Quinoline Alkaloids. Part 26.[1] Pseudobases from the Reaction of Furoquinolinones with Methyl Iodide. A new Route to 3-(3-Methyl-2-oxobutyl)-quinolin-2(1*H*)-ones[2]

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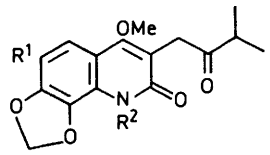
Reaction of 2-isopropyl-9-methylfuro[2,3-*b*]quinolin-4(9*H*)-ones (**5**) with methyl iodide gave salts believed to be pseudobase hydriodides (**7**), which were converted with base into 4-methoxy-1-methyl-3-(3-methyl-2-oxobutyl)quinolin-2(1*H*)-ones (**6**); the analogous pseudobase derivative (**12**) from the furoquinoline alkaloid skimmianine gives the furoquinolin-4-one isoskimmianine on further reaction with methyl iodide. The mechanisms of these reactions and of the acid-catalysed rearrangement of furoquinolinones (**5**) are discussed.

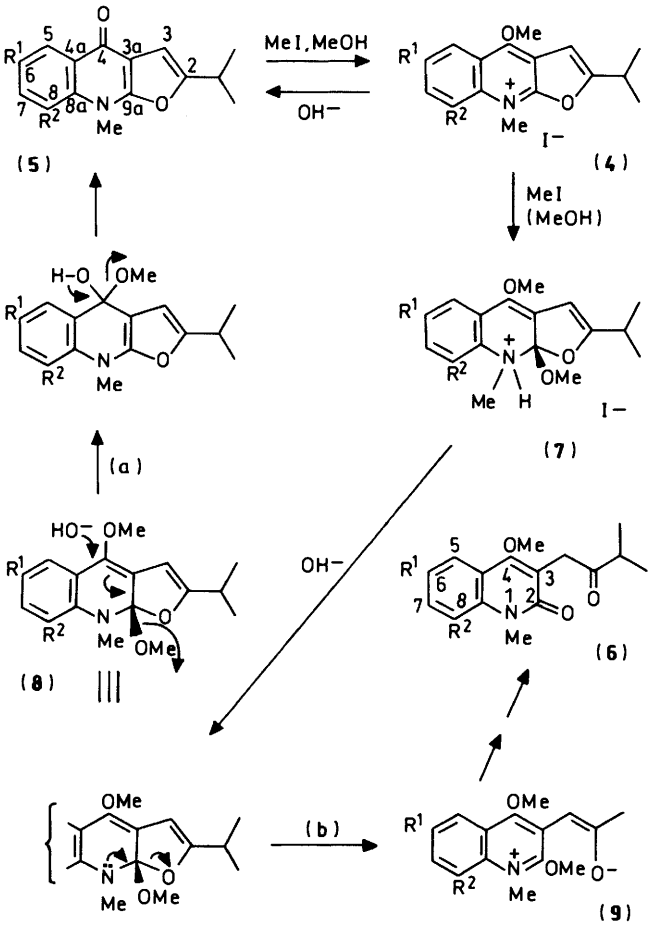
Several quinolin-2-one alkaloids containing a ketonic group in a hemiterpenoid side-chain occur in rutaceous plants. Thus, lunidonine (**1**) was obtained first from *Lunasia amara*[3] and was later isolated from *Ptelea trifoliata*;[4] *N*-demethyl-lunidonine (**2**)[4] and 6-methoxylunidonine (**3**)[5] also occur in the latter species. We planned to develop a general preparation of these



