REDUCTION OF 3-SUBSTITUTED QUINOLINES WITH TRIETHYLAMMONIUM FORMATE*

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Reduction of 3-substituted quinoline derivatives, containing electron donating substituents (*Ia*—*Id*), as well as of the quaternary salts *VIb* and *VIc*, with triethylammonium formate afforded mainly the corresponding 1-formyl-1,2,3,4-tetrahydroquinolines *II* or their 1-methyl derivatives. Analogous reductions of quinoline derivatives, containing electron withdrawing groups (*e.g. Im*) gave 1,4-dihydroquinolines *IV* in addition to 1,2,3,4-tetrahydroquinoline derivatives. Quaternary salts of 3-substituted derivatives with electron withdrawing substituents (*e.g. VId*) were reduced exclusively to 1-alkyl-1,4-dihydroquinolines *IV*.

In our previous papers of this series we described reductions of the following 2-,3- and 4-substituted quinolines with triethylammonium formate: acids[1], nitriles[2], their quaternary salts[2], and acetylquinolines[3]. In the present work we describe the reductions of further quinoline derivatives with the aim to study the effect of substituent in the position 3.

To this end we reduced 3-dimethylaminoquinoline (*Ia*), 3-methoxyquinoline (*Ib*), 3-quinolinol (*Ic*), 3-bromoquinoline (*Id*) and ethyl quinoline-3-carboxylate (*Im*) with triethylammonium formate. Reduction of *Ia* afforded a mixture of 1,2,3,4-tetrahydro-3-quinolinol (*IIa*) and 1-formyl-1,2,3,4-tetrahydro-3-quinolinol (*IIc*). The same products, together with 1-formyl-1,2,3,4-tetrahydro-3-quinolyl formate (*IId*), were obtained by reduction of 3-quinolinol (*Ic*). In both cases we assume a primary formation of 1,2-dihydroquinolines *IIIa*, *IIIb* and 1,4-dihydroquinolines *IVa*, *IVb*. The dihydroquinoline derivatives *IIIb* and *IVb* have a common ketone form *V* which is reduced to the tetrahydro derivative *IIa* and further formylated to *IId*. In the reduction of *Ia* the primarily formed enamines *IIIa* and *IVa* undergo hydrolysis to the ketone *V*. This ketone is again reduced to *IIa* which is partially formylated to *IIc*. Reduction of 3-methoxyquinoline (*Ib*) with triethylammonium formate afforded a mixture of 1-formyl-3-methoxy-1,2-dihydroquinoline (*IIIc*) and 1-formyl-3-methoxy-1,2,3,4-tetrahydroquinoline (*IIe*). This reduction obviously proceeds again *via* the dihydro derivatives *IIId* and *IVc*. The derivative *IIId* is not reduced further,

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undergoing only formylation to *IIIc*, whereas the 1,4-dihydro derivative *IVc*, as an enamine, is further reduced with simultaneous formylation to *IIe*.

The infrared spectrum of *IIa* in tetrachloromethane displayed absorption bands $\nu(OH)_{free} = 3640\ cm^{-1}$ and $\nu(OH)_{bonded} = 3570\ cm^{-1}$. Since on dilution the intensity ratio of both these bands remained constant, we can exclude the presence of an intermolecular hydrogen bond. Under given conditions, 1,2,3,4-tetrahydroquinolinol (*IIa*) apparently exists as a mixture of two conformers, one with pseudoequatorial hydroxyl which cannot form an intramolecular hydrogen bond, and another one with pseudoaxial hydroxyl which can form this bond. In accord with this assumption, the coupling constants $^3J_{2a,3} = 4$ Hz and $^3J_{4a,3} = 5$ Hz, in the ^{1}H-NMR spectrum of *IIa* differ from the common values for 3-substituted 1,2,3,4-tetrahydroquinolines with a pseudoequatorial substituent[4]. We assume an analogous situation also in the tetrahydro derivatives *IIc*–*IIe*.

