Mechanism of Plancher's Rearrangement. I. Twofold Wagner-Meerwein Type Rearrangement of Indolenines

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Although, Plancher's rearrangement, which was described as early as 1898, has been much discussed[1], it is unfortunate that there are found many misunderstandings about the scope of this rearrangement, because of lack of definitive studies. In 1898, Plancher[2] obtained a indolenium iodide, m. p. 237°C, from 2-ethyl-3-methylindole (I) and 2-methyl-3-ethylindole (II) by heating with methyliodide at 120°C.

He assigned the structure of 1, 2, 3-trimethyl-3-ethylindolenium iodide (III) to the indolenium iodide, on a non-confirmative chemical base, but whatever structure it has, migration of the subsituents has to be assumed, in order to explain the formation of the same indolenium iodide, m. p. 237°C, from both I and II.

Another type of rearrangement was established when Plancher[3] obtained two indolenium iodides, m. p. 186° and 232°C, from 2-isopropyl-3-methylindole (IV) by heating with methyliodide at 85~90°C for 2 days.

He posturated the formation of the two intermediate indolenines VII and VIII which would give corresponding indolenium iodides V and VI with methyliodide. Although the structure of the indolenium iodides (V or VI) remained unestablished, the conversion of the indolenium iodide, m. p. 186°C, into the isomeric indolenium iodide, m. p. 232°C, was achieved by heating at 180~190°C for 10 min. From these and other experiments, Plancher could draw the following conclusion[4]: 1) The indolenium iodide with the lower melting point can be converted into the isomeric indolenium iodide with the higher melting point. 2) The heavier substituent migrates to the β-position. However, his conclusion 2) can be hardly justified without further strenuous studies, since the structures of these indolenium iodides were only presumed on nothing but some analogies, except on one occasion; i.e. 1,2,3-trimethyl-3-phenylindolenium iodide (X). By heating 2-phenylindole (IX) with methyliodide at 120°C, Plancher[5] obtained an indolenium iodide, m. p. 226~227°C, which

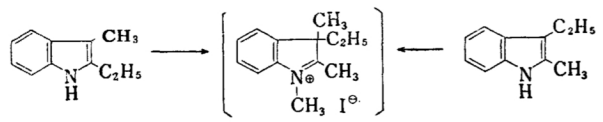


Fig. 1.

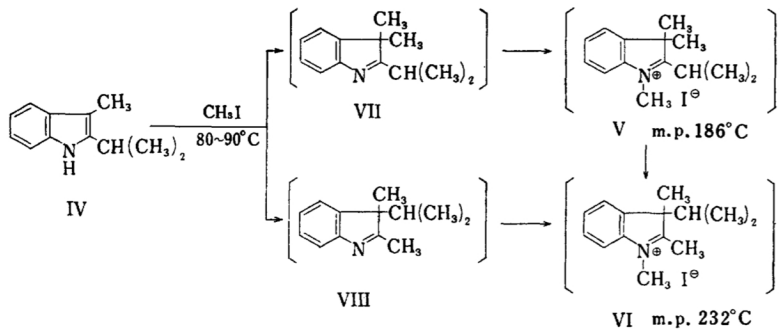


Fig. 2.

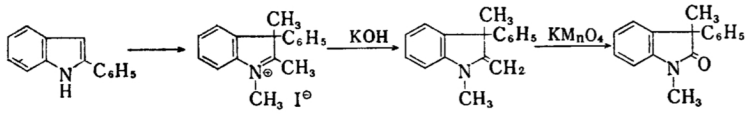
1) For general discussion of Plancher's rearrangement and other related rearrangement reactions, see P. L. Julian, E. W. Meyer and H. C. Pring, "The Chemistry of Indoles" in R. Elderfield, "Heterocyclic Compounds", Vol. 3, John Wiley & Sons., Inc., New York (1952), p. 1.

2) G. Plancher, *Gazz. chim. ital.*, **28**, II, 374 (1898); *Chem.-Zentr.*, **1899**, I, 282.

3) G. Plancher, *Atti. accad. Lincei*, (5), **11**, II, 182 (1902); *Chem.-Zentr.*, **1902**, I, 1322.

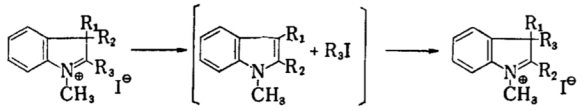
4) G. Plancher, *Atti. acced. Lincei*, (5), **9**, 115 (1900), *Chem.-Zentr.*, **1900**, I, 867. See also a brief discussion of Julian, Ref. 1.

