LII.—*Limonene Nitrosocyanides and their Derivatives.*

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In a "preliminary notice of some new derivatives of pinene and other terpenes" (*Proc.*, 1902, **18**, 163), it was shown by Tilden and Burrows that whilst pinene nitrosochloride yields with potassium cyanide a crystalline nitrosocyanide, a mixture of the isomeric limonene nitrosochlorides gives a liquid product.

By modifying the conditions of experiment, it has since been found that the separate limonene nitrosochlorides yield corresponding crystalline nitrosocyanides, the investigation of which I have continued at the request of Professor Tilden.

The following table contains a statement of the principal physical characters of the limonene nitrosochlorides, as determined by Wallach and Conrady, together with those of the new compounds derived from them by processes the details of which will be found in the experimental part of this paper :

Compound.	Dextro- and lævo-, m. p.	Racemic, m. p.	Dextro- [α] _D .	Lævo- [α] _D .
Limonene (Wallach and Conrady)	—	—	+106·8°	-105·0°
α -Nitrosochloride „ „	103—104°	—	+313·4	-314·8
β -Nitrosochloride „ „	not	definite	+240·3	-242·2
α -Nitrosocyanide	90—91°	81°	+152·7	-152·2
Benzoyl α -nitrosocyanide.....	108	96	+126·3	-127·2
β -Nitrosocyanide	140—141	159—160	-31·6	+30·6
Benzoyl β -nitrosocyanide.....	121	98	-108·2	+108·7
α -Amide	138	155	+174·9	-174·0
Benzoyl α -amide	152	150	+241·7	-242·0
α -Carboxylic acid	97	116	+102·9	-103·9
Dihydrocarboxime	88·5	115	+9·45	-9·25

The α - and β -nitrosochlorides both yield the same two isomeric nitrosocyanides, referred to in this paper as the α - and β -modifications,

and these two compounds are produced from the α -nitrosochloride in the same proportion as from the β -nitrosochloride. These remarks apply equally to the derivatives of *d*- and *l*-limonenes.

This observation is in accord with the account given by Wallach (*Annalen*, 1889, 252, 113, and 1892, 270, 181) of the production of two isomeric nitrolamines from limonene α - and β -nitrosochlorides respectively.

The *d*- and *l*- α -nitrosocyanides behave quite normally as nitriles, giving on hydrolysis the corresponding amides and acids. The acids are characterised by the readiness with which they part with carbon dioxide, yielding the normal oxime of *d*- and *l*-dihydrocarvones.

The β -nitrosocyanides are, however, produced in such small quantity that material sufficient for the preparation of the corresponding amides and acids has not been accumulated, but on hydrolysis with caustic potash these cyanides yield the oximes of dihydrocarvone identical with those obtained from the α -acids.

The following scheme will elucidate the relationship of the new compounds :

In order to discuss the nature of the isomerism of these nitrosochlorides and nitrosocyanides, the formula recently established by W. H. Perkin, jun. (*Trans.*, 1904, 85, 654), may be assumed.

The α - and β -nitrosocyanides formed from these two nitrosochlorides in the manner already indicated are unimolecular, and their isomerism can only be accounted for on the *cis*- and *trans*-hypothesis, the more fusible isomeride (m. p. 90—91°) being assumed to be the *cis*-compound and the less fusible (m. p. 140—141°) isomeride its *trans*-correlative.

The isomerism of the nitrolamines must be accounted for in a similar way.

A remarkable resemblance exists between the limonene α -nitrosocyanides and their derivatives and the nitrosocyanide prepared by Wallach (*Annalen*, 1888, **248**, 164) from amylene nitrosate.

The acid obtained by hydrolysing the cyanide in each case happens to melt at the same temperature, 97°, and both at this temperature pass into oximes with vigorous evolution of carbon dioxide. As already stated, the limonene α -acid gives the normal oxime of dihydrocarvone, whilst the acid from amylene nitrosocyanide yields the oxime of methyl *isopropyl* ketone, $(\text{CH}_3)_2\text{CH}\cdot\text{C}(\text{NOH})\cdot\text{CH}_3$.

