334. *Quinolizines. Part III.*[1] *The Synthesis of* 1-*Alkyl- and* 1-*Aryl-quinolizinium Salts.*

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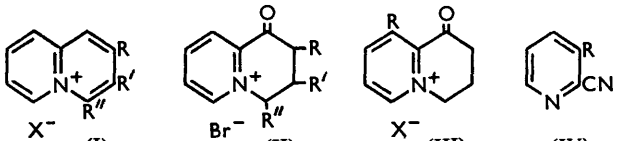
Some γ-2′-pyridylbutyraldehyde diethyl acetals have been prepared. With boiling hydrobromic acid they give, in most cases, 1,2-dihydroquinolizinium derivatives, and thence the quinolizinium salts. 1-Methylquinolizinium picrate has also been obtained by a modification of a previous quinolizinium synthesis.[2]

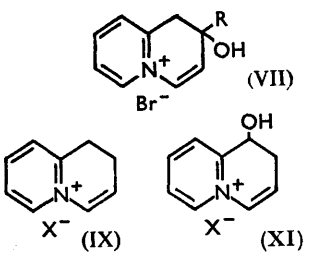
We have reported [1] the preparation of quinolizinium salts (I) bearing alkyl or aryl groups in the 2-, 3-, or 4-position, by the action of boiling acetic anhydride on ketones of type (II). Although this method represents a possible route to 1-substituted quinolizinium salts (XVII), the precursor (III) would have to be prepared from a 3-substituted 2-cyanopyridine (IV) and such compounds are difficult to prepare in quantity. In the present paper we report attempts to find a more convenient route to 1-alkyl- and 1-aryl-quinolizinium salts (XVII).



(I) (II) (III) (IV)

By preparing hydroxy-acetals of type (V) we hoped to obtain, after cyclisation with acid and dehydration of the cyclised alcohol, 1-substituted quinolizinium salts (cf. V ⟶ XVI ⟶ XVII). When our preliminary experiments were complete Nesmeyanov and Rybinskaia reported [3] the preparation of hydroxy-acetals of type (VI; R = Me, Pr^n, or Ph), which were cyclised in boiling hydrobromic acid to the hydroxy-compound (VII) and these were dehydrated to give 2-substituted quinolizinium salts (I; R = Me, Pr^n, or Ph, R′ = R″ = H).

(V) 2-C_5H_4N·CR(OH)·$[CH_2]_2$·$CH(OEt)_2$
(VI) 2-C_5H_4N·CH_2·CR(OH)·CH_2·$CH(OEt)_2$
(VIII) 2-C_5H_4N·$[CH_2]_3$·$CH(OEt)_2$
(X) R·$[CH_2]_2$·$CH(OEt)_2$



(VII) (IX) (XI)

First we treated γ-2′-pyridylbutyraldehyde diethyl acetal [4] (VIII) with boiling concentrated hydrobromic acid for 3 hr., but could not isolate any pure material. 18 hours' reaction gave 1,2-dihydroquinolizinium picrate (IX; X = picrate) but only in poor yield [the 1,2-dihydro-structure is assumed from the mode of formation and from the difference in ultraviolet absorption of the product from that of 3,4-dihydro-1-methylquinolizinium picrate (XX; X = picrate)].

Next we tried to prepare the parent quinolizinium cation by cyclisation of γ-hydroxy-γ-2′-pyridylbutyraldehyde diethyl acetal (V; R = H) with subsequent dehydration of the hydroxy-compound (XI). We obtained the acetal (V; R = H) by a novel reaction.