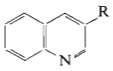
3-Bromoquinoline (*Id*) was reduced with triethylammonium formate to give 1-formyl-1,2,3,4-tetrahydroquinoline (*IIf*). The same product is formed also in the reduction of quinoline with triethylammonium formate in the presence of Raney nickel[5]. This reduction of 3-bromoquinoline is analogous to the similar reduction of β-bromostyrene to ethylbenzene[6]. The results of reductions of 3-substituted quinolines, containing electron donating substituents, together with the results, obtained previously with ethylquinoline (*Ie*), 3-vinylquinoline (*If*) and 3-(1-hydroxyethyl)quinoline (*Ig*), are presented in Table I.

TABLE I

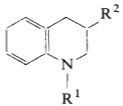
Reduction of 3-Substituted Quinoline Derivatives with Triethylammonium Formate

Derivatives	Product	Derivatives	Products
Ia	*IIa, IIc*	*Ik*[a]	*IIc, IIIf*
Ib	*IIe, IIIc*	*Il*[a]	*IIg, IIh, IIIe*
Ic	*IIa, IIc, IId*	*Im*	*IIk, IIj, IVf*
Id	*IIf*	*IVf*	*IIj*
Ie[a]	*IIg, IIIe*	*VIa*[b,d]	*IVg*
If[a]	*IIg, IIh, IIIe*	*VIa*[b,e]	*IIp, IIq, IVg*
Ig[a]	*IIg, IIh, IIIe*	*VIb*	*IIr*
Ih[a]	*IIf*	*VIc*	*IIs*
Ii[b]	*IIi, IIj, IVd*	*VId*	*IVh*
Ij[c]	*IIg, IIh, III, IIm, IIn, IIIe, IVe*	*VII*[f]	*IVi*

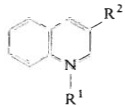
[a] Ref.[1]; [b] ref.[2]; [c] ref.[3]; [d] 60°C, 15 min; [e] 160°C, 6 h; [f] ref.[7].



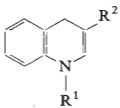
Ia, R = $N(CH_3)_2$
Ib, R = OCH_3
Ic, R = OH
Id, R = Br
Ie, R = C_2H_5
If, R = $CH{=}CH_2$
Ig, R = $CHCH_3$ | OH
Ih, R = COOH
Ii, R = CN
Ij, R = $COCH_3$
Ik, R = CH_2CH_2COOH
Il, R = $CH{=}CHCOOH$
Im, R = $COOC_2H_5$
In, R = $COOCH_3$



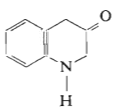
IIa–b, R^1 = H
IIc–o, R^1 = CHO
IIp–s, R^1 = CH_3
IIa, R^2 = OH
IIb, R^2 = OCHO
IIc, R^2 = OH
IId, R^2 = OCHO
IIe, R^2 = OCH_3
IIf, R^2 = H
IIg, R^2 = C_2H_5
IIh, R^2 = $=CHCH_3$
IIi, R^2 = $CONH_2$
IIj, R^2 = COOH
IIk, R^2 = $COOC_2H_5$
IIl, R^2 = $COCH_3$
IIIm, R^2 = $CHCH_3$ | OCHO
IIn, R^2 = $CHCH_3$ | OH
IIo, R^2 = CH_2CH_2COOH
IIp, R^2 = $CONH_2$
IIq, R^2 = COOH
IIr, R^2 = CH_3
IIs, R^2 = OCH_3



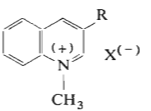
IIIa, R^1 = H, R^2 = $N(CH_3)_2$
IIIb, R^1 = H, R^2 = OH
IIIc, R^1 = CHO, R^2 = OCH_3
IIId, R^1 = H, R^2 = OCH_3
IIIe, R^1 = CHO, R^2 = C_2H_5
IIIf, R^1 = CHO, R^2 = CH_2CH_2COOH



