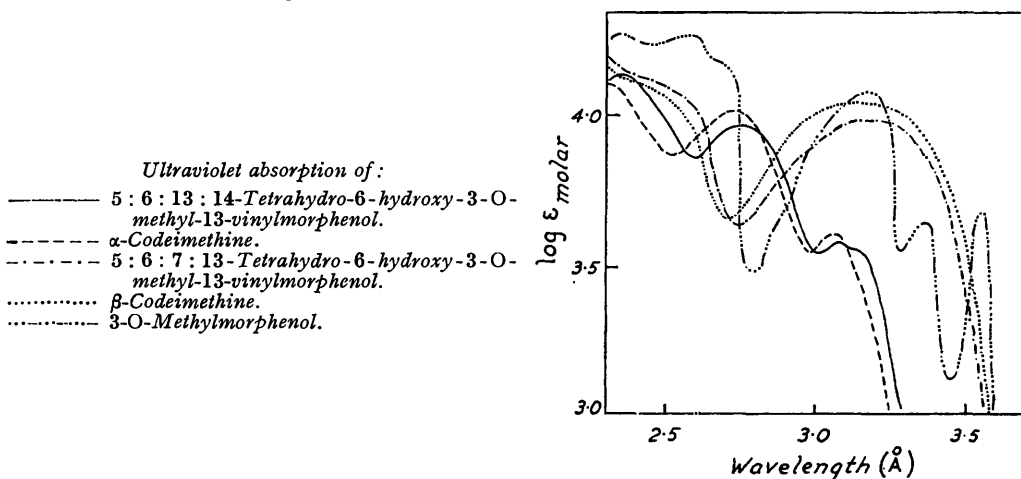


384. *The Morphine-Thebaine Group of Alkaloids. Part VII.* A
New Method of Systematic Degradation to Nitrogen-free Products.*

By K. W. BENTLEY, J. C. BALL, and J. P. RINGE.

Thermal decomposition of methine *N*-oxides has been shown to be a general method for the production of nitrogen-free compounds in the morphine series. Elimination of the side-chain, which sometimes takes place during Hofmann degradation, has not been observed, and compounds inaccessible by exhaustive methylation have been prepared. In this way eleven methines of the morphine-thebaine group have been degraded to the corresponding vinyl compounds and dihydrothebainone dihydromethine converted into thebenone, but the method failed for two phenolic bases.

FOLLOWING the successful production by Mamlock and Wolfenstein,¹ Cope, Foster, and Towle,² Cope, Pike, and Spencer,³ and Rogers⁴ of simple olefins and *NN*-dialkylhydroxylamines, by thermal decomposition of tertiary amine oxides, we decided to study the general applicability of this reaction to the preparation of nitrogen-free derivatives of alkaloids. For this the morphine series provides a number of suitable and easily accessible bases, which would be particularly valuable because of the ease with which morphine derivatives suffer molecular rearrangement.



The *N*-oxide of dihydrocodeine methine (I) readily decomposed at 150°, the product being 5 : 6 : 7 : 8 : 13 : 14-hexahydro-6-hydroxy-13-vinyl-3-O-methylmorphenol (II) which showed the same m. p. and $[\alpha]_D$ as the nitrogen-free product of exhaustive methylation

* Part VI, *J.*, 1956, 1863.

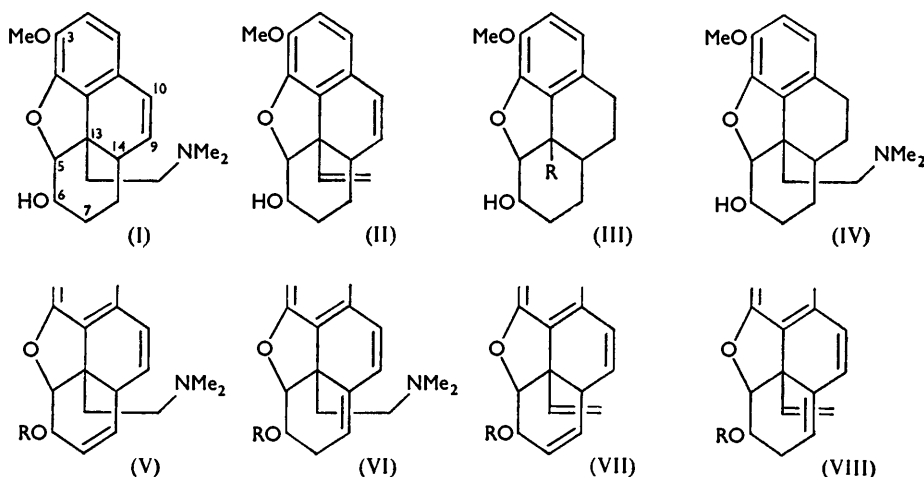
¹ Mamlock and Wolfenstein, *Ber.*, 1900, **33**, 159.

