[CONTRIBUTION FROM OTAGO UNIVERSITY]

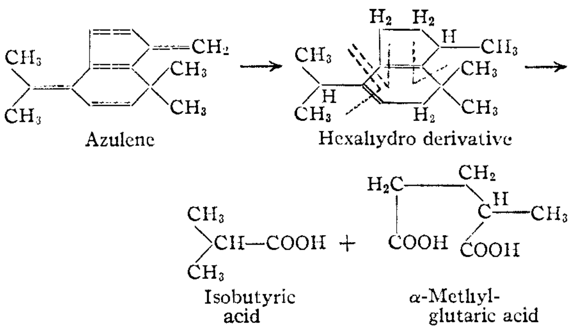
Studies in the Chemistry of Azulene

BY KENNETH STEWART BIRRELL

Owing to the highly condensed system of conjugated double bonds which would appear to be present in the peculiar blue hydrocarbon azulene, $C_{15}H_{18}$, and the consequent difficulty in obtaining by oxidation fragments sufficiently large to convey information regarding the skeleton present,[1,2] it is necessary to perform degradation experiments on related compounds less highly unsaturated, and some work along these lines will be described in this paper. The question as to the number of azulenes actually existent[1,2] which was raised in the preliminary note[3] must be regarded as still in doubt since distance from the source of supplies has prevented further work on this point. In this account "azulene" will mean the hydrocarbon obtained by sulfur dehydrogenation of the sesquiterpene guaiene (m. p. 31.5°, picrate m. p. 122°, styphnate m. p. 105°).

Melville[4] ozonized the colorless reduced azulene which had taken up 2.7 molecules of hydrogen (corresponding to the disappearance of the conjugated system responsible for the color) and obtained two acids in the form of their *p*-phenylphenacyl esters[5] corresponding to C_3H_7COOH and $C_{14}H_{21}COOH$, the first ester having since been shown to be that of isobutyric acid. In a repetition of the ozonolysis of this same reduced azulene in the present work the acidic products were subdivided into: (a) steam volatile, (b) water-soluble, (c) ether soluble. (a) gave formic acid (0.09 mole) and the *p*-phenylphenacyl ester of isobutyric acid. (b) gave the *p*-phenylphenacyl ester of a dibasic acid $C_6H_{10}O_4$. As none of these esters of the $C_6H_{10}O_4$ acids has been prepared, it was necessary to prepare likely synthetic specimens for comparison, and as a result it seemed fairly conclusive that the ester isolated was that of α-methylglutaric acid. (c) gave about 10 mg. of *p*-phenylphenacyl ester of m. p. 143°, identical with that of m. p. 144.5° obtained by Melville ($C_{14}H_{21}COOH$ acid). The ether-soluble neutral portion after careful fractionation gave no crystalline derivatives with the usual carbonyl reagents.

It would appear that the tentative formula originally proposed for the hydrocarbon by Ruzicka and van Veen[6] gives the most satisfactory explanation of the facts now known regarding azulene, although minor objections may be raised against it. On the basis of this structure, the above changes may be formulated thus



The mechanism for the formation of the $C_{14}H_{21}$-COOH acid from a reduced azulene was postulated by Melville[4] as analogous to the oxidation of α-fenchene to α-fenchenylanic acid.

Ozonolysis of azulene after the hydrocarbon had taken up 4 molecules of hydrogen gave 0.6 mole of formic acid and 0.05 g. of a crystalline acid whose equivalent weight (227) was fairly close to the value required for an acid $C_{14}H_{21}COOH$ (234) but it was not found possible to determine whether this acid would give the *p*-phenylphenacyl ester (m. p. 144.5°) originally obtained by Melville. The neutral fractions were as intractable as those mentioned previously. Formic acid is considered to arise in these experiments by the oxidation of an extracyclic methyl group, as any methylene groups would be expected to undergo fairly early reduction during hydrogenation.