(**1**) R^1 = H, R^2 = Me
(**2**) R^1 = R^2 = H
(**3**) R^1 = OMe, R^2 = Me

compounds from furoquinolinium salts (**4**), in the expectation that reaction of hydroxide ion at C-9a would result in cleavage of the furan ring. The 4,6,8-trimethoxyfuroquinolinium iodide (**4a**), m.p. 184—189 °C, was obtained by refluxing the quinolin-4-one (**5a**) with methyl iodide in methanol, but treatment of the quaternary salt with sodium hydroxide in aqueous methanol gave back the quinolin-4-one (**5a**) almost quantitatively; apparently cleavage of the 4-methoxy group occurred in preference to nucleophilic attack at C-9a. When the furoquinolinone (**5a**) was refluxed in methyl iodide alone a precipitate formed slowly; crystallisation of the product from methanol–ether gave a new salt, m.p. 141—143 °C, which on reaction with base gave back the quinolin-4-one (**5a**) (25%) and the required ketone (**6a**) (60%). The structure of the latter compound was indicated by i.r. absorption at 1 715 (ketonic CO) and 1 658 cm^{-1} (quinolin-2-one CO) and by the ^1H n.m.r. spectrum. Reaction of the furoquinolin-4-ones (**5b**) and (**5c**) with methyl iodide gave salts (**7b**) and (**7c**), respectively, but increasing time of reflux was required in the series (**5a**) ⟶ (**5b**) ⟶ (**5c**). Compounds (**7b**) and (**7c**) were converted into ketones (**6b**) (81%) and (**6c**) (70%), respectively, by treatment with sodium hydroxide. Although the synthetic objectives were obtained in this way it was clearly of interest to examine the structures and properties of the new salts.

In the case of the compound formed by reaction of the 6,8-dimethoxyfuroquinolin-4-one (**5a**) with methyl iodide, n.m.r. spectroscopy indicated that the most probable structure (**7a**) is that of a hydriodide salt of a pseudobase.[6] Thus, in the ^1H n.m.r. spectrum (Table 1), three-proton singlets at δ 4.74, 4.09, and 3.96 were assigned to methoxy groups at C-4, C-8, and C-6, respectively and confirmed by substantial n.O.e. (20—23% enhancement) arising by interaction with protons at C-3, C-7, and C-5, respectively. A three-proton singlet at δ 4.67 is due to the $\overset{+}{N}HMe$ group [compared with 3.84 for $=\overset{+}{N}(Me)-$ in methiodide (**4a**)] and a high-field resonance at 3.59, which is



a; R^1 = R^2 = OMe
b; R^1 = OMe, R^2 = H
c; R^1 = R^2 = H
d; R^1 = H, R^2 = OMe

Scheme 1.

absent from the spectrum of the methiodide, is attributed to the methoxy group at C-9a. The ^{13}C n.m.r. spectrum (see Experimental section) supports structure (**7a**) and was assigned completely on the basis of off-resonance decoupling at 0 and 8 p.p.m. and by comparison with the ^{13}C n.m.r. spectra of related hemiterpenoid quinolines.[7] The assignment of the C-2 resonance was apparent from long-range couplings to protons at C-3 and C*H*Me_2. A key feature of the ^{13}C spectrum is the

Table 1. ^{1}H N.m.r. chemical shifts (δ) of compounds (**4a**) and (**7**) in $CDCl_3$ and (**12**) in CD_3OD

Compound	Arom. 5-H	Other ArH	–CH=	9a-OMe	4-OMe	6-OMe	8-OMe	$\overset{+}{N}$Me	$CHMe_2$	$CHMe_2$
(**7a**)	7.25	7.01	7.37	3.59	4.74	3.96	4.09	4.67	3.22	1.25
(**4a**)	7.34	7.34	7.52		4.59	3.97	4.08	3.84	3.10	1.40
(**7b**)	7.80	8.30, 7.60	7.30	3.60	4.70	3.94		4.60	3.30	1.40
(**7c**)	8.55—7.50		7.40	3.60	4.75			4.52	3.30	1.43
(**12**)	7.75	8.32	8.10, 7.70	3.50	4.70		4.10	4.60*		

* Also a signal at 4.00 (7-OMe).

resonance at δ_C 107.1 (C-9a), which shows long-range coupling to the olefinic proton at C-3 and has a chemical shift comparable in value with that observed for quaternary carbons of ortho esters (*e.g.* δ_C 112.5 for triethyl orthoformate[8] and δ_C 119.0 for the orthoacetate group of the terpenoid phragmalin[9]) when allowance is made for reduced deshielding by a nitrogen compared with an oxygen atom. Salts (**7b**) and (**7c**) derived from other furoquinolinones have similar ^{1}H n.m.r. spectra (Table 1).