² Cope, Foster, and Towle, *J. Amer. Chem. Soc.*, 1949, **71**, 3929.

³ Cope, Pike, and Spencer, *ibid.*, 1953, **75**, 3212.

⁴ Rogers, *J.*, 1955, 769.

prepared by Rapoport.⁵ This compound on hydrogenation absorbed two mols. of hydrogen and afforded the 13-ethyloctahydro-derivative (III; R = Et), also obtained by the hydrogenation of the octahydro-13-vinyl compound (II; R = CH:CH₂) which was prepared by decomposition of the *N*-oxide of α -tetrahydrocodeimethine (IV). α - (V; R = H) and β -Codeimethine (VI; R = H) were degraded in the same way through the *N*-oxides to 5 : 6 : 13 : 14- (VII; R = H) and 5 : 6 : 7 : 13-tetrahydro-6-hydroxy-3-*O*-methyl-13-vinylmorphenol (VIII; R = H) respectively. The presence of the α - and β -codeimethine chromophores in these two products is shown by their ultraviolet spectra (see Figure). These two compounds are not accessible by normal Hofmann exhaustive methylation during which the side-chain is eliminated with production of a fully aromatic phenanthrene derivative. The compound (VII; R = H) was converted into the isomeride (VIII; R = H) under the conditions required for the $\alpha \rightarrow \beta$ -codeimethine transformation, and both substances on catalytic hydrogenation absorbed three mols. of hydrogen and gave the 13-ethyloctahydro-derivative (III; R = Et). α -Codeimethine methyl ether (V; R = Me) likewise afforded, through the *N*-oxide, 5 : 6 : 13 : 14-tetrahydro-6-methoxy-3-*O*-methyl-13-vinylmorphenol (VII; R = Me) which in boiling alkali furnished the isomer (VIII; R = Me), also obtained by the decomposition of the *N*-oxide of β -codeimethine



methyl ether (VI; R = Me). The two nitrogen-free products (VII and VIII; R = Me) on hydrogenation absorbed three mols. of hydrogen and gave the same 13-ethyloctahydro-compound; this was also prepared by the reduction of octahydro-6-methoxy-3-*O*-methyl-13-vinylmorphenol, which was the product of thermal decomposition of α -tetrahydrocodeimethine methyl ether *N*-oxide and was obtained by Rapoport⁵ by dry distillation of α -tetrahydrocodeimethine methyl ether methohydroxide and was reduced by him to the 13-ethyl compound.

The *N*-oxides of dihydrothebaine methine (IX) and dihydrothebaine dihydromethine (X) were degraded to the 13-vinyl compounds (XI) and (XII) respectively. These compounds were shown to be identical with the products of the corresponding Hofmann degradations,^{6, 7, 8} (a) by hydrolysis to the related ketones (XIII) and (XIV) followed by catalytic reduction to the same 13-ethyl-derivative (XV), and (b) by reduction of the compound (XI) to the phenolic ethylhexahydromorphol derivative (XVI), followed by hydrolysis to the ketone (XVII).