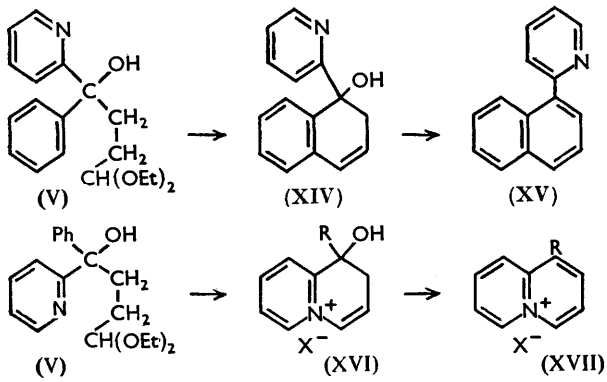
[1] Part II, Glover and Jones, *J.*, 1958, 3021.
[2] Boekelheide and Gall, *J. Amer. Chem. Soc.*, 1954, **76**, 1832.
[3] Nesmeyanov and Rybinskaia, *Doklady Akad. Nauk. S.S.S.R.*, 1957, **116**, 93.
[4] Jones and Law, *J.*, 1958, 3631.

β-Bromopropionaldehyde diethyl acetal (X; R = Br) reacted smoothly with lithium in dry ether. Adding to pyridine-2-aldehyde a solution containing an excess of this lithium reagent (X; R = Li) afforded a complex from which a 61% yield of the hydroxy-acetal (V; R = H) was obtained. However, attempts to cyclise this to the 1,2-dihydro-1-hydroxyquinolizinium salt (XI) gave only tars. In the hope that the unsaturated acetal (XII) might be more readily cyclised, the hydroxy-acetal (V; R = H) was heated with acetic anhydride; after hydrolysis of the acetic anhydride, a picrate was obtained whose analyses appear to indicate that it is the picrate of 4-acetoxy-4-2′-pyridylbutyraldehyde (XIII; R = Ac, R′ = H).

$2\text{-}C_5H_4N\cdot CH{:}CH\cdot CH_2\cdot CH(OEt)_2$ (XII)

$2\text{-}C_5H_4N\cdot CR'(OR)\cdot[CH_2]_2\cdot CHO$ (XIII)

We next prepared the hydroxy-acetal (V; R = Ph) by interaction of the lithium reagent (X; R = Li) with 2-benzoylpyridine. When this acetal was boiled with hydrobromic acid for 5 hr. it afforded much tar and a material from which two isomeric picrates were prepared. The higher-melting was identified by analysis and mixed melting point as α-2-pyridylnaphthalene picrate,[5] formed by the reactions (V) ⟶ (XIV) ⟶ (XV). The lower-melting picrate was smoothly converted into a perchlorate by anionic exchange; its ultraviolet absorption spectrum was similar to that of 2-phenylquinolizinium perchlorate,[1] therefore it is considered to be the desired 1-phenylquinolizinium picrate (XVII; R = Ph, X = picrate). In impure samples were found traces of a third picrate; this was suspected of being an intermediate, so the acetal (V; R = Ph) was then boiled with hydrobromic acid for 1·5 hr. only and then gave only the third picrate; analyses were in closest agreement with a formulation $C_{15}H_{15}O_2N$ + picrate and of the possible intermediates (XIII; R = H, R′ = Ph), (XIV), and (XVI), the first appears the most likely.



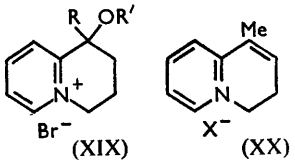
Attempts to prepare the hydroxyvaleraldehyde diethyl acetal (V; R = Me) by a similar reaction were unsuccessful. When a solution of the lithium reagent (X; R = Li) was added to a solution of 2-acetylpyridine, a complex was formed, but decomposition of this complex gave only 2-acetylpyridine. Since 2-acetyl-5-methylpyridine has been reported [6] to react normally with methylmagnesium iodide, we assume that the failure of the above reaction is due to some complex formation between the lithium ion and the 2-acetylpyridine. In confirmation of the above report we treated 2-acetylpyridine with 3-ethoxypropylmagnesium bromide or chloride: each gave a good yield of the pyridyl-alcohol (XVIII; R = Me) which was cyclised by treatment with boiling hydrobromic acid and subsequent heating of the intermediate bromo-amine in chloroform, giving the tetrahydrohydroxyquinolizinium bromide (XIX; R = Me, R′ = H). This was dehydrated to a 3,4-dihydro-1-methylquinolizinium salt (XX), and the picrate (XX;

[5] Bradsher and Beavers, *J. Amer. Chem. Soc.*, 1956, **78**, 2459.
[6] Oparin *J. Russ. Phys. Chem. Soc.*, 1929, **61**, 2011; *Chem. Abs.*, 1930, **24**, 4785.