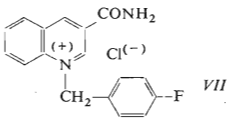
IVa–f, R^1 = H
IVg–h, R^1 = CH_3
IVi, R^1 = $CH_2C_6H_4F(p)$
IVa, R^2 = $N(CH_3)_2$
IVb, R^2 = OH
IVc, R^2 = OCH_3
IVd, R^2 = CN
IVe, R^2 = $COCH_3$
IVf, R^2 = $COOC_2H_5$
IVg, R^2 = CN
IVh, R^2 = $COOCH_3$
IVi, R^2 = $CONH_2$



V



VIa, R = CN, X = OSO_3CH_3
VIb, R = CH_3, X = OSO_3CH_3
VIc, R = OCH_3, X = I
VId, R = $COOCH_3$, X = I



VII

Of 3-substituted quinolines with electron withdrawing substituents, 3-quinolinecarboxylic acid[1] (*Ih*) afforded on reduction only the product *IIf*, arising by decarboxylation and subsequent reduction and formylation. 3-Quinolinecarbonitrile[2] (*Ii*) and 3-acetylquinoline[3] (*Ij*) gave the corresponding 1,4-dihydroquinolines *IVd* and *IVe*, respectively, in addition to products of further reduction. Analogously reacted[1] 3-quinolinepropionic acid (*Ik*) and 3-quinolineacrylic acid (*Il*). The results are given in Table I.

Ethyl 3-quinolinecarboxylate (*Im*) was reduced to a mixture from which we isolated, in addition to the 1,4-dihydro derivative *IVf*, ethyl 1-formyl-1,2,3,4-tetrahydro--3-quinolinecarboxylate (*IIk*) and the corresponding acid *IIj*. Prolonged reaction time in the case of the ester *Im* resulted in formation of the tetrahydro acid *IIj* as the main product; this compound was also the sole reduction product arising from ethyl 1,4-dihydro-3-quinolinecarboxylate (*IVf*).

In our previous paper we described reduction of 3-quinolinecarbonitrile methyl methosulfate (*VIa*) with triethylammonium formate[2]. After a shorter reaction time we isolated the 1,4-addition product *IVg* whereas longer reduction afforded also the tetrahydroquinolines *IIp* and *IIq*. Analogous results were obtained also in the reduction of 1-substituted 3-aminocarbonylquinolinium halides with formic acid in the presence of triethylamine[7]. Reduction of methyl 3-quinolinecarboxylate methiodide (*VId*) afforded the 1,4-addition product *IVh*. Of quaternary salts of 3-substituted quinolines, containing electron donating substituents, we reduced 3-methylquinoline methomethyl sulfate (*VIb*) and 3-methoxyquinoline methiodide (*VIc*) which afforded the 1-methyl-1,2,3,4-tetrahydroquinoline derivatives *IIr* and *IIs*, respectively.

The already described[1-3], as well as the present, reductions of 3-substituted quinolines show that the electrophilic position in the quinoline molecule depends on the nature of the substituent. It seems that electron accepting groups in the position 3 make the position 4 more electrophilic than the position 2; this is indicated by the formation of 1,4-dihydroquinoline derivatives. Electron donor groups in position 3 make the effect of the quinoline nitrogen atom more pronounced and the reaction thus affords 1,2-dihydroquinolines. In the mentioned reductions of quaternary salts, the electron accepting substituents in the position 3 have a dominant effect, in spite of strong electron acceptor influence of the quaternary nitrogen atom: the reaction thus leads to the 1,4-dihydroquinolines *IVg* and *IVh*.

We can conclude that the triethylammonium formate reduction of quaternary salts of 3-substituted quinolines, containing electron accepting substituents, is suitable for preparation of 1-alkyl-1,4-dihydroquinolines, contrary to the reduction with sodium borohydride which affords 1-alkyl-1,2-dihydroquinoline derivatives[8].

EXPERIMENTAL

Gas–liquid chromatography was performed on a Chrom II instrument (170 × 0·6 cm column, 15% poly(1,4-butanediol)succinate on Chromaton N-AW), flame-ionisation detector, carrier gas nitrogen. Thin-layer chromatography was carried out on Silufol UV 254 and 366 sheets (silica gel containing luminiscence indicator on an aluminium foil, binder starch). Spots were detected by Universal UV-Lampe Camag (Muthenz, Switzerland) at 254 and 366 nm. Column chromatography was performed on Silpearl UV 254. The IR spectra were measured on a Perkin–Elmer spectrophotometer Model 325, ^{1}H-NMR spectra on a Varian XL-100-15 (100·1 MHz) instrument at 37°C with tetramethylsilane as internal standard, UV spectra on a UV Specord (Zeiss, Jena) spectrometer in ethanol. The temperature data are uncorrected.

