UDC 547.837.2.07

107. **Yuichi Kanaoka**: Application of the Robinson Dehydrogenation Reaction. II.[1] Oxidative Cyclization of Some Phenethyl- and Phenylpropyl-amines.

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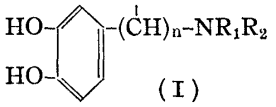
Robinson dehydrogenation reaction consists in the oxidative cyclization of some amines having suitable catechol structure as shown in formula (I), to give polynuclear-condensed nitrogen compounds by means of such a mild oxidizing agent as chloranil.[1,2]

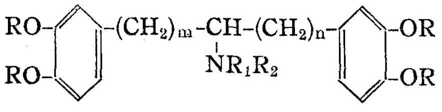
Recently, there have been numerous descriptions concerning the reactions of this type, which include the chemistry of melanine,[3] synthetic applications covering some alkaloids,[4] and reactions between amines and quinones.[5]



(I)

The present paper describes the application of the Robinson dehydrogenation reaction on arylaliphatic non-cyclic nitrogen compounds in order to elucidate some fundamental aspects of this reaction.

The main structural requirements for the reaction seem to be the ability to form a stable ring system and a sufficient basic property of nitrogen atom to undergo nucleophilic attack towards the catechol ring. In an attempt to investigate the effect of the number of methylenes (n) and the nature of substituents on the nitrogen atom (R_1 or R_2) in (I) on reactivity or yield of this reaction, following various amines (II~X; R=H or Me) were prepared and examined.



R = H or Me

	m	n	R_1	R_2
(II)	1	1	H	H
(III)	1	1	H	Me
(IV)	1	1	Me	Me
(V)	1	2	H	H
(VI)	1	2	H	Me
(VII)	1	2	Me	Me
(VIII)	2	2	H	H
(IX)	2	2	H	Me
(X)	2	2	Me	Me
(XI)	1	1	H	CHO
(XII)	1	1	CHO	Me
(XIII)	1	2	H	CHO
(XIV)	1	2	CHO	Me
(XV)	2	2	H	CHO
(XVI)	2	2	CHO	Me

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* Kita-12-jo, Nishi-5-chome, Sapporo (金岡祐一).

1) Part I. S. Sugasawa, Y. Kanaoka: This Bulletin, **3**, 266(1955).

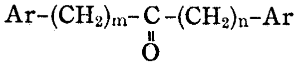
2) R. Robinson, S. Sugasawa: J. Chem. Soc., **1932**, 789; *et seq.*

3) H. Raper: Biochem. J., **21**, 89(1937); R. I. T. Cromatie, J. Harley-Mason: J. Chem. Soc., **1953**, 3525, *et seq.*; A. Robertson, *et al.*; *Ibid.*, **1954**, 1947, *et seq.*; G.R. Clemo, *et al.*: *Ibid.*, **1952**, 3464, *et seq.*

4) J. D. BuLock, J. Harley-Mason: J. Chem. Soc., **1951**, 712; J. Harley-Mason: *Ibid.*, **1953**, 200, 1465; **1954**, 1165, 3651; **1955**, 374; E. J. Forbes: *Ibid.*, **1956**, 513.

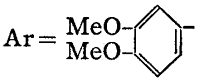
5) F. Kehrmann, M. Cordone: Ber., **46**, 3009(1913); A.G. Green: J. Chem. Soc., **1913**, 925; L. Horner, *et al.*: Ann., **608**, 128(1957); etc.

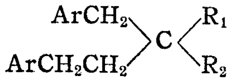
The ketones (XVII, XVIII, XIX) were converted to formamido derivatives (XI, XIII, XV) by the Leuckart reaction and hydrolysed to give primary amines (II, VIII) or reduced with lithium aluminum hydride to give secondary amines (III, VI, IX). (III, VI, IX) were again formylated by Sugasawa's method⁶⁾ with formamide to give (XII, XIV, XVI) and then reduced as above to produce tertiary amines (IV, VII, X). Since hydrolysis of (XIII) was troublesome, (V) was prepared from (XX) by the Curtius method via (XXI), (XXII), and (XXIII).



