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ADDITION OF HYDROGEN CYANIDE TO 9-METHYL-Δ^4-OCTALONE-3 AND 9β-METHYL-8β-HYDROXY-Δ^4-OCTALONE-3

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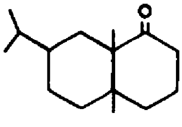
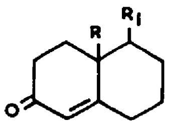
Abstract—Addition of hydrogen cyanide to 9-methyl-Δ^4-octalone-3 (IIb), as a model, yielded both *cis*- and *trans*-ketonitriles the configurations of which are assigned on the basis of IR spectra of the hydrolysed products. Similar addition of hydrogen cyanide to 9β-methyl-8β-hydroxy-Δ^4-octalone-3 (IIc) gave the corresponding *cis*- and *trans*-hydroxy-keto-nitriles, configurations of which were proved by their conversion into *cis*- and *trans*-keto-nitriles obtained in the model study. In contrast to the model experiment where the *trans*-product predominated, the *cis*-isomer was the major product of addition to IIc.

RECENT elucidation of the structure of valeranone[1] or jatamansone[2] as I has led to a new type of sesquiterpene with the unique feature of two angular methyl groups in a decalin system. This is presumably an artefact of a naturally occurring sesquiterpene belonging to the eudalene group. With a view to synthesizing it, conjugate additions of hydrogen cyanide to 9-methyl-Δ^4-octalone-3 (IIb), as a model, and 9β-methyl-8β-hydroxy-Δ^4-octalone-3 (IIc) have been studied. The publications of Nagata *et al.*[3,4] describe the addition of hydrogen cyanide to cholestenone[3] yielding both *cis*- and *trans*-isomers of the corresponding cyanoketone and also the conversion[4] of the angular cyano group into methyl, the latter step being included in our projected synthesis. However, publications by Kundu and Dutta[5] and Meyer and Schnautz[6] on the cyanide addition to the $\Delta^{1,9}$-octalone-2 (IIa) have prompted us to report our results on similar additions to IIb and IIc.



I



II (a), R = R$_1$ = H
(b), R = CH$_3$, R$_1$ = H
(c), R = CH$_3$, R$_1$ = OH

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[1] [a] J. Krepinsky, V. Herout and F. Sorm, *Tetrahedron Letters* No. 3, 9 (1960); [b] J. Krepinsky, M. Romanuk, V. Herout and F. Sorm, *Ibid.* No. 7, 9 (1960); [c] J. Krepinsky, M. Romanuk, V. Herout and F. Sorm, *Ibid.* No. 5, 169 (1962); [d] J. Krepinsky, M. Romanuk, V. Herout and F. Sorm, *Coll. Czech. Chem. Comm.* **27**, 2638 (1962).

[2] [a] T. R. Govindachari, B. R. Pai and S. Rajadurai, *Chem. Ber.* **91**, 908 (1958); [b] T. R. Govindachari, K. K. Purushothaman and S. Rajadurai, *Ibid.* **92**, 1662 (1959); [c] T. R. Govindachari, B. R. Pai, K. K. Purushothaman and S. Rajadurai, *Chem. & Ind.* 1059 (1960); [d] T. R. Govindachari, B. R. Pai, K. K. Purushothaman and S. Rajadurai, *Tetrahedron* **12**, 105 (1961); [e] C. Djerassi, T. R. Govindachari, B. R. Pai, K. K. Purushothaman, *Tetrahedron Letters* No. 6, 226 (1961).

[3] W. Nagata, S. Hirai, H. Itazaki and K. Takeda, *J. Org. Chem.* **26**, 2413 (1961).

[4] W. Nagata, S. Hirai, H. Itazaki and K. Takeda, *Liebigs Ann.* **641**, 196 (1961).

[5] N. G. Kundu and P. C. Dutta, *J. Chem. Soc.* 533 (1962).

[6] W. L. Meyer and N. G. Schnautz, *J. Org. Chem.* **27**, 2011 (1962).

The addition of hydrogen cyanide to 9-methyl-Δ^4-octalone-3 (IIb) gave a mixture of *trans*- and *cis*-9-methyl-10-cyanodecalone-3, slightly contaminated with the octalone (IIb). Resolution of this mixture afforded the pure *trans*-cyanoketone (IIIa), m.p. 107–108°, and the *cis*-cyanoketone (IVa), m.p. 136–137°, in the approximate ratio of 15:1. The non-identity of IIIa and IVa was proved by comparison of their IR spectra (Fig. 1) and determination of the mixture m.p. Purification of the residual gum from the mother liquor by chromatography furnished mainly the *trans*-isomer (IIIa). Predominance of the *trans*-isomer in this experiment has been confirmed by other workers.[3,5–7]