3-Dimethylaminoquinoline (*Ia*)

Formic acid (4·35 g; 0·08 mol), followed by 36% formaldehyde (4·3 g; 0·052 mol), was added to 3-aminoquinoline[9] (2·9 g; 0·02 mol) under cooling (0°C) and stirring. The mixture was heated to 80°C on a water bath for 24 h, acidified (cooling) with hydrochloric acid (1 : 1) and extracted with ether. The aqueous layer was made alkaline, the product extracted with ether, the extract dried over magnesium sulfate, taken down and the residue distilled; yield 2·1 g (60·7%) of *Ia*, b.p. 117—122°C/0·05 Torr (7·6 Pa), m.p. 54·5—55·5°C; reported[8] b.p. 126—128°C/13 Torr. For $C_{11}H_{12}N_2$ (172·2) calculated: 76·71°C, 7·02% H, 16·26% N; found: 76·92% C, 7·22% H, 16·39%N.

Picrate: m.p. 226—227°C (ethanol–acetone), reported[8] m.p. 224—226°C.

Reduction of 3-Dimethylaminoquinoline (*Ia*)

A mixture of *Ia* (3·45 g; 0·02 mol) and triethylammonium formate[5] (26 g; 0·3 mol) was heated to 150°C for 5 h. Triethylammonium formate was distilled off *in vacuo*, the residue made alkaline with sodium carbonate and the product taken up in benzene. The benzene extract afforded 1·2 g (34%) of *IIc*, m.p. 90·5—91·5°C (ethyl acetate–hexane). For $C_{10}H_{11}NO_2$ (177·2) calculated: 67·78% C, 6·26% H, 7·90% N; found: 67·73% C, 6·46% H, 8·01% N. IR spectrum ($CHCl_3$), cm^{-1}: 3 600 and 3 400 ν(OH), 1 677 (ν(C=O) in NCHO. ^{1}H-NMR spectrum ($CDCl_3$), ppm: 2·60 (bs, 1 H) OH, 2·98 (m, 2 H, $^2J = 16$, $^3J_{4a,3} = 5$, $^3J_{4e,3} = 5$) $CH_2(4)$ AB; 3·58—4·08 (m, 2 H) $CH_2(2)$; 4·32 (m, 1 H) CH(3); 7·20 (bs, 4 H) benzene ring; 8·82 (s, 1 H) CHO. The aqueous layer afforded 0·6 g (20·1%) of *IIa*, m.p. 87°C; reported[10] m.p. 87°C. IR spectrum (CCl_4), cm^{-1}: 3640 $\nu(OH)_{free}$, 3 570 $\nu(OH)_{assoc.}$, 3 450 ν(NH). ^{1}H-NMR spectrum ($CDCl_3$), ppm: 2·0—3·8 (b, 2 H) NH and OH; 2·92 (m, 2 H, $^2J = 16$ Hz, $^3J_{4a,3} = 5$, $^3J_{4e,3} = 4$ Hz) $CH_2(4)$ AB; 3·10—3·45 (m, 2 H) $CH_2(2)$; 4·23 (m, 1 H) CH(3); 6·45—7·11 (m, 4 H) benzene nucleus.

