PREPARATION OF SOME DERIVATIVES OF BENZO[ij]QUINOLIZINE*

Alexandra ŠILHÁNKOVÁ, Petr TRŠKA, Daniela VLKOVÁ and Miloslav FERLES

Department of Organic Chemistry,
*Institute of Chemical Technology, 166 28 Prague 6*

Reaction of 1,2,3,4-tetrahydroquinoline with 1-chloro-2,3-epoxypropane afforded 1-(3-chloro--2-hydroxypropyl)-1,2,3,4-tetrahydroquinoline (*IIb*) which was thermolabile and on heating *in vacuo* was converted into 2,3,6,7-tetrahydro-1*H*,5*H*-benzo[ij]quinolizin-2-ol (*Ib*). This compound reacted with acetic anhydride and *p*-toluenesulfonyl chloride to give 2-acetoxy-2,3,6,7--tetrahydro-1*H*,5*H*-benzo[ij]quinolizine (*Ic*) and 2-(*p*-toluenesulfonyloxy)-2,3,6,7-tetrahydro--1*H*,5*H*-benzo[ij]quinolizine (*Id*), respectively. N,N-Bis(3-chloro-2-hydroxypropyl)aniline (*IIIb*) on heating gave a mixture of *cis*- and *trans*-2,3,6,7-tetrahydro-1*H*,5*H*-benzo[ij]quinolizine-2,6--diols (*Ie*). The corresponding 4-methoxyaniline derivative afforded analogously a mixture of *cis*- and *trans*-9-methoxy-2,3,6,7-tetrahydro-1*H*,5*H*-benzo[ij]quinolizine-2,6-diols (*If*). Dehydration with potassium hydroxide converted the diols *Ie* into 1*H*,7*H*-benzo[ij]quinolizine (*VIa*), the diols *If* into 9-methoxy-1*H*,7*H*-benzo[ij]quinolizine (*VIb*). Treatment of *Ib* with phosphorus pentoxide led to 2,3,6,7-tetrahydro-1*H*,5*H*-benzo[ij]quinolizine (julolidine, *Ia*).

Some derivatives of 1,2,3,4-tetrahydroquinoline represent (besides N,N-disubstituted anilines) suitable starting compounds for the synthesis of partially reduced benzo[ij]-quinolizines. Of hydroxy derivatives of 2,3,6,7-tetrahydro-1*H*,5*H*-benzo[ij]quinolizine (julolidine; *Ia*) which have been the subject of our synthetic studies, only the 8-hydroxy[1], 2,6-dihydroxy-9-phenyl and 2,6-dihydroxy-9-methyl derivatives[2] are known as yet. About one hundred years ago Reissert[3] used for the at that time unknown 3*H*,5*H*-benzo[ij]quinolizine (*IV*) the name julol; this was later changed by Mann and Smith[4] to juline. However, neither this parent compound nor the isomeric 1*H*,5*H*-benzo[ij]quinolizine (*V*) nor 1*H*,7*H*-benzo[ij]quinolizine (*VIa*) have been described so far.
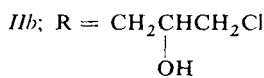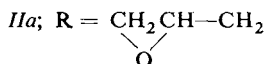
Trying to reproduce the described[5] preparation of 1-(2,3-epoxypropyl)-1,2,3,4--tetrahydroquinoline (*IIa*) from 1,2,3,4-tetrahydroquinoline and 1-chloro-2,3-epoxy-propane we found that the reaction product was not the desired epoxy derivative *IIa* but 1-(3-chloro-2-hydroxypropyl)-1,2,3,4-tetrahydroquinoline (*IIb*) as shown by the ¹H NMR and mass spectra. The reaction thus proceeds in the same way as with aniline and its derivatives[6,7]. The obtained product *IIb* was thermolabile and on heating