The mechanism of the process by which the isomeric nitrosocyanides are formed from the limonene bimolecular nitrosochlorides is not yet fully elucidated, but it may be regarded as probable that at the moment of separation of the two semi-molecules of the nitrosochloride a double link is temporarily formed by the removal of the elements of hydrogen chloride:

This is immediately followed by the addition of hydrogen cyanide, while the bisnitroso-compound changes into the oxime :

whether the *cis*- or *trans*-form of nitrosocyanide is produced would depend, according to this hypothesis, on which of the two bonds temporarily formed is saturated by the addition of the hydrogen cyanide, and it may be supposed that the nitrosocyanide, which is formed in the smaller proportion, namely, the β -compound, would be the product of this succession of changes. The α -nitrosocyanide might be formed in a similar manner, but it appears more probable that this results from the direct substitution of CN for the chlorine of the nitrosochloride. Support is found for the above hypothesis as to the formation of a temporary double linking in the researches of von Baeyer (*Ber.*, 1893, **26**, 2861).

It is noteworthy that whilst the optical activity of the α -nitrosocyanides is in the same sense as that of the nitrosochlorides from which they are derived, the β -nitrosocyanides have specific rotation opposite in sign to that exerted by the corresponding nitrosochlorides.

Several other questions remain for further investigation, among them an inquiry as to the nature of the union between the two semi-molecules of the nitrosochlorides.

The substitution or withdrawal of the chlorine certainly renders the bisnitroso-linking unstable, but it does not appear to follow in all cases that the presence of the chlorine prevents the assumption of the oxime constitution by the nitroso-group, or that on the removal of the chlorine the derivative is necessarily unimolecular.

EXPERIMENTAL.

Preparation of the Isomeric Limonene Nitrosocyanides.

The *d*-limonene employed in these experiments was the fraction of sweet orange oil boiling at 174—176°, having sp. gr. 0.8664 at 15°, and α_D 100°22.5' in a 1-dm. tube, whence $[\alpha]_D$ 115.2°; a solution in chloroform gave $[\alpha]_D$ 119.9°. The *l*-limonene obtained from Messrs. Schimmel distilled at 172—176°, had a sp. gr. 0.8658 at 19°, and gave α_D -97°27' in a 1-dm. tube, whence $[\alpha]_D$ -112.3°.

These hydrocarbons were converted into the nitrosochlorides by Wallach's process (*Annalen*, 1889, **252**, 108), but in quantities twenty times those mentioned, addition of hydrochloric acid being temporarily

discontinued when the precipitation of the nitrosochloride induces a rapid rise of temperature; at the conclusion of the operation, 100 c.c. of alcohol were added, 75 grams of the isomeric products being thus obtained from every 100 c.c. of hydrocarbon. In order to separate the α - and β -nitrosochlorides, 150 grams of the mixture were added to 450 grams of chloroform, which dissolved the major portion, forming a deep blue liquid, the undissolved portion consisting of crude β -nitrosochloride, which was reprecipitated by methyl alcohol from the solution in 10 parts of chloroform, and finally washed with dry ether.

The bulk of both the α - and β -compounds was, however, obtained from the first solution in chloroform, from which, by adding methyl alcohol, the β -nitrosochloride was precipitated, together with the greater quantity of the α -compound, which is finally purified by dissolution in ether and precipitation with methyl alcohol, 68–70 grams of the α -nitrosochloride and 40–42 grams of the β -nitrosochloride being obtained from 150 grams of the crude mixture. Owing to the large production of a yellow oil, which arises from the action of potassium cyanide on the limonene nitrosochlorides, it has been necessary to modify the method of preparation previously indicated (Trans., 1904, 85, 931). The following process gives the best results.