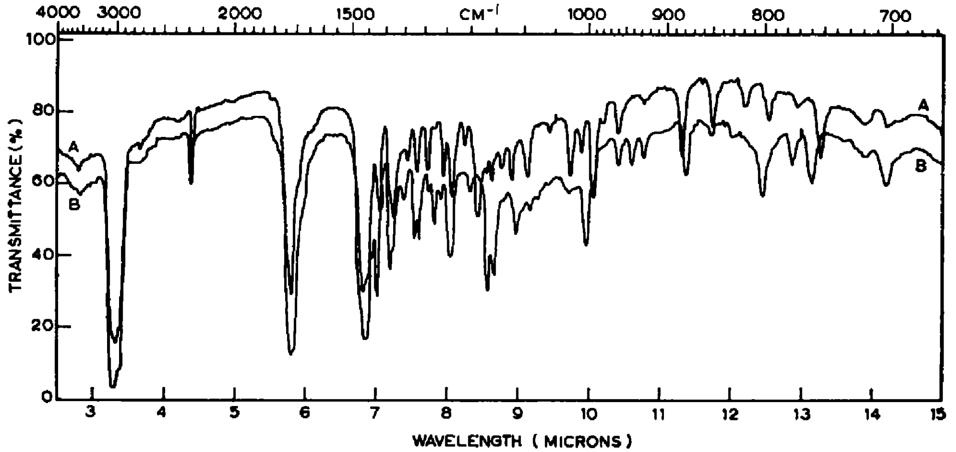
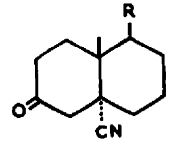
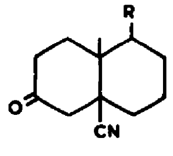


FIG.1. I.R. SPECTRA OF A-III a, B-IV a (NUJOL MULL)



III (a), R = H
(b), R = OH



IV (a), R = H
(b), R = OH

On refluxing the cyanoketone, m.p. 107–108°, with concentrated hydrochloric acid, a crystalline product, m.p. 177°, was obtained in 36% yield. Alkaline saponification of the ethylene ketal of IIIa was not successful. The IR spectrum (Fig. 2) of the hydrolysis product in chloroform solution or in nujol mull exhibited absorption bands at 3460 cm^{-1} (bonded —OH stretching) and 1776 cm^{-1} (C=O stretching for γ-lactone) and did not show any band in the region 1700–1725 cm^{-1} (C=O stretching for six membered cyclic ketone and acid dimer), thus indicating that the keto acid was present entirely in the lactol form (V). IR spectrum of the keto acid, obtained by Nagata *et al.*[8] from the *trans*-isomer of the cyanide addition product of cholestenone,

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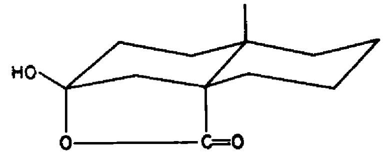
[7] A. Bowers, *J. Org. Chem.* **26**, 2043 (1961).

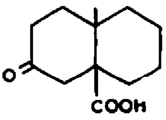
[8] W. Nagata, S. Hirai, H. Itazaki and K. Takeda, *Liebigs Ann.* **641**, 148 (1961).



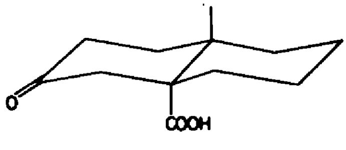
V

also showed that it existed entirely as the lactol. These workers confirmed the *trans*-configuration by an optical rotatory dispersion study of their product. By analogy, we have assigned the *trans*-configuration to the cyanoketone, m.p. 107–108°.

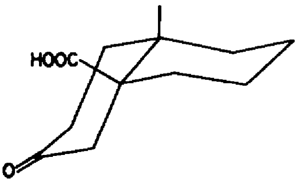
The cyanoketone, m.p. 136–137°, on refluxing with concentrated hydrochloric acid furnished a crystalline product, m.p. 157°, in 34% yield. The IR spectrum (Fig. 2) of the latter in nujol mull exhibited bands at 3050 cm^{-1} (broad), 1724 cm^{-1} (C=O stretching for six-membered cyclic ketone) and 1696 cm^{-1} (C=O stretching for acid dimer), thus indicating that this product was present entirely as the keto acid (VI) in the solid state. But its IR spectrum (Fig. 2) in chloroform solution exhibited an additional shoulder at 1770 cm^{-1} (C=O stretching for γ-lactone) besides the bands at 3226 cm^{-1}, 1724 cm^{-1} and 1695 cm^{-1}. A study of the molecular (Dreiding) models showed that (i) the formation of a lactol is most favoured in the *trans*-chair form (VII), (ii) it is less favoured in the *cis*-(S)-chair form (VIII), but the lactol formation is possible and (iii) lactol formation is not possible in the *cis*-(NS)-chair form (IX). In support of the aforementioned observation it may be stated that the IR spectrum of the keto acid, obtained by Nagata *et al.*[8] from the *cis*-isomer of the cyanide addition product of cholestenone, in chloroform solution showed a shoulder at 1762 cm^{-1}, a strong band for ring ketone and one at 1710 cm^{-1} for the acid carbonyl. IR spectra of the keto acid (VI) in nujol mull and in chloroform solution led us to conclude that the cyanoketone, m.p. 136–137°, has the *cis*-configuration, the corresponding keto acid (conformation VIII and/or IX) being at equilibrium in chloroform with some of the ketol related to conformation VIII.