5) G. Plancher, *Gazz. chim. ital.*, **28**, II, 391 (1898); *Chem.-Zentr.*, **1899**, I, 283.



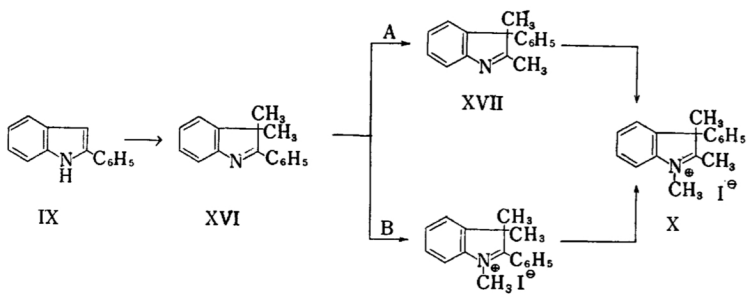
IX X XI XII

Fig. 3.



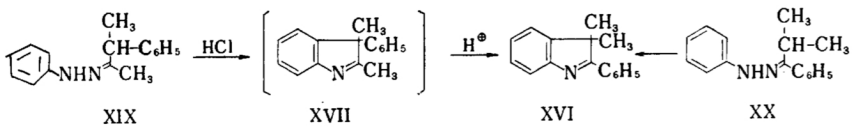
XIII XIV XV

Fig. 4.



IX XVI XVII XVIII X

Fig. 5.



XIX XVII XVI XX

Fig. 6.

he thought to be 1, 2, 3-trimethyl-3-phenylindolenium iodide (X) as the result of rearrangement involving an exchange of methyl with phenyl group. But the structure of this indolenium iodide was left to be determined by chemical means until Boyd-Barrett[6] (1932) repeated Plancher's experiment and oxidized the product with alkaline potassium permanganate (via the intermediate XI) to form 1, 3-dimethyl-3-phenyloxyindole (XII), the nitro derivative of which was found to be identical with the one obtained by the umambiguous synthetic route.

The mechanism of the rearrangement of indolenium compounds proposed by Plancher[7] is illustrated in Fig. 4. According to this mechanism, the formation of iodobenzene and its subsequent reaction with 1,2,3-trimethylindole to secure 1, 2, 3-trimethyl-3-phenylindolenium iodide (X), though it is highly improbable, is an inevitable consequence to explain the formation of X from 2-phenylindole. Julian[8] pointed out another conceivable route from IX to X, assuming that 3, 3-dimethyl-2-phenylindolenine (XVI) is the intermediate and that rearrangement involving an exchange of methyl with the phenyl group takes place at this point (Fig. 5, route A).

This Julian's alternative postulated the migration of the substituents of indolenine which has not been demonstrated in any indolenine with umambiguous constitution[9], and it is unfortunate

6) H. S. Boyd-Barrett, *J. Chem. Soc.*, **1932**, 321.

7) G. Plancher, *Atti, accad. Lincei*, (5), **11**, 183 (1902); *Chem.-Zentr.*, **1902**, I, 1322.

8) See Ref. 1, p. 106.

9) M. Garry, *Ann. chim.*, **17**, 5 (1942); *Chem. Abstr.*, **36**, 6875 (1942), obtained two indolenines; 3,3-diphenyl-2-methylindolenine, m. p. 145°C, picrate, m. p. 210°C, and isomeric indolenine presumingly 2, 3-diphenyl-3-methylindolenine, m. p. 108°C, picrate, m. p. 155°C, from 1-anilino-1-phenylethylketone by heating with aniline and aniline hydrochloride at 160~165°C, but unfortunately she did not mention their possible interconversion. According to Julian's description, "she apparently assumed. and let it to the reader to assume, that the shifts involved in her synthesis took place *before* cyclization to the indolenines". But the recent study of the mechanism of Bishler's indole synthesis seems to suggest that the skeleton change of the anilinoketone would not occur *during* or *before* the cyclization. [F. Weygand and E. Richter, *Chem. Ber.*, **88**, 499 (1955).]. From the present achievement, it is safely assumed that the first formed 3, 3-diphenyl-2-methylindolenine rearranges to give 2, 3-diphenyl-3-methylindolenine under the reaction condition.

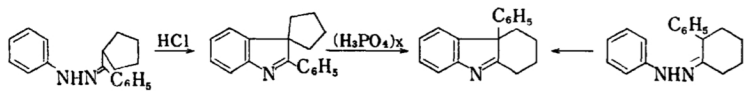


Fig. 7.

