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140. Synthesis of 4-Oxo-1,2,3,4-tetrahydropyridine (2,3-Dihydro-4(1*H*)pyridinone)

by **Akhtar Haider, Georges Cornuz** and **Hugo Wyler**

Institut de chimie organique, Université de Lausanne, Rue de la Barre 2, 1005 Lausanne

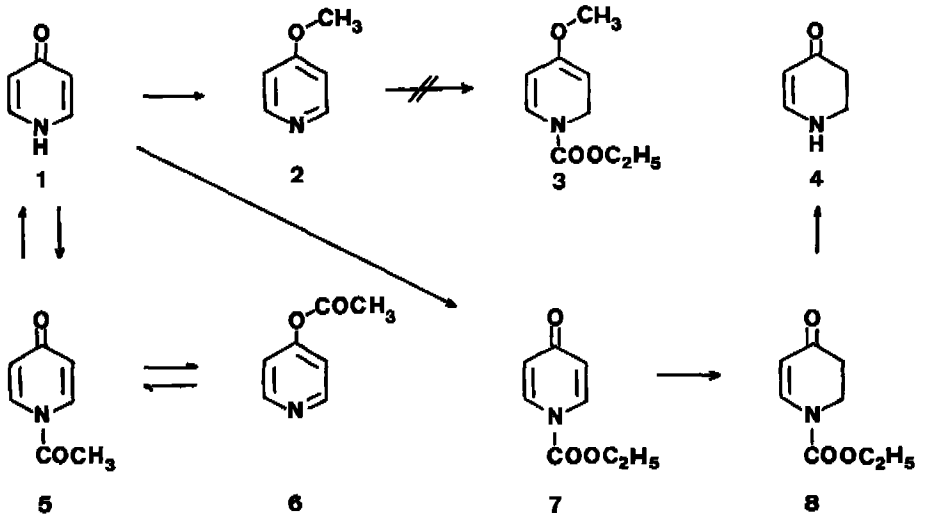
(7. V. 75)

Summary. N-Ethoxycarbonyl-4-pyridone is reduced to N-ethoxycarbonyl-4-oxo-1,2,3,4-tetrahydropyridine by sodium borohydride in *t*-butyl alcohol containing ethyl chloroformate. Saponification of the product leads to 4-Oxo-1,2,3,4-tetrahydropyridine.

1. Introduction. – Some N-alkylated 4-Oxo-1,2,3,4-tetrahydropyridines have been most successfully synthesized by reduction of the corresponding N-alkyl pyridones with hydroaluminates. A first example was given by *Winterfeldt* [1] who reduced N-[2-(indol-3-yl)-ethyl]-4-pyridone with lithium aluminium hydride to the corresponding N-alkyl-4-oxo-1,2,3,4-tetrahydropyridine. Other N-alkyl-4-oxo-1,2,3,4-tetrahydropyridines were prepared by *Tamura et al.* [2] treating N-alkyl pyridones with lithium triethoxy aluminium hydride. Such compounds have also been obtained by other procedures: An example by *Hebky et al.* [3] showed that they are accessible by catalytic hydrogenation of pyridones; *Stütz et al.* [4] found an opposite mode of access: dehydrogenation of an N-alkyl piperidone occurred following a peracid and acetic anhydride/base treatment by means of a modified type of the *Polonovsky* reaction. A total synthetic route to some 2,6-disubstituted 4-oxo-1,2,3,4-tetrahydropyridines is reported by *Sugiyamas* group [5] condensing *Schiff*-bases with dialkali salts of β-diketones.

A preparation of 4-oxo-1,2,3,4-tetrahydropyridine (**4**) is not yet reported in the literature. In our approach to the synthesis of this compound we intended to adopt an elegant procedure used by *Fowler* [6] in the preparation of dihydropyridines: he reacted pyridine in methanol at −65° with sodium borohydride and methyl chloroformate and obtained exclusively N-methoxycarbonyl-1,2-dihydropyridine. We were hopeful that application of the same reaction with ethyl chloroformate to 4-methoxypyridine (**2**) would lead to the corresponding dihydropyridine **3** which on hydrolysis would liberate the 4-oxo-1,2,3,4-tetrahydropyridine (**4**).

