

from rearrangement of the triphenylmethyl ether of *o*-cresol, m. p. 162–163°.

2. This study supports the evidence of Boyd and Hardy,<sup>4</sup> who conclude the migrating radical

has not entered the side chain when triphenylmethyl *o*-tolyl ether undergoes rearrangement.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

## The Utilization of Aliphatic Nitro Compounds. (I) The Production of Amines and (II) The Production of Oximes<sup>1</sup>

BY KENNETH JOHNSON WITH ED. F. DEGERING

The nitroparaffins were studied by a number of investigators following their first production by Victor Meyer<sup>2</sup> in 1872. The preparation of these compounds, however, was such that not very large amounts were available for experimentation and in many cases the investigators were not very thorough. With the work of Hass, Hodge and Vanderbilt,<sup>3</sup> begun in 1930, a process was perfected whereby the paraffin hydrocarbons were nitrated directly, making the nitroparaffins available at a lower cost and in greater abundance. The possibility of industrial development of this process brought about renewed interest in the study of nitroparaffins and their derivatives and a broad investigation was begun. The work reported here is a part of that much larger work.

### I. Reduction of Nitroparaffins to Amines

A number of investigators<sup>3,4</sup> have reported the reduction of nitroparaffins with different reagents and under different experimental conditions, but in every case the yields of isolatable products have been small.

(a) **Reduction with Iron and Hydrochloric Acid.**—After several preliminary experiments the following apparatus and procedure were adopted: a three-necked flask is equipped with a mercury-seal stirrer (motor driven) and a reflux condenser. A trap containing standard hydrochloric acid is arranged to absorb any amines which might pass through the condenser. To 35 g. of 40-mesh iron filings are added 75 ml. of water and 10 ml. of concd. hydrochloric acid. After the evolution of hydrogen has stopped, one-sixth of a mole of the nitroparaffin is added and, with

rapid stirring, the mass is heated at 100° for thirteen to fifteen hours. The solution is then made alkaline and the amine distilled out into standard hydrochloric acid. The conversion is calculated from the amount of hydrochloric acid required for neutralization. In another series of experiments, 1 g. of ferric chloride was added to the reaction mixtures.

The reaction mixture was evaporated to dryness, and the hydrochlorides of the amines extracted with butanol. No ammonium chloride remained as a residue. The amine hydrochlorides were further identified by titration with silver nitrate, from which data the molecular weight was calculated, and by a Van Slyke determination of amino nitrogen.

(b) **Catalytic Hydrogenation.**—These nitroparaffins were also reduced with hydrogen to give yields of 92–98% of the theoretical, by dissolving 0.25–0.33 mole of nitroparaffin in 175 ml. of methyl or ethyl alcohol and treating with hydrogen in a Parr bomb under 6–110 atmospheres over 7.5 g. of Raney nickel<sup>5</sup> for two to five hours, at 40–50°, with rocking. The non-formation of ammonia and the identity and yields of the amines were established as in the reductions with iron and hydrochloric acid.

Other catalysts were studied, but the results were unsatisfactory.<sup>6</sup>

The following nitro compounds were reduced in this way: nitromethane, nitroethane, 1- and 2-nitropropane, 1- and 2-nitrobutane, and 1- and 2-nitro-2-methylpropane. Percentage conversions of 82–94% were obtained in the absence of, and 93–97% in the presence of, ferric chloride. The titration gave the calculated molecular weight with an average deviation of only 1% and with an extreme deviation of 2.3%, while the amino nitrogen was found in every case to be either the exact amount required by the formula or within 1% thereof.

### II. Reduction of Nitroparaffins to Oximes

The partial reduction of primary and secondary nitroparaffins produces oximes.<sup>7,8</sup> A number of reducing agents were tried, but the procedure adopted is: to 100 ml. of glacial acetic acid and 15 ml. of 1-nitropropane, add 35 g. of zinc dust, stir, and reflux for six hours. Hydrolyze the oxime by adding 25 ml. of water, then 5 ml. of concd. sulfuric acid, and heating. Distil the aldehyde and

(1) Abstracted from a portion of a Thesis submitted to the Faculty of Purdue University by Kenneth Johnson in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1937. This research project was sponsored by The Commercial Solvents Corporation under the general supervision of Jerome Martin and H. B. Hass. Presented before the Division of Industrial Engineering Chemistry of the American Chemical Society at the Baltimore meeting, April 3–7, 1939.

(2) Victor Meyer, *Ber.*, **5**, 203, 514, 1029, 1034 (1872).

(3) Hass, Hodge and Vanderbilt, *Ind. Eng. Chem.*, **28**, 339 (1936).

(4) Meyer, *Ann.*, **171**, 1 (1874); Kahn and Meyer, *Chem. Abs.*, **21**, 3205 (1927).

(5) Covert and Adkins, *THIS JOURNAL*, **54**, 4116 (1932).

