[CONTRIBUTION FROM THE UNIVERSITY OF OTAGO]

The Dehydrogenation of the Sesquiterpenes of Wintera Colorata

BY JAMES MELVILLE

The constituents of the essential oil of *Wintera Colorata* have already been described.[1] The sesquiterpene fraction has been further investigated, particularly in regard to its behavior on dehydrogenation. Ruzicka[2] has obtained by the action of sulfur on different sesquiterpenes three hydrocarbons, *viz.*, cadalene, eudalene (in yields up to 50%) and azulene (in yields varying from a trace up to 20%). Very little is known of the last hydrocarbon and a study of its formation from the sesquiterpene mixture in this essential oil was the end in view when this investigation was undertaken.

Fractionation of the sesquiterpene was attempted by means of distillation under reduced pressure, but gave results comparable with those of many other investigators. No clear-cut separation was obtained although three fractions with boiling point ranges of about four degrees were collected. The preparation of crystalline hydrochlorides and hydrobromides was also attempted but without success. Thus for all practical purposes it was found that no pure sesquiterpene could be obtained from the mixture.

The molecular refractivity of the fractions obtained by distillation agrees very well with that calculated for a dicyclic sesquiterpene. To confirm this result the four fractions were hydrogenated in the presence of finely divided palladium according to Shaefer's method.[3] Hydrogenation showed the presence of two double bonds, one of which takes approximately twenty times as long to saturate as the other.

The experiments on dehydrogenation were all carried out on the original mixture, as a preliminary dehydrogenation of each of the fractions with sulfur gave the same quantity of azulene. Three of the methods, *viz.*, exhaustive bromination, treatment with iodine, and anhydrous copper sulfate, gave no azulene. The three other methods, catalytic, with selenium, and with sulfur gave yields of 2, 3 and 5%, respectively. Catalytic dehydrogenation was carried out by heating the sesquiterpene with finely divided palladium at 200° for several hours. The maximum yield obtained was 2%. Heating the sesquiterpene mixture with selenium for twelve hours at 260° gave a 3% yield of azulene. In view of the work by Ruzicka and Haagen-Smit[4] it is possible that this azulene is not identical with that formed by the action of sulfur.

Sulfur, which is by far the most generally used dehydrogenating agent in

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(1) Melville, *J. Soc. Chem. Ind.*, **51**, 210T (1932).

(2) Ruzicka, *Helv. Chim. Acta*, **5**, 345 (1922).

(3) Shaefer, *Ind. Eng. Chem., Anal. Ed.*, **2**, 115 (1930).

(4) Ruzicka and Haagen-Smit, *Helv. Chim. Acta*, **14**, 1104 (1931).

this field, gave the best yield of azulene. A series of experiments was carried out using varying amounts of sulfur from theoretical down to one-fourteenth of the theoretical. These experiments showed that with one-third of the theoretical amount (Expt. 4) quite as good a yield is obtained as when the theoretical amount is used. With less than this quantity the yield decreased proportionately to the amount of sulfur used. In all those experiments where the quantity of sulfur was in excess of the critical quantity required to give the maximum yield of azulene, the azulene-freed reaction product gave a precipitate with picric acid which proved to be cadalene picrate (m. p. 116°). In those cases where the quantity of sulfur is the optimum or below the optimum for the production of azulene, no cadalene could be detected in the reaction product.

Hence it is obvious, in this case at least, that dehydrogenation with sulfur is a selective phenomenon in which all the azulene-producing sesquiterpene is dehydrogenated before the cadalene-producing sesquiterpene is attacked. The best yield of cadalene was obtained when the theoretical quantity of sulfur was used and amounted to 7%. In those experiments where less than the theoretical quantity of sulfur was used, further dehydrogenation of the azulene-free product brought the yield of cadalene up to the value obtained with the theoretical quantity. The equation for the dehydrogenation of the sesquiterpenes is

$$C_{15}H_{24} + 3S = C_{15}H_{18} + 3H_2S$$

Based on the sesquiterpene taken the yield of azulene is 5%. Calculated on the amount of sulfur used, however, the yield of azulene in Expt. 4 is 16%, which is almost as high as Ruzicka[5] obtains from guaiene. It is noteworthy in this connection that no sesquiterpene yielding crystallizable derivatives from which the pure hydrocarbon can be recovered, gives azulene on dehydrogenation. The nearest approach is guaiene, which is prepared from the crystalline sesquiterpene alcohol, guaiol.

Experimental

Fractional Distillation.—This was carried out with a number of different still heads. The most satisfactory was made from a glass tube 30 cm. in length and 1.5 cm. in diameter, insulated with cotton wool and loosely packed with Al rings. A dephlegmator through which air was passed was placed in the top in order to keep the reflux : distillation ratio about 15:1.

TABLE I

Fraction	Yield, cc.	B. p. (12 mm.), °C.	d^{20}_{20}	n^{20}_D	M_α
A	40	120–124	0.9083	1.4980	65.8
B	30	126–129	.9073	1.5010	66.1
C	33	130–133	.9136	1.5059	66.3
D	25	134–137	.9160	1.5075	66.6

M_α calculated for $C_{15}H_{24}$ and two double bonds is 66.3 so that the agreement is fairly good.

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(5) Ruzicka, *Helv. Chim. Acta*, **9**, 118–140 (1926).