3-Methoxyquinoline (*Ib*)

A solution of 3-quinolinol[11] (12 g; 0·083 mol) in tert-butyl alcohol (320 ml) was added dropwise under stirring to a cooled solution of diazomethane (prepared from 58 g of N-methyl-N-nitrosourea) in ether (1 l). The mixture was stirred for 7h at −20°C and set aside overnight. The solvent was distilled off, the residue dissolved in ether and filtered, the filtrate was shaken with a dilute sodium hydroxide solution, the ethereal solution dried over magnesium sulfate and taken down. Distillation afforded 9·8 g (74%) of yellow *Ib*; b.p. 94°C/0·1 Torr (13 Pa). For $C_{10}H_9NO$ (159·2) calculated: 75·45% C, 5·70% H, 8·80% N; found: 75·47% C, 5·74% H, 8·76% N. IR spectrum (neat), cm^{-1}: 2960, 2940 $\nu(CH_3)$, 2845 $\nu(CH_3)$ in OCH_3, 1375 $\delta(CH_3)$, 1030 $(COCH_3)$. ^{1}H-NMR spectrum ($CDCl_3$), ppm: 3·87 (s, 3 H) OCH_3; 7·30 (d, 1 H, $J = 2$ Hz) CH(4); 7·41 to. 7·77 (m, 3 H) CH(5, 6, 7); 7·97—8·13 (m, 1 H) CH(8), 8·67 (d, 1 H, $J = 3$ Hz) CH(2).

Reduction of 3-Methoxyquinoline (*Ib*)

A stirred mixture of *Ib* (4 g; 0·025 mol) and triethylammonium formate (32·4 g; 0·375 mol) was heated to 150°C for 10 h. The usual work-up procedure afforded 2·6 g of a yellowish liquid, b.p. 122–125°C/0·1 Torr (13 Pa), which was separated on silica gel (chloroform with 2% of methanol). The following fractions were isolated: *a*) *IIIc*, b.p. 123–126°C/0·1 Torr (13 Pa), 1 g (21·2%), m.p. 40–45°C. For $C_{11}H_{11}NO_2$ (189·2) calculated: 69·83% C, 5·86% H, 7·40% N; found: 69·89% C, 6·11% H, 7·13% N. IR spectrum ($CHCl_3$), cm^{-1}: 2980, 2950 $\nu(CH_3)$, 2850 $\nu(CH_3)$ in OCH_3, 1670 ν(C=O) in NCHO, 1655 ν(C=C). ^{1}H-NMR spectrum ($CDCl_3$), ppm: 3·74 (s, 3 H) OCH_3; 4·40 (s, 2 H) CH_2(2); 5·56 (s, 1 H) CH(4); 7·09 (bs, 4 H) benzene nucleus; 8·60 (s, 1 H) CHO. b) *IIe*, b.p. 108°C/0·1 Torr (13 Pa), 0·9 g (18·8%). For $C_{11}H_{13}NO_2$ (191·2) calculated: 69·09% C, 6·85% H, 7·32% N; found: 69·13% C, 6·75% H, 7·58% N. ^{1}H-NMR spectrum ($CDCl_3$), ppm: 2·98 (m, 2 H, $^2J = 16$, $^3J_{4a,3} = 5$) CH_2(4) AB; 3·40 (s, 3 H) OCH_3; 3·54–3·90 (m, 2 H) CH_2(2); 4·04 (m, 1 H) CH(3); 6·9–7·1 (m, 4 H) benzene nucleus: 8·78 (s, 1 H) CHO. IR spectrum ($CHCl_3$), cm^{-1}: 2840 $\nu(CH_3)$ in OCH_3, 1670 ν(C=O) in NCHO.

Reduction of 3-Quinolinol (*Ic*)

