to —20° deposited no solid except a little benzene. On evaporating further the red solid appeared before the volume had been reduced to 10 cc. No salts containing other metals could be obtained from the addition compound.

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[CONTRIBUTION FROM THE LABORATORY OF THE DODGE & OLCOTT CO.]

AZULENE, A BLUE HYDROCARBON. II.

BY ALFRED E. SHERNDAL.

Received March 24, 1915.

Since the publication of the preliminary notice of the isolation of the remarkable new hydrocarbon which occurs in so many of the essential oils,[1] the following further work has been carried out, and is described below:

(1) The preparation of a picrate, and its analysis.

(2) The preparation of artificial blue oils from various oils of the sesquiterpene type.

(3) The isolation and identification, by means of the picrate, of azulene from the blue sections of the oils of cubebs, camphor, and from the artificial blue gurjun oil.

(4) The complete reduction of azulene to a colorless dihydrosesquiterpene.

The picrate is readily formed by combining the alcoholic solutions of its constituents, and crystallizes out almost immediately in the form of jet black, shiny needles, melting without decomposition at about 120°, and containing one mol of picric acid to one mol of azulene. This ready formation of a picrate is strong evidence that the hydrocarbon possesses an aromatic structure, since only this class of hydrocarbons has been found to yield additive compounds with picric acid, etc.[2] No true picrates of the hydroaromatic hydrocarbons have been prepared, the so-called picrates of pinene and thymene,[3] being in reality picric acid esters, from which the original hydrocarbons cannot be regenerated. They also differ from the picrates of the aromatic hydrocarbons in conditions of formation, stability, etc. The picrate of azulene, on the other hand, resembles the true additive compounds of picric acid with the aromatic hydrocarbons in ease of formation, decomposition by water or dilute alkalies with regeneration of the original hydrocarbon, melting point, etc. It provides an excellent means of establishing the identity of the blue substances isolated from various oils, and of effecting a final and complete purification of the blue hydrocarbon.

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[1] THIS JOURNAL, 37, 167 (1915).

[2] Bruni, *Chem. Ztg.*, 30, 569 (1906); Küster, *Ber.*, 27, 1101 (1894).

[3] Lextreit, *Compt. rend.*, 102, 555 (1886); Semmler, "*Die aetherischen Öle,*" II, 253.

The method of preparation was as follows: To a solution of 1.0 g. picric acid in 20 cc. 95% alcohol, was added 1.0 g. azulene dissolved in 5 cc. alcohol. In a few minutes the mixture set to a mass of crystals which dissolved again when warmed on the water bath, and on cooling separated out in short, shiny, black needles. These were filtered off on the pump, and dried *in vacuo* over sulfuric acid. Yield, 0.73 g.; m. p. 118°. The picrate dissolves readily in alcohol, acetone and ether with a green color; in benzene and ethyl acetate with a blue color. The green color of the solutions is probably due to partial decomposition in the moist solvents. For the same reason, if dilute alcohol is used in the preparation, a substance with a lower m. p. is obtained, more or less contaminated by oil. Carbon tetrachloride and benzine dissolve out the azulene and leave the picric acid undissolved. To determine the amount of picric acid in the compound, it was decomposed by warm water containing a measured amount of barium hydrate, made up to definite volume, filtered, and the excess of barium hydrate determined by titrating an aliquot portion of the filtrate with standard hydrochloric acid, using phenolphthalein as indicator.

0.445 g. picrate, decomposed by warm water containing 17.6 cc. 0.1 N $Ba(OH)_2$, made up to 100 cc., filtered, and 50 cc. of the filtrate titrated with 0.1 N HCl. Required, 3.5 cc.

Found: 54.3% picric acid. Calc. for 1 mol picric acid: 53.5%; for 2 mol: 69.8%; for $^1/_2$ mol: 36.6%.

The picrate accordingly contains one mol picric acid to one of the hydrocarbon.