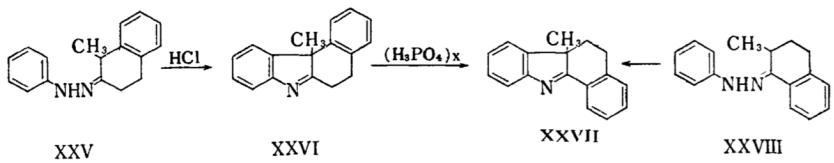


Fig. 8.

that sometimes Plancher's rearrangement was understood as this sort of rearrangement of indolenines only to cause many confusions[10].

This paper is concerned with demonstration of this migration of substituents of indolenines to elucidate the mechanism of Plancher's rearrangement. In order to obtain 2, 3-dimethyl-3-phenylindolenine (XVII), Fisher-Brunner's method was applied on 3-phenylbutane-2-one (XIX) under various conditions using zinc chloride, alcoholic hydrogen chloride and borontrifluoride etherate as catalyst.

Even under very mild condition (with alcoholic hydrogen chloride at 0°C), all attempts failed only to afford 3, 3-dimethyl-2-phenylindolenine (XVI)[11], apparently resulting from the intermediate indolenine XVII by rearrangement reaction involving an exchange of the phenyl with the methyl group.

The view that 3-phenylbutane-2-one would rearrange to isobutyrophenone and then its phenylhydrazone (XX) would cyclize to XVI seems untenable, since the fact that the entirely reversed process is predominant in acidic condition was firmly established recently[12].

Also it is hard to find any reasonable sequence which would explain a possible migration of substituents in the cyclization steps of Fischer-Brunner's synthesis, which has a common feature with Fischer's indole synthesis extensively studied by Carlin et al.[13] At any rate, route A (Fig. 5) which assumes hypothetical rearrangement XVI → XVII has to be abandoned[14].

Although this is the first case, in which a rearranged indolenine is obtained in Fischer-Brunner's indolenine synthesis, the first example of the rearrangement of an indolenine to the other indolenine, both with established structures, was encountered in the isomerization of XXII to XXIII.

Spiro-(cyclopentane-1, 3'-*pseudo*-2'-phenylindole)[15](XXII) (λ_{max} 310 mμ)[16] which was synthesized from cyclopentylphenylketone phenylhydrazone (XXI) by Fischer-Brunner's synthesis by saturating its alcoholic solution with dry hydrogen chloride, was found to convert, when heated with polyphosphoric acid[17], into 11-phenylcarbazolenine (XXIII) which in turn was prepared from 2-phenylcyclohexanone phenylhydrazone (XXIV).

Another interesting rearrangement was demonstrated when 11b-methyl-5, 6-dihydro-11b-benzo-[*c*]carbazole[18] (XXVI) which could be prepared from α-methyl-β-tetralone phenylhydrazone (XXV), was heated with polyphosphoric acid

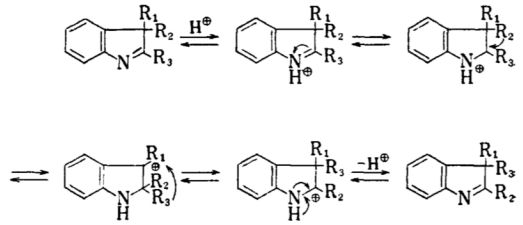


Fig. 9.

10) For example, B. Witkop and J. B. Patrick, *J. Am. Chem. Soc.*, 73, 1358 (1951), discussed the rearrangement of indolenine as Plancher's rearrangement.

11) An attempt was made to prepare 2, 3-dimethyl-3-phenylindolenine (XVII) by alkylation of 2-methyl-3-phenylindole with sodium amide and methyliodide in liquid ammonia only to afford 1, 2-dimethyl-3-phenylindole. Also another attempt to obtain the indolenine XVII by Grignard synthesis from 2-methyl-3-phenylindole was found fruitless.

12) S. Barton and C. R. Portor, *J. Chem. Soc.*, 1956, 2483.

13) R. B. Carlin, W. D. Henley and D. P. Carlson, *J. Am. Chem. Soc.*, 79, 5712, (1957); and also his preceeding papers on the same subject.

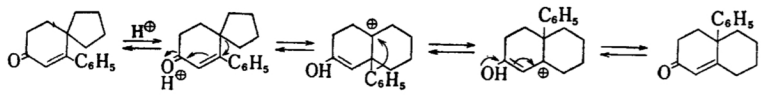
14) The fact that the rearrangement actually takes place by route B (Fig. 5) was established by our experiment which follows. To avoid unnecessary confusion, the term of "Plancher's rearrangement" should be used to indicate solely the *rearrangement of indolenium compounds* such as illustrated XVIII→X (Fig. 5).

