Quinoline Alkaloids. Part XV.[1] Reactions of a Quinoline Isoprenyl Epoxide with Hydride Reagents. Asymmetric Synthesis and Stereochemistry of Lunacridine and Related *Lunasia* Alkaloids

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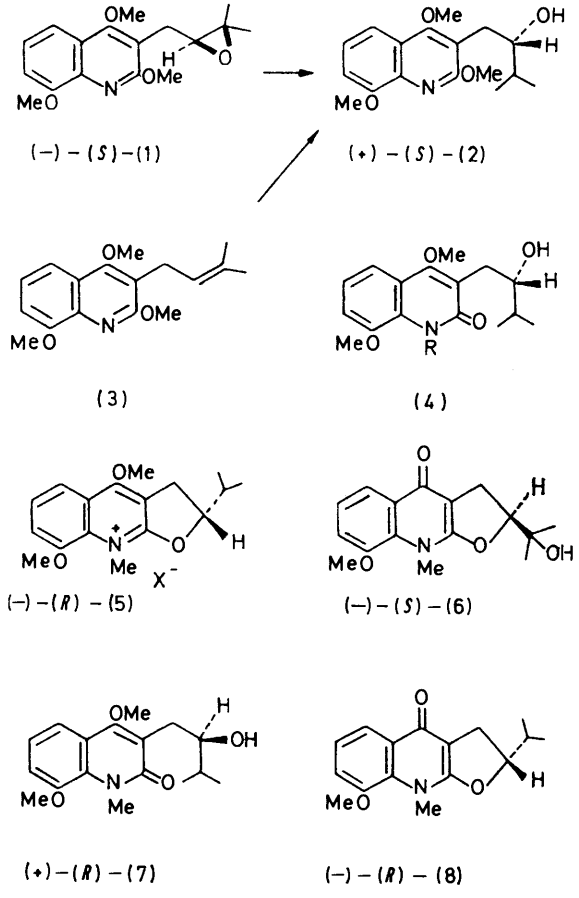
Reaction of (−)-3-(2,3-epoxy-3-methylbutyl)-2,4,8-trimethoxyquinoline, of known configuration, with diborane–lithium borohydride or with lithium aluminium hydride–aluminium chloride gave a secondary alcohol which was converted into (−)-lunacridine. The stereochemistry of *Lunasia* alkaloids is discussed. Reductive displacement of 4-methoxy-groups in 2,4,8-trimethoxyquinoline derivatives occurs with lithium aluminium hydride. Rearrangement products obtained from the quinoline epoxide with mixed hydrides and with acid are described.

ISOPRENOID epoxides have been shown to be intermediates in the cyclisation of squalene to triterpenes and steroids,[2] and the role of biological epoxidation in the formation of other natural isoprenoids has been discussed,[3,4] although in these cases *in vivo* evidence is not available. In the 3-isoprenylquinoline series, an *in vitro* model, involving oxidation of 3-isoprenyl-2-quinolones with optically active peroxy-acids resulted in the asymmetric synthesis of hydroxyisopropyldihydrofuranoquinoline alkaloids, such as (6), and the pyranoisomers, but in these reactions the intermediate epoxides cyclised rapidly through the 2-quinolone oxygen atom and were not isolated.[1,4] Application of the reaction to 2,4-dimethoxyquinoline derivatives leading to an asymmetric synthesis of the isoprenyl diol alkaloid, orixine, required preparation of epoxides such as (1).[5] The biosynthetic interest and ready availability of these optically active epoxides led us to examine their reactions, and we now report a study of the reduction of the quinoline epoxide (1), $[\alpha]_D$ −0·84°, obtained by reaction of the isoprenylquinoline (3) with (+)-peroxycamphoric acid and shown previously to have the (*S*)-configuration.[1]

