Mechanism of Plancher's Rearrangement. II[1]. Twofold Wagner-Meerwein Type Rearrangement of Indolenium Compounds

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A novel conversion, by heating at 180~190°C, of an indolenium iodide, m.p. 186°C into an isomeric indolenium iodide, m.p. 232°C, both were obtained by the interaction of 2-isopropyl-3-methylindole and methyliodide was first described by Plancher[2], although the structures of these indolenium iodides were left unsettled.

But on only one occasion was the structure of the rearranged indolenium iodide established: Boyd-Barrett[3] oxidized the indolenium iodide III, obtained from 2-phenylindole (I) by heating with methyliodide at 120°C, to 1, 3-dimethyl-2-phenyloxyindole, and thus confirmed the structure of the rearranged indolenium III proposed by Plancher[4].

Plancher[2] explained the formation of 1, 2, 3-trimethyl-3-phenylindolenium iodide (III) from 2-phenylindole (I) by the sequence of reactions: decomposition of the first formed 1, 3, 3-trimethyl-2-phenylindolenium iodide (II) into iodobenzene and 1, 2, 3-trimethylindole and a recombination of which together with iodobenzene to form III.

It is obvious that such mechanism is hardly tenable, and Julian[5] suggested another mechanism which assumed that 3, 3-dimethyl-2-phenylindolenine is the first intermediate and its rearrangement involving an exchange of the phenyl with the methyl group would give 2, 3-dimethyl-3-phenylindolenine. But the fact that the conversion of 3, 3-dimethyl-2-phenylindolenine into 2,3-dimethyl-2-phenylindolenine, which would give III with methyliodide, however, was proved just opposite to the case[6], leaving only one possible mechanism remaining, i.e. the conversion of the intermediate 1, 3, 3-trimethyl-2-phenylindolenium iodide (II) into III, by a twofold Wagner-Meerwein type rearrangement formulated in Fig. 1. To testify this possibility, Leuch's experiment[7] was repeated in order to obtain 1, 3, 3-trimethyl-2-phenylindolenium iodide (II) from 3, 3-dimethyl-2-phenylindolenine and methyliodide.

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[1] Part I: M. Nakazaki, K. Yamamoto and K. Yamagami, This Bulletin, 33, 466 (1960).

[2] G. Plancher, *Atti, accad. Lincei,* (5) **11**, III, 182 (1902); *Chem.-Zentr.*, **1902**, I, 1322.

[3] H. S. Boyd-Barrett, *J. Chem. Soc.*, **1932**, 321.

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

[5] 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. 106. The introductory part of the preceding paper gives a brief historical survey of Plancher's rearrangement.

[6] M. Nakazaki, K. Yamamoto and K. Yamagami, This Bulletin, 33 466 (1960).

[7] H. Leuchs, A. Heller and A. Hoffmann, *Ber.*, **62**, 871 (1932).

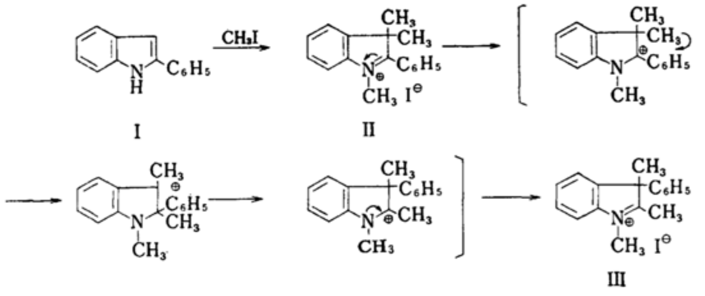

Fig. 1.

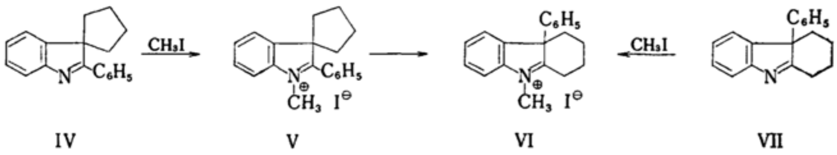

Fig. 2.

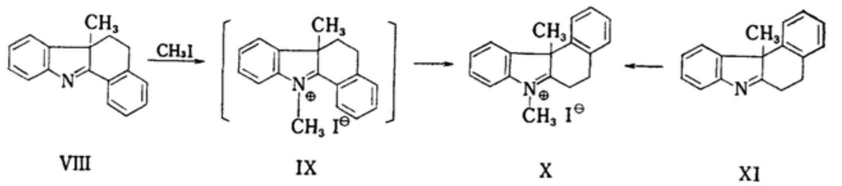

Fig. 3.