A stirred mixture of *Ic* (ref.[11]) (5·1 g; 0·035 mol) and triethylammonium formate (45·4 g; 0·525 mol) was heated to 155°C for 9 h. The usual work-up procedure afforded 2·7 g of a product, b.p. 160–170°C/0·1 Torr (13 Pa) which was separated on silica gel (chloroform). The following fractions were obtained: *a*) *IId*, b.p. 150°C/0·1 Torr (13 Pa), 0·6 g (8·4%). For $C_{11}H_{11}NO_3$ (205·2) calculated: 64·38% C, 5·40% H, 6·83% N; found: 64·28% C, 5·63% H, 7·06% N. IR spectrum ($CHCl_3$), cm^{-1}: 1735 ν(C=O) in OCHO, 1677 ν(C=O) in NCHO. ^{1}H-NMR spectrum ($CDCl_3$), ppm: 3·10 (m, 2 H, $^2J = 16$, $^3J_{4e,3} = 4{\cdot}5$, $^3J_{4a,3} = 4$ Hz) CH_2(4) AB; 3·67 (dd, 1 H, $^2J = 14$, $^3J_{2a,3} = 3{\cdot}5$ Hz) 2-H_a; 4·30 (dd, 1 H, $^3J_{2e,3} = 5$ Hz) 2-H_e, CH_2(2) AB; 5·46 (m, 1 H) CH(3); 7·18 (bs, 4 H) benzene nucleus; 7·97 (s, 1 H) OCHO; 8·81 (s, 1 H) NCHO. *b*) *IIc*, m.p. 90–91°C (ethyl acetate–hexane), 0·8 g (24·2%), identical with authentic compound. The aqueous layer after extraction of the reaction mixture with benzene was acidified with hydrochloric acid, decolorised with charcoal and the filtrate taken down. The residue was extracted with boiling ethanol, the solvent was driven off *in vacuo*, the residue made alkaline and the product taken up in chloroform. Evaporation of the solvent afforded 0·7 g (13·4%) of *IIa*, m.p. 88°C, identical with the authentic compound.

Reduction of 3-Bromoquinoline (*Id*)

A mixture of *Id* (ref.[12]) (6·7 g; 0·032 mol) and triethylammonium formate (41·5 g; 0·48 mol) was heated to 165–170°C for 13 h. After cooling, the separated triethylamine hydrobromide (4·60 g; 78·9%) was filtered, m.p. 246–247°C (ethanol); reported[13] m.p. 248°C. The filtrate after filtration of triethylamine hydrobromide was distilled *in vacuo* to remove the triethylammonium formate; the usual work-up of the residue afforded 3 g (58·2%) of *IIf*, b.p. 102–104°C / / 0·1 Torr (13 Pa), identical with the authentic[1] *IIf*.

Reduction of Ethyl 3-Quinolinecarboxylate (*Im*)

A stirred mixture of *Im* (7 g; 0·035 mol) and triethylammonium formate (45·1 g; 0·522 mol) was heated to 165–170°C for 5·5 h. Triethylammonium formate was distilled off *in vacuo*, the residue made alkaline with a sodium hydrogen carbonate solution, the separated product filtered, washed with water and dried over phosphorus pentoxide. Crystallisation from light petroleum–ethyl

acetate gave 1·7 g (23·9%) of *IVf*, m.p. 140–141°C; reported[8] m.p. 142–143°C. IR spectrum (KBr), cm^{-1}: 1710–1630 (N–C=C–$CO_2C_2H_5$). UV spectrum (ethanol): 340 nm. ^{1}H-NMR spectrum ($CDCl_3$), ppm: 1·26 (t, 3 H, $J = 7$) CH_3; 3·72 (s, 2 H) CH_2(4); 4·16 (q, 2 H, $J = 7$) CH_2CH_3; 6·24 (bs, 1 H) NH; 6·46–7·35 (m, 5 H) benzene nucleus and CH(2); (hexadeuteriodimethyl sulfoxide): 1·14 (t, 3 H, $J = 7$) CH_3; 3·56 (s, 2 H) CH_2(4); 4·02 (q, 2 H, $J = 7$) $C\underline{H}_2CH_3$; 6·58–7·10 (m, 4 H) benzene nucleus; 7·18 (d, 1 H, $^3J_{NH,CH(2)} = 6$) CH(2); 8·80 (d, 1 H) NH. The mother liquor from *IVf* was taken down, the residue extracted with ether and the extract dried over magnesium sulfate. Distillation afforded 2 g of the product, b.p. 145–150°C/0·1 Torr (13 Pa), which consisted, according to ^{1}H-NMR spectrum, of *Im* and *IIk*. This mixture was shaken with ethereal hydrogen chloride, the solution filtered, the filtrate shaken with a sodium hydrogen carbonate solution and dried over magnesium sulfate. Work-up of the ethereal extract afforded 1 g (12·3%) of *IIk*, b.p. 142°C/1 Torr (133 Pa). For $C_{13}H_{15}NO_3$ (233·3) calculated: 66·94% C, 6·48% H, 6·00% N; found: 67·17% C, 6·70% H, 5·86% N. IR spectrum ($CHCl_3$), cm^{-1}: 1670 ν(C=O) in NCHO. ^{1}H-NMR spectrum ($CDCl_3$), ppm: 1·28 (t, 3 H, $J = 7$) CH_3; 2·76–3·20 (m, 3 H) CH(3) and CH_2(4); 3·54–3·92 (m, 1 H) 2-H_a; 4·18 (q, 2 H, $J = 7$) $C\underline{H}_2CH_3$; 4·06–4·50 (m, 1 H) 2-H_e; 7·18 (bs, 4 H) benzene nucleus; 8·79 (s, 1 H) CHO. The aqueous solution was acidified with hydrochloric acid, the separated product filtered and dried over phosphorus pentoxide; yield 1·4 g (19·5%) of *IIj*, m.p. 164–165°C (ethyl acetate–ethanol), no melting point depression on admixture with an authentic specimen[1].