Asymmetric Synthesis of Lunacridine and Stereochemistry of Lunasia *Alkaloids.*—The hydroxyisoprenylquinoline, lunacridine, and the related compounds lunasine, lunacrine, and hydroxylunacridine were isolated from *Lunasia* species, and the structures of the alkaloids but not their absolute stereochemistry were determined.[6] (±)-Lunacridine [as (7)] was synthesised by hydroboration of a 3-isoprenyl-2-quinolone,[7] and we have now carried out an asymmetric synthesis. Brown and Yoon [8] showed that borohydride-catalysed reaction of diborane with trisubstituted epoxides favoured anti-Markovnikov ring opening, and application of the reaction to the epoxide (1) furnished the secondary alcohol (2) (67%), $[\alpha]_D$ +0·85°. The structure of the compound was indicated by its n.m.r. spectrum (Table) and was verified by preparation of the racemate from the isoprenylquinoline (3) by reaction with diborane followed by treatment with hydrogen peroxide. The accepted mechanism of the Brown–Yoon reaction implies retention



of configuration at the chiral centre, and the (+)-secondary alcohol accordingly is assigned the (*S*)-configuration (2). Selective cleavage of the 2-methoxy-group with hydrogen chloride then afforded the corresponding 2-quinolone (4; R = H) (95%), $[\alpha]_D$ −0·37°. Reaction of the 2-quinolone (4; R = H) with diazomethane furnished the trimethoxyquinoline (2) (47%)

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[2] E. J. Corey, W. E. Russey, and P. R. O. De Montellano, *J. Amer. Chem. Soc.*, 1966, **88**, 4750, 4751; E. E. Van Tamelen, J. D. Willett, R. B. Clayton, and K. E. Lord, *ibid.*, p. 4752.
[3] 'Recent Developments in the Chemistry of Natural Phenolic Compounds,' ed. W. D. Ollis, Pergamon, Oxford, 1961, pp. 36, 83.
[4] R. M. Bowman, J. F. Collins, and M. F. Grundon, *Chem. Comm.*, 1967, 1131.
[5] R. M. Bowman and M. F. Grundon, *J. Chem. Soc.* (*C*), 1967, 2368.
[6] S. Goodwin and E. C. Horning, *J. Amer. Chem. Soc.*, 1959, **81**, 1908; H. C. Beyerman and R. W. Rooda, *Proc. k. ned. Akad. Wetenshap.*, 1959, *B*62, 427; 1960, *B*63, 154; J. R. Price, *Austral. J. Chem.*, 1959, **12**, 458.
[7] E. A. Clarke and M. F. Grundon, *J. Chem. Soc.*, 1964, 438.
[8] H. C. Brown and N. M. Yoon, *J. Amer. Chem. Soc.*, 1968, **90**, 2686.

and the *N*-methyl-2-quinolone (4; R = Me) (32%), $[\alpha]_D$ −0·19°. The (−)-enantiomer predominating in the latter product must have the (*S*)-configuration shown, since the two reaction steps from the (*S*)-2,4-dimethoxyquinoline (2) do not involve the chiral centre. The alkaloid (+)-lunacridine, accordingly, is the (*R*)-enantiomer (7). This work and known transformations lead to an assignment of stereochemistry to other *Lunasia* alkaloids. Thus, the quaternary alkaloid more highly substituted alcohol,[12] and in the reaction with the epoxide (1), we expected to obtain the tertiary alcohol (9; R = OMe). In practice, the 2,8-dimethoxyquinoline (9; R = H) was isolated (63%), and the dimethoxy-compound (9; R = OMe), which was prepared for comparison by oxymercuration of the isoprenylquinoline (3), was not detected. The structure of the dimethoxyquinoline (9; R = H) was established by spectroscopy. Thus, the n.m.r. spectra of the tertiary

N.m.r. spectral assignments (τ values; 100 MHz)

Compound	Solvent	Arom. 3-H	Arom. 4-H	ArC*H*$_2$	>C*H*·OH	ArCH$_2$·C*H*$_2$	>C*H*Me$_2$	OMe	>CMe$_2$
(2)	CCl_4			7·23 (q)	6·44 (m)		8·35 (m)	5·94 (s) 6·07 (s) 6·11 (s)	9·03 (d)
(9; R = OMe)	$(CD_3)_2SO$			7·22 (m)		8·12 (m)		5·96 (s) 6·05 (s) *	8·84 (s)
(9; R = H)	$(CD_3)_2SO$		2·0 (s)	7·24 (m)		8·24 (m)		5·97 (s) 6·05 (s)	8·83 (s)
2,8-Dimethoxyquinoline	CCl_4	3·16 (d, *J* 9 Hz)	2·14 (d, *J* 9 Hz)					5·92 (s) 6·00 (s)	
4,8-Dimethoxyquinoline [a]	$CDCl_3$	3·26 (d, *J* 5 Hz)						5·94 (s) 6·00 (s)	
(10) [b]	$CDCl_3$			6·88 (s)				5·86 (s) 5·95 (s) 6·06 (s)	9·06 (s)
(11)	$CDCl_3$			6·12 (d)			7·22 (m)	5·92 (s) 5·96 (s) 6·08 (s)	8·86 (d)
(12) [c]	$CDCl_3$			6·95 (q)	5·60 (t)			5·84 (s) 5·94 (s) 6·00 (s)	

* Integration indicates two methoxy-groups.

