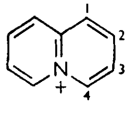
623. *Synthesis and Properties of Dehydropyridocolinium Salts.*

By A. Richards and T. S. Stevens.

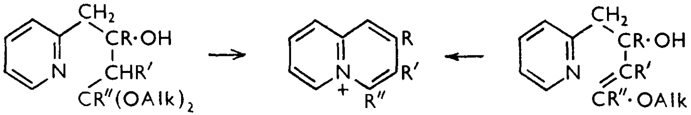
Several dehydropyridocolinium salts (I) have been prepared by treating the enol ether or the monoacetal of a β-diketone with 2-picolyl-lithium and cyclising the resulting alcohol with acid. Their reactions, especially with anionoid reagents, have been examined.

Replacement by nitrogen of a carbon atom common to both rings of the naphthalene system gives the dehydropyridocolinium ion (I). Salts of this cation were first prepared by Boekelheide and Gall[1] in moderate yield; we have now prepared homologues by a more effective process[2] and studied some of their reactions. The synthetic method was essentially an adaptation of that employed by McLamore and Woodward[3] for the synthesis of sempervirine metho-salts. A β-oxo-aldehyde or -ketone is converted into the mono-acetal and/or the enol ether and this treated with picolyl-lithium; the product, usually of low stability and often an unresolved mixture, is cyclised by alcoholic picric acid:

$$\text{R·CO·CHR'·COR''} \begin{cases} \xrightarrow{\text{MeOH-HCl}} \text{R·CO·CHR'·CR''(OAlk)}_2 \text{ (II}a\text{)} \longrightarrow \text{(III}a\text{)} \\ \xrightarrow{\text{H·C(OEt)}_3\text{-FeCl}_3} \text{R·CO·CR'{:}CR''·OAlk (II}b\text{)} \longrightarrow \text{(III}b\text{)} \end{cases}$$



(I)



(IIIa) (IIIb)

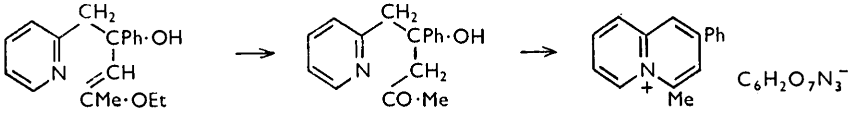
---

[1] Boekelheide and Gall, *J. Amer. Chem. Soc.*, 1954, **76**, 1832; Boekelheide and Ross, *ibid.*, 1955, **77**, 5691.

[2] Preliminary communication, *Chem. and Ind.*, 1954, 905.

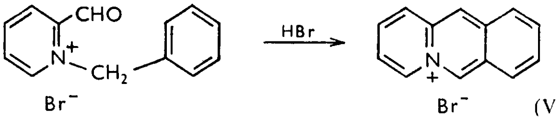
[3] McLamore and Woodward, *J. Amer. Chem. Soc.*, 1949, **71**, 349.

The dehydropyridocolinium salts, assembled in Table 2, are all substituted in position 2, owing to more difficult accessibility of initial materials for those unsubstituted in this position. The method failed in the case (9) of 3-methyl-2-phenyldehydropyridocolinium salts. In case (8) the product of attempted cyclisation with picric acid gave analyses correct for the picrate of the ketone (IV), indicating simple hydrolysis of the enol ether. When refluxed with acetic anhydride and sulphuric acid this product yielded the quaternary picrate (V).



(IV) (V)

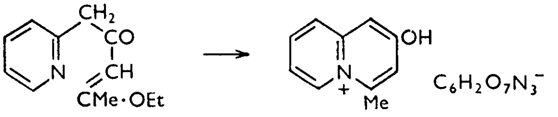
Bradsher and Beavers[4] prepared 2 : 3-benzodehydropyridocolinium **bromide** by dehydrating pyridine-2-aldehyde benzylobromide:



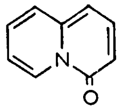
(VI)

A similar dehydration of the corresponding allylobromide would give an unsubstituted dehydropyridocolinium salt, but we failed to effect this with hydrobromic, sulphuric, or polyphosphoric acid.