Analogous reduction of *Im* (4 g; 0·02 mol) with triethylammonium formate (25·8 g; 0·3 mol) (165–170°C, 13 h) afforded the ester *IIk* (0·2 g; 4·3%), the dihydro derivative *IVf* (0·2 g; 5%) and the acid *IIj* (1·6 g; 39·2%).

Similar reduction of *IVf* (0·7 g; 3·45 mmol) (165–170°C, 15 h) gave 0·4 g (56·6%) of the acid *IIj*, m.p. 164°C.

3-Methoxyquinoline Methiodide (*VIc*)

A mixture of *Ib* (5·1 g; 0·032 mol), methyl iodide (10 g; 0·07 mol) and methanol (100 ml) was refluxed for 10 h. After cooling, the separated crystals were filtered, yielding 6·1 g (63%) of *VIc*, m.p. 213°C (methanol). For $C_{11}H_{12}INO$ (301·1) calculated: 43·88% C, 4·02% H, 42·14% I, 4·65% N; found: 44·09% C, 4·15% H, 41·85% I, 4·90% N.

The compound *VIc* (5·1 g; 0·017 mol) was reduced in the usual manner (80–100°C, 45 min) yielding 2 g (66·4%) of *IIs*, b.p. 83–85°C/0·1 Torr (13 Pa). For $C_{11}H_{15}NO$ (177·3) calculated: 74·54% C, 8·53% H, 7·90% N; found: 74·79% C, 8·47% H, 8·18% N. IR spectrum (neat), cm^{-1} 2825 ν(CH_3) in OCH_3, 1105ν(C–O–C). ^{1}H-NMR spectrum ($CDCl_3$), ppm: 2·61–3·33 (m, 4 H) CH_2(4) and CH_2(2); 2·89 (s, 3 H) NCH_3; 3·42 (s, 3 H) OCH_3; 3·57–3·93 (m, 1 H) CH(3); 6·70–7·20 (m, 4 H) benzene nucleus.

3-Methylquinoline Methyl Methosulfate (*VIb*)

A mixture of 3-methylquinoline[15] (5 g; 0·035 mol), dimethyl sulfate (4·4 g; 0·035 mol) and benzene (50 ml) was refluxed for 4 h. The product was filtered, yield 8·8 g (94%), m.p. 129°C (ethyl acetate–ethanol). For $C_{12}H_{15}NO_4S$ (269·3) calculated: 53·52% C, 5·61% H, 5·20% N, 11·91% S; found: 53·76% C, 5·89% H, 5·06% N, 11·94% S.

