TABLE III

ANALYSIS OF HONEYS BY OXIDATION METHODS

Honey, numbering as in Table I	1	2	3	4	5	6
Total solids by ref. index. %						
(a) Schönrock table	80.00	82.2	82.3	77.9.	83.4	83.8
(b) Marvin table	81.5	83.7	84.0	79.2	85.0	85.5
Total solids by oven drying	81.0	83.2	83.8	78.6	84.3	93.9
Analysis by Jackson and Mathews method						
Fructose	38.3	40.7	38.7	35.8	43.5	28.4
Glucose	38.6	35.2	37.2	37.3	31.5	36.1
Total reducing sugars	77.0	75.9	75.9	73.1	75.0	64.5
Analysis by Becker and Englis method						
Fructose	40.7	45.2	41.3	40.7	49.2	33.5
Glucose	35.9	30.8	35.0	33.1	26.0	29.7
Total reducing sugars	76.6	76.0	76.3	73.8	75.2	63.2
Sucrose	1.1	1.0	4.4	1.2	2.9	2.7
Dextrins	..	2.8	..	..	..	..
Undet. matter	4.4	6.3	3.1	3.6	6.2	18.1

The quantity of dextrin and gum precipitated by methanol was small but its removal was helpful for smooth distillation. With proper care, however, reliable analytical results were obtainable without this step, as in runs 3 and 5.

Analysis by Oxidation Methods.—With the exception of the previously mentioned method for fructose by Becker and Englis,[3] the procedures used are described in detail in the handbook of the A. O. A. C.[8] The total solids were estimated by the oven-drying procedure (*in vacuo* at 70°) after dispersing the sample on quartz sand in an aluminum dish. As a check on the drying method, the refractive value of each sample was taken and the apparent solids found from the sucrose table of Schönrock and a special table for honey proposed by Marvin.[9] This table gives results in better accord with the drying method.

Total reducing sugars were estimated by the method of Lane and Eynon.[10] Sucrose was found from the increase in reducing sugar after hydrolysis with hydrochloric acid at room temperature.

These results are presented in Table III.

Summary

Six samples of honey have been analyzed by a distillation method and by oxidation methods. The distillation method gives lower values for the monosaccharides and higher values for the disaccharides than are shown by the oxidation methods when it is assumed that sucrose is the only disaccharide present. The presence of maltose or some other reducing disaccharide is indicated as a general component of the several samples. Some higher saccharides are also indicated. The suggestion is made that the variance in results obtained by two selective oxidation methods for fructose is associated with the reducing disaccharides which are present in honey. The distillation method is a valuable technique for checking and pointing out deficiencies in other processes for carbohydrate estimation.

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(8) "Methods of Analysis," A. O. A. C., 5th ed., 1940.

(9) G. E. Marvin, *American Bee J.*, 212 (1934).

(10) Lane and Eynon, *J. Soc. Chem. Ind.*, **42**, 32T (1923).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND PURDUE RESEARCH FOUNDATION, PURDUE UNIVERSITY]

Nitration of 2,3-Dimethylbutane[1]

BY M. H. DANZIG AND H. B. HASS

The successful vapor-phase nitration of ethane, propane and the two butanes was accomplished by Hass, Hodge and Vanderbilt.[2] The nitrations of *n*-pentane and isopentane were reported by Hass and Patterson[3] and Seigle and Hass,[4] respectively. In every case these investigators found the mono nitration products expected as predicted by the activated complex theory of nitration.[5]

The vapor-phase nitration procedure is now being expanded to the hexanes. This paper deals specifically with the nitration of 2,3-dimethylbutane. This hydrocarbon is of interest not only because it serves as further evidence of the generalizations previously reported regarding the identity of nitroparaffins obtained under these conditions but also because it possesses two tertiary hydrogen atoms. It is important to know whether these tertiary hydrogen atoms are replaced in the nitration process to form the corresponding dinitroparaffin. This compound can be reduced to 2,3-dimethyl-2,3-butanediamine, an interesting synthetic intermediate.

Konovalov[6] has reported the nitration of 2,3-dimethylbutane with nitric acid at 125°[7] to give 2,3-dimethyl-2-nitrobutane and 2,3-dimethyl-2,3-dinitrobutane, the latter is a solid melting at 208°.

Five compounds are to be expected when this hydrocarbon is subjected to vapor-phase nitra-

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(1) This article contains material from the doctoral thesis of M. H. Danzig.