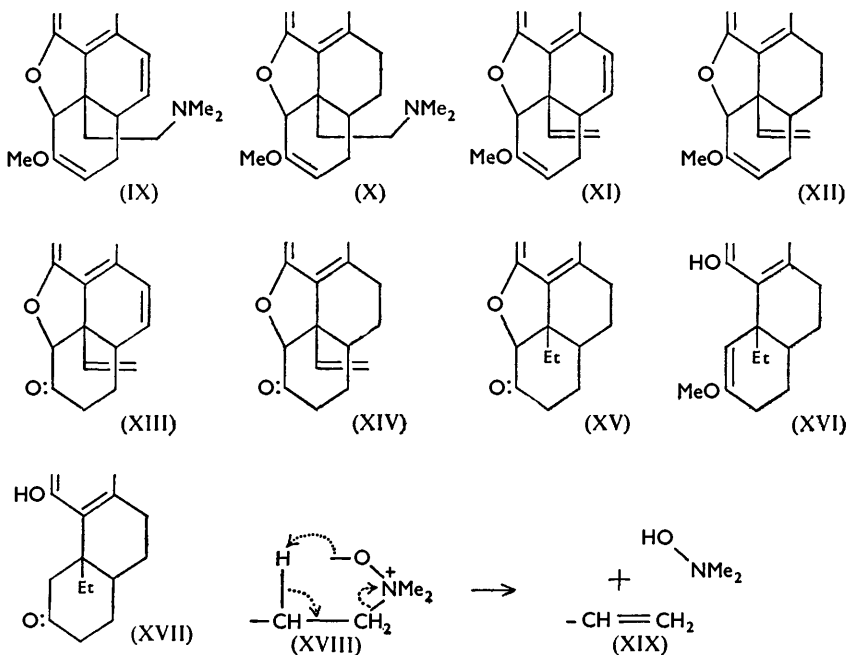
⁵ Rapoport, *J. Org. Chem.*, 1948, **13**, 714.

⁶ Cahn, *J.*, 1930, 702.

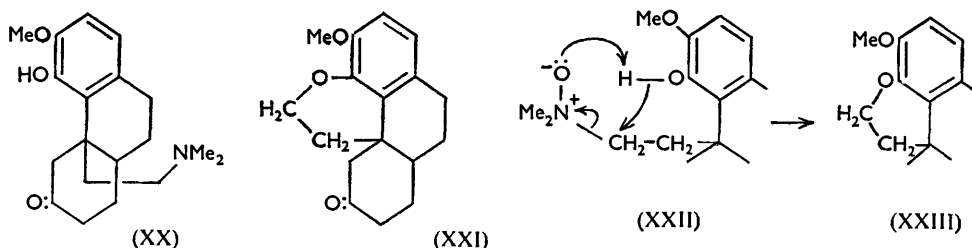
⁷ Sargent and Small, *J. Org. Chem.*, 1951, **16**, 1031.

⁸ Wieland and Kotake, *Annalen*, 1925, **444**, 69.

Since decomposition of the *N*-oxides presumably proceeds by the cyclic process (XVIII) \rightarrow (XIX) it was thought possible that 13-vinyl compounds might result from the degradation of 4-hydroxy-compounds in the morphine series, instead of the cyclic ethers of the thebenone type which are invariably the product of the Hofmann degradation of such



compounds. However, degradation of dihydrothebaine dihydromethine (XX) *via* the *N*-oxide afforded a good yield of thebenone (XXI), a process that presumably proceeds as shown in (XXII) \rightarrow (XXIII).



Two other cases of the formation of oxide rings during Hofmann degradation have been reported, namely, the production of codiran (XXIV) from γ -tetrahydrocodeimethine⁹ [the C₍₆₎-epimer of (IV)], and of "dihydrohydroxycodeone" (XXV) from dihydro-14-hydroxycodeinone methine (XXVI).^{10,11} Degradation of the last-named base (XXVI) *via* the *N*-oxide, gave, however, a good yield of the non-cyclised alcohol (XXVII), which was hydrogenated as usual to the ethyloctahydro-alcohol (XXVIII). That the methine (XX) suffers oxide-ring closure during degradation *via* the *N*-oxide but that the methine (XXVI) does not may be due either to the difference in acidity of the two hydroxyl groups or to steric reasons.

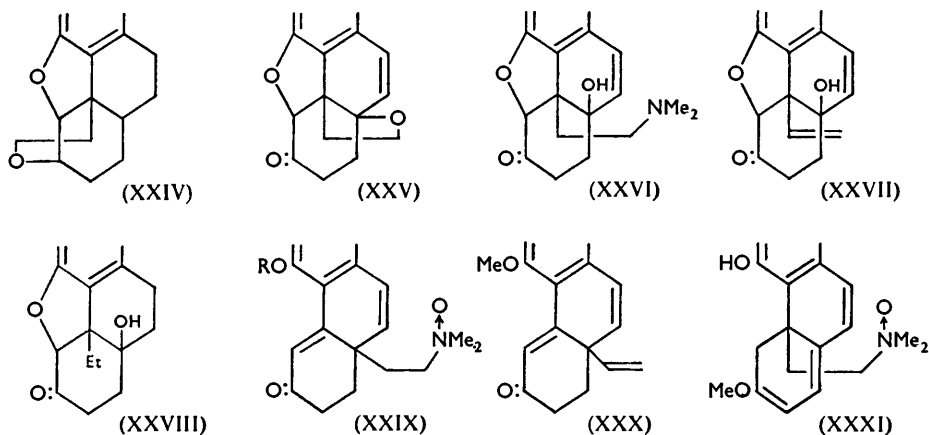
The degradation of metathebaine methyl ether methine *N*-oxide (XXIX; R = Me)