$Ar-(CH_2)_m-\overset{\displaystyle O}{\overset{\|}{C}}-(CH_2)_n-Ar$

	m	n
(XVII)	1	1
(XVIII)	1	2
(XIX)	2	2

Ar =


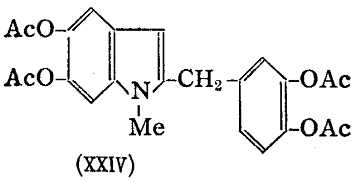


	R_1	R_2
(XX)	CO_2Et	CO_2Et
(XXI)	CO_2H	CO_2H
(XXII)	H	CO_2Me
(XXIII)	H	$CONHNH_2$
(V)	H	NH_2

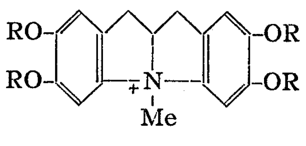
Oxidation was carried out by the general procedure, products being isolated after methylation or acetylation. In the course of the reaction, a reddish brown coloration appeared on addition of the agent and this disappeared rapidly, in accord with the proposed mechanism.²⁾ This characteristic color transformation was called for the sake of convenience "positive color test for Robinson dehydrogenation reaction." On the other hand, this color transformation was not effected occasionally, resulting in persistent color deepening, when it was called "negative." Since it was found that the reaction was brought about successfully when the color test was positive and otherwise not, this test could be of diagnostic value to show the applicability of the reaction.

In the case of primary amines (II, V, VIII), probably due to the competitive side reaction, the color change was negative and nothing definite was obtained, forming a resinous material. This result was consistent with the preliminary experiment, which showed that primary amines reacted with chloranil producing a colored precipitate.

Of secondary amines (III, VI, IX), (VI) gave no definite result with negative color test. In the case of (III), though chloranil gave no definite result, (XXIV) was obtained with potassium ferricyanide as the reagent, after acetylation. This result showed that the initially formed cyclized base did not undergo the second cyclization to give the possible product (XXV) arising from the double ring-closure, but was oxidized secondarily with formation of an indole derivative, thus suggesting also that non-basic nitrogen atom such as in indole could not participate any more in the oxidative cyclization.



(XXIV)



(XXV)

The oxidation of (IX) gave the methiodide in a low yield after methylation, analytical and spectral data of which eliminated both of the structures (XXVI) and (XXVII) for it, thus leaving only uncertain possibility of some secondarily oxidized product such as (XXVIII). The isolation of the product of double ring-closure of (IX) to give (XXVII) appeared unlikely in view of Sugasawa's report⁷⁾ that (XXX) could not be isolated successfully from the cyclization product of (XXIX), but the cyclized product was obtained when the hydrogenated

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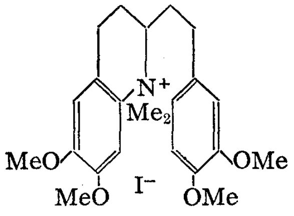
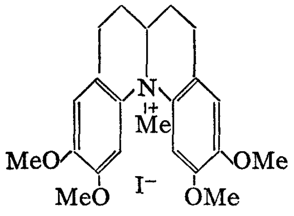
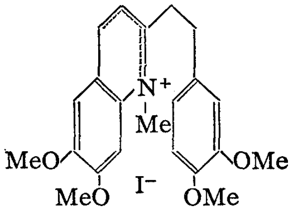
6) S. Sugasawa, H. Shigehara : Yakugaku Zasshi, **62**, 531(1942).
7) S. Sugasawa, N. Sugimoto : Proc. Imp. Acad. (Tokyo), **18**, 656(1942).