Twenty grams of the pure α - or β -nitrosochloride were ground to a fine powder with 12 grams of potassium cyanide; alcohol was gradually added up to 120 c.c., the mixture being kept at 25–30°. Potassium chloride was soon deposited, whilst the liquid assumed a pale yellow colour, which deepened as the reaction proceeded, the nitrosochloride gradually disappearing; the α -nitrosochloride was completely changed in about 5 days, the β -compound requiring about 15 days, but these rates are influenced very considerably by variation in temperature. Pouring the alcoholic solution into water precipitated a colourless oil, which soon became semi-solid and weighed 18 grams; washing with light petroleum and crystallisation from the same solvent furnished two optically active nitrosocyanides, of which the preponderating modification formed thick prisms (7 grams) melting at 90–91°, the remainder (0.5 gram) crystallising in slender needles and melting at 140–141°. The less fusible isomeride is also deposited in part from the light petroleum washings, and purified by solution in chloroform and precipitation with petroleum. When the reaction is carried out above 30°, this isomeride is not readily produced. Attempts have been made to increase the yield of the nitrosocyanides by dissolving the α -nitrosochloride in ether, mixtures of alcohol with ether and of water with ether, instead of alcohol, and no better results were obtained by substituting different metallic cyanides for potassium cyanide. The α - and β -nitrosochlorides both give rise to approximately

30—35 per cent. of α -nitrosocyanide, accompanied by 2—3 per cent. of the β -modification, the remaining 60 per cent. being transformed into an oil the composition of which has not been determined.

The dextro-compound has been already described (Trans., 1904, 85, 932). Both the *d*- and *l*- α -nitrosocyanides crystallise from dilute alcohol in long, colourless, transparent, four-sided prisms, also from light petroleum in flattened prisms, readily soluble in ether, chloroform, and hot petroleum, sparingly so in cold petroleum, and insoluble in water. They melt at 90—91° without decomposition, fusing again at the same temperature. The compounds are soluble in dilute aqueous alkali, and are reprecipitated by the addition of dilute acid; a solution of bromine in chloroform is readily decolorised, and halogen acids are fixed by the cyanides. When crushed, the α -nitrosocyanides become very electrified, clinging tenaciously to the vessel. Towards hot aqueous or alcoholic potash they behave like normal nitriles, being readily hydrolysed to the corresponding amide or acid with evolution of ammonia.

The α -nitrosocyanides gradually dissolve with evolution of heat in concentrated sulphuric acid, producing a yellow, and finally a deep red, colour; on pouring the solution into water, the liquid remains clear, but on neutralising with ammonia a white, gelatinous precipitate is formed, which has not been further investigated. When heated with dilute acids, the nitrosocyanides readily yield hydroxylamine together with dark coloured, uncrystallisable products.

The α -nitrosocyanides are optically active, the sign of the rotation being the same as that of the nitrosochlorides from which they are derived.

0.5692 gram of the dextro- α -nitrosocyanide, dissolved and made up to 25 c.c. with chloroform, gave a mean rotation of $+6^{\circ}57.3'$ at 18.5° in a 2-dm. tube, whence $[\alpha]_D + 152.7^{\circ}$.

0.5524 gram of the lævo- α -nitrosocyanide in a similar way at 19° gave a mean rotation of $-6^{\circ}43.5'$, whence $[\alpha]_D - 152.2^{\circ}$.

0.1084 [*d*-] gave 14.2 c.c. nitrogen at 19.5° and 760 mm. N = 15.02.

0.1526 [*l*-] „ 19.6 c.c. „ 16° „ 760 mm. N = 14.98.

$C_{11}H_{16}ON_2$ requires N = 14.58 per cent.

Molecular weight determinations by the cryoscopic method gave :

	Weight of benzene.	Weight of substance.	Depression Δ .	Molecular weight.
Laevo-	19.29	0.0780	0.110	180.1
„	19.29	0.1812	0.235	195.9
Dextro-	20.68	0.0466	0.080	138.0
„	20.68	0.1096	0.170	152.6
„	20.68	0.1784	0.250	168.7
„	19.8	0.2204	0.300	181.8
„	19.8	0.3318	0.420	195.4

$C_{11}H_{16}ON_2$ requires 192.

0.0991 gram in 19.3 grams of naphthalene gave $\Delta = 0.1875^\circ$ for the dextrorotatory compound, whence M.W. = 191.6.

In their unimolecular character, therefore, the *d*- and *l*- α -nitrosocyanides resemble the limonene nitrolamines.

The *benzoyl* derivatives, $CN \cdot C_{10}H_{15} : NO \cdot CO \cdot C_6H_5$:

The *d*- and *l*- α -nitrosocyanides readily yield benzoyl derivatives by the Schotten-Baumann method; these crystallise from dilute alcohol in thin leaves or plates melting at 108° . They are readily soluble in chloroform and ether, and may also be crystallised from petroleum.