⁹ Rapoport and Payne, *J. Amer. Chem. Soc.*, 1952, **74**, 2630.

¹⁰ Freund and Speyer, *J. prakt. Chem.*, 1916, **94**, 135.

¹¹ Schöpf and Borkowsky, *Annalen*, 1927, **452**, 249.

afforded a poor yield of 6 : 7 : 8 : 14-tetrahydro-3 : 4 : dimethoxy-6-oxo-14-vinylphenanthrene (XXX), whose ultraviolet absorption (see p. 1969) proves the absence of rearrangements. This substance has been reported (isolated only as the phenylhydrazone) to be produced during exhaustive methylation of metathebainone methyl ether methine.¹²



Degradation of metathebainone methine *N*-oxide (XXIX; R = H) resulted in extensive oxidation of the phenolic nucleus, and thermal decomposition of β -dihydrothebaine methine *N*-oxide (XXXI) involved spontaneous inflammation; the method is therefore not generally suitable for the degradation of phenols. Basic material was frequently isolated in small amounts from the products of decomposition of the *N*-oxides: this was invariably the parent base.

The presence of vinyl groups was in every case proved by hydrogenation and in several cases by the diagnostic infrared absorption band (see Table).

Vinyl infrared absorption bands (μ).

Vinyl compound prepared from :		Vinyl compound prepared from :	
dihydrocodeine methine	10.85	dihydrothebaine methine (after hydrolysis) ..	10.83
α -codeimethine methyl ether	10.77	dihydrothebaine dihydromethine (after hydrolysis)	10.77
β -codeimethine	10.87	metathebainone methyl ether methine ...	10.77
dihydrothebaine methine	10.83		

The thermal decomposition of non-phenolic *N*-oxides is thus seen to be a reliable and valuable alternative to Hofmann degradation for the preparation of nitrogen-free products. In no case so far examined is the abnormal product obtained where Hofmann degradation leads to loss of the side-chain.

EXPERIMENTAL

General Procedure.—(a) *Preparation of the N-oxide.* The tertiary amine was heated with 30% hydrogen peroxide (1—2 ml. per g.) on the steam-bath until a homogeneous water-soluble solution was obtained. The excess of hydrogen peroxide was removed at *ca.* 100°/20 mm.

(b) *Decomposition of the N-oxide.* The unpurified oxide was heated gradually in an oil-bath at 0.1 mm. until decomposition began, usually at 140—150°, but sometimes as low as 115°, then at the decomposition temperature for about 30 min. *NN*-Dimethylhydroxylamine was collected in a liquid-air trap. The residue in the flask was straightway extracted with cold 2*N*-hydrochloric acid and ether, the insoluble residue being rejected. The ether extract was washed with hydrochloric acid and the acid extract shaken with ether. The combined ether extracts were washed with dilute aqueous sodium carbonate (which frequently removed some colour, though nothing was ever recovered from it on acidification) and water, dried (Na_2SO_4), and evaporated. The neutral residue frequently crystallised. Small amounts of basic material were frequently recovered when the acid extracts were worked up in the usual way.

¹² Knorr and Pschorr, *Ber.*, 1905, **38**, 3172.