The method of isolating azulene which was described in the first paper gives at least an approximation of the amount contained in the blue oil. As already shown, an intensely blue fraction which was examined, yielded about 0.28% azulene. Following the same procedure with a dark bluish green fraction of oil of cubebs, the amount of azulene which could be isolated amounted to only 0.03%. This shows strikingly enough how oils containing only a trace of the substance, might be intensely colored and still show the characteristics of a homogeneous substance. To give an idea of the color intensity of azulene, 0.064 g. of the pure hydrocarbon was dissolved in a liter of benzine, and an ammoniacal solution of copper sulfate made up to match it in depth of color. The latter solution contained 0.24 g. $CuSO_4$ to the liter and matched the azulene solution almost exactly both in depth and shade of the color, showing only a slightly less purple nuance.

The azulene was extracted from the oil of cubebs as follows: 250 g. of the oil were dissolved in 200 cc. of benzine, shaken out thoroughly in a separating funnel with 25 cc. of about 63% H_2SO_4, allowed to settle during a half hour, and the acid solution then drawn off. This was then diluted with water, and extracted with benzine. The same operation was repeated three times, and the final extraction of the diluted acid made with ether. On evaporation of the ether, a residue of 0.073 g. was left, *i. e.*, 0.03% of the cubebs oil taken. This residue was mixed with a solution of 0.07 g. picric acid in 2 cc. absolute alcohol. The black crystalline mass which soon separated was recrystallized from a little alcohol, yielding then the characteristic black, shiny needles of azulene picrate, m. p. 122°.

The production of blue oils from products which do not originally show any blue color, has already been referred to. Wallach,[1] found that the hydrocarbon obtained by dehydrating guaiol with zinc chloride or phosphorus pentoxide, showed a strong blue color, and ascribed the color to the presence of a small amount of some substance containing oxygen. Gadamer,[2] in a similar manner, obtained a blue product by dehydrating atractylol, and noted also, that guaiene, by the absorption of oxygen, took on a blue color. α-Gurjunene, when heated under pressure with air or oxygen, yields a blue oil.[3] All these colorations are undoubtedly due to the presence of small amounts of azulene, formed from the hydrocarbons by an oxidative process. Another reaction which produces azulene, was suggested in the previous paper, namely the action of sulfuric acid in acetic anhydride. By means of this reaction, blue oils were prepared from the oils of amyris, guaiac-wood, and gurjun, and from the latter azulene was isolated and identified by means of the picrate. The sesquiterpene fraction of oil of eucalyptus also gave a greenish blue oil, while from oil of cedar-wood and caryophyllene of clove oil the distillates showed no trace of blue or green color. The method of procedure was as follows:

10 cc. of gurjun oil were mixed with an equal volume of acetic anhydride and 2 cc. of strong sulfuric acid was added gradually, keeping the flask cool by ice water. A violent reaction took place; the mixture took on an intense purple color which changed to a dark blue, and sulfur dioxide was given off. After standing for some time, steam was passed through the acid mixture, and a distillate of 4 cc. of a dark blue oil was thus obtained. By extracting the azulene from this oil in the usual way, *i. e.*, by dissolving in benzine and extracting with 63% sulfuric acid, a yield of about 0.04% of the gurjun oil taken was obtained. The product gave a picrate which crystallized in coarse, black needles with blunt ends, melting at 122°. The blue oils from guaiac, amyris, and heavy eucalyptus sesquiterpene were made in the same way.

This is far from being a smooth reaction, which is not surprising con-

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[1] *Ann.*, **279**, 379 (1894).

[2] *Arch. Pharm.*, **241**, 33 (1903).