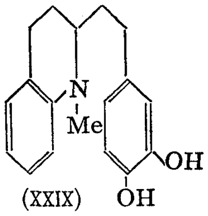
material (XXXI) was used.

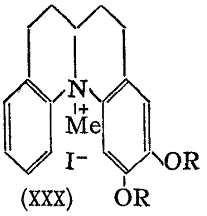
These relatively poor results with secondary amines may be ascribed to the side or secondary oxidative reaction. The former is likely owing to the sensitive nature of the starting material to oxidation and the latter to the one of the product.

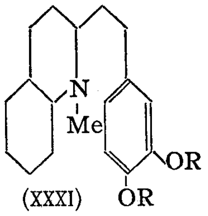

(XXVI)


(XXVII)


(XXVIII)

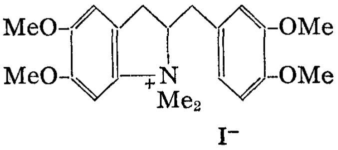

(XXIX)

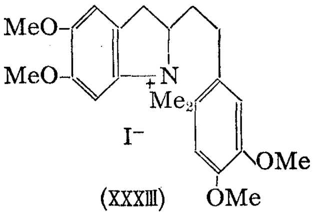

(XXX)

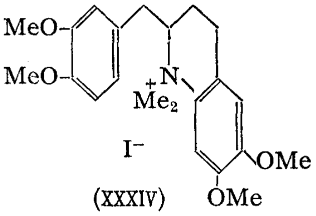

(XXXI)

As for tertiary amines (IV, VII, X), (IV) readily gave the methiodide (XXXII) with positive color test. (VII) similarly gave the methiodide (XXXIII). On decomposition by heating, (XXXIII) produced the material which gave positive Ehrlich's color test as in the case of decomposition of (XXXII), thus excluding the possible alternative structure (XXXIV). (X) gave (XXVI) though in a rather poor yield.

It is shown from these results that the Robinson dehydrogenation reaction may be applied most smoothly to tertiary amines, whereby five-membered ring is likely to be preferentially formed over a six-membered one.


(XXXII)


(XXXIII)


(XXXIV)

The author expresses his deep gratitude to Prof. S. Sugasawa of the University of Tokyo for his unfailing guidance throughout this work. He is also grateful to Prof. Y. Ban for his encouragement and Mr. M. Terashima for his kind cooperation. Thanks are also due to Messrs. O. Yonemitsu, T. O-ishi, and T. Kimura for the measurement of infrared and ultraviolet spectra, and to Mr. K. Narita of the University of Hokkaido and members of the Analytical Room of Tokyo Research Laboratory, Tanabe Seiyaku Co. Ltd., for microanalytical data.

Experimental

1,1-Bis(3,4-dimethoxybenzyl)-methylamine (II)[8]

[1,1-Bis(3,4-dimethoxybenzyl)-dimethylamine (III)—To a solution of N-[bis(3,4-dimethoxybenzyl) methyl]formamide (XI)[8] (4 g.) in anhydr. tetrahydrofuran (60cc.), $LiAlH_4$ (0.8 g.) suspended in dehyd. Et_2O (20 cc.) was added while cooling and stirring, and the mixture was warmed for 4 hr. Excess hydride was decomposed by adding calcd. amount of water, the solvent was removed *in vacuo*, and the residue was extracted with Et_2O. Et_2O layer was extracted with dil. HCl, the aqueous layer was basified with NaOH, and again extracted with Et_2O. The extract was washed, dried, and evaporated, leaving (III) as slightly colored syrup (2.9 g.). Picrate : Yellow prisms, m.p. 216~217° (from EtOH). *Anal.* Calcd. for $C_{20}H_{27}O_4N \cdot C_6H_3O_7N_3$: C, 54.53; H, 5.26; N, 9.75. Found : C, 54.7;H,5.2;

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[8] S. Sugasawa. K. Kakemi : Yakugaku Zasshi, **60**, 35(1940).

