1) Phenazine is not obtained by the reaction between nitrobenzene and aniline, in spite of the change of the conditions.

2) In the case of 1-methoxyphenazine, the reaction between one mole each of nitro and amino compounds produces the best yield, in spite of the solvent used.

3) In the case of 2-methoxyphenazine, the reaction between 0.5 mole of nitrobenzene and 1 mole of *p*-anisidine produces the best yield and the increase of nitrobenzene produces only 2-methoxyphenazine mono-N-oxide. No remarkable change was observed even when potassium ferricyanide, iron powder, and active charcoal were added to the reaction, and only mono-N-oxide was obtained.

The author wishes to thank Dr. M. Ishidate for his encouragement.

Experimental

Phenazine Mono-N-oxide—i) A mixture of aniline (9.3 g.) and nitrobenzene (12.8 g.) was refluxed for 7 hrs. in toluene (150 cc.) with powdered potassium hydroxide (40 g.). After the reaction, the toluene solution was filtered, while hot, from the precipitate and steam-distilled. The crude crystalline substance deposited in the remaining aqueous solution was filtered and then purified on alumina by benzene. The eluate was evaporated and recrystallized from ligroine. 0.8 g. of phenazine mono-N-oxide was obtained as yellow needles, m.p. 221~222°(decomp.).

ii) A mixture of aniline (9.3 g.) and nitrobenzene (12.3 g.) was kept standing for 3 days at room temperature in the presence of powdered potassium hydroxide. It was dissolved in water, steam-distilled, and purified on alumina. 0.5 g. of phenazine mono-N-oxide was obtained.

2-Methoxyphenazine Mono-N-oxide—i) A mixture of *p*-anisidine (12.3 g.) and nitrobenzene (6.15 g.) was refluxed with 16.4 g. of potassium ferricyanide for 7 hrs. in toluene. The isolation of it was made by the ordinary procedure. 1.0 g. of 2-methoxyphenazine mono-N-oxide was obtained.

ii) A mixture of *p*-anisidine (12.3 g) and nitrobenzene (12.3 g.) was refluxed with iron powder (11.0 g.) for 7 hrs. in toluene. 4.5 g. of 2-methoxyphenazine mono-N-oxide was obtained.

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Munemitsu Tomoeda :

Synthesis and Nitration of 1-Methyl-5,6,7,8-tetrahydronaphthalene.

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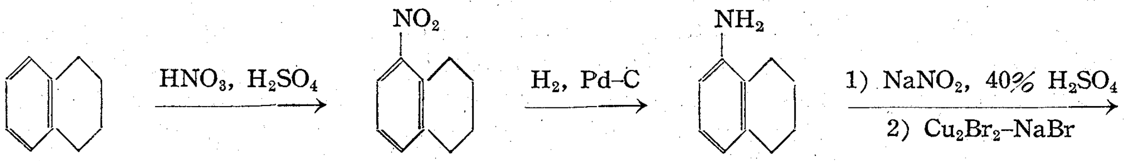
This report is concerned with the synthesis and nitration of 1-methyl-5,6,7,8-tetrahydronaphthalene (V).

(V) was obtained from monobromo-5,6,7,8-tetrahydronaphthalene by Veselý[1)], but the product was contaminated with 2-methyl isomer, for the starting material was a mixture of 1-bromo- and 2-bromo-5,6,7,8-tetrahydronaphthalene. Now the pure 1-bromo compound (IV) was synthesized from tetrahydronaphthalene (I) through three steps and converted to (V) by the Grignard reaction. By fractional distillation under reduced pressure, (V) was separated from the by-product which is supposedly tetrahydronaphthalene. (V) gave b.p. 112~114° at 18 mm. and total yield from (I) was 15.5%.



(I) (II) (III)

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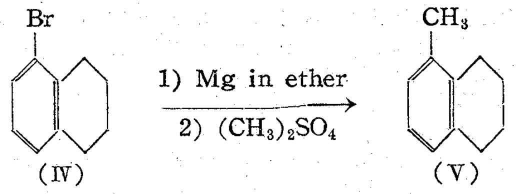
* Katakasu, Fukuoka (友枝宗光).