[3] *Ber.*, **47**, 2252 (1914).

sidering the reagents used, but it shows, as do the other methods of producing blue oils, the nature of the reaction which results in the formation of azulene, namely, a splitting off of hydrogen by oxidative action, which results in the formation of new double bonds. In the terpene series we have the same reaction, that is, the oxidative removal of two hydrogen atoms from the compound $C_{10}H_{16}$, resulting in the formation of cymol, $C_{10}H_{14}$. This also is not a quantitative reaction, the yield of cymol being as a rule very low. But by such means the terpenes are converted into an aromatic molecule, which is structurally closely related to them. Now, all indications point to the conclusion that azulene also is an aromatic hydrocarbon. Its empirical formula, isomeric with the naphthalene homolog $C_{10}H_8.C_5H_{10}$, its picrate, its high specific gravity, its behavior towards sulfuric acid, are all evidence of aromatic structure. Once this is clear, the striking analogy between the conversion of the terpenes $C_{10}H_{16}$ on the one hand, to the benzene homolog cymol, and on the other hand the conversion of the sesquiterpene $C_{15}H_{24}$ to the aromatic molecule $C_{15}H_{18}$, isomeric with a naphthalene homolog, becomes immediately apparent. The similarity of the reactions by which these conversions are affected adds still more to the analogy. Compare, for instance, the formation of cymol from camphor, with the production of the blue oil from guaiol, both by the action of P_2O_5; the formation of cymol from turpentine by heating under pressure with CO_2, with the formation of a blue oil by heating gurjunene under pressure with air or oxygen; the production of cymol from various terpenes by the action of sulfuric acid, with the formation of azulene by the action of sulfuric acid and acetic anhydride on various sesquiterpenes. The assumption is certainly not far-fetched that an analogous oxidative process takes place in all these cases, which although not smooth, yet from both classes of hydroaromatic compounds, tends to produce aromatic molecules of which the cyclic terpenes and sesquiterpenes, respectively, can be said to be hydro-derivatives. That the nucleus of the azulene molecule is not very different from that of the sesquiterpene from which it is produced, is indicated by the experiment described below, in which its reduction to a colorless dihydrosesquiterpene is effected.

If we could write formulae to illustrate the structure of the various types of sesquiterpenes, it would doubtless help to give an insight into the structure of azulene. The proposed formulae for the sesquiterpenes are, however, based upon such meager experimental evidence, that they cannot be accepted as in the slightest degree conclusive. Some experimental evidence of their close relation to the terpenes and isoprene, was given by Semmler,[1] who succeeded in identifying terpinene in the degradation products formed by heating the gurjunene sesquiterpenes under

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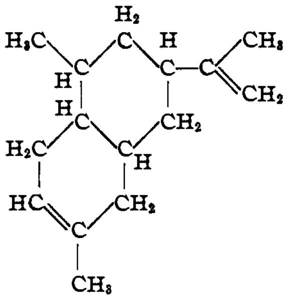
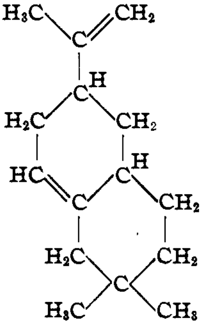
[1] *Ber.*, 47, 2252 (1914).

pressure. In general they are assumed to be hydro-naphthalene derivatives. Semmler,[1] in reviewing the possible condensations of three isoprene molecules, brings into consideration, on the basis of unpublished experimental data, the formula



as the type of most of the sesquiterpenes, and states that this type can, under certain conditions, be readily converted into a naphthalene derivative. To another smaller class of sesquiterpenes he ascribes the type formula:



from which no naphthalene derivatives have as yet been obtained. It is evident that in these main types, pinene camphene, or tanacetone rings can take the place of ethylene bonds. The sesquiterpenes also probably include open chain and monocyclic compounds with a corresponding number of double bonds. The number of ethylene bonds, and consequently the ring structure, mono-, bi-, or tricyclic, is determined by the molecular refraction, and in recent times the elegant method of reduction by hydrogen in the presence of finely divided platinum or palladium, has provided an additional means for determining the state of unsaturation, the monocyclic sesquiterpenes being thereby reduced to the saturated molecule $C_{15}H_{30}$, the bicyclic to $C_{15}H_{28}$, the tricyclic to $C_{15}H_{26}$. By this method it was demonstrated that azulene is tricyclic, that is, it contains four double bonds. It was reduced quantitatively to the saturated molecule $C_{15}H_{26}$, which then showed the characteristics of a tricyclic dihydro-sesquiterpene. The reduction was carried out as follows:

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[1] *Ber.*, **36**, 1038 (1903).