2. Results. – a) *Reactions.* 4-Methoxy-pyridine (**2**) was prepared according to a known procedure [7] by treatment of 4-pyridone (**1**) with diazomethane in methanol and was obtained pure after steam distillation as its hydrochloride. When this compound was treated with sodium borohydride and ethyl chloroformate in methanol at −60°, as described by *Fowler* [6], we obtained to our surprise about 10–15% of N-ethoxycarbonyl-4-oxo-1,2,3,4-tetrahydropyridine (**8**) instead of the expected N-ethoxycarbonyl-4-methoxy-1,2-dihydropyridine (**3**); the rest was identified as 4-pyridone (**1**). The oily reduction product was separated by chromatography on silica gel with methylene chloride/methanol 19:1 (Rf 0.74) from the slowly migrating pyridone (Rf 0.05). The relatively modest yield could not be increased to more than 25% even with a large excess of the sodium borohydride.



It seemed obvious that the reduction product did not arise directly from 4-methoxy-pyridine (**2**) but from 4-pyridone (**1**) liberated in this reaction. This was confirmed by an experiment with 4-pyridone itself; the yield in that case was still poor. However when we applied the reduction procedure to N-ethoxycarbonyl-4-pyridone (**7**) the yield became almost quantitative. The starting material was prepared by reaction of the sodium salt of 4-pyridone with ethyl chloroformate in *t*-butyl alcohol. The N-ethoxycarbonyl-pyridone **7** was stirred with a 10-fold excess of sodium borohydride and of ethyl chloroformate in *t*-butyl alcohol at room temperature; the endpoint of the reaction became evident from the disappearance of the spot of the starting material

on a thin layer chromatogram (after about 2 days). N-Ethoxycarbonyl-4-oxo-1,2,3,4-tetrahydropyridine (**8**) was obtained pure after chromatography in about 70% yield. The reduction proceeded as well in DMF and THF as solvents; in ethanol a reaction took place only after heating and with poor yield (22%), no reaction was observable in ether or without a solvent. The presence of ethyl chloroformate in this reaction was essential; with sodium borohydride alone in *t*-butyl alcohol N-ethoxycarbonyl-4-pyridone (**7**) decomposed to give 4-pyridone (**1**).

Under mild conditions – diluted KOH in aqueous methanol at pH 12- the N-ethoxycarbonyl-4-oxo-1,2,3,4-tetrahydropyridine was rapidly saponified to give 4-oxo-1,2,3,4-tetrahydropyridine (**4**); the oily product was purified by chromatography on silicagel with methylene chloride/methanol 3:1 (Rf 0.4).

b) *Structures.* The structure of the N-ethoxycarbonyl-4-pyridone (**7**) could principally be assigned by comparison of its NMR.-spectrum with that of known N-acetyl-4-pyridone (**5**), as described by *Fleming* & *Philippides* [8]: the NMR.-spectrum in $CDCl_3$ shows two doublets centered at 8.15 and 6.35 ppm (8 Hz) characteristic of the A_2X_2-system of the protons at C(3) and C(5) respectively at C(2) and C(6), in addition to the proton signals of the ethoxy group (1.46/*t* and 4.53/*q*). N-Ethoxycarbonyl-4-pyridone (**7**) is stable in that solvent whereas N-acetyl-4-pyridone (**5**) tautomerises rapidly to an equilibrium with 4-acetoxy-pyridine (**6**), as reported to happen slowlier in methylene chloride [8]. Some doubt on the structure arose from the UV.-spectrum: both the N-acetyl- and the N-ethoxycarbonyl-4-pyridone have in their UV.-spectra a triplet like fine structure which reminds rather of the spectrum of pyridine derivatives[1]). The IR.-spectrum used as criterium by *Fleming et al.* [8] could not help further in our case[2]). We gained conclusive evidence only from a comparison of ^{13}C-NMR.-spectra.