In an attempt to prepare a dehydropyridocolinium salt unsubstituted in position 2 by a modified method, ethyl β-ethoxycrotonate was treated with picolyl-lithium, giving (VII). Numerous attempts to reduce the carbonyl group of this compound failed, as did experiments on the simpler 2-acetonylpyridine. With picric acid, the ketone (VII) itself gave an unstable product having the composition of 2-hydroxy-4-methyldehydropyridicolinium picrate (VIII).



(VII) (VIII)



(IX)

When the methiodide of pyridine, quinoline, or acridine is treated with silver oxide in water, the quaternary hydroxide reaches equilibrium with the pseudo-base; the ammonium hydroxide predominates in the first case, the pseudo-base in the last. The loss in resonance energy consequent on dearomatisation of a pyridine ring diminishes in the order given, and the pseudo-base further tends, with rising molecular weight, to separate from aqueous solution or to pass into organic solvents. Formation of a pseudo-base from dehydropyridocolinium hydroxide would destroy the aromaticity of both rings, and there was no indication of its production when the iodide in aqueous solution was treated with silver oxide or warmed with 10N-sodium hydroxide. The iodide did, however, reduce alkaline ferricyanide, giving a small amount of material doubtfully identifiable as (IX);[5] this may be regarded as evidence for the presence of at least a trace of pseudo-base in equilibrium with the ammonium hydroxide. Likewise there was no evidence of the formation of a pseudo-cyanide when dehydropyridocolinium iodide was treated with potassium cyanide solution. With *n*-butylmagnesium bromide dehydropyridocolinium iodide gave only a small amount of unstable brown oil; the metho-salts of quinoline and

---

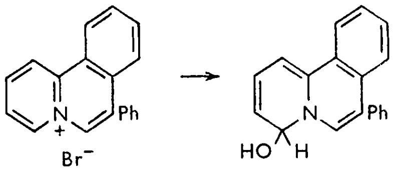
[4] Bradsher and Beavers, *J. Amer. Chem. Soc.*, 1955, **77**, 4812.

[5] Boekelheide and Lodge, *ibid.*, 1951, **73**, 3681.

acridine, but not those of pyridine, readily afford *C*-alkyl-*N*-methyl-dihydro-bases with Grignard reagents.

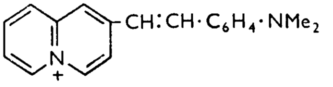
In the case of 3-phenyl-1 : 2-benzodehydropyridocolinium bromide [6] (X), slightly more favourable to production of a pseudo-base, the ammonium hydroxide solution deposited an amorphous benzene-soluble product after 2 days. The compound (X) reduced alkaline ferricyanide, but gave no pseudo-cyanide with sodium cyanide. On the other hand 2 : 3-benzodehydropyridocolinium iodide (as VI) quickly afforded an unstable pseudo-base which was soon oxidised in air, and with sodium cyanide it gave an amorphous product, apparently the pseudo-cyanide. The iodide also reduced alkaline ferricyanide. Unsuccessful attempts were made to induce the pseudo-base to condense, in the same way as berberine, with nitromethane and other " reactive methylene compounds."

1 : 2-Dimethylquinolinium salts, on treatment with alkali, give 1 : 2-dihydro-1-methyl-2-methylenequinolines, but neither 2-methyl-, 2-ethyl-3-methyl-, nor 2 : 3-dimethyl-dehydropyridocolinium salts behaved in this way, and in other respects they resembled the unsubstituted compound in their behaviour towards anionoid reagents. The methyl group of the 2-methyl compound showed however the reactivity of a 4-methyl substituent in a pyridine ring in condensing with *p*-dimethylaminobenzaldehyde and with *NN*-dimethyl-*p*-nitrosoaniline, giving compounds (XI) and (XII) respectively. These highly coloured products were decolorised reversibly by dilute acids, owing no doubt to exclusion by protonation of the second nitrogen atom from the conjugated system.