X = picrate) was dehydrogenated by palladium–charcoal in boiling butanol to 1-methylquinolizinium picrate (XVII; R = Me, X = picrate). The perchlorate (XVII; R = Me, X = ClO_4) showed the characteristic quinolizinium absorption in the ultraviolet region. In one experiment the dehydration procedure was modified; on cooling the acetic anhydride solution crystals separated. These were shown by analysis to be the acetate (XIX; R = Me, R′ = Ac). The synthesis reported above is a modification of that used by Boekelheide and Gall in their synthesis of quinolizinium salts.[2]

Since 3-ethoxypropylmagnesium bromide reacted successfully with 2-acetylpyridine, attempts were made to prepare a Grignard reagent of type (X; R = MgX). Neither 3-bromo- nor 3-chloro-propionaldehyde diethylacetal could be made to react with magnesium in ether, but in tetrahydrofuran the chloroacetal gave the Grignard reagent smoothly. This, with 2-acetylpyridine, gave a complex from which the hydroxy-acetal (V; R = Me)

$2\text{-}C_5H_4N\cdot CR(OH)\cdot[CH_2]_3\cdot OEt$
(XVIII)



(XIX)

(XX)

was obtained in 48% yield. This acetal with boiling hydrobromic acid gave a gum from which the picrate of the cyclic alcohol (XVI; R = Me, X = picrate) was obtained. The unpurified gum [assumed to be the bromide (XVI; R = Me, X = Br)] was boiled in acetic anhydride containing a trace of sulphuric acid, affording 1-methylquinolizinium as picrate, identical with that obtained by the method reported above. The overall yield from the hydroxy-acetal (V; R = Me) was 54%, so that this sequence of reactions offers a satisfactory route to the 1-alkylquinolizinium salts.

In an attempt to prepare 1-phenylquinolizinium picrate by an unambiguous route, 2-benzoylpyridine was treated with 3-ethoxypropylmagnesium bromide, giving the phenylpyridyl-alcohol (XVIII; R = Ph). However, attempts to cyclise this compound to the hydroxyquinolizinium compound (XIX; R = Ph, R′ = H) were unsuccessful.

Experimental

M. p.s were determined on a Kofler block. Reactions with lithium reagents were performed in dry nitrogen.

1,2-Dihydroquinolizinium Picrate (IX; X = *Picrate*).—A solution of γ-2′-pyridylbutyraldehyde diethyl acetal[4] (2 g.) in 48% aqueous hydrobromic acid (25 ml.) was boiled under reflux for 18 hr. After evaporation to dryness under reduced pressure the residue was treated with water and chloroform. The aqueous layer was evaporated under reduced pressure to small volume and treated with saturated aqueous sodium picrate. The precipitated picrate and the supernatant liquor were heated on a boiling-water bath, and the clear supernatant liquor was decanted. The residual gummy picrate was treated with acetone and set aside overnight, after which filtration gave a solid yellow *picrate* (140 mg.), recrystallising from water as yellow prisms, m. p. 183° (Found: C, 50·0; H, 3·5. $C_{15}H_{12}O_7N_4$ requires C, 50·1; H, 3·4%), $\lambda_{max.}$ 3150, 3290, 3570 Å ($\log_{10}\varepsilon$ 3·94, 4·2, 4·15) in ethanol.