in vacuo lost hydrogen chloride under formation of 2,3,6,7-tetrahydro-1H,5H-
-benzo[ij]quinolizin-2-ol (*Ib*) which was identified by ^{1}H NMR and mass spectro-
scopy. The alcohol *Ib* was not stable at room temperature when exposed to the air
and light and, like julolidine (*Ia*) itself, it was slowly converted into a red polymeric
compound. However, on storage in a brown bottle at −19°C, the compound re-
mained unchanged for several weeks. Reaction of the alcohol *Ib* with acetic anhydride
in pyridine gave liquid 2-acetoxy-2,3,6,7-tetrahydro-1H,5H-benzo[ij]quinolizine (*Ic*),
treatment of *Ib* with *p*-toluenesulfonyl chloride in pyridine gave crystalline 2-(*p*-
-toluenesulfonyloxy)-2,3,6,7-tetrahydro-1H,5H-benzo[ij]quinolizine (*Id*).
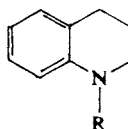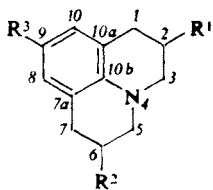
Ia, R^1 = R^2 = R^3 = H
Ib; R^1 = OH, R^2 = R^3 = H
Ic; R^1 = OCOCH$_3$, R^2 = R^3 = H
Id; R^1 = OTs, R^2 = R^3 = H
Ie; R^1 = R^2 = OH, R^3 = H
If; R^1 = R^2 = OH, R^3 = OCH$_3$

IIa; R = CH$_2$CH—CH$_2$
                    \ /
                     O

IIb; R = CH$_2$CHCH$_2$Cl
                    |
                   OH

Reaction of the alcohol *Ib* with phosphorus pentoxide in toluene afforded julolidine
(*Ia*) in 50% yield. The formation of this reduced base may be explained by dis-
proportionation of the primary dehydration product under simultaneous formation
of benzoquinolizinium phosphate. Similar disproportionation reactions of substituted
1-methyl-1,2-dihydro- and 1,4-dihydroquinolines induced by polyphosphoric acid
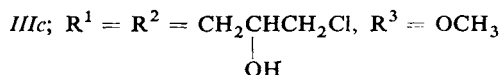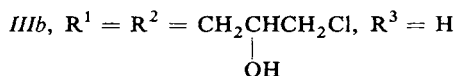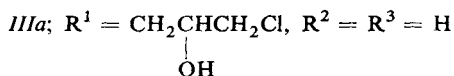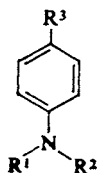are known[8,9].

2,3,6,7-Tetrahydro-1H,5H-benzo[ij]quinolizine-2,6-diols (*Ie*) were prepared by re-
action of aniline and 1-chloro-2,3-epoxypropane. This reaction is known to give
the corresponding monosubstituted[10−12] (*IIIa*) or disubstituted[6,7] (*IIIb*) aniline.
An experiment at 40°C afforded, after column chromatography, crystalline N-(3-
-chloro-2-hydroxypropyl)aniline (*IIIa*), previously described[10−12] as an unstable
brown oil. In our hands, the pure compound remained unchanged for several months
when stored in the dark.

The disubstituted aniline *IIIb* was best prepared from aniline and 1-chloro-2,3-epoxy-
propane in ethanol[7]. The literature[6] reports (without further evidence) two different
isomers, m.p. 94°C and 91·5°C, which were separated by many crystallizations,
whereas Hrehorowicz[7] neglected the isomerism and described a single reaction product

melting at 92−93°C. The ^{1}H NMR and ^{13}C NMR spectra showed that the mentioned reaction gave a mixture of two diastereoisomers from which we obtained by repeated crystallization an isomer of m.p. 91−92°C. The attempted purification of the second isomer by column chromatography or crystallization was unsuccessful. The presence of other possible structures, considered in ref.[6], can be excluded on the basis of the tabulated ^{13}C NMR shift increments together with the signal assignment by the APT technique[23].

IIIa; $R^1 = CH_2CHCH_2Cl$, $R^2 = R^3 = H$
$\quad\quad\quad\quad\quad\quad$ OH

IIIb, $R^1 = R^2 = CH_2CHCH_2Cl$, $R^3 = H$
$\quad\quad\quad\quad\quad\quad\quad$ OH

IIIc; $R^1 = R^2 = CH_2CHCH_2Cl$, $R^3 = OCH_3$
$\quad\quad\quad\quad\quad\quad\quad$ OH

IV

V
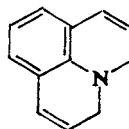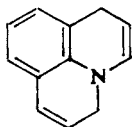
VIa; R = H
VIb; R = OCH$_3$

Heating of the substituted aniline *IIIb in vacuo* to 180°C (bath temperature) brought about evolution of hydrogen chloride. The reaction gave a mixture o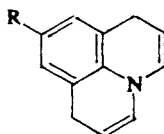f two compounds which, according to the mass, ^{1}H NMR and ^{13}C NMR spectra, were *cis*- and *trans*-2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]quinolizine-2,6-diols *(Ie)*. The reaction took place within a narrow temperature range, batches of more than 1 g gave lower yields. Therefore, we carried out the cyclization according to the method used for the preparation of 3-hydroxy-1,2,3,4-tetrahydroquinoline and its derivatives[13,14]. The aniline *IIIb* was heated in bromobenzene in the presence of equimolecular amount of N,N-diethylaniline. This method gave much higher yields than the direct heating, however, no increase in the yield was observed in the preparation of *Ib*