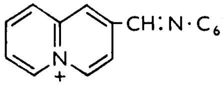


(X)

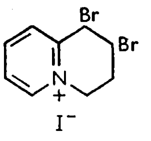
All the dehydropyridocolinium ions studied gave orange, crystalline dibromoiodides, $[B]^+[IBr_2]^-$, when the iodides were treated with bromine in acetic acid. The bright orange compound which Boekelheide and Ross [1] obtained by treating 3 : 4-dihydrodehydropyridocolinium iodide with bromine and formulated as (XIII) closely resembles the original salt in its ultraviolet absorption, and is no doubt in fact the related dibromoiodide (XIV; $X = IBr_2$). The 3-methylene group in this would be expected to be reactive, and condensation with nitrosodimethylaniline was effected, giving the red-brown anil (XV).



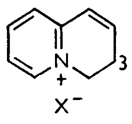
I$^-$ (XI)



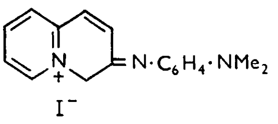
I$^-$ (XII)



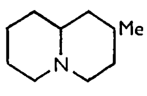
(XIII)



(XIV)



(XV)



(XVI)

Reduction of the dehydropyridocolinium and the 2-ethyl-3-methyldehydropyridocolinium ions with lithium aluminium hydride gave no definable product, but 2-methyldehydropyridocolinium iodide was hydrogenated over platinum oxide to octahydro-2-methylpyridocoline (XVI).

---

[6] Bradsher and Beavers, *J. Amer. Chem. Soc.*, 1955, **77**, 453.

EXPERIMENTAL

Difficulty was encountered in the analysis of many of the compounds described, which had often to be mixed with copper oxide to effect complete combustion.

4-*Methyl*-3-*oxovaleraldehyde* (*Case* 2).—A mixture of methyl *iso*propyl ketone (1 mol.) and ethyl formate (1 mol.) was added slowly to sodium wire (1 atom) under ether at 0°. After 48 hr. the pale yellow sodium salt was collected and the liberated *oxo-aldehyde* dried in ether (Na_2SO_4) and distilled. The unstable liquid, b. p. 54°/20 mm., gave a deep violet colour with ferric chloride (Found: C, 63·0; H, 7·9. $C_6H_{10}O_2$ requires C, 63·2; H, 8·8%).

Reactions with Ethyl Orthoformate.[12]—*Case* 1. Sodio-formylacetophenone (24 g.) was decomposed with acid and the free oxo-aldehyde, dried in ether (Na_2SO_4 and a little K_2CO_3), was used without further purification; ethyl orthoformate (20 g.), ethanol (20 ml.), and ferric chloride (0·5 g.) were added to the residue from evaporation of the ethereal solution, and the mixture was boiled for 10 min. The cooled solution was poured into cold aqueous sodium hydroxide and shaken with ether without delay; the ether layer was washed with alkali until a neutralised portion of the washings gave no colour with ferric chloride, washed with water, dried (Na_2SO_4), and distilled. The product (6·8 g.), b. p. 110—114°/0·04 mm., was probably a mixture of ethoxymethyleneacetophenone and formylacetophenone diethyl acetal (Found: C, 72·1; H, 7·4. Calc. for $C_{11}H_{12}O_2$: C, 75·0; H, 6·8. Calc. for $C_{13}H_{18}O_3$: C, 70·3; H, 8·1%). It decolorised bromine in carbon tetrachloride, afforded no dimedone derivative, and with alcoholic ferric chloride gave a colour only after some time. The same method was used in other cases (see Table 1), except nos. 1 and 8.

TABLE 1. *Initial and intermediate compounds.*

Case	Dicarbonyl compound	Intermediate (II)	B. p./mm.	Intermediate (III), b. p./mm.
1	Me·CO·CH_2·CHO	Acetal [7]	—	see exptl. part
2	Me_2CH·CO·CH_2·CHO	Mixture	90—112°/40	114—120°/0·5
3	Me_3C·CO·CH_2·CHO [8]	Mixture	92—96°/10	100—108°/0·05
4	Ph·CO·CH_2·CHO	Mixture	100—114°/0·04	*a*
5	Me·CO·CHMe·CHO [9]	Mixture	90—98°/10	100—112°/0·02
6	Me·CO·CH_2·COMe	Enol ether	74—78°/30 [b]	108—116°/0·5
7	Et·CO·CHMe·CHO	Mixture	92—96°/10	128—134°/0·2
8	Ph·CO·CH_2·COMe	Enol ether [10]	—	M. p. 78° [c]
9	Ph·CO·CHMe·CHO [11]	Mixture	100—106°/0·05	M. p. 62—63° [d]

