tube were added 5.75 g. of phosphorus pentachloride and 6.85 g. of N-2-bromoethyl-p-nitrobenzamide.[12] The mixture was heated for 120 hr. To this mixture was added 2.33 g. of aniline dissolved in 70 ml. of benzene. After an additional 24 hr. of refluxing, the phosphorus oxychloride which was formed and benzene were evaporated by means of a water aspirator and water bath. The resulting brown oil was poured into 250 ml. of hot water, the solution neutralized with ammonium hydroxide, and the organic material extracted with chloroform. The chloroform extracts were filtered through a norit pad and evaporated. The yellow crystalline residue was recrystallized twice from 50% aqueous ethanol and melted at 109–111°. A crude yield of 3.1 g. was obtained.

Anal. Calcd. for $C_{15}H_{13}N_3O_2$: N, 15.71. Found 15.71.

Acid methanolysis of I. To a mixture of 50 ml. of methanol and 36 mg. of concentrated sulfuric acid was added 100 mg. of I. The mixture was refluxed 3 hr., neutralized with several drops of 30% sodium hydroxide, the solvent evaporated, and the residue washed with water and filtered. A yield of 98.9 mg. of crude N p-nitrophenyl-N′-2-methoxyethylbenzamidine melting at 87–89° was obtained. An infrared spectrum of the crude product was identical with spectrum of an authentic sample of the amidine. Recrystallization of the crude product from cyclohexane gave crystals melting 95–97°.

N-p-nitrophenyl-N′-2-methoxyethylbenzamidine. To 3.25 g. of N-p-nitrophenylbenzimidoyl chloride was added 1.60 g. of 60% aqueous 2-methoxyethylamine. After the reaction subsided, the mixture was allowed to cool to room temperature and 40 ml. of water was added. The mixture after standing overnight gave 3.4 g. of material melting at 80–85°. Recrystallization from cyclohexane gave crystals melting at 95–97°.

Anal. Calcd. for $C_{16}H_{17}N_3O_3$: N, 14.04. Found 14.51.

Acid methanolysis of 1-p-nitrobenzoylaziridine. To a solution of 14 mg. of 98% sulfuric acid in 60 ml. of methanol was added 384 mg. of 1-p-nitrobenzoylaziridine. The reaction mixture was allowed to stand 13 hr. at room temperature, the solvent was then evaporated, and the residue was washed and filtered. A yield of 422 mg. of N-2-methoxyethyl-p-nitrobenzamide melting at 109–113° and having an infrared identical with an authentic sample[13] was obtained.

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DEPARTMENT OF CHEMISTRY
BUCKNELL UNIVERSITY
LEWISBURG, PENNSYLVANIA

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"1-Phenylazetidine" and an Unusual Hofmann-Martius Reaction

A. FISCHER, R. D. TOPSOM, AND J. VAUGHAN

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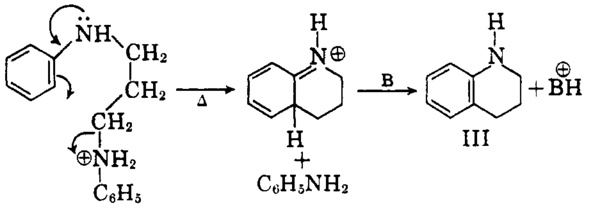
In 1899 Scholtz[1] claimed to have prepared 1-phenylazetidine [N-phenyltrimethyleneimine (I)] by the reaction of 1,3-dibromopropane with aniline. Not only is this the sole recorded preparation of an azetidine from the reaction of a dihalide with an amine,[2] but on no other occasion has the isolation of any N-aryl derivative of this ring been claimed. Scholtz obtained the compound, in small yield, as a low-boiling fraction when distilling his main reaction product, which was N,N'-diphenyltrimethylenediamine (II). Hanssen[3] had previously prepared the diamine (II) by this method but failed to distill it owing to extensive decomposition. Veer[4] later carried out the same preparation. He differed from Hanssen in distilling the diamine (II) quite readily, and differed from Scholtz in obtaining only aniline, and no trace of the cyclic compound (I), in the very small first runnings of his distillation.

In repeating Scholtz's preparation, we found that during the distillation of diamine (II), the "low-boiling" fraction could be separated into aniline, and a material answering to Scholtz's description of the azetidine (I). This description, however, also fits the secondary amine 1,2,3,4-tetrahydroquinoline (III), with which the compound was readily identified.

When the diamine (II) was carefully freed from acid (following Veer's[4] procedure of repeated water and ether extractions) it could, indeed, be distilled unchanged, but the monohydrobromide of II was found to break down smoothly at 230–250° into aniline and the reduced quinoline (III). With smaller amounts of hydrobromic acid present, decomposition of II was less rapid and although breakdown was still perceptible with "catalytic" quantities, it was found convenient to use 0.1 mol. hydrobromic acid. Under these conditions the yield of purified III, over several runs, was 50% of theory (on scheme below), with an apparently quantitative yield of aniline.

It seems likely that formation of the compound (III) is the result of an interesting Hofmann-Martius reaction:



On this scheme, the results obtained by Hanssen, Scholtz, and Veer are understandable, because incomplete removal of acid from the diamine (II) should result, at distillation temperature, in reaction of the type postulated. It is of interest that Scholtz prepared the o-tolyl analog of II. His predistillation treatment of this compound resembled that of Veer and consequently no breakdown products of distillation were reported. We find that addition of 0.1 mol. hydrobromic acid to this

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(2) S. A. Ballard and D. S. Melstrom, in *Heterocyclic Compounds* (ed. Elderfield), John Wiley & Sons, Inc., New York, 1950, Vol. 1, p. 87.