The permanganate oxidation of two small samples of the sesquiterpene guaiene (this substance is very probably a mixture of two sesquiterpenes) gave acetone and oxalic acid in yields roughly equimolecular with the azulene obtainable from the guaiene on sulfur dehydrogenation, but the other neutral products had to be left on account of lack of time. It is considered that this bicyclic sesquiterpene merits further investiga-

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(1) Ruzicka and Rudolf, *Helv. Chim. Acta*, **9**, 118–140 (1926).

(2) Ruzicka and Haagen-Smit, *ibid.*, **14**, 1104–1122 (1931).

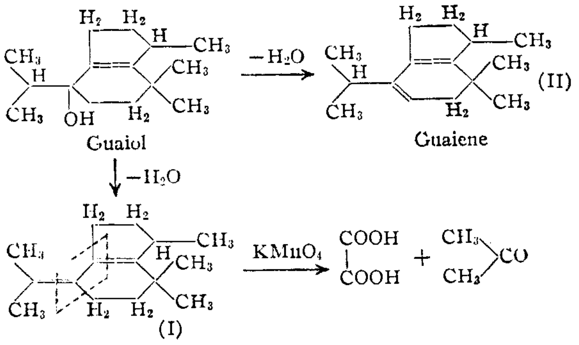
(3) Birrell, THIS JOURNAL, **56**, 1248 (1934).

(4) Melville, *ibid.*, **55**, 3288 (1933).

(5) Drake and Bronitsky, *ibid.*, **52**, 3715 (1930).

(6) Ruzicka and van Veen, *Ann.*, **476**, 70 (1929).

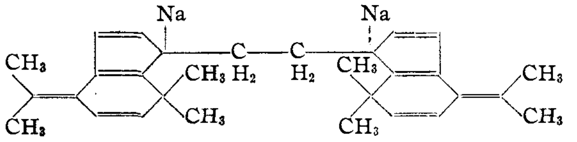
tion. The above results are regarded as consistent with the formulation



(I) may be considered as the parent of azulene which would be produced directly on dehydrogenation (see structure quoted earlier).

The objection to the persistence of a *gem*-dimethyl grouping in a dehydrogenation product may be met by considering (a) that where one of the *gem*-dimethyl groups has to be split off on dehydrogenation it forms an obstacle to the formation of an aromatic ring, *cf* the cyclization and dehydrogenation of vitamin A to give 1,6-dimethylnaphthalene, with loss of one of the *gem*-dimethyl groups from the β-ionone ring [*Biochem. J.*, **26,** 1194 (1932)]. It has been fairly conclusively shown by earlier workers that azulene does not contain a benzenoid ring. (b) A hydrocarbon such as (I) may quite feasibly dehydrogenate without effect on the *gem*-dimethyl grouping and the resulting quinonoid structure is in good agreement with the intense color of the substance.

Further work was done on the alkali-metal derivatives of azulene and some related compounds (see Melville, Ref. 4). Analysis of the sodio and potassio derivatives indicated formulas $(C_{15}H_{18}M)_x$, M = Na or K. Decomposition of the sodio derivative with aqueous ether gave a small amount of yellow crystalline material of m. p. 141°, which was not sufficiently stable to permit of a Rast molecular weight determination, but the formula may probably be $C_{30}H_{38}$. Oxidation of the carboxylated potassio derivative gave acetone, acetic acid and probably oxalic acid, but no formaldehyde, these oxidation products occurring in approximately the same yields as from azulene itself (Ruzicka and Haagen-Smit[2]). No dibasic acid was isolated. These facts may be explained by postulating that azulene gives a sodio derivative of the formula



A relatively large yield of acetic acid is not readily accounted for, and this may perhaps be best explained by postulating a wandering of one of the *gem*-dimethyl groups prior to oxidative fission. For instance, 1,1-dimethyl-4-methylene-$\Delta^{2,5}$-cyclohexadiene is very readily changed to γ-cumene (1,2,4-trimethylbenzene).[7] The former hydrocarbon possesses a similar structure to the 6-membered ring in the azulene formula quoted. This explanation may also apply to the formation of acetic acid by the oxidation of azulene itself.[2]

Experimental

Isolation and Purification of Azulene.—The azulene was prepared from commercial guaiacum wood oil as described by Melville[8] but the hydrocarbon was purified by recrystallization as indicated in the author's preliminary note:[3] 600 g. of oil gave 15 g. of azulene of m. p. 30–31°. Analysis to check purity gave: C, 90.77; H, 9.16. Calcd. for $C_{15}H_{18}$: C, 90.86; H, 9.14.

