

CIX.—*Contributions to the Chemistry of the Terpenes.*
Part V. The Action of Chromyl Chloride on
Terpinene and on Limonene.

By GEORGE GERALD HENDERSON and WILLIAM CAMERON.

IN continuation of the investigation of the products formed by the action of chromyl chloride on terpenes, of which accounts have already been communicated to the Society (Trans., 1903, **83**, 1299; 1907, **91**, 1871; 1908, **93**, 288), we have recently examined the behaviour of terpinene towards that oxidising agent, with somewhat unexpected results. When a dilute solution of chromyl chloride (2 mols.) in dry carbon disulphide is added slowly to terpinene (1 mol.) largely diluted with the same solvent, there is considerable evolution of heat, and a solid compound separates. The solid is of a greyish-brown colour when dry, and on exposure to air quickly takes up moisture and undergoes decomposition. On treatment with water, it yields an insoluble, brown, oily liquid of an aromatic odour, while chromic chloride passes into solution. When this liquid oxidation product, after purification by distillation with steam, is mixed with a saturated solution of sodium hydrogen sulphite, about one-half remains unattacked, and the rest forms a bisulphite compound, which separates quickly in small, pearly plates. From this compound an aldehyde of the formula $C_{10}H_{12}O$ was prepared in the usual manner. Investigation of the properties of the aldehyde led to the conclusion that it is not the expected derivative of terpinene, but is, indeed, no other than α -*p*-tolylpropaldehyde, $C_6H_4Me \cdot CHMe \cdot CHO$. It has already been shown by Errera (*Gazzetta*, 1889, **19**, 528; 1891, **21**, 76) and by Miller and Rohde (*Ber.*, 1890, **23**, 1070; 1891, **24**, 1356) that this aldehyde is one of the substances produced by the action of water on the solid compound, $C_{10}H_{14} \cdot 2CrO_2Cl_2$, which is formed when a dilute solution of cymene in carbon disulphide is treated with a similar solution of chromyl chloride.

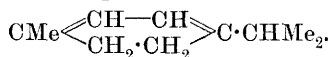
The portion of the liquid oxidation product which did not react with sodium hydrogen sulphite was washed with water, dried, and fractionally distilled under diminished pressure, with the result that three distinct liquid substances were separated from it. The liquid of lowest boiling point, of which the quantity was small, was proved to be cymene. The second fraction, which was also a very small one, contained an oxidation product of the formula $C_9H_{12}O$, which presumably is a ketone, since it forms a semi-carbazone. The third compound, which was present in by far the

largest proportion, was found to be a ketone of the formula $C_9H_{10}O$, and was ultimately identified as *p*-tolyl methyl ketone, $COMe \cdot C_6H_4Me$. This ketone has also been obtained from cymene by Errera and by Miller and Rohde, being produced along with α -*p*-tolylpropaldehyde by the action of water on the additive compound, $C_{10}H_{14} \cdot 2CrO_2Cl_2$.

According to these results, terpinene on oxidation with chromyl chloride yields the same chief products as are formed by treatment of cymene with that reagent. It might therefore appear not improbable that the hydrocarbon employed in our experiments was in reality cymene, and not terpinene; that, however, was not the case. We used for oxidation two different specimens of terpinene. One of these, supplied by Schuchardt, was presumably prepared from pinene by the usual process of treatment with sulphuric acid. To obtain the other we used the method of Genvresse (*Compt. rend.*, 1902, **134**, 360), according to which pinene was heated for some time with about one-fourth of its weight of crystallised arsenic acid, the mixture then subjected to distillation in a current of steam, and the terpinene collected, dried, and distilled. Before use each specimen was carefully distilled through a "pear" fractionating column, and only the fraction which boiled at 179—181° was used for oxidation. Other physical properties of this fraction were determined, with the following results:

$$d_{20}^{20} = 0.845; n_D = 1.48521; \text{mol. refract. } 45.6.$$

Moreover, the liquid resinified quickly on standing, and, when treated with nitrous acid, readily gave a copious yield of the characteristic crystalline terpinene nitrosite, melting at 155°. There is no doubt that the substance in our hands was ordinary terpinene, which, according to Wallach (*Annalen*, 1908, **362**, 285), is mainly composed of α -terpinene,



It must also be noted that the specimens of terpinene cannot have contained more than a very small proportion of cymene, and yet the yields of α -*p*-tolylpropaldehyde and of *p*-tolyl methyl ketone obtained from them were not very far from being quantitative. In short, it is impossible to account for the formation of such quantities of these compounds on the supposition that they were directly derived from cymene present as an impurity in the terpinene.

Our experiments, therefore, have shown that chromyl chloride acts quite differently on terpinene on the one hand, and on pinene and camphene on the other. Each of the latter hydrocarbons yields an additive compound of the formula $C_{10}H_{16} \cdot 2CrO_2Cl_2$;

terpinene, on the contrary, is, for the most part, first oxidised to cymene, and the cymene then reacts with the chromyl chloride to form the compound $C_{10}H_{14} \cdot 2CrO_2Cl_2$. Probably a small proportion of the terpinene is at the same time converted into a compound, $C_{10}H_{16} \cdot 2CrO_2Cl_2$, which on treatment with water yields the ketone $C_9H_{12}O$ referred to above.

