XXVI.—*The Oxidation of Certain Sesquiterpenes with Chromyl Chloride and Chromic Acid.*

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THE action of chromyl chloride on the simple terpenes, as is the case with aromatic hydrocarbons, results in the formation of compounds of the formula $C_{10}H_{16},2CrO_2Cl_2$, which on treatment with water yield mixtures of oxidation products of the terpene and, as a rule, some chlorinated compounds (J., 1922, **121**, 2717; 1924, **125**, 107). Extending this work to the sesquiterpenes cadinene, β-caryophyllene, and cedrene, we now find that additive products are formed just as in the former instances, but there is a greater absorption of the reagent. The additive compound $C_{15}H_{24},2CrO_2Cl_2$ apparently is contaminated with $C_{15}H_{24},3CrO_2Cl_2$, or perhaps with $C_{15}H_{22},2CrO_2Cl$. The amount of oxidising reagent required in its formation indicates the former. These compounds are not so sensitive to atmospheric moisture as those obtained from the simple terpenes and aromatic hydrocarbons; but when they are decomposed by water they yield only a relatively small amount of tractable oxidation product.

Étard (*Ann. Chim. Phys.*, 1881, **22**, 218) states that the chromyl chloride additive product of toluene is decomposed by ether, ethyl chloride being evolved. We find, however, that ether carefully dried over sodium has no action whatever either on the toluene additive compound or on the new series of compounds we have prepared.

β-Caryophyllene forms an additive *compound* having the approximate composition $C_{15}H_{24},2\frac{1}{2}CrO_2Cl_2$. On decomposition with water, this yields a *ketone*, $C_{15}H_{24}O$ (which gave a crystalline *semicarbazone*), an *unsaturated ketone*, $C_{15}H_{20}O_2$, caryophyllene alcohol, and some chlorinated oxidation products, but no aldehyde.

From cedrene, an additive *compound* of similar composition was obtained, which on decomposition yielded a *compound*, $C_{15}H_{24}O$, which gives a *semicarbazone*, together with chlorinated products. The compound $C_{15}H_{24}O$ does not give an acid upon further oxidation with nitric acid, and is therefore probably not an aldehyde.

When the additive *compound* obtained from cadinene was decomposed, in addition to a small quantity of an acid, a 10% yield of a steam-volatile, *neutral product* was obtained which did not give a crystalline semicarbazone. Owing to the difficulty of preparing this hydrocarbon, we did not consider that the yields justified the continuation of this part of the investigation, and it seemed probable that a direct oxidation with chromic acid might lead to more valuable results.

Wallach (*Annalen*, 1887, **238**, 87) found that, on oxidation with chromic acid, cadinene gave a mixture of lower fatty acids. With potassium dichromate and sulphuric acid mixture, we obtained products which were entirely acid. On careful oxidation with chromic anhydride, however, we obtained a *compound*, b. p. 180—196°/12 mm., the composition of which agrees with the formula $C_{15}H_{24}O_2$. No definite evidence of the presence of ketonic or hydroxyl groups could be obtained. When treated with metallic sodium, the compound polymerised. This compound closely resembles the hydroxy-ketone described by Ruzicka and Stoll (*Helv. Chim. Acta*, 1924, **7**, 94).

EXPERIMENTAL.

In each case described below, the additive compound was prepared by allowing the reagents to react in carbon tetrachloride solution at such dilution (10%) as allowed the course of the reaction to be carefully controlled.

Action of Chromyl Chloride on β-Caryophyllene.—β-Caryophyllene, b. p. 119°/9 mm., $n^{15°}$ 1·5030, $[\alpha]_D^{15°}$ $-$ 5·2°, gave an additive product which had the approximate composition $C_{15}H_{24},2\frac{1}{2}CrO_2Cl_2$ and remained unaltered when different proportions of chromyl chloride were used (Found: Cr, 21·0, 20·9, 21·3. $C_{15}H_{24},2CrO_2Cl_2$ requires Cr, 20·0%. $C_{15}H_{24},3CrO_2Cl_2$ requires Cr, 23·3%). It was decomposed in the usual way. The steam-distilled oil (17 g. from 75 c.c. of caryophyllene) was fractionated at 1 mm., and a main product (10 g.), b. p. 120—140°, Cl, 5%, was collected. This fraction was practically freed from chlorine by refluxing with zinc dust in alcoholic solution for a month. The oil thus purified distilled mainly at 100—110° (A) and 110—125° (B) at 0·5 mm. (A), which was saturated, was treated (5 g.) in the usual way with semicarbazide acetate, being allowed to stand 2 months. After removal of the solvent and uncombined oil, the residue was recrystallised from methyl alcohol, and the resulting semicarbazone (1 g.), after further purification from benzene, melted at 234° (Found: C, 69·3; H, 10·0; N, 15·4. $C_{16}H_{27}ON_3$ requires C, 69·4; H, 9·8; N, 15·2%).

