Summary

The distribution ratios at 0 and −19.5° of seven fatty acids and five esters of β-methoxyethanol have been determined between 2,2,4-trimethylpentane and β-methoxyethanol. The distribution ratios at 0 and −19.5° of four esters of methanol have been determined between 2,2,4-trimethylpentane and methanol.

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[CONTRIBUTION FROM THE UNIVERSITY OF OTAGO]

Azulene[1]

BY JAMES MELVILLE

Our knowledge of the chemistry of the blue hydrocarbons known as the azulenes is practically summed up in two papers by Ruzicka and his collaborators,[2] who give a full bibliography of earlier work on the subject.

The azulene used in this investigation was obtained partly by the dehydrogenation of the sesquiterpenes of the essential oil of *Wintera Colorata*[3] and partly by the dehydrogenation *in toto* of guaiacum wood oil. The picrates of the azulene from both sources melted at 121–122°, as did also a mixture of the two, so that the materials are identical. It is probably the sulfur–guaiazulene described by Ruzicka and hereinafter will be called azulene.

The hydrogenation curve of azulene was traced, following the procedure developed by Lebedev and his collaborators.[4] Three hydrogenations were carried out and, although they show slight variations among themselves, the curves have the same general characteristics. A typical example is shown in Fig. 1. There is a short induction period with a slow rate of hydrogenation, rising to give a fairly steady but slowly decreasing rate up to the critical point. The critical point, which can easily be determined as the point at which the blue color disappears, occurs at 55% hydrogenation. A slight but definite increase in the rate was observed immediately after the critical point (*cf.* diisopropenyl and piperylene).

The rate of hydrogenation decreases fairly sharply to a very low value at a point corresponding to 72% saturation, *i. e.*, 3.6 double bonds, and continues to decrease until full saturation is attained. No distinct break occurs at 80% saturation as implied by Sherndal,[5] and the materials described in the literature as octahydroazulene are probably mixtures of this material with hexa- and decahydroazulene.

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[1] This work was carried out while the author was the holder of the John Edmond Fellowship.

[2] Ruzicka and Rudolph, *Helv. Chim. Acta*, **9**, 118 (1926); Ruzicka and Haagen-Smit, *ibid.*, **14**, 1104 (1931).

[3] Melville, THIS JOURNAL, **55**, 2462 (1933).

[4] Lebedev and collaborators, *J. Chem. Soc.*, 823, 2190 (1928).

[5] Sherndal, THIS JOURNAL, **37**, 1537 (1915).

The formation of formaldehyde, formic acid and acetone by the oxidation of azulene with ozone as reported by Ruzicka, was confirmed, showing that the molecule contains both a methylene and an isopropylene group. It is obvious, however, that apart from the determination of these two side chains, very little information can be obtained by the action of ozone on such a highly unsaturated compound as azulene. Hence azulene was reduced with hydrogen as far as the critical point, giving a mixture which probably consisted of a large percentage of hexahydro- with smaller amounts of di-, tetra-, octo-, and decahydroazulene. No acetone, formic acid or formaldehyde could be detected among the oxidation products of this mixture with ozone.

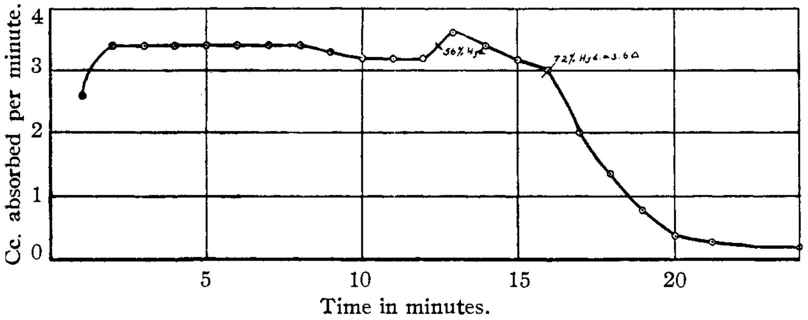

Fig. 1.—Hydrogenation curve of azulene to 3.8 double bonds (accuracy of volume measurements, ±0.2 cc.).