When a solution of 3, 3-dimethyl-2-phenylindolenine and methyliodide in methanol was heated at 100°C for 4 hr., there were obtained, in contrary to expectation, colorless prisms, m.p. 226~227°C[8], beside Leuch's indolenium iodide, yellow needles, m.p. 203°C, in about the same amount. Since the indolenium iodide with m.p. 226~227°C was proved to be 1, 2, 3-trimethyl-3-phenylindolenium iodide (III) by Boyd -Barrett's degradative experiment[3], the isomeric yellow indolenium iodide, m. p. 203°C which was a sole product Leuchs could isolate, was to be assigned the structure of 1, 3, 3-trimethyl-2-phenylindolenium iodide (II). These structure assignments were further confirmed by their ultraviolet absorption spectra, which show clearly a bathochromic shift (III, $\lambda_{\max}$ 276 mμ and II, $\lambda_{\max}$ 297 mμ) due to conjugation with the phenyl group (Fig. 5).

The conversion of II to III was realised when a methanolic solution of II was heated in a sealed tube at 120~150°C for 1/2 hr., and this is the first case where indolenium compound was rearranged into the isomeric indolenium compound both with known constitutions, exchanging substituents between 2- and 3-position of the indolenium nucleus. Another smooth isomerization was established when *spiro*-(cyclopentane-1, 3′-*pseudo*-2′-phenylindole) methoiodide (V), prepared from the corresponding indolenine IV, with methyliodide, was heated in methanolic solution at 160°C for 3 hr. in a sealed tube to give 11 - phenyltetrahydrocarbazolenine methoiodide (VI), which could be prepared from 11-phenyltetrahydrocarbazolenin (VII) and methyliodide.

Although it was unsuccessful to obtain the methoiodide of 6a-methyl-5, 6-dihydro-6a-benzo-[*a*] carbazole (IX) in crystalline form, it could be isomerized by heating its methanolic solution at 150°C for 5 hr. to the isomeric 11b-methyl-5, 6-dihydro-11b-benzo [*c*] carbazole methoiodide (X) provided from the corresponding indolenine XI with methyliodide. The mechanism of these rearrangements of indolenium iodides can be sought in the twofold Wagner-Meerwein type rearrangement[9] illustrated in Fig. 4.

Situated between two substituents at 1- and 3-position of indolenium compounds the substituents at 2-position suffer a considerable steric repulsion from both sides and the most bulky group (R_3) would tend to migrate to 2-position,

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[8] In the repetition of Plancher's experimet, Boyd-Barrett (Ref. 3) obtained a yellow indolenium iodide, m. p. 196°C as a minor product. Apparently this is the intermediate 1, 3, 3-trimethyl-2-phenylindolenium iodide (II), but any structural study as well as its possible rearrangement III was not tried.

[9] Twofold Wagner-Meerwein type rearrangement was also demonstrated in indolenines (ref. 6) and 2, 3-disubstituted indoles M. Nakazaki, This Bulletin, 33, 461 (1960) A *spiro* type intermediate has to be assumed in the case of the rearrangement IX→X.

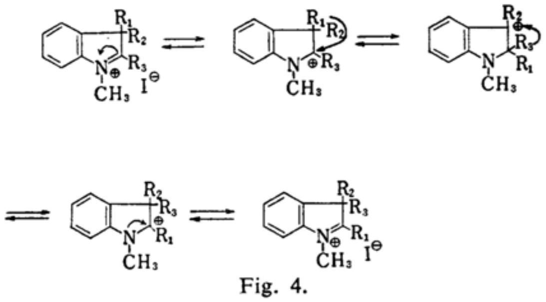

Fig. 4.

compelling the least bulky group (R_1) to 2-position (Fig. 4).

This steric effect would be strong enough[10] so as to compensate for the mesomeric stabilization effect of the phenyl group conjugated with the indolenium nucleus.