0.5092 gram of the *l*-benzoyl derivative, when dissolved and made up to 25 c.c. with chloroform, gave a mean rotation of $-5^\circ 11'$ at 15° in a 2-dem. tube, whence $[\alpha]_D - 127.2^\circ$.

0.5478 gram of the *d*-benzoyl derivative, treated in the same manner at 19° , gave a mean rotation of $+5^\circ 32.25'$, whence $[\alpha]_D + 126.3^\circ$.

0.1496 [*d*-] gave 12.4 c.c. nitrogen at 20.5° and 767 mm. $N = 9.55$.

0.1728 [*l*-] „ 14.6 c.c. „ 18° „ 760 mm. $N = 9.76$.

$C_{18}H_{20}O_2N_2$ requires $N = 9.46$ per cent.

The *methyl ether*, $CN \cdot C_{10}H_{15} : NO \cdot CH_3$, of the *d*- α -nitrosocyanide is a viscous oil, which is readily prepared by the action of methyl iodide and caustic potash in methyl alcohol, also by the use of silver oxide.

The *ethyl ether*, $CN \cdot C_{10}H_{15} : NO \cdot C_2H_5$, prepared in the same way, is also an oil. On passing dry hydrogen chloride through a solution of this ether in methyl alcohol, the characteristic hydrochloride is precipitated; it crystallises from dilute alcohol in large, hexagonal plates which melt at 44° . This compound was produced with the object of comparing it with the hydrochloride which is formed by the yellow oil obtained in the preparation of the nitrosocyanides, it being possible that ether formation takes place during the separation of the two halves of the bimolecular nitrosochloride. The hydrochloride of the yellow oil, however, melts at about 165° and does not resemble the foregoing substance.

The *hydrochloride* of *d*- α -nitrosocyanide, $CN \cdot C_{10}H_{15}(NOH)Cl$, is

readily obtained by adding the elements of hydrogen chloride; it crystallises from dilute alcohol in thin, transparent plates which melt at 56° .

The preparation of these compounds has been described. They crystallise in fine, woolly needles from chloroform on addition of petroleum, and in somewhat longer needles from dilute alcohol.

In order to effect a complete separation of the β -nitrosocyanide from the α -compound, the crude mixture is dissolved in a little chloroform and light petroleum added; the β -isomeride, being the less soluble, is precipitated, whilst small quantities of the α -nitrosocyanide with oily matter remain in solution. The melting point gradually rises after each precipitation until it reaches $140\text{--}141^{\circ}$ with no perceptible decomposition, but distinct softening takes place at 138° . Recrystallisation from hot light petroleum depresses the melting point, probably owing to slight decomposition. The d - and l - β -nitrosocyanides are less soluble in all ordinary solvents than the corresponding α -nitrosocyanides. They resemble the latter, however, in their solubility in dilute aqueous alkalis, being reprecipitated on addition of dilute mineral acids; if boiled with dilute acids, however, they yield hydroxylamine, but not so readily as the α -nitrosocyanides.

Action of Aqueous Alkali.—Although the quantity of the β -isomeride is small, it has been found that, on treatment with 25 per cent. aqueous potassium hydroxide, like the α -nitrosocyanide, it readily evolves ammonia, and most probably the corresponding acid is formed. The acid, however, has not been isolated, but only the product of its decomposition, namely, the oxime of dihydrocarvone, which melts at 88.5° , and is identical with that obtained by the hydrolysis of the α -nitrosocyanide.

The limonene β -nitrosocyanides are optically active, but in the opposite sense to the nitrosochlorides from which they are derived.

0.4672 gram of the d - β -nitrosocyanide, when dissolved and made up to 25 c.c. with chloroform, gave a mean rotation of $-1^{\circ}11'$ at 19° in a 2-dm. tube, whence $[\alpha]_D - 31.6^{\circ}$.

0.4528 gram of the l - β -nitrosocyanide in a similar manner gave a mean rotation of $+1^{\circ}6.5'$ at 19° , whence $[\alpha]_D + 30.6^{\circ}$.

0.1246 [d] gave 16.1 c.c. nitrogen at 19.5° and 773 mm. $N = 15.07$.