(6) Adkins and Connor, *ibid.*, **53**, 1091 (1931).

(7) Konowaloff, *J. Chem. Soc.*, **76**, 733 (1899).

(8) Ponzio, *ibid.*, **82**, 334 (1902).

identify by its reaction with  $\text{H}_2\text{NOH}\cdot\text{HCl}$ . The conversion to aldehyde is 43%.<sup>9</sup>

### Summary

All the nitroparaffins available from the nitration of propane, butane, and isobutane have been reduced to the corresponding amines by the use of iron and hydrochloric acid and catalytic hydrogenation. These processes produce good

(9) Pemberton, Card and Craven, *J. Soc. Chem. Ind.*, **54**, 163T (1935).

yields of easily purified products and require only simple technique. The results indicate that primary, secondary, and tertiary nitroparaffins can be reduced to give almost quantitative yields of the corresponding amines.

The conversion of nitroparaffins to oximes gives, in general, rather low yields because of the simultaneous formation of the amines.

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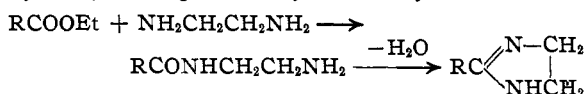
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## Preparation and Cyclization of Monoacylethylenediamines. II

BY SAMUEL R. ASPINALL

It has been shown<sup>1</sup> that the best method of preparing 2-substituted-4,5-dihydroimidazoles is by dehydrating monoacylated ethylenediamines.



The investigation herein reported was undertaken to determine the extent of the applicability of this method. As a result of this and previous work<sup>1</sup> it is shown that an ester may be converted to the corresponding 4,5-dihydroimidazole in an over-all yield of about 75% when R is any one of such divergent groups as:  $\text{CH}_3-$ ,  $\text{C}_2\text{H}_5-$ , *n*- $\text{C}_3\text{H}_7-$ ,  $(\text{C}_2\text{H}_5)_2\text{CH}-$ ,  $(\text{iso-C}_3\text{H}_7)_2\text{CH}-$ ,  $\text{C}_6\text{H}_5-$ , *p*- $\text{CH}_3\text{C}_6\text{H}_4-$ , or  $\text{C}_6\text{H}_5\text{CH}_2-$ . The yield of 2-diphenylmethyl-4,5-dihydroimidazole from ethyl diphenylacetate was considerably lower. Because reaction conditions for this series of experiments were more or less arbitrarily fixed in order to give comparable data, the yield reported for any given experiment is not necessarily the best obtainable.

Two slight changes in the procedure heretofore employed<sup>1</sup> have resulted in simplification and generally higher yields. (a) The reaction of ethylenediamine and esters of six or more carbon atoms which are branched in the alpha position requires higher temperatures than heretofore used. This effect is presumably due to the condition usually described as steric hindrance. (b) If the mixture of monoamide and diamide resulting from the reaction of ethylenediamine and an ester is treated in the usual way with lime, the yields are somewhat higher than those obtained by dehydrating the isolated monoamide with

lime. This fact is in accord with earlier observations<sup>2</sup> that ethylenediamides yield some 4,5-dihydroimidazole when heated at a high temperature with acid binding materials.

A typical experiment is now carried out as follows: 2-diethylmethyl-4,5-dihydroimidazole. Forty-eight grams ( $\frac{1}{3}$  mole) of ethyl diethylacetate and 60 g. (1 mole) of ethylenediamine are heated at 215° for twenty-four hours, and the low boiling material consisting of ethyl alcohol and excess ethylenediamine removed at diminished pressure. The remaining 39 g. of monoamide and diamide is heated with 94 g. ( $\frac{2}{3}$  mole) of calcium oxide at 225° for fifteen hours in an atmosphere of nitrogen. The organic products are extracted from the lime with alcohol, the solvent removed, and the product distilled at low pressure. 2-Diethylmethyl-4,5-dihydroimidazole, which distills as a pure white oil, solidifies immediately on cooling and is obtained as glistening white needles from petroleum ether.

It was earlier<sup>1</sup> pointed out that although the lower aliphatic monoacylethylenediamines are distillable under ordinary laboratory vacuum conditions, the corresponding aromatic derivatives are not, because the latter dehydrate to the 4,5-dihydroimidazole configuration at a temperature below that required for their distillation. It has now been found the behavior of the higher and phenylated aliphatic derivatives upon distillation is somewhat variable and depends upon structural features. (a) A higher aliphatic monoacylethylenediamine containing an alkyl group branched in the alpha position may be smoothly distilled at constant temperature to yield a distillate whose purity and homogeneity were demonstrated by quantitative conversion to simple derivatives. Presumably the steric factors which inhibit the initial reaction between the ester and

(1) Hill and Aspinall, *THIS JOURNAL*, **61**, 822 (1939).

(2) Chitwood and Reid, *THIS JOURNAL*, **57**, 2424 (1935).