(2) H. B. Hass, E. B. Hodge and B. M. Vanderbilt, *Ind. Eng. Chem.*, **28**, 339 (1936).

(3) H. B. Hass and J. A. Patterson, *ibid.*, **30**, 67 (1938).

(4) L. W. Seigle and H. B. Hass, *ibid.*, **31**, 648 (1939).

(5) H. B. Hass and E. F. Riley, *Chem. Rev.*, **32**, 373 (1943).

(6) M. Konovalov, *J. Russ. Phys.-Chem. Soc.*, **37**, 1119–1125 (1905).

(7) The statement in Brooks' "Chemistry of the Non-Benzenoid Hydrocarbons," p. 61, and Ellis' "Chemistry of Petroleum Derivatives," Vol. I, p. 1043, that "diisopropyl reacts readily with nitric acid at 20°" cannot be found in the reference given[8] (M. Konovalov, *J. Russ. Phys.-Chem. Soc.*, **37**, 1119–1125 (1905)). It does occur, however, in an article by Markownikoff (W. B. Markownikoff, *Chem. Zentr.*, **70**, I, 1064 (1899); *Ber.*, **32**, 1441–1445 (1899)), who used fuming nitric acid (specific gravity 1.53). Experiments in this laboratory have shown that while 2,3-dimethylbutane seems to be unattacked by ordinary nitric acid at room temperature, a vigorous exothermic action is observed when fuming nitric acid is employed under these conditions.

(8) I. M. Heilbron, *Dictionary of Organic Compounds*, Vol. 1, p. 570, Oxford University Press, 1934.

tion by substitution of a hydrogen atom or of an alkyl group. No dinitroalkane has so far been observed to be formed in vapor-phase nitration at high temperature. An examination of the reaction products from the nitration of 2,3-dimethylbutane disclosed but five nitroparaffins and no evidence for dinitroparaffin formation, thus serving as an additional confirmation of these empirical rules. The five nitroparaffins resulting from the vapor-phase nitration are nitromethane, 2-nitropropane, 3-methyl-2-nitrobutane, 2,3-dimethyl-2-nitrobutane, and 2,3-dimethyl-1-nitrobutane.

Identification of the Products

Two ketones were observed in the nitration products. Acetone was identified by the melting point of the 2,4-dinitrophenylhydrazone (127°). 3-Methyl-2-butanone was recognized by its boiling point, 95°, the positive test for a carbonyl group, and by the melting point of the 2,4-dinitrophenylhydrazone (117°). These ketones could be formed by the oxidation of 2-nitropropane and 3-methyl-2-nitrobutane, respectively.

The two olefins capable of being formed without carbon skeleton change were identified. 2,3-Dimethyl-1-butene (boiling point 56° (748 mm.)) and 2,3-dimethyl-2-butene (boiling point 73° (748 mm.)) decolorized bromine water and dilute permanganate solution.

Nitromethane was recognized by its boiling point (101° (750 mm.)) and by the formation of a deep red color due to the presence of the sodium salt of methazonic acid when nitromethane is treated with concentrated sodium hydroxide.

2-Nitropropane was identified by its boiling point (120.8° (760 mm.)). It gave the blue pseudonitrole color test indicative of a secondary nitro compound.

3-Methyl-2-nitrobutane, whose boiling point was 60° (22 mm.) (156.4° (760 mm.) calcd.), is identical with the compound obtained by Seigle and Hass[4] in the vapor-phase nitration of isopentane. It was characterized by the blue color of the pseudonitrole formed by the addition of alcoholic sodium hydroxide followed by a few crystals of sodium nitrite and later acidification with nitric acid. The nitro compound was identified conclusively by reduction to the corresponding amine in the following manner. Thirty-five grams of iron filings, 75 ml. of water and 10 ml. of con-concentrated hydrochloric acid were introduced into a 250-ml. three-necked flask. When the bubbling of the hydrogen gas ceased, 26 ml. of the nitro compound was added. A mercury-sealed stirrer was employed effectively to stir the solution and keep volatile gases from escaping. The reaction temperature was kept at 98° for four hours. The solution was made alkaline with sodium hydroxide and extracted with ether. After the ether was evaporated an amine was distilled whose boiling point was 84°. This corresponds to the boiling point of 3-methyl-2-butylamine.