Degradation of Dihydrocodeine Methine N-Oxide.—Dihydrocodeimethine (10.72 g.) was converted into the *N*-oxide with 30% hydrogen peroxide (20 ml.). The oxide decomposed at 140–150°, giving the hexahydro-13-vinyl compound (2.16 g.), which solidified and formed needles, m. p. 102° (from *n*-hexane), $[\alpha]_D^{20} + 78^\circ \pm 1.5^\circ$ (*c* 1.42 in EtOH). Rapoport⁵ gives m. p. 102–103°, $[\alpha]_D^{20} + 77.1^\circ$. The product was hydrogenated in methanol over platinum oxide, 2 mols. of hydrogen being absorbed, and the 13-ethyloctahydro-compound (III; R = Et) obtained as a colourless oil; this was purified by distillation at 0.05 mm. and characterised as the 3 : 5-dinitrobenzoate, yellow prisms, m. p. 115° (from methanol), $[\alpha]_D^{20} + 169^\circ \pm 3^\circ$ (*c* 0.61 in CHCl₃) (Found : C, 61.4; H, 5.3; N, 5.9. C₂₄H₂₄O₈N₂ requires C, 61.5; H, 5.1; N, 6.0%).

Degradation of α -Tetrahydrocodeimethine N-Oxide.— α -Tetrahydrocodeimethine (3.9 g.) was converted into the *N*-oxide with 30% hydrogen peroxide (4 ml.). This on decomposition furnished 1.5 g. of 5 : 6 : 7 : 8 : 9 : 10 : 13 : 14-octahydro-6-hydroxy-3-*O*-methyl-13-vinylmorphenol (III; R = CH₂CH₃) as a pale yellow viscous oil, $[\alpha]_D^{20} + 16.5^\circ \pm 0.5^\circ$ (*c* 1.49 in EtOH), characterised as the 3 : 5-dinitrobenzoate, yellow prisms, m. p. 146° (from methanol) (Found : C, 61.7; H, 4.9; N, 5.7. C₂₄H₂₂O₈N₂ requires C, 61.8; H, 4.7; N, 6.0%). The vinyl compound was catalytically hydrogenated : 1 mol. of hydrogen was absorbed and the 13-ethyloctahydro-compound (III; R = Et) was obtained (3 : 5-dinitrobenzoate, m. p. and mixed m. p. 115°).

Degradation of α -Tetrahydrocodeimethine Methyl Ether N-Oxide.— α -Tetrahydrocodeimethine methyl ether (5 g.) and 30% hydrogen peroxide (5 ml.) gave the amine oxide, which, on decomposition, afforded 2.7 g. of pale yellow 5 : 6 : 7 : 8 : 9 : 10 : 13 : 14-octahydro-6-methoxy-3-*O*-methyl-13-vinylmorphenol, b. p. 170°/0.05 mm., $[\alpha]_D^{21} + 1.27^\circ$ (*c* 1.57 in CHCl₃). On catalytic hydrogenation over platinum oxide in methanol this absorbed 1 mol. of hydrogen and gave the 13-ethyloctahydro-compound, prisms, m. p. 51–53° (lit.,⁵ m. p. 51–52°).

A base (0.75 g.) was also obtained and shown to be α -tetrahydrocodeimethine methyl ether, by conversion into the methiodide, colourless needles, m. p. and mixed m. p. 244–245°, $[\alpha]_D^{20} - 42^\circ$ (*c* 0.24 in EtOH) {lit.,¹³ m. p. 247° (decomp.), $[\alpha]_D^{20} - 40^\circ$ in aq. EtOH}.

Degradation of α -Codeimethine N-Oxide.— α -Codeimethine *N*-oxide [from α -codeimethine (14.2 g.) and 30% hydrogen peroxide (15 ml.)] on decomposition afforded 5 : 6 : 13 : 14-tetrahydro-6-hydroxy-3-*O*-methyl-13-vinylmorphenol as a pale brown oil (2.2 g.), $[\alpha]_D^{20} - 125^\circ$ (*c* 1.56 in EtOH), characterised as 3 : 5-dinitrobenzoate, yellow prisms, m. p. 165° (from methanol) (Found : C, 62.4; H, 4.0; N, 6.0. C₂₄H₁₈O₈N₂ requires C, 62.3; H, 3.9; N, 6.1%).

3 Mols. of hydrogen were absorbed when this substance (0.39 g.) was hydrogenated in ethanol over platinum oxide (0.05 g.), the product being the 13-ethyloctahydro-compound whose 3 : 5-dinitrobenzoate had m. p. and mixed m. p. 116° (from methanol).