15) For the nomenclature of *spiro* compounds, see *Chem. Abstr.*, 39, 5885, 5888 (1945).

16) U. V. spectrum of 3, 3-dimethyl-2-phenylindolenine: λ_{max} 306 mμ (log ε 4.177). B. Witkop, J. B. Patrick and H. M. Kissman, *Chem. Ber.*, 85, 953 (1952).

17) When indolenine synthesis using polyphosphoric acid was applied on cyclopentylphenylketone-phenylhydrazone, 11-phenyltetrahydrocarbazolenine was formed directly.

18) According to the nomenclature of A. M. Patterson and L. T. Capell, "The Ring Index", Reinhold Publishing Corp., New York (1940), p. 331.



XXIX XXX

Fig. 10.

at 180°C for 5 min. The rearranged indolenine was found to be identical with 6a-methyl-5, 6-dihydro-6a-benzo[*a*]carbazole[18] (XXVII) provided from β-methyl-α-tetralone phenylhydrazone (XXVIII) by usual method.

The mechanism of the migration of the substituents of indolenines can be readily explained by twofold Wagner-Meerwein type rearrangement initiated by the attack of a proton on the nitrogen atom of the indolenine nucleus as formulated in Fig. 9[19-21].

Since undoubtedly all steps are in equilibrium, the thermodynamical stability of the products would be the predominant factor to determine the direction of the migration, and it would be safely assumed that mesomeric stabilization of the phenyl group is responsible in the case of XVII → XVI and XXVI → XXVII. The seemingly contradictory attitude of XXII toward acid can be reasoned when the inspection of its Stuart's model reveals that a considerable steric repulsion is observed between the phenyl group and the hydrogens of 3, 4-position of cyclopentyl group of XXII, i.e. this is the case where steric effects suppress mesomeric stabilization of the phenyl group[22].

Harmonious with this result is the smooth transformation[23] of 6-phenyl-*spiro*(4, 5)decen-6-one-8 (XXIX) to 10-phenyl-2-keto-$\Delta^{1,9}$-octahydronaphthalene (XXX) by heating with polyphosphoric acid.

Experimental[24]

3-Phenylbutane-2-one.—A mixture of 16.3 g. of methyliodide and 30 cc. of absolute ether was added dropwise to a mixture of 6.4 g. of magnesium and 30 cc. of absolute ether at room temperature. To the chilled Grignard solution, a mixture of 24.5 g. of α-methyl benzylcyanide[25] and 30 cc. of ether was added, and the reaction mixture was kept at room temperature for 4 hr. The Grignard complex was destroyed by the addition of diluted sulfuric acid and extracted with ether. The ethereal extract was washed with 5% sodium carbonate solution and water and dried over anhydrous sodium sulfate. Removal of the solvent afforded an oil which was distilled in vacuo to give 21.2 g. of 3-phenylbutane-2-one, b. p. 107~115°C/20 mmHg[26].

3, 3-Dimethyl-2-phenylindolenine (XVI) from 3-Phenylbutane-2-one Phenylhydrazone.—*By zinc chloride method*[27].—A mixture of 11.8 g. of 3-phenylbutane-2-one and 8.6 g. of phenylhydrazine was heated on a water bath for 40 min. The mixture became turbid and the separation of water drops was observed. Then the mixture was extracted with ether and dried over anhydrous sodium sulfate. After the solvent was evaporated completely, the residue was dissolved in 160 cc. of absolute ethanol and 80 g. of zinc chloride was added. The mixture was refluxed for 20 hr. and the alcohol was removed. The residue was made basic by the addition of concentrated ammonia solution to precipitate basic material. This was extracted with ether, and the ether extract was washed with water and dried over anhydrous potassium carbonate. Removal of the solvent afforded a residue which was distilled in vacuo to give 2.3 g. of a pale yellow liquid, b. p. 110~139°C/2 mmHg.

Found: C, 86.05; H, 7.27; N, 6.77. Calcd. for $C_{16}H_{15}N$: C, 86.84; H, 6.83; N, 6.33%.

The picrate was recrystallized to yield crystals, m. p. 170~172°C, which was found identical with the picrate of 3, 3-dimethyl-2-phenylindolenine, m. p. 167~168°C, prepared from an authentic 3, 3-dimethyl-2-phenylindolenine[28] (XVI), by mixed melting point determination.