[a] Arom. 2-H at 1·25 (d, *J* 5 Hz). [b] C*H*$_2$·OH at τ 7·22 (s). [c] =C(Me)− at τ 8·12 (s) and =CH$_2$ at τ 5·04 and 5·18.

(−)-lunasine (5) reacts with base to give (+)-lunacridine (7), and on heating furnishes (−)-lunacrine (8), by reactions in which the chiral centre is not involved.[6] The three alkaloids, therefore, have the (*R*)-configuration. The fourth alkaloid of this type isolated from *Lunasia* species, (−)-hydroxylunacrine was shown by ozonolysis to be the (*S*)-enantiomer (6).[9]

The biosynthesis of hydroxyisopropylfuroquinoline alkaloids, such as (6), occurs apparently by oxidative cyclisation of 3-isoprenyl-2-quinolones,[10] but the biosynthetic route to isopropylfuro-derivatives of the lunacrine and lunasine type is unknown. Direct cyclisation of a 3-isoprenyl-2-quinolone has been suggested,[11] and other possibilities include dehydration of an hydroxyisopropyl derivative, *e.g.* (6), to an endo- or an exo-cyclic olefin followed by reduction of the double bond. The work described here does not support the involvement of a terminal olefin as an intermediate in the biosynthesis of lunacrine in *Lunasia* species, since the requisite tertiary alcohol, (*S*)-hydroxyluncrine would be expected to furnish (*S*)-lunacrine and not the (−)-(*R*)-enantiomer occurring in *Lunasia*.

Reduction with Lithium Aluminium Hydride.—Lithium aluminium hydride usually attacks trisubstituted epoxides at the secondary centre with the formation of the alcohols (9; R = OMe) and (9; R = H) (Table) were essentially identical in the τ 7—9 region, but the latter compound showed one less resonance in the methoxy-region and a singlet at τ 2, characteristic of a C-4 proton in a quinoline (see later). The mass spectrum displays a parent ion peak at *m/e* 275, a base peak at 160, probably arising by fragmentation of the side chain and loss of the 8-methoxy-group (*cf.* 8-methoxyquinoline), and a major fragment at 59 ($Me_2C{=}OH^+$).

The unusual reaction of the trimethoxyquinoline epoxide (1) with lithium aluminium hydride thus involves selective displacement of the 4-methoxy-group; the greater reactivity of 4-substituents in 2,4-disubstituted quinolines in nucleophilic substitution reactions has been observed previously.[13] Reductive displacement of the 4-methoxy-group in the trimethoxy-tertiary alcohol (9; R = OMe) also occurs with lithium aluminium hydride, and 2,4,8-trimethoxyquinoline behaves similarly yielding a dimethoxyquinoline. Formulation of the product as 2,8-dimethoxyquinoline was indicated by the presence in the n.m.r. spectrum of a doublet at τ 2·1 (H-4) and by its lack of identity with the isomeric 2,4- and 4,8-dimethoxyquinolines. The latter compound was prepared by hydrogenation of 2-chloro-4,8-dimethoxyquinoline. From the n.m.r. spectrum it appears that H-2 (doublet at τ 1·25) experienced more

[9] J. F. Collins and M. F. Grundon, *Chem. Comm.*, 1969, 1078; *J.C.S. Perkin I*, 1973, 161.

[10] J. F. Collins and M. F. Grundon, *Chem. Comm.*, 1969, 621.

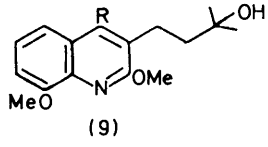
[11] *E.g.* T. A. Geissman and D. H. G. Crout, 'Organic Chemistry of Secondary Plant Metabolism,' Freeman, Cooper and Co., San Francisco, 1969, p. 482.

