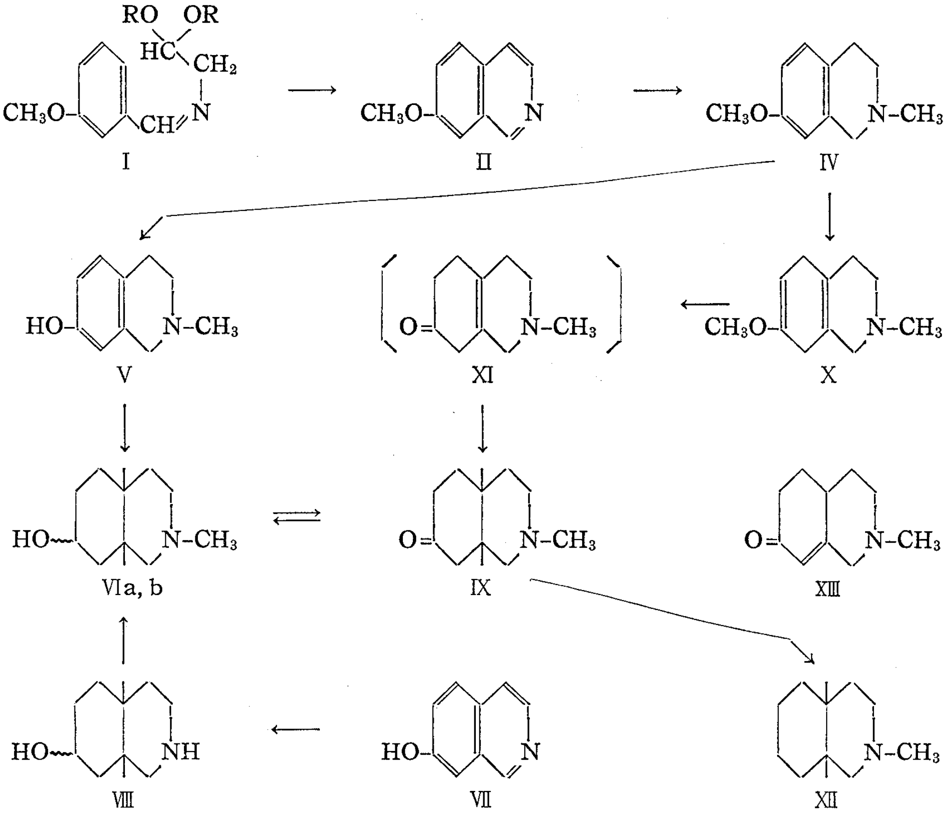
UDC 547.833.3.02

97. **Masao Okamoto and Masayo Yamada**: Stereochemistry of Decahydroisoquinolines and Related Compounds. III.[*2] Syntheses of *cis*-2-Methyl-decahydro-7-isoquinolinols.

(*Kyoto College of Pharmacy*[*1])

Previously, Clarke and Pinder[1)] reported that 2-methyl-7-methoxy-1,2,3,4-tetrahydroisoquinoline (IV), on reduction by Birch reduction followed by hydrolysis with diluted sulfuric acid, yielded 2-methyl-2,3,4,4*a*,5,6-hexahydro-7(1*H*)-isoquinolone (XIII), which was catalytically hydrogenated over platinum oxide in acetic acid to 2-methyl-2,3,4,4*a*,5,6,8,8*a*-octahydro-7(1*H*)-isoquinolone (IX). On the other hand, Ochiai and Nakagome[2)] reported that XIII, prepared by the same way as employed by Clarke, *et al.*, was converted by catalytic hydrogenation over palladium-barium sulfate in ethanol to IX, but when platinum oxide in ethanol was used, 2-methyl-decahydro-7-isoquinolinol (VI) was obtained. In order to clarify this discrepancy, the following two points have to be taken into consideration. (a) While Clarke, *et al.* identified XIII and IX as the methiodides, Ochiai, *el al.* characterized them as the semicarbazone and the picrate (see Table I). Therefore, it is not possible to confirm by direct comparison whether the compounds described by Clarke, *et al.* are identical with those reported by Ochiai, *et al.* (b) In either of these investigations, no experimental evidence on the configuration of the ring juncture in IX was presented. The aim of this work is to clarify these ambiguities.