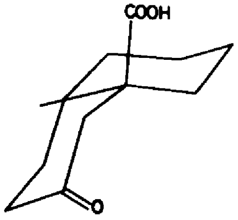
VI



VII



VIII



IX

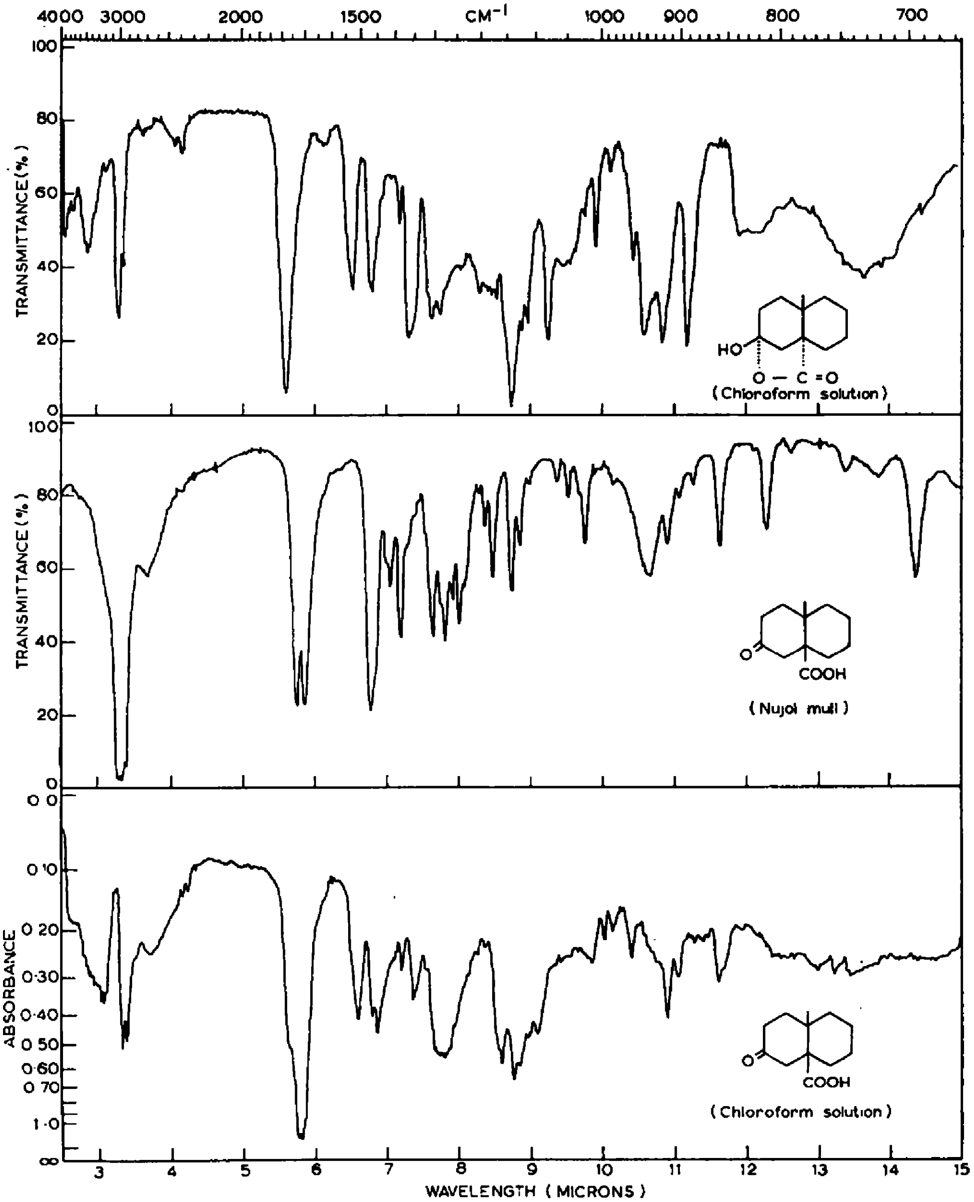


FIG 2

Products obtained by similar hydrogen cyanide addition to 9β-methyl-8β-hydroxy-Δ^4-octalone-3 (IIc) may be resolved by chromatography[9] into two crystalline fractions in the approximate ratio of 16:1, non-identity of these fractions being proved in the usual manner.