Analogously, treatment of 4-methoxyaniline with 1-chloro-2,3-epoxypropane afforded N,N-bis(3-chloro-2-hydroxypropyl)-4-methoxyaniline[15] (*IIIc*) which, according to the ^{13}C NMR spectrum, was a mixture of diastereoisomers with one isomer strongly predominating. In boiling bromobenzene, this mixture gave *cis*- and *trans*-9-methoxy-2,3,6,7-tetrahydro-1H,5H-benzo[*ij*]quinolizine-2,6-diols (*If*).

Both the diol mixtures *Ie* and *If* were dehydrated analogously as described[16] for 1-methyl-3-hydroxy-1,2,3,4-tetrahydroquinoline. On heating with solid potassium hydroxide *in vacuo* to 180—200°C, the diol *If* was dehydrated and afforded 9-methoxy-1H,7H-benzo[*ij*]quinolizine (*VIb*) which was unstable and turned dark on exposure to the air; in nitrogen atmosphere at −18°C it decomposed within 2—3 hours.

When the diol *Ie* was dehydrated under the same conditions as the 9-methoxy derivative *If*, the product was contaminated with the starting compound. Good results were obtained when working under less diminished pressure which allowed to obtain the dehydration temperature without distillation of the starting diol. The arising 1H,7H-benzo[*ij*]quinolizine (*VIa*) was even less stable than the 9-methoxy derivative *VIb* (it immediately turned brown on the air) and could be handled only under nitrogen. The instability of the bases *VI* resembles the behaviour of 1-methyl--1,4-dihydroquinoline and their ^{1}H NMR spectra confirm the assumed structure. The chemical shifts of ^{1}H protons as well as coupling constants are in an excellent agreement with data published for 1-methyl-1,4-dihydroquinoline[17−20] which are considered typical and sufficiently reliable for distinguishing between the 1,2- and 1,4-dihydro forms.

EXPERIMENTAL

The temperature data are uncorrected. Infrared spectra were measured on a Perkin Elmer 325 spectrophotometer in chloroform or tetrachloromethane; the absorption maxima are given in cm^{-1}. ^{1}H NMR Spectra were taken on a Varian XL-100-15 instrument (100·1 MHz) at 35°C, ^{13}C NMR spectra were obtained with a Tesla 567 (25·14 MHz) spectrometer. The chemical shifts are given in δ (ppm) relative to tetramethylsilane and coupling constants in Hz. Mass spectra were measured on a Gas Chromatograph-Mass Spectrometer type 9000 LKB (Stockholm) and on an AEI MS 902 S instrument (direct inlet). The ions are given in m/z (relative intensity, %). Thin-layer chromatography was performed on Silufol UV 254 sheets (silica gel Silpearl, containing a luminiscent indicator on aluminium foil, binder starch), detection with a Universal-UV-Lampe Camag (Muttenz, Switzerland) at 254 and 366 nm, or with iodine vapours.

1-(3-Chloro-2-hydroxypropyl)-1,2,3,4-tetrahydroquinoline (*IIb*)

A stirred mixture of 1,2,3,4-tetrahydroquinoline[21] (6·6 g; 0·05 mol), 1-chloro-2,3-epoxypropane (9·3 g; 0·10 mol) and water (0·25 ml) was heated to 55—65°C for 8 h. After removal of the unreacted 1-chloro-2,3-epoxypropane by distillation *in vacuo*, the residue was mixed with water (10 ml), saturated potassium hydroxide solution was added, and the solution was extracted three times with dichloromethane. The combined organic extracts were dried over magnesium sulfate and the solvent was removed *in vacuo* (maximum bath temperature 55°C), affording

8·9 g (79%) of a crude product which decomposed on attempted distillation. According to thin-layer chromatography (benzene–methanol 95 : 5), the reaction product was contaminated with other compounds and therefore a part was purified on a silica gel column. The obtained *IIb* was a colourless viscous liquid, turning brown on the air. ^{1}H NMR Spectrum (δ, C^{2}HCl$_3$): 6·82—7·08 and 6·68 (2 m, 4 H) aromatic H; 3·94—4·22 (m, 1 H) CH—O; 3·50—3·72 (m, 2 H) CH$_2$Cl; 3·10—3·46 (m, 4 H) 2 × CH$_2$N; 2·74 (t, 2 H, $J = 6$) H at C$_{(4)}$ of the heterocyclic ring; 2·57 (d, 1 H, $J = 5$) O—H; 1·76—2·06 (m, 2 H) H at C$_{(3)}$ of the heterocyclic ring. IR Spectrum (CHCl$_3$, cm^{-1}): 3 580 ν(OH, free), 3 490 ν(OH bonded). Mass spectrum (m/z; rel. intensity, %): 225 (M$^+$) (9), 146 (M$^+$—CHOHCH$_2$Cl) (100).