N, 9.85.

N-[Bis(3,4-dimethoxybenzyl)methyl]-N-methylformamide (XII)—(III) (2 g.) was heated with formamide (5cc.) at 180° in an oil bath for 4 hr. After cool, hydr. EtOH was added and allowed to stand overnight. Separated solid was recrystallized from hydr. EtOH to prisms, m.p. 124∼125°; yield, 1.5 g. *Anal.* Calcd. for $C_{21}H_{27}O_5N$: N, 3.75. Found : N, 3.9.

1,1-Bis(3,4-dimethoxybenzyl)-trimethylamine (IV)—(XII) (1.4 g.) was reduced as in the case of (III), giving slightly colored syrup (IV) (1 g.).

Picrate : Yellow prisms (from EtOH), m.p. 169°. *Anal.* Calcd. for $C_{21}H_{29}O_4N \cdot C_6H_3O_7N$: C, 55.09; H, 5.48; N, 9.51. Found : C, 54.95; H, 5.5; N, 9.65.

Methiodide : Pale yellow prisms (from MeOH-Et_2O), m.p. 202°. *Anal.* Calcd. for $C_{22}H_{32}O_4NI$: N, 2.79. Found : N, 3.0.

[1-(3,4-Dimethoxybenzyl)-1-(3,4-dimethoxyphenethyl)]-dimethylamine (VI)—(VI) was obatined as in the case of (III) from 9 g. of N-[1-(3,4-dimethoxybenzyl)-1-(3,4-dimethoxyphenethyl)methyl]-formamide (XIII)[9] as colorless syrup (6 g.).

Hydrochloride : Colorless needles (from EtOH-Et_2O), m.p. 153∼154°. *Anal.* Calcd. for $C_{21}H_{29}O_4N \cdot HCl$: C, 63.71; H, 7.64; N, 3.54. Found : C, 63.5; H, 8.0; N, 3.9.

N-Methyl-N-[1-(3,4-dimethoxybenzyl)-1-(3,4-dimethoxyphenethyl)methyl]-formamide (XIV)—(XIV) of 1 g. was obtained from 1.4 g. of (VI) as in the case of (XII). Colorless needles (from hydr. EtOH), m.p. 127∼128°. *Anal.* Calcd, for $C_{22}H_{29}O_5N$: C, 68.19; H, 7.54; N, 3.62. Found : C, 68.0; H, 7.5; N, 3.7.

[1-(3,4-Dimethoxybenzyl)-1-(3,4-dimethoxyphenethyl)]-trimethylamine (VII)—As in the case of (III), (VII) (0.7 g.) was obtained from (XIV) (0.8 g.) as colorless solid, m.p. ca. 60∼63.°

Methiodide : Colorless prisms (from MeOH-Et_2O), m.p. 164∼166°. *Anal.* Calcd. for $C_{23}H_{34}O_4NI$: C, 53.59; H, 6.65; N, 2.72. Found : C, 53.65; H, 6.5; N, 2.9.

N-[Bis(3,4-dimethoxyphenethyl)methyl]-formamide(XV)—Bis(3,4-dimethoxyphenethyl) ketone(XXIX) (5 g.) was treated with formamide as in the case of (XII) to give (XV) in 90% yield. Colorless needles (from aq. MeOH), m.p. 125∼126°. *Anal.* Calcd. for $C_{22}H_{29}O_5N$: C, 68.19; H, 7.54; N, 3.62. Found: C, 68.2; H, 7.8; N, 3.55.

1,1-Bis(3,4-dimethoxyphenethyl)-methylamine (VIII)—(XV) (5 g.) was warmed with 15% HCl (75 cc.) in a water bath for 7 hr. The mother liquor was extracted with AcOEt to remove the unreacted material, the aqueous layer was basified with Na_2CO_3, and taken up in AcOEt. The extract was washed, dried, and evaporated, leaving (VIII) as slightly brownish oil, 4.2 g. or 91%.