γ-Hydroxy-γ-2′-pyridylbutyraldehyde Diethyl Acetal (V; R = H).—The lithium reagent from β-bromopropionaldehyde diethyl acetal[7] (40 g.; freshly distilled) and lithium (2·7 g.) in anhydrous ether (200 ml.) was added slowly to a cold, stirred solution of pyridine-2-aldehyde (10 g.) in anhydrous ether (100 ml.). The mixture was subsequently stirred for 1 hr. and left overnight. The complex obtained was decomposed by water, and the ethereal layer was dried (Na_2SO_4) and distilled, giving the *acetal*, b. p. 173—176°/12 mm., 113°/0·1 mm. (13·7 g., 61%) (Found: C, 64·8; H, 8·9. $C_{13}H_{21}O_3N$ requires C, 65·2; H, 8·8%). The *acetal picrate* crystallised from absolute ethanol as needles, m. p. 116—117° (Found: C, 48·6; H, 4·7. $C_{19}H_{24}O_{10}N_4$ requires C, 48·7; H, 5·2%).

[7] Nef, *Annalen*, 1904, **335**, 363.

γ-Acetoxy-γ-2′-pyridylbutyraldehyde Picrate (XIII; R = Ac, R′ = H).—γ-Hydroxy-γ-2′-pyridylbutyraldehyde diethyl acetal (2 g.) was boiled in acetic anhydride (15 ml.) for 10 min. After addition of water the solvent was removed under reduced pressure. The residue was dissolved in the minimum quantity of 2N-hydrochloric acid, diluted, and treated with an excess of saturated aqueous sodium picrate. The *picrate* (1·7 g., 58%) crystallised from water as prisms, m. p. 130—131° (Found: C, 46·8; H, 3·6. $C_{17}H_{16}O_{10}N_4$ requires C, 46·8; H, 3·7%).

2-Benzoylpyridine.—A cooled, stirred solution of 2-cyanopyridine (20 g.) in dry ether (150 ml.) under nitrogen was treated dropwise with the Grignard reagent from bromobenzene (40 g.) in dry ether (400 ml.). The mixture was stirred for 1 hr. and left overnight. The Grignard complex was hydrolysed by ice-cold 5N-hydrochloric acid, the whole basified, and the base extracted with ether and dried (Na_2SO_4). Distillation gave 2-benzoylpyridine, b. p. 107°/0·1 mm. (30 g., 85%).

2-Acetylpyridine.—This, b. p. 84—86°/16 mm., was similarly prepared in 77% yield from 2-cyanopyridine and methylmagnesium iodide.

γ-Hydroxy-γ-phenyl-γ-2′-pyridylbutyraldehyde Diethyl Acetal (V; R = Ph).—A cooled, stirred solution of 2-benzoylpyridine (15 g.) in anhydrous ether (100 ml.) was treated dropwise with the lithium reagent from β-bromopropionaldehyde diethyl acetal [7] (40 g.) and lithium (2·7 g.) in anhydrous ether (200 ml.). Worked up as described for compound (V; R = H) the *hydroxy-acetal* was obtained as an oil, b. p. 160°/0·1 mm. (17 g., 66%) (Found: C, 72·2; H, 8·1. $C_{19}H_{25}O_3N$ requires C, 72·3; H, 8·0%).

On one occasion, under the conditions described above but with the lithium reagent added rapidly to the benzoylpyridine, the material, isolated in 80% yield, had b. p. 130—134°/0·1 mm. and solidified. Recrystallisation from light petroleum (b. p. 60—80°) gave prisms of phenyl-2-pyridylmethanol, m. p. 74° (lit.,[8] m. p. 76—78°). The picrate crystallised from absolute ethanol as prisms, m. p. 169° (lit.,[8] m. p. 169°).

