a suitable arrangement copper was again deposited on both tubes across the joint until they were completely united by a solid mass of deposited copper. It was found very convenient to use as a plating vessel a short section of glass tubing, 3 cm. in diameter, closed at the bottom with a 1-hole rubber stopper. That part of the glass tube to be plated extended through the hole in the stopper into the bath. By sliding the tube up or down through the stopper and by adjusting the height of the liquid, it was very easy to regulate the deposit to the desired position and extent. A copper-sulfate acid bath was used and the current density was kept below 0.1 ampere per sq. cm. It was necessary to remove the tube from the bath and file the deposit occasionally until it became perfectly smooth across the joint. Such a connection is perfectly solid and the glass is free from all heating strains.

A joint of this type was built into a thermostat regulator a year ago and has been entirely satisfactory. A similar joint was made between copper-plated steel tubing, 6 mm. in diameter, and soft glass of the same size. The metal end was soldered shut and the glass tube sealed directly to a manometer system in which a vacuum of less than 1 mm. was produced. During a week of observation no trace of a leak was evident.

Violent changes of temperature, because of the different coefficients of expansion of the glass and metal, evidently tend to weaken the vacuum tightness of the joint. It will stand a reasonable amount of heat, however, as shown by the fact that the above joint became quite hot when the metal tube was soldered within 7.5 cm. of the glass.

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[Contribution from the Laboratory of Plant Chemistry, University of Wisconsin]

EXPERIMENTS ON AZULENE[1]

By Roland E. Kremers

Received May 15, 1922

Historical

The blue pigment which is associated with the high-boiling fractions of certain volatile oils has long been known to chemists. Various conjectures as to its nature have been put forward and, indeed, the problem was at one time considered settled by the discovery of copper salts in oils distilled through untinned copper condensers. Even in recent years, no definite knowledge was at hand, and the substance was considered to contain

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[1] An abstract based on part of a monograph submitted by Roland E. Kremers to the Graduate Faculty of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1921.

oxygen in spite of the fact that unmistakable blue fractions were obtained as by-products in reactions which produced hydrocarbons from alcohols.

It is accordingly all the more remarkable that in 1915 Sherndal[2a] not only succeeded in isolating a pure blue compound, $C_{15}H_{18}$, but also carried out a number of important reactions. Following Sherndal's first paper, Augspurger[3] applied the same method of isolation and obtained a blue hydrocarbon, also $C_{15}H_{18}$, from the high-boiling fractions of milfoil oil. He also reduced azulene to a colorless hydrocarbon, $C_{15}H_{28}$, by the method of Skita. However, because of most untimely illness and death, Augspurger never fully published his results.

In the meantime Sherndal's second paper[2b] appeared, contributing a notable advance in the description of azulene picrate and of a reduced hydrocarbon, $C_{15}H_{26}$, obtained according to the method of Paal. This was the state of affairs when the writer resumed the work in the Wisconsin Laboratory.[4] Two general methods of approach were used, one the study of the physical properties of azulene, and the other the study of its chemical behavior.

Physical Properties

Boiling Point.—Sherndal stated that azulene was not volatile without decomposition. Although this statement has not been definitely disproved, it was found possible to distil a quantity of hydrocarbon at a constant boiling point and with a clean-cut separation from a non-blue and almost non-volatile residue. Two determinations were carried out in connection with the final purification of azulene: (1) 57 g. of distillate; b. p., 135.6° at 1.1 mm. (2) 17 g. of distillate; b. p., 167–168.4° at 11.0 mm.

Density.—The density of azulene was determined by the pycnometer method, and found to be d_4^{25} 0.98771, d_{25}^{25} 0.98465.

Absorption Spectrum.—Several measurements of the absorption spectrum were made.[5] The same characteristic spectrographs were obtained in each instance. The values recorded in Table I were read from a Hilger Type C spectrograph in the Chemical Laboratory of Vanderbilt University.

Index of Refraction. Optical Activity.—In spite of repeated efforts to measure the index of refraction and the optical activity, no results were

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[2] Sherndal, This Journal, **37**, (a) 167, (b) 1537 (1915).

[3] Augspurger, *Science* (N. S.) **42**, 100 (1915).

[4] The writer wishes to express his gratitude for the inspiration and helpful guidance received from his father in the course of this research, and to acknowledge his indebtedness to Professor E. R. Miller, formerly Chemist for the Wisconsin Pharmaceutical Experiment Station, who left at his disposal several liters of oil of milfoil.