Degradation of β -Codeimethine N-Oxide.— β -Codeimethine *N*-oxide (from β -codeimethine, 5.1 g., and 30% hydrogen peroxide, 10 ml.) decomposed at 148°, giving 1.07 g. of a brown oil, which crystallised. Recrystallisation from *n*-hexane afforded 5 : 6 : 7 : 13-tetrahydro-6-hydroxy-3-*O*-methyl-13-vinylmorphenol (VIII; R = H), m. p. 107–108°, $[\alpha]_D^{21} + 434^\circ \pm 2^\circ$ (*c* 0.84 in CHCl₃), $+ 498^\circ \pm 1^\circ$ (*c* 0.98 in EtOH) (Found : C, 75.9; H, 6.2. C₁₇H₁₆O₃ requires C, 76.1; H, 6.0%).

On catalytic reduction in methanol over platinum oxide this absorbed 3 mols. of hydrogen and yielded the last-mentioned 13-ethyloctahydro-compound (III; R = Et) {3 : 5-dinitrobenzoate, m. p. and mixed m. p. 116°, $[\alpha]_D^{22} + 165^\circ \pm 3^\circ$ (*c* 0.45 in CHCl₃)}.

*Isomerisation of 5 : 6 : 13 : 14-Tetrahydro-6-hydroxy-3-*O*-methyl-13-vinylmorphenol.*—This compound (0.5 g.) from α -codeimethine was boiled under reflux for 2 hr. with potassium hydroxide (1 g.) in 60% ethanol (10 ml.). The mixture was cooled and diluted with water, and the product extracted with ether, from which a brown oil was recovered. On crystallisation from *n*-hexane, this yielded the 5 : 6 : 7 : 13-tetrahydro-isomer, m. p. 108° alone or mixed with a specimen prepared as above from β -codeimethine.

Degradation of α -Codeimethine Methyl Ether N-Oxide.—This oxide [from α -codeimethine methyl ether (6 g.) and 30% hydrogen peroxide (7 ml.)] decomposed at 145°, giving 2.4 g. of brown crystals from which 5 : 6 : 13 : 14-tetrahydro-6-methoxy-3-*O*-methyl-13-vinylmorphenol (VII; R = Me) was obtained as pale brown prisms, m. p. 115° (from methanol), $[\alpha]_D^{21} - 256^\circ$ (*c* 1.22 in CHCl₃) (Found : C, 76.6; H, 6.5. C₁₈H₁₈O₃ requires C, 76.6; H, 6.4%).

Hydrogenation (3 mols.) of this product in glacial acetic acid over platinum oxide, distillation, crystallisation from methanol, and sublimation gave the 13-ethyloctahydro-compound having m. p. 52–53° alone or mixed with a specimen prepared from α -tetrahydrocodeimethine methyl ether, $[\alpha]_D^{23} - 43^\circ$ (*c* 1.66 in EtOH) (Found : C, 74.8; H, 8.3. Calc. for C₁₈H₂₄O₃ : C, 75.0; H, 8.2%) {lit.,⁵ m. p. 51–52°, $[\alpha]_D^{20} - 44^\circ$ (in EtOH)}.

¹³ Faltis and Suppan, *Pharm. Monatsh.*, 1923, 4, 189.

Degradation of β -Codeimethine Methyl Ether N-Oxide.—Decomposition of the *N*-oxide from β -codeimethine methyl ether (6.6 g.; and 10 ml. of 30% hydrogen peroxide) began at 115° and was rapid at 130°. 2.0 g. of neutral material were obtained, which yielded 5 : 6 : 7 : 13-tetrahydro-6-methoxy-3-*O*-methyl-13-vinylmorphenol (VIII; R = Me) a light brown oil, b. p. 200°/0.05 mm., $[\alpha]_D^{18} + 498^\circ \pm 1^\circ$ (*c* 0.42 in EtOH) (Found : C, 76.3; H, 6.5. $C_{18}H_{18}O_3$ requires C, 76.6; H, 6.4%).

Catalytic reduction (3 mols.) of this material in methanol over platinum oxide was slow; it gave the 13-ethyl-14-hydroxy-compound, m. p. 53° alone and mixed with a specimen prepared from α -tetrahydrocodeimethine methyl ether.

*Isomerisation of 5 : 6 : 13 : 14-Tetrahydro-6-methoxy-3-*O*-methyl-13-vinylmorphenol.*—This compound (0.37 g.) was boiled under reflux with potassium hydroxide (2 g.) in 80% ethanol (6 ml.) for 2 hr. The product recovered on dilution with water and ether-extraction was a yellow oil, identified as the 5 : 6 : 7 : 13-tetrahydro-isomer by its ultraviolet spectrum.