50 cc. of 50% alcohol and 0.2 g. of colloidal palladium were placed in a shaking flask connected with a gas buret, the whole apparatus filled with hydrogen at ordinary pressure, and shaken by a mechanical arrangement till no more hydrogen was absorbed. With a current of hydrogen running through the flask, 2.552 g. of azulene were introduced, the apparatus closed, and the shaking continued until the absorption of hydrogen ceased. The reduction required about twelve hours' shaking, the rate of absorption being uniform throughout and stopping suddenly. At 0°, 760 mm. about 1200 cc. hydrogen were absorbed. Calc. for H_8: 1146 cc. When the reduction was complete, as shown by the sudden break in the absorption of hydrogen, the mixture was distilled in a current of steam and the oil collected in a narrow graduated tube. In this way were obtained about 2.5 cc. of oil with only a very faint green tint and the following constants:

Sp. gr. at 25°, 0.8935; n_{D20} 1.490, O. R. $\pm$ 0.

The oil was insoluble in 63% sulfuric acid, gave an intense coloration with acetic anhydride containing a trace of sulfuric acid, and also with bromine in acetic acid solution.

Comparing these constants with those of other tricyclic dihydro-sesquiterpenes, it will be seen that the sp. gr. is considerably lower, indicating a differing structure. The color reaction also shows that we have to do with a peculiar structure.

The work of Deussen and Philipp,[1] Semmler and Spornitz,[2] Semmler and Jakubowicz,[3] on the sesquiterpenes of gurjun oil, gives interesting data for comparison with the dihydro-sesquiterpene from azulene. Deussen and Philipp found that oil of gurjun consists of two sesquiterpenes. Semmler and Jakubowicz then showed that these were both tricyclic, the crude oil, on reduction by hydrogen and platinum, absorbing only two hydrogen atoms and yielding a dihydro product with sp. gr. at 20° 0.909; n_D 1.49; b. p. 115–117 at 7 mm. They succeeded further in separating the crude oil with the following characters: sp. gr. 0.922; O. R. —55°; n_D 1.507, into the two tricyclic sesquiterpenes:

β-Gurjunene; sp. gr., 0.9348; O. R. + 74.5°; n_D 1.50275. α-Gurjunene, sp. gr., 0.918; O. R. — 95°.

The β-gurjunene, which forms about 33% of the oil, resembles cedrene closely, but is not chemically identical. It does not give the color reactions characteristic of crude gurjun oil, and yields no blue oil on heating under pressure. Its reduction product by hydrogen and platinum has the characters:

Sp. gr., 0.9258; n_D 1.49775; b. p., 120° at 8 mm.

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[1] *Ann.*, **374**, 105 (1910).

[2] *Ber.*, **47**, 1029 (1914).

[3] *Ibid.*, **47**, 1141 (1914).

α-Gurjunene gives the color reactions of the crude oil, and on heating under pressure with air or oxygen yields a blue oil.

From these data the approximate constants of the dihydro-α-gurjunene can be derived: Sp. gr. at 20° 0.900; n_D 1.492, which agree with those of the dihydro derivative from azulene. Summing up the characteristics of α-gurjunene, we find: (1) it gives the color reactions characteristic of crude gurjun oil; (2) it yields azulene on heating under pressure with oxygen; (3) it is reduced to a tricyclic dihydro-sesquiterpene with constants and chemical behavior such as color reactions, similar to those of the reduction product from azulene. All these properties differ from those of other tricyclic sesquiterpenes such as β-gurjunene and cedrene. It is possible that other sesquiterpene types may be inverted by the reagents used, and so show some of the same properties.

