Grignard reaction of bromobenzene and $C^{14}$ labeled carbon dioxide.[2] As esterification of benzoic acid and meta nitration[3] of the resulting ester are readily effected, direct reduction of the methyl and ethyl *m*-nitrobenzoates to *m*-toluidine was attempted.

In 1948, Huang-Minlon[4] reported a modification of the Wolff–Kishner reaction in which nitrobenzaldehydes were reduced to toluidines by hydrazine hydrate in diethylene glycol, this solvent permitting a high refluxing temperature. The success of this reaction and the report by McFadyen and Stevens[5] that certain esters are reduced to aldehydes *via* formation of their benzenesulfonyl hydrazides prompted the present investigation of the effect of hydrazine on *m*-nitrobenzoate esters. This has resulted in a new reductive method whereby *m*-toluidine is prepared by simple distillation of an alkaline solution of the methyl or ethyl *m*-nitrobenzoate and hydrazine in diethylene glycol.

In the belief that the reaction might go through a hydrazidine intermediate which is competitively hydrolyzed and reduced by the alkali, an attempt was made to improve the yield by distilling off excess water from the initial mixture of glycol, nitroester and hydrazine hydrate, and then replacing the potassium hydroxide solution with an equivalent amount of sodium diethylene glycolate, prepared by the reaction of metallic sodium with diethylene glycol. After fifteen minutes of refluxing, the flask was allowed to cool, 2 ml. of water added, and steam distillation carried out as described below. However, this resulted in no increase in yield.

To attempt to extend the scope of this reaction, it was tried on several other compounds (Table I). On the unsubstituted aromatic and aliphatic esters, ethyl benzoate and methyl laurate, the method was unsuccessful, resulting only in hydrolysis to the corresponding acid. Attempted reduction of an equimolar mixture of nitrobenzene and ethyl benzoate gave only aniline and benzoic acid. Two grams each of the methyl *o*- and *p*-nitrobenzoates gave only approximately 0.05 g. of the corresponding *o*- and *p*-toluidines. Attempted reduction of methyl salicylate and methyl *m*-hydroxybenzoate, resulted in no reduction product.

TABLE I

EFFECT OF HYDRAZINE ON VARIOUS ESTERS

| Compound | Redn. product | % yield |
|---|---|---|
| Ethyl benzoate | None | |
| Methyl laurate | None | |
| Methyl *o*-hydroxybenzoate | None | |
| Methyl *m*-hydroxybenzoate | None | |
| Methyl *o*-nitrobenzoate | *o*-Toluidine | Appx. 4 |
| Methyl *m*-nitrobenzoate | *m*-Toluidine | 25 |
| Methyl *p*-nitrobenzoate | *p*-Toluidine | Appx. 4 |
| Ethyl *m*-nitrobenzoate | *m*-Toluidine | 25 |

Reduction of methyl *m*-nitrobenzoate labeled with $C^{14}$ in the carboxyl group gave $C^{14}$ labeled *m*-toluidine containing the same molar specific activity as the nitro ester.

## Experimental

***m*-Toluidine.**—All procedures unless otherwise indicated followed that described below for the preparation of *m*-toluidine, and used the same mole ratios of materials.

In a 200-ml., round-bottom, standard glass-taper flask 2 g. of methyl *m*-nitrobenzoate was dissolved in 12 ml. of diethylene glycol and 3 ml. of 85% hydrazine hydrate was added. After one minute of gentle heating and swirling of the flask to ensure complete mixing, a concentrated aqueous solution containing 2 g. of potassium hydroxide was added and the flask attached to a 20-cm. Vigreux column whose side arm extended to the bottom of an ice-bath cooled receiver.

The mixture was heated over a small bunsen flame so that vapor began to condense in the side arm in five to ten minutes and shortly thereafter droplets of the *m*-toluidine appeared in the distillate. This steam distillation was continued until no water remained in the reaction mixture, as evidenced by the rise of distillation temperature from the initial 99–100°.

The organic material in the distillate was separated from the aqueous phase by ether extraction. Removal of the ether by evaporation left 0.30 g. (25%) of *m*-toluidine, b. p. 201° at 756 mm., which readily reacted with acetic anhydride to give a white solid of m. p. 65°, not depressed on mixture with an authentic sample of N-acetyl-*m*-toluidine; literature: *m*-toluidine b. p. 203°, acetamide, deriv. m. p. 65°.

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[2] Dauben, Reid and Yankwich, *Ind. Eng. Chem., Anal. Ed.*, **19**, 828 (1947).

[3] Gilman and Blatt, "Organic Syntheses," Coll. Vol. I, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., p. 372.

[4] Huang-Minlon, THIS JOURNAL, **70**, 2802 (1948).

[5] McFadyen and Stevens, *J. Chem. Soc.*, 584 (1936).

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# Hydrogen Peroxide Vapor Explosions—Determination of Explosive Composition[1]

BY CHARLES N. SATTERFIELD, GEORGE M. KAVANAGH, RALPH N. KINGSBURY AND HYMAN RESNICK

The occurrence of a homogeneous gas decomposition in hydrogen peroxide vapor, a reaction easily obscured by the heterogeneous decomposition on the walls, has recently been deduced by McLane.[2] His experiments, conducted at high temperature, under low pressure, and with carefully prepared surfaces, indicate that the usual wall decomposition is accompanied by some homogeneous reaction. Direct observation of explosions and flames in vapor containing hydrogen peroxide has been reported by Hart.[3] In an investigation of the nature of the decomposition reaction, measure-

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[1] This work is supported by funds from the Office of Naval Research.