The ^{13}C-NMR.-spectrum of a fresh solution of N-acetyl-4-pyridone (**5**) in deuteriomethylene chloride shows the signal of C(4) at 182.6 beside those of C(2) + C(6) at 136.6 and of C(3) + C(5) at 120.9 ppm.; in the equilibrated mixture the new signals of the 4-acetoxy-pyridine (**6**) showed up at 141.7 (C(2) + C(6)), 119.6 (C(3) + C(5)) and 153.7 (C(4)) ppm. (The shifts of the acetyl carbon atoms 170.0 resp. 170.4 were of no diagnostic value). The corresponding signals in deuteriochloroform were found to be shifted upfield by 3 ppm (*N-acetyl-4-pyridone*. C(4): 179.6; C(2) + C(6): 133.6; C(3) + C(5): 118.1. - *4-acetoxy-pyridine* C(4): 150.7, C(2) + C(6): 138.4, C(3) + C(5): 116.5). The resonance spectrum of N-ethoxycarbonyl-4-pyridine **7** in deuteriochloroform unequivocally shows the presence of the C(4)-carbonyl at 179.5 beside those of the other ring carbons C(2) + C(6) at 134.2 and C(3) + C(5) at 118.0.

Our reduction product **8** is characterised by NMR.-spectroscopy: Apart from the presence of the multiplets characteristic for the ethoxy group two doublets (8 Hz) at

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[1]) UV. (CH_2Cl_2) of **5**: Max 295.5 and 286, Infl. at 278; UV. ($CHCl_3$) of **6**: Max 287 and 279, Infl. at 272.
The UV.- spectrum of N-ethoxycarbonyl-4-pyridone (**7**) in methanol has the same characteristics as that in chloroform or methylene chloride. The UV.-spectrum of N-acetyl-4-pyridone (**5**) in methanol, observable only within the first minutes, changes rapidly into one maximum at 256 nm of the 4-pyridone formed by methanolysis.

[2]) *Fleming et al.* [8] reported for N-acetyl-pyridone **5** in CH_2Cl_2-solution a band at 1750 cm^{-1} and for acetoxy-pyridine **6** another at 1775 cm^{-1}. The N-ethoxycarbonyl-pyridone **8** in CH_2Cl_2 or KBr gives a band at 1765 cm^{-1}.

5.35 and 7.88 ppm represent the olefinic protons on C(5) and C(6); the methylenic protons on C(2) and C(3) appear as two triplets (7 Hz) at 4.05 (partially superimposed with the quartet of the methylene protons in the ethoxy group) and at 2.56 ppm. In the IR.-spectrum (KBr) the band 1725 may be attributed to the ester carbonyl vibration, those at 1670 and 1602 to the unsaturated ketone function. The mass-spectrum confirms the molecular weight with the mass peak 169 (as parent peak); other fragment peaks arise from loss of ethyl, ethoxycarbonyl and HCN. Its UV.-spectrum in methanol shows only one maximum at 286.5 (ε = 16500).

The spectral data of the 4-oxo-1,2,3,4-tetrahydropyridine (**4**) agree well with those of known substituted derivatives; this concerns notably its UV.-spectrum in methanol with a maximum at 313 nm (18400) [1] [2] [5] and the IR.-spectrum showing the bands assigned for vinylogous amides AV-I 1620 and AV-II 1570–80 [9]. The NMR.-spectrum ($CDCl_3$) shows the olefinic protons on C(5) and C(6) as a doublet 4.99 (7 Hz) resp. a triplet 7.26 (7 Hz). To the methylenic protons at C(2) and C(3) correspond a double-triplet centered at 3.60 (8 and 2 Hz) and a triplet at 2.45 ppm. The NH-proton signal appears as a very broad hump, (6.0–6.6). In the ^{13}C-NMR.-spectrum, the singlets 41.6, 35.7, 192.2, 98.2 and 151.9 correspond in this order to the carbon atoms C(2) to C(6).