2,3-Dimethyl-2-nitrobutane was identified by its boiling point (169°) and by its melting point (7.0°). It was insoluble in sodium hydroxide as expected of a tertiary nitro compound. This is identical with the nitroparaffin obtained by Konovalov[6] in the nitration of 2,3-dimethylbutane at 125°. Upon reduction with iron and hydrochloric acid, 2,3-dimethyl-2-butylamine was obtained boiling at 104° (765 mm.).

2,3-Dimethyl-1-nitrobutane has not been previously described in the literature. Its boiling point is 176° (760 mm.), refractive index $n^{20}\text{D}$ 1.4330, specific gravity 20°/4° 0.9638. An elementary analysis gave the percentages of carbon, hydrogen and nitrogen: Calcd.: C, 54.98; H, 9.96; N, 10.68. Found: C, 54.7; H, 9.8; N, 10.7.

The structure of this compound was proved by its hydrolysis by means of 85% sulfuric acid to the known compound, 2,3-dimethylbutyric acid (boiling point 189° (756 mm.)). The procedure followed was that of Lippincott and Hass.[9] The acid was converted to the acyl halide by means of thionyl chloride and the latter was converted to the solid amide with concentrated ammonia (melting point 128°; literature value 129.0°[5]).

Discussion

In order to insure a pure hydrocarbon, free from olefins, 2,3-dimethylbutane, kindly supplied by The Texas Co., was washed with cold, concentrated sulfuric acid and rectified through a Lecky–Ewell column. The fraction boiling from 57.5 to 58.0° was employed.

The apparatus built for the vapor-phase nitration was of all glass construction. Essentially it was identical with the one developed in this Laboratory and described previously.[2,3]

The mixture of nitroparaffins obtained from the reaction product was separated into its components by rectification under diminished pressure in a modified Podbielniak column. As a precautionary measure, one gram of boric acid was added to each batch of nitro compound rectified; this procedure prevented decomposition during the distillation.

The nitration of 2,3-dimethylbutane was carried out at various temperatures. The average conversion per pass, based upon the amount of nitric acid reacting at 408°, was 17.5%. The average mole ratio of hydrocarbon to nitric acid was 1.58. When nitration was attempted at higher temperatures, particularly at bath temperature of 430°, a great deal of oxidation was noticed. Also at this temperature a white, crystalline substance separated out in the coils of the condensing system. This water-soluble material was identified as an inorganic nitrate.

It was found that the highest conversion to nitro compounds was obtained at a temperature of 410° and a contact time of 1.2 seconds.

The materials used were the pure hydrocarbon

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[9] S. B. Lippincott and H. B. Hass, *Ind. Eng. Chem.*, **31**, 118 (1939).

and ordinary c. p., concentrated (68%) nitric acid.

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Summary

The nitroparaffins obtained in the high-temperature, non-catalytic, vapor-phase nitration of 2,3-dimethylbutane were identified as nitromethane, 2-nitropropane, 3-methyl-2-nitrobutane, 2,3-dimethyl-2-nitrobutane and 2,3-dimethyl-1-nitrobutane.

The isolation of these five products and the absence of a dinitroparaffin serve as additional confirmation of the generalizations concerning the vapor-phase nitration of aliphatic hydrocarbons.

LAFAYETTE, INDIANA RECEIVED JULY 14, 1944

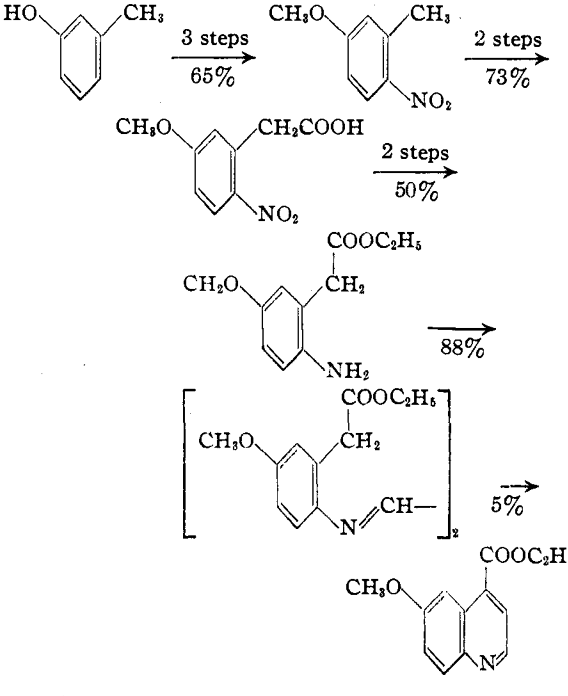
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

A Synthesis of Ethyl Quininate from *m*-Cresol

BY C. F. KOELSCH

Of the several methods which have been used for synthesizing ethyl quininate or quininic acid,[1-6] that of Thielepape and Fulde[6] is the best, but since it requires the isolation and purification of numerous intermediates, a simpler synthesis is desirable.