[*1] Nakauchi-cho, Yamashina-misasagi, Higashiyama-ku, Kyoto (岡本正夫, 山田真代).
[*2] Part II. S. Kimoto: This Bulletin, **10**, 362 (1962).
1) C.B. Clarke, A.R. Pinder: J. Chem. Soc., **1958**, 1967.
2) E. Ochiai, T. Nakagome: Yakugaku Zasshi, **78**, 1438 (1958).

Hydrogenation of the isoquinolines, 2-methyl-1,2,3,4-tetrahydro-7-isoquinolinol (V), 7-isoquinolinol (VII), and IV, was carried out in three ways. According to Mirza's method,[3] IV was prepared by reduction of the methiodide (III) of 7-methoxyisoquinoline (II) with sodium borohydride in methanol in an excellent yield (91 %), and then converted into V by boiling with concentrated hydrochloric acid at 175~180° in a sealed tube. Hydrogenation of V over Raney-nickel in methanol solution at high pressure and elevated temperature gave rise to the alcohol (VI), b.p.$_4$ 115~116°, which was separated by alumina chromatography into the two isomeric alcohols, VIa, b.p.$_5$ 117.5~118° (methiodide, m.p. 279~280°) and VIb, b.p.$_5$ 111° (methiodide, m.p. 264~266°). These alcohols, on oxidation with chromic anhydride in acetic acid, afforded the ketone (IX), b.p.$_4$ 90~92° (methiodide, m.p. 278~279°; picrate, m.p. 186~188°), whose picrate agreed with that prepared by Ochiai, *et al.*, but whose methiodide did not correspond to that recorded by Clarke, *et al.* The ketone (IX) was then converted by Wolff-Kishner reduction modified by Huang-Minlon[4] to *cis*-2-methyl-decahydroisoquinoline (XII). The ketone (IX), on hydrogenation over platinum oxide in ethanol, gave back to the two isomeric alcohols (VIa, VIb). Therefore, it is clear that both the ketone (IX) and the two isomeric alcohols (VIa, VIb) have *cis* configuration at the ring juncture since the configuration was not supposed to change in this oxidation and reduction process. 7-Isoquinolinol (VII), on hydrogenation in methanol solution over Raney-nickel at high pressure and high temperature, followed by methylation with formalin and formic acid, afforded exclusively one isomer (VIb), which was converted to the *cis* ketone (IX). However, it was found that either of the two methiodides of VI was not agreeable with the methiodide described by Ochiai, *et al.*, and hence more detailed examination on this point had to be made. In the previous paper,[*2] it was reported that stereospecific hydrogenation of 2-methyl-1,3,4,7,8,8*a*-hexahydro-6(2*H*)-isoquinolone (XV) over palladium-charcoal in acidic solution, gave *cis*-2-methyl-1,3,4,4*a*,5,7,8,8*a*-octahydro-6(2*H*)-isoquinolone (XVI), but when this hydrogenation was carried out in neutral solution, *trans* isomer (XVII) was obtained. Therefore, it was thought advisable to reinvestigate such reaction starting from XIII. According to the procedure recorded in the literatures,[1,2] hydrolysis of 2-methyl-7-methoxy-1,2,3,4,5,8-hexahydroisoquinoline (X) (IR μ[*3] : 5.83 (medium), 5.98 (strong)) was effected with 10% sulfuric acid at 140° for 5 hours, whereupon the resulting oil (IR μ :

Table I. Physical Data of 2-Methyl-2,3,4,4*a*,5,6-hexahydro-7(1*H*)-isoquinolone (XIII) and 2-Methyl-2,3,4,4*a*,5,6,8,8*a*-octahydro-7(1*H*)-isoquinolone (IX).