The major isomer of 9β-methyl-8β-hydroxy-10-cyanodecalone-3, m.p. 158°, was hydrolysed with concentrated hydrochloric acid to yield a crystalline product, m.p.

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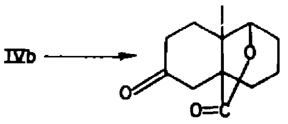
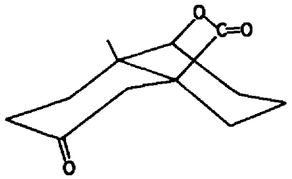
[9] C. Djerrassi and W. Rittel, *J. Amer. Chem. Soc.* **79**, 3528 (1957).

145°, in 84% yield. Its IR spectrum in nujol mull, with absorption bands at 1786 cm^{-1} (C=O stretching for γ-lactone), 1724 cm^{-1} (C=O stretching for six membered cyclic ketone), and the percentage composition showed it to be the keto lactone (X).



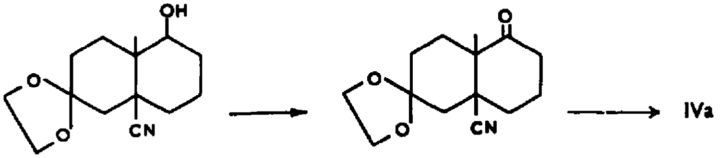
X



XI

Because of the ease of formation in excellent yield, the keto lactone (X) has been assigned the conformation (XI) and hence the hydroxy keto nitrile, m.p. 158–159°, the *cis*-configuration.

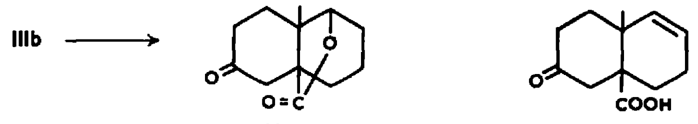
Recently the stereochemistry of ring junction of valeranone or jatamansone has been proved to be *cis*.[10,11] As either the hydroxy-keto-nitrile (IVb) or the keto lactone (X) was intended to serve as a starting material for the synthesis of I, it was necessary to prove the steric configuration of the ring fusion in IVb. For this purpose 9β-methyl-8β-hydroxy-10-cyanodecalone-3 (IVb) was converted into the previously described *cis*-cyano ketone (IVa) by the following sequence of reactions.



XII XIII

The ethylene ketal (XII) of IVb was oxidized with chromium trioxide[12] to furnish the keto ethylene ketal nitrile (XIII) which on Wolff-Kishner reduction[13] followed by deketalization gave the *cis*-keto nitrile, m.p. 136–137°, identical in all respects with the authentic *cis*-keto nitrile (IVa).

The other isomer of 9β-methyl-8β-hydroxy-10-cyanodecalone-3, m.p. 189°, on similar hydrolysis gave a liquid lactone (XIV) and a crystalline unsaturated acid (XV), m.p. 174°, in 30% and 10% yields respectively. It was not possible to assign definite configuration to this hydroxy-cyanoketone (IIIb) on the basis of hydrolysis products.



VIX XV

The nature of ring junction of this compound was shown to be *trans* by a sequence of reactions similar to that applied to the *cis*-hydroxy keto nitrile (IVb). The ethylene

[10] J. Krepinsky, M. Romanuk, V. Herout, F. Sorm and E. Hohne, *Coll. Czech. Chem. Comm.* **28**, 3122 (1963).

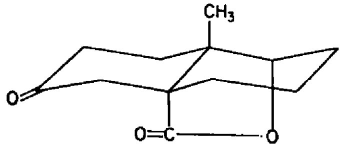
[11] H. Hikino, Y. Hikino, Y. Takeshita, K. Meguro and T. Takemoto, *Chem. Pharm. Bull.* **11**, 1207 (1963).

[12] G. I. Poos, G. E. Arth, R. E. Beyler and L. H. Sarett, *J. Amer. Chem. Soc.* **75**, 423 (1953).

[13] Haung-Minlon, *J. Amer. Chem. Soc.* **68**, 2487 (1946).

ketal (XVI) of IIIb was oxidized to the keto ethylene ketal nitrile (XVII), m.p. 163°, and was found to be different from the previous product (XIII). Wolff-Kishner reduction of XVII, followed by deketalization gave the *trans*-keto nitrile, m.p. 107–108°, identical with the authentic *trans*-keto nitrile (IIIa).

