened on exposure to light, but sufficient spectral information was gathered to permit the red liquid to be described as N-(1-ethoxyvinyl)-4-pyridone (IV). In the infrared spectrum, peaks were observed at 1640 (conjugated ketone) and 1290 cm^{-1} (vinyl ether), while the ultraviolet contained a maximum at 277 mμ, somewhat displaced from the band at 256 mμ in 4-pyridone. Again the nuclear magnetic resonance spectrum held the expected signals at δ 1.38 (methyl), 4.04 (aliphatic methylene), 4.17 and 4.45 (vinyl methylene), 6.36 (two ring hydrogens near oxygen), and 8.05 (two ring hydrogens near nitrogen). In conclusion, 2- and 4-pyridone add to ethoxyacetylene to afford both O and N substitution, but do not react in a Diels-Alder fashion under the conditions described here.



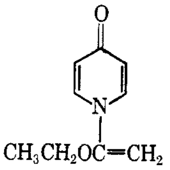
I



II



III



IV

Experimental Section[20]

2-Acetoxypyridine (I) and N-(1-Ethoxyvinyl)-2-pyridone (II).—A solution of 2-pyridone (18.0 g, 0.189 mole) and ethoxyacetylene (33 ml, furnished as a 62% hexane azeotrope from the Humphrey Chemical Company) in chloroform (100 ml) under anhydrous conditions was refluxed for 20 days, at which time there was added additional ethoxyacetylene (20 ml). By 27 days the 2-pyridone had disappeared from the reaction liquid as judged by thin layer chromatographic screening. The chloroform was removed under reduced pressure and the residual black oil was distilled to yield 2-acetoxypyridine [17.4 g, 67%; clear liquid; bp 74–76° (0.95 mm) (lit.[8] 110–112° (10 mm)); $n^{21}\text{D}$ 1.5032; the ultraviolet spectrum gave λ_{max} 227 (ϵ 1760), 258 (2640), 264 sh (2100), and 303 broad mμ (786); the infrared spectrum gave 3080 w (aromatic CH), 3015 w, 2935 w (acetoxy CH), 1768 s (C═O), 1628 m (C═C), 1595 s, 1573 m, 1471 s (CH$_3$), 1435 s (C═N), 1371 s (CH$_3$), 1195 vs (C–O–C), 1146 m, 1045 m, 1012 m, 995 m, 915 m, 841 m, (CH), 770 m, and 740 m cm^{-1}; the nmr spectrum showed peaks at δ 2.27 (methyl, singlet, area 3), 7.21 (ring hydrogen 3, doublet, area 1, J = 8 and 1 cps), 7.23 (ring hydrogen 5, pair of doublets with fine structure, area 1, J = 8, 5, and 1 cps), 7.82 (ring hydrogen 4, doublet of triplets, area 1, J = 8, 8, and 2 cps), 8.48 (ring hydrogen 6, pair of doublets, area 1, J = 5 and 2 cps)] and N-(1-ethoxyvinyl)2-pyridone [10.2 g, 33%; yellow oil; bp 108–110° (1.2 mm); $n^{21}\text{D}$ 1.5421; the ultraviolet spectrum λ_{max} gave 227 (ϵ 6100) and 303 broad mμ (4530); the infrared spectrum gave 3120 w (aliphatic CH), 3080 w, 3010 w, 2975 m, 2930 w, 2895 w, 2880 w, 1670 s (C═O), 1598 s, 1533 s, 1385 m, 1286 s, 1210 m, 1141 m, 1090 s, 1045 m, 977 m, 856 m (═CH$_2$), and 762 m cm^{-1}; the nmr spectrum showed peaks at δ 1.32 (methyl, triplet, area 3, J = 7 cps), 4.00 (aliphatic methylene, quartet, area 2, J = 7 cps), 4.47 and 4.40 (vinyl methylene, AB pattern, area 2, J = 3 cps), 6.27 (ring hydrogen 5, triplet, area 1, J = 1 cps), 6.55 (ring hydrogen 3, doublet, area 1, J = 10 cps), 7.50 (ring hydrogen 4, pair of doublets, area 1, J = 10 and 7 cps), and 7.55 (ring hydrogen 6, doublet, area 1, J = 7 cps).

Anal. Calcd for $C_9H_{11}NO_2$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.15; H, 6.62; N, 8.30.