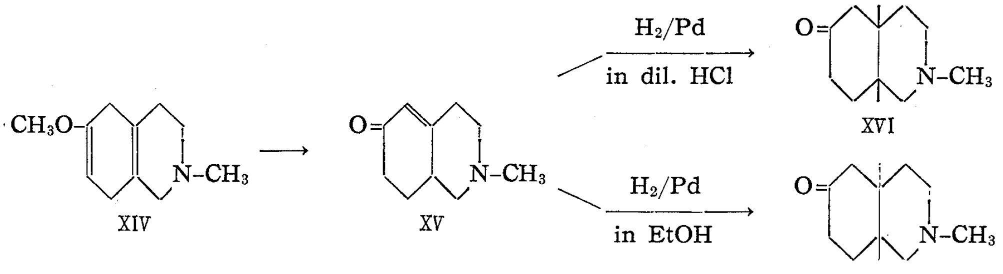
		Clarke, *et al.*	Ochiai, *et al.*	The authors
XIII	b.p. (/mm.)	58~60°/0.05	135°/7	
	UV : λ_{max} mμ (log ε)	222 (3.708)[a]	230.5 (3.854)[b]	
	IR : $\nu_{C=C}$ cm^{-1}	1665	1678	
	ν_{CO} cm^{-1}	1710	1720	
	Methiodide (m.p.)	205~208°	——	
	Semicarbazone (m.p.)	——	210°	
IX	b.p. (/mm.)	61~62°/0.03	100~110/3[c]	90~92°/4
	IR : ν_{CO} cm^{-1}	1703	1693	1708
	Methiodide (m.p.)	258~259°	——	278~279°
	Picrate (m.p.)	——	186~188°	186~188°

a) Measured in methanol. *b*) Measured in ethanol.
c) This boiling point represents bath temperature.

[*3] See examples for IR absorption spectra of enol ethers in 6μ region—2-methyl-6-methoxy-1,2,3,4,5,8-hexahydroisoquinoline (XIV) : 5.88μ (medium), 6.01 μ (strong), (in our hands); $\Delta^{5,8}$-phenolic dihydrothebaine : 5.9 μ (weak), 6.0 μ (medium), (G. Stork : J. Am. Chem. Soc., **74**, 768 (1952)).

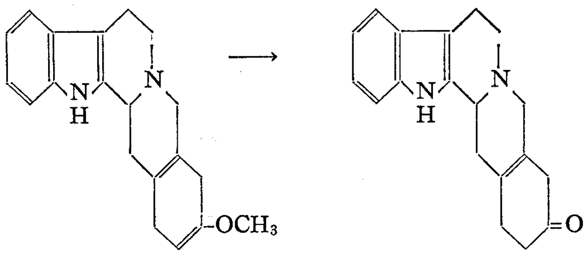
3) R. Mirza : J. Chem. Soc., **1957**, 4400.

4) Huang-Minlon : J. Am. Chem. Soc., **68**, 2487 (1946).

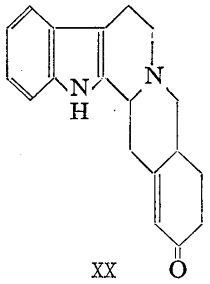


XIV XV XVI XVII

5.81 (strong), 5.97 (medium), 6.13 (weak)) changed in a short time to a dark brown resinous liquid, which afforded neither pure methiodide nor semicarbazone. The infrared absorption spectrum showed that this unstable oil may be a mixture of the unsaturated ketone (XI) and the conjugated ketone (XIII). This observation was in keeping with the fact that the infrared absorption spectrum of XV also showed α,β-unsaturated ketone bands at 6.0 μ (strong) and at 6.13 μ (medium). However, hydrolysis of X at 80° for 0.5 hour gave an oil, b.p$_3$ 108~109° (IR μ : 5.81 (CO), no bands near 6.0 μ; UV λ_{max}^{EtOH} mμ (ε): 217 (2400), 278 (447)), which did not produce any crystalline derivatives. Clarke, *et al.*[1] reported that the hexahydro ketonic base (XIII) gave a methiodide (m.p. 205~208°) and had maxima at 1710 cm^{-1} (CO) and 1665 cm^{-1} (C=C). In contrast, the corresponding hexahydro ketonic base obtained by us showed an absorption typical of a six-membered ring ketone (1710 cm^{-1})[5] and no appreciable absorption band of an α,β-unsaturated ketone (1684~1674 cm^{-1})[5] in the infrared spectrum. However, on prolonged hydrolysis, the intensity of this saturated carbonyl band decreased and the unsaturated carbonyl band became significant. The abnormal ultraviolet absorption spectra of α,β-unsaturated ketonic bases such as XIII and XV was already reported by Clarke, *et al.*[1] and Georgian.[6] The hexahydro ketonic base obtained by us had an absorption maximum at 217 mμ which situated at shorter wavelength than that of the corresponding base (XIII) obtained by Clarke, *et al.* (cf. Table I). When this base was catalytically hydrogenated to the saturated ketonic base (IX), this absorption maximum shifted toward more shorter wavelength region (<210 mμ), and the intensity of the other absorption maximum (278 mμ, ε: 447) decreased to that of the normal unconjugated carbonyl band (278 mμ, ε: 42). Leonard, *et al.*[7,8] reported that a β,γ-unsaturated bridged-ring ketone showed abnormally a high extinction coefficient (ε : 300~500) at 280 mμ region and 1-ethyl-1,2,5,6-tetrahydropyridine had 218 mμ (ε : 1700). On the basis of these spectrophotometric data, it seems reasonable to assume that the hexahydro ketonic base obtained by us should be formulated by the $\Delta^{9(10)}$-unsaturated ketonic base (XI). In order to investigate this problem in more detail, further investigation is now in progress, and the results will be reported in later papers.