[2] C. K. McLane, *J. Chem. Phys.*, **17**, 379 (1949).

[3] A. B. Hart, *Nature*, **63**, 876 (1949).

ments are being made of the pressures and compositions of vapors that will support explosive decomposition. Experimental results are reported here concerning the compositions of vapors at atmospheric pressure containing principally hydrogen peroxide and water, plus a small amount of oxygen, that may be exploded by a hot wire.

### Experimental

In the experimental procedure, a vapor stream is passed through a flask and the effluent is analyzed at frequent intervals before the explosion is attempted. The vapor stream is supplied from a boiling aqueous hydrogen peroxide solution of high purity. Decomposition is kept to a minimum by keeping the amount of liquid in the boiler at any one time small relative to the boiling rate.

The vapors produced in the boiler are passed through the explosion flask and thence through a condenser. The concentration and volume of the condensate are determined while the volume of any non-condensable gas, assumed to be oxygen, is measured by a wet-test gas meter. These measurements are combined to give a complete vapor analysis as well as a material balance which can be used to check the steady-state operation of the system. It is assumed that negligible decomposition occurs in the explosion flask and condenser.

Initiation of the explosions in these experiments was accomplished by a platinum wire 0.01″ in diameter and 5 cm. long, which was welded across two 0.04″ diameter platinum leads sealed through glass into the explosion flask. Explosion was attempted by passing a current of 5 amperes through the wire, causing it to glow at a red heat.

In performing the experiments, hydrogen peroxide vapors were passed continuously through the explosion flask and analyzed until the measurements showed that steady state had been obtained. An attempt to explode the vapor was then made. After the attempt, the current through the wire was shut off and approximately thirty seconds allowed for the system to reach its previous steady state before ignition was again tried. At high hydrogen peroxide concentrations, the vapor will explode violently with complete destruction of the apparatus; however, with the vapor concentrations covered in the table below, the maximum effect has been an audible "pop." When the concentration was close to the explosion limit, no noise was heard; and the question as to whether or not an explosion had occurred was decided by close observation of the fog formed in the condenser. It has been possible to distinguish clearly between two cases on heating the wire: either (1) the fog is suddenly expelled from the condenser, or (2) there is no noticeable disturbance in the condenser. If there is a sudden expulsion of fog from the condenser, an explosion is considered to have occurred even though there has been no audible report.

**Results.**—The results are presented in Table I, which shows the vapor compositions studied and the observations on repeated explosion attempts with that vapor, at one atmosphere total pressure.

TABLE I

| Partial press. in vapor, mm. | | | Observations | |
|---|---|---|---|---|
| $H_2O_2$ | $H_2O$ | $O_2$ | Explosion | Attempts |
| 153 | 517 | 99 | 0 | 10 |
| 178 | 550 | 22 | 0 | 10 |
| 198 | 559 | 5 | 1 | 9 |
| 198 | 557 | 6 | 3 | 10 |
| 204 | 487 | 69 | 10 | 10 |
| 222 | 524 | 19 | 10 | 10 |
| 226 | 523 | 15 | 10 | 10 |
| 231 | 518 | 6 | 10 | 10 |

The variation in the oxygen concentration in the vapor is due to improving operational technique which caused a decreasing amount of decomposition in successive runs. From energy considerations, reaction between water or oxygen and any of the species that could be present in this reacting mixture are unlikely; from this it would be expected that the oxygen to water ratio in the diluent gas should have little effect on the limit of explosive composition in terms of the partial pressure of hydrogen peroxide. This assumption is supported by the results obtained.

**Discussion.**—The results indicate definitely that with this experimental system, there is a reproducible explosion limit in the vicinity of 198 mm. partial pressure of hydrogen peroxide. In considering the significance of the results, it must be remembered, however, that the physical characteristics of the ignition system may appreciably affect the measured ignition limits.

The mechanism of the explosive reaction has not been thoroughly investigated, but a branched chain explanation seems unlikely because of energy considerations. It is probable that the reaction is carried through the mixture by unbranched chains—perhaps corresponding to the mechanism proposed by Haber and Willstätter for liquid phase decomposition,[4] with the initiating reaction in this case a breaking of the O–O bond in the hydrogen peroxide.[5,2] A continually increasing number of these chains may be thermally initiated as a result of the large heat of decomposition, thus producing an explosion which is essentially thermal in nature.

[4] F. Haber and R. Willstätter, *Ber.*, **64B**, 2844 (1931).

[5] P. Giguere, *Can. J. Research*, **25B**, 135 (1947).

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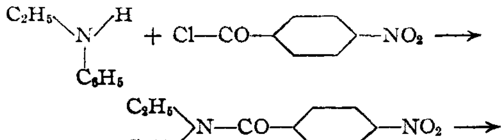
## Synthesis of 4-(N-Ethylamino)-N-ethyl-N-phenylbenzamide[1]

BY W. A. SCHROEDER AND PHILIP E. WILCOX

In the course of recent experiments it was necessary to prepare 4-(N-ethylamino)-N-ethyl-N-phenylbenzamide (III) for which no method of synthesis seems to have been described in the literature. Two other new compounds, 4-nitro-N-ethyl-N-phenylbenzamide (I) and 4-amino-N-ethyl-N-phenylbenzamide (II), were intermediates in the synthesis of the desired compound. The series of reactions was



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