Ozonolysis of Partially Reduced Azulene (2.7 molecules of hydrogen absorbed).—The substance was ozonized in carbon tetrachloride solution. Formic acid was present in the solvent (removed *in vacuo*) to the extent of 0.246 g. = 0.09 mol. (Hg_2Cl_2 method). Prolonged distillation of the fission products of the ozonide gave isobutyric acid, identified as *p*-phenylphenacyl ester of m. p. 86°, identical with a synthetic specimen, m. p. 89°. The water-soluble acid (0.8 g.) recovered from the sodium salt, distilled at 140–165° (11 mm.) as a viscous partly crystalline material (0.42 g.) giving 0.15 g. of *p*-phenylphenacyl ester of m. p. 132°.

Anal. Calcd. for $C_{34}H_{30}O_6$: C, 76.37; H, 5.66, corresponding to a dibasic acid $C_6H_{10}O_4$. Found (micro): C, 76.13, 76.37; H, 5.74, 5.81.

Adipic acid gives a *p*-phenylphenacyl ester of m. p. 148°, mixed m. p. with above ester 125–138°. α,α-Dimethylsuccinic acid gives a *p*-phenylphenacyl ester of m. p. 146°, mixed m. p. with above ester 124–135°. α-Methylglutaric acid gives a *p*-phenylphenacyl ester of m. p. 132–133°, mixed m. p. with above ester 132°.

α,α-Dimethylsuccinic and α-methylglutaric acids were prepared by the condensation of the appropriate derivatives of malonic and acetoacetic esters with the appropriate bromo esters.

Oxidation of Guaiene.—Guaiene (4.2 g.) b. p. 134–136° (22 mm.) distilled over sodium was treated at room temperature with 4% potassium permanganate (325 cc.). Acetone was concentrated in the product by distillation, 0.036 g. being found by the method of Denigès. Oxalic acid was isolated via its silver salt from the potassium salts in the residue, crystallizing in prisms of, m. p. 99°,

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[7] Von Auwers and Ziegler, *Ann.*, **425,** 217–280 (1921).

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

identical with authentic hydrated oxalic acid. The anhydrous acid (m. p. 187° dec.) gave an equiv. wt. by titration of 49.

Analysis of Sodio and Potassio Derivatives.—The solution and suspension of the alkali-metal derivatives were separated from excess metal by decantation or filtration through glass wool in the absence of air, and the alkali formed by decomposition with water titrated: 0.2556 g. of azulene combined with 0.325 g. of sodium. $(C_{15}H_{18}Na)_2$ requires 0.289 g. 0.2387 g. of azulene combined with 0.398 g. of potassium. $(C_{15}H_{18}K)_2$ requires 0.470 g.

Analysis and Oxidation of the Carboxylated Alkali-Metal Derivatives.—0.1058 g. of the carboxylated sodio derivative gave 0.0293 g. of sodium sulfate. Equivalent wt. of corresponding acid, 256. $(C_{15}H_{18}COOH)_2$ requires equiv. wt. 243.

3.5 g. of the potassium salt of the above acid was treated with 4% aqueous potassium permanganate. Acetone was concentrated by distillation, the yield being 0.125 molecular; equiv. wt. of steam volatile acid, 64, and 0.81 g. Ba salt gave 0.2 g. of *p*-phenylphenacyl ester of m. p. 110° identical with a specimen from pure acetic acid. The residue from steam distillation required in the cold 132 cc. of 0.1 *N* potassium permanganate, which would be equiv. to 0.59 g. of oxalic acid, if this were the only reacting substance.

