sodium hydroxide and again steam distilled. As in the preceding cases, the steam is passed in until the distillate comes over clear. The distillate is extracted with ether, the ether is evaporated and the resulting quinoline is weighed. Although in the various processes the material is usually further purified by distillation, in our work the results are based on comparisons of the yield at this stage.

Graphs.—The effect of the time of heating upon the yield of quinoline is shown in Fig. 1. The effect of varying the amount of sulfuric acid is shown in Fig. 2. The effect of the quantity of glycerol upon the yield of quinoline is shown in Fig. 3. The concentration of the acetic acid has no decided effect upon the yield of quinoline.

Theory of Modification

The authors believe and experiments indicate that the violence of the ordinary Skraup reaction is due to the sudden liberation of acrolein resulting from the action of sulfuric acid upon the glycerol. The acetic acid was introduced in an effort to form a glycerol mono or diacetate and thereby remove a large proportion of the glycerol from the reaction sphere. Acetic acid was used because it is quite stable and relatively cheap.

Summary

1. A modification of the Skraup process which may be conducted with safety has been developed.

2. The variation of the yield under different conditions has been studied.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF COLORADO]

THE NITRATION OF PIPERONAL

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In a former paper[2] it was reported that commercial *o*-nitropiperonal yielded two benzylidene derivatives when treated with anthranilic acid in alcohol solution. The one was a yellow crystalline compound melting at 128° and the other yellowish-brown crystals melting at 185°. These two benzylidene products, in turn, reacted with acetic anhydride to form the corresponding nitropiperonylacet-keto-dihydrobenzmetoxazines melting at 206 and 165°, respectively. The conclusion was that Kahlbaum's

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[1] Extract from a thesis by Margaret S. Klemme submitted to the Graduate School of the University of Colorado in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Ekeley, Rogers and Swisher, THIS JOURNAL, **44**, 1756 (1922). The *o*-nitropiperonal used was Kahlbaum's product. Material from the same lot was used in these experiments.

o-nitropiperonal contained a small amount of a second isomeric nitropiperonal. Further study of the matter was desirable. To this end the above reactions were repeated and verified. The two benzylidene anthranilic acids melting at 128 and 185°, respectively, were hydrolyzed, the former yielding *o*-nitropiperonal melting at 98.5° and the latter a compound melting at 143° which showed the reactions of an aldehyde and gave the following analysis: calcd. for $C_8H_5NO_5$: N, 7.18. Found: N, 7.17. In addition fractional crystallizations were carried out with a quantity of Kahlbaum's *o*-nitropiperonal melting as an impure substance at 80°. The fractionations were carried out in ethyl alcohol, with the result that a yellow crystalline product was obtained melting at 143° and another, the major portion, melting at 98.5°. Both were nitropiperonals and yielded the above described benzylidene compounds with anthranilic acid which, in turn, were transformed into the benzmetoxazine derivatives. The one melting at 143° gave the following analysis: calcd. for $C_8H_5NO_5$: N, 7.18. Found: N, 7.22. The benzmetoxazine derivatives made from it gave the following analysis: calcd. for $C_{15}H_{10}N_2O_6$: N, 8.91. Found: N, 8.89.

We are unable to find anything in the literature on the nitration of piperonal since Fittig and Remsen's paper of 1871. A systematic study of the nitration products of piperonal then seemed advisable and this paper is a report of the results from the nitration of piperonal under twenty-one different experimental conditions. In no case was it possible to isolate from the reaction product a nitropiperonal melting at 143°. We have been unable to obtain from Kahlbaum the method of nitration used in preparing their product, so that we do not know the conditions under which it was formed. Our experiments show that besides *o*-nitropiperonal, there were formed in varying quantities, according to the nitration method used, nitropiperonylic acid, mononitromethylenecatechol, dinitromethylenecatechol, and under one set of conditions an isomeric mononitromethylenecatechol, hitherto unknown.

Experimental

The nitrations were carried out by adding small portions at a time of powdered piperonal to the nitration mixture at the temperatures indicated in each case. The raw nitration product after removal from the nitration mixture was washed and first treated with potassium hydroxide solution to obtain any acid product. Next it was treated with sodium bisulfite solution to remove aldehydes. The remaining solids were then subjected to distillation with steam. The non-volatile residue was purified, examined qualitatively and identified. In case two products were found, they were separated by fractional crystallization. The yields of the several nitration products were determined by weighing the product. The original filtrate was evaporated to dryness and oxalic acid determined.

I. Fifty g. piperonal, 250 cc. HNO_3 (sp. gr. 1.31) at 23°, stood for two hours when temperature finally rose to 40°. Yields: nitropiperonal, 40 g.; mononitromethylenecatechol,[3] m. p. 144°, 5 g., obtained by Jobst and Hess by nitrating piperonylic acid.

II. Fifty g. piperonal, 250 cc. HNO_3 (sp. gr. 1.31), at 2–4°. Yields: nitropiperonal, 50 g.; mononitromethylenecatechol, 4 g.; oxalic acid, small amount.