Hydrochloride : Colorless needles (from MeOH-Et_2O), m.p. 139∼141°. *Anal.* Calcd. for $C_{21}H_{29}O_4N \cdot HCl$: C, 63.70; H, 7.64; N, 3.54. Found : C, 63.6; H, 7.5; N, 3.6.

1,1-Bis(3,4-dimethoxyphenethyl)-dimethylamine (IX)—(XIII) (8 g.) was reduced as in the case of (III) to give (IX) (5 g.) as colorless syrup.

Hydrochloride : Colorless prisms (from MeOH-Et_2O), m.p. 141∼142°. *Anal.* Calcd. for $C_{22}H_{31}O_4N \cdot HCl$: C, 64.45; H, 7.90; N, 3.41. Found : C, 63.9; H, 7.6; N, 3.9.

1,1-Bis(3,4-dimethoxyphenethyl)trimethylamine (X)—(IX) (1.5 g.) was treated with formamide as in the case of (XII) to give (XVI) as colorless syrup (1.3 g.). This was reduced without purification with $LiAlH_4$ (0.4 g.) as above, producing (X) as faintly colored syrup (1 g.).

Methiodide : Colorless needles (from MeOH-Et_2O), m.p. 137∼138°. *Anal.* Calcd. for $C_{24}H_{36}O_4NI$: C, 54.45; H, 6.86; N, 2.64. Found : C, 54.85; H, 7.0; N, 2.2.

Diethyl 2-(3,4-Dimethoxybenzyl)-2-(3,4-dimethoxyphenethyl)malonate (XX)—A solution of diethyl malonate (16 g.) in dehyd. EtOH (10 cc.) was added slowly, while cooling and stirring, to EtONa, prepared from dehyd. EtOH (30 cc.) and Na (1.28 g.). The mixture was warmed slightly to dissolve the precipitating salt, cooled again, then 3,4-dimethoxyphenethyl bromide (12.5 g.) in dehyd. EtOH (10 cc.) was added with stirring. After refluxing for 5 hr., most of EtOH was removed *in vacuo*, water added, and extracted with benzene. The benzene layer was washed, dried, evaporated, and the residue was distilled. Diethyl 2-(3,4-dimethoxyphenethyl)malonate was obtained as viscous oil, b.p. 191∼195°; 11.2 g. or 75%.

In a manner similar to that described above, (XX) was obtained from the above ester (14 g.) and NaOEt, prepared from Na (0.5 g.) and dehyd. EtOH (30 cc.), and 3,4-dimethoxybenzyl chloride (9.4 g.) in dehyd. EtOH (10 cc.). Yield, 13.4 g. or 66%, of feathers (from hexane), m.p. 85∼87°. *Anal.* Calcd. for $C_{26}H_{34}O_8$: C, 65.80; H, 7.22. Found : C, 65.7; H, 6.9.

Methyl 2-(3,4-Dimethoxybenzyl)-2-(3,4-dimethoxyphenethyl)acetate (XXII)—A mixture of KOH (2 g.), 80% EtOH (20 cc.), and (XX) (5.4 g.) was refluxed for 8 hr. After removal of EtOH *in vacuo*, water added, and acidified with dil. HCl. The crude malonic acid (XXI) separated as yellowish solid; yield, 4 g. This acid was heated in an oil bath at 150° for 30 min., cooled, and recrystallized from benzene-hexane to give 80% of the acetic acid as needles, m.p. 108∼111°. 2-(3,4-Dimethoxybenzyl)-

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9) Y. Kanaoka, M. Terashima, T. Kimura : This Bulletin, **7**, 648(1959).

2-(3,4-dimethoxyphenethyl)acetic acid. *Anal.* Calcd. for $C_{21}H_{26}O_6$: C, 67.36; H, 7.00. Found : C, 67.7; H, 7.1.