[5] The courteous assistance of Dr. Ingersoll and Dr. Peterson of the Department of Physics, University of Wisconsin, in helping the writer to master the technique of spectrum photography, is gratefully acknowledged.

obtained. The intense color of azulene and its solutions made accurate readings impossible.

Table I

Absorption Spectrum of Azulene

0.0001 *N* soln.												
Mm.	Log mm.	Limits of transmission in 1/λ										
2	0.30	...	...	...	...	...	...	...	...	...	...	425
4	0.60	...	...	...	...	...	...	...	...	...	...	425
6	0.78	...	...	...	...	...	...	...	...	400	410	425
8	0.90	...	...	...	...	...	...	...	...	400	...	...
10	1.00	...	...	...	...	...	...	338	375	390	...	...
20	1.30	...	...	...	...	...	...	337	375	386	...	...
30	1.48	...	...	...	...	...	...	336	...	...	...	...
40	1.60	...	...	...	...	...	...	329	...	...	...	...
50	1.70	282	283	293	297	303	308	326	...	...	...	...
60	1.78	282	283	293	297	303	308	326	...	...	...	...
80	1.90	281	283	291	297	303	308	326	...	...	...	...
100	2.00	280	283	290	297	301	308	326	...	...	...	...
120	2.08	280	284	289	...	...	308	326	...	...	...	...
140	2.15	280	284	289	...	...	313	321	...	...	...	...
160	2.20	280	284	289	...	...	313	319	...	...	...	...
180	2.25	280	285	289	...	...	314	319	...	...	...	...
200	2.30	279	285	286	...	...	...	...	...	...	...	...
220	2.34	279	...	...	...	...	...	...	...	...	...	...
240	2.38	279	...	...	...	...	...	...	...	...	...	...
260	2.42	279	...	...	...	...	...	...	...	...	...	...
280	2.45	279	...	...	...	...	...	...	...	...	...	...
400	2.60	278	...	...	...	...	...	...	...	...	...	...
600	2.78	277	...	...	...	...	...	...	...	...	...	...

Chemistry of Azulene

Isolation.—The method of Sherndal was slightly modified as follows.

One hundred cc. of high-boiling blue fraction was diluted with 400 cc. of heptane and cooled to 0°; sirupy phosphoric acid was added and the mixture stirred constantly. After complete disappearance of the blue color, the acid layer was separated. The regenerated azulene was extracted with ether and the solution treated with phosphoric acid as before. The azulene regenerated a second time was taken up with ether; the solution was washed with water, bicarbonate solution and again with water, dried over anhydrous calcium chloride, and subjected to distillation. The 1915–16 oil yielded 1.6% azulene, and the 1919 oil yielded 1.47%.

Identification.—The picrate was formed according to Sherndal's directions. Although the product possessed all the apparent characteristics as described by him, the melting point was found to be lower and not constant with each preparation. The range was from 110° to 115°.

Reduction.—The reduction of unsaturated compounds has become a standard method of determining the number of rings and double bonds in a molecule. It was the more important in this instance since as yet no direct physical evidence had been obtained because of the intense color of azulene. Various methods were tried as follows.

1. *By Palladium Hydrogen.*—As previously noted, both Sherndal and Augspurger claimed the ready reduction of azulene by palladium hydrogen, but disagreed as to the formula of the product. The writer encountered considerable difficulty in reducing azulene by the Skita method, but finally obtained enough reduced hydrocarbon to distil. The reduction mixtures from several runs were distilled with steam as long as colorless oil was obtained. This was separated, dried over calcium chloride, and distilled in a vacuum; b. p., 130–140° (20 mm.); d^{22}, 0.8920; n^{22}, 1.4870; r, 0.3224. (Lorenz and Lorentz formula.)

TABLE II

MOLECULAR REFRACTION[6] OF AZULENE

Formula	M. R. obs.	M. R. calc.	Difference
$C_{15}H_{24}$	65.77	62.67	+3.10
$C_{15}H_{26}$	66.42	64.87	+1.55
$C_{15}H_{28}$	67.06	67.07	−0.01
$C_{15}H_{30}$	67.70	69.27	−1.57

SHERNDAL'S REDUCED AZULENE

Formula	M. R. obs.	M. R. calc.	Difference
$C_{15}H_{24}$	66.00	62.67	+3.33
$C_{15}H_{26}$	66.65	64.87	+1.78
$C_{15}H_{28}$	67.30	67.07	+0.23
$C_{15}H_{30}$	67.95	69.27	−1.32

Sherndal recorded for reduced azulene not distilled in a vacuum d_{25}, 0.8935; n^{20}, 1.490; r, 0.3236.