2,3,6,7-Tetrahydro-1*H*,5*H*-benzo[*ij*]quinolizin-2-ol (*Ib*)

A stirred mixture of 1,2,3,4-tetrahydroquinoline (5 g; 38 mmol), 1-chloro-2,3-epoxypropane (6·9 g; 75 mmol) and water (0·18 ml) was heated to 60—75°C for 7h. After this time, thin-layer chromatography showed that all 1,2,3,4-tetrahydroquinoline had reacted. The unreacted 1-chloro-2,3-epoxypropane was distilled off under reduced pressure and the residue was heated *in vacuo* to 190°C. At this temperature rapid evolution of hydrogen chloride occurred. After 15 min, the dark reaction mixture was cooled, diluted with water, made alkaline with 40% sodium hydroxide and extracted three times with dichloromethane. The organic layer was dried over magnesium sulfate, taken down and the residue distilled, affording 2·8 g (39%) of a liquid, b.p. 109—110°C/1·3 Pa, which solidified on standing overnight in a refrigerator. Two crystallizations from pentane gave the product *Ib*, m.p. 59·5—60°C, unstable on exposure to air and light. For C$_{12}$H$_{15}$NO (189·3) calculated: 76·16% C, 7·99% H, 7·40% N; found: 76·13% C, 7·96% H, 7·68% N. ^{1}H NMR Spectrum (δ, C^{2}HCl$_3$): 6·69—6·86 and 6·42—6·66 (2 m, 3 H) H aromatic; 4·16 (bm, 1 H) CH—O; 3·00—3·22 (m, 4 H) H at C$_{(3)}$ and C$_{(5)}$; 2·90—3·00 and 2·64—2·88 (2 m, 4 H) H at C$_{(1)}$ and C$_{(7)}$; 2·42 (s, 1 H) O—H; 1·84—2·14 (m, 2 H) H at C$_{(6)}$. IR Spectrum (CHCl$_3$, cm^{-1}): 3 540, ν(OH free); 3 620 ν(OH bonded). Mass spectrum (m/z, rel. intensity, %): 189 (M$^+$) (100); 188 (M$^+$—1) (52), 170 (M$^+$—19) (34). 2,3,6,7-Tetrahydro-1*H*,5*H*-benzo[*ij*]quinolizin-2-ol, hydrochloride m.p. 152—158°C (acetone-2-propanol 4 : 1). For C$_{12}$H$_{16}$ClNO (225·7) calculated: 63·85% C, 7·14% H, 15·71% Cl, 6·21% N; found: 63·63% C, 7·28% H, 15·52% Cl, 6·30% N. ^{1}H NMR Spectrum (δ, hexadeuteriodimethyl sulfoxide): 6·68—7·00 (m, 3 H) aromatic H; 4·13 (bm, 1 H) CH—O; 3·12—3·42 (m, 4 H) H at C$_{(3)}$ and C$_{(5)}$; 2·46—3·12 (m, 5 H) 4 H at C$_{(1)}$ and C$_{(7)}$, O—H; 1·80 to 2·14 (m, 2 H) 2 H at C$_{(6)}$.

2-Acetoxy-2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]quinolizine (*Ic*)

A mixture of *Ib* (0·2 g; 1·1 mmol), pyridine (0·6 ml) and acetic anhydride (0·4 g; 4·2 mmol) was set aside at room temperature for two days. Pyridine and the unreacted acetic anhydride were removed *in vacuo* and the residue was distilled to give 0·15 g (61%) of a yellow viscous liquid, b.p. 106—109°C/2·6 Pa, unstable on exposure to the air. For C$_{14}$H$_{17}$NO$_2$ (231·2) calculated: 72·70% C, 7·41% H, 6·06% N; found: 72·95% C, 7·24% H, 6·23% N. ^{1}H NMR Spectrum (δ, C^{2}HCl$_3$): 6·70—6·90 and 6·40—6·64 (2 m, 3 H) aromatic H; 5·06—5·38 (m, 1 H) H at C$_{(2)}$; 2·64—3·44 (m, 8 H) H at C$_{(1)}$, C$_{(3)}$, C$_{(5)}$, C$_{(7)}$; 1·82—2·16 (m, 5 H) 2 H at C$_{(6)}$ and CH$_3$CO. Mass spectrum (m/z, rel. intensity, %): 231 (M$^+$) (23); 171 (M$^+$—CH$_3$COOH) (28); 170 (100).