1) C. A., **28**, 5815 (1934); *ibid.*, **30**, 8202 (1936).

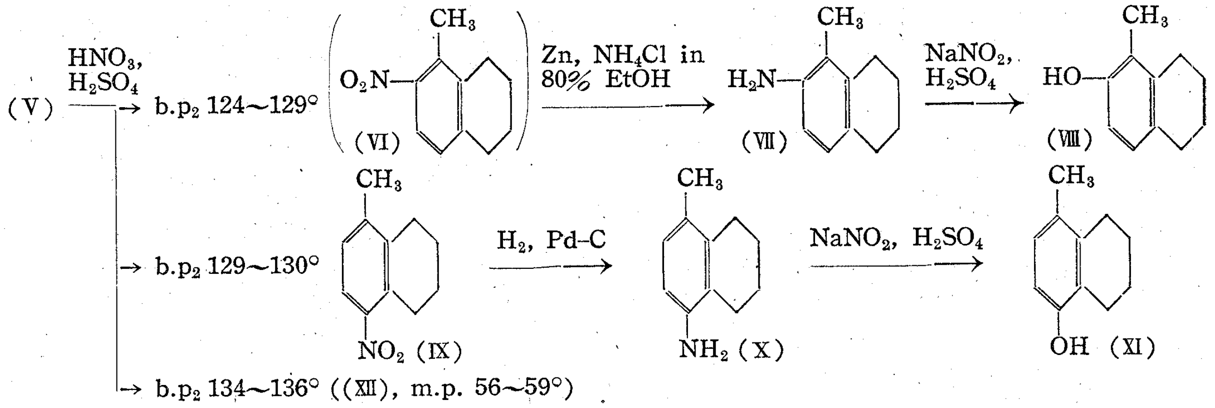


Nitrating (V) with a mixture of nitric acid and sulfuric acid, an oily product was obtained and separated to three fractions by distillation under reduced pressure.

The first fraction was assumed to consist of 1-methyl-2-nitro-5,6,7,8-tetrahydronaphthalene (VI) and was reduced with zinc and aqueous alcohol for the purpose of obtaining methyltetraline quinol. The existence of quinol-like substance could not be proved, but a little quantity of an amine sulfate was obtained. Its structure was proved as 1-methyl-2-amino-5,6,7,8-tetrahydronaphthalene (VII) sulfate by converting to 1-methyl-2-hydroxy-5,6,7,8-tetrahydronaphthalene (VIII) which was identical with its authentic sample. So it is clear that the first fraction contains some quantity of (VI).

From the second fraction, a crystalline substance, which was supposed to be 1-methyl-4-nitro-5,6,7,8-tetrahydronaphthalene (IX), was obtained with a good yield. (IX) was converted to 1-methyl-4-amino-5,6,7,8-tetrahydronaphthalene (X), which was then converted to 1-methyl-4-hydroxy-5,6,7,8-tetrahydronaphthalene (XI).

From the third fraction, yellow crystals (XII) were obtained. They melted at 56~59° after recrystallization from methanol and the microanalytical data showed that N was 9.39.% The structure of this compound will be discussed in future.



The author's thanks are due to Prof. Momose for his advice and encouragement during the course of this work and to members of the analytical room of this Institute for the microanalytical work.

Experimental

1-Methyl-5 6,7,8-tetrahydronaphthalene (V)—200 g. of (IV), b.p$_4$ 107~110°, was added to a solution of 23 g. of Mg in 500 cc. of anhyd. ether. After Mg dissolved, 148 g. of Me_2SO_4 in 200 cc. of ether was added while stirring. After the reaction ended, the ether solution was decomposed with dil. HCl, and shaken with $NaHCO_3$ solution, then with water, and dried over anhyd. $CaCl_2$. Concentrating the ether solution, an oily product remained and was fractionated by distillation under reduced pressure. (V) was a colorless liquid, b.p$_{18}$ 112~114°, and weighed 73 g.