The uncombined oil on evaporation deposited crystals which, after washing with ligroin, melted at 92—95° and did not depress the melting point of an authentic specimen of caryophyllene alcohol.

The higher fraction (B) gave a non-crystalline semicarbazone which, after removal of solvent and uncombined oil, was distilled in steam with oxalic acid, and the regenerated oil collected. It was unsaturated ; b. p. 118°/1 mm. (Found : C, 77·8 ; H, 9·4. $C_{15}H_{20}O_2$ requires C, 77·6 ; H, 8·9%).

Action of Chromyl Chloride on Cedrene.—Cedrene, b. p. 123—125°/8 mm., $d_{4^\circ}^{20^\circ}$ 0·9361, $[\alpha]_D^{17^\circ}$ − 55·4°, n^{17° 1·50170, gave an additive compound similar to the one described above. When it was decomposed, steam-distillation of the product gave an oil which contained chlorine (Found : Cl, 4·2%). The chlorine content was reduced to 0·5% by refluxing in alcohol with zinc dust for 8 weeks. The oil then distilled at 93°/0·15 mm., and the distillate contained no chlorine; n^{15° 1·5462 (Found : C, 81·0; H, 10·6; *M*, cryoscopic in benzene, 224, in camphor, 223. $C_{15}H_{24}O$ requires C, 81·7; H, 11·0%; *M*, 220).

The oil gave a good yield of an amorphous semicarbazone, which was dissolved in methyl alcohol to free it from the solid condensation product which semicarbazide forms with itself, purified with animal charcoal, and added to a large excess of water. This retained the last traces of the condensation product and precipitated the *semicarbazone* as a white powder (Found : C, 70·4; H, 10·0; N, 14·4. $C_{16}H_{27}ON_3$ requires C, 69·4; H, 9·8; N, 15·2%).

Action of Chromyl Chloride on Cadinene.—Cadinene, b. p. 130—134°/10 mm., $d_{4^\circ}^{20^\circ}$ 0·9189, $n_D^{20^\circ}$ 1·5097, $[\alpha]_{5461}^{18^\circ}$ − 125°, regenerated from the dihydrochloride, m. p. 118°, gave an additive compound of similar composition to those described above. On decomposition, it yielded a small quantity of a non-crystalline acid, and a neutral product in about 10% yield, consisting of a steam-volatile oil, which was mixed with semicarbazide acetate, but even after prolonged treatment no crystalline semicarbazone could be obtained.

Chromic Acid Oxidation of Cadinene.—Chromic anhydride (70 g.) dissolved in a little water and diluted with acetic acid was slowly added with constant stirring to cadinene (50 g.) in glacial acetic acid (250 g.) during 1 hour, the temperature being kept below 50° by occasional cooling. Finally the mixture was heated on the water-bath until green, and water added. The neutral product was isolated and purified by fractional distillation at 0·5 mm. After removal of unchanged cadinene (dihydrochloride, m. p. 118°) and a small amount of acid, a light yellow oil was obtained, b. p. 180—196°/12 mm., $n_D^{6\cdot5^\circ}$ 1·5095 (Found: C, 76·6; H, 10·2. $C_{15}H_{24}O_2$ requires C, 76·3; H, 10·2%).

This oil was unsaturated towards bromine and alkaline permanganate. It did not give a semicarbazone, neither did it react with *p*-nitrobenzoyl chloride, or with phenylcarbimide. Addition of finely divided sodium produced polymerisation.

The acid products of the oxidation were isolated and purified.

The chief product gave the following analysis: C, 59·2; H, 8·4%. The silver salt gave Ag, 35·4%.

Cadinene (10 g.) in acetic acid (50 c.c.) was treated with potassium dichromate (20 g.) and sulphuric acid (14 c.c.) in aqueous acetic acid. The reaction was similar to that described above. After a little unchanged cadinene had been removed, there resulted only an acid product which appears to be identical with the acid described above (Found: C, 59·7; H, 8·6%. Silver salt gave Ag, 35·1%).

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