[12] L. W. Trevoy and W. G. Brown, *J. Amer. Chem. Soc.*, 1949, **71**, 1675; E. L. Eliel and J. P. Freeman, *ibid.*, 1952, **74**, 923; E. L. Eliel and M. Perick, *ibid.*, 1960, **82**, 1362.

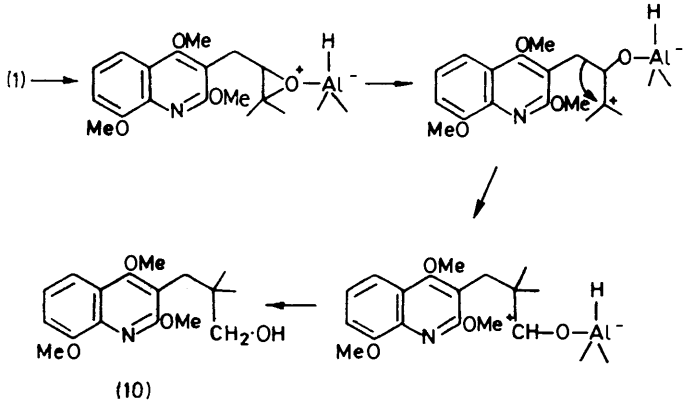
[13] F. J. Buchmann, *J. Amer. Chem. Soc.*, 1942, **64**, 1357.

deshielding by the nitrogen atom than the H-4 in the 2,8-dimethoxyquinoline, and this difference may be generally useful in distinguishing between such isomers. The 8-methoxy-group apparently stabilises the transition state leading to reductive displacement of a 4-methoxy-group, since 2,4-dimethoxyquinoline, 2,4-dimethoxy-3-methylquinoline and 2,4-dimethoxy-3-(3-methylbut-2-enyl)quinoline were unaffected by lithium aluminium hydride under the same conditions.

Reduction with Mixed Hydrides.—Studies of the reaction of epoxides with mixed hydrides obtained from lithium aluminium hydride–aluminium chloride indicate that for a 3 : 1 ratio of the reagents the active species is aluminium hydride.[14] This results predominantly in the formation of the less highly substituted alcohol from trisubstituted epoxides, and we applied the procedure to the epoxide (1). The secondary alcohol (2) was obtained but in lower yield (41%) than from the reaction of the epoxide with lithium aluminium hydride–sodium borohydride (see before). A second product (39%) proved to be the primary alcohol (10). The mass spectrum showed a parent ion peak at *m/e* 305 and a major fragment at 232 (benzylic cleavage, $M - C_4H_9O$). In the n.m.r. spectrum (Table) the absence of coupling in the τ 6·5—9·0 region is consistent with the structure of the side chain. The signal at 6·88 (three protons) is attributed to CH_2·OH and O*H*, and became equivalent to two protons when the sample was shaken with deuterium oxide. The resonance at τ 7·22 (ArCH_2) is similar in chemical shift to that of the corresponding protons in the

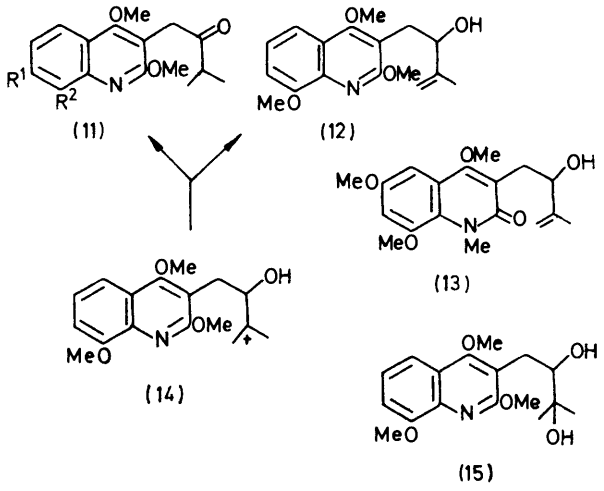


(9)



(10)

tertiary alcohol (9; R = OMe) (Table). By analogy with the reaction of β-di-isobutylene oxide with lithium aluminium hydride–aluminium chloride,[15] the primary alcohol (10) is formed by migration, presumably by the mechanism shown. It seems likely that a stronger Lewis acid than aluminium hydride, either H_2AlCl or $HAlCl_2$, is responsible for the rearrangement.



