XIX.—*Isomeric Nitroso-terpenes.*

By WILLIAM A. TILDEN, D.Sc. (Lond.), and
W. A. SHENSTONE, F.C.S.

AN immense number of hydrocarbons, described as terpenes, and having the composition and molecular weight indicated by the formula $C_{10}H_{16}$, are known, but our knowledge of their properties and constitution is at present extremely imperfect, and some method by which they may be identified and classified is very desirable.

The nitroso-terpene obtained by Tilden (*Chem. Soc. J.*, 1875, p. 514), from common dextrogyrate turpentine oil, stands alone at the present time as an example of a well-defined crystalline derivative obtained from a terpene by a direct process of substitution. By preparing and studying in detail a number of the corresponding isomeric compounds from other hydrocarbons of the same class, we hope to be able to throw some light on their mutual relations.

The present paper contains an account of the methods employed. The crystallographic characters of the nitroso-terpenes hitherto obtained are under investigation by Professor N. Story-Maskelyne, and a complete description of these products is reserved until their examination shall be finished.

We have operated upon terpenes obtained from various essential oils, which were supplied from trustworthy sources, and were believed to be perfectly genuine and unadulterated. The oils of juniper, savin, caraway, and sage were of English production, those of lemon, bergamot, and sweet orange (*Essence de Portugal*) were the best obtainable in commerce. These oils contain terpenes which are divisible into two classes. In the one we have those, of which common turpentine is the type, boiling under ordinary pressure at 160° or thereabouts. In the other class we have terpenes represented by the hydrocarbon from orange-peel, boiling at 174° . The turpentines are said to yield acetic and terephthalic acid when oxidised, whilst it has been shown by Wright that hesperidene (orange-peel terpene) yields neither toluic nor terephthalic acid, but a body resembling camphor.

Preparation of the Nitroso-chlorides of the Terpenes.

The preparation of these compounds is the first step towards the production of the nitroso-substitution derivatives. The general formula of the nitroso-chlorides is $C_{10}H_{16}(NO)Cl$, and they are formed by the direct union of nitrosyl chloride with the hydrocarbon. They cannot, however, be regarded as mere products of addition containing nitrosyl

chloride united to the terpene in the same manner as water of crystallisation is united with a salt. For none of them are in the slightest degree affected by contact with water or alcohol, both of which instantly decompose not only nitrosyl chloride itself, but various molecular compounds which nitrosyl chloride forms with other bodies, such as anthracene.

The nitrosyl chloride required for the preparation of these compounds is obtained, as formerly described, by acting upon common salt with "chamber crystals," or with sulphuric acid saturated with nitrous anhydride. We find it best to place in a flask, having a side tube to convey away the gas, a quantity of common salt wetted with strong hydrochloric acid, and to allow the nitrous sulphuric acid to drop in upon the mixture, which after a time may be gently heated.

One important condition for the successful preparation of the nitroso-chlorides of the terpenes is that the temperature of the liquid be kept throughout the experiment at a few degrees below zero. In operating upon rectified turpentine oil as in the original experiments, some difficulty was experienced in preventing the hydrocarbon from becoming heated under the influence of the nitrosyl chloride. We now find that the process becomes more manageable if the hydrocarbon is diluted with several times its volume of some solvent, such as chloroform or spirit of wine, the choice of the liquid being determined by a preliminary experiment on a small scale.

The process we now adopt is one or other of the following. The terpene is dissolved in three or four times its bulk of chloroform,* cooled by means of ice and salt to about -10° , and then saturated with nitrosyl chloride passed in at such a rate that the temperature is not caused to rise appreciably. The liquid, which becomes bright green, is tested from time to time by mixing a few drops of it with several times its bulk of spirit of wine. When a white crystalline precipitate makes its appearance, the quantity of which is not increased perceptibly when a subsequent testing is made after the further action of the gas, the whole of the chloroform solution is poured into two or three times its volume of methylated spirit, and allowed to stand for half an hour. The ensuing precipitate, which is quite white, and which consists of minute prismatic crystals, is then filtered off, washed with rectified spirit, and dried by pressure and exposure to the air.