Hydrogenation.—About 0.5 g. of the fraction to be examined was taken in each case with 0.2 g. of freshly prepared finely divided palladium, using glacial acetic acid as solvent. Electrolytic hydrogen was used throughout. The different fractions gave the following results.

Fraction	Wt. taken, g.	H_2 absorbed, g.	Calcd. for 2 double bonds
A	0.571	0.0114	0.0113
B	.551	.0110	.0108
C	.645	.0129	.0126
D	.560	.0116	.0110

Fraction D differs from the theoretical value by more than the experimental error, this being probably due to the presence of a small amount of monocyclic sesquiterpene.

The time required for saturation was about twelve hours, the first bond requiring only half an hour.

Dehydrogenation with Sulfur.—In all the experiments described below 15 g. of the sesquiterpene mixture was taken. This was introduced together with the sulfur into a 100-cc. Claisen flask and heated under somewhat reduced pressure to 180° when dehydrogenation begins. Reduced pressure causes the sesquiterpene to boil with the result that nearly all the sulfur dissolves before the reaction sets in, the dehydrogenation then going very smoothly and rapidly. A soda-lime tower connected to the receiver absorbs all the hydrogen sulfide given off so that the reaction need not be carried out in the fume cupboard. The temperature is raised to 250° over half an hour, the pressure meanwhile being reduced as far as possible without causing the liquid to distil. In this way the reaction can be completed and the liquid distilled over within an hour and a quarter—only one-third of the time required by the usual method. The distillate was diluted with petroleum ether and shaken with 10 cc. of 50% sulfuric acid in two stages when the azulene was wholly extracted giving a red solution. Dilution of this with water gave azulene which was then converted into its picrate. After three crystallizations from alcohol it melted at 121°.[6] The azulene-free distillate was distilled over sodium and treated with picric acid, when in Expts. 1 to 3 cadalene picrate crystallized out and was purified by crystallization from alcohol (m. p. 115°).

Expt.	Quantity of sulfur, g.	Azulene formed (as picrate), g.	Yield, %	Cadalene as picrate, g.	Yield, %
1	7 (theoretical)	1.6	5	2.5	7
2	3.5	1.7	5.5	0.25	0.7
3	2.5	1.7	5.5	Tiny ppt.	
4	2.3	1.7	5.5	No ppt., slight darkening of soln. on addn. of picric	
5	2.1	1.6	5	No trace of cadalene	
6	1.2	1.1	4		
7	0.5 (theoretical 1/14)	0.7	2.4		

The yield of azulene in Expts. 6 and 7 could be brought up to 5% by further treatment with sulfur. In no case, whether in single dehydrogenations as in 1 to 4, or in those cases where a second dehydrogenation was carried out with production of azulene, was there any trace of cadalene observed until all the azulene had been formed. The source of the cadalene could not be determined. It is probably not cadinene as saturation of the azulene free oil (from Expt. 4 above) with hydrogen chloride under conditions which gave cadinene dihydrochloride with a genuine sample of cadinene, gave no crystalline derivative.

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[6] *Cf.* guaiazulene, Ruzicka and Haagen-Smit, *Helv. Chim. Acta,* **14,** 1104 (1931).

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Summary

The production of azulene and cadalene by dehydrogenation of the sesquiterpene mixture of *Wintera Colorata* has been investigated. Dehydrogenation with sulfur is shown to be selective, all the azulene being formed before any cadalene can be detected.

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Organo-Mercuri Acetylides and their Use in the Identification of Organo-Mercury Halides

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When acetylene is passed into an alkaline solution of mercuric iodide in potassium iodide,[1] a white flocculent precipitate is obtained which has the formula C_2Hg, and which when dry is extremely explosive. Monosubstituted acetylenes react with alkaline solutions of mercuric iodide or cyanide with the formation of salts of the general formula $(R{-}C{\equiv}C{-})_2Hg$.[2] Hilpert and Grüttner have reported that pentamethylene-1,5-di-mercurinitrate in alcoholic ammonia solution reacts with acetylene with the formation of pentamethylene-di-mercuri-acetylide.[3] While investigating the use of various organic mercury compounds as catalysts in the conversion of acetylene into acetaldehyde, Nieuwland and Toussaint[4] obtained a white precipitate by the action of acetylene on ethylmercuric chloride in an alcoholic potassium hydroxide solution. The present investigation was undertaken to determine the composition of this and similar compounds and to see whether or not this reaction was general for aliphatic, aromatic and mixed aliphatic–aromatic mercury halides. It was hoped that if the reaction was general, the resulting acetylenic compounds might possess properties which would render them suitable as derivatives for identifying substituted mercury halides.

The action of acetylene on substituted mercury halides in alkaline solution may result in the replacement of one or both of the acetylene hydrogens by organo-mercury groups. Ten different substituted mercury halides were treated with acetylene, and in each case a mercuric acetylide was obtained in good yield. Analysis indicates that in every instance both

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(1) Keiser, *Am. Chem. J.*, **15**, 535 (1893).
(2) Johnson and McEwen, THIS JOURNAL, **48**, 469 (1926).
(3) Hilpert and Grüttner, *Ber.*, **47**, 184 (1914).
(4) Nieuwland and Toussaint, unpublished work.