XVIII XIX



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[5] L. T. Bellamy : "The Infrared Spectra of Complex Molecules" 2nd. Edd. p. 147 (1958).
[6] V. Georgian : Chem & Ind. (London), **1954**, 930.
[7] N. J. Leonard, D. M. Locke : J. Am. Chem. Soc., **77**, 437 (1955).
[8] R. C. Cookson, N. S. Warigar : J. Chem. Soc., **1956**, 2302.

18-Oxo-15(20)-yohimbene (XIX) was easily prepared by acid hydrolysis of 3-methoxy-1,4,5,7,8,13,13*b*,14-octahydrobenzo[*g*]indolo[2,3-*a*]quinolizine (XVIII) and had UV : λ_{max}^{EtOH} mμ (log ε) : 225 (4.66), 283 (3.92), 290 (3.83) and IR (KBr) : 1710 cm^{-1} (CO).[9] In this case, the migration of the double bond of the β,γ-unsaturated ketonic base (XIX) leading to the formation of 18-oxo-19(20)-yohimbene was not observed, while under a similar condition[10] 17-oxo-15(16)-yohimbene (XX) was easily obtained from the corresponding enol ether.

Hydrogenation of XI over palladium-charcoal either in acidic solution or in neutral solution at 3 kg./cm^2 of hydrogen pressure gave exclusively the same saturated *cis* ketone (IX), which was in contrast to the hydrogenation of 6-oxo-derivative (XV).

In view of the fact that *cis*-decahydro-7-isoquinolinol derivatives were obtained exclusively by the above three different methods, it seems reasonable to assume that these *cis* isomers were unexpectedly more stable than corresponding *trans* isomers.

Experimental[*4]

3-Methoxybenzylideneaminoacetaldehyde Dimethyl Acetal (I, R=CH_3)——3-Methoxybenzaldehyde[11] (29.5 g.) was heated with aminoacetaldehyde dimethyl acetal (26 g.) on the water bath for 1 hr. The mixture was taken up in benzene (500 cc.), and the solution was dried over anhyd. Na_2SO_4 and evaporated. Distillation of the residue at 130~140°/7 mm. Hg yielded 45.5 g. (88.6 %) of I.

7-Methoxyisoquinoline (II) and the Methiodide (III)——The acetal (I) (25.5 g.) was added dropwise under stirring to 76.5% H_2SO_4 (102 g.), maintained at 30~40°. Stirring was continued at the same temp. for 9 hr. The mixture was poured into H_2O and after shaking with Et_2O, the aqueous solution was made alkaline with 20% NaOH and extracted with Et_2O. The Et_2O extract was dried over anhyd. Na_2SO_4 and evaporated. The residual liquid (II) distilled at 111°/3 mm. Hg (lit.[12] : b.p$_{34}$ 132~136°). Yield, 15.8 g. or 87 %. The picrate, m.p. 193~195° (lit.[12] : m.p. 194~195°). Treatment of II (27 g.) with MeI (30 g.) in dehyd. EtOH (60 cc.) gave the methiodide (III), which upon recrystallization from EtOH formed colorless needles, m.p. 189~191° (almost quantitative).

2-Methyl-7-methoxy-1,2,3,4-tetrahydroisoquinoline (IV)——To a solution of III (40 g.) in MeOH (800 cc.), $NaBH_4$ (18.5 g.) was added with stirring under cooling with water, and the mixture was gently refluxed for 7.5 hr. After cooling, it was poured into H_2O (4 L.) and extracted with $CHCl_3$. The extract was washed with H_2O, dried over anhyd. Na_2SO_4, and evaporated. The residue (IV) distilled at 112~116°/6 mm. Hg (lit.[1]: b.p$_{10}$ 131~135°). Yield, 21.4 g. or 91 %. The hydrochloride, m.p. 200~201° (lit.[1] : m.p. 200~201°).