The author extends his thanks to Dr. J. K. H. Inglis for advice and kindly criticism during this investigation, and also to Mr. J. Melville, who arranged for micro-analyses to be done.

Summary

1. Azulene reduced until 2.7 molecules of hydrogen were taken up and then ozonized gave formic acid (in small yield), isobutyric acid, α-methylglutaric acid and the $C_{14}H_{21}COOH$ acid obtained by Melville.[4]

2. A reduced azulene (four molecules of hydrogen absorbed) gave with ozone formic acid (0.6 mole) and in poor yield possibly the same acid $C_{14}H_{21}COOH$ as before.

3. The sesquiterpene guaiene gave on oxidation with permanganate, acetone and oxalic acid in roughly equimolecular proportions and neutral products not investigated.

4. The sodio derivative of azulene probably has the formula $(C_{15}H_{18}Na)_2$ and gives with aqueous ether an unstable crystalline hydrocarbon. The carboxylated potassio derivative, probably $(C_{15}H_{18}COOK)_2$, gives with potassium permanganate, acetone, acetic acid and (probably) oxalic acid.

5. The facts now known regarding the hydrocarbon may best be explained by the formula originally proposed by Ruzicka for elemazulene, although this structure is not free from minor objections.

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[A COMMUNICATION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

The Michael Condensation. III. The Addition of Simple Ketones[1]

BY DAVID B. ANDREWS AND RALPH CONNOR

In earlier communications[2,3] it has been shown that the order of reactivity of active methylene groups in the Michael condensation is not only a function of the number of labilizing groups attached to them but is dependent also upon other structural influences. This created an interest in the reactivity of simple ketones as representatives of the class of addenda possessing only one activating group. The addition of simple ketones to various acceptors is reported in a number of earlier papers[4,5] but the compounds and conditions used were so varied that no definite comparisons of the influence of structure upon the reactivity of these compounds could be drawn. Therefore a brief investigation of the reaction of a number of ketones with α,β-unsaturated ketones was undertaken with the purpose of comparing the behavior of these substances with the compounds containing two activating groups which have previously been investigated.[3]

In view of the influence[3] of substitution of

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(1) This communication is abstracted from the thesis submitted by David B. Andrews in partial fulfilment of the requirements for the degree of Master of Chemistry at Cornell University in June, 1934.

(2) Connor, THIS JOURNAL, **55**, 4597 (1933).

(3) Connor and Andrews, *ibid.*, **56**, 2713 (1934).

(4) (a) Knoevenagel and Weissgerber, *Ber.*, **26**, 444 (1893); (b) Cornelson and Kostanecki, *ibid.*, **29**, 241 (1896); (c) Kostanecki and Rossbach, *ibid.*, **29**, 1488, 2245 (1896); (d) Stobbe, *ibid.*, **34**, 653 (1901); (e) Abell, *J. Chem. Soc.*, **83**, 360 (1903); (f) Ekeley and Carpenter, THIS JOURNAL, **48**, 2375 (1926); (g) Kostanecki and Podrajansky, *Ber.*, **29**, 2248 (1896).

(5) (a) Stobbe, *J. prakt. Chem.*, [2] **86**, 209, 218 (1912); (b) Stobbe and Rosenburg, *ibid.*, **86**, 226 (1912); (c) Georgi, *ibid.*, **86**, 232 (1912); (d) Striegler, *ibid.*, **86**, 241, 257 (1912); (e) Rosenburg, *ibid.*, **86**, 250 (1912); (f) Cruikshanks, *ibid.*, **86**, 269 (1912); (g) Georgi and Schwyzer, *ibid.*, **86**, 273 (1912); (h) Stobbe, *ibid.*, **89**, 184 (1914); (i) Schwyzer and Cruikshanks, *ibid.*, **89**, 189 (1914); (j) Cruikshanks, *ibid.*, **89**, 194 (1914); (k) Allen and Sallans, *Can. J. Research*, **9**, 574 (1933).