19) An intermediate possessing *spiro* structure is to be assumed in the case of XXVI→XXVII, and it seems noteworthy to compare with the dienone-phenol rearrangement of 2-keto-4a-methyl-2, 4a, 5, 6-tetrahydrobenzo[*c*]phenathrene in which the transformation which requires a *spiro* intermediate is inhibited. C. Djerassi and T. T. Grossnickel, *J. Am. Chem. Soc.*, **76**, 1741 (1954). See also Ref. 14 in the preceeding paper on the rearrangement of 2, 3-disubstituted indoles.

20) A novel cleavage reaction of benzyl and *t*-butyl group is recently reported when R_1 (Fig. 9) is benzyl and *tirt*-butyl, and the same sort of cleavage reaction was demonstrated on 11-benzyltetrahydrocarbazolenine and 11-*tirt*-butyltetrahydrocarbazolenine. M. Nakazaki, S. Isoe and K. Tanno, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **76**, 1262 (1955).

21) The mechanism of Brunner-Robinson-Suginome's rearrangement (conversion of 3, 3-dimethylindolenine into 2, 3-dimethylindole) is the special case where R_3 is a hydrogen atom. K. Brunner, *Monatsh.*, **17**, 255 (1896); R. Robinson and H. Suginome, *J. Chem. Soc.*, **1932**, 298.

22) B. Witkop and J. B. Patrick, *J. Am. Chem. Soc.*, **73**, 1558 (1951), tried the rearrangement of 11-methyltetrahydorocarbazolenine in a hope to get *spiro*-(cyclopentane-1′, 3-*pseudo*-2′-methylindole) but in vain. This can be attributed to the stability of 11-methyltetrahydrocarbazolenine in respect of the steric effect as well as the small migration aptitude of the methyl group.

23) M. Nakazaki and S. Isoe, unpublished experiment.

24) All the melting points are uncorrected values. All ultraviolet spectra were measured with an EPS-2 Hitachi selfrecording spectrophotometer and infrared spectra on a Perkin Elmer Model 12C. The analyses were performed in the Microanalytical Laboratory of the Institute of Polytechnics, Osaka City University.

25) B. p. 106~112°C/11 mmHg or 71~79°C/2 mmHg. Prepared following the procedure of H. M. Crawford, *J. Am. Chem. Soc.*, **56**, 140 (1934).

26) W. D. Kumler, L. A. Strait and E. L. Alpen, *J. Am. Chem. Soc.*, **72**, 1463 (1950).

27) Following Leuch's procedure to synthesize 3, 3-dimethyl-2-phenylindolenine from isobutyrophenone phenylhydrazone. H. Leuchs, A. Heller and A. Hoffman, *Ber.*, **62**, 877, (1929).

28) B. p. 178~182°C/9 mmHg. Picrate, m. p. 167~168°C. Prepared by polyphosphoric acid method. H. M. Kissman, D. W. Farnsworth and B. Witkop, *J. Am. Chem. Soc.*, **74**, 3948 (1952).

By borontrifluoride etherate method[29].—To a mixture of 2.7 g. of 3-phenylbutane-2-one phenylhydrazone[30] and 30 cc. of acetic acid, 2.1 g. of borontrifluoride etherate was added and refluxed for 3 hr. After the solvent was removed in vacuo, the residue was dissolved in ether and basic material was extracted with 2 N hydrochloric acid solution. To the cooled acidic solution, 2 N sodium hydroxide solution was added to liberate the basic substance, and extracted with ether. After the ethereal solution was washed with water and dried over anhydrous potassium carbonate, the solvent was removed. The residue was distilled in vacuo to give a pale yellow oil, 1.2 g., b. p. 145~155°C/2 mmHg. The picrate, m. p. 168~169°C was prepared to be found identical with the picrate of 3,3-dimethyl-2-phenylindolenine (XVI) by mixed melting point determination.

Synthesis with hydrochloric acid in ethanol.—A solution of 2 g. of 3-phenylbutane-2-one phenylhydrazone[30] in 40 cc. of absolute ethanol was chilled in an ice bath and was saturated with dried hydrogen chloride. After being allowed to stand at room temperature for 2 days (15°C), the solvent was removed in vacuo (below 40°C). Water was added to the residue and extracted with ether. The aqueous layer was made basic by the addition of 2 N sodium hydroxide solution and extracted with ether. The ethereal extract was washed with water and dried over anhydrous potassium carbonate. After removal of the solvent, the residue was distilled to afford a liquid, b. p. 135~145°C/1.5 mmHg, infrared spectrum of which could overlap in every detail on that of 3,3-dimethyl-2-phenylindolenine. The identity was further confirmed by the mixed melting point determination of their picrates.