2-Methyl-1,2,3,4-tetrahydro-7-isoquinolinol (V)——The compound (IV) (5 g.) was heated at 175~180° with conc. HCl (45 cc.) in a sealed tube for 26 hr. After the solution was evaporated to dryness *in vacuo*, the crystalline residue was dissolved in H_2O (40 cc.) and the solution was made alkaline with Na_2CO_3. The precipitated phenolic base (V) was collected by suction and recrystallized from Me_2CO to give colorless prisms, m.p. 171~173° (lit.[13] : m.p. 171~172°). Yield, 3.6 g. or 80 %.

Hydrogenation of V——A solution of V (4 g.) in MeOH was catalytically hydrogenated at 175° and 131 kg./cm^2 (initial H_2 pressure, 89 kg./cm^2) over Raney-Ni prepared from Ni-Al alloy (6.3 g.) for 8 hr. After cooling, the filtered solution was evaporated *in vacuo*. The residual oil was dissolved in Et_2O and the solution was shaken with 30% NaOH, dried over Na_2SO_4 and evaporated. Distillation of the residual oil gave 2-methyl-decahydro-7-isoquinolinol (VI) as a colorless, viscous liquid (3.1 g.), b.p$_4$ 115~116°. The oil was chromatographed through a column (45×3 cm.) of alumina (150 g.) and eluted with $CHCl_3$. The IR spectrum of VIa was different from that of VIb. The fraction (A) was regarded as a mixture of VIa and VIb from its IR spectrum. The methiodides of VIa and VIb were recrystallized

Fr. No.	Eluting solvent (cc.)	Eluate (g., b.p$_5$)	Methiodide (m.p.)
1~13 (VIa)	$CHCl_3$ 130	1.0, 117.5~118°	279~280°
14~43 (A)	$CHCl_3$ 400	1.0	
44~98 (VIb)	$CHCl_3$ 1100	0.5, 111°	264~266°

[*4] All melting points are uncorrected.

9) T. Naito, O. Nagase : Yakugaku Zasshi, **80**, 629 (1960).

10) G.R. Clemo, G.A. Swan : J. Chem. Soc., **1946**, 617; *Ibid*., **1949**, 491, 1723.

11) R.N. Icke, C.E. Redemann, B.B. Wisegarrer, G.A. Alles : Org. Synth., **29**, 64 (1949).

12) P. Fritsch : Ann., **286**, 1 (1895).

13) F.L. Pyman, F.G.P. Remfry : J. Chem. Soc., **101**, 1605.

respectively from EtOH to form colorless needles. The elemental analyses of these methiodides gave identical data. *Anal.* Calcd. for $C_{10}H_{19}NO\cdot CH_3I$: C, 42.45; H, 7.13. Found : C, 42.68; H, 7.21, and C, 42.57; H, 7.21.

Oxidations of VIa and VIb with CrO_3 in AcOH gave the same corresponding ketone (IX), b.p$_4$ 90∼92°, which formed the methiodide as colorless needles, m.p. 278∼279° (*Anal.* Calcd. for $C_{10}H_{17}NO\cdot CH_3I$: C, 42.73; H, 6.52. Found : C, 43.02; H, 6.72) and the picrate, m.p. 186∼188°, undepressed on admixture with an authentic sample supplied by Ochiai.

Hydrogenation of VII——The compound (VII)[14] (10 g.) in MeOH (200 cc.) was catalytically hydrogenated at 170° and 165 kg./cm^2 (initial H_2 pressure, 110 kg./cm^2) over Raney-Ni, prepared from Al-Ni alloy (22 g.) for 8 hr. After cooling, the filtered solution was evaporated. The residual oil was dissolved in Et_2O and the solution was shaken with 30% NaOH, dried over anhyd. Na_2SO_4, and evaporated. Distillation of the residual oil gave a colorless, viscous oil (5.5 g.), b.p$_3$ 108∼115°, and a colorless, more viscous oil (2 g.), b.p$_{0.001}$ 170∼180° (bath temperature). The former base (VIII), by treatment with MeI in EtOH, afforded the methiodide, m.p. 264∼266°, which was identical with that of VIb, but the latter high boiling fraction gave no crystalline salts, such as a methiodide, a picrate and a hydrochloride, and so was not examined further.