3. Discussion. – The specific reduction of N-alkylated 4-pyridones to their dihydro stages by hydroaluminates as reported by *Winterfeldt* [1] and *Tamura et al.* [2] corresponds to the behaviour of vinylogous amide systems. In the case of 1-(dimethylamino)-4-methyl-1-penten-3-one *Martin et al.* [10] noticed specific reduction of just the double bond on treatment with $LiAlH_4$ in ether. They interpret their result as a primary 1,4-attack of the reagent to the conjugated carbonyl system leading to an intermediary stable enolate anion; the actual end products must be liberated on contact with water during the usual workup procedure. This reasonable assumption may further be illustrated by the known 1,4-addition of *Grignard* reagents to vinylogous amides [11]. In our case of N-ethoxycarbonyl-4-oxo-1,2,3,4-tetrahydropyridine (**7**) the reduction pathway may be considered analogous to that of N-alkylpyridones. The reaction seems to proceed slowlier however; in contrast to the previous procedures we use *t*-butyl alcohol as solvent instead of ethers; the postulated intermediary enolate anion is obviously stable under theses conditions since no further reduction is observed.

The presence of acylating agent in our reaction mixture was found to be crucial otherwise cleavage of the acyl group is the result. Whereas excess sodium borohydride may reduce ester groups, though less readily than ketones [12], cleavage of heterocyclic amides are reported to occur with $LiAlH_4$ [13]. The reduction of 4-pyridone itself is blocked by formation of the corresponding salt which must be as unreactive to the reducing agent as is known to be the case with amide salts [14]. The observed cleavage reaction of 4-methoxy-pyridine (**2**) by sodium borohydride and chloroformate in methanol is not completely rationalized.

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^{13}C-NMR.-spectra were recorded by Dr. *Jean-Pierre Kintzinger* and *Claude Delseth*; MS. were taken by *H. Serra*. We wish to thank them for their indispensable aid.

Experimental Part

Melting points are observed under a microscope and corrected. Spectroscopic measurements: UV. (*Beckman* DB) Max = maximum, Infl. = inflection, Min = minimum, in nm (ε); IR. (*Beckman* IR 20 A) in cm^{-1}, strong intensities without special remark, medium = *m*, weak = *w*, br. = broad; NMR. (*Varian* A60 A and *Brucker* HX 90 FT); ^{1}H-chemical shifts in δ (ppm) referred to internal TMS/multiplicity: *s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, (coupling constants in Hz), relative number of protons (assignement); ^{13}C-chemical shifts in ppm from internal TMS (assignment); MS. (*CEC* 21–490) at 70 ev, mass peak *m/e* (intensivity in % relative to base peak = 100). Thinlayer chromatography (TLC.) on silica gel GF 254 *Merck*; column chromatography on silica gel 60 *Merck* (0.2–0.5 mm).

N-Acetyl-4-pyridone (**5**) (see [8]). The preparation of N-acetyl-4-pyridone was improved using commercial 4-pyridone purified by sublimation in high vacuum which was reacted in acetic anhydride pyridine at 35–40° for 30 min. After another 3 h at room temp. the solvent was completely removed by adiabatic distillation in a closed evacuated system of two bridged round bottom flasks leaving pure N-acetyl-pyridone, m.p. 80°. (lit 125 135°). – ^{13}C-NMR. (CD_2Cl_2): 24.4 (C-methyl); 120,9 (C(3),C(5)); 136,6 (C(2),C(6)); 170,0 (CO acetyl); 182,6 (C(4)). – ^{13}C-NMR. ($CDCl_3$): (from equilibrated mixture with 4 acetoxypyridine): 21,6 (C-methyl); 118,1 (C(3), C(5)); 133,6 (C(2), C(6)); 166,3 (CO-acetyl) 179,6 (C(4)).