In view of the confirmation of the *trans*-configuration of hydroxy-cyanoketone (IIIb), the formation of its hydrolysis products may be rationalized by assuming that lactonization proceeds *via* the unsaturated keto acid (XV), so that the liquid lactone (XIV) has the conformation (XVIII).



XVIII

EXPERIMENTAL[14]

trans- *and* cis-9-*Methyl*-10-*cyanodecalone*-3 (IIIa *and* IVa)

To a stirred solution of 9-methyl-Δ^4-octalone-3 (40 g) and acetic acid (22 g) in 95% ethanol (200 ml), cooled in a freezing mixture (ice and salt), a solution of KCN (40 g) in water (118 ml) was added over a period of 2 hr. After stirring for 3 hr, the reaction mixture was left at room temp for about 48 hr, when it turned deep red. It was then diluted with water and saturated with $(NH_4)_2SO_4$. The separated oil was thoroughly extracted with chloroform and the extract was washed with water and saturated brine solution. The residue, obtained after removal of the solvent, was distilled *in vacuo* to yield 3 g of the unchanged IIb, b.p. 120–140°/1 mm, and the cyanoketone (33 g), b.p. 160°/1 mm. The second fraction solidified on trituration with pet. ether to give IIIa, m.p. 99–103°. On crystallization from pet. ether the product melted at 107–108°. IR bands at 2268 cm^{-1} (C≡N) and 1724 cm^{-1} (C═O) (Found: C, 75·19; H, 8·96; N, 7·64. $C_{12}H_{17}NO$ requires: C, 75·36; H, 8·91; N, 7·33%).

2,4-*Dinitrophenylhydrazone* of IIIa was obtained as yellow needles from ethanol (95%), m.p. 205° (Found: N, 19·11. $C_{18}H_{21}N_5O_4$ requires: N, 18·86%).

The *semicarbazone* crystallized from ethanol aq, m.p. 232° (Found: N, 22·81. $C_{13}H_{20}N_4O$ requires: N, 22·58%).

Concentration of the mother liquor gave needle shaped crystals (0·8 g) of IVa which on crystallization from ether melted at 136–137°. IR bands at 2268 cm^{-1} (C≡N) and 1724 cm^{-1} (C═O) (Found: C, 75·94; H, 8·48; N, 7·75. $C_{12}H_{17}NO$ requires: C, 75·36; H, 8·91; N, 7·33%).

2,4-*Dinitrophenylhydrazone* of IVa was obtained as orange yellow needles from ethanol (95%), m.p. 230° (Found: N, 18·98. $C_{18}H_{21}N_5O_4$ requires: N, 18·86%).

The *semicarbazone* crystallized from ethanol (95%), m.p. 223° (Found: N, 22·74. $C_{13}H_{20}N_4O$ requires: N, 22·58%).

The residual gum obtained from the mother liquor after separation of the *cis*-product (IVa) was chromatographed on neutral alumina.[9] Elution with pet. ether–benzene (4:1) afforded IIb, and elution with pet. ether–benzene (1:1) and benzene gave further quantities of the *trans*-product (IIIa).

Hydrolysis of trans-9-*methyl*-10-*cyanodecalone*-3 (IIIa). A mixture of 1 g of the cyanoketone (IIIa) and conc HCl (100 ml) was refluxed for 20 hr. The HCl was removed (red. press.) and the residue after dilution with saturated brine solution was thoroughly extracted with ether. The aqueous layer was then saturated with NH_4Cl and extracted with ether. The combined ether extract was washed with sat. $NaHCO_3$ aq and the solution cooled in a freezing mixture (ice and salt) and acidified with 10% ice-cold HCl aq followed by saturation with NH_4Cl and extraction with ether. The ether

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[14] M.ps are not corrected. The IR spectra were taken with a Perkin-Elmer Infracord, Model 137. Petroleum ether used had b.p. 40–60°. Microanalyses were carried out by Messrs. B. R. Seetharamia and D. P. Bose of this department.

extract was washed with brine solution and dried (Na_2SO_4). Removal of the solvent gave a solid residue (0·4 g) which on crystallization from ether furnished the pure *lactol of* 9-*methyl*-10-*carboxydecalone*-3 (V), m.p. 177° (Found: C, 68·19; H, 8·21. $C_{12}H_{18}O_3$ requires: C, 68·57; H, 8·57%).

