

3. The application of ozonization makes possible an improved technique for determining the structure of uracil compounds. The advantages gained experimentally become apparent when one is called upon to separate and identify the products of oxidation.

4. The urea configuration of the pyrimidine nucleus is not destroyed by the action of ozone.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, HOLY CROSS COLLEGE]

THE EFFECT OF SUBSTITUENTS ON CERTAIN PHYSICAL PROPERTIES OF BENZENE PICRATE¹

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Only a few of the aromatic hydrocarbons may be identified from their picrates. The reason for this is that very few aromatic hydrocarbons form picrates which are stable and can be purified by crystallization from suitable solvents. Most of the aromatic hydrocarbons form picrates which are decomposed by solvents or on standing in air.

The influence of substituents on the color of benzene picrate was studied by Franzen.² From a study of the absorption spectrum of a mixture of picric acid and a number of aromatic hydrocarbons and their halogen derivatives, he found that an increase in the number of alkyl groups in general causes an increase in the depth of the color produced. He also found that *m*-derivatives are the brightest, and that *p*-derivatives are the darkest.

Compounds of picric acid with aromatic hydrocarbons were studied by Efrenov³ by means of thermal analysis of the binary mixtures. He found that molecular quantities of the substances usually reacted, but diphenyl, diphenylmethane and triphenylmethane do not give picrates.

Kendall⁴ explains the existence of the picrates by the formation of oxonium salts. The existence and stability of the addition compounds were determined from the freezing-point curve. The melting point was determined by distectic points on the fusion curve, *i. e.*, the temperature at which crystallization begins. The molecular composition of the picrates was found to be of the general type 1:1.

In our study with picrates, we have prepared the picrates of several

¹ Some of the experimental results described in this paper are taken from a thesis submitted to the Faculty of Holy Cross College by E. S. Hauber in partial fulfillment of the requirements for the degree of Master of Science.

² Hartig Franzen, *J. prakt. Chem.*, **98**, 67-80 (1918).

³ N. N. Efrenov, *J. Russ. Phys.-Chem. Soc.*, **50**, 1, 372-421 (1918).

⁴ Kendall, *THIS JOURNAL*, **38**, 1314 (1916).

aromatic hydrocarbons, and have taken a melting point of the picrate formed before decomposition took place. The colors of the picrates in the same series were compared in an effort to determine whether or not the substitution of different groups on the benzene ring had any effect on the color of the picrate. In preparing the picrates, a method was used which may be applied to the preparation of picrates of all aromatic hydrocarbons. Wherever possible, the color and the melting points of these picrates were compared with those which could be prepared and purified by crystallization from suitable solvents.

Experimental

All temperatures given are uncorrected.

Picric acid containing 3% of water was dried in an oven at 100° for six hours. All liquid hydrocarbons were dried over anhydrous calcium chloride for twenty-four hours and were freshly distilled. Solid hydrocarbons were crystallized from suitable solvents until they gave a sharp melting point. Equimolecular quantities of the hydrocarbon and picric acid were heated until fusion took place. The melting point of the addition compound was the temperature at which crystallization began, which is in reality the freezing point. The method for the determination of the freezing point was that of Beckmann. A large test-tube containing the two constituents was placed under a reflux condenser. The test-tube was surrounded by a larger test-tube immersed in a bath of concentrated sulfuric acid. The temperature of the sulfuric acid bath was cooled, after fusion took place, at the rate of about one-half a degree per minute below 100°, and at about one to two degrees per minute above 100°. Three determinations were made of each picrate. Wherever possible, these picrates were compared in color and melting point to picrates prepared according to Mulliken.⁵ Many picrates prepared could not be found in the literature.

General Procedure.—Ten millimoles of the hydrocarbon and ten millimoles of picric acid were intimately mixed in a test-tube and placed under a reflux condenser. A thermometer was inserted in the mixture. The mixture was gently heated in the sulfuric acid bath until fusion took place, and the bath was then cooled slowly. The freezing point of the picrate was taken on solidification of the mixture. The same mixture was liquefied and the freezing point taken three times in succession in order to check on compound formation.