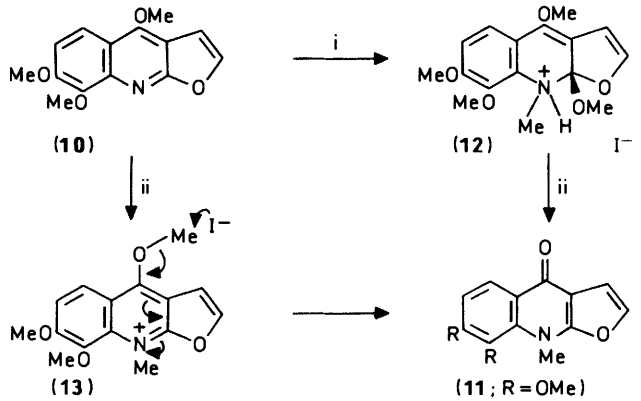
When tested with silver nitrate solution, compound (**7a**) was shown to contain iodide ion. Elemental analysis of the salts gave a value for the percentage of carbon ~2% higher than required by structures (**7a**—**c**), perhaps indicating partial loss of hydrogen iodide.

When the methiodide (**4a**) was refluxed with methyl iodide for 24 h, partial conversion into the pseudobase derivative (**7a**) was shown by t.l.c. to occur. The normal methiodides (**4**) are therefore likely to be intermediates in the formation of compounds (**7**) from furoquinolinones (**5**); if some methanol is formed by hydrolysis of methyl iodide during the prolonged reaction, a possible mechanism involves addition of methanol to the $-\overset{+}{N}(Me)=C$ bond of the methiodides (**4**) favoured by the aprotic medium, followed by transfer of a proton from oxygen to nitrogen. A possible route to the furoquinolin-4-ones (**5**) then involves addition of hydroxide ion at C-4 of pseudobases (**8**), followed by elimination of the methoxy group at this centre [route (a)] (Scheme 1). Alternatively, splitting of the C–O bond of compounds (**8**) [route (b)] can result after subsequent hydrolysis of the 2-methoxyquinoline derivative (**9**) in conversion into ketones (**6**).

Since the reactions of isopropylfuroquinolin-4-ones (**5**) with methyl iodide were reminiscent of the traditional method of converting furoquinoline alkaloids, *e.g.* (**10**), into the isoalkaloids, *e.g.* (**11**), by heating at 80 °C in a sealed tube with methyl iodide,[10] we refluxed skimmianine (**10**) with methyl iodide (Scheme 2). A pseudobase hydriodide structure (**12**) was assigned to the crystalline product on the basis of the ^{1}H n.m.r. spectrum (Table 1); reaction of this compound with methyl iodide at 80 °C gave the *N*-methylfuroquinolin-4-one isoskimmianine (**11**; R = OMe) (62% yield). The iso rearrangement is usually regarded as occurring through a methiodide such as (**13**), as shown in Scheme 2, but the present results indicate that a pseudobase derivative may also participate.

Dehydration of Dihydro(hydroxypropan-2-yl)furoquinolin-4-ones.—Isopropylfuroquinolin-4-ones (**5**) that were required as starting compounds for this study were prepared by dehydration of the corresponding dihydro(hydroxypropan-2-yl)furoquinolin-4-ones (**14**), as described previously.[11] Since, however, the method was found to be more complex than anticipated, a discussion is warranted.

Reaction of the 6,8-dimethoxy derivative (**14a**) with conc. sulphuric acid for 1 h gave the furoquinolinone (**5a**) (53%),