1,2-Dimethyl-3-phenylindole.—To a suspension of sodium amide prepared from 200 cc. of liquid ammonia and 0.78 g. of sodium, 5 g. of 2-methyl-3-phenylindole[31] was added with 10 cc. of ether. After a mixture of 3.4 g. of methyliodide and 10 cc. of ether was added dropwise in a period of 20 min., the reaction mixture was allowed to stand at room temperature overnight to evaporate the liquid ammonia. After 200 cc. of water was added, the mixture was extracted with ether. The ethereal extract was washed with 2 N hydrochloric acid to remove basic material (very small amount, discarded). After this has been washed with 5% sodium carbonate solution and water, the ether extract was dried over anhydrous sodium sulfate. Removal of the solvent gave crystals (4 g.), which were recrystallized from ethanol. m. p. 111~112.5°C.

Found: C, 87.38; H, 7.03; N, 6.33. Calcd. for $C_{16}H_{15}N$: C, 86.84; H, 6.38; N, 6.33%.

The picrate was recrystallized from ethanol to give brown black needles, m. p. 199~201°C.

Found: N, 12.40. Calcd. for $C_{22}H_{18}O_7N_4$: N, 12.44%.

***Spiro*-(cyclopentane-1,3'-*pseudo*-2'-phenylindole) (XXII).**—A mixture of 5 g. of cyclopentylphenylketone[32] and 3.4 g. of phenylhydrazine was heated on a water bath for 1 hr. and the water generated was removed by azeotropic distillation with benzene. After the benzene was removed completely in vacuo, the residue was dissolved in 60 cc. of absolute ethanol and the chilled solution was saturated with dry hydrogen chloride. Then 100 cc. of water was added to the semisolid mass, and washed with ether. The aqueous layer was made basic by the addition of 2 N sodium hydroxide solution, and extracted with ether. The ether extract was washed with water and dried over anhydrous sodium sulfate. After the solvent was evaporated, the residue was distilled at reduced pressure to give 4.9 g. of a pale yellow liquid, b. p. 164~167°C/1 mmHg. U. V. spectrum: λ_{max} mμ (log ε), 239 (4.28), 247(4.23), 310(4.28). λ_{min} 258 mμ (log ε 3.89) in ethanol (Fig. 11).

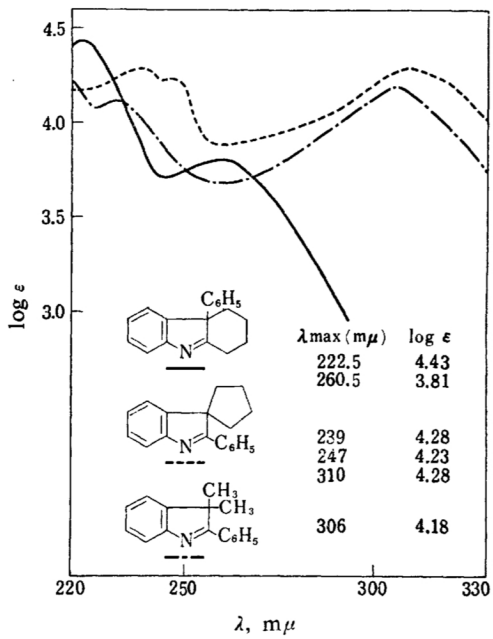


Fig. 11.

Found: C, 87.11; H, 7.21; N, 6.16. Calcd. for $C_{18}H_{17}N$: C, 87.41; H, 6.93; N, 5.55%.

The picrate was recrystallized from ethanol to give yellow crystals, m. p. 175°C.

Found: C, 61.18; H, 4.35; N, 11.74. Calcd. for $C_{24}H_{20}O_7N_4$: C, 60.50; H, 4.23; N, 11.76%.

11-Phenyltetrahydrocarbazolenine (XXIII).—*From 2-phenylcyclohexanone phenylhydrazone (XXIV).*—A mixture of 10 g. of 2-phenylcyclohexanone[33] and 7.3 g. of phenylhydrazine was

29) This attempt seems to be the first instance where borontrifluoride etherate was successfully employed for sythesis of indolenine, whereas this reagent has been frequently used for Fisher's indole synthesis. H. R. Snyder and C. W. Smith, ibid., **65**, 2454 (1943).

30) B. p. 160~170°C/2 mmHg; m. p. 76~78.5°C (from ethanol-water). Found: N, 11.83. Calcd. for $C_{16}H_{18}N_2$: N, 11.76%.