A stirred mixture of *VIb* (5·6 g; 0·02 mol) and triethylammonium formate (26 g; 0·30 mol) was heated to 120°C for 15 min, cooled, poured into water and the product taken up in benzene. Work-up of the extract afforded 2·6 g (80·6%) of *IIr*, b.p. 103°C/11 Torr (1·5 kPa). For $C_{11}H_{15}N$ (161·3) calculated: 81·94% C, 9·38% H, 8·68% N; found: 81·68% C, 9·48% H, 8·75%

N. ^{1}H-NMR spectrum ($CDCl_3$), ppm: 1·03 (d, 3 H, $J = 7$) CH_3; 1·90—2·60 (m, 2 H, $^2J = 16$, $^3J_{4a,3a} = 10$) 3-H_a, 4-H_a; 2·64—2·98 (m, 2 H, $^3J_{4e,3a} = 5$) 4-H_e, 2-H_a; 2·86 (s, 3 H) NCH_3, 3·02—3·26 (m, 1 H, $^2J = 12$ Hz) 2-H_e; 6·44—7·18 (m, 4 H) benzene nucleus.

Methyl 3-Quinolinecarboxylate Methiodide (*VId*)

A mixture of the ester *In*[14] (7·3 g; 0·039 mol), methyl iodide (6·5 g; 0·046 mol) and methanol (70 ml) was heated in a sealed ampoule to 95°C for 12 h. The usual isolation afforded 10·4 g (84·5%) of *VId*, m.p. 197—198°C (methanol). For $C_{12}H_{12}INO_2$ (329·1) calculated: 43·79% C, 3·67% H, 38·56% I, 4·26% N; found: 44·09% C, 3·68% H, 38·56% I, 4·17% N.

Reduction of *VId* (6·5 g; 0·02 mol; 60—70°C, 20 min) gave 3·4 g (89·7%) of *IVh*, b.p. 135 to 140°C/0·5 Torr (65 Pa). For $C_{13}H_{13}NO_2$ (203·2) calculated: 70·92% C, 6·45% H, 6·89% N; found: 71·02% C, 6·68% H, 6·89% N. IR spectrum ($CHCl_3$), cm^{-1}: 1680 and 1645 (N—C=C—CO_2CH_3). ^{1}H-NMR spectrum ($CDCl_3$), ppm: 3·16 (s, 3 H) NCH_3; 3·70 (s, 3 H) OCH_3; 3·75 (s, 2 H) CH_2(4); 6·60—7·16 (m, 4 H) benzene nucleus; 7·18 (s, 1 H) CH(2).

The elemental analyses were carried out in Analytical Department of this Institute (Dr L. Helešic, Head), the ^{1}H-NMR *spectra were performed under supervision of Dr P. Trška.*

REFERENCES

1. Kocián O., Ferles M.: This Journal *43*, 1413 (1978).
2. Ferles M., Kocián O.: This Journal *44*, 2238 (1979).
3. Kocián O., Ferles M.: This Journal *44*, 1167 (1979).
4. Kocián O.: *Thesis*. Prague Institute of Chemical Technology, Prague 1978.
5. Ito K.: Yakugaku Zasshi *86*, 1166 (1966); Chem. Abstr. *66*, 75 899 (1967).
6. Cortese N. A., Heck F. R.: J. Org. Chem. *42*, 3491 (1977).
7. Gizzi L., Joullié M. M.: Tetrahedron Lett. *1969*, 3117.
8. Kikugawa Y., Kuramoto M., Saito I., Yamada S.: Chem. Pharm. Bull. *21*, 1914 (1973).
9. Renshaw R. R., Friedman H. L.: J. Amer. Chem. Soc. *61*, 3320 (1939).
10. Bendz G., Culvenor C. C. J., Goldsworthy L. J., Kirby K. S., Robinson R.: J. Chem. Soc. *1950*, 1130.
11. Cragoe E. J., Robb C. M.: Org. Syn., Col. Vol. *5*, 635 (1973).
12. Eisch J. J.: J. Org. Chem. *27*, 1318 (1962).
13. Wagner L.: Z. Krystalogr., Kristallgeometrie, Kristallphys., Kristallchem. *43*, 148 (1907); Chem. Zentralbl. *1907*, I, 129.
14. Chiavarelli S., Marini-Bettolo G. B.: Gazz. Chim. Ital. *82*, 86 (1952).
15. Utermohlen W. P.: J. Org. Chem. *8*, 544 (1943).

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