The above acid was esterified with dry HCl-MeOH as usual, giving 90% of (XXII), needles (from benzene-ligroine), m.p. 64~65°. *Anal.* Calcd. for $C_{22}H_{28}O_6$: C, 68.02; H, 7.27. Found : C, 68.6; H, 7.1.

2-(3,4-Dimethoxybenzyl)-2-(3,4-dimethoxyphenethyl)acetohydrazide (XXIII)—(XXII) was refluxed with excess of anhyd. hydrazine (b.p. 115~116°) in AmOH solution in an oil bath for 8 hr. From the residue (XXIII) was obtained as needles (from EtOH), m.p. 114~116° in 82% yield. *Anal.* Calcd. for $C_{21}H_{28}O_5N_2 \cdot H_2O$: C, 62.05; H, 7.44; N, 6.89. Found : C, 61.7; H, 7.5; N, 7.3.

Benzylurethan of (XXIII); Benzyl N-[1-(3,4-Dimethoxybenzyl)-1-(3,4-dimethoxyphenethyl) methyl]carbamate—To a solution of (XXIII) (0.7 g.) in 10% H_2SO_4 (20 cc.) and AcOH (44 cc.), Et_2O (35 cc.) was added and to this mixture a solution of $NaNO_2$ (0.37 g.) in water (3 cc.) was added dropwise under ice-cooling and stirring. Et_2O layer was separated and the aqueous layer was extracted with Et_2O. The combined Et_2O extract was washed with 10% $NaHCO_3$ under cooling, dried ($MgSO_4$). To this was added benzyl alcohol (0.25 g.), Et_2O removed *in vacuo*, and the mixture was refluxed with dehyd. benzene (30 cc.) for 3 hr. From the residue the urethan was obtained as colorless needles (form MeOH), m.p. 102~103°; 0.8 g. or 93%. *Anal.* Calcd. for $C_{28}H_{33}O_6N$: C, 70.32; H, 6.93; N, 2.92. Found : C, 70.5; H, 6.95; N, 3.2.

1-(3,4-Dimethoxybenzyl)-1-(3,4-dimethoxyphenethyl)methylamine (V)—The urethan (1 g.) was catalytically hydrogenated in EtOH solution with Pd-charcoal. Conc. HCl (0.2 cc.) was added, the catalyst was removed by filtration, and the solvent removed *in vacuo*. The residue was dissolved in warm dil. HCl, extracted with AcOEt after cooling, the aqueous layer was basified with 10% NaOH, and the product was isolated by means of Et_2O. (V), colorless prisms (from dehyd. Et_2O), m.p. 86~87°. Yield, 0.5 g. or 69%. *Anal.* Calcd. for $C_{20}H_{27}O_4N$: C, 69.56; H, 7.82. Found : C, 69.7; H, 8.05.

Hydrochloride : Colorless needles (from MeOH-Et_2O), m.p. 123°. *Anal.* Calcd. for $C_{20}H_{27}O_4N \cdot HCl$: N, 3.67. Found : N, 3.5.

N-Formyl derivative obtained from (V) in usual way was identical with (XIII) prepared from (XVIII).

General Procedure of Oxidation

a) **Demethylation**—The methoxyl compound (1 part) was mixed with 48% HBr (5~10 parts by weight) and the whole was heated at 130~140°(oil bath temp.) for 1.5 hr. The reaction mixture was evaporated *in vacuo*, water added, and evaporated again. The residue, after drying over alkali in a vacuum desiccator, was recrystallized, or used for next oxidation without purification.

b) **Oxidation (with Chloranil)**[1,2]—A solution of the hydrobromide (1 g.) of above demethylated compound in 95% EtOH (ca. 50 cc.) was mixed with AcOK (1.3~1.5 moles), warmed gently, and filtered. Chloranil (0.9~1 mole) was dissolved in hot EtOH (100~150 cc.) and the solution cooled with stirring so as to cause a fine crystallization; it was then added to the above filtrate with stirring at a room temp. during about 0.5 hr. Usually a reddish brown coloration appeared, then disappeared rapidly (positive), and sometimes kept deepening (negative).