Hydrolysis of cis-9-*methyl*-10-*cyanodecalone*-3 (IVa). Treatment of 0·6 g IVa with conc HCl (50 ml as before gave 0·33 g of a crystalline product which on crystallization from ether, furnished 9-*methyl*-10-*carboxydecalone*-3 (VI), m.p. 157° (Found: C, 68·62; H, 8·63. $C_{12}H_{18}O_3$ requires: C, 68·57; H, 8·57%).

trans-*and* cis-9-*Methyl*-8-*hydroxy*-10-*cyanodecalone*-3 (IIIb *and* IVb)

A solution of IIc (8·4 g) and acetic acid (4 g) in 95% ethanol (80 ml) was treated with a solution of KCN (7·7 g) in water (20 ml) as described before, except that the stirring was continued for longer time (8 hr), and the product worked up as in the previous case yielded a brown solid, which on chromatography over neutral alumina[*] (250 g) gave 4·5 g of IVb, m.p. 145–150° by elution with benzene and benzene–ether (50:50). This was purified by crystallization from ethyl acetate, m.p. 158–159°. IR bands at 3650 cm⁻¹ (O—H), 2268 cm⁻¹ (C≡N) and 1724 cm⁻¹ (C═O) (Found: C, 69·39; H, 8·08; N, 7·11. $C_{12}H_{17}NO_2$ requires: C, 69·56; H, 8·21; N, 6·76%).

2,4-*Dinitrophenylhydrazone* of IVb was obtained as yellow needles from ethanol (95%), m.p. 220° (Found: N, 18·05. $C_{18}H_{21}N_5O_5$ requires: N, 18·09%).

The *semicarbozane* crystallized from ethanol (95%), m.p. 236° (Found: N, 21·22. $C_{13}H_{20}N_4O_2$ requires: N, 21·21%).

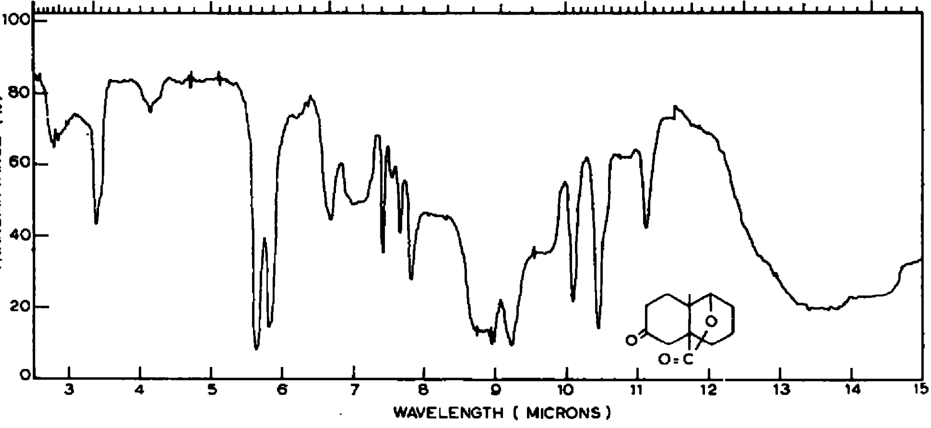
Elution with benzene–ether (20:80) gave a mixture of *cis*- and *trans*-hydroxy-cyanoketones (0·3 g), from which 0·1 g of IIIb, m.p. 189°, along with some amount of the *cis*-addition product (IVb) could be obtained by fractional crystallization. IR bands at 3650 cm⁻¹ (O—H), 2268 cm⁻¹ (C≡N) and 1724 cm⁻¹ (C═O) (Found: C, 69·46; H, 8·51; N, 6·54. $C_{12}H_{17}NO_2$ requires: C, 69·56; H, 8·21; N, 6·76%).

Elution with ether–chloroform (50:50) and chloroform afforded additional 0·2 g of the crystalline *trans*-product (IIIb), m.p. 184°.

2,4-*Dinitrophenylhydrazone* of IIIb was obtained from 95% ethanol, m.p. 196° (Found: N, 18·31 $C_{18}H_{21}N_5O_5$ requires: N, 18·09%).

The semicarbazone was crystallized from aqueous ethanol, m.p. 220° (Found: N, 20·85. $C_{13}H_{20}N_4O_2$ requires: N, 21·21%).

Hydrolysis of cis-9-*methyl*-8-*hydroxy*-10-*cyanodecalone*-3 (IVb). Hydrolysis of 9·65 g of IVb by refluxing with conc HCl (200 ml) as before afforded a crystalline solid (6 g) which on crystallization gave the pure *lactone of* 9-*methyl*-8-*hydroxy*-10-*carboxydecalone*-3 (X), m.p. 145° (Found: C, 69·31; H, 7·57. $C_{12}H_{16}O_3$ requires: C, 69·23; H, 7·69%).



I R. SPECTRUM OF X (CHLOROFORM SOLUTION)

FIG. 3.