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diamine leads to smooth decomposition at 240° to give 8-methyl-1,2,3,4-tetrahydroquinoline in 50–60% yield. The recovery of *o*-toluidine appears to be somewhat above that expected on the simple reaction scheme.

It may be added that in the initial preparation of II by Hanssen's route,[3] yield of the diamine could be increased to 85% by use of excess aniline, recovery of which was satisfactory.

EXPERIMENTAL

N,N'-diphenyltrimethylenediamine (II). On our scale of preparation, high yields proved possible when the ratio of aniline:1,3-dibromopropane was *ca.* 10:1. Aniline (128.0 g.) and dibromopropane (25.0 g.) were heated together on a steam bath. After 30 min., solid aniline hydrobromide suddenly appeared in mass. The material was diluted with 300 ml. diethyl ether and shaken with ammonia. The ethereal extract was then washed with water, dried over anhydrous potassium carbonate, and ether removed by distillation at normal pressure. Distillation at 20 mm. allowed recovery of aniline (102.2 g. = 97% of initial excess) and further fractionation of the residue at 0.1 mm. gave 23.8 g. of the required compound (II) (85% theory, b.p. 189–192° at 1 mm.; n_D^{14} 1.6257).

Rearrangement of II. It was found convenient to work with a molar ratio of hydrobromic acid:*N,N'*-diphenyltrimethylenediamine of 1:10. To 14.3 g. of II was added 0.5 ml. hydrobromic acid (S.G. 1.7) and the mixture was heated (oil bath) in a simple Claissen distillation apparatus under 12 mm. pressure. Between 230° and 240° (oil bath temperature), nearly all the reaction material decomposed to give 13.1 g. of distillate. This distillate was carefully fractionated under reduced pressure to yield 6 g. aniline and 4.3 g. of III (51% of theory; b.p. 122–124°/15 mm., 130°/21 mm.; hydrochloride m. 180–181°; benzoylated under Schotten-Baumann conditions to give benzoyl derivative m.p. 76°): lit. b.p. of 1,2,3,4-tetrahydroquinoline, b.p. 245–250° at 755 mm.; hydrochloride, m.p. 181°; benzoyl derivative, m.p. 76°.

Rearrangement of N,N'-di-o-tolyltrimethylenediamine. To 16.3 g. of this diamine (prepared, in similar manner to II, in 78% yield) was added 0.5 ml. hydrobromic acid in 25 ml. ether. After shaking well, the ether was removed, and the residual liquid decomposed as for compound II. Rearrangement took place smoothly at 240–250° (oil bath), giving 14.6 g. distillate. Fractionation of this distillate finally gave 7.75 g. *o*-toluidine and 4.85 g. of 8-methyl-1,2,3,4-tetrahydroquinoline (53% yield). The reduced quinoline (n_D^{19} 1.5870) was fully characterized by a benzoyl derivative m.p. 108.5°, hydrochloride m.p. 215°, and by dehydrogenation (standard procedure using sulphur) to 8-methylquinoline (n_D^{23} 1.6148, picrate m.p. 205° unchanged by addition of authentic sample).

Department of Chemistry
University of Canterbury
Christchurch, N. Z.

The Rate of Hydrolysis of 1,2-Naphthoquinone-1-imine

Charles C. Irving

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Although the ease of hydrolysis of quinone imines to quinones has been recognized qualitatively,[1,2] no quantitative data are available concerning the rate of this reaction, as quinone imines generally cannot be obtained sufficiently pure for rate measurements. However, the availability of the pure *o*-quinone imine, 1,2-naphthoquinone-1-imine,[3] has permitted a determination of its rate of hydrolysis in aqueous solvents.

1,2-Naphthoquinone-1-imine was stable for several hours in 95% ethanol but was rapidly hydrolyzed to the *o*-quinone in alcohol–water mixtures which contained less than 75% ethanol. The first order rate constants for the hydrolysis of 1,2-naphthoquinone-1-imine are listed in Table I. After 1,2-naphthoquinone-1-imine had been completely hydrolyzed (thirty minutes in 10% ethanol), only 1,2-naphthoquinone could be detected in the solution by ultraviolet spectrophotometry.

TABLE I

RATE CONSTANTS FOR THE HYDROLYSIS OF 1,2-NAPHTHOQUINONE-1-IMINE IN AQUEOUS ETHANOL AT 25°

Ethanol concentration (% by volume)	$10^4 \cdot k_{obs}$ (sec.$^{-1}$)
95	0.57
75	1.3
55	4.8
40	8.7
25	14.9
10	34.8

In contrast to the moderate stability of 1,2-naphthoquinone-1-imine in 95% ethanol, 1,2-naphthoquinone-1-benzimide was unstable in this solvent. The instability of 1,2-naphthoquinone-1-benzimide in 95% ethanol was not due to its hydrolysis but to the formation of an adduct, *N*-(x-ethoxy-2-hydroxy-1-naphthyl)benzamide, m.p. 160–161°. The isolation of this adduct has been reported previously.[4]

Nevertheless, *N*-acylated derivatives of 1,2-naphthoquinone-1-imine were more resistant towards hydrolysis in aqueous systems than the *o*-quinone imine itself. 1,2-Naphthoquinone-1-benzimide was stable for as long as two hours in 20% aqueous dioxane. The quinone imide was also stable in mixtures of 0.1 *M* phosphate buffer-dioxane (8:2, by volume) of *p*H 6.1 and 7.3 for a minimum of twenty minutes, this being the longest time interval over which observations were

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