After 1~2 hr.'s standing, 10% HCl (5 cc.) or HCl-MeOH (2~3 cc.) was added, a small amount of precipitate was filtered off, and the filtrate was evaporated *in vacuo*. The residue was dissolved in 5% HCl under warming if necessary and evaporated *in vacuo*. When the above residue was insoluble in dil. HCl, it was extracted several times with peroxide-free Et_2O to remove dihydrochloranil. The residue thus obtained was methylated or acetylated.

c) **Methylation**—Above oxidation product (0.5 g.) was suspended in water (3 cc.), aq. KOH (5 cc., 33%) added, and the mixture was shaken until a clear solution resulted. Me_2SO_4 (3 cc.) was then added and the whole shaken vigorously, whereby exothermic reaction occurred. After this procedure (aq. K_2CO_3 5 cc., 33% and Me_2SO_4, 3 cc.) was repeated twice, aq. K_2CO_3 (15 cc., 33%) was added to decompose excess of reagent and warmed in a water bath if necessary. When cool, the separated product was taken up in $CHCl_3$ (20 cc., twice), $CHCl_3$ layer extracted with water (10 cc., 3 times), and the aqueous layer was filtered. To this KI (1 g.) was added and the mixture was stored in an ice chest overnight to precipitate the methiodide. This salt was collected, washed with water, dried in a desiccator, and recrystallized from MeOH-Et_2O.

d) **Acetylation**—A mixture of the oxidation product (0.5 g.), Ac_2O (5 cc.), and a few drops of pyridine was refluxed for 1.5 hr., decomposed with ice (2~3 hr.), extracted with benzene, and worked up as usual.

Oxidation of (II, V, VI, VIII; R=H)—On addition of chloranil, reddish violet coloration developed, which deepened as the reaction proceeded (color-test, negative), finally giving a dark purple precipitate, from which nothing definite was isolated.

Oxidation of (III; R=H); 1-Methyl-2-(3,4-diacetoxybenzyl)-5,6-diacetoxyindole (XXIV)—To a solution of the hydrobromide of (III; R=H) (0.75 g.) in water (50 cc.) a mixture of $K_3Fe(CN)_6$ (1.35 g.), $NaHCO_3$ (0.7 g.), and water (30 cc.) was added under stirring, during 0.5 hr. After stirring for 0.5

hr., the whole was extracted with AcOEt (30 cc., 3 times), dried, and evaporated. The residue (0.4 g.; purple with Ehrlich's color-test) was mixed with dehyd. pyridine (3 cc.) and Ac_2O (2 cc.), the mixture was allowed to stand for 2 days, and worked up as usual. After purification through alumina column, (XXIV) was obtained as colorless pillars (from benzene-hexane), m.p. 191~193°. Yield, 0.3 g. or 33%. *Anal.* Calcd. for $C_{24}H_{23}O_8N$: C, 63.57; H, 5.11; N, 3.09. Found : C, 63.7; H, 5.35; N, 2.9. UV λ_{max}^{EtOH} mμ (log ε) : 227 (4.54), 288.5 (3.99).

N-Acetyl-1,1-bis(3,4-diacetoxybenzyl)dimethylamine was also prepared from (III; R=H) for comparison. Colorless needles (from benzene-hexane), m.p. 133~134°. *Anal.* Calcd. for $C_{25}H_{27}O_9N$: C, 61.85; H, 5.60; N, 2.89. Found : C, 62.05; H, 5.6; N, 2.85. UV λ_{max}^{EtOH} 272 mμ (log ε 3.35).