3-*Ethylenedioxy-9-methyl-8-hydroxy-*10*-cyanodecalin* (XII)

A mixture of 0·9 g of IVb, ethylene glycol (0·6 g), *p*-toluenesulphonic acid (0·05 g) and dry benzene (100 ml) was refluxed in a flask fitted with a continuous water separator until no more water separated (15 hr). The cooled reaction mixture was washed with 10% NaHCO$_3$ aq and water. After removal of the solvent the residue (1 g) was crystallized from benzene to furnish XII, m.p. 105–106°. IR bands at 3450 cm^{-1} (O—H), 2268 cm^{-1} (C≡N), and 1105 and 1076 cm^{-1} (ethylene ketal) (Found: C, 67·21; H, 8·00; N, 5·95. C$_{14}$H$_{21}$NO$_3$ requires: C, 66·92; H, 8·42; N, 5·57%).

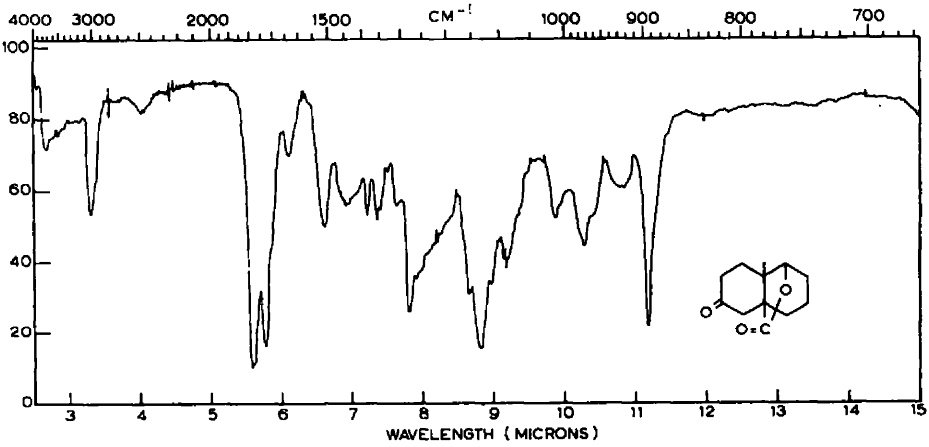
3-*Ethylenedioxy-9-methyl-*10*-cyanodecalone-*8 (XIII)

To the complex of CrO$_3$ (0·8 g) and anhydrous pyridine (10 ml) a solution of XII (0·4 g) in pyridine (6 ml) was added. The solution which darkened immediately, was allowed to stand overnight at room temp and then poured into water. The aqueous solution was extracted with ethyl acetate and the extract washed thoroughly with water. Removal of the solvent *in vacuo* gave XIII (0·33 g, yield 84%), which on crystallization from ethyl acetate–pet ether furnished the pure product (XIII), m.p. 132–133°. IR bands at 2273 cm^{-1} (C≡N), 1721 cm^{-1} (C=O), and 1101 and 1086 cm^{-1} (ethylene ketal) (Found: C, 67·72; H, 7·79; N, 5·89. C$_{14}$H$_{19}$NO$_3$ requires: C, 67·47; H, 7·81; N, 5·62%).

Wolff-Kishner reduction of 3-*ethylenedioxy-9-methyl-*10*-cyanodecalone-*8 (XIII)

A mixture of 0·12 g of XIII and diethylene glycol (5 ml) containing KOH (0·34 g) and 60% hydrazine hydrate (1 ml) was heated under reflux for 2 hr at 130 to 140° (inner temp). The temp was raised to 180–190° by removal of the volatile matter and the mixture heated under reflux at that point for 2 hr. Most of the diethylene glycol was distilled off, and the residue was treated with dil HCl aq and heated for 30 min at 100°. After cooling, the mixture was poured into saturated brine solution and extracted with chloroform. Removal of the solvent afforded a crystalline material (0·07 g, yield 52%), m.p. 110–116°. Recrystallization from pet. ether, using animal charcoal gave the pure colourless crystals of IVa, m.p. 136–137°.

Hydrolysis of trans-*9-methyl-8-hydroxy-*10*-cyanodecalone-*3 (IIIb). A mixture of 0·45 g of IIIb and conc HCl was refluxed and the product worked up as before to afford an oily residue (0·22 g). This was extracted thoroughly with 5% NaHCO$_3$ aq and the insoluble material was extracted with benzene. The benzene extract was washed with water and brine solution. The gum obtained after removal of the solvent was subjected to short-path distillation, (m)b.p. 125–135°/(2·31 × 10^{-3} mm) to give 0·15 g of the liquid *lactone of* 9*-methyl-8-hydroxy-*10*-carboxydecalone-*3 (XIV). IR bands at 1786 cm^{-1} (γ-lactone) and 1724 cm^{-1} (C=O) (Found: C, 69·02; H, 7·71. C$_{12}$H$_{16}$O$_3$ requires: C, 69·23; H, 7·69%).