2-(*p*-Toluenesulfonyloxy)-2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]quinolizine (*Id*)

p-Toluenesulfonyl chloride (1·05 g; 5·5 mmol) was added to a solution of *IIIa* (1 g; 5·3 mmol) in pyridine (1 ml). After standing at room temperature in the dark for 3 days, water (30 ml) was

added, followed by an excess of saturated solution of sodium hydrogen carbonate. The mixture was extracted with ether (3 × 15 ml), the ethereal layer was washed with water, dried over magnesium sulfate and taken down. The residue was mixed with cyclohexane, affording 1·3 g (72%) of the *p*-toluenesulfonate *Id* which was twice crystallized from cyclohexane. Yield 1·1 g of the product m.p. 87—87·5°C. For $C_{19}H_{21}NO_3S$ (343·4) calculated: 66·45% C, 6·16% H, 4·08% N, 9·33% S; found: 66·72% C, 6·14% H, 3·84% N, 9·66% S.

Reaction of *Ib* with Phosphorus Pentoxide

A solution of *Ib* (1 g; 5·3 mmol) in toluene (5 ml) was added dropwise to a boiling suspension of phosphorus pentoxide (10 g) in toluene (20 ml). After boiling for 30 min, the solvent was distilled off, the residue heated to 150—160°C for 2·5 h and decomposed with ice. Traces of toluene were removed by steam-distillation, the residue was made alkaline with 40% sodium hydroxide, extracted with dichloromethane (4×) and the extract dried over magnesium sulfate. The solvent was removed by distillation leaving a red residue (0·45 g; 49·5%). Purification by chromatography on a column of silica gel in benzene afforded an oil which solidified on standing in a refrigerator. According to the ^1H NMR, IR and mass spectra, the product was identical with *Ia* prepared by the described procedure[22].

N-(3-Chloro-2-hydroxypropyl)aniline (*IIIa*)

A mixture of aniline (2·5 g; 27 mmol) and 1-chloro-2,3-epoxypropane (10 g; 0·11 mol) was kept at 40°C for 16 h. The unreacted 1-chloro-2,3-epoxypropane was distilled off at 55°C (bath) and 1·3 kPa. Thin-layer chromatography in benzene revealed that the yellow residue (6·7 g) was a mixture of compounds. A part of this mixture (2·1 g) was chromatographed on a column of silica gel (benzene and benzene with 4% of ethyl acetate) affording 0·85 g (40%) of *IIIa*, m.p. 38·5—39·5°C (pentane). The literature[10−12] reports this compound as an oil, solidifying at −10°C and decomposing on attempted distillation. For $C_9H_{12}ClNO$ (185·6) calculated: 58·22% C, 6·51% H, 19·09% Cl, 7·54% N; found: 58·44% C, 6·50% H, 18·85% Cl, 7·42% N. ^1H NMR Spectrum (δ, C^2HCl_3): 7·00—7·26 (m, 2 H) H at $C_{(3)}$ and $C_{(5)}$ of the aromatic nucleus; 6·50—6·75 (m, 3 H) H at $C_{(2)}$, $C_{(4)}$ and $C_{(6)}$ of the aromatic nucleus; 3·86—4·09 (m, 1 H) CH—O; 3·56—3·60 (d, $J = 4$, 2 H) CH_2Cl; 3·02—3·40 (m, 4 H) N—CH_2, NH, OH, after shaking with ^2H_2O only 2 H. IR Spectrum ($CHCl_3$, $cm^{−1}$): 3 590 $\nu(OH)$; 3 430 $\nu(NH)$. Picrate: m.p. 170 to 172°C (ethanol), ref.[10] states m.p. 174°C, ref.[13] 171—174°C.

Further chromatographic fractions gave 1·17 g (56%) of a compound, m.p. 58—75°C, which on crystallization from cyclohexane melted at 72—82°C. Its ^1H NMR spectrum was identical with that of the mixture of stereoisomeric anilines *IIIb*.