(11) (12) (13) (14) (15)

Acid-catalysed Reactions.—Although the trisubstituted epoxide from 1-methylcyclohexene was reduced to the secondary alcohol, 2-methylcyclohexanol, with platinum and hydrogen in the presence of perchloric acid or of sulphuric acid,[16] the epoxide (1) did not undergo this reaction. The only products isolated were the ketone (11; R^1 = H, R^2 = OMe) and the allylic alcohol (12). The structure of the ketone was indicated by the similarity of its n.m.r. spectrum in the τ 6·1—9·0 region to the spectra of orixinone (11; R^1R^2 = O·CH_2·O), containing the same side-chain,[17] and by its identity with the product formed by oxidation of the secondary alcohol (2) with chromic acid. The n.m.r. spectrum of the second product (12) establishes the structure of the side-chain. The mass spectrum, with a molecular ion peak at *m/e* 303 and peaks at 233 (70%, $M - C_4H_6O$), 232 (100%, $M - C_4H_6O - H\cdot$), and 218 (45%, $M - C_4H_6O - \cdot CH_3$) is similar to that of the quinoline alkaloid ptelefolin (13), with an identical side chain.[18] It is apparent that the rearrangement of the epoxide (1) to the ketone (11; R^1 = H, R^2 = OMe) and the allylic alcohol (12) occurs in the acidic solvent *via* the cation (14). When the epoxide in ethyl acetate was treated with sulphuric acid, in the absence of platinum and hydrogen, the same products (11; R^1 = H, R^2 = OMe) and (12) were formed; in this case the diol (15) was also isolated; this was identical with the compound obtained previously.[1]

EXPERIMENTAL

N.m.r. spectra were determined with a Varian HR-100 spectrometer (tetramethylsilane as internal standard) and mass spectra with an A.E.I. MS 902 instrument. Optical rotations were measured on a Bendix-NPL Automatic polarimeter (type 143) fitted with a precision control unit capable of measurement to $\pm 2 \times 10^{-4}$ deg.

[14] E. C. Ashby and J. Prather, *J. Amer. Chem. Soc.*, 1966, **88**, 729.
[15] E. C. Ashby and B. Cooke, *J. Amer. Chem. Soc.*, 1968, **90**, 1625.
[16] F. J. McQuillin and W. O. Ord, *J. Chem. Soc.*, 1959, 3169.
[17] W. R. Donnelly and M. F. Grundon, *J.C.S. Perkin I*, 1972, 2116.
[18] J. Reisch, K. Szendrei, V. Paray, I. Novak, and E. Minker, *Tetrahedron Letters*, 1970, 3365.

The epoxide (1), prepared as described previously,[1] was obtained as needles, m.p. 78—80°, $[\alpha]_D$ −0·84°.

3-(2-*Hydroxy*-3-*methylbutyl*)-2,4,8-*trimethoxyquinoline* (2). —(*a*) Diborane, generated externally, was passed during 3 h into the allylquinoline (3) [7] (600 mg) in tetrahydrofuran (5 ml). The solution was stirred with 2N-sodium hydroxide (5 ml) and 30% hydrogen peroxide (3 ml) for 1 h under nitrogen, and then the product was recovered with dichloromethane. Chromatography on silica gel and elution with ether–light petroleum (b.p. 40—60°) gave the allylquinoline (3) (29 mg), m.p. and mixed m.p. 52—55°, and then the *alcohol* (2) in prisms from light petroleum (b.p. 40—60°) (614 mg, 97%), m.p. 66—68° (Found: C, 67·2; H, 7·5; N, 4·7. $C_{17}H_{23}NO_4$ requires C, 66·9; H, 7·6; N, 4·6%).

(*b*) Diborane, generated externally, was passed during 2 h into a solution of the (−)-epoxide (1) (600 mg) in tetrahydrofuran (8 ml) at 0° containing a large excess of lithium borohydride. The mixture was kept at 0° for 24 h, M-sulphuric acid–tetrahydrofuran (1 : 1; 10 ml) was added, the aqueous layer was saturated with potassium carbonate, and the tetrahydrofuran phase was separated and evaporated. Chromatography of the product on silica gel and elution with ether–light petroleum (b.p. 40—60°) (1 : 4) gave unchanged epoxide (20 mg), m.p. and mixed m.p. 75—77°, a mixed fraction (80 mg), and then the alcohol (2) (402 mg, 67%), m.p. and mixed m.p. 65—66°, $[\alpha]_D$ +0·85°.