Experimental[11]

1, 3, 3-Trimethyl-2-phenylindolenium Iodide (II) and 1, 2, 3-Trimethyl-3-phenylindolenium Iodide (III).—A mixture of 12.7 g. of 3, 3-dimethyl-2-phenylindolenine[12], 24.2 g. of methyliodide and 77 cc. of methanol was heated at 100°C. for 4 hr. in a sealed tube. After the solvent was removed on a water bath, the residue was recrystallized from methanol-ethyl acetate. From the more soluble fraction yellow needles were obtained and recrystallization from water (aqueous solution was colorless, whereas the methanolic solution was yellow) gave 3.6 g. of yellow needles, m. p. 202~203°C. (literature[7]: 203°C). Ultraviolet spectrum of 1, 3, 3-trimethyl-2-phenylindolenium iodide: λ_{max} 297 mμ (log ε 3.97) in methanol (Fig. 5).

Found: C, 56.24; H, 5.07. Calcd. for $C_{17}H_{18}NI$: C, 56.21; H, 4.99%.

From the less soluble fraction, there were obtained colorless prisms which were recrystallized from methanol, m.p. 226~227°C (literature[3]: 227°C). This iodide is rather sensitive to air and gradually changes to pink in color. U. V. spectrum of 1, 2, 3-trimethyl-3-phenylindolenium iodide: λ_{max} 276 mμ (log ε 3.84) in methanol (Fig. 5).

Found: C, 56.73; H, 5.37. Calcd. for. $C_{17}H_{18}NI$: C, 56.21; H, 4.99%.

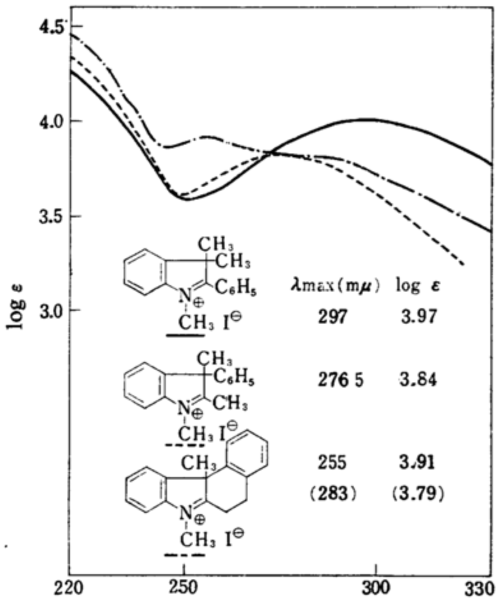

Fig. 5.

Rearrangement of 1,3,3-Trimethyl-2-phenylindolenium Iodide (II).—The indolenium iodide II (0.5 g.) was dissolved in 6 cc. of methanol and heated at 120~150°C for 3 hr., and then at 180°C for 1/2 hr. in a sealed tube. The original yellow color of the reaction mixture changed to violet-red. After removal of the solvent, the residue was dissolved in a small amount of methanol, and ethyl acetate was added to precipitate prisms (m.p. 222~224°C) with faint pink color, which was recrystallized from methanol to raise the melting point to 224~226°C. This was found identical with 1, 2, 3-trimethyl-3-phenylindolenium iodide (III) by mixed melting point determination and the comparison of infrared spectra.

***Spiro*-(cyclopentane-1, 3′-*pseudo*-2′-phenylindole)**

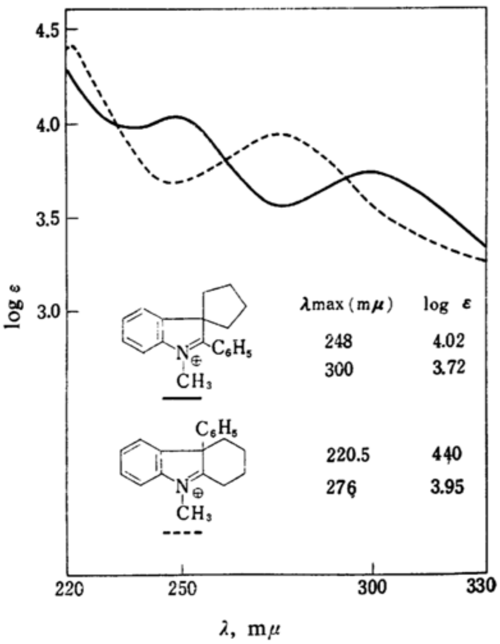

Fig. 6.

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[10] Even in the indolenine IV, without the repulsion from the substituent at 1-position, the steric strain is sufficient enough to be responsible for the smooth rearrangement of the isomeric indolenine VII (Ref. 6).