Nitration of 1-Methyl-5,6,7,8-tetrahydronaphthalene (V)—To 73 g. of (V), a mixture of 58 g. of HNO_3 (d=1.35) and 128 g. of H_2SO_4 (d=1.84) was added while stirring, maintaining the solution temperature below −5°. Adding 200 cc. of carbon tetrachloride, upper layer was separated and washed with $NaHCO_3$ solution, then with water and dried over anhyd. $CaCl_2$. Concentrating the filtrate, an oil remained and was fractionated to three fractions by distillation under reduced pressure, i.e. b.p$_2$ 124~129°, 129~130°, and 134~136°. The yields of each fraction were 4 g., 35 g., and 5 g., respectively.

1-Methyl-2-amino-5,6,7,8-tetrahydronaphthalene (VII) Sulfate—The first fraction, b.p$_2$ 124~129°, was reduced with zinc powder and ammonium chloride in boiling 80% EtOH during 30 mins. After cooling, the alcoholic solution was acidified with 20% H_2SO_4 and a white crystalline substance precipitated. After recrystallization from EtOH, it formed needles, m.p. 270~271° (decomp.). (cor.) *Anal.* Calcd. for $C_{11}H_{11}N \cdot 1/2\,H_2SO_4$: N, 6.95. Found : N, 7.23.

1-Methyl-2-hydroxy-5,6,7,8-tetrahydronaphthalene (VIII)—To the solution of 100 mg. of (VII) in 10 cc. of 10% H_2SO_4, 0.4 cc. of 10% sodium nitrite solution was added below 0°, and then the solution temperature was elevated to 100°. After cooling, the brown oily product was extracted with ether and the ether solution was washed with water and dried over anhyd. sodium sulfate. Concentrating the filtrate, the residue crystallized after adding petroleum benzine. Recrystallization from petroleum benzine yielded needles, m.p. 111~112°, and it was proved to be identical with 1-methyl-2-hydroxy-5,6,7,8-tetrahydronaphthalene by mixed fusion with the one synthesized in the author's laboratory by the Harukawa-Ishikawa method[2].

1-Methyl-4-nitro-5,6,7,8-tetrahydronaphthalene (IX)—The second fraction, b.p$_2$ 129~130°, crystallized. Recrystallization from petroleum ether yielded pale yellow prisms, m.p. 70~71.5°. *Anal.* Calcd. for $C_{11}H_{13}ON_2$: C, 69.09; H, 6.85; N, 7.33. Found : C, 68.95; H, 6.66; N, 7.54.

1-Methyl-4-amino-5,6,7,8-tetrahydronaphthalene (X) Sulfate—300 mg. of (IX) and 100 mg. of 10% palladium-charcoal in 10 cc. of ethyl acetate was shaken with hydrogen. After absorbing ca. three equivalent volumes of hydrogen, the filtrate was concentrated. An oil remained and was distilled during 128~130° at 2 mm. Adding 10% H_2SO_4 (X) crystallized with a quantitative yield. Recrystallization from alcohol yielded needles, m.p. 193° (decomp.)(cor.). *Anal.* Calcd. for $C_{11}H_{11}N \cdot 1/2\,H_2SO_4$: N, 6.95. Found : N, 6.67.

Picrate of (X), yellow needles from EtOH, m.p. 195~196° (decomp.).(cor.) *Anal.* Calcd. for $C_{17}H_{18}O_7N_4$: N, 14.36. Found : N, 13.96.

1-Methyl-4-hydroxy-5,6,7,8-tetrahydronaphthalene (XI)—To 400 mg. of (X) in 10 cc. of 10% H_2SO_4 1.4 cc. of 10% sodium nitrite solution was added below 0° and the solution temperature was elevated to 90°. After cooling, the solution was extracted with ether and the ether solution was washed with water, then dried over anhyd. sodium sulfate. b.p. of (XI) was 118~120° at 3 mm. and it crystallized after distillation, weighning 150 mg. Recrystallization from petroleum benzine yielded needles, m.p. 86~88°. *Anal.* Calcd. for $C_{11}H_{14}O$: C, 81.43; H, 8.70. Found : C, 81.40; H, 8.31.

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[2] J. Pharm. Soc. Japan, **70**, 49 (1950).