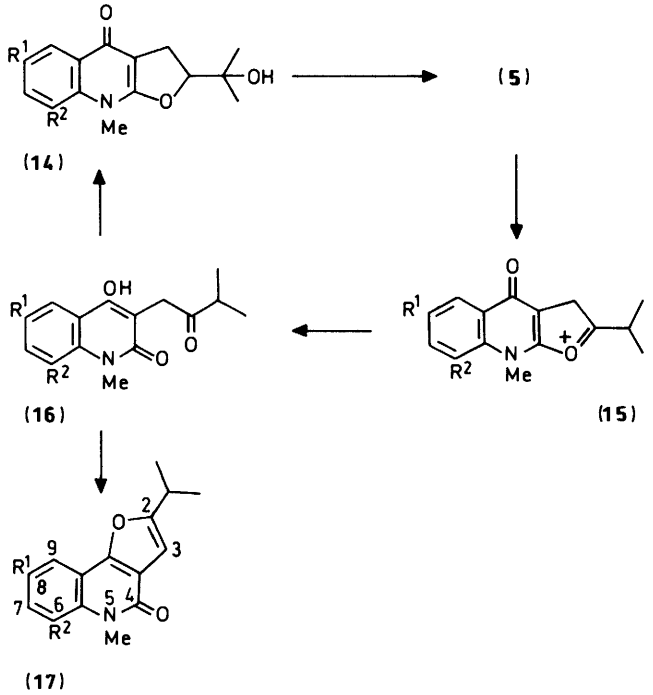
Scheme 2. *Reagents and conditions:* i, MeI, reflux; ii, MeI, 80 °C

but in this case an isomeric compound was also isolated, in 20% yield. The minor product was shown to be the angular quinolinone (**17a**) by the i.r. absorption at 1 660 cm^{-1} and by the absence in the ^{1}H n.m.r. spectrum of a signal lower than δ 6.99; by contrast, the linear quinolinone (**5a**) showed in the ^{1}H n.m.r. spectrum a doublet at δ 7.65, which is attributed to the proton at C-5 adjacent to the carbonyl group. Similar dehydration of dihydro(hydroxypropan-2-yl)furoquinolin-4-one (**14c**) (isoplatydesmine) and its 6-methoxy derivative (**14b**) also gave the corresponding linear and angular furoquinolinones that were identified by i.r. and ^{1}H n.m.r. spectroscopy (Table 2).

The proportion of the two isomers obtained depended on the reaction time. Thus, in the case of dehydration of the 6-methoxyquinolin-4-one (**14b**), the yields of linear furoquinolinone (**5b**) and angular furoquinolinone (**17b**) after treatment with conc. sulphuric acid for 2 min were 85 and 14%, respectively; after 30 min 42 and 38%; and after 1 h 20 and 75%. These results suggest that the linear compounds (**5**) undergo acid-catalysed rearrangement to the angular isomers (**17**). In support of this proposal we found that reaction of the linear 6,8-dimethoxyfuroquinolinone (**5a**) with conc. sulphuric acid for 2 h gave a product that was shown by ^{1}H n.m.r. spectroscopy to contain the linear quinolinone (**5a**) and the angular quinolinone (**17a**) in the ratio 2:1. The linear compound (**5a**) was unaffected by sodium hydroxide, indicating that the base used in the work-up procedure was not responsible for the rearrangement. A plausible mechanism (Scheme 3) involving formation of protonated enol ethers (**15**), cleavage to the ketones (**16**), and then cyclisation to the more stable angular furoquinolinones (**17**) is analogous to the mechanism proposed[12] for rearrangement of the furoquinolinone isodictammine (**11**; R = H) with polyphosphoric acid. Reaction of the 8-methoxyquinolin-4-one (**5d**) with hydrobromic acid at 75 °C gave the isopropylfuroquinolinone (**17d**) in 35% yield, apparently by a similar route.

Table 2. ^{1}H N.m.r. chemical shifts (δ) of compounds (**5**) and (**17**) in $CDCl_3$

Compound	Arom. 5-H or 9-H	Other ArH	-CH=	OMe	NMe	C*H*Me$_2$	CH*Me*$_2$
(**5a**)	7.65	6.79	6.65	4.15, 3.95	3.95	3.15	1.36, 1.27
(**17a**)	6.99	6.62	6.65	3.97, 3.90	3.93	3.12	1.44, 1.30
(**5b**)	8.05	7.50—7.30	6.70	3.95	3.95	3.10	1.35, 1.25
(**17b**)	7.30	7.20—7.10	6.62	3.70	3.89	3.10	1.40, 1.30
(**5c**)	8.50	7.65—7.05	6.60		3.78	2.95	1.35, 1.23
(**17c**)	7.96	7.55—7.20	6.65		3.77	3.14	1.43, 1.31
(**17d**)		7.70—6.88	6.64	4.00	3.91	3.12	1.36



a; $R^1 = R^2 = OMe$
b; $R^1 = OMe$, $R^2 = H$
c; $R^1 = R^2 = H$
d; $R^1 = H$, $R^2 = OMe$

Scheme 3.