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

[12] B. p. 178~179°C/9 mmHg. Picrate, m. p. 167~168°C. Prepared following Witkop's procedure. [H. M. Kissman, D. W. Farnworth and B. Witkop, *J. Am. Chem. Soc.*, **74**, 3948 (1952)].

Methoiodide (V).—A mixture of 1 g. of *spiro*-(cyclopentane-1, 3′-*pseudo*-2′-phenylindole)[13], 1.0 g. of methyliodide and 10 cc. of methanol was heated at 100°C for 2 hr. in a sealed tube. After the solvent was removed from the dark green reaction mixture, the residue was recrystallized from ethanol to give yellow needles (0.55 g.), m.p. 186.5∼188°C. U. V. spectrum: $\lambda_{\max}$ mμ(log ε), 248 (4.02), 300 (3.72) in ethanol (Fig. 6).

Found: C, 58.51; H, 5.36; N, 3.59. Calcd. for $C_{19}H_{20}NI$: C, 58.70; H, 5.18; N, 3.60%.

11-Phenyltetrahydrocarbazolenine Methoiodide (VI).—A mixture of 1.0 g. of phenyltetrahydrocarbazolenine[14] 1.0 g of methyliodide and 10 cc. of methanol was heated at 100°C. for 3 hr. in a sealed tube. After removal of the solvent, the green residue was dissolved in methanol and decolorized with sulfur dioxide.

Then small amount of water was added to precipitate needles, which were recrystallized from water to give colorless needles, m.p. 116∼118°C (decomp.). U. V. spectrum: $\lambda_{\max}$ mμ(log ε), 220.5 (4.40), 276 (3.95) in ethanol (Fig. 6).

Found: C, 56.26; H, 5.60; N, 3.67. Calcd. for $C_{19}H_{20}NI \cdot H_2O$: C, 56.03; H, 5.45; N, 3.44%.

Rearrangement of *Spiro*-(cyclopentane-1, 3′-*pseudo*-2′-phenylindole) Methoiodide (V).—A mixture of 0.4 g. of the indolenium iodide V and 6 cc. of methanol was heated at 160°C for 3 hr. and at 200°C for 15 min. in a sealed tube. After removal of the solvent, the green residue was extracted with boiling water. The aqueous solution was treated with Norit and was concentrated to give colorless needles which were recrystallized from water., m.p. 116∼118°C. This was found identical with the 11-phenyltetrahydrocarbazolenine methoiodide (m.p. 116∼117°C) by mixed melting point determination (m.p. 116∼118°C).

11b-Methyl-5, 6-dihydro-11b-benzo[*c*]carbazole (X).—A mixture of 0.2 g. of the indolenine XI[15], 0.4 g. of methyliodide and 4 cc. of methanol was heated at 100°C. for 3 hr. in a sealed tube. After removal of the solvent, a small amount of ether was added to the residue and was allowed to stand with occasional trituration. The crystals precipitated were collected and recrystallized from ethanol to give m.p. 202∼204°C. U. V. spectrum: $\lambda_{\max}$ 255 mμ(log ε 3.91) with a plateau at 283 mμ (3.79) in ethanol (Fig. 5).

Found: C, 57.81; H, 5.18; N, 4.20. Calcd. for $C_{18}H_{18}NI$: C, 57.61; H, 4.83 N, 3.73%.

Rearrangement of 6a-Methyl-5, 6-dihydro-6a-benzo[*a*]carbazole Methoiodide (IX).—A mixture of 0.5 g. of the indolenine VIII[16], 1.0 g. of methyliodide and 4 cc. of methanol was heated at 100°C for 3 hr. in a sealed tube. After the solvent was removed at reduced pressure, the residue was washed with ether. After various fruitless attempts to crystallize, the viscous residue was dissolved in 6 cc. of methanol and heated at 150°C for 5 hr. in a sealed tube. The solvent was evaporated and a small amount of ether was added to the residue and triturated. The crystals were collected, and recrystallized from ethanol to give crystals melting at 202∼204°C, which was found identical with the indolenium iodide X by mixed melting point determination and the comparison of their infrared spectra.

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[13] B.p. 164∼167°C/1 mmHg. Picrate, m.p. 175°C. Ref. 6.

[14] M. p. 126°C. Picrate, m. p. 182∼183°C. Ref. 6.

[15] B. p. 160∼165°C/2 mmHg. Picrate, m. p. 167∼167.5°C, Ref. 6.

[16] B. p. 160∼194°C/2 mmHg. Picrate, m. p. 169∼170°C. Ref. 6.