Aliphatic Derivatives of Benzene.—The picrates of the aliphatic derivatives of benzene were prepared from equimolecular amounts of the hydrocarbon and picric acid according to the Beckmann method.

⁵ Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York City, 1916, Vol. 2, p. 33.

They were also prepared by crystallizing the picrate from a boiling saturated solution of picric acid in the hydrocarbon according to Fritzsche.⁶

TABLE I
ALIPHATIC DERIVATIVES OF BENZENE PICRATE

Substance	Color	Form	M. p., °C.
Benzene	Colorless	Needles	83.9
Toluene	Light yellow	Plates	88.2
Ethylbenzene	Light yellow	Plates	96.6
Propylbenzene	Yellow	Plates	103.5
<i>o</i> -Xylene	Lemon-yellow	Needles	88.5
<i>m</i> -Xylene	Lemon-yellow	Needles	90-91.5
<i>p</i> -Xylene	Lemon-yellow	Needles	90.5
Hemimellitine	Yellow	Needles	89.5
Pseudocumene	Yellow	Needles	96-97
Mesitylene ^a	Bright yellow	Leaflets	96.6
1,2,3,4-Tetramethylbenzene ^b	Golden-yellow	Prisms	92-95
Pentamethylbenzene ^c	Golden-yellow	Prisms	131
Hexamethylbenzene ^d	Orange-yellow	Plates	170

^a Schultz, Wurth, *Chem. Centr.* I, 1443 (1905). ^b This stable picrate crystallizes from boiling alcohol [A. Tohl, *Ber.*, 21, 905 (1888)]. ^c This stable picrate crystallizes from boiling alcohol [Jacobson, *ibid.*, 20, 898 (1887)]. ^d This picrate loses hexamethylbenzene at 100-110°. Alcohol removes picric acid. Friedel and Crafts [*Ann. chim.*, [6] 10, 417 (1887)].

The picrates in Table I are all unstable, decomposing in air, excepting the tetra-, penta- and hexamethylbenzene picrates, which decompose slightly above their melting points. The position of the methyl groups in dimethylbenzene does not have any appreciable effect on the color of the picrates. Separation of the methyl groups in trimethylbenzene raises the melting point of the picrate.

The isomers of the polymethylbenzenes such as cumene and *p*-cymene form no picrates, as all attempts to prepare them failed.

Benzene derivatives containing a double bond in the side chain such as styrene and indene form very explosive picrates.

Hydroxy Derivatives of Benzene.—The hydroxy derivatives of benzene yield picrates which crystallize into beautiful yellow to red crystals from a deep red solution. These equimolecular compounds are highly dissociated on fusion, as is evidenced by the flatness of the maximum on the freezing point curve.⁷

The picrates of the hydroxy derivatives of benzene were prepared from equimolecular amounts of the hydrocarbon and picric acid according to the Beckmann method. All formed needle crystals.

Naphthalene and Anthracene Derivatives.—The picrates of the naphthalene and anthracene derivatives were prepared from equimolecular

⁶ Fritzsche, *Jahresb.*, 456 (1857).

⁷ Kendall, *THIS JOURNAL*, 38, 1314 (1916).

TABLE II
 HYDROXY DERIVATIVES OF BENZENE PICRATE

Substance	Color	M. p., °C.
Phenol	Yellow	83.1
Pyrocatechol	Orange-yellow	122
Resorcinol ^a	Orange-yellow	89-90
Hydroquinone ^b	Light yellow	115-117
Pyrogallol	Lemon-yellow	128-129 ^c
Hydroxyquinol	Orange-red	96
Phloroglucinol	Brown	101-103
<i>o</i> -Cresol	Orange-yellow	88
<i>m</i> -Cresol ^e	Yellow	61.6
<i>p</i> -Cresol ^d	Bright red	64-65
Orcinol	Orange-yellow	92
1,2,4-Xylenol ^e	Chrome-yellow	83.8
1,3,2-Xylenol	Orange-yellow	50-53
1,4,2-Xylenol	Orange	81-82

^a Decomposed by water, ethyl ether and ethyl alcohol. ^b Decomposed by benzene.
^c Decomposes in air, ethyl alcohol, ethyl ether and benzene. ^d Unstable at its maximum,
 m. p. 65.6° by extrapolation. ^e Can be crystallized from alcohol.