These tables show that the hydrocarbon resulting from the complete reduction of azulene has the formula $C_{15}H_{28}$ as claimed by Augspurger and that it is therefore bicyclic. Azulene itself is also to be considered as a compound containing 2 rings.

2. *By sodium amalgam.*—The conjugated double bonds of the fulvene type of structure to be suggested for azulene would ordinarily be interpreted as requiring the possibility of reduction by sodium and alcohol. Sherndal, however, stated emphatically that this could not be done, a fact which the writer repeatedly confirmed. It was finally established, at least qualitatively, that the reduction is readily effected by sodium amalgam as evidenced by the complete disappearance of the blue color. This observation was made too near the end of the investigation to permit of further study.

3. *Non-reduction by aluminum amalgam.*—Thiele[7] states that the conjugated double bond of the fulvenes is not reduced by aluminum amalgam unless the ω-carbon atom carries a phenyl or carboxyl group. Several attempts were made to reduce azulene by the aluminum-mercury couple,

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[6] Atomic refractions according to Landolt-Börnstein-Roth, "Physikalisch-chemische Tabellen," J. Springer, **1912**, p. 1039.

[7] Thiele, *Ann.*, **347**, 249 (1906).

but without the slightest success. This fact is of value in eliminating possible isomers.

Oxidation.—Like the reduction experiments, oxidation was undertaken in order to obtain an insight into the structural elements of azulene. The following reagents were used without success before more promising conditions were found: nitric acid, d. 1.2; nitric acid in acetic acid; chromic acid in acetic acid; 5% permanganate solution; 1% permanganate in acetone solution; and 1% permanganate solution acidified by sulfuric acid. Finally, much more favorable conditions were found in Wallach's alkaline permanganate method[8] of oxidizing nopinene to nopinic acid. The following is given as an example of its application.

Four g. of freshly distilled azulene was shaken vigorously with 36 g. of permanganate and 10 g. of sodium hydroxide dissolved in 1200 cc. of water. The exothermic reaction proceeded readily and appeared to be complete in about a half hour. At the end of 2 hours' standing, the manganese oxides had settled, leaving a clear light straw-colored solution. Distillation with steam removed a small quantity of semi-solid blue oil. The alkaline mixture was then concentrated to about 400 cc. by heating on the water-bath, whereupon sulfur dioxide was passed in until the oxides had just dissolved. Carbon dioxide was liberated, and only a small precipitate remained to be removed by filtration.

This residue was composed of 2 substances, one coarse and grayish-white, the other fine and slimy. The former was separated mechanically and was found to contain manganese; 50% sulfuric acid dissolved it; ether removed from this solution a grayish ash-free acid; m. p., 105° without decomposition.

The volatile acids were obtained by steam distillation of the solution acidified by the sulfur dioxide. The distillate was neutralized by sodium hydroxide and the sodium salts recovered by evaporation.

The identification of the substances thus obtained was greatly hindered by the very low yields. Of the solid acid only about 0.05 g. resulted. The melting point and the formation of a fluorescent solution after fusion with sulfuric acid and resorcinol indicate a homolog of phthalic acid, possibly a methylphthalic acid.

Acetic acid was probably present in the volatile fraction. A small quantity of sodium salt when heated with alcohol and sulfuric acid produced the odor of ethyl acetate. A silver salt prepared from the sodium salt assayed 62.3% of silver, which may be interpreted as corresponding to an impure silver acetate.

By repeated fractionation of the aqueous distillate resulting from the removal of the neutral substances from the reaction mixture, a fraction was finally obtained which gave a qualitative test for acetone, that is, it yielded iodoform when treated with iodine and sodium hydroxide.

Attempts at the Preparation of New Derivatives.—Azulene readily enters into reaction with the following reagents commonly employed in the characterization and identification of unsaturated molecules: bromine,

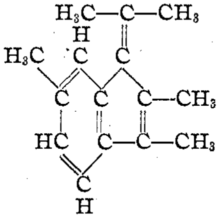
[8] Wallach, *Ann.*, **356**, 228 (1907).

nitrogen trioxide and nitrosyl chloride. No well-defined products were obtained, because the insolubility and instability which characterize them made purification impossible with only small quantities available for experiment. The so-called nitrosite appears as the most promising point of attack for further trials.

