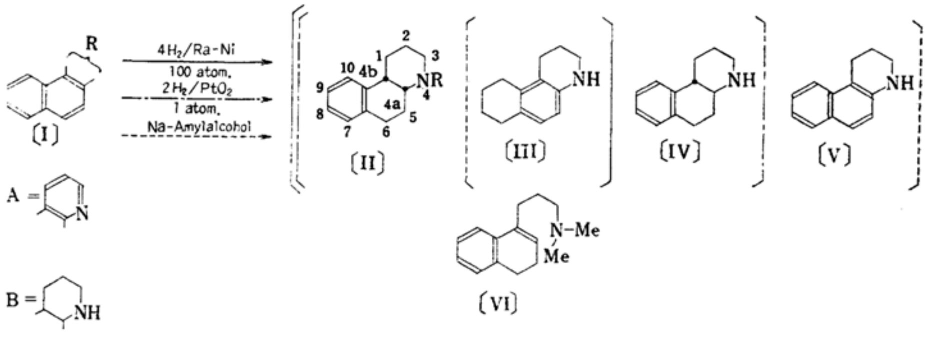
The Syntheses and Exhaustive Methylation of cis- and trans-1, 2, 3, 4, 5, 6, 4a, 4b-Octahydrobenzo [f] quinoline[1]

By Tadashi MASAMUNE
and Masato KOSHI*

(Received July 10, 1959)

A recent paper[2] has described the preparation and also Hofmann's exhaustive methylation of 4-methyl-1, 2, 3, 4, 5, 6, 4a, 4b-octahydrobenzo [f] quinoline (II) R=Me. The stereochemistry of the ring fusion is tentatively assigned as *cis*.

The present paper undertakes to report the syntheses and exhaustive methylation of *cis*- and *trans*-1, 2, 3, 4, 5, 6, 4a, 4b-octahydrobenzo [f] quinoline (II) R=H and (IV). These bases are interesting as 5, 6-benzoderivatives of decahydroquinoline.



---

* Present address: Central Research Laboratory of Tōyōkōatsu Industries, Inc., Totsuka-ku, Yokohama.

[1] Part X of "The Condensed Polynuclear Perhydrocompounds Containing Nitrogen"; Part IX, T. Masamune, This Bulletin, **30**, 491 (1957).

[2] N. A. Nelson, J. E. Ladbury and R. S. Hsi, *J. Am. Chem. Soc.*, **80**, 6633 (1958).

Hydrogenation of benzo[f]quinoline[3] (I) R=A using a catalyst of Raney nickel (150°C) under 100 atm. initial pressure resulted in conversion into the mixture of octahydrobenzo[f]quinoline, consuming four molecular equivalents of hydrogen. From the ethereal solution of oily mixture, *cis*-octahydrobenzo[f]quinoline (II) R=H was isolated as carbonate. *cis*-1,2,3,4,5,6,4a,4b-Octahydrobenzo[f]quinoline[4], which was analyzed as the hydrochloride (Found: C, 64.46; H, 8.09. Calcd. for $C_{13}H_{17}N\cdot HCl\cdot H_2O$; C, 64.65; H, 8.28%.), can be regenerated from the carbonate by adding aqueous caustic alkali. Overall yield, 4.8%. The evaporation of the solvent from mother ethereal solution gave 1,2,3,4,7,8,9,10-octahydrobenzo[f]quinoline (III) in yield of 88%, but no *trans* isomeride could be isolated. On the other hand, hydrogenation of 1,2,3,4-tetrahydrobenzo[f]quinoline[5] (I) R=B in glacial acetic acid with platinum oxide as a catalyst at ordinary pressure, gave the mixture of *cis* and *trans* isomers of octahydrobenzo[f]quinoline in poor yield (*cis* and *trans* 2.4% each). The main product was 1,2,3,4,7,8,9,10-octahydrobenzo[f]quinoline. Yield, 86%. The separation of *cis* and *trans* isomerides was carried out most conveniently by means of the difference between the speed of carbonate formation of the *cis*- and *trans*-bases; thus, on exposing the mixture of *cis* and *trans* isomerides to air for a few hours the *cis* isomeride forms the carbonate preferentially.

Furthermore, the reduction of benzo[f]quinoline to octahydro-derivatives by sodium and amylalcohol, which has been first described by Bamberger and Müller[3] was reexamined. In this case, *trans*-1,2,3,4,5,6,4a,4b-octahydrobenzo[f]quinoline (IV) (2.9%) (Found: C, 83.25; H, 9.12; Calcd. for $C_{13}H_{17}N$: C, 83.43; H, 9.08%.), 1,2,3,4,7,8,9,10-octahydrobenzo[f]quinoline (III) (29%) and 1,2,3,4-tetrahydrobenzo[f]quinoline (V) (39%) were obtained respectively from the reaction mixture.