N,N-Bis(3-chloro-2-hydroxypropyl)aniline (*IIIb*)

The title compound (17·4 g; 42%) was prepared from aniline (13·9 g; 0·15 mol) and 1-chloro-2,3-epoxypropane (30·4 g; 0·33 mol) in ethanol (15 ml) as described in the literature[12]. The product was separated by repeated crystallization into two portions: *a)* isomer A, m.p. 91—92°C, homogeneous according to ^{13}C NMR spectrum; and *b)* a mixture of diastereoisomers A and B (2 : 1, ^{13}C NMR), melting at 63—64°C. Isomer A: ^1H NMR spectrum (δ, C^2HCl_3): 7·09—7·27 (m, 2 H) H at $C_{(3)}$ and $C_{(5)}$ of the aromatic nucleus; 6·55—6·77 (m, 3 H) H at $C_{(2)}$, $C_{(4)}$ and $C_{(6)}$ of the aromatic nucleus; 4·66 (s, 2 H) 2 × OH, temperature dependent; 4·12 (bm, 2 H) 2 × CHO; 3·46 (d, $J = 4$, 4 H) 2 × CH_2Cl. ^{13}C NMR Spectrum (δ, C^2HCl_3): 46·6 CH_2Cl, 57·8 CH_2N;

69·4 CH—O; 112·7$C_{(2)}$ aromatic; 117·6 $C_{(4)}$ aromatic; 129·5 $C_{(3)}$ aromatic. ^{13}C NMR Spectrum of the isomer B (after subtraction of the spectrum of A) (δ, C^{2}HCl$_3$): 47·2 (CH$_2$Cl; 55·9 CH$_2$N; 69·0 CH—O; 114·4 $C_{(2)}$ aromatic; 118·5 $C_{(4)}$ aromatic; 129·5 $C_{(3)}$; 148·4 $C_{(1)}$ aromatic. IR Spectrum (CHCl$_3$, cm^{-1}): 3 580 ν(OH free); 3 370 ν(OH bonded).

N,N-Bis(3-chloro-2-hydroxypropyl)-4-methoxyaniline (*IIIc*)

This compound was prepared in the same way as described for *IIIb*; m.p. 111—112°C (reported[15] m.p. 109—111°C). According to ^{13}C NMR spectrum, the product was a 9 : 1 mixture of two isomers. ^{1}H NMR Spectrum (δ, C^{2}HCl$_3$): 6·61—6·84 (m, 4 H) H of aromatic ring; 4·04 (bm, 2 H) 2 × CH—O; 3·72 (s, 3 H) O—CH$_3$; 3·48 (d, $J = 4$) 2 × N—CH$_2$; 2·98—3·96 (m) 2 × × CH$_2$—Cl and 2 × OH (2·98—4·04 15 H total). ^{13}C NMR Spectrum of the predominating isomer (δ, C^{2}HCl$_3$): 47·1 CH$_2$Cl; 55·9 CH$_3$O; 58·7 CH$_2$N; 69·7 CH—O; 115·3 and 116·9 $C_{(2)}$, $C_{(3)}$, $C_{(5)}$, $C_{(6)}$ of aromatic nucleus; 153·5 $C_{(4)}$ aromatic.

cis- and *trans-*9-Methoxy-2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]quinolizine-2,6-diols (*If*)

A solution of *IIIc* (10 g; 32 mmol) and N,N-diethylaniline (8·9 g; 64 mmol) in bromobenzene (400 ml) was refluxed for 40 h. After cooling, the reaction mixture was shaken with 5% HCl (130 ml), the aqueous layer was extracted with benzene, made alkaline with 40% sodium hydroxide and N,N-diethylaniline was extracted with benzene. The aqueous layer was continuously extract-ed for 25 h, the ethereal extract was dried over magnesium sulfate and taken down. The obtained yellow crystals (4·35 g, 57%), m.p. 142—148°C, were a mixture of *cis-* and *trans-If* (thin-layer chromatography in benzene-methanol 9 : 1). ^{1}H NMR Spectrum (δ, hexadeuteriodimethyl sulfoxide): 6·26 (s, 2 H) H of aromatic nucleus; 4·8 (2 H 2 × OH) the shape and position of the signal are concentration and temperature dependent; 3·90 (bm, 2 H) 2 × CHO; 3·52 (s, 3 H) O—CH$_3$; 2·30—3·21 (m, 8 H) H at $C_{(1)}$, $C_{(3)}$, $C_{(5)}$, $C_{(7)}$. ^{13}C NMR Spectrum (δ, DMSO-d$_6$): isomer A (more populated): 37·0 $C_{(1)}$, $C_{(7)}$; 55·3 CH$_3$O; 56·9 $C_{(3)}$, $C_{(5)}$; 63·0 $C_{(2)}$, $C_{(6)}$; 113·1 $C_{(8)}$, $C_{(10)}$; 121·3 $C_{(10a)}$, $C_{(7a)}$; 135·9 $C_{(10b)}$; 151·2 $C_{(9)}$. Isomer B (minor amount): 36·5 $C_{(1)}$, $C_{(7)}$; 55·3 CH$_3$O; 56·3 $C_{(3)}$, $C_{(5)}$; 62·7 $C_{(2)}$, $C_{(6)}$; 113·1 $C_{(8)}$, $C_{(10)}$; 120·8 $C_{(7a)}$, $C_{(10a)}$; 135·9 $C_{(10b)}$; 150·9 $C_{(9)}$. IR Spectrum (KBr pellet, cm^{-1}): 3 320 ν(OH bonded). Mass spectrum (m/z, relative intensity, %): 235 (M$^+$) (78), 220 (M$^+$—15) (100). For $C_{13}H_{17}NO_3$ (235·3) calculated: 66·36% C, 7·28% H, 5·95% N; found: 66·67% C, 7·56% H, 6·20% N. Attempted chromatographic separation of the mixture on a column of silica gel resulted in decomposition of the material.