 TABLE III
 DERIVATIVES OF NAPHTHALENE AND ANTHRACENE PICRATES

Substance	Color	Form	M. p., °C.
Naphthalene ^a	Yellow	Needles	149
α -Methylnaphthalene	Lemon-yellow	Needles	140-141
β -Methylnaphthalene	Lemon-yellow	Needles	115-116
α -Ethylnaphthalene	Lemon-yellow	Needles	97.4
β -Ethylnaphthalene	Yellow	Needles	69-70
α -Propylnaphthalene	Yellow	Needles	140-141
β -Propylnaphthalene	Yellow	Needles	89-90
α -Butylnaphthalene	Orange-yellow	Needles	104-105
β -Butylnaphthalene	Orange-yellow	Needles	71-73
1,4-Dimethylnaphthalene	Orange-yellow	Prisms	139-140
2,6-Dimethylnaphthalene	Orange-yellow	Needles	141-142
1,2,6-Trimethylnaphthalene	Orange-yellow	Needles	121-122
α -Naphthol	Orange-yellow	Needles	188.5
β -Naphthol	Orange-yellow	Needles	155.5
Anthracene	Ruby-red	Needles	138
Hexamethylantracene	Dark brown	Needles	203
Phenanthrene	Orange-yellow	Needles	132.8
Acenaphthene ^b	Orange-red	Needles	160.5
Stilbene ^c	Red	Needles	90-91
Fluorene ^d	Red-brown	Prisms	77
Pyrene	Red	Needles	220

^a This picrate crystallizes from ethyl acetate in yellow prisms and plates, from ethyl ether in yellow crystals, and from ethyl alcohol in monoclinic prisms and needles.
^b Flat needles from ethyl alcohol. ^c Red needles from alcohol or ether. Decomposes on fusion at 92.8°. ^d This picrate crystallizes from ethyl ether in red-brown prisms, and it is unstable.

amounts of the hydrocarbon and picric acid according to the Beckmann method. The picrates were also prepared from a solution of the hydrocarbon and picric acid in boiling alcohol, and their physical properties were compared with the physical properties of the picrates prepared according to the Beckmann method. The colors and melting points of the corresponding picrates were found to be identical.

Although the melting points of the β -naphthalene derivatives are higher than those of the α -naphthalene derivatives, the β -naphthalene picrates have a lower melting point than the corresponding α -naphthalene picrates.

Summary

The addition of hydroxyl groups to benzene picrate lowers the melting point and deepens the color of the picrate formed. The addition of methyl groups to benzene picrate raises the melting point of the product and deepens the color of the picrate less than the hydroxyl group. The addition of methyl groups to a side chain of benzene picrate gradually increases the melting point and deepens the color of the picrate, and this increase is more rapid than when a corresponding number of methyl groups are substituted in the ring. The symmetrical trihydroxy- and trimethylbenzene picrates are the darkest, and the color of the picrates becomes lighter as we approach the 1,2,3-derivatives. The same deepening in color was obtained with the methyl derivatives of naphthalene. The β -naphthalene picrates possess lower melting points than the α -naphthalene picrates. Unsaturation in the side chain yields a very unstable picrate. The heavier the molecule the deeper the color of the picrate.

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THE CATALYTIC HYDROGENATION OF ORGANIC COMPOUNDS OVER COPPER CHROMITE

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Nickel has been the only base metal catalyst which has offered much promise for the hydrogenation of pure organic compounds in the liquid phase, although several oxides and mixtures of oxides have been used for the hydrogenation of carbon monoxide in the gas phase at temperatures above 300°. In connection with a study of the action of some of these oxides in inducing the condensation of acetaldehyde at 360°,¹ it seemed advisable to investigate them with respect to their efficiency for catalyzing hydrogenations in the liquid phase. This latter study has resulted in the discovery that a combination of copper and chromium (oxides) is in many

¹ Adkins, Kinsey and Folkers, *Ind. Eng. Chem.*, 22, 1046 (1930).