III. Fifty g. piperonal, 250 cc. HNO_3 (sp. gr. 1.38), without cooling, temperature rising finally to the boiling point, 91° at Boulder. Yields: nitropiperonal, 35 g.; mononitromethylenecatechol, 5 g.; oxalic acid, 7.7 g.

IV. Fifty g. piperonal, 250 cc. HNO_3 (sp. gr. 1.38), below 45°. Yields: nitropiperonal, 51.7 g.; mononitromethylenecatechol, 10 g.; oxalic acid, 2.6 g.

V. Fifty g. piperonal, 250 cc. HNO_3 (sp. gr. 1.403), at 0–10°. Yields: nitropiperonal, 50 g. Non-aldehyde portion gave mononitromethylenecatechol, 8 g., and a small amount of a compound melting at 100°, and shown by properties and analysis to be dinitromethylenecatechol,[4] obtained by Jobst and Hess by nitrating piperonylic acid.

VI. Fifty g. piperonal, 500 cc. HNO_3 (sp. gr. 1.403), at 0–10°. Yields: nitropiperonal, 49.1 g.; mononitromethylenecatechol, 13.3 g.; a trace of dinitro, a trace of a compound melting at 172° (see IX) and a small amount of oxalic acid.

VII. Fifty g. piperonal, 250 cc. HNO_3 (sp. gr. 1.403), at 0–10° in sunlight. Yields: nitropiperonal, 46.6 g.; mononitromethylenecatechol, 10 g.; a trace of the dinitro; a trace of the compound melting at 172°; oxalic acid 2 g.

VIII. Fifty g. piperonal, 250 cc. HNO_3 (sp. gr. 1.43), below 40°. Yields practically the same as in VII.

IX. Fifty g. piperonal, 250 cc. HNO_3 (sp. gr. 1.43), on ice for a week. Yields: nitropiperonal, trace; nitropiperonylic acid, m. p. 172°, 35 g.; oxalic acid 7.5 g. · Nitropiperonylic acid was obtained by Jobst and Hess[5] by the nitration of piperonylic acid.

X. Fifty g. piperonal, 250 cc. fuming HNO_3 at 30–70°. As was to be expected, there was severe oxidation, the yields being nitropiperonal, 25 g.; dinitromethylenecatechol, 4 g.; oxalic acid, 30 g.

XI. Fifty g. piperonal, 250 cc. fuming HNO_3, on ice three days. Yields, nitropiperonal, 16.5 g.; dinitromethylenecatechol, 20 g.; a small amount of the mononitro; oxalic acid, 10 g.

XII. Fifty g. piperonal, 250 cc. fuming HNO_3, at 0°, the piperonal being added very slowly during ten hours. Yields: nitropiperonal, 9 g.; dinitromethylenecatechol, 8 g., oxalic acid, 14 g.; 20 g. of a yellow crystalline compound melting at 70°. This was separated from the dinitromethylenecatechol by fractional crystallization and was shown by its properties and analysis to be an isomer of mononitromethylenecatechol.

Anal. Calcd. for $C_7H_5O_4N$: N, 8.40. Found: N, 8.44.

XIII. Fifty g. piperonal, 250 cc. fuming HNO_3, at -5°. Yields: nitropiperonal, 45 g.; dinitromethylenecatechol 13.3 g.; oxalic acid, 1 g.

XIV. Fifty g. piperonal, 250 cc. HNO_3 (sp. gr. 1.403), 250 cc. H_2SO_4 (sp. gr. 1.82), below 10°. Yields: nitropiperonal, 15 g.; dinitromethylenecatechol, 32.5 g.; a trace of nitropiperonylic acid, a small amount of oxalic acid.

XV. Fifty g. piperonal, 250 cc. HNO_3 (sp. gr. 1.403), 250 cc. H_2SO_4 (sp. gr. 1.82) below 0°. Yields: nitropiperonal, 25 g.; dinitromethylenecatechol, 12 g.; some oxalic acid.

XVI. Fifty g. piperonal, 250 cc. fuming HNO_3, 250 cc. H_2SO_4 (sp. gr. 1.48), at 0°. Yields: nitropiperonal, 20 g.; dinitromethylenecatechol, 5.8 g.; oxalic acid, 35 g.

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[3] Fittig and Remsen, *Ann.*, **159**, 134 (1871); Jobst and Hess, *Ann.*, **199**, 73 (1879); Salway, *J. Chem. Soc.*, **95**, 1163 (1909).

[4] Jobst and Hess, *Ann.*, **199**, 75 (1879).

[5] Jobst and Hess, *Ann.*, **199**, 70 (1879).

XVII. Fifty g. piperonal, 250 cc. fuming HNO_3 into which SO_2 had been led for twelve hours, at 0°.[6] Yields: nitropiperonal, 38.3 g.; dinitromethylenecatechol 20 g.; oxalic acid, 1 g.

