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,[8] 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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(1) L. F. Fieser and M. Fieser, *Organic Chemistry*, 3rd Ed., Reinhold Publishing Corporation, New York, N. Y., 1956, p. 715.

(2) N. V. Sidgwick, T. W. J. Taylor, and W. Baker, *The Organic Chemistry of Nitrogen*, Oxford University Press, Oxford, England, 1937, p. 97.

(3) A. Lüttringhaus and H. Wulff, *Angew. Chem.*, **67**, 274 (1955).

(4) C. C. Irving and H. R. Gutmann, *J. Biol. Chem.*, **234**, 2878 (1959).

made. Increasing the final pH to 8.3 in the buffered solvent system resulted in the slow hydrolysis of 1,2-naphthoquinone-1-benzimide (rate constant: 0.67×10^{-4} sec.$^{-1}$ at 25°). The rate of hydrolysis of 1,2-naphthoquinone-1-acetimide in the buffered aqueous dioxane at pH 8.3 was almost three times faster (rate constant: 1.80×10^{-4} sec.$^{-1}$ at 25°) than the rate of hydrolysis of 1,2-naphthoquinone-1-benzimide in the same solvent system. After a solution of 1,2-naphthoquinone-1-acetimide in buffered aqueous dioxane at pH 8.3 had stood for several hours, the visible spectrum of the solution was identical with that of a solution of 1,2-naphthoquinone.

EXPERIMENTAL

1,2-Naphthoquinone,[5] 1,2-naphthoquinone-1-imine,[3] 1,2-naphthoquinone-1-acetimide[4] and 1,2-naphthoquinone-1-benzimide[6] were prepared by published methods. Dioxane was purified according to Fieser.[7] The visible and ultraviolet spectra were recorded on a Beckman Model DR Spectrophotometer.

1,2-Naphthoquinone-1-imine in aqueous ethanol. A comparison of the ultraviolet absorption spectra of 1,2-naphthoquinone and 1,2-naphthoquinone-1-imine is shown in Fig. 1. The rate of decrease in absorbance at 259 mμ was used to measure the rate of hydrolysis of 1,2-naphthoquinone-1-imine in aqueous ethanolic solutions. The concentration of 1,2-naphthoquinone-1-imine was calculated from the equation:

$$[\mathrm{QI}]_t = \frac{\mathrm{E}_t - [\mathrm{QI}]_0 \cdot \epsilon_{\mathrm{Q}}}{\epsilon_{\mathrm{QI}} - \epsilon_{\mathrm{Q}}}$$

where

$[\mathrm{QI}]_t$ = concentration (mol. per l.) of 1,2-naphthoquinone-1-imine at time, t
E_t = absorbance at time, t
$[\mathrm{QI}]_0$ = initial concentration (mol. per l.) of 1,2-naphthoquinone-1-imine
ϵ_{QI} = molar extinction coefficient of 1,2-naphthoquinone-1-imine at 259 mμ (log ϵ = 4.30)
ϵ_{Q} = molar extinction coefficient of 1,2-naphthoquinone at 259 mμ (log ϵ = 4.17).

The first order rate constants were calculated from the data obtained from the plot of the log of the concentration of 1,2-naphthoquinone-1-imine versus time in minutes. The rate plots were linear for the time intervals observed: 60 min. for 95–40% ethanol, 30 min. for 25% ethanol and 10 min. for 10% ethanol.

1,2-Naphthoquinone-1-acetimide and 1,2-naphthoquinone-1-benzimide in aqueous dioxane. 1,2-Naphthoquinone-1-acetimide and 1,2-naphthoquinone-1-benzimide have absorption maxima at 360 mμ in aqueous dioxane (20% dioxane by volume). The position of the maxima did not shift as the pH of the solution was changed from 6.1 to 8.3. The concentrations of solutions of 1,2-naphthoquinone-1-acetimide (log ϵ_{360} = 3.58) and of 1,2-naphthoquinone-1-benzimide (log ϵ_{360} = 3.68) were determined from their absorbancies at 360 mμ. Since the rate of hydrolysis of these quinone imides was only slight, absorption at 360 mμ due to the hydrolysis product, 1,2-naphthoquinone, was negligible during the initial time periods.[8]

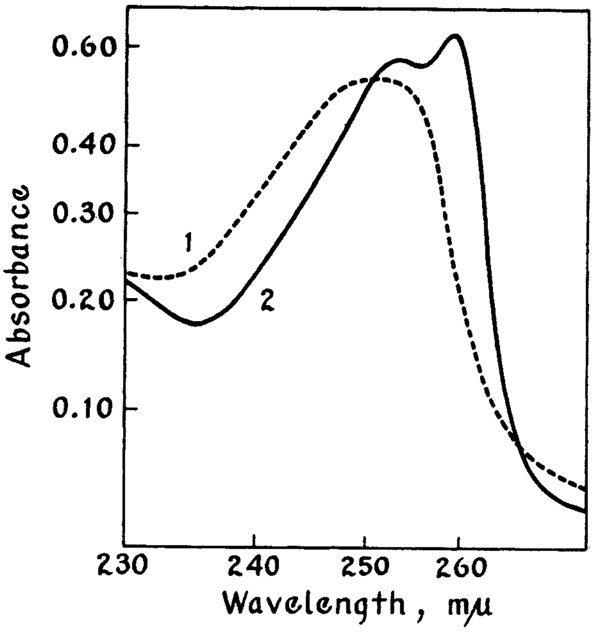

Fig. 1. Ultraviolet absorption spectra of 1,2-naphthoquinone (1) and 1,2-naphthoquinone-1-imine (2) in 95% ethanol

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UNIVERSITY OF MINNESOTA
MINNEAPOLIS

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(5) L. F. Fieser, *Org. Syntheses*, **Coll. Vol. II**, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 430.

(6) R. Adams and J. M. Stewart, *J. Am. Chem. Soc.*, **74**, 5876 (1952).

(7) L. F. Fieser, *Experiments in Organic Chemistry*, 3rd Ed., D. C. Heath and Company, New York, N. Y., 1955, p. 285, procedure (a).

(8) Present address: Radioisotope Service, VA Medical Teaching Hospital, Memphis 15, Tennessee.

2-Imino-4-oxo-5-thiazolidineacetic Acid and Its Derivatives

A. N. ARAKELIAN, H. DUNN, JR., L. L. GRIESHAMMER, AND L. E. COLEMAN

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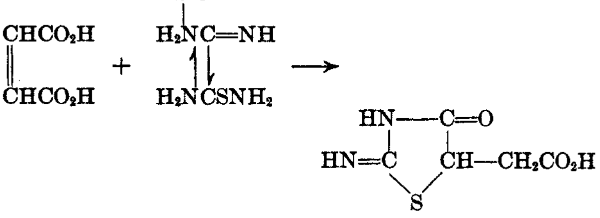
Tambach[1] and Andreash[2] in 1894–1895 reported that thiourea reacts in the enol form with maleic acid or fumaric acid to yield the 2-imino-4-oxo-5-thiazolidineacetic acid, I. Structure was proved



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(1) R. Tambach, *Lieb. Ann.*, **280**, 233 (1894).

(2) R. Andreash, *Monatsch.*, **16**, 789 (1895).