1-Phenylquinolizinium Picrate (XVII; R = Ph, X = *Picrate*) *and α-2-Pyridylnaphthalene* (XV) *Picrate.*—A solution of the acetal (V; R = Ph) (3 g.) in 48% aqueous hydrobromic acid (25 ml.) was boiled under reflux for 5 hr. Evaporation to dryness under reduced pressure gave a residue which was treated with water and filtered from a black solid. The filtrate was washed with chloroform and evaporated under reduced pressure. Two methods were used to work up the residue. (*a*) The residue was dissolved in a small volume of water and treated with an excess of a saturated aqueous sodium picrate. The precipitate and the supernatant picrate solution were heated for some time at 100° and then filtered hot. From the filtrate, on cooling, crystallised *1-phenylquinolizinium picrate* (0·21 g.), needles (from absolute ethanol), m. p. 128°, rising to 160° on drying at 118°/0·1 mm. (Found: C, 58·1; H, 3·2. $C_{21}H_{14}O_7N_4$ requires C, 58·05; H, 3·25%), $\lambda_{max.}$ 2310 Å ($\log_{10}$ ε 4·4) in water. The *perchlorate*, obtained by anionic exchange on an Amberlite I.R.A.-400 column, crystallised from absolute ethanol–ethyl acetate as needles, m. p. 150—151° (Found: C, 58·5; H, 3·9. $C_{15}H_{12}O_4NCl$ requires C, 58·9; H, 4·0%), $\lambda_{max.}$ 2930, 3220, 3300 Å ($\log_{10}$ ε 3·87, 4·02, 4·13) in water.

The material undissolved by the hot sodium picrate solution was crystallised first from water and then from absolute ethanol, forming yellow needles, m. p. 194—195° (recorded [5] m. p. of α-2-pyridylnaphthalene picrate 198°) (Found: C, 58·3; H, 3·2. Calc. for $C_{21}H_{14}O_7N_4$: C, 58·05; H, 3·25%). A mixed m. p. with a synthetic sample of α-2-pyridylnaphthalene picrate showed no depression.

(*b*) If the residue was treated with alcoholic picric acid and the precipitate collected and digested with hot water as above the main product isolated was the α-2-pyridylnaphthalene picrate (0·32 g.) with a much smaller quantity of 1-phenylquinolizinium picrate (0·09 g.).

In one experiment the hydroxy-acetal (VII; R = Ph) was boiled with hydrobromic acid for a shorter time (1·5 hr.). Working up by method (*a*) gave a *picrate*, m. p. 168°, as prisms from absolute ethanol (Found: C, 52·8, 52·9; H, 3·7, 3·5. $C_{21}H_{18}O_9N_4$ requires C, 53·6; H, 3·9%).

Treatment of 2-Acetylpyridine with 3,3-Diethoxypropyl-lithium.—To a cooled, stirred solution of 2-acetylpyridine (10 g.) in anhydrous ether (100 ml.) was added dropwise the lithium reagent from β-bromopropionaldehyde diethyl acetal (40 g.). A white complex was formed and was decomposed next morning by water. After drying (Na_2SO_4) the ethereal layer was distilled: 2-acetylpyridine (6 g.) was recovered. None of the expected alcohol was obtained.

5-Ethoxy-2-2′-pyridylpentan-2-ol (XVIII; R = Me).—2-Acetylpyridine (10 g.) in anhydrous ether (50 ml.) was added under nitrogen to the stirred Grignard reagent from 3-ethoxypropyl

[8] Gilman and Spatz, *J. Org. Chem.*, 1951, **16**, 1485

bromide [10] (20 g.) in anhydrous ether (250 ml.). Stirring was continued for 1 hr. after the addition, and the mixture then left overnight. The complex was decomposed by cold 5N-hydrochloric acid, and the aqueous layer was basified and extracted with ether. The ethereal extract was dried (Na_2SO_4) and distilled, giving the *pyridylpentanol* (10·5 g., 59%), b. p. 160—162°/17 mm. (Found: C, 69·05; H, 9·3. $C_{12}H_{19}O_2N$ requires C, 68·9; H, 9·15%). The yield was similar when the Grignard reagent from 3-ethoxypropyl chloride was used, and since this can be obtained from 3-ethoxypropanol in better yield (73%) than the bromide (60%) it is the preferred reagent.

