This hypothesis was based upon color considerations and apparently affords a thoroughly adequate explanation of the observed differences in color in tautomeric forms of aminated dyes. Direct evidence of structure of the type illustrated in Formula I is lacking, although a closely analogous structure has been demonstrated in the complexes which basic dyes form with cyclic derivatives containing phenolic groups.[5]

A compound of the structural type represented by Formula I would be expected to be relatively inert. The writer's hypothesis, accordingly, supplies an explanation of the observed lack of chemical reactivity in the violet form of brilliant cresyl blue, and this inactivity, in turn, supports the validity of the hypothesis.

Summary

The violet and blue forms of brilliant cresyl blue, which exist in tautomeric equilibrium in aqueous solutions of the dye, have been isolated. The former tautomer is chemically inert whereas the latter is reactive. These facts are held to support the author's hypothesis that the tautomerism is one between structure of addition product type and structure of ammonium salt type.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF CORNELL COLLEGE]

THE WURTZ REACTION. FACTORS INVOLVED IN THE PREPARATION OF OCTANE

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The work herein described is concerned with an attempt to determine the factors which govern the successful carrying out of a Wurtz reaction. The preparation of octane from butyl bromide offers such an opportunity.

The preparation of 2,5-dimethylhexane from *iso*butyl iodide and sodium as described by Würtz[1] opened up to the organic chemist a valuable method for the preparation of the higher aliphatic hydrocarbons. Fittig and others soon adapted the reaction for use in the synthesis of mixed aromatic aliphatic and higher aromatic hydrocarbons.

Schorlemmer,[2] using butyl iodide and sodium, was the first to use the reaction in the preparation of normal octane. He compared his product with those octanes formed through the hydrogenation of methylhexylcarbinol and suberic acid and proved their identity.

The mechanism of the Würtz-Fittig reaction has received much study

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[5] Holmes and Hann (awaiting publication). This paper will probably be published in the October, 1928, issue of *Stain Technology*.

[1] Wurtz, *Ann.*, **96**, 365 (1855).

[2] Schorlemmer, *Ann.*, **161**, 280 (1872).

within the last few years and a good picture of the situation will be found in a recent article by Bachmann and Clarke.[3]

Discussion of Experimental Work

In order to determine the importance of the various factors which govern the formation of octane, a number of variables have been studied in connection with a standard procedure; these include the relative masses of sodium and butyl bromide, the amount of solvent (diethyl ether), temperature, time, area and diameter of the sodium, dryness of reagents, agitation, influence of methyl cyanide and the method of recovery of octane from the reaction mass.

As the result of this study, a method has been developed for the preparation of large amounts of octane, with yields of 65–70% based upon butyl bromide. Octane thus prepared has the following physical constants: b. p., 124.2–124.8°; $n_D^{20} = 1.3961$; $d_4^{20} = 0.7044$.

The data tabulated on the following pages indicate that: 1. optimum yields of octane are obtained when the sodium is used in excess; the excess need not be greater than 50 mole per cent. This holds for sodium used either as 2 mm. wire, shot or thin shavings.

2. A volume of ether two and a half times the volume of butyl bromide is necessary for keeping the reaction mixture sufficiently fluid to agitate. More is unnecessary and less may result in a loss of octane due to local overheating.

3. Low temperatures appear to favor the production of octane; higher temperatures give greater quantities of unsaturated hydrocarbons. At 0° high yields of octane result. At this temperature the blue intermediate compound is not formed. An accurate temperature study is hard to make without changing more than one variable at a time. An attempt was made to use the higher ethers as solvents, but was not successful because of the difficulty of separating those ethers from the octane. It should be stated here that the ethers up to the *iso*-amyl ether are stable to the action of sodium for several hours at the reflux temperature.

4. Each set of operating conditions has a maximum time for optimum yield. Too long operation may even cause a loss of octane for there is some evidence that octane is slowly acted upon by sodium at its reflux temperature.

5. The finer the sodium wire, and consequently the greater the area, the more rapid is the formation of octane. Wire finer than 0.5 mm. is difficult to prepare with the ordinary sodium press. Wire of 2 mm. diameter is easily prepared and satisfactory for most uses.

6. Traces of water present in the reaction mixture cut down the yields far more than would be predicted on the basis of the primary reaction

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[3] Bachmann and Clarke, THIS JOURNAL, **49**, 2089 (1927).

between sodium and water. On the other hand, ether prepared by washing with water, drying over phosphorus pentoxide and distilling over sodium does not yield as much octane as does ether dried over calcium chloride and distilled over sodium.

