Notes

Yoshinori Kidani : Studies on Phenazines. VIII.* Some Observations in the Phenazine Synthesis by the Improved Wohl–Aue Reaction.

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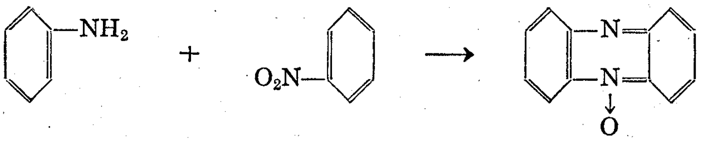
The synthesis of mono–[1] and di–methoxyphenazines by the improved Wohl–Aue reaction[2] has already been reported, while the mechanism of this condensation reaction will be enlarged upon later.

When nitro derivatives, starting materials, condense with amino derivatives in this reaction, the former seems to participate in the oxidative action spontaneously. Therefore, the yield of the phenazine derivatives produced, in order to examine the condition, has been investigated by changing the mole numbers of nitro compounds to the corresponding amino compounds under the same conditions, such as reaction period, temperature, and solvents (toluene or xylene).

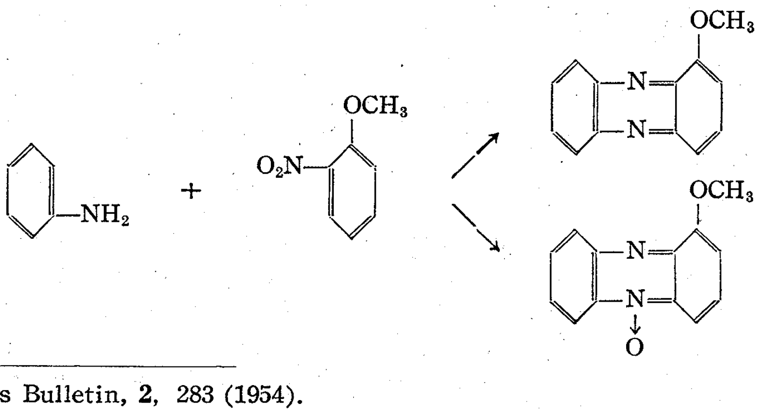
Nitrobenzene and aniline were condensed in order to obtain phenazine, but the main product was phenazine mono–N–oxide and a fair amount of azobenzene was produced, besides a trace of phenazine. No phenazine was obtained. The details are shown in Table I.

TABLE I.

	Aniline	Nitrobenzene	Solvent	Alkali	Phenazine mono–N–oxide
i)	9.3 g. (1 mole)	12.3 g. (1 mole)	toluene	KOH	0.8 g.
ii)	〃	6.1 g. (0.5 mole)	〃	〃	0.6 g.
iii)	〃	12.3 g. (1 mole)	no solvent	〃	0.5 g.
iv)	〃	〃	〃	NaOH	0.3 g.
v)	〃	〃	xylene	KOH	0.8 g.
vi)	〃	6.1 g. (0.5 mole)	〃	〃	0.5 g.



In the reaction of *o*–nitroanisole and aniline, starting materials, 0.5, 1, and 1.5 moles of *o*–nitroanisole were added to 30 g. of powdered sodium hydroxide, respectively, with 1 mole of aniline and refluxed for 7.5 hrs. of reaction period in 150 cc. of toluene. The results are shown in Table II.



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* Part Ⅶ : This Bulletin, **2**, 283 (1954).

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[1] I. Yoshioka : J. Pharm. Soc. Japan, **72**, 1128 (1952); **73**, 24 (1953).

[2] Wohl, Aue : Ber., **34**, 2442 (1901).

TABLE II.

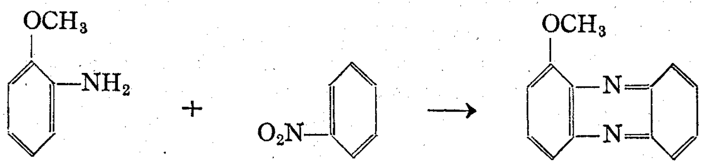
	Aniline	*o*–Nitroanisole	1–Methoxyphenazine	Yield
i)	9.3 g.	7.65 g. (0.5 mole)	0.7 g.	3.3%
ii)	〃	15.3 g. (1 mole)	1.4 g.	6.6%
iii)	〃	22.95 g. (1.5 mole)	0.8 g.	3.8%

In case of i), phenazine was produced and in case of ii), and iii), 1–methoxyphenazine mono–N–oxide[3] was obtained as by products. The results showed that the yield of 1–methoxyphenazine was best when one mole each of nitro derivatives was reacted.