Experimental

^{1}H N.m.r. spectra were determined with a Perkin-Elmer R12 (60 MHz) or R32 (90 MHz) spectrometers with tetramethylsilane as internal standard, i.r. spectra with a Perkin-Elmer 457 spectrophotometer, and mass spectra with an AE1 MS9 instrument.

Dehydration of 2-(1-*Hydroxy*-1-*methylethyl*)-9-*methyl*-2,3-*dihydrofuro*[2,3-b]*quinolin*-4(9H)-*ones* (**14**).—A solution of the dihydrofuroquinolin-4-one (**14a**)[13] (0.49 g) in conc. sulphuric acid (5 ml) was kept for 1 h, diluted with water (20 ml), made basic with 2M-aqueous sodium carbonate, and extracted with chloroform. Evaporation of the solvent and crystallisation from methanol–ether gave 2-*isopropyl*-6,8-*dimethoxy*-9-*methylfuro*[2,3,b]*quinolin*-4(9H)-*one* (**5a**) (0.15 g), m.p. 140—142 °C; $\nu_{max.}$(KBr) 1 640 cm^{-1} (C=O) (Found: C, 67.3; H, 6.1; N, 4.4. $C_{17}H_{19}NO_4$ requires C, 67.7; H, 6.35; N, 4.6%). Evaporation of the methanol–ether solution and preparative t.l.c. (p.l.c.) of the residue on silica with chloroform gave a further quantity of the furoquinolin-4-one (**5a**) (0.095 g, total yield 53%), R_F 0.16, and 2-*isopropyl*-6,8-*dimethoxy*-5-*methylfuro*[3,2-c]-*quinolin*-4(5H)-*one* (**17a**) (0.09 g, 20%) (from ethyl acetate), m.p. 129—130 °C; $\nu_{max.}$(KBr) 1 660 cm^{-1} (C=O) (Found: C, 67.5; H, 6.2; N, 4.9%). After treatment with conc. sulphuric acid for 2 h, compound (**5a**) (50 mg) was shown by t.l.c. and ^{1}H n.m.r. spectroscopy to be converted into a mixture of (**5a**) and (**17a**) in the ratio 2:1.

Application of the procedure to the dihydrofuroquinolin-4-one (**14b**)[13] gave 2-*isopropyl*-6-*methoxy*-9-*methylfuro*[2,3-b]-*quinolin*-4(9H)-*one* (**5b**) (from ethyl acetate), m.p. 187—189 °C; $\nu_{max.}$(KBr) 1 630 cm^{-1} (Found: C, 70.0; H, 6.4; N, 4.9. $C_{16}H_{17}NO_3$ requires C, 70.8; H, 6.3; N, 5.2%), and the angular furoquinolin-4-one (**17b**) (from ethyl acetate), m.p. 181 °C; $\nu_{max.}$ 1 660 cm^{-1}, which was not characterised fully.

Dehydration of the dihydrofuroquinolin-4-one (**14c**)[14] with conc. sulphuric acid for 3 min gave 2-*isopropyl*-9-*methylfuro*-[2,3-b]*quinolin*-4(9H)-*one* (**5c**) (83%), m.p. 145—146 °C (from ethyl acetate); $\nu_{max.}$(KBr) 1 630 cm^{-1} [Found: M^+, 241.1087 (58.7%). $C_{15}H_{15}NO_2$ requires *M*, 241.1103] and 2-isopropyl-5-methylfuro[3,2-*c*]quinolin-4(5*H*)-one (**17c**) (25%), m.p. 112—118 °C, identical (^{1}H n.m.r. and i.r.) with an authentic sample.[1]