7. Agitation speeds up materially the octane-producing reaction.

8. Methyl cyanide has no positive action in the formation of octane. In fact, octane was not obtained from the reaction mixture containing five drops of the cyanide. This is somewhat different from the experience of Michael.[4] In the preparation of butyl and *iso*-amyl benzene on the other hand, methyl cyanide has no effect on the yield of hydrocarbon.

9. Small amounts of octane are easily recovered from the reaction mixture by distillation at the conclusion of the experiment. Larger amounts are best obtained after the sodium is first destroyed, either with dilute alcohol or with water, as recommended by Bartow and Sellards.[5]

Chemicals Used

Butyl Bromide.—Butyl bromide was prepared from *n*-butanol according to the method described in "Organic Syntheses," Vol. I, p. 5; $d_4^{20} = 1.2740$; $n_D^{20} = 1.4381$.

Sodium.—J. T. Baker metal, used as 2 mm. wire.

Diethyl Ether.—U. S. P. dried over calcium chloride and distilled and kept over sodium.

Procedure

The solvent ether, 50 cc. (0.472 mole), is placed in a 500-cc. round-bottomed flask equipped with a double neck addition tube and a reflux condenser, and the sodium, 6.9 g. (0.3 mole), added. The butyl bromide, 21.9 cc. (0.202 mole), is run in over a period of two minutes. In a short time, the mixture is at the reflux temperature where it is maintained during the required time. If the mixture is to be agitated, a special three-necked addition tube bearing a mercury seal replaces the two-necked tube. At the end of the time set for the reaction, the condenser is turned down and volatile materials distilled. These are separated by fractional distillation, two fractionations being sufficient. The fraction coming over between 110 and 130° is collected as crude octane and the octane content estimated by the refractive index. Reference is made to an octane–butyl bromide refractive index curve drawn from values obtained on mixtures of known composition and tested in an Abbé refractometer, using the sodium light and at a tempera-

Table I

Physical Constants of Mixtures of Octane and Butyl Bromide

Octane, %	Butyl bromide, %	Density, 20°	Refractive index, 20° (sodium light)
100.00	...	0.7044	1.3961
95.07	4.93	.7239	1.4000
83.35	16.65	.7607	1.4011
51.91	48.09	.8940	1.4091
32.00	68.00	1.0064	1.4189
15.41	84.59	1.1229	1.4276
6.53	93.47	1.2058	1.4330
...	100.00	1.2740	1.4381

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[4] Michael, *Am. Chem. J.*, **25**, 419 (1901).

[5] Bartow and Sellards, This Journal, **27**, 371 (1905).

ture of 20°. When the reaction is carried on for two and a half hours, a yield of octane of 70% is consistently obtained.

Experimental Data

1. VARIATION IN SODIUM–BUTYL BROMIDE RATIO

Concentration in moles					
Sodium	Butyl bromide	Ether	Time, hours	Yield, % octane	Notes
0.1	0.202	0.472	2.5	18.4	
.3	.202	.472	2.5	71.3	
.3	.202	.472	2.5	71.5	
.35	.202	.472	2.5	72.2	
.5	.202	.472	2.5	66.5	
.6	.202	.472	2.5	73.0	

2. TIME–YIELD RELATION

0.3	0.202	0.472	0.5	14.7	Diameter wire, 2 mm.
.3	.202	.472	1.75	41.5	
.3	.202	.472	2.5	71.3	
.3	.202	.472	0.5	27.3	Diameter wire, 1 mm.
.3	.202	.472	1.0	62.4	
.3	.202	.472	1.5	66.8	
.3	.202	.472	0.5	66.4	Diameter wire, 0.5 mm.
.3	.202	.472	1.0	75.3	
.3	.202	.472	2.0	73.6	
.55	.330	.472	1.0	36.6	Sodium as shot
.55	.330	.472	2.5	73.2	
.55	.330	.472	5.0	71.8	
.55	.330	.472	10.0	69.4	
.55	.330	.472	24.0	70.0	

3. SIZE OF THE SODIUM WIRE

0.3	0.202	0.472	0.5	71.3	0.5 mm. sodium wire
.3	.202	.472	.5	41.5	1.0 mm. sodium wire
.3	.202	.472	.5	14.7	2.0 mm. sodium wire

4. INFLUENCE OF WATER ON YIELD

0.27	0.180	0.236	0.5	47.4	No water
.27	.180	.236	.5	37.6	0.1 cc. water
.27	.180	.236	.5	30.3	.5 cc. water
.27	.180	.236	.5	4.1	1.0 cc. water
.27	.180	.236	.5	3.5	2.0 cc. water

5. AGITATION OF THE REACTION MIXTURE

0.3	0.24	0.36	2.5	22.6	No agitation
.3	.24	.36	5.0	44.5	No agitation
.3	.24	.36	2.5	41.4	Agitation
.3	.24	.36	5.0	72.8	Agitation