Degradation of Dihydrothebaine Methine N-Oxide.—Dihydrothebaine methine (6 g.) and 30% hydrogen peroxide (7 ml.) were heated on the steam-bath. The resulting amine oxide decomposed at 150°, giving 2.3 g. of almost colourless neutral product, which gave 5 : 8 : 13 : 14-tetrahydro-6-methoxy-3-*O*-methyl-13-vinylmorphenol (XI) as pale cream plates, m. p. 123—124° (from methanol), $[\alpha]_D^{25} - 238^\circ$ (*c* 1.15 in EtOH) (Cahn⁶ gives m. p. 120—121°; Sargent and Small,⁷ m. p. 123—124.5°).

This was hydrogenated (2.05 mols.) in methanol over platinum oxide to the 13-ethyl-7 : 8 : 9 : 10 : 13 : 14-hexahydro-compound, prisms, m. p. 167—168° (from methanol), $[\alpha]_D^{21} + 21^\circ$ (*c* 0.24 in EtOH) {Sargent and Small⁷ give m. p. 171—173°, $[\alpha]_D^{20} + 23.8^\circ$ (in EtOH)}. Hydrolysis of this enol ether with dilute alcoholic hydrochloric acid afforded 13-ethyl-5 : 6 : 7 : 8 : 9 : 10 : 13 : 14-octahydro-3-*O*-methyl-6-oxomorphol (XVII), needles, m. p. 148—149° (from methanol) (Cahn,⁶ m. p. 148—150°; Sargent and Small,⁷ m. p. 154—155°).

5 : 8 : 13 : 14-Tetrahydro-6-methoxy-3-*O*-methyl-13-vinylmorphenol itself was hydrolysed with dilute alcoholic hydrochloric acid to 5 : 6 : 7 : 8 : 13 : 14-hexahydro-3-*O*-methyl-6-oxo-13-vinylmorphenol (XVIII), prisms, m. p. 149—150° (from ethanol) (lit.,⁶ m. p. 149°), reduced (methanol; palladised strontium carbonate; 2 mols.) to 13-ethyl-5 : 6 : 7 : 8 : 9 : 10 : 13 : 14-octahydro-3-*O*-methyl-6-oxomorphenol (XV), needles, m. p. 113—114° (from methanol) (Cahn⁶ gives m. p. 113°).

Degradation of Dihydrothebaine Dihydromethine N-Oxide.—Dihydrothebaine dihydromethine *N*-oxide (from 6 g. of amine and 7 ml. of 30% hydrogen peroxide) decomposed at 145—150°, giving 3.1 g. of 5 : 8 : 9 : 10 : 13 : 14-hexahydro-6-methoxy-3-*O*-methyl-13-vinylmorphenol (XII), cream-coloured prisms, m. p. 120—121° (from methanol), $[\alpha]_D^{18} - 104^\circ$ (*c* 1.05 in EtOH) (Wieland and Kotake⁸ give m. p. 119°).

Hydrolysis with dilute alcoholic hydrochloric acid then afforded 5 : 6 : 7 : 8 : 9 : 10 : 13 : 14-octahydro-3-*O*-methyl-6-oxo-13-vinylmorphenol (XIV), needles, m. p. 129—130° (from ethanol), $[\alpha]_D^{19} - 25^\circ$ (*c* 1.17 in $CHCl_3$) (Found : C, 75.7; H, 6.8. Calc. for $C_{17}H_{18}O_3$: C, 75.6; H, 6.7%) {lit., m. p. 125—127°, $[\alpha]_D - 23.8^\circ$ (in EtOH)}. The *semicarbazone* was obtained as white prisms, m. p. 193—194°, from methanol (Found : C, 66.3; H, 6.6; N, 12.8. $C_{18}H_{21}O_3N_3$ requires C, 66.0; H, 6.4; N, 12.8%). Reduction (1 mol.) of this hydrolysis product over palladised strontium carbonate in methanol gave 13-ethyl-5 : 6 : 7 : 8 : 9 : 10 : 13 : 14-octahydro-3-*O*-methyl-6-oxomorphenol (XV), colourless needles, m. p. 113—114° (from methanol), identical with the product prepared above in stages from dihydrothebaine methine.