31) B. p. 194~196°C/3 mmHg; m. p. 78~79°C. Picrate m. p. 139~141°C. And also see the preceding paper.

32) B. p. 135~136°C/10 mmHg; m. p. of 2,4-dinitrophenylhydrazone, 142°C, [prepared from cyclopentane carboxylic acid chloride by Friedel-Crafts synthesis. (D. H. Hey and O. C. Musgrave, *J. Chem. Soc.*, **1949**, 3156. B. p. 136~140°C/16 mmHg; m. p. of 2,4-dinitrophenylhydrazone, 142~143°C).].

33) B. p. 140~146°C/10 mmHg (60% yield). Prepared following Newman's procedure. M. S. Newman and M. D. Frabman, *J. Am. Chem. Soc.*, **69**, 1550 (1944).

heated on a water bath for 1 hr. The water generated was removed by azeotropic distillation with benzene, and the benzene was removed by distillation in vacuo of a water pump. The residue was dissolved in 100 cc. of absolute ethanol, and saturated with dry hydrogen chloride. A considerable amount of ammonium chloride was observed to precipitate. After the reaction mixture was allowed to stand at room temperature for 10 hr., the solvent was removed in vacuo (below 40~45°C). The residue was dissolved in 250 cc. of water and washed with ether, and the aqueous layer was made basic by the addition of 2 N sodium hydroxide solution and extracted with ether. After the ethereal extract was washed with water and dried over anhydrous potassium carbonate, the solvent was removed to give crystals, which were recrystallized from ethanol-water, m. p. 126~127°C. I. R. spectrum: 6.3 μ. U. V. spectrum: λ_{max} mμ (log ε), 222.5 (4.42), 260.5 (3.81), λ_{min} 245 mμ (3.72) in ethanol (Fig. 11).

Found: C, 87.47; H, 7.02; N, 5.69. Calcd. for $C_{18}H_{17}N$: C, 87.41; H, 6.93; N, 5.66%.

The picrate was recrystallized from ethanol to give yellow prisms, m. p. 182~183°C.

Found: C, 60.48; H, 4.44; N, 11.78. Calcd. for $C_{24}H_{20}O_7N_4$: C, 60.50; H, 4.23; N, 11.76%.

From cyclopentylphenylketone phenylhydrazone (XXI).—To 29 g. of polyphosphoric acid, a mixture of 15 g. of cyclopentylphenylketone[32] and 9.8 g. of phenylhydrazine was added. The temperature of the reaction mixture rose spontaneously up to 150°C, and the reaction mixture was kept at this temperature for 10 min. in an oil bath. The viscous mass was dissolved in water and washed with ether. The acidic aqueous layer was made basic by the addition of 2 N sodium hydroxide solution, and was extracted with ether. After the ether extract was washed with water and dried over anhydrous sodium sulfate, the ether was distilled off. The residue was recrystallized from ethanol-water to give needles, m. p. 122~124°C (7.7 g.) which was proved identical with 11-phenyltetrahydrocarbazolenine (XXIII) prepared from 2-phenylcyclohexanone phenylhydrazone (XXIV).

From rearrangement of spiro-(cyclopentane-1,3'-pseudo-2'-phenylindole) (XXII).—A mixture of 1.4 g. of indolenine XXII and 7 g. of polyphosphoric acid was heated at 155°C for 10 min. in an oil bath. The reaction mixture was dissolved in water by warming on a water bath. The acidic aqueous layer was made basic by the addition of 2 N sodium hydroxide solution to precipitate needles (1.0 g.), which were collected and recrystallized from ethanol-water to give m. p. 124°C. The mixed melting point with 11-phenyltetrahydrocarbazolenine was 124°C.

11b-Methyl-5, 6-dihydro-11b-benzo[*c*]carbazole (XXVI).—A mixture of 8.1 g. of α-methyl-β-tetralone[34] and 5.5 g. of phenylhydrazine was heated on a water bath for 2 hr., and the generated water was removed by azeotropic distillation with benzene. After the solvent was removed in vacuo, the residue was dissolved in 70 cc. of absolute ethanol, and was saturated with dry hydrogen chloride. After being allowed to stand at 5°C overnight, the reaction mixture was poured into 350 cc. of ice water and washed with ether. The aqueous layer was made basic and was extracted with ether. The ether extract was washed with water and dried over anhydrous potassium carbonate. Removal of the solvent gave a viscous liquid, which was distilled in vacuo to afford 4.1 g. of a viscous pale yellow liquid, b. p. 159~163°C/1 mmHg. I. R. spectrum: 6.3 μ. U. V. spectrum: λ_{max} 248 mμ (log ε 4.02) in ethanol (Fig. 12).