[a] Could not be distilled; pale yellow after passage through alumina column. [b] Lit., b. p. 69—70°/10 mm. [c] Lemon-yellow needles of 4-*ethoxy*-2-*phenyl*-1-2′-*pyridylpent*-3-*en*-2-*ol* (Found: C, 76·3; H, 7·6; N, 4·8. $C_{18}H_{21}O_2N$ requires C, 76·3; H, 7·4; N, 4·9%). [d] Colourless needles of 4-*ethoxy*-3-*methyl*-2-*phenyl*-1-2′-*pyridylbut*-3-*en*-2-*ol* (Found: C, 76·7; H, 7·4; N, 4·9%).

Reactions with Picolyl-lithium.—*Case* 1. 4 : 4-Dimethoxybutan-2-one (25 g.) in ether (50 ml.) was added at 0° with stirring to ethereal 2-picolyl-lithium [13] from lithium (3 g.), bromobenzene (32 g.), and picoline (19 g.). After 1 hour's stirring at room temperature, ice was added and the organic material extracted with ether and dried (Na_2SO_4). Distillation afforded a golden-yellow oil (13·5 g.), b. p. 110—115°/0·2 mm., which darkened quickly in air. The diethyl acetal (4 g.) gave similarly a product (3·1 g.), b. p. 112—116°/0·15 mm. In the other cases a larger excess of picolyl-lithium was used, with otherwise the same procedure.

Ring-closure to Dehydropyridocolinium Salts.—The product (III) was boiled for a few minutes with ethanolic picric acid; in cases 1—7 (see Table 2) the dehydropyridocolinium picrate separated in good yield at once or on cooling, and crystallised from ethanol in yellow needles. In case 8 the product so obtained, m. p. 154°, appeared to be 4-*oxo*-2-*phenyl*-1-2′-*picolylpentan*-2-*ol picrate* (IV) (Found: C, 54·6; H, 4·2; N, 12·1. $C_{22}H_{20}O_9N_4$ requires C, 54·6; H, 4·2; N, 11·6%); since it lost no weight at 78°/0·5 mm. in 6 hr., it was not a solvate. The picrate was refluxed for 10 min. with acetic anhydride containing a drop of sulphuric acid and poured into

---

[7] Royals and Brannock, *J. Amer. Chem. Soc.*, 1953, **75**, 2050.

[8] Couturier and Vignon, *Compt. rend.*, 1905, **140**, 1695.

[9] Benary, Meyer, and Charisius, *Ber.*, 1926, **59**, 108, 600.

[10] Claisen, *Ber.*, 1926, **59**, 144.

[11] Claisen and Meyerowitz, *Ber.*, 1889, **22**, 3277.

[12] Claisen, *Ber.*, 1907, **40**, 3903.

[13] Walter, *Org. Synth.*, 1943, **23**, 83.

water, the picrate (V) being obtained which, recrystallised from methanol, had the composition and properties recorded in Table 2.

Dehydropyridocolinium iodides were prepared by warming the same precursors with hydriodic acid (freshly distilled from red phosphorus); the solution was evaporated to dryness in a vacuum, the residue dissolved in hot ethanol and treated with sulphur dioxide to remove free iodine, and the solid which separated on cooling was crystallised from ethanol. 2-Methyldehydropyridocolinium iodide, pale yellow needles, had m. p. 136—138°, and with picric acid yielded the picrate identical with that prepared directly. 2 : 3-*Dimethyldehydropyridocolinium iodide*, colourless plates, melted at 222—224° (dec.) (Found: N, 4·9. $C_{11}H_{12}NI$ requires N, 4·9%), and 2-*ethyl*-3-*methyldehydropyridocolinium iodide*, colourless needles, at 186—187° (Found: C, 48·6; H, 4·7; N, 4·5. $C_{12}H_{14}NI$ requires C, 48·2; H, 4·7; N, 4·7%).