Analogy with the reaction studied by Kulisch,[7] who obtained quinoline in 35–40% yields from *o*-toluidine and glyoxal, suggested that ethyl quininate might be obtained from ethyl 2-amino-5-methoxy-α-toluate and glyoxal. This has now been realized, but the yield of the desired ester is disappointingly low. The reactions investigated in the present research are summarized in the formulas shown.



Experimental

The direct nitration of *m*-cresol[8,9,10] was unsatisfactory, for even when the conditions described by Schultz and Lehrburger[8] were used, the yield of 4-nitro-3-methylphenol was never better than that (29%) obtained by Blaikie and Perkin,[10] and considerable amounts of the isomeric nitrocresols[9] were obtained. The following procedure, based in part on an old observation of Robertson,[11] furnished 3-methyl-4-nitroanisole simply and in yields of 60–66%.

A stirred mixture of 54 g. of *m*-cresol, 150 ml. of acetic acid and 20 ml. of sulfuric acid was treated at 8–10° with a solution of 35 g. of sodium nitrite in a little water. After a few minutes the mixture was poured into ice-water, and the crystalline nitroso compound was pressed out on a filter. It was then added in portions to a stirred mixture of 50 ml. of nitric acid (d. 1.42) and 150 ml. of water at 40–50°; stirring was continued for a few minutes or as long as nitric oxide was evolved. The resulting crude nitrocresol, isolated by pouring in water and pressing out on a filter, was suspended in 200 ml. of water at 40–45° and stirred while 60 ml. of methyl sulfate and a solution of 35 g. of sodium hydroxide in 90 ml. of water were added alternately and in portions. The crude product was washed with water, dried, and then distilled, giving 50–56 g. of pure 3-methyl-4-nitroanisole, m. p. 55°.

Considerable simplification in the conversion of this substance into 5-methoxy-2-nitro-α-toluic acid has been attained. A suspension of sodium ethoxide from 7 g. of powdered sodium and 15 g. of dry alcohol in 75 ml. of dry ether was treated with 45 g. of ethyl oxalate and then with 50 g. of finely powdered 3-methyl-4-nitro-anisole. After ten minutes the mixture became solid; the sodio derivative is yellow if the starting materials are dry, and not red as described by Blaikie and Perkin.[10] The mixture was heated at 45° for four hours, then treated with 200 ml. of ice-water. Ten per cent. hydrogen peroxide was added until the deep red color was discharged; then small amounts of 30% sodium hydroxide and hydrogen peroxide were added alternately until the alkali no longer restored the red color. About 85% of the calculated amount of oxidant was required. The solution was mixed with "Hyflo,"

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(1) Pictet and Misner, *Chem. Ztg.*, **35**, 147 (1911); *Ber.*, **45**, 1800 (1912).

(2) Kaufmann, *ibid.*, **45**, 1805 (1912); **51**, 116 (1918); **55**, 614 (1922); *cf.* Cohen and King, *Proc. Roy. Soc.* (London), **B125**, 49 (1938).

(3) Halberkann, *Ber.*, **54**, 3090 (1921).

(4) Rabe, Huntenburg, Schultze and Volger, *ibid.*, **64**, 2487 (1931); *cf.*, Cohen and King, *loc. cit.*

(5) v. Schelven, English Patent 388,087; *Chem. Zentr.*, **104**, II, 3195 (1933); *cf.* Silberg, *Bull. soc. chim.*, [5] **3**, 1767 (1936).

(6) Thielepape and Fulde, *Ber.*, **72**, 1432 (1939).

(7) Kulisch, *Monatsh.*, **15**, 276 (1894).

(8) Schultz and Lehrburger, *Ber.*, **40**, 4322 (1907).

(9) Khotinsky and Jacopson-Jacopmann, *ibid.*, **42**, 3098 (1909).

(10) Blaikie and Perkin, *J. Chem. Soc.*, **125**, 296 (1924).

(11) Robertson, *ibid.*, **81**, 1477 (1902).