4-Acetoxy-pyridine. Spectral properties observed in equilibrated mixture with N-acetyl-4-pyridone: ^{13}C-NMR. (CD_2Cl_2): 23,9 (C-methyl); 119,6 (C(3), C(5)); 141,7 (C(2), C(6)); 153,7 (C(4)); 170,4 (CO-acetyl). – ^{13}C-NMR. ($CDCl_3$): 21 (C-methyl); 116,5 (C(3), C(5)); 138,4 (C(2), C(6)); 150,7 (C(4)); 166,8 (CO-acetyl). – UV. (CH_2Cl_2): Max 295,5 (23500), 286 (24500); Infl. 278 (18600); Min 291 (17600). – UV. ($CHCl_3$): Max 294, 284; Infl. 277; Min 290. – UV. (CH_3OH): Max 256 (21200).

N-Ethoxycarbonyl-4-pyridone (**7**). 0.5 g of NaH (20 mmol) ground in a mortar are added at once to a stirred solution of 1,44 g of 4-pyridone (15.2 mmol, sublimated commercial product) in 10 ml of *t*-butyl alkohol which is then heated to 50° on a water bath. Ethyl chloroformate 2 ml (20 mmol) is added dropwise; the heating bath is allowed to return to room temperature. After 1½ h 25 ml H_2O are added; the pH value of the resulting solution 8.5 was immediately adjusted to 6.9 with a few drops of 2% HCl. Repeated extraction with ether (a total 180 ml) followed by usual drying procedure gave 1,62 g of solid product; m.p. 85° (yield, 64%), Rf 0.4 (methylene chloride/MeOH 19:1). – UV. ($CHCl_3$): Max 272 (11400), 279 (14780), 287 (13150); Min 249 (2520), 273 (14370), 283,5 (8300). – UV. (CH_3OH): Infl. 270 (16040); Max 275,5 (18400), 283 (16000); Min. 231 (570), 280 (12800). – IR. (KBr): 1765, 1640–60, 1598, 1470, 1465 *m* infl., 1450 *m* infl., 1398 *m*, 1372, 1347, 1270–1300, 1180–1190, 1147 *m*, 1100, 1118, 1000, 975 infl., 960, 811 *m*, 770, 725 *m*, 620, 459, 325. – IR. (CH_2Cl_2): 1765, 1650–60, 1608, 1370, 1342 *m*, 1250–80, 1180, 1140 *w*, 1095 *m*, 1010 *m*, 995 *m*, 870 *m*, 850, 612 *m*. – ^{1}H-NMR. ($CDCl_3$): 1.46/*t* (J = 7), 3 H (CH_3-ethyl); 4.53/*q* (J = 7), 2 H (CH_2O); 6,35/*d* (J = 8) part of A_2X_2, 2 H (H—C(3), H—C(5)); 8.15/*d* (J = 8) part of A_2X_2, 2 H (H—C(2), H—C(6)). – ^{13}C-NMR. ($CDCl_3$): 14.0 (CH_3); 65.5 (CH_2O); 118.0 C(3), C(5); 134.2 (C(2), C(6)); 149.1 (C ethoxycarbonyl); 179.5 (C(4)). – MS.: 167 (14.2), 122 (2.5), 108 (2.8), 95 (18.5), 80 (9.9), 67 (76), 53 (5.9), 39 (27.8), 29 (100).