6. INFLUENCE OF METHYL CYANIDE

0.3	0.202	0.472	0.5	13.6	
.3	.202	.472	.5	16.7	
.3	.202	.472	.5	..	Five drops methyl cyanide
.3	.202	.472	.5	..	Five drops methyl cyanide

Separation of Octane from Reaction Mixture.—No great difference is noted in the yield of octane in runs which have come to an end, when the octane is recovered by distillation on the one hand and by destruction of excess sodium by water and separation of the water insoluble layer on the other. The latter method is much safer when working with large quantities of materials. It has been the experience in this Laboratory that a rapid evolution of octane may occur in the distillation process when the temperature of the sodium mass reaches a certain point. Under such conditions fires may be expected.

Discussion

Constant yields of octane have not been obtained when the solvent ether is completely omitted from the reaction mixture. At times, however, 70% yields of octane have been reached by adding the butyl bromide slowly to the sodium in the standard set-up or by adding sodium in small amounts to the bromide and allowing the mixture to reflux. When the apparatus is fixed for distilling rather than for refluxing, octane mixed with some unchanged bromide may be distilled from the sodium as fast as butyl bromide is added. The octane yield under these conditions is between 50 and 70%.

Large quantities of octane may be prepared in the following way. Twenty moles (1480 g.) of ether, dried over calcium chloride and distilled over sodium, is placed in a five liter round-bottomed flask equipped with an addition tube, a four foot reflux condenser and an agitator. Sodium cut thin with a sodium knife is added to the amount of 12.1 moles (278 g.) and then 8.3 moles (1137 g.) of dry butyl bromide run in over fifteen minutes. The mixture is refluxed with agitation for ten hours and then the excess sodium destroyed by slowly adding water to the contents of the flask. The layers are separated; the ether layer is dried with calcium chloride and fractionally distilled.

Fractions are collected up to 55, 55–110, 110–130, 130–180, 180–210, 210–250 and 250–300°. After a second fractionation, a yield of 450 cc. of octane is obtained. This is 68% on the basis of butyl bromide. The ether recovery is better than 75%.

Butene is also formed and this is recovered by bubbling the reaction gases through bromine. Dibromobutane is recovered; this boils between 160 and 170° and has a refractive index of 1.5151 at 20°. A typical run gave 26 g. of dibromobutane. The literature gives 166° for 1,2-dibromobutane.

A saturated hydrocarbon boiling at 295–300° is recovered to the extent of about one gram. This may be a hexadecane. Three grams of another saturated hydrocarbon, boiling point 210–215°, is also found. The dodecanes boil at that point.

Sodium bromide is recovered from the aqueous layer by crystallization.

The recovery is practically quantitative and the quality of the product satisfactory for use in making butyl bromide.

Conclusions

1. A study has been made of the factors influencing the formation of octane from butyl bromide by the Wurtz reaction.
2. Based upon this study, a method has been developed for the formation of octane in rather large amounts and with yields of 65–70% based upon butyl bromide.
3. Butene and at least two higher saturated hydrocarbons are also formed. The boiling points of the hydrocarbons suggest dodecane and hexadecane.

MOUNT VERNON, IOWA

[CONTRIBUTION FROM THE LABORATORY OF FOODS AND SANITATION, UNIVERSITY OF WISCONSIN]

CAROTIN: A PIGMENT OF HONEY[1]

BY H. A. SCHUETTE AND PHYLLIS A. BOTT

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Color and quality in honey have from time immemorial borne an inverse relationship to each other in the minds of the average consumer, the more deeply pigmented honeys, as a rule, commanding a lesser price. As a result of this, the practice of designating its color has become universal in the grading of honey to the end that certain loosely defined names for these colors have come into use. It is only within recent years, however, that these colors have been defined with the aid of a spectrophotometer.[2]

Since these color designations are but an attempt to describe the pigmentation of a particular honey, and since this pigmentation is due wholly if not in part to red, orange or yellow coloring matters, it seemed but reasonable to assume that the latter are of the carotinoid type. To harmonize this assumption with factual evidence was the purpose of the study herein recorded.

Experimental

A highly pigmented buckwheat honey, described in trade parlance as amber colored, was selected for study since it seemed to offer the greater promise for the recovery of the necessary quantity of pigment for identification.

Attempts at removal of the coloring matter by precipitation with those clarifying agents which are commonly used in "purifying" a sugar con-

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[1] Constructed from a thesis submitted by Miss Bott to the Faculty of the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degree of Master of Science, June, 1924.

[2] E. L. Sechrist, U. S. Dept. Agr., *Dept. Circ. 364*, **1925**, p. 3.