I R. SPECTRUM OF XIV (CHLOROFORM SOLUTION)

FIG. 4.

The bicarbonate extract was cooled (ice and salt) and acidified with ice-cold dil HCl and extracted with benzene. The benzene extract was washed with ice-cold water and saturated brine solution. On removal of the solvent a solid residue (0·05 g), m.p. 163–170°, which on crystallization from ether furnished the pure *9-methyl-10-carboxy-*Δ^7*-octalene-3-one* (XV), m.p. 174°. IR bands at 3050 cm^{-1} (O—H), 1724 cm^{-1} (C=O), 1696 cm^{-1} (acid dimer) and 1613 cm^{-1} (unsaturation) (Found: C, 68·96; H, 7·73. $C_{12}H_{16}O_3$ requires: C, 69·2; H, 7·6%).

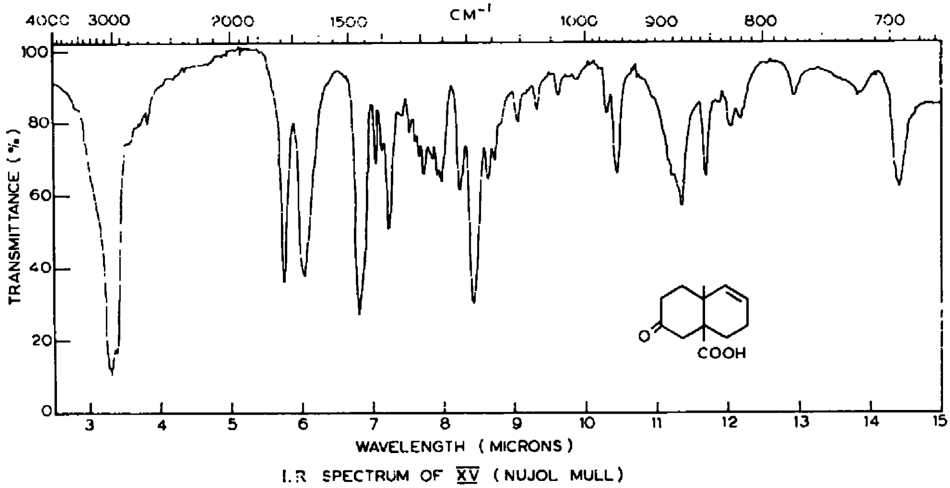


FIG. 5.

3-*Ethylenedioxy-9-methyl-8-hydroxy-10-cyanodecalin* (XVI)

A mixture of 0·5 g of IIIb ethylene glycol (0·8 ml), *p*-toluenesulphonic acid (0·05 g) and dry benzene (50 ml) was refluxed and the product worked up as for the preparation of XII, to obtain a crystalline solid (0·55 g), m.p. 168–170°. Crystallization from ether furnished the pure ethylene ketal (XVI), m.p. 172°. IR bands at 3450 cm^{-1} (O—H), 2273 cm^{-1} (C≡N), and 1105 cm^{-1} (ethylene ketal) (Found: C, 67·46; H, 8·3; N, 5·69. $C_{14}H_{21}NO_3$ requires: C, 66·92; H, 8·41; N, 5·57%).

3-*Ethylenedioxy-9-methyl-10-cyanodecalone-8* (XVII)

A solution of 0·09 g XVI in pyridine (2 ml) was treated with the complex of CrO_3 (0·12 g) and pyridine (3 ml) and the product worked up as for the preparation of XIII to afford a crystalline solid (0·07 g, yield 84%), m.p. 160°. After two crystallizations from ethyl acetate–pet. ether the pure ketal ketone (XVII), m.p. 163°, was obtained. The product (XVII) was different from XIII; the mixture was depressed, the IR spectra were not identical and they behaved differently on thin layer chromatograms. IR bands at 2273 cm^{-1} (C≡N), 1721 cm^{-1} (C=O) and 1105 and 1078 cm^{-1} (ethylene ketal) (Found: C, 67·45; H, 7·88; N, 6·08. $C_{14}H_{19}NO_3$ requires: C, 67·47; H, 7·81; N, 5·62%).

Wolff-Kishner reduction of 3-*ethylenedioxy-9-methyl-10-cyanodecalone-8* (XVII). A mixture of 0·13 g XVII, diethylene glycol (5 ml) containing KOH (0·34 g) and 60% hydrazine hydrate (1 ml) was heated and the product worked up as for the preparation of IVb to furnish a crystalline product (0·07g, yield 52%), m.p. 99–102°. On crystallization from pet. ether IIIa, m.p. 107°, was obtained.