This process we have found applicable to some varieties of turpentine, and especially to the terpene from juniper oil, but not to the terpenes from caraway, bergamot, lemon, and sweet orange. In these latter cases the hydrocarbon is mixed with five or six times its bulk of methylated spirit, a quantity generally sufficient to dissolve nearly the whole of it, and the liquid is then cooled to about -10° . On

* In the case of common turpentine, half its bulk of chloroform is sufficient.

passing nitrosyl chloride gas into this solution, it assumes a pale green colour, and after a time becomes almost pasty, from the formation of crystals of the nitrosochloride, slight effervescence attending the end of the operation. This precipitate is collected and pressed from a small quantity of green oily matter, and then washed with spirit. If required in a state of perfect purity, it may be dissolved in chloroform and crystallised out again by mixing the solution with alcohol.

The Nitroso-terpenes.

1. *Nitroso-australene*.—Ordinary American dextrogyrate turpentine oil was employed. Those portions which come over below 160° or 161° may be used. Different samples vary slightly in their action upon the polarised ray. The first specimen operated upon had the specific rotatory power* $[\alpha]_D = +17.5^{\circ}$. The nitroso-chloride, the analysis of which has already been published (*loc. cit.*) melts at about 103° , but is thereby decomposed, yielding a brown liquid, which does not solidify on cooling. When this substance is warmed with rectified spirit, small quantities of alcoholic potash being added till the whole of it has just dissolved, it loses the elements of hydrochloric acid, and is converted into nitroso-australene (designated in the former paper simply nitroso-terpene). The alkaline liquid being neutralised and evaporated, yields crystals of this compound, the analysis and crystallographic characters of which have already been published. It melts at 129° (corr.) and its alcoholic solution has no action on polarised light.

2. *Nitroso-terebenthene*.—French turpentine was re-distilled, those portions being collected which passed over between 156° and 160° . A column 100 mm. long of this liquid was found to deviate the polarised ray 33.7° to the left. When treated with the nitrosyl chloride, this hydrocarbon yields a much smaller quantity of nitroso-chloride than the dextrogyrate turpentine. And the reason of this seemed to be that a greater amount of heat is developed, so that it is more difficult to prevent the liquid from becoming suddenly hot, and so destroying the product. It is interesting to notice, in connection with this fact, that the specific rotatory power of this hydrocarbon in a state of partial purity, as observed by us, is more than twice as great as that of the dextrogyrate variety, though in the opposite direction. The numbers given by Berthelot are for pure australene $[\alpha]_D = +21.5^{\circ}$, and for pure terebenthene $[\alpha]_D = -42.3^{\circ}$.

The nitrosochloride obtained has properties similar to those of the

* The rotatory powers of the substances mentioned in this paper were determined by means of a Wild's polaristobometer, using as source of light a Bunsen-flame tinged yellow by means of a bead of sodium chloride and borax.

corresponding compound obtained from dextrogyrate turpentine. It is a white crystalline powder, which, when acted upon by alcoholic potash yields nitrosoterebenthene of the formula, $C_{10}H_{15}(NO)$. It agrees in most of its characters with nitroso-australene. Thus its alcoholic solution is optically inactive, and the melting point is the same, the actual determination being 128.8° (corrected). The crystals obtained by slow evaporation of its alcoholic solution are, however, easily distinguishable from those of nitroso-australene obtained in the same way. Their different appearance is, however, probably not due to any fundamental difference of crystalline structure, but to a peculiarity of habit, the cause of which has not yet been found out. Their description must be postponed until the measurements are complete, but we may mention that, although the specimens in our possession have been several times recrystallised, we have not observed the formation of crystals having the same appearance as those of the first discovered compound, nitroso-australene.

3. Terpenes from oil of sage (*Salvia officinalis*). We are indebted to Mr. M. M. Pattison Muir for small quantities of two terpenes from this essential oil.

A. Boiling point, $158-160^{\circ}$. 100 mm. gave a rotation of 32.2° to the left. This substance behaves in every respect like the terpene from French turpentine. The crystals of the nitroso-derivative have the same aspect and melting point (129°), and the alcoholic solution is optically inactive. The observed rotatory power of this terpene being so nearly equal to that of terebenthene, we believe these two hydrocarbons to be not merely isomeric but identical.

B. Boiling point, $168-176^{\circ}$. 100 mm. rotate the plane of polarisation 17.7° to the left. We have not been successful in obtaining a solid nitroso-derivative from this hydrocarbon. The action of the nitrosyl chloride causes effervescence, and the production of brown oily substances. It is not improbably a mixture containing polymeric hydrocarbons.