Oxidation of (IX)—The hydrobromide of (IX; R=H) (2 g.) was treated with AcOK (0.8 g.) and chloranil (1.25 g.) as described in the general procedure. The color deepened without fading (negative). After methylation there was obtained methiodide as pale yellow fine needles (from MeOH-Et_2O), m.p. 207~210°(decomp.). Yield, 0.27 g. or 12%. *Anal.* Found : C, 52.9; H, 5.4; N, 3.0. (Calcd. for $C_{22}H_{28}O_4NI$ (XXVIII; Γ_2) : C, 53.43; H, 5.09; N, 2.73). UV λ_{max}^{EtOH} mμ(log ε) : 275(3.55), 284(3.49), 355.5 (4.33).

Oxidation of (IV); 1,1-Dimethyl-2-(3,4-dimethoxybenzyl)-5,6-dimethoxyindolinium Iodide (XXXII)—The hydrobromide of (IV; R=H) (0.8 g.) was treated with AcOK (0.3 g.) and chloranil (0.45 g.) as usual, whereby initial color faded distinctly on every addition, thus showing the positive color-test. After the usual procedure, the methiodide was obtained as colorless needles (from MeOH-Et_2O), m.p. 213°(decomp.). Yield, 0.55 g. or 61%. *Anal.* Calcd. for $C_{21}H_{28}O_4NI$: C, 51.96; H, 5.82; N,3.27. Found: C, 52.0; H, 5.8; N, 3.0. UV λ_{max}^{EtOH} mμ(log ε) : 280.5(3.93), 284(3.91).

(XXXII) (2 mg.) was heated to melt and dissolved in EtOH (0.5 cc.), which developed reddish purple on Ehrlich's color-test.

Oxidation of (VII; R=H); 1,1-Dimethyl-2-(3,4-dimethoxyphenethyl)-5,6-dimethoxy-indolinium Iodide (XXXIII)—On oxidation, (VII; R=H) gave as in the case of (XXXII), the methiodide forming slightly colored prisms (from MeOH-Et_2O), m.p. 189~191°(decomp.). Yield, 0.3 g. or 60%. *Anal.* Calcd. for $C_{22}H_{30}O_4NI$: C, 52.91; H, 6.05; N, 2.80. Found : C, 52.7; H, 6.2; N, 3.0. UV λ_{max}^{EtOH}mμ(log ε) : 277(3.90), 280.5(3.94). Its decomposition product showed positive Ehrlich's test as above.

Oxidation of (X; R=H); 1,1-Dimethyl-2-(3,4-dimethoxyphenethyl)-6,7-dimethoxy-1,2,3,4-tetrahydroquinolinium Iodide (XXVI)—The hydrobromide of (X; R=H) (0.6 g.) was treated with AcOK (0.3 g.) and chloranil (0.3 g.) as above. Reddish purple coloration appeared, fading of which was not observed clearly. After 0.5 hr., reddish colored substance began to precipitate out accompanied with gradual discoloration. After working up as usual, the methiodide was obtained as faint yellow needles (from MeOH-Et_2O), m.p. 150~152°(decomp.). Yield, 0.13 g. or 21%. *Anal.* Calcd. for $C_{23}H_{32}O_4NI$: C, 53.79; H, 6.31; N, 2.73. Found : C, 53.8; H, 6.1; N, 2.6. UV λ_{max}^{EtOH} mμ(log ε) : 278(3.70), 286.5(3.63).

Summary

Varied aliphatic non-cyclic amines (II~X) were prepared and oxidized in the hope of elucidating some fundamental aspects of the Robinson dehydrogenation reaction. In the case of tertiary amines the cyclization was brought about most smoothly, whereby five-membered ring was likely to be formed preferentially over a six-membered one. In secondary amines, yields were varied presumably due to side or secondary reactions, while primary amines were shown to be unsuitable for this reaction.

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