0.1020 [l] „ 13.3 c.c. „ 19° „ 762 mm. $N = 15.03$.

$C_{11}H_{16}ON_2$ requires $N = 14.58$ per cent.

Determinations of the molecular weight in benzene gave the following results :

	Weight of benzene.	Weight of substance.	Depression Δ .	Molecular weight.
Dextro-	18.94	0.0979	0.115	220.2
„	18.94	0.1911	0.215	229.9
Laevo-	20.68	0.0840	0.095	209.5
„	20.68	0.1542	0.165	221.4

$C_{11}H_{16}ON_2$ requires 192.

The *benzoyl* derivatives, $CN \cdot C_{10}H_{15} : NO \cdot CO \cdot C_6H_5$, are readily prepared by the Schotten-Baumann reaction, which crystallises from dilute alcohol in beautiful, long, silky needles melting at 121° , and yielding a somewhat soft, coherent mass when crushed. 0.5042 gram of the *d*-benzoyl dissolved and made up to 25 c.c. with chloroform gave a mean rotation of $-4^\circ 22'$ at 18° and in a 2-dcm. tube, whence $[\alpha]_D - 108.2^\circ$.

0.5324 gram of the *l*-benzoyl, in a similar manner, gave a mean rotation of $+4^\circ 38'$ at 18.15° , whence $[\alpha]_D + 108.7^\circ$. The sign of rotation is the same as that of the corresponding nitrosocyanides.

0.1635 [*d*] gave 14.1 c.c. nitrogen at 19° and 765 mm. $N = 9.97$.

0.1618 [*l*] „ 13.8 c.c. „ 15° „ 743 mm. $N = 9.76$.

$C_{18}H_{20}O_2N_2$ requires $N = 9.46$ per cent.

The *d*- and *l*- α -Amides, $C_{10}H_{15} \begin{smallmatrix} \text{NOH} \\ \diagup \text{CO} \cdot \text{NH}_2 \end{smallmatrix}$.

Twenty grams of the *d*- or *l*-limonene α -nitrosocyanide were heated on the steam-bath for about 8 days in a reflux apparatus with 25 grams of potassium hydroxide, dissolved in absolute alcohol, when the solution gave no precipitate on acidification with dilute hydrochloric acid. During the process, small quantities of ammonia were evolved, the liquid developing a brown colour, and on adding acetic acid the solution yielded a semi-solid paste which soon became crystalline. The crude product, weighing 17.5 grams, was dissolved in chloroform and precipitated with petroleum, and on repeating this operation several times, the amide became colourless and separated in tufts of slender, bulky needles. It crystallises in somewhat larger needles on adding petroleum to an ethereal solution, and melts at 138° with slight decomposition. Alcohol dissolves it very readily, dilution precipitating it incompletely; it is soluble also in dilute aqueous alkalis and acids. It readily decolorises a solution of bromine in chloroform and unites with halogen hydrides.

The *d*- and *l*- α -amides are optically active in the same sense as the nitrosocyanides and nitrosochlorides from which they are derived.

0.5050 gram of the *d*- α -amide, dissolved in chloroform and made

up to 25 c.c., gave a mean rotation of $+7^{\circ}4'$ at 17° and in a 2-dcm. tube, whence $[\alpha]_D +174.9^{\circ}$.

0.5242 gram of the *l*- α -amide, in a similar manner, gave a mean rotation of $-7^{\circ}17.8'$ at 19° , whence $[\alpha]_D -174.0^{\circ}$.

0.1258 [*d*-] gave 14.6 c.c. nitrogen at 24° and 766 mm. $N=13.13$.

0.1280 [*l*-] „ 15.0 c.c. „ 15° „ 744 mm. $N=13.43$.

$C_{11}H_{18}O_2N_2$ requires $N=13.33$ per cent.

The *methyl ether* is a viscous liquid resembling the methyl ether of the α -nitrosocyanide.

The *benzoyl* derivatives are prepared by the Schotten-Baumann reaction and crystallise from dilute alcohol in rhombic prisms, which melt sharply at 152° without decomposing. They are optically active, the introduction of the acyl group increasing the rotation strongly.

0.4180 gram of the *d*-benzoyl, dissolved in chloroform and made up to 25 c.c., gave a mean rotation of $+8^{\circ}5'$ at 19° and in a 2-dcm. tube, whence $[\alpha]_D +241.7^{\circ}$.