The ether-soluble fraction of the fission products contained both acidic and neutral substances. The neutral material (b. p. *ca.* 130° (3 mm.)) could not be induced to form derivatives with any of the carbonyl reagents, and was not further investigated. It is probably analogous to the oxide $C_{15}H_{22}O$ isolated by Ruzicka from the ozonide of guaiol and may be derived from a hexahydroazulene.[6] From the acidic part two fractions were separated by distillation and converted into their *p*-phenylphenacyl esters.[7] The analysis of the ester of the lower boiling acid agrees very well with the figures for the isobutyric ester of *p*-phenylphenacyl alcohol. The second ester is a compound $C_{29}H_{32}O_3$, which would be derived from an acid $C_{14}H_{21}$-COOH, *i. e.*, one having the same number of carbon atoms as azulene, but eight hydrogen atoms less than the fatty acid with fifteen carbon atoms. The carboxyl group can be most easily explained by the oxidation of the methylene group to a carboxyl group as occurs in the oxidation of fenchene with ozone. To explain the shortage of hydrogen atoms it is probable that the material is bicyclic and has two double bonds which as in Ruzicka's compound $C_{15}H_{22}O$ have resisted ozonolysis. Using Ruzicka's formula for elemazulene, the reaction may be represented

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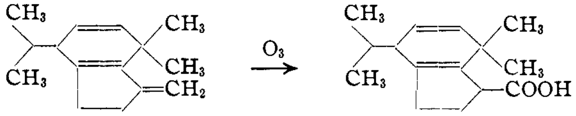
(6) Ruzicka and Haagen-Smit, *Helv. Chim. Acta*, **14**, 1122 (1931).

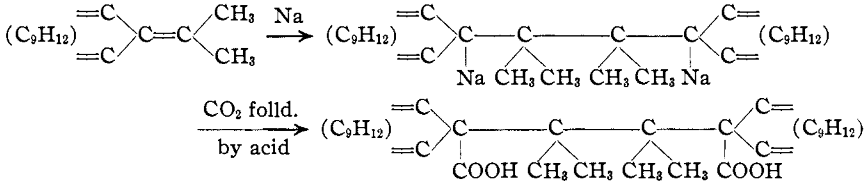
(7) Drake and Bronitsky. THIS JOURNAL, **52**, 3715 (1930).



The author is convinced of the utility of this oxidation of partially hydrogenated azulene as an aid to elucidating its structure. More information could undoubtedly be gained if the mixture of acids were treated directly with *p*-phenylphenacyl bromide, omitting the preliminary distillation which causes considerable decomposition, and possibly complete loss of one or more acids which may have been present. *p*-Phenylphenacyl bromide is particularly to be recommended as a reagent for the gummy acids which often occur in ozone oxidations.

Kremers noticed that when a solution of azulene is allowed to stand over metallic sodium, a brown crust which regenerates azulene with hydroxylic solvents forms on the surface of the metal. On shaking an ethereal solution of azulene with powdered sodium, the blue color of azulene gave place to a grayish-brown, while a fine powder settled out whenever shaking was stopped. Air causes the immediate reappearance of the blue color, but hydroxylic solvents do not, as stated by Kremers, regenerate azulene. By the action of carbon dioxide an apparently non-crystalline acid was obtained (m. p. *ca.* 100°). Its equivalent weight showed its probable formula to be $(C_{15}H_{18})_2(COOH)_2$.

No acetone was obtained when this acid was oxidized with ozone but both formaldehyde and formic acid were present among the oxidation products. Hence the sodium has attached itself to the isopropylene double bond. Assuming a fulvene structure for azulene as postulated by Ruzicka, then by analogy with Schlenk's[8] work on the action of sodium with dimethylfulvene, the formation of the sodio derivative of azulene would be as follows



With alcohol the sodio derivative forms a green compound, which does not give a picrate.

Maleic anhydride, which reacts readily with the fulvenes, gave only a green amorphous mass when refluxed with azulene in benzene solution for twenty-four hours. The lack of reactivity in such a highly conjugated system is probably due to the dicyclic character of azulene.

One property of azulene has not been discussed by any of the investi-

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[8] Schlenk, *Ann.*, **463**, 1 (1928).

gators of this substance, *viz.*, its solubility in 50% sulfuric and 80% phosphoric acids. Several unsaturated hydrocarbons[9] dissolve in concentrated sulfuric acid to give highly colored solutions from which the original material cannot be regenerated by dilution. Carotin is the one exception, but even carotin is quite insoluble in 50% sulfuric acid. It would appear that azulene is unique in this respect.

Experimental

Preparation of Azulene from Guaiac Wood Oil.—The oil, without any preliminary fractionation, was dehydrogenated in a 2-liter Pyrex Claisen flask in batches of 600 g., each batch being treated with 250 g. of sulfur. The technique for the preparation of pure azulene is as described in a previous paper.[3] The specimen for analysis was further purified by two redistillations followed by several recrystallizations of the picrate; boiling point (12 mm.) 169°.

Anal. Calcd. for $C_{15}H_{18}$: C, 90.9; H, 9.1. Found: C, 90.7; H, 9.1.

Hydrogenation.—This was carried out in a modification of Schafer's apparatus.[10] In a typical case 0.123 g. of azulene was dissolved in absolute alcohol containing about 0.1 g. of metallic palladium catalyst and absorbed 51.0 cc. of hydrogen at N. T. P. at the break in the hydrogenation curve. Four double bonds were hydrogenated in four hours but the rate of hydrogenation at this point though very small was quite definite.