N-Ethoxycarbonyl-4-oxo-1,2,3,4-tetrahydropyridine (**8**). N-Ethoxycarbonyl-4-pyridone (0.85 g, 0.005 mol), sodium borohydride (1 g, 0.05 mol), ethyl chloroformate (5.42 g, 0.05 mol) and *t*-butyl alkohol (5.2 g) are stirred for 2 days at room temp. (25°) until the UV.-spectrum of a probe diluted in methanol no longer shows the caracteristic fine structure of the starting material. Addition of water (10 ml) followed by ether extraction gives 0,71 g of slightly yellow oil. By TLC. (CH_2Cl_2/MeOH 19:1) only one migrating spot Rf 0.74 is seen in the UV.; another spot remains on the starting point. The product is chromatographed on a column of silica gel (130 g) with CH_2Cl_2/MeOH 19:1; the slightly yellow band contains 0.59 g of N-ethoxycarbonyl-4-oxo-1,2,3,4-tetrahydropyridine, Rf 0.74, (yield 70%). – UV. (MeOH): Max 286.5 (16500); Min 230 (1800). – IR. (film): 2950, 2920, 2850, 1725, 1670, 1602, 1465 *m*, 1425 *m*, 1400 *m*, 1379, 1340, 1322, 1300, 1214, 1182, 1105 *m*, 1022 *m*, 810 *m*, 766 *m*, 730 *m*. – ^{1}H-NMR. ($CDCl_3$): 1.35/*t* (J = 7), 3 H (CH_3-ethyl); 2.56/*t* (J = 7) 2 H (H—C(3)); 4,05/*t* (J = 7), 2 H (H—C(2)); 4.33/*q* (J = 7), 2 H (CH_2-ethyl); 5.35/*d* (J = 8), 1 H (H—C(5)); 7,88/*d* (J = 8) 1 H (H—C(6)). – MS.: 169 (Mol peak) (100), 96 (57), 82 (50), 69 (91), 41 (37), 29 (96).

In another preparation no ethyl chloroformate was added. After stirring 167 mg of **7**, 38 mg $NaBH_4$ in 4 ml *t*-butyl alkohol for 2 h a diluted specimen of the solution in methanol showed only one absorption max. at 256 nm and the TLC. revealed just one spot corresponding to 4-pyridone.

4-Oxo-1,2,3,4-tetrahydropyridine (**4**). To 117 mg (0.69 mmol) of N-ethoxycarbonyl-4-oxo-1,2,3,4-tetrahydropyridine in 8 ml methanol are added 4 aliquots of 0.2 ml each of a solution of 0.5 g KOH in 4.5 ml 90% methanol (2.1N). Progress of hydrolysis was controlled 5 min. after each addition by UV.-spectrum in methanol and by TLC. of a spot test on silica gel with methylene chloride/methanol 3:1.; whereas in the spectrum gradual shift of the maximum was noticed from 287 to 313 nm, chromatography clearly indicated product formation (Rf 0.4) and disappearance of starting material (Rf 0.8). The final solution was evaporated and the product dissolved in methylene chloride/methanol 3:1 was passed on a column of 18 g silica gel. The 5 ml fractions containing compound with Rf 0.4 gave a total of 62 mg (0.64 mmol) of oily dihydro-4-pyridone (yield 92%). – UV. (MeOH): Max 313 (18400). – IR. (film): 3440 (shoulder), 3220 3260, 3040, 2840 *m*, 1700 *w* br., 1620, 1570–1580, 1535, 1455 *m*, 1410, 1355, 1320, 1285, 1250, 1180, 1102 *w*, 1055 *w*, 1020, 905 *w*, 800, 755 *m*, 660 *m* br., 620. – ^{1}H-NMR. ($CDCl_3$): 2.45/*t* (J = 8), 2 H (H—C(3)); 3.60/*d* × *t* (J – 8; J – 2), 2 H (H—C(2)); 4.99/*d* (J = 7), 1 H (H—C(5)); 7.26/*t* (J = 7), 1 H (H—C(6)); 6.0–6.6/br. *s*, 1 H (NH). – ^{13}C-NMR. ($CDCl_3$): 35.7 (C(3)); 41.6 (C(2)); 98.2 (C(5)); 151.9 (C(6)); 192.2 (C(4)).

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