When nitro and amino groups were reversed, that is, nitrobenzene and *o*–anisidine were condensed by the same method, though a fair amount of azo and azoxy compounds were produced, 1–methoxyphenazine was obtained, besides a trace of 1–methoxyphenazine mono–N–oxide. In these reactions, xylene was used as a solvent, instead of toluene.

TABLE III.

	o–Anisidine	Nitrobenzene	1–Methoxyphenazine	Yield
i)	12.3 g.	12.3 g. (1 mole)	1.25 g.	6.0%
ii)	〃	6.19 g. (0.5 mole)	0.7 g.	3.3%

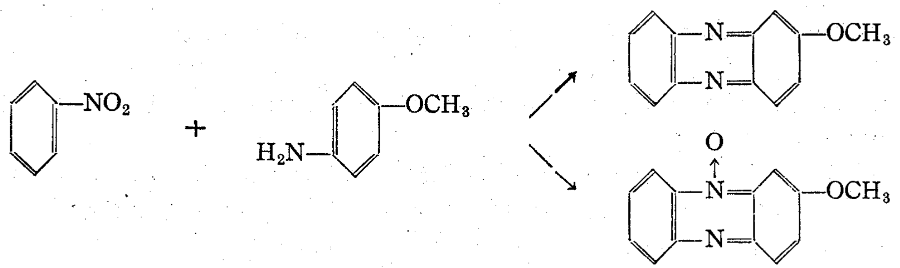


The results of the condensation between nitrobenzene and *p*–anisidine were examined. The condition of the reaction was the same as that of 1–methoxyphenazine (Table IV).

TABLE IV.

	p–Anisidine	Nitrobenzene	2–Methoxyphenazine	2–Methoxyphenazine mono–N–oxide
i)	12.3 g.	6.15 g. (0.5 mole)	1.4 g.	0 g.
ii)	〃	12.3 g. (1 mole)	0 g.	1.4 g.
iii)	〃	6.15 g.	〃	1.0 g.*
iv)	〃	12.3 g.	〃	a) 2.5 g.** b) 4.5 g.**
v)	〃	〃	〃	3.1 g.***

* 16.4 g. (0.5 mole) of potassium ferricyanide was used as an oxidizing agent.
** a) 2.7 g. and b) 11.0 g. of iron powder was used, respectively, as a reducing agent.
*** 12 g. of active charcoal was used.



2–Methoxyphenazine was obtained when 0.5 mole of nitrobenzene was condensed with 1 mole of *p*–anisidine but other experiments using 1 mole each ended in obtaining its mono–N–oxide.

The mono–N–oxide was also produced when 0.5 mole of potassium ferricyanide was added to 0.5 mole of nitrobenzene to the reaction as an oxidizing agent. Iron powder and active charcoal was used, respectively, as a reducing agent but the yield of mono–N–oxide unexpectedly increased. The reason for the increased yield of mono–N–oxide was that the reaction was carried out under agitation, to make it more effective.

Above results are summarized as follows :

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[3] Position of the oxide was discussed in the previous paper[1].

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.

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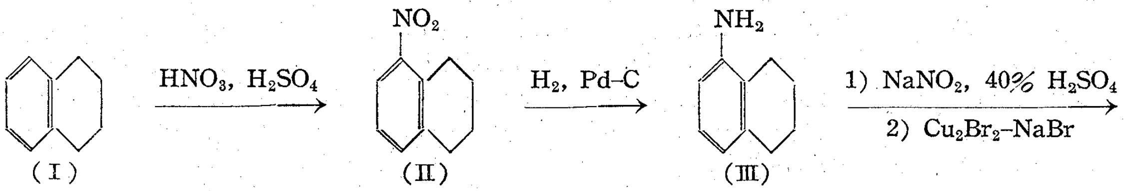
This report is concerned with the synthesis and nitration of 1-methyl-5,6,7,8-tetrahydronaphthalene (V).

(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%.



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