In the course of this work we were struck with the resemblance between the properties of the aldehyde and of the ketone formerly obtained by oxidising limonene with chromyl chloride (Trans., 1907, 91, 1871), and of the α -*p*-tolylpropaldehyde and *p*-tolyl methyl ketone respectively, which were similarly formed from terpinene. In particular, the semicarbazones of the two aldehydes and ketones exhibited this resemblance in a striking manner. The aldehyde derived from limonene was found to boil at $221\text{--}222^\circ/755$ mm., and its semicarbazone to melt at 156° ; α -*p*-tolylpropaldehyde boils at 222° under atmospheric pressure, and its semicarbazone melts at 155° ; the melting point of a mixture of the two semicarbazones was the same. Former analyses of the limonene aldehyde gave results which agreed rather better with the figures calculated for the formula $C_{10}H_{14}O$ than with those corresponding with the formula $C_{10}H_{12}O$, but, on the other hand, determinations of the percentage of nitrogen in its semicarbazone favoured the adoption of the latter formula. In their other properties the two aldehydes agree fairly closely, the only notable difference observed between them being that the limonene aldehyde underwent partial oxidation on exposure to air, yielding a small proportion of a crystalline acid, whilst the other does not appear to oxidise at all readily in these circumstances. Taking the available evidence into account, we conclude that the aldehyde derived from limonene consists for the most part of α -*p*-tolylpropaldehyde, but that a small proportion of a different aldehyde is mixed with this. The two ketones also resemble each other closely. The ketone derived from limonene was found to boil at about $112^\circ/20$ mm., whilst *p*-tolyl methyl ketone boils at about $109^\circ/14$ mm. The semicarbazone of each ketone crystallises with 1 mol. of methyl alcohol, which is quickly lost on exposure to air; after heating at 100° to expel methyl alcohol, each semicarbazone melts at $204\text{--}205^\circ$, and a mixture of the two compounds melts at the same temperature. Analysis of the limonene ketone gave results which pointed to the formula $C_9H_{12}O$ rather than to $C_9H_{10}O$; but the percentage of nitrogen contained in its semicarbazone agreed closely with that calculated for the corresponding derivative of a ketone of the formula $C_9H_{10}O$. Hence it appears that the ketone derived from limonene is *p*-tolyl methyl ketone.

Limonene, therefore, when treated with chromyl chloride under the conditions formerly described, is, to a large extent at least, oxidised to cymene, which then forms the solid, $C_{10}H_{14} \cdot 2CrO_2Cl_2$. While resembling terpinene in this respect, it differs considerably from the latter in other ways. As already stated, the yields of α -*p*-tolylpropaldehyde and *p*-tolyl methyl ketone obtained from terpinene are very good, but the solid compound derived from limonene gives, on treatment with water, much resinous matter and only very small quantities of the aldehyde and the ketone. Further, more than half of the oxidation product of terpinene is composed of the aldehyde, while the ketone is the chief constituent of the liquid obtained from limonene.

EXPERIMENTAL

The method of preparing and decomposing the solid produced by the action of chromyl chloride on terpinene was essentially the same as that employed in the case of pinene and limonene, which has already been described (Trans., *loc. cit.*). The brown, oily liquid formed by treatment of the solid compound with water was purified by distillation in a current of steam, almost the whole quantity passing over, and only a little resinous matter being left in the flask. The purified liquid, now in the form of a clear, yellow oil, was mixed with a saturated solution of sodium hydrogen sulphite, and the bisulphite compound, which crystallised quickly in lustrous, pearly leaflets, was collected with the aid of the pump and washed with alcohol and with ether. The part of the liquid oxidation product which remained was treated repeatedly with the sodium hydrogen sulphite solution until no more crystals were formed, and as a result it was found that fully one-half of the original liquid consisted of an aldehyde. The bisulphite compound was heated with sodium carbonate solution in a current of steam, the aldehyde extracted from the distillate with ether, the ethereal solution washed, dried, evaporated, and the aldehyde finally purified by distillation under diminished pressure in a current of dry carbon dioxide. The aldehyde thus prepared is a colourless liquid with a peculiar odour. Its boiling point is 222° at atmospheric pressure; $d_{20}^{20} = 0.984$; $n_D = 1.51436$; mol. refract. = 45.3 . It is practically insoluble in water, but freely soluble in alcohol or ether, and it exhibits the characteristic properties of aldehydes. Oxidation does not take place at all readily when it is exposed to air. Analysis showed the formula of the compound to be $C_{10}H_{12}O$:

0.2576 gave 0.7654 CO_2 and 0.1886 H_2O . C = 81.04; H = 8.14.

0.3080 gave 0.9130 CO₂ and 0.2230 H₂O. C = 80.84; H = 8.05.

C₁₀H₁₂O requires C = 81.0; H = 8.1 per cent.