1,2,3,4-*Tetrahydro*-1-*hydroxy*-1-*methylquinolizinium Bromide* (XIX; R = Me, R′ = H).—A solution of the pentanol (XVIII; R = Me) (3 g.) in 48% aqueous hydrobromic acid (20 ml.) was boiled under reflux for 0·5 hr. The solution was evaporated to dryness under reduced pressure, the residue dissolved in water and basified by aqueous sodium carbonate, and the liberated bromo-amine was extracted by benzene. The dried (Na_2SO_4) benzene solution was boiled under reflux until a solid separated. Filtration gave the *tetrahydroquinolizinium bromide* (1·05 g., 30%) as a colourless solid, crystallising from absolute ethanol–ethyl acetate as prisms, m. p. 156° (Found: C, 49·2; H, 5·8. $C_{10}H_{14}ONBr$ requires C, 49·2; H, 5·9%), $\lambda_{max.}$ 2660 Å ($\log_{10}\varepsilon$ 3·83) in water. The *picrate* crystallised from absolute ethanol as prisms, m. p. 128° (Found: C, 49·15; H, 4·1. $C_{16}H_{16}O_8N_4$ requires C, 49·0; H, 4·1%).

1-*Acetoxy*-1,2,3,4-*tetrahydro*-1-*methylquinolizinium Bromide* (XIX; R = Me, R′ = Ac).—A solution of 1,2,3,4-tetrahydro-1-hydroxy-1-methylquinolizinium bromide (1 g.) in acetic anhydride (6 ml.) containing a drop of sulphuric acid was boiled under reflux for 10 min. The solution was cooled and the solid was filtered off. Treatment of the filtrate with ethyl acetate precipitated more solid which was filtered off and added to the initial precipitate. The combined precipitates crystallised from ethyl acetate–ethanol as prisms, m. p. 212° (0·8 g., 68%) (Found: C, 50·4; H, 5·8. $C_{12}H_{16}O_2NBr$ requires C, 50·35; H, 5·6%), $\lambda_{max.}$ 2680 Å ($\log_{10}\varepsilon$ 3·91) in water. The *picrate*, prepared by treating the solid bromide with saturated aqueous sodium picrate, crystallised from absolute alcohol as prisms, m. p. 142° (Found: C, 49·6; H, 4·2. $C_{18}H_{18}O_9N_4$ requires C, 49·8; H, 4·2%).

3,4-*Dihydro*-1-*methylquinolizinium Picrate* (XX).—A solution of the hydroxyquinolizinium bromide (XIX; R = Me, R′ = H) (1 g.) in acetic anhydride (20 ml.) containing a drop of sulphuric acid was boiled under reflux for 0·5 hr., then cooled, water was added, and the volume reduced to 3 ml. under reduced pressure. Dilution followed by addition of saturated aqueous sodium picrate gave the dihydroquinolizinium picrate, crystallising from absolute ethanol as prisms, m. p. 114—115° (0·8 g., 53%) (Found: C, 50·8; H, 3·8. $C_{16}H_{14}O_7N_4$ requires C, 51·35; H, 3·8%), $\lambda_{max.}$ 3325 Å ($\log_{10}\varepsilon$ 4·18) in 95% ethanol.

Dehydrogenation of 3,4-*Dihydro*-1-*methylquinolizinium Picrate*.—A solution of the dihydroquinolizinium picrate (0·4 g.) in butanol was boiled under reflux for 3 hr. with 5% palladium–charcoal [11] (0·4 g.). The solution was then filtered hot and cooled, 1-methylquinolizinium picrate crystallising (0·11 g., 27%). Recrystallised from absolute ethanol it had m. p. 149°, and was identical with that prepared as described below.