TABLE 2. *Dehydropyridocolinium picrates.*

	Substituents					Found (%)			Required (%)		
Case	2	3	4	M. p.	Formula	C	H	N	C	H	N
1	Me	—	—	161°	$C_{16}H_{12}O_7N_4$	51·8	3·7	14·8	51·6	3·3	15·1
2	Pr^{i}	—	—	156—167	$C_{18}H_{16}O_7N_4$	—	—	13·9	—	—	14·0
3	Bu^{t}	—	—	184	$C_{19}H_{18}O_7N_4$	54·8	4·3	13·6	55·1	4·3	13·5
4	Ph	—	—	171	$C_{21}H_{14}O_7N_4$	57·6	3·7	12·8	57·9	3·2	12·9
5	Me	Me	—	216 dec.	$C_{17}H_{14}O_7N_4$	52·7	3·9	14·3	52·9	3·6	14·5
6	Me	—	Me	150—151	,,	52·9	3·9	14·5	,,	,,	,,
7	Et	Me	—	189·5	$C_{18}H_{16}O_7N_4$	53·7	4·2	14·2	54·0	4·0	14·0
8	Ph	—	Me	226 dec.	$C_{22}H_{16}O_7N_4$	58·8	3·8	12·9	58·9	3·6	12·5

In case 9, no dehydropyridocolinium salt could be obtained by treatment either with ethanolic picric acid or with mineral acid.

Pyridine-2-*aldehyde Allylobromide.*—Pyridine-2-aldehyde (2·2 g.) and allyl bromide (2·4 g.) were mixed and kept at room temperature for 4 weeks. The viscous, hygroscopic gum, which contained ionic bromine, slowly resinified when refluxed with 45% hydrobromic acid, rapidly with 50% sulphuric acid. Treatment with polyphosphoric acid at 100—120° for 12 hr. yielded, after dilution and neutralisation, only a little gummy picrate.

2-*Hydroxy*-4-*methyldehydropyridocolinium Picrate.*—Ethereal picolyl-lithium, prepared from lithium (1 g.), bromobenzene (12 g.), and 2-picoline (7 g.), was added to ethyl β-ethoxycrotonate [14] in ether so as to maintain gentle refluxing. 4-Ethoxy-1-2′-pyridylpent-3-en-2-one (VII), isolated as usual, was a dark oil, b. p. 126—132°/0·1 mm.; the *methiodide* had m. p. 126° after crystallisation from ethanol–ether (Found: C, 44·8; H, 5·3; N, 4·0; I, 36·5. $C_{13}H_{18}O_2NI$ requires C, 44·9; H, 5·2; N, 4·0; I, 36·6%). The base (VII) showed strong absorption bands at 1050—1060, 1111, and 1665 cm.$^{-1}$, in agreement with the assigned structure; the methiodide absorbed strongly at the first two frequencies, and also at 1630, 1658, and 3395 cm.$^{-1}$, suggesting enolisation of the ketomethylene system. With alcoholic picric acid, the base (VII) yielded a picrate, m. p. 136°, which gave a black gum on attempted recrystallisation; it appeared to be 2-*hydroxy*-4-*methyldehydropyridocolinium picrate* (VIII) (Found: C, 49·4; H, 3·5; N, 14·2. $C_{16}H_{12}O_8N_4$ requires C, 49·5; H, 3·1; N, 14·4%). Attempted reduction of the base (VII) by lithium aluminium hydride in ether, by aluminium *iso*propoxide in propan-2-ol–toluene, and by aluminium amalgam in moist ether, all gave unchanged ketone recognised as the picrate (VIII). Similar treatment left 2-acetonylpyridine [15] unchanged.

Reactions with Alkali.—Dehydropyridocolinium iodide was shaken with water and silver oxide for 15 min. No benzene-soluble material was obtained; the aqueous solution, which had pH 10, contained no iodide ions, precipitated silver oxide from silver nitrate solution, and with picric acid gave dehydropyridocolinium picrate. A concentrated aqueous solution of the same iodide gave no benzene-soluble product when warmed with excess of 10N-sodium hydroxide.