Though no rigid proof can be given for the configuration of the above isomers,

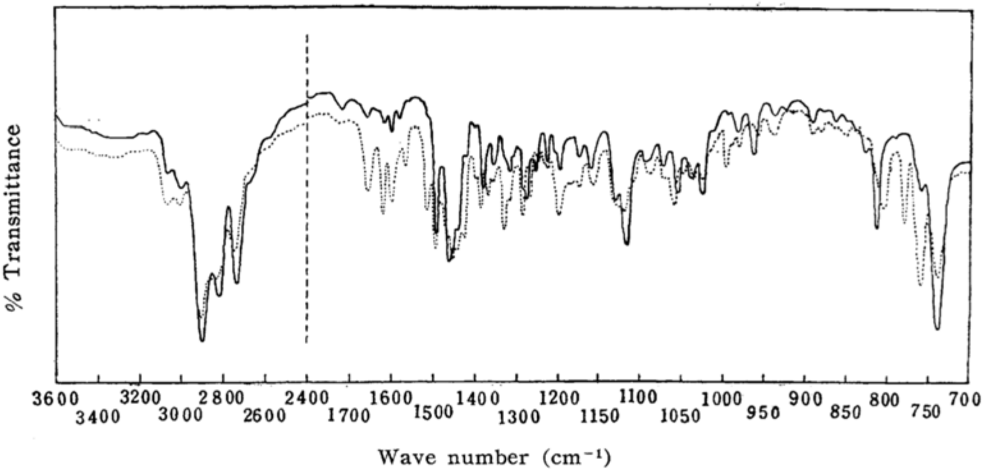


Fig. 1. The infrared spectra of *cis*- and *trans*-4-methyl-1,2,3,4,5,6,4a,4b,-octahydrobenzo[f]quinolines.
cis: ------ *trans*: ——

TABLE I. PHYSICAL CONSTANTS OE THE *trans* AND *cis* ISOMERS AND THEIR DERIVATIVES

	cis, (°C)	*trans*, (°C)
1,2,3,4,5,6,4a,4b-Octahydrobenzo[f]quinoline	b. p. 160～165/5 mm.	m. p. 88～90[b]
Benzoate	m. p. 96～97	m. p. 100～102
Picrate	m. p. 197～198.5	m. p. 189～190
Hydrochloride	m. p. 258～259	m. p. 251～253[c]
N-Methylate picrate	m. p. 165～167	m. p. 210～212
Methiodide	m. p. 295[a]	m. p. 238～240

a) N. A. Nelson et al.[2] record m. p. 295°C (decomp.).
b) E. Bamberger et al.[3] record m. p. 91°C.
c) E. Bamberger et al.[3] record m. p. 252°C.

---

[3] E. Bamberger and R. Müller, *Ber.*, **24**, 2648 (1891).

[4] Analysis of free base was difficult, owing to rapid absorption of atmospheric carbon dioxide.

[5] E. Bamberger and R. Müller, *Ber.*, **24**, 2641 (1891).

in view of the reduction conditions and other considerations[2)] there is little doubt that the higher melting product resulting from the reduction with sodium-alcohol system is the *trans* isomeride. The infrared spectra of *cis*- and *trans*-*N*-methyl-octahydrobenzo[f]quinoline are shown in the figure. Physical constants of the *cis* and *trans* isomers and their derivatives are given in Table I.

Exhaustive methylation of *cis*-octahydrobenzo[f]quinoline has been recently carried out by Nelson et al.[2)] who found that distillation of *cis*-octahydro-4-methylbenzo-[f]quinoline methohydroxide produced 1-(3-dimethylaminopropyl)-3,4-dihydronaphthalene (VI). In the present investigation the Hofmann degradation of *cis*- and *trans*-octahydro-4-methylbenzo[f]-quinoline methohydroxides gave the same oily product in yields of 43% and 32%, respectively, boiling at 150~155°C/4 mm. (picrate m.p. 87~88°C), which was identified as 1-(3-dimethylaminopropyl)-3,4-dihydronaphthalene (VI), and no other compound could be isolated.

Examination of a model of the feasible structures for *cis*- and *trans*-*N*-methyl-octahydrobenzo[f]quinoline shows that in *cis* configuration the necessary conformational requirement for easy Hofmann fission is satisfied by elimination of any one of the equatorial 2-hydrogen, 4b-hydrogen and 5-hydrogen and in *trans* configuration by elimination of the equatorial 2-hydrogen.

Thus, in the exhaustive methylation of both *cis*- and *trans*-octahydrobenzo[f]-quinolines the preferential elimination of a β-proton on C 4b shows vividly that the influence of the electronic character of aromatic substituent at position C 4b is superior to the necessary co-planar *trans*-arrangement for easy Hofmann fission. Several examples[6)] of this type of elimination have already been reported. Detailed results of the matters discussed in the present paper will be reported elsewhere.

Department of Chemistry
Faculty of Science
Hokkaido University
Sapporo

---

6) T. Masamune, This Bulletin, **30**, 491 (1957) and references given there; H. Booth, F. E. King and J. Parrick, *J. Chem. Soc.*, **1958**, 2302.