Ozonolysis of Azulene.—Azulene (6 g.) was ozonized in the usual way using carbon tetrachloride as solvent. This was removed at as low a temperature as possible and the ozonide decomposed by warming with 30 cc. of water. The aqueous solution was shown to contain acetone by the formation of the dibenzylidene derivative (m. p. 111°). The resorcin and gallic acid tests for formaldehyde were both positive while the presence of formic acid was shown by the mercuric oxide method.[11]

Partial Reduction of Azulene with Subsequent Ozonolysis.—Azulene (12 g.) was reduced with palladium and hydrogen in alcohol until the color had just disappeared, the partially reduced azulene distilling at 124–127° (11 mm.). Eleven grams of this material was ozonized in the usual way, and the ozonide decomposed by heating with water for two hours at a temperature not exceeding 45°. A small amount of ether was added to separate the water-insoluble substances.

Aqueous Solution.—No formaldehyde, formic acid, or acetone could be detected by the above methods. On evaporating 50 cc. to 2 cc. a solution was obtained which gave an immediate Schiff's test and with semicarbazide acetate gave a yellow microcrystalline semicarbazone melting at about 234° with decomposition.

Ethereal Solution.—The acid and neutral portions were separated by extraction with dilute sodium carbonate solution. The free acids (4 g.) were then distilled and two fractions were obtained: 0.5 cc., b. p. 55–65° (10 mm.), and 1.0 cc., b. p. *ca.* 180° (1.5 mm.). The method is wasteful as there was a considerable residue in the distillation flask. The two fractions were then converted to their *p*-phenylphenacyl esters by Drake's method. The first fraction gave a mass of crystals on cooling, which after several recrystallizations from 80% alcohol was finally obtained in colorless leaflets melting at 84° (uncorr.).

Anal. Calcd. for $C_{18}H_{18}O_3$: C, 76.6; H, 6.4. Found (micro): C, 76.6; H, 6.3.

The second ester was recrystallized from fairly large quantities of 95% alcohol giving as a final product buff-colored needles melting at 144.5° (uncorr.).

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[9] Kuhn and Winterstein, *Helv. Chim. Acta*, **11**, 150 (1928).

[10] Schaefer, *Ind. Eng. Chem., Anal. Ed.*, **2**, 115 (1930).

[11] Mulliken, "The Identification of Pure Organic Compounds," Vol. I, pp. 24, 83, 149.

Anal. (Micro) Calcd. for $C_{29}H_{22}O_3$: C, 81.3; H, 7.45. Found: C, 81.4; H, 7.4.

The neutral fraction of the ethereal extract distilled at 125–145° (3 mm.) with considerable decomposition. It could not be induced to form crystalline derivatives with any of the ordinary carbonyl reagents.

Sodio Derivative.—Azulene (6 g.) in anhydrous ether was shaken in the absence of air with 2 g. of powdered sodium until the blue color had been replaced by a light brownish-gray. The solution, which regenerated azulene immediately on exposure to air, was treated with carbon dioxide. The precipitated sodium salt was washed with ether and dissolved in water, giving a brown solution from which hydrogen chloride precipitated the free acid in gray flocculent masses. The acid did not appear to be crystalline but melted fairly definitely at 100°. Its equivalent weight, by titration against baryta, was approximately 270 but an accurate end-point was impossible owing to the color of the solution. Calcd. for $(C_{15}H_{18})_2(COOH)_2$: 243.

The acid (4 g.) was oxidized with ozone and the ozonide treated as before. Formaldehyde and formic acid were both found to be present, but no trace of acetone could be obtained. Time did not permit of investigation of the other fission products of the ozonide.

The author wishes to thank Dr. J. K. H. Inglis for his kindly advice and criticism throughout this investigation. He wishes also to acknowledge his indebtedness to Mr. F. R. Meldrum, who prepared the *p*-phenylphenacyl bromide, and to Mr. Williams of Imperial College, London, who carried out the two microanalyses.

Summary

1. The hydrogenation curve of azulene has been investigated and shows a break when 3.5–3.7 double bonds have been saturated. The critical point occurs at 55% hydrogenation.

2. Oxidation of a partially reduced azulene with ozone gave no acetone or formic acid; a neutral non-ketonic compound and two acids C_3H_7COOH and $C_{14}H_{21}COOH$ were isolated from the fission products.

3. Azulene reacts with sodium to form a sodio derivative which regenerates azulene with oxygen. Carbon dioxide forms with this sodio derivative an acid $(C_{15}H_{18})_2(COOH)_2$. From an oxidation of this acid it appears that the azulene molecule has been attacked at the isopropylene group.

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