[*With Kevin J. James*]. A mixture of dihydrofuroquinolin-4-one (**14d**) [(±)-balfourodine][15] (6.24 g) in 48% hydrobromic acid (10 ml) was heated at 75 °C for 4 h and diluted with water (20 ml). After neutralisation, extraction with chloroform gave an oil, which was chromatographed on alumina. Elution with light petroleum (b.p. 40—60 °C)–ether (3:2) gave 2-*isopropyl*-6-*methoxy*-5-*methylfuro*[3,2-c]*quinolin*-4(5H)-*one* (**17d**) as needles (0.079 g, 35%), m.p. 75 °C; $\nu_{max.}$(KBr) 1 665 cm^{-1} (Found: C, 70.8; H, 6.4; N, 5.2. $C_{16}H_{17}NO_3$ requires C, 70.8; H, 6.3; N, 5.2%). The ^{1}H n.m.r. data for compounds (**5**) and (**17**) are given in Table 2.

Reactions of the Furoquinolin-4-*ones* (**5**) *with Methyl Iodide*.—(*a*) A solution of the furoquinolin-4-one (**5a**) (70 mg) in methanol (10 ml) and methyl iodide (2 ml) was refluxed for 12 h and evaporated. Crystallisation of the residue from methanol–ether gave 2-*isopropyl*-4,6,8-*trimethoxy*-9-*methylfuro*[2,3-b]-*quinolinium iodide* (**4a**) (78 mg) m.p. 184—189 °C (Found: C, 49.1; H, 5.25; N, 3.3. $C_{18}H_{22}INO_4$ requires C, 48.8; H, 5.0; N, 3.2%). The methiodide (40 mg) in 2M-methanolic sodium hydroxide was kept for 16 h to give the furoquinolin-4-one (**5a**) (26 mg, 95%).

(*b*) The furoquinolin-4-one (**5a**) (75 mg) in methyl iodide (5 ml) was refluxed for 24 h. Evaporation and crystallisation of the residue from methanol–ether gave the *pseudobase hydriodide* (**7a**) (64 mg), m.p. 141—143 °C; δ_C($CDCl_3$) 165.1 (C-2), 161.2 (C-4), 158.4 (C-6), 157.8 (C-8a), 152.2 (C-8), 122.8 (C-3a), 122.0 (C-4a), 107.1 (C-7), 107.1 (C-9a), 100.9 (C-3), 95.3 (C-5), 61.9 (4-OMe), 57.2 (8-OMe), 56.1 (6-OMe), 54.0 (9a-OMe), 40.3 ($\overset{+}{N}$Me), 28.2 (*C*HMe$_2$), and 20.3 (CH*Me*$_2$) (Found: C, 50.0; H, 5.4; N, 2.8. $C_{19}H_{26}INO_5$ requires C, 48.1; H, 5.5; N, 2.9%).

The quinolinium iodide (**4a**) was refluxed with methyl iodide

for 24 h; t.l.c. of the product on silica with chloroform-methanol (10:1) showed the presence of the pseudobase salt (**7a**), R_F 0.2.

The furoquinolin-4-one (**5b**) was refluxed with methyl iodide for 48 h to give the *pseudobase hydriodide* (**7b**) as needles, m.p. 160—162 °C (from methanol–ether) (Found: C, 50.6; H, 5.5; N, 3.3. $C_{18}H_{24}INO_4$ requires C, 48.0; H, 5.3; N, 3.1%). After refluxing with methyl iodide for 4 days, the furoquinolin-4-one (**5c**) gave the *salt* (**7c**), m.p. 131—135 °C (from methanol–ether) (Found: C, 51.3; H, 4.0; N, 3.8. $C_{17}H_{22}INO_3$ requires C, 49.2; H, 5.3; N, 3.3%).