3-(2-*Hydroxy*-3-*methylbutyl*)-4,8-*dimethoxy*-2-*quinolone* (4; R = H).—The secondary alcohol (2) (800 mg), $[\alpha]_D$ +0·46°, in ether (200 ml) was saturated with dry hydrogen chloride. After 12 h the solvent was evaporated off and a solution of the residue in dichloromethane was washed with N-sodium carbonate and evaporated. Trituration with ether gave the 2-quinolone (720 mg, 95%), m.p. 163—165°, $[\alpha]_D$ −0·37°, identical (mixed m.p. and i.r. spectrum) with an authentic sample.[7]

3-(2-*Hydroxy*-3-*methylbutyl*)-4,8-*dimethoxy*-N-*methyl*-2-*quinolone* (*Lunacridine*) (4; R = Me).—The 2-quinolone (4; R = H) (680 mg) in methanol (80 ml) was treated with an excess of diazomethane and, after 12 h, the solvent was evaporated off and the residue was chromatographed on silica gel. Elution with ether–light petroleum (b.p. 40—60°) (7 : 3) gave first 3-(2-hydroxy-3-methylbutyl)-2,4,8-trimethoxyquinoline (2) (360 mg, 47%) and then the 2-quinolone (4; R = Me) (246 mg, 32%), m.p. 72—74°, $[\alpha]_D$ −0·19°, shown to be lunacridine by mixed m.p. and by a comparison of i.r. spectra with a sample of the racemate, m.p. 72—74°.[7]

3-(3-*Hydroxy*-3-*methylbutyl*)-2,4,8-*trimethoxyquinoline* (9; R = OMe).—A solution of the allylquinoline (3) (2·3 g) and mercury(II) acetate (3·18 g) in tetrahydrofuran (18 ml) and water (8 ml) was stirred at ambient temperature for 2 h, and sodium borohydride in aqueous sodium hydroxide was added. After filtration, the aqueous layer was saturated with sodium chloride, and the organic layer was evaporated. Chromatography of the product on silica gel and elution with ether furnished the tertiary *alcohol* (2·18 g, 90%), m.p. 78—81° (prisms from di-isopropyl ether) (Found: C, 66·8; H, 7·5; N, 4·5. $C_{17}H_{23}NO_4$ requires C, 66·9; H, 7·6; N, 4·6%).

3-(3-*Hydroxy*-3-*methylbutyl*)-2,8-*dimethoxyquinoline* (9; R = H).—(*a*) A solution of the epoxide (1) (600 mg) in ether (50 ml) was added dropwise over 20 min to a suspension of lithium aluminium hydride (700 mg) in ether (50 ml). The mixture was stirred for 4 h, excess of hydride was decomposed with water, and the product was recovered with ether. Chromatography on silica gel and elution with ether–light petroleum (b.p. 40—60°) (1 : 2) gave the *dimethoxyquinoline* (350 mg, 63%), m.p. 95—96° (prisms from di-isopropyl ether) (Found: C, 69·0; H, 7·7. $C_{16}H_{21}HO_3$ requires C, 69·8; H, 7·7%).

(*b*) Reaction of the tertiary alcohol (9; R = OMe) (250 mg) with lithium aluminium hydride as in (*a*) gave the dimethoxyquinoline (9; R = H) (70 mg, 30%), m.p. and mixed m.p. 94—95°. The starting compound was recovered in 34% yield.

2,8-*Dimethoxyquinoline*.—2,4,8-Trimethoxyquinoline (3·0 g) in tetrahydrofuran reacted with lithium aluminium hydride in the usual way and gave 2,8-*dimethoxyquinoline* (126 mg, 5%), m.p. 33—35° [prisms from light petroleum (b.p. 40—60°)]. A satisfactory analysis was not obtained (Found: C, 68·9; H, 5·8. $C_{11}H_{11}NO_2$ requires C, 69·8; H, 5·8%), but the structure was confirmed by the n.m.r. spectrum (Table).