cis- and *trans-*2,3,6,7-Tetrahydro-1*H*,5*H*-benzo[*ij*]quinolizine-2,6-diols (*Ie*)

Analogously to the preparation of *If*, compound *IIIb* (5·56 g; 0·02 mol) was treated with N,N-di-ethylaniline (5·96 g; 0·04 mol) in bromobenzene (400 ml), affording a mixture of diols *Ie*(1·87 g; 45%), m.p. 136—142°C. For $C_{12}H_{15}NO_2$ (205·2) calculated: 70·22% C, 7·37% H, 6·82% N; found: 70·15% C, 7·36% H, 6·82% N. ^{1}H NMR Spectrum (δ, hexadeuteriodimethyl sulfoxide): 6·60 (d, $J = 6$, 2 H) H at $C_{(8)}$ and $C_{(10)}$; 6·20—6·42 (m, 1 H) H at $C_{(9)}$; 4·8 (bm, 2 H) temperature dependent, 2 × O—H; 3·65—4·04 (bm, 2 H) CH—O; 2·36—3·20 (m, 8 H) H at $C_{(1)}$, $C_{(3)}$, $C_{(5)}$, $C_{(7)}$. It Spectrum (KBr pellet): 3 280 cm^{-1} ν(OH bonded). Mass spectrum (m/z, relative intensity, %): 205 (M$^+$) (100), 204 (M$^+$—1) (14), 186 (M$^+$—19) (36). ^{13}C NMR Spectrum (δ, hexadeuterio-dimethyl sulfoxide): isomer A (principal isomer): 36·6 $C_{(1)}$, $C_{(7)}$; 56·4 $C_{(3)}$, $C_{(5)}$; 62·7 $C_{(2)}$, $C_{(6)}$; 116·2 $C_{(9)}$; 119·4 $C_{(7a,10a)}$, 127·3 $C_{(8)}$, $C_{(10)}$; 141·4 $C_{(10b)}$. Isomer B (minor isomer): 36·2 $C_{(1)}$, $C_{(7)}$; 56·0 $C_{(3)}$, $C_{(5)}$; 62·4 $C_{(2)}$, $C_{(6)}$; 115·7 $C_{(9)}$; 119·0 $C_{(7a)}$, $C_{(10a)}$; 127·2 $C_{(8)}$, $C_{(10)}$; 141·3 $C_{(10b)}$.

9-Methoxy-$1H,7H$-benzo[ij]quinolizine (*VIb*)

A mixture of *If* (0·50 g; 2 mmol) and finely ground potassium hydroxide (0·5 g) was heated at 1·3 Pa. A greenish liquid distilled at bath temperature 180—200°C. It solidified on cooling to give 0·28 g (66%) of yellow-green crystals, m.p. 42—46°C, relatively stable in a nitrogen atmosphere but rapidly turning dark on exposure to air, even at $-18°$C. For $C_{13}H_{13}NO$ (199·3) calculated: 78·36% C, 6·58% H, 7·03% N; found: 78·27% C, 6·74% H, 6·81% N. ^{1}H NMR Spectrum (δ, deuteriochloroform): 3·46—3·52 (m, 4 H) H at $C_{(1)}$ and $C_{(7)}$; 3·70 (s, 3 H) OCH$_3$; 4·50 (dt, $J_{2,3} = J_{5,6} = 8$, $J_{1,2} = J_{6,7} = 4$, 2 H) H at $C_{(2)}$, $C_{(6)}$; 5·96 (dt, $J_{2,3} = J_{5,6} = 8$, $J_{1,3} = J_{5,7} = 2$, 2 H) H at $C_{(3)}$, $C_{(5)}$; 6·33 (s, 2 H) H aromatic at $C_{(8)}$ and $C_{(10)}$. IR Spectrum (CCl$_4$, cm^{-1}): 1 670 ν(C=C).