Reactions of Pseudobase Salts (**7**) *with Sodium Hydroxide*.—A solution of compound (**7a**) (100 mg) in 2M-methanolic sodium hydroxide (14 ml) was kept for 8 h. The products were obtained by evaporation of methanol, addition of water, and extraction with chloroform; p.l.c. on silica with chloroform–methanol (10:1) gave 4,6,8-*trimethoxy*-1-*methyl*-3-(3-*methyl*-2-*oxobutyl*)-*quinolin*-2(1H)-*one* (**6a**) as needles (42 mg, 60%), R_F 0.91; m.p. 92—98 °C (from cyclohexane); $\nu_{max.}$ 1 715 ($CH_2C{=}O$) and 1 658 cm^{-1} (NC=O); $\delta_H(CDCl_3)$ 6.95 (1 H, d, ArH), 6.74 (1 H, d, ArH), 3.90 (14 H, s, 3 × OMe, NMe, and CH_2), 2.88 (1 H, m, $CHMe_2$), and 1.2 (6 H, d, $CHMe_2$) (Found: C, 64.7; H, 6.8; N, 3.8. $C_{18}H_{23}NO_5$ requires C, 64.8; H, 6.95; N, 4.2%); and then the furoquinolin-4-one (**5a**) (17 mg, 25%).

Application of the procedure to compound (**7b**) (113 mg) gave 4,6-*dimethoxy*-1-*methyl*-3-(3-*methyl*-2-*oxobutyl*)*quinolin*-2(1H)-*one* (**6b**) as prisms (79 mg, 81%), R_F 0.46; m.p. 86—87 °C (from cyclohexane); $\nu_{max.}$ 1 700 and 1 640 cm^{-1}; $\delta_H(CDCl)$ 7.82 (3 H, br s, ArH), 3.90 (s) and 3.70 (s) (11 H, 2 × OMe, NMe, and CH_2), 2.90 (1 H, m, $CHMe_2$), and 1.20 (6 H, d, $CHMe_2$) (Found: 67.2; H, 6.85; N, 4.8. $C_{17}H_{21}NO_4$ requires C, 67.3; H, 7.0; N, 4.6%); and the furoquinolin-4-one (**5b**) (10 mg, 12%).

Application of the procedure to compound (**7c**) (100 mg) gave 4-*methoxy*-1-*methyl*-3-(3-*methyl*-2-*oxobutyl*)*quinolin*-2(1H)-*one* (**6c**) as needles (46 mg, 70%), R_F 0.52; m.p. 80—81 °C (from cyclohexane); $\nu_{max.}$ 1 705 and 1 640 cm^{-1}; $\delta_H(CDCl_3)$ 7.9—7.1 (4 H, m, ArH), 3.90 (3 H, s, OMe), 3.85 (2 H, s, CH_2), 3.70 (3 H, s, NMe), 7.85 (1 H, m, $CHMe_2$), and 1.22 (6 H, d, $CHMe_2$) (Found: C, 70.5; H, 7.4; N, 5.3. $C_{16}H_{19}NO_3$ requires C, 70.3; H, 7.0; N, 5.1%); and the furoquinolin-4-one (**5c**) (15 mg, 25%).

Reactions of Skimmianine (**10**).—A solution of skimmianine (**10**) (50 mg) in methyl iodide was refluxed for 6 h and evaporated; crystallisation from methanol–ether gave the *pseudobase hydriodide* (**12**) as needles (33 mg), m.p. 166—167 °C (Found: C, 49.8; H, 5.0; N, 3.8. $C_{16}H_{20}INO_5$ requires C, 44.3; H, 4.6; N, 3.2%). The salt (**12**) (30 mg) was heated in a sealed tube with methyl iodide at 80 °C for 5 h. Evaporation of methyl iodide and p.l.c. of the residue on silica with chloroform–methanol (10:1) gave isoskimmianine (**11**; R = OMe) (12 mg, 67%), m.p. 188—190 °C (lit.,[16] 189—190 °C); $\delta_H(CDCl_3)$ 8.33 (1 H, d, 5-H), 7.03 (1 H, d, 6-H), 7.23 (1 H, d) and 7.20 (1 H, d) (2- and 3-H), 4.17 (3 H, s), 3.99 (3 H, s), and 3.86 (3 H, s) (2 × OMe and NMe).

Acknowledgements

We thank Drs. N. J. McCorkindale and D. S. Rycroft for the ^{13}C n.m.r. spectroscopic data, and the Department of Education for Northern Ireland for a postgraduate studentship (to J. L. G.).

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Received 19*th September* 1988; *Paper* 8/03602K