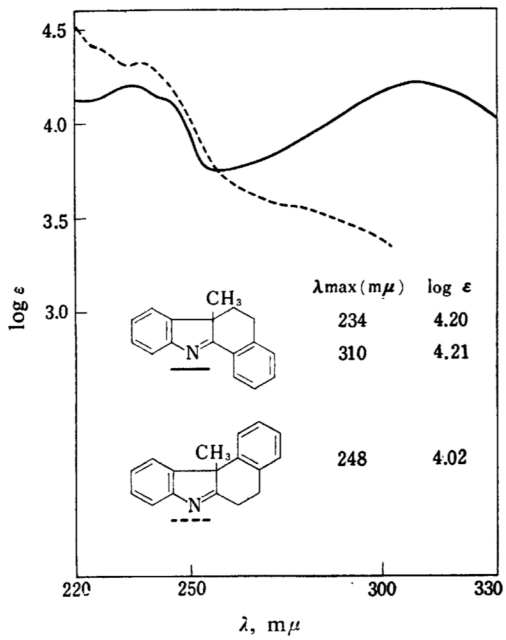


Fig. 12.

Found: C, 86.31; H, 6.83; N, 6.06. Calcd. for $C_{17}H_{15}N$: C, 87.51; H, 6.48; N, 6.00%.

The picrate was recrystallized from ethanol to give yellow prisms, m. p. 167~167.5°C.

Found: C, 59.91; H, 4.03; N, 12.31. Calcd. for $C_{25}H_{18}O_7N_4$: C, 59.74; H, 3.92; N, 12.12%.

6a-Methyl-5, 6-dihydro-6a-benzo[*a*]carbazole (XXVII).—When 30 g. of polyphosphoric acid was added to a mixture of 5.2 g. of β-methyl-α-tetralone[35] and 3.6 g. of phenylhydrazine, a considerable generation of heat was observed to cause the reaction temperature to rise to 165°C. After this rather violent reaction subsided, 200 cc. of water was added to dissolve the viscous reaction mass. The acidic aqueous solution was washed with ether, and was made basic to precipitate an oil, which was extracted with ether. The ether extract was washed with water and dried over anhydrous sodium sulfate. Removal of the solvent gave brown viscous residue which was distilled to give 3.4 g. of a pale yellow oil, b. p. 160~164°C/2 mmHg. I. R. spectrum:

34) B. p. 137~142°C/10 mmHg. Prepared following the procedure of J. English and G. Cavaglieri, *J. Am. Chem. Soc.*, 65, 1085 (1943).

35) B. p. 116~120°C/2 mmHg. Prepared following the procedure of W. E. Bachmann and D. G. Thomas, ibid., 63, 598 (1941).

6.5 μ. U. V. spectrum : λ_{max} mμ (log ε), 234(4.20), 310(4.21). λ_{min} 256 mμ (log ε 3.76) in ethanol (Fig. 12).

Found : C, 86.41 ; H, 6.69 ; N, 6.11. Calcd. for $C_{17}H_{15}N$: C, 87.51 ; H, 6.48 ; N, 6.00%.

The picrate was recrystallized from ethanol to give yellow prisms, m. p. 169~170°C. The mixed melting point with the picrate of 11b-methyl-5,6-dihydro-11b-benzo[*c*]carbazole (m. p. 167~167.5°C) was 156~159°C.

Found : C, 59.62 ; H, 4.12 ; N, 12.54. Calcd. for $C_{23}H_{18}O_7N_4$: C, 59.74 ; H, 3.92 ; N, 12.12%.

From rearrangement of 11b-methyl-5,6-dihydro-11b-benzo[c]carbazole (XXVI)—A mixture of 0.4 g. of the indolenine XXVI and 2 g. of polyphosphoric acid was heated at 180°C for 15 min. in an oil bath. After water was added, the aqueous solution was freed from a small amount of unsoluble resinous material by filtration.

The solution was made basic with 2 N sodium hydroxide solution, and the turbid mixture was extracted with ether. The ethereal extract was washed with water and dried over anhydrous sodium sulfate. After the ether wae removed, the residue was converted into picrate, without further purification, by the addition of ethanolic picric acid. The picrate was recrystallized from ethanol to give yellow prisms, m. p. 166~167°C, which was proved identical with the picrate of 6a-methyl-5,6-dihydro-6a-benzo[*a*]carbazole (m. p. 169~170°C) by mixed melting point determination.

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