XVIII. Fifty g. piperonal, 250 cc. HNO_3 (sp. gr. 1.403), 250 cc. glacial acetic acid[7] at 25°. Yields: nitropiperonal, 40 g.; mononitromethylenecatechol, 10 g.; a trace of the dinitro; oxalic acid, 1 g.

XIX. Fifty g. piperonal, 250 cc. HNO_3 (sp. gr. 1.403), acetic acid, 166 g., acetic anhydride,[8] 166 g. at 25°. Yields: nitropiperonal, 47 g.; mononitromethylenecatechol, 8.3 g.; a trace of the dinitro; some oxalic acid.

XX. Fifty g. piperonal, 250 cc. HNO_3 (sp. gr. 1.403) and $HgNO_3$[9] 11.8 g. at 20°. Yields: nitropiperonal, 50 g.; mononitrocatechol, 13.3 g.; a trace of oxalic acid. No phenolic compounds were formed.

XXI. Fifty g. piperonal, 250 cc. HNO_3 (sp. gr. 1.403), 250 cc. H_2SO_4 (sp. gr. 1.48), $HgNO_3$, 11.8 g., at 0°. Yields: no nitropiperonal; mononitromethylenecatechol, 6.6 g.; dinitro, 26.6 g.; some oxalic acid.

It was noticed that nitropiperonal on exposure to sunlight changes to a brown color. Since the isomeric nitropiperonal isolated from Kahlbaum's product is brownish-yellow, it was thought that it might have been formed from the ordinary form through a light reaction. Ordinary nitropiperonal was, therefore, exposed in thin layers to sunlight and to ultraviolet light, but on recrystallizing the brown product only nitropiperonal, m. p. 98.5°, and a brown tarry residue were obtained.

Summary

1. An isomer of the ordinary nitropiperonal has been isolated and found to melt at 143°. It was found in the commercial Kahlbaum nitropiperonal, m. p. 80°, both by means of derivatives made therefrom and by fractional crystallization of the Kahlbaum product.

2. In an attempt to prepare the isomeric nitropiperonal, piperonal was nitrated under varying conditions of temperature and of nitric acid concentrations with and without sulfuric acid in the presence and absence of catalytic agents and in the presence and absence of sunlight.

3. Besides *o*-nitropiperonal, mononitro and dinitromethylenecatechol, nitropiperonylic acid and an isomeric mononitromethylenecatechol may be obtained by nitrating piperonal.

4. Increase in temperature in general causes an increase in oxidation products.

5. Beyond a nitric acid of sp. gr. 1.38, increase in acid concentration causes an increase in oxidation products.

6. The presence of nitrosulfonic acid causes a decrease in oxidation and an increase in nitration, the presence of glacial acetic acid causes an

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[6] Varma and Kulkarni, This Journal, **47**, 143 (1925).

[7] Witt and Utermann, *Ber.*, **39**, 3901 (1906); Orton, *J. Chem. Soc.*, **81**, 806 (1902).

[8] Orton, *Ber.*, **40**, 370 (1907).

[9] Wolffenstein and Böters, *Ber.*, **46**, 586 (1913); Davis, Worrall, Drake, Helmkamp and Young, This Journal, **43**, 594 (1921).

increase in the nitration, but the best yield of nitropiperonal was obtained with nitric acid of sp. gr. 1.38 at 45°.

7. No trace of the isomeric nitropiperonal, m. p. 143°, present in Kahlbaum's commercial product, m. p. 80°, was obtained in any of the experiments.

8. That the isomeric nitropiperonal was probably formed as an intermediate product in the experiment using fuming nitric acid at 0° is indicated by the isolation of an isomeric mononitromethylenecatechol from the reaction mixture.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY]

EQUILIBRIUM IN THE REACTION $C_2H_6 \rightleftarrows C_2H_4 + H_2$[1]

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Bone and Coward[4] have shown that ethane is rather rapidly decomposed at 675°, and that the primary products of decomposition are ethylene and hydrogen; and it is well known that ethylene and hydrogen combine quantitatively to form ethane in the presence of catalysts from room temperature up to at least 350°.[5] The indications are, therefore, that the reaction $C_2H_6 \rightleftarrows C_2H_4 + H_2$ is reversible somewhere within the temperature region between 350 and 675°, and that equilibrium should be determinable. Indeed, Berthelot[6] has reported that dissociation and formation of ethane both occur at a low red heat. These results have encouraged us to attempt the measurement of equilibrium in this reaction.

Methods and Apparatus

The work of Bone and Coward having proved that prolonged heating of ethane or ethylene gives rise to by-products such as methane, it was necessary to show that the reaction under consideration was the main reaction under the conditions of our experiments. We therefore carried out forward and reverse reactions at each temperature, making a check-up of

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[4] Bone and Coward, *J. Chem. Soc.*, **93**, 1197 (1908).

[5] Sabatier and Senderens, *Ann. chim. phys.*, [8] **4**, 344 (1905).

[6] Berthelot, *Ann. chim.*, [4] **9**, 431 (1886).