Methylation of VIII (5.5 g.) with 85% HCOOH (15 cc.), 36% aqueous HCHO (6 cc.) and HCOONa (6 g.) for 15 hr. on the steam bath gave the above-mentioned alcoholic base (VIb) (4.2 g.) (methiodide, m.p. 264∼266°).

Oxidation of the above obtained alcoholic base VIb (9.6 g.) with CrO_3 (5 g.) in AcOH (35 cc.) at 60∼70° for 9 hr. gave the ketonic base, b.p$_3$ 80∼87° (6.0 g.), which on purification by means of alumina chromatography using $CHCl_3$ as an eluting solvent, furnished exclusively the *cis* ketonic base (IX), b.p$_4$ 90∼92° (picrate, m.p. 186∼188°).

Reduction of IX by Wolff-Kishner Method modified by Huang-Minlon——A mixture of IX (1 g.), 81% hydrazine hydrate (20 cc.), and triethylene glycol (20 cc.) was refluxed at 140° for 5 hr. cooled, and the mixture was transferred to a small distillation flask. To the mixture, KOH (5 g.) was added, the temperature was gradually raised to 210° during 3 hr., and the distillate (160∼210°) was extracted with Et_2O. The extract was dried over anhyd. Na_2SO_4. Evaporation of the Et_2O gave XII (0.5 g.), b.p$_7$ 71∼73°. Its picrate, m.p. 202∼204°, was undepressed on admixture with an authentic sample of *cis*-2-methyldecahydroisoquinoline.

Reduction of IX to VIa and VIb——A solution of IX (920 mg.) in EtOH (30 cc.) was shaken with PtO_2 in H_2 at room temperature. The hydrogen uptake (1 mol.) ceased after 3 hr. The filtered solution was evaporated and the residual oil (0.8 g.) was dissolved in $CHCl_3$ and passed through a column (35×2 cm.) of alumina (100 g.). The column was eluted with $CHCl_3$-MeOH (99:1) (700 cc.) and MeOH (200 cc.). The $CHCl_3$-MeOH fraction gave VIa, b.p$_3$ 102∼104° (100 mg.) (methiodide, m.p. 279∼280°) and the other fraction gave VIb, b.p$_4$ 104∼112° (500 mg.) (methiodide, m.p. 264∼266°). These methiodides were identical with those of VIa and VIb, respectively.

2-Methyl-7-methoxy-1,2,3,4,5,8-hexahydro-isoquinoline (X)——A solution of IV (9.4 g.) in MeOH (37.5 cc.) was added gradually to a solution of liquid NH_3 (500 cc.) and anhyd. Et_2O (50 cc.) under stirring during 15 min. and Na (7.5 g.) was added in small pieces with vigorous stirring each time the blue color of the solution disappeared (2 hr.). Then H_2O (180 cc.) was added to the mixture, and the solution was kept overnight. The deposited colorless prisms (X), m.p. 45∼50° (lit.[1] : m.p. 50∼51°), were collected by suction, and an additional amount of X was obtained by extraction of the filtrate with Et_2O. Total yield, 8.88 g. or 93.7%. The methiodide, m.p. 220∼221° (lit.[1] : m.p. 222°).

Hydrolysis of X to XI——A solution of X (2 g.) and 10% H_2SO_4 (30 cc.) was heated at 80° for 0.5 hr. under N_2. The mixture was cautiously basified with Na_2CO_3 and extracted with Et_2O. After evaporation of the Et_2O, the residual oil (XI) distilled at 108∼109°/3 mm.Hg. Yield, 1.7 g. or 91%. IR ($CHCl_3$) μ : 5.80 (CO), no absorption band near 6.0 μ. UV λ_{max}^{EtOH} mμ (ε) : 217 (2400), 278 (447). It was observed that XI changed to a pale yellow compound, which became a dark colored, viscous liquid in a few days.