$1H,7H$-Benzo[ij]quinolizine (*VIa*)

A mixture of *Ie* (0·20 g; 0·97 mmol) and ground potassium hydroxide (0·6 g) was heated at 1·6 kPa. At bath temperature 190—205°C a compound distilled which solidified immediately on the cooling finger to a bright yellow-crystalline compound, m.p. 48—50°C (115 mg; 70%). The product turned rapidly brown on the air. No elemental analysis was obtained since the product decomposed during the weighing. ^{1}H NMR Spectrum (δ, C^{2}HCl$_3$): 3·54 (m, 4 H) H at $C_{(1)}$, $C_{(7)}$; 4·58 (dt, $J_{2,3} = J_{5,6} = 8$, $J_{1,2} = J_{6,7} = 4$, 2 H) H at $C_{(2)}$, $C_{(6)}$; 5·94 (dt, $J_{2,3} = J_{5,6} = 8$, $J_{1,3} = J_{5,7} = 2$, 2 H) H at $C_{(3)}$, $C_{(5)}$; 6·62—6·90 (m, 3 H) H aromatic at $C_{(8)}$, $C_{(9)}$, $C_{(10)}$. IR Spectrum (CCl$_4$, cm^{-1}): 1 670 ν(C=C).

REFERENCES

1. Valenta Z., Deslongchamps P., Ellison R. A., Weisner K.: J. Amer. Chem. Soc. *86*, 2533 (1964).
2. Vorozhtsov N. N., Kutkevichus S. I.: Zh. Obshch. Khim. *27*, 2152 (1957).
3. Reissert A.: Ber. Deut. Chem. Ges. *24*, 841 (1891).
4. Mann F. G., Smith B. B.: J. Chem. Soc. *1951*, 1898.
5. Geschickter C. F., Pierce J. S., Reid E. E.: U.S. 3 056 792 (1962); Chem. Abstr. *58*, 9036 (1963).
6. I. G. Farbenind. A.-G.: Fr. 819 403 (1937); Chem. Abstr. *32*, 2144 (1938).
7. Hrehorowicz E.: Pr. Inst. Przem. Org. *2*, 313 (1970); Chem. Abstr. *78*, 57 906 (1973).
8. Gogte V. N., Salama M. A., Tilak B. D.: Tetrahedron *26*, 173 (1970).
9. Gogte V. N., More K. M., Tilak B. D.: Indian J. Chem. *12*, 327 (1974).
10. Merchant J. R., Choughuley S. V., Vaghani K. D.: Curr. Sci. *29*, 142 (1960); Chem. Abstr. *54*, 20 828 (1960).
11. McKelvey J. B., Webre B. G., Benerito R. R.: J. Org. Chem. *25*, 1424 (1960).
12. Triggle A. M., Triggle D. J.: J. Med. Chem. *10*, 285 (1967).
13. Pennington F. C., Tridle G. L., Boyd S. D., Bowersox W., Aniline O.: J. Org. Chem. *30*, 2801 (1965)
14. Pennington F. C., Martin L. J., Reid R. E., Lapp T. W : J. Org. Chem. *24*, 2030 (1959).
15. Everett J. L., Ross W. C. J.: J. Chem. Soc. *1949*, 1972.
16. Davies D. V., Savige W. E.: J. Chem. Soc. *1950*, 890.
17. Bunting J. W., Meathreal W. G.: Tetrahedron Lett. *1971*, 133.
18. Bunting J. W., Meathreal W. G.: Can. J. Chem. *50*, 917 (1972).
19. Coales R. M., Johnson E. F.: J. Amer. Chem. Soc. *93*, 4016 (1971).

20. Cook M. J., Katritzky A. R., Linda P., Tack R. D.: J. Chem. Soc., Perkin Trans. *2*, 1973, 1080.
21. Bamberger E., Williamson S.: Ber. Deut. Chem. Ges. *27*, 1458 (1894).
22. Glass D. B., Weissberger A.: Org. Syn. Coll. Vol. III, 504 (1955).
23. Trška P., Sklenář V., Hájek M.: Chem. Listy *77*, 874 (1983).

Translated by M. Tichý.