4. Terpene from oil of juniper (*Juniperus communis*). English oil of juniper was submitted to fractional distillation, and about one-third of the whole was separated, boiling below 160° . This portion consists of the terpene sufficiently pure. It showed a rotation of about 1° to the left for a column 100 mm. long. When diluted with chloroform and treated with the gas, this hydrocarbon gave a crystalline nitroso-chloride much more readily and in larger quantity than either of the terpenes previously described. After washing and reprecipitation from chloroform it was analysed. .3701 gram gave .2613 gram of $AgCl$, corresponding with 17.46 per cent. of chlorine. $C_{10}H_{16}NOCl$ requires 17.6 per cent. Decomposed with alcoholic potash in the usual way, it gave a crystalline nitroso-compound, which we believe

to be identical with nitroso-terebenthene. It was found to melt at 128.5° . Its alcoholic solution is optically inactive, and the crystals have the same form as those of nitroso-terebenthene. The hydrocarbons, however, from which these two compounds are obtained, by no means agree in physical properties, the turpentine having a much greater rotatory power than the juniper terpene, and giving out a greater amount of heat under the influence of the nitrosyl chloride.

Comparing together the four terpenes thus far described, we find that, as regards the facility with which they yield nitrosochlorides, they stand in the inverse order of their action on polarised light, the juniperene, which is almost destitute of such action, giving out less heat, and furnishing a larger yield of nitroso-chloride than the others. Next to juniperene comes right-handed turpentine, and lastly the left-handed turpentine and sage terpene, which are equal.

With these facts in view we thought it probable that, by destroying the rotatory power of an active hydrocarbon, we should get a liquid which would yield a nitroso-derivative very readily. We have, therefore, treated a quantity of both dextro- and lævo-gyrate turpentine with sulphuric acid, and after washing submitted the product to fractional distillation. The fractions which came over at $156-159^{\circ}$, and of which, by the way, only a very small quantity was obtained, were quite colourless and destitute of rotatory power, and correspond with the hydrocarbon which has been described as terebene. This liquid, submitted to the action of nitrosyl chloride under various conditions, gave no crystalline nitroso-chloride. The attempt will be renewed, but for the present it is sufficient to state that terebene certainly differs from the terpenes in its behaviour with this reagent.

5. *Nitroso-hesperidene*.—*Essence de Portugal* submitted to distillation yielded about three-fifths of its bulk, boiling at $174-175^{\circ}$. A column 100 mm. long gave a rotation of 85.9° to the right. Nitrosyl chloride passed into a mixture of the hydrocarbon, with about five volumes of methylated spirit, caused a copious crystalline deposit of nitroso-chloride. After thorough washing with spirit of wine, the chlorine was determined. .8748 gram gave .6221 gram of silver chloride, indicating 17.5 per cent. of chlorine. This agrees with the formula, $C_{10}H_{16}NOCl$, which requires 17.6 per cent.

When treated with alcoholic potash this compound behaves differently from the nitrosochlorides hitherto described. It gives by this process no crystalline nitroso-compound, but a brown, viscid, oily body, which we have not felt disposed to examine more closely at present, but which almost certainly consists of or contains a liquid nitroso-hesperidene isomeric with the crystalline variety. This latter we have succeeded in obtaining, though at great expense of material, by another process. The dry nitroso-chloride melts at about 103°

and forms a green liquid, which, if kept at the melting point even for a few seconds, enters into violent ebullition from the escape of gas, and yields nothing but brown viscid products. If, however, the melted chloride is cooled quickly by immersing the tube in cold water, a semi-solid crystalline mass results. The solid portion does not, however, consist of unaltered nitroso-chloride, but of the nitroso-terpene deprived of the elements of hydrochloric acid, a little of which escapes in fumes. The liquid products formed at the same time have not yet been examined. They are brown and have a peculiar aromatic odour.

In order therefore to prepare crystallised nitroso-hesperidene, the nitroso-chloride is heated in test-tubes in portions not exceeding about a gram each. As soon as the compound is completely melted and the liquid becomes yellowish, the tube is at once plunged into cold water. After standing a few hours, the honey-like mass in each tube is dissolved out with alcohol and the united solutions set aside. Large flat, probably orthorhombic, prisms are deposited. They are more than twice as soluble in alcohol as any of the compounds previously described, and the tendency of the compound to form large crystals is quite remarkable. It may be sublimed, but an attempt to determine the vapour-density in the barometer vacuum of Hofmann's apparatus failed, as the temperature of boiling aniline vapour was not sufficiently high to volatilise it, and it is first polymerised and then becomes brown at higher temperatures.