An aqueous solution of 3-phenyl-1 : 2-benzodehydropyridocolinium bromide, treated with silver oxide, gave no benzene-soluble material at once. The strongly alkaline aqueous filtrate (pH >10) yielded phenylbenzodehydropyridocolinium picrate with picric acid; when a portion was kept for 2 days, the solution, now neutral, had deposited brown, amorphous, benzene-soluble matter.

---

[14] Michael and Carlson, *J. Amer. Chem. Soc.*, 1935, **57**, 159.

[15] Beets, *Rec. Trav. chim.*, 1944, **63**, 120.

Addition of saturated potassium iodide solution to a hot aqueous solution of 2 : 3-benzodehydropyridocolinium bromide yielded the crystalline iodide. This, dissolved in water, was shaken with silver oxide under nitrogen for 15 min. and the undissolved organic material extracted with benzene, giving a neutral, halogen-free aqueous solution. The orange benzene extract, which darkened rapidly in air, yielded with picric acid benzodehydropyridocolinium picrate. An aqueous solution of the iodide gave with sodium hydroxide solution an orange precipitate, m. p. 80—83° after shrinking at 70°, which did not crystallise and with picric acid gave benzodehydropyridocolinium picrate.

Benzodehydropyridocolinium iodide (330 mg.) was mixed with nitromethane (100 mg.) and potassium hydroxide (150 mg.) in methanol, and the orange solution kept overnight. No condensation product could be isolated at this stage or after 1 hour's refluxing. No condensation was observed in similar experiments with 2 : 4-dinitrotoluene, acetone, acetophenone, diethyl malonate, or ethyl acetoacetate.

Addition of potassium ferricyanide (500 mg.) and potassium hydroxide (200 mg.) in water to aqueous dehydropyridocolinium iodide (180 mg.) gave a dark solution from which benzene extracted a small quantity of water-soluble solid, m. p. 70—75°, which gave an unstable picrate, m. p. 130—140°. The aqueous solution gave Prussian blue with ferric chloride. 3-Phenyl-1 : 2-benzodehydropyridocolinium bromide also reduced ferricyanide. 2 : 3-Benzodehydropyridocolinium iodide gave similarly a white amorphous precipitate, the filtrate from which contained ferrocyanide ion. The precipitate, which decomposed in air, and in hot solvents, may have been dimeric (*M*, cryoscopic in C_6H_6, 410).

Solutions of dehydropyridocolinium or 3-phenyl-1 : 2-benzodehydropyridocolinium salts with aqueous sodium cyanide gave no pseudo-cyanide even after long storage. With 2 : 3-benzodehydropyridocolinium iodide an unstable red precipitate was obtained; this dissolved in benzene and, when warmed with picric acid, gave benzodehydropyridocolinium picrate.

2-Methyldehydropyridocolinium iodide was refluxed in ethanol with *p*-dimethylaminobenzaldehyde (slight excess) and a drop of piperidine for 4—5 hr. The red solution deposited, on cooling, 2-p-*dimethylaminostyryldehydropyridocolinium iodide* (XI), claret-coloured needles, slightly soluble in water to a yellow solution; these had m. p. 316° after crystallisation from methanol (Found: C, 56·1; H, 4·9; N, 6·9. $C_{19}H_{19}N_2I$ requires C, 56·7; H, 4·7; N, 7·0%). A similar reaction with *p*-nitrosodimethylaniline gave dark brown needles, m. p. 230—232°, of 2-*formyldehydropyridocolinium iodide* p-*dimethylaminoanil* (XII) (Found: C, 53·1; H, 4·3; N, 10·1. $C_{13}H_{18}N_3I$ requires C, 53·6; H, 4·5; N, 10·4%), slightly soluble in cold water to a cherry-red solution changed to pale yellow by hydrochloric acid.