4-Acetoxypyridine (III) and N-(1-Ethoxyvinyl)-4-pyrdone (IV).—A solution of 4-pyridone (18.0 g, 0.189 mole) and ethoxyacetylene (33 ml) in chloroform (200 ml) under anhydrous conditions was refluxed for 5 days, at which time there was added additional ethoxyacetylene (15 ml). By 12 days the 4-pyridone had disappeared from the reaction liquid as judged by thin layer chromatographic screening. The chloroform was removed under reduced pressure and the residual black oil was distilled to yield 4-acetoxypyridine [10.6 g, 41%; bp 120–125° (2.1 mm); white needles, unstable to air; mp 130–133° (sealed capillary) and 135–145° (open capillary) (lit.[19] mp 140–150°); in the latter case, the recovered sample possessed an infrared spectrum consistent with a mixture of both 4-pyridone and 4-acetoxypyridine; the ultraviolet spectrum gave λ_{max} 256 mμ (ϵ 15,100); the infrared spectrum gave 3080 w, 3065 w (aromatic CH), 2920 w (acetoxy CH), 1727 s (C═O), 1662 s (C═C), 1635 s (C═C), 1601 s, 1555 m, 1578 w (CH$_3$), 1400 m (C═N), 1372 s (CH$_3$), 1339 m, 1255 s, 1191 s (C–O–C), 1075 s, and 850 s cm^{-1} (CH)] and N-(1-ethoxyvinyl)-4-pyridone [5.4 g, 17%; red oil; bp 140–148° (0.75 mm); $n^{20}\text{D}$ 1.5784; the ultraviolet spectrum gave λ_{max} 277 mμ (ϵ 5630); the infrared spectrum gave 2980 w (CH), 1640 s (C═O), 1590 s (C═C), 1470 m (CH$_3$), 1407 m, 1368 m, 1341 m (CH$_3$), 1290 s, 1186 s, 1130 w, 1111 w, 1095 m, 1042 s, 978 m, and 848 s (CH) cm^{-1}; the nmr spectrum showed peaks at δ 1.38 (methyl, triplet, area 3, J = 7 cps), 4.04 (aliphatic methylene, quartet, area 2, J = 7 cps), 4.17 and 4.45 (vinyl methylene, AB pattern, area 2, J = 4 cps), 6.36 (ring hydrogens 3 and 5, doublet, area 2, J = 8 cps), and 8.05 (ring hydrogens 2 and 6, doublet, area 2, J = 8 cps).

Anal. Calcd for $C_9H_{11}NO_2$: C, 65.44; H, 6.71; N, 8.48. Found: C, 64.84; H, 6.68; N, 8.27.

Registry No.—I, 3847-19-6; II, 14210-19-6; III, 14210-20-9; IV, 14210-21-0; ethoxyacetylene, 927-80-0; 2-pyridone, 142-08-5; 4-pyridone, 108-96-3.

---

[19] F. Arndt and A. Kalischek, *Ber.*, **63**, 587 (1930).

[20] The boiling and melting points are uncorrected. The infrared spectra were determined as neat films or in pressed potassium bromide disks with a Perkin-Elmer Model 421 spectrophotometer, ultraviolet spectra were measured in 95% ethanol on a Cary Model 14 spectrophotometer, and nuclear magnetic resonance spectra were obtained on a Varian A-60 spectrometer. Thin layer chromatography utilized silica gel G as the support, chloroform–methanol (1:1) for elution, and iodine vapor for development. Microanalyses were provided by the Microanalytical Laboratory, Department of Chemistry, Stanford University.

Hydrogenolysis by Hydrogen Transfer. Role of Palladium–Charcoal on Halogenated Benzo–Pyridine System

UMA PRASANNA BASU AND BHABATOSH BHATTACHARYA

Bengal Immunity Research Institute, Calcutta-16, India

Received April 13, 1967

In a systematic investigation on the synthesis of isoquinoline derivatives,[1–3] it has been observed that when 5-chloro-3-methyl-3,4-dihydroisoquinoline (IIIa) was subjected to dehydrogenation with palladium–charcoal (Pd–C) in tetralin or diphenyl ether in a carbon dioxide atmosphere, not only dehydrogenation but also dehalogenation occurs, yielding 3-methylisoquinoline (IVe)[4] in place of the expected 5-chloro-3-

---

[1] T. N. Ghosh and B. Bhattacharya, *J. Indian Chem. Soc.*, **37**, 111 (1960).

[2] T. N. Ghosh, B. K. Ghosh, and B. Bhattacharya, *J. Sci. Ind. Res., India*, **21B**, 133 (1962).

[3] B. Bhattacharya, *Indian J. Chem.*, **2**, 25 (1964); B. Bhattacharya, *ibid.*, in press.

[4] S. Gabriel and A. Neumann, *Ber.*, **25**, 3563 (1892).