The semicarbazone of the aldehyde, C₁₀H₁₂:N·NH·CO·NH₂, crystallises in small, colourless prisms, which melt at 155°. It is readily soluble in cold, very easily so in hot, methyl alcohol:

0.1156 gave 19.9 c.c. N₂ at 16° and 767 mm. N = 20.8.

0.1345 „ 23.8 c.c. N₂ „ 17° „ 764 mm. N = 20.6.

C₁₁H₁₅ON₃ requires N = 20.5 per cent.

The properties of this aldehyde correspond precisely with those of *α-p*-tolylpropaldehyde, C₆H₄Me·CHMe·CHO, and the two substances behave in the same manner towards oxidising agents. By heating for a considerable time with silver oxide, each is converted into the corresponding *α-p*-tolylpropionic acid, C₆H₄Me·CHMe·CO₂H, small, colourless crystals which melt at 41—42°; when boiled with dilute nitric acid, each is oxidised to *p*-toluic acid, and when oxidised with potassium permanganate each yields terephthalic acid. In short, there can be no doubt that the aldehyde obtained by oxidising terpinene with chromyl chloride is *α-p*-tolylpropaldehyde, or, in other words, is a derivative of cymene and not of terpinene.

The ethereal solution of that part of the liquid oxidation product of terpinene which remained after the removal of the aldehyde by means of sodium hydrogen sulphite was washed, dried, and evaporated. The residual liquid was fractionally distilled under diminished pressure in a current of dry carbon dioxide, and after several distillations yielded three fractions of almost constant boiling point, whilst a small quantity of a thick residue containing some chlorinated product was left. The chief constituent was a colourless, rather oily liquid with a pleasant odour, which distilled at 109°/14 mm., and showed the character of a ketone. Several concordant analyses gave results agreeing fairly well with those required by the formula C₉H₁₀O, but as the compound was not quite pure but contained traces of a chlorinated product of which the separation was troublesome, its semicarbazone was prepared and analysed. These analyses left no doubt that the formula of this ketone is C₉H₁₀O.

The semicarbazone of the ketone, C₉H₁₀:N·NH·CO·NH₂, crystallises from methyl alcohol in lustrous, colourless prisms containing one molecule of alcohol of crystallisation, which quickly become opaque and break down to a powder on exposure to air. After being heated for some time at 100°, the melting point of the semicarbazone is 204—205°. It is not readily soluble in hot, and very sparingly so in cold, methyl alcohol:

0·1370 gave 26·6 c.c. N_2 at 18° and 760 mm. $N = 22\cdot4$.

0·1420 „, 27·1 c.c. N_2 „, 17° „, 762 mm. $N = 22\cdot2$.

$C_{10}H_{13}ON_3$ requires $N = 22\cdot0$ per cent.

To determine the proportion of alcohol of crystallisation, a quantity of the crystals was quickly dried with filter paper, weighed, and heated at 100° :

0·3670 lost 0·0520. $MeOH = 14\cdot1$.

$C_{10}H_{13}ON_3 \cdot MeOH$ requires $MeOH = 14\cdot4$ per cent.

The phenylhydrazone of the ketone was also prepared. It crystallises from dilute alcohol in delicate, colourless needles, which melt at $88-89^\circ$.

The properties of the ketone, $C_9H_{10}O$, obtained by the oxidation of terpinene, as well as those of its semicarbazone and phenylhydrazone, agree so closely with the properties of *p*-tolyl methyl ketone, $COMe \cdot C_6H_4Me$, and of its corresponding derivatives, that there can be no doubt as to the identity of the two compounds.

The other two substances separated from the ketone by fractional distillation constituted only a small proportion of the mixture. The first of these, a colourless liquid which boiled at 176° under atmospheric pressure, proved to be cymene, probably some of that formed from the terpinene, which had escaped further oxidation owing to part of the chromyl chloride having been consumed in converting the terpinene into cymene. The other substance, which distilled at $100^\circ/14$ mm., is a colourless liquid with a strong odour somewhat like that of peppermint. It appears to be a *ketone*, since it readily forms a crystalline semicarbazone. Although the quantity was too small to permit of thorough purification of the substance, the results of analysis agreed fairly well with those calculated for the formula $C_9H_{12}O$:

0·2604 gave 0·7530 CO_2 and 0·2048 H_2O . $C = 78\cdot86$; $H = 8\cdot74$.

0·2398 „, 0·6962 CO_2 „, 0·1890 H_2O . $C = 79\cdot15$; $H = 8\cdot75$.

$C_9H_{12}O$ requires $C = 79\cdot4$; $H = 8\cdot8$ per cent.

The *semicarbazone* of this ketone, $C_9H_{12} \cdot N \cdot NH \cdot CO \cdot NH_2$, crystallises from alcohol in very small, colourless prisms, which melt at $200-201^\circ$. It is only sparingly soluble in alcohol:

0·1158 gave 22·3 c.c. N_2 at 19° and 754 mm. $N = 21\cdot9$.

$C_{10}H_{15}ON_3$ requires $N = 21\cdot8$ per cent.

We are indebted to the Research Fund Committee of the Carnegie Trust for a grant which met the cost of the materials used.

CHEMISTRY DEPARTMENT,

THE GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.