Degradation of Dihydrothebainone Dihydromethine N-Oxide.—This *N*-oxide (from 2.76 g. of base and 5 ml. 30% hydrogen peroxide) decomposed at 140°, giving thebenone (1.0 g.) (XXI), colourless prisms, m. p. 130° (undepressed on mixing with an authentic specimen of m. p. 134°), $[\alpha]_D^{19.5} + 61^\circ \pm 2^\circ$ (*c* 0.68 in EtOH) {lit.,¹⁰ $[\alpha]_D^{23} + 64.4^\circ$ (in EtOH)}. The benzylidene derivative had m. p. 163° (lit.,¹⁰ 162°) and the piperonylidene derivative, m. p. 183° (lit.,⁸ 185—186°).

Dihydro-14-hydroxycodeinone Methine.—Freund and Speyer give insufficient details for successful repetition of this preparation. Dihydro-14-hydroxycodeinone (5 g.) and methyl iodide (10 ml.) were heated at 125° in a sealed tube for 4 hr. The excess of methyl iodide was removed, the residue extracted with warm methanol, the extract evaporated to dryness, and the residual methiodide dissolved in water. Potassium hydroxide pellets were added to the boiling aqueous solution until a yellow oil separated; this was extracted with chloroform from the cooled solution. The chloroform extract was washed with water, dried (Na_2SO_4), and evaporated; the residue crystallised from light petroleum (b. p. 80—90°), the methine being obtained as prisms, m. p. 115° (lit., 115°).

Degradation of Dihydro-14-hydroxycodeinone Methine N-Oxide.—The oxide (from 3.14 g. of methine and 6 ml. of 30% hydrogen peroxide) decomposed at 150°, giving 0.55 g. of 5 : 6 : 7 : 8 : 13 : 14-*hexahydro-14-hydroxy-3-O-methyl-6-oxo-13-vinylmorphenol* (XXVII), prisms, m. p. 107—108° (from moist ether), $[\alpha]_D^{18.5} -59^\circ \pm 1.5^\circ$ (*c* 0.64 in CHCl₃) (Found: C, 67.5; H, 6.2. C₁₇H₁₈O₄.H₂O requires C, 67.2; H, 6.5%) ("dihydrohydroxycodeone,"¹¹ m. p. 214—215°, $[\alpha]_D^{20} -140.8^\circ$ in CHCl₃).

Catalytic reduction (2 mols.) of this product in methanol over platinum oxide gave 13-*ethyl-5 : 6 : 7 : 8 : 9 : 10 : 13 : 14-octahydro-14-hydroxy-3-O-methyl-6-oxomorphenol* (XXVIII), colourless needles, m. p. 204° (from ethanol), $[\alpha]_D^{20.5} -94^\circ \pm 1^\circ$ (*c* 0.56 in CHCl₃) (Found: C, 70.4; H, 7.6. C₁₇H₂₂O₄ requires C, 70.4; H, 7.6%) ("tetrahydrohydroxycodeone,"¹¹ m. p. 150—153°, $[\alpha]_D$ not given).

Degradation of Metathebainone Methyl Ether Methine N-Oxide.—This oxide (from 5.3 g. of methine and 6 ml. of 30% hydrogen peroxide) on decomposition at 150° afforded 0.5 of neutral product and 2.2 g. of the parent base. The neutral material was chromatographed on alumina : a yellow band rapidly separated and was eluted with benzene, giving a yellow oil. This crystallised from aqueous ethanol. The dry material, better recrystallised from light petroleum (b. p. 50—60°), gave 6 : 7 : 8 : 14-*tetrahydro-3 : 4-dimethoxy-6-oxo-14-vinylphenanthrene* (XXX) as pale yellow prisms, m. p. 97—98°, $[\alpha]_D^{20} -983^\circ$ (*c* 0.49 in CHCl₃) (Found: C, 76.2; H, 6.5. C₁₈H₁₈O₃ requires C, 76.6; H, 6.4%). Absorption max. at 2650 and 3220 Å (ϵ 35,200 and 11,800), cf. metathebainone methyl ether methine 2650 and 3320 Å (ϵ 18,200 and 8940) and contrast metathebainone 2300 and 2970 Å (ϵ 15,140 and 16,600). The 2 : 4-*dinitrophenyl-hydrazone* was obtained as deep red prisms, m. p. 234° (from ethanol-chloroform) (Found: C, 62.0; H, 4.9. C₂₄H₂₂O₆N₄ requires C, 62.3; H, 4.8%).

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