Hydrogenation of XI to IX——i) The compound (XI) (1.7 g.), b.p$_3$ 108∼109°, in EtOH (50 cc.) was catalytically hydrogenated over 10% Pd-C (1 g.) at 3 kg./cm^2. After H_2 absorption ceased, the catalyst was filtered off and the filtrate was evaporated. The residual oil distilled at 109∼114°/6 mm.Hg. Alumina-chromatographic purification of the distillate, using $CHCl_3$ as an eluting solvent, gave IX, b.p$_5$ 100∼103°, IR ($CHCl_3$) μ : 5.85 (CO), (methiodide, m.p. 278∼279°; picrate, m.p. 186∼188°) together with a very small amount of VIb (methiodide, m.p. 264∼266°), IR spectrum of which showed a hydroxyl band at 2.75 μ but no carbonyl band.

ii) A solution of XI (1.7 g.) in 5% HCl (50 cc.) was catalytically hydrogenated over 10% Pd-C (1 g) at 2.4 kg./cm^2. After the uptake of H_2 ceased, the catalyst was filtered off and the filtrate was cautiously basified with NaOH and extracted with Et_2O. The dried Et_2O solution was evaporated. Distillation of the residual oil gave only IX (1.0 g.), b.p$_5$ 90° (methiodide, m.p. 278∼279°).

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14) R.B. Woodward, W. von E. Doering : J. Am. Chem. Soc., **67**, 860 (1945).

The authors wish to express their cordial gratitude to Prof. S. Kimoto for his kind guidance and unfailing encouragement. Thanks are also due to Prof. Emeritus E. Ochiai, University of Tokyo for his kind supply of the comparison samples, to the members of Analytical Center, University of Kyoto for elemental microanalyses and to Mr. J. Ōno and Miss S. Kataoka, for their technical assistance. A part of expenses of the present work was defrayed by a Grant-in-Aid for Scientific Research from the Ministry of Education, which is gratefully acknowledged.

Summary

Hydrogenation of isoquinolines, 2-methyl-1,2,3,4-tetrahydro-7-isoquinolinol (V), 7-isoquinolinol (VII), 2-methyl-7-methoxy-1,2,3,4-tetrahydroisoquinoline (IV), was carried out in three different ways. It was clarified that 2-methyl-2,3,4,4*a*,5,6,8,8*a*-octahydro-7(1*H*)-isoquinolone (IX) and a pair of corresponding 2-methyl-decahydro-7-isoquinolinols (VIa and VIb), thus obtained, possessed *cis* configuration at ring juncture. In addition, hydrolysis products of 7-methoxy-1,2,3,4,5,8-hexahydroisoquinoline (X) were discussed.

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98. **Masuo Akagi, Setsuzo Tejima, and Masanobu Haga** : On the Relative Rates of Displacement Reaction of Primary *p*-Tosyloxy Groups of Hexapyranose Derivatives with Sodium Iodide in Acetone Solution.

(*Faculty of Pharmaceutical Sciences, School of Medicine, Hokkaido University*[*1])

The tosylates (*p*-toluenesulfonates) of carbohydrates have been studied by many investigators due to peculiar characteristics which make them of great importance in carbohydrate chemistry.

Especially the displacement reaction of primary tosyloxy groups with sodium iodide in acetone was known as "Oldham and Rutherford rule"[1] and well studied for the preparation of sugar halohydrins and for the confirmation of primary hydroxyl structure.

On this subject, Tipson[2] described in his elaborate review on sugar sulfonates that it seems to be some configurational effects among sugars and anomers. That is, in hexose series, allose, altrose, mannose, and glucose derivatives react more easily with sodium iodide than galactose derivatives. Moreover, in the case of anomeric derivatives, Tipson also speculated that β-D-glucose and β-D-galactose derivatives are more reactive than the corresponding α-anomers from the reaction conditions and yields reported by different authors.

In a recent paper from this laboratory[3] the primary tosyloxy group of D-glucose derivatives was shown to replace easily by potassium thioacetate in acetone. However the authors observed the failure of this reaction for corresponding D-galactose derivatives.[4]

[*1] Nishi-5-chome, Kita-12-jo, Sapporo, Hokkaido (赤木満洲雄, 手島節三, 羽賀正信).

1) J.W.H. Oldham, J.K. Rutherford : J. Am. Chem. Soc., **54**, 366 (1932).

2) R.S. Tipson : "Advances in Carbohydrate Chemistry" **8**, 107 (1953). Academic Press Inc., New York.

3) M. Akagi, S. Tejima, M. Haga : This Bulletin, **10**, 562 (1962).

4) *Idem* : *Ibid.*, (1963) to be published.