In one characteristic this compound differs notably from those previously described. Although the terpene from which this compound is derived is dextrorotatory, the alcoholic solution of this derivative is lævorotatory. 1 part of nitrosohesperidene dissolved in 9 parts by weight of alcohol of 84 per cent. gave a solution the specific gravity of which at 10° was ·8609. 200 mm. of this solution gave as the mean of four observations $\alpha_D = -6^\circ 19'$, whence $[\alpha]_D = -36\cdot6^\circ$.

Nitroso-hesperidene dissolved in rectified spirit gives no precipitate with hydrochloric acid gas or solution. Its chloroform solution mixed with bromine leaves, after evaporation, a semi-crystalline mass of dibromide, $C_{10}H_{15}(NO)Br_2$.

The melting point of hesperidene was in one case found to be $70\cdot1^\circ$, and another sample, probably purer, 71° (corr.).

The results of its combustion are as follows:—3536 gram gave ·9340 gram of CO_2 , and ·2964 gram of OH_2 .

	Calculated.	Experiment.
C_{10}	72·72	72·02
H_{15}	9·09	9·3
NO	18·19	—

6. *Terpene from Caraway*.— $2\frac{1}{4}$ lbs. of English oil of caraway (*Carum carui*) submitted to distillation gave about 7 fluid ounces of hydrocarbon boiling below 178° , and 100 mm. column of which gave a rotation of $+ 11^{\circ}$.

This terpene was treated in precisely the same manner as the hydrocarbon from orange-peel. It gave a nitrosochloride, the chlorine of which was determined and found to agree with the requirements of the general formula $C_{10}H_{16}NOCl$. After heating in the manner already described, it yields a crystallisable nitrosoterpene which is in every respect identical with that obtained from hesperidene. It melts at 71° , rotates the polarised ray in the same direction and to the same extent, and in solubility and crystalline form agrees fully with that compound.

7. *Bergamot*.—The best commercial oil of bergamot (*Citrus bergamia*) was submitted to distillation. About three-fifths came over below 190° . This gave about a fourth of its bulk below 180° , and this, after treatment with sodium for some hours, came over almost entirely below 176° . 100 mm. of this hydrocarbon rotates 75.6° to the right. When treated with nitrosyl chloride in the same manner as hesperidene, it gave a nitroso-chloride which melted at about 98° , and after heating gave a honey-like mass from which the nitroso-compound was extracted. This compound, like nitroso-hesperidene, melts at 71° and is lævogyrate, but when crystallised from spirit it gives none of the broad flat prisms so characteristic of the compounds from orange and caraway. At present it has been obtained only in concentric or parallel groups of very long thin prisms, which have not yet been examined with the goniometer.*

8. *Lemon*.—Essence of lemon gives a large quantity of a terpene boiling at 173 — 176° , and of which 100 mm. were found to rotate the polarised ray 61.5° to the right. This terpene does not yield the nitrosochloride readily by any process at present tried. A few grams, however, have been obtained and the chlorine determined. It gave 17.13 per cent., thus agreeing with the general formula. It does not yield a crystalline product after treatment with alcoholic potash, and the result of heating the small quantity in our possession was unsatisfactory. Further information about this compound has therefore yet to be obtained.

9. *The Essential Oil of Savin* (*Juniperus Sabina*), a coniferous plant, was thought likely to yield derivatives similar to those of turpentine and juniper, but at present attempts to produce them have been unsuccessful.

Since the above was written, we have prepared a large quantity of this compound, and we now find that it yields crystals of the same form as the nitroso-compounds from the terpenes of sweet orange and caraway.

We believe the results we have described are sufficient to show that the method we have adopted is competent to fulfil the purpose to which we have endeavoured to apply it, namely, to distinguish the isomeric terpenes from one another and to effect a classification of these bodies. We believe that the result of the further application of this method will be to show that a great many of the natural terpenes are merely physical isomerides not differing from one another in chemical constitution, and we think it probable that the number of distinct chemical species, at least among the natural terpenes, will prove to be not so great as is sometimes supposed.

Nitroso-australene from common turpentine, and nitroso-hesperidene from sweet orange peel, may be regarded as typical compounds. Experiments, which have for their object the determination of the rational formulæ of these compounds, are now in progress.