Dibromoiodides.—The dehydropyridocolinium iodide in acetic acid was treated with a 10% solution of bromine in the same solvent, and the precipitate recrystallised from ethanol, giving the following *dibromoiodides*: *dehydropyridocolinium*, orange needles, m. p. 182—184° (Found: C, 25·9; H, 2·3; N, 3·9. $C_9H_8NIBr_2$ requires C, 25·9; H, 2·0; N, 3·4%); 2-*methyldehydropyridocolinium*, orange plates and needles, m. p. 100—101° (Found: C, 27·6; H, 2·4; N, 3·3; Hal, 66·2. $C_{10}H_{10}NIBr_2$ requires C, 27·8; H, 2·3; N, 3·2; Hal, 66·6%); 2 : 3-*dimethyldehydropyridocolinium*, pale orange needles and plates, m. p. 160° (decomp.) (Found: C, 29·5; H, 2·9; N, 3·5. $C_{11}H_{12}NIBr_2$ requires C, 29·7; H, 2·7; N, 3·1%); 2-*ethyl*-3-*methyldehydropyridocolinium*, yellow needles, m. p. 98° (Found: C, 31·8; H, 3·2; N, 3·4. $C_{12}H_{14}NIBr_2$ requires C, 31·4; H, 3·1; N, 3·1%); 2 : 3-*benzodehydropyridocolinium*, orange needles, m. p. 222—224° (Found: C, 33·5; H, 2·8; N, 3·1. $C_{13}H_{10}NIBr_2$ requires C, 33·4; H, 2·2; N, 3·0%). With iodine in ethanol, 2-ethyl-3-methyldehydropyridocolinium iodide gave the *tri-iodide*, m. p. 85° (Found: N, 2·4. $C_{12}H_{14}NI_3$ requires N, 2·5%).

3 : 4-Dihydrodehydropyridocolinium iodide gave the dibromide, m. p. 142°, as described by Boekelheide and Ross [1] for their presumed 1 : 2-dibromo-1 : 2 : 3 : 4-tetrahydropyridocolinium iodide (Found: C, 25·6; H, 2·6; N, 3·6. Calc. for $C_9H_{10}NIBr_2$: C, 25·8; H, 2·4; N, 3·4%). It showed absorption maxima at 211 (log ε 4·43) and 311 mμ (log ε 3·94), agreeing closely with the recorded figures for dihydrodehydropyridocolinium iodide and contrasting with those for tetrahydro-2-hydroxydehydropyridocolinium iodide.

3 : 4-*Dihydrodehydropyridocolinium tri-iodide*, prepared in and crystallised from ethanol, formed dark magenta plates, m. p. 133° (decomp.) (Found: C, 21·1; H, 2·2. $C_9H_{10}NI_3$ requires C, 21·1; H, 1·9%). The monoiodide (0·5 g.) was refluxed for 4 hr. in ethanol with *p*-nitrosodimethylaniline (0·3 g.) and a drop of piperidine. On concentration and cooling, the red solution deposited 3-p-*dimethylaminophenylimino*-3 : 4-*dihydrodehydropyridocolinium iodide*, red-brown

needles, m. p. 224—225° (decomp.) after crystallisation from ethanol (Found: C, 52·6; H, 4·9; N, 10·2. $C_{17}H_{18}N_3I$ requires C, 52·2; H, 4·6; N, 10·7%). The anil dissolved sparingly in water to a yellow solution, readily in acids to a colourless solution turned yellow by alkali.

Hydrogenation of Dehydropyridocolinium Iodide.—The iodide (140 mg.) in methanol rapidly absorbed 5 mols. of hydrogen over Adams catalyst (50 mg.). The product afforded a yellow picrate, needles (from ethanol), m. p. 150—151° (Found: C, 50·25; H, 5·8; N, 14·5. Calc. for $C_{16}H_{21}O_7N_4$: C, 50·4; H, 5·5; N, 14·7%). Clemo and Metcalfe [16] give 158° as the m. p. of octahydro-2-methylpyridocoline picrate prepared otherwise; the two products may differ stereochemically.

We thank the Department of Scientific and Industrial Research for a Maintenance Allowance (to A. R.).

THE UNIVERSITY, SHEFFIELD, 10.

[*Received, April* 18*th*, 1958.]

---

[16] Clemo and Metcalfe, *J.*, 1937, 1518.