4,8-*Dimethoxyquinoline*.—A solution of 4,8-dimethoxy-2-quinolone (920 mg) in phosphoryl chloride (6 ml) was refluxed for 30 min. The solvent was evaporated off, the residue was treated with water, and the product was recovered with dichloromethane. Crystallisation from ether–light petroleum (b.p. 40—60°) afforded 2-*chloro*-4,8-*dimethoxyquinoline* in needles (956 mg, 96%), m.p. 138—140° (Found: C, 58·1; H, 4·7; Cl, 15·6; N, 6·3. $C_{11}H_{10}ClNO_2$ requires C, 59·1; H, 4·5; Cl, 15·8; N, 6·3%).

A solution of the chloroquinoline (150 mg) in ethanol (1 ml) containing potassium hydroxide (6·3 g) was hydrogenated over Raney nickel for 16 h. The solution was filtered, the solvent was removed, the product in ether was washed with water, and the ether was evaporated off. 4,8-Dimethoxyquinoline was obtained from di-isopropyl ether in needles (100 mg, 79%), m.p. 145—147°; for n.m.r. see Table.

Reaction of the Epoxide (1) *with Lithium Aluminium Hydride–Aluminium Chloride*.—A suspension of lithium aluminium hydride (400 mg, 10 mmol) in ether (25 ml) was added to aluminium chloride (450 mg, 3·6 mmol) in ether (25 ml) at 0°. The mixture was stirred at 0° for 1 h, the precipitate was allowed to settle, and a portion of the solution (22 ml) was treated dropwise with a solution of the epoxide (1) (1·0 g) in ether (22 ml). The mixture was stirred at ambient temperature for 3 h, the excess of hydride was decomposed with ice, and the ether solution was evaporated. Chromatography of the residue on silica gel and elution with ether–light petroleum (b.p. 40—60°) (1 : 4) gave unchanged epoxide (141 mg, 14%), m.p. and mixed m.p. 76—78°, and then 3-(2-hydroxy-3-methylbutyl)-2,4,8-trimethoxyquinoline (466 mg, 47%), m.p. and mixed m.p. 67—69°. Further elution furnished 3-(3-*hydroxy*-2,2-*dimethylpropyl*)-2,4,8-*trimethoxyquinoline* (383 mg, 39%), m.p. 102—104° (prisms from ether–light petroleum), which did not give satisfactory analytical figures (Found: C, 65·9; H, 7·7. $C_{17}H_{23}NO_4$ requires C, 66·9; H, 7·6%). The structure was confirmed by n.m.r. and mass spectrometry (Table and Discussion section).

2,4,8-*Trimethoxy*-3-(3-*methyl*-2-*oxobutyl*)*quinoline* (11; R^1 = H, R^2 = OMe).—The secondary alcohol (2) (73 mg) and a 6% solution of chromium trioxide in 2N-sulphuric acid (40 ml) were stirred for 7 h and then diluted with water. The *ketone* was recovered with ether and separated from light petroleum (b.p. 40—60°) in prisms (31 mg, 43%), m.p. 66—68° (Found: C, 66·9; H, 6·9; N, 4·8. $C_{17}H_{21}NO_4$ requires C, 67·3; H, 7·0; N, 4·6%).

Reaction of the Epoxide (1) *with Acid.*—A solution of the epoxide (1) (250 mg) in ethyl acetate (20 ml) containing 1 drop of sulphuric acid was stirred at room temperature for 18 h. The solvent was evaporated off and the residue was chromatographed on silica gel. Elution with ether–light petroleum (b.p. 40—60°) gave the ketone (11; R^1 = H, R^2 = OMe) (28 mg, 11%), m.p. and mixed m.p. 66—68°, and then 3-(2-*hydroxy*-3-*methylbut*-3-*enyl*)-2,4,8-*trimethoxyquinoline* (90 mg, 36%), m.p. 113—114° (needles from ether–light petroleum). The structure was indicated by n.m.r. and mass spectroscopy (Table and Discussion section). Elution with ether furnished the diol (15), obtained as needles (from di-isopropyl ether) (44 mg, 17%), m.p. 141—143°, identical (mixed m.p. and i.r. spectrum) with an authentic sample.[1]

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