It seems quite probable, however, that the α-gurjunene is the type which produces azulene, and that the dihydro-sesquiterpene formed by the complete reduction of azulene is identical with dihydro-α-gurjunene, although further experiments are necessary to demonstrate any such identity.

In the present state of our knowledge of the structure of the sesquiterpenes and the experimental data on azulene, an attempt to ascribe a structural formula to the latter is necessarily purely speculative. Certain bases for a discussion of the possibilities are, however, not lacking, for instance:

(1) It is closely related to the sesquiterpenes in structure, as shown by the mode of formation and its reduction product.

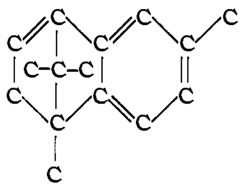
(2) It is tricyclic and consequently contains four ethylene bonds.

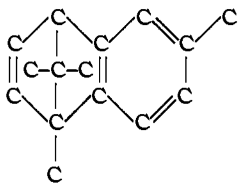
(3) It possesses an aromatic nucleus, indicated by the ready formation of a picrate.

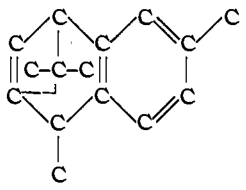
(4) It contains no hydroaromatic conjugate double bonds, since it is not reducible by sodium in alcohol.

(5) It has a peculiar arrangement of the double bonds which accounts for its intense color, such color intensity being exhibited by no hitherto discovered hydrocarbon.

If we take, for the time being, the type formulae suggested by Semmler, and consider the possibilities of oxidizing to a tricyclic, tetra- or pentocean molecule $C_{15}H_{18}$, which could be reconciled with the above requirements, we arrive at structures such as the following:







Whether or not the azulene molecule has some such structure, can only be determined by further study, perhaps from its oxidation products. Its formation from the sesquiterpenes can aid but little in this direction, so long as their structure is so little known, but a synthesis from substances of known structure does not seem impossible. In this connection the formation of the blue oil by the dry distillation of calcium adipate, (Hentschel and Wislicenus),[1] is interesting. Such a synthesis would seem to give the greatest promise in indicating the structure of this remarkable substance, and would at the same time give additional evidence as to the structure of the sesquiterpenes to which it is related.

Two obvious typographical errors crept into the first article on azulene, in connection with the molecular weight determination (p. 169). This determination was made by Dr. Farnau of New York University, and the values found agreed well with those calculated for $C_{15}H_{18}$, 198.

BAYONNE, N. J.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

THE CONSTITUTION OF THE SO-CALLED DITHIOURIMIDO-ACETYLACETONE.

BY WILLIAM J. HALE.

Received April 8, 1915.

The principal product resulting from the condensation of urea and acetylacetone has been called by Evans[2] acetylacetone-urea. The constitution of this substance, a 2-ketopyrimidine, has been thoroughly investigated by de Haan and others.[3] At the same time de Haan recognized in the reaction product the presence of two new distinct substances. One of these new compounds was found to be a 2-ketopyrimidine-urea and identical in all respects with the second product which Evans had obtained by the use of a slightly acid condensing medium, and to which he had assigned the structure corresponding to a diurimido-acetylacetone. In all cases it is to be assumed that, during these condensations, one molecule of acetylacetone and one molecule of urea proceed directly to the formation of a pyrimidine ring, and that afterwards another molecule of urea condenses with this pyrimidine ring to form either a simple ureide derivative or a second ring leading to a compound of the diureino type.

According to Evans, the principal product in the condensation of thiourea and acetylacetone is a 2-thiopyrimidine [II] (acetylacetone-thiourea). By use of a small amount of acid he further secured the product corresponding to his diurimido-acetylacetone, namely, dithiourimido-

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[1] *Ann.*, 275, 312 (1893).

[2] *J. prakt. Chem.*, [2] 48, 489 (1893).

[3] *Rec. trav. chim.*, 27, 162 (1908); THIS JOURNAL, 36, 104 (1914).