γ-*Hydroxy*-γ-2′-*pyridylvaleraldehyde Diethyl Acetal* (V; R = Me).—A solution of the Grignard reagent from 3-chloropropionaldehyde diethyl acetal [9] (27 g.) and magnesium (3·9 g.) in tetrahydrofuran (120 ml.) was prepared under nitrogen and stirred for 1 hr. after addition of the chloro-compound. 2-Acetylpyridine (10 g.) in tetrahydrofuran (50 ml.) was added slowly, the solution being boiled for a further 15 min. and then stirred until it had reached room temperature. The mixture was hydrolysed with an aqueous mixture of ammonia and ammonium chloride, and the aqueous layer washed with ether. The combined organic layer and ether extracts were dried (Na_2SO_4) and distilled, giving the *hydroxyvaleraldehyde diethyl acetal* (10 g., 48%), b. p. 116°/0·4 mm. (Found: C, 66·45; H, 8·9; N, 5·15. $C_{14}H_{23}O_3N$ requires C, 66·4; H, 9·15; N, 5·5%).

1-*Methylquinolizinium Picrate* (XVII; R = Me, X = *Picrate*).—A solution of the acetal (V; R = Me) (3 g.) in 48% aqueous hydrobromic acid (25 ml.) was boiled under reflux for 3 hr. Working up as described for the phenylquinolizinium compound gave an aqueous solution which on evaporation yielded a brown gum; this was treated with alcohol and evaporated to dryness, but failed to crystallise. A sample, dissolved in water and treated with saturated aqueous

[9] Witzemann, Evans, Hass, and Schroeder, *Org. Synth.*, Coll. Vol. II, p. 137.
[10] Hurd and Fowler, *J. Amer. Chem. Soc.*, 1939, **61**, 249.
[11] Schwyzer, *Helv. Chim. Acta*, 1952, **35**, 867.

sodium picrate solution, gave 1,2-*dihydro*-1-*hydroxy*-1-*methylquinolizinium picrate* (XVI; R = Me, X = picrate), crystallising from absolute alcohol as prisms, m. p. 152—153° (Found: C, 49·2; H, 3·7. $C_{16}H_{14}O_8N_4$ requires C, 49·2; H, 3·6%).

The major portion of the gum was boiled in acetic anhydride (15 ml.) containing a trace of concentrated sulphuric acid for 0·5 hr. The cooled solution was treated with ether, and the black oil which was precipitated was separated and treated with saturated aqueous sodium picrate. The solution and the precipitated picrate were heated in a boiling-water bath and filtered hot; cooling the filtrate gave 1-*methylquinolizinium picrate* which on recrystallisation from absolute ethanol formed needles (2·4 g., 54% overall yield from the acetal), m. p. 149° (Found: C, 51·5; H, 3·1. $C_{16}H_{12}O_7N_4$ requires C, 51·6; H, 3·25%) $\lambda_{max.}$ 2290, 2920, 3190, 3320 ($\log_{10}$ ε 4·54, 3·77, 4·25, 4·48) in 95% ethanol. The *perchlorate*, obtained by anionic exchange, crystallised from absolute ethanol–ethyl acetate as colourless needles, m. p. 168—169° (Found: C, 49·1; H, 4·2. $C_{10}H_{10}O_4NCl$ requires C, 49·3; H, 4·1%), $\lambda_{max.}$ 2290, 2890, 3160, 3300 Å ($\log_{10}$ ε 4·34, 3·61, 4·1, 4·29) in water.

4-*Ethoxy*-1-*phenyl*-1-2′-*pyridylbutan*-1-*ol* (XVIII; R = Ph).—A solution of 2-benzoylpyridine (10 g.) in anhydrous ether (50 ml.) was added slowly with stirring, under nitrogen, to the Grignard reagent from 3-ethoxypropyl bromide [10] (15 g.) in anhydrous ether (200 ml.). Worked up as for compound (XVIII; R = Me), the *alcohol* (11 g., 74%) had b. p. 140°/0·05 mm. (Found: C, 75·2; H, 8·1; N, 5·45. $C_{17}H_{21}O_2N$ requires C, 75·25; H, 7·8; N, 5·2%).

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