Reaction with Sodium.—It was observed that a heptane solution of azulene on standing over sodium becomes decolorized and deposits a brown crust on the metal. By the addition of alcohol and water, azulene was regenerated. This unexpected reaction explains the earlier contention that the blue oils must owe their color to an oxygenated substance, because distillation over sodium removed the color.

Structure of Azulene

Formula and Summary.—The following structural formula is suggested for azulene



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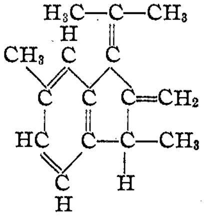


because it rationalizes the known facts concerning the compound, which, may be summarized as follows: (1) color and complex absorption spectrum; (2) high density and boiling point; (3) formation of a picrate; (4) reduction to a bicyclic hydrocarbon; (5) reduction by sodium amalgam; (6) non-reduction by aluminum amalgam; (7) formation of a phthalic acid on oxidation; (8) formation of acetic acid on oxidation; (9) formation of acetone on oxidation; (10) formation of carbon dioxide on oxidation; (11) reaction with bromine, nitrous oxide and nitrosyl chloride; (12) reaction with sodium.

Conclusion

In conclusion the writer wishes to emphasize the many theoretical problems connected with the elucidation of the structure of azulene, of which the following may be mentioned: the genetic relations of azulene to the sesquiterpenes, and the question of the structure of that whole group; the relation of color to structure; the explanation of azulene's toxic properties and their possible therapeutic value. Further studies are in progress both on the properties of azulene itself and also on its reactions, which it is hoped will ultimately lead to its synthesis.

Summary

The boiling point, density, and absorption spectrum of azulene have been measured. Through the reduction by palladium hydrogen, it has been shown that azulene is bicyclic. Permanganate oxidation yielded substances characterized as phthalic acid, acetone, acetic acid, and carbon dioxide. Azulene has been shown to behave as an unsaturated compound. In conformity with these facts a benzfulvene structure has been tentatively assigned to it.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL RESEARCH, PARKE, DAVIS AND COMPANY, NO. 14]

GAMMA-CHLOROPROPYL URETHANS AND A SYNTHESIS OF THE 1,3-OXAZINE RING

BY ARTHUR W. DOX AND LESTER YODER

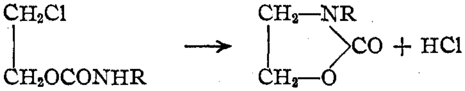
Received June 8, 1922

Of the numerous possible halogen-substituted propyl carbamates only 2 are described in the literature, namely, β,γ-dichloropropyl and β,β'-dichloro*iso*propyl carbamate.[1] The latter has come into therapeutic use as a hypnotic[2] and appears on the market under the name "Aleudrin." Homologs of γ-chloropropyl carbamate, namely, γ-chloro-α-ethylpropyl and γ-chloro-α-propylpropyl carbamate have been reported by Puyal and Montagne.[3]

Two methods have been used in the preparation of these urethans: (1) treatment of the substituted alcohol with phosgene and conversion of the resulting chlorocarbonate into the urethan by ammonia, (2) treatment of the alcohol with urea chloride.

For the preparation of the corresponding carbanilates, or phenylurethans, another method is available which consists in the simple addition of phenyl isocyanate to the alcohol. This method was used by Johnson and Langley[4] for the preparation of a number of dihalogen propyl and *iso*propyl carbanilates.

An interesting observation reported by Otto, and later extended by Johnson and Langley, is the fact that β-halogen alkyl carbanilates when treated with alkali lose halogen acid with ring closure to form oxazoles.



The only instance where a γ-halogen alkyl carbanilate has been subjected to this treatment with alkali was the γ-chloro-β-bromopropyl carbanilate where a β-halogen was also present.[4] In this case it was the β- and not the γ-halogen that reacted.

[1] Otto, *J. prakt. Chem.*, [2] **44**, 20 (1891).

[2] Ger. pat., 271,737, 1911; U. S. pat., 1,108,676, **1914**.

[3] Puyal and Montagne, *Bull. soc. chim.*, **27**, 857 (1920).

[4] Johnson and Langley, *Am. Chem. J.*, **44**, 352 (1910).