0.4176 gram of the *l*-benzoyl, in a similar manner, gave a mean rotation of $-8^{\circ}5'$, whence $[\alpha]_D -242.0^{\circ}$.

0.2210 [*d*-] gave 18.2 c.c. nitrogen at 24° and 760 mm. $N=9.23$.

0.1667 [*l*-] „ 13.7 c.c. „ 15° „ 745 mm. $N=9.42$.

$C_{13}H_{22}O_3N_2$ requires $N=8.91$ per cent.

The *hydrochloride* of the *d*- α -amide crystallises from dilute alcohol in slender needles and melts at $100-101^{\circ}$ without decomposing.

Twenty grams of the *d*- or *l*- α -nitrosocyanide were dissolved in 150 c.c. of 25 per cent. aqueous potassium hydroxide and boiled during 24 hours; when the reaction had proceeded several hours, the liquid gave rise to an oil which partly crystallised on allowing the contents of the flask to cool. The oil had a distinct odour of caraway (carvone), or probably of dihydrocarvone. The alkaline liquid, cooled with ice and carefully neutralised with dilute hydrochloric acid, gave 9 grams of the acid in a crystalline and almost colourless condition, together with 2.5 grams of impure acid; the by-products although partly crystalline, have not been fully investigated. The acid was purified by dissolution in a small quantity of alcohol, the solution cooled below 0° , and gradually diluted with water, which precipitated nacreous leaflets melting at 97° and evolving carbon dioxide. Re-

crystallisation was effected as quickly as possible, as the acids decompose in solution and slowly evolve carbon dioxide.

0.1738 [*d*-] gave 10.8 c.c. nitrogen at 17.5° and 751 mm. $N = 7.11$.

0.1739 [*l*-] „ 10.5 „ „ „ 15° „ 745 mm. $N = 6.92$.

$C_{11}H_{17}O_3N$ requires $N = 6.63$ per cent.

The acids rotate the plane of polarisation in the same direction as the hydrocarbons from which they arise.

0.5636 gram of the *d*-acid, dissolved and made up to 25 c.c. with chloroform, gave a mean rotation of $+4^{\circ}38.3'$ at 20° and in a 2-dcm. tube, whence $[\alpha]_D + 102.9^{\circ}$.

0.5732 gram of the *l*-acid gave a mean rotation of $-4^{\circ}46'$, whence $[\alpha]_D - 103.9^{\circ}$.

The rotations of these acids are not constant owing to the decomposition which takes place so readily in solution. In one case, in the course of 45 minutes, the rotation fell from $+4^{\circ}50'$ to $4^{\circ}20'$.

The *ammonium* salts were precipitated on passing ammonia into dried ethereal solutions of the acids. Aqueous solutions give precipitates with soluble salts of the heavy metals, but the compounds are not characteristic.

The *silver* salts prepared from aqueous solutions of the ammonium salts and silver nitrate separate in the form of colourless, bulky precipitates. They become brown on exposure to light. For analysis, the substance was washed with alcohol followed by ether, and then dried in a vacuum.

0.3134 [*d*-] gave 0.1058 Ag. $Ag = 33.76$.

0.1666 [*l*-] „ 0.0560 Ag. $Ag = 33.61$.

$C_{11}H_{16}O_3NAg$ requires $Ag = 33.93$ per cent.

The silver salts are soluble in ammonia; the aqueous or ammoniacal solutions rapidly blacken on heating.

The *methyl ester* of the *d*-acid was prepared from the silver salt and methyl iodide diluted with methyl alcohol, absence of diluent involving a vigorous action with blackening and destruction of the substance. The methyl ester melts at 65° and softens at 62°, being difficult to obtain pure owing to admixture with other decomposition products of the acid; it is soluble in dilute aqueous alkali.

0.1983 gave 11.6 c.c. nitrogen at 19° and 758 mm. $N = 6.69$.

$C_{12}H_{19}O_3N$ requires $N = 6.20$ per cent.

The readiness with which solutions of the acids lose carbon dioxide in chloroform, ether, or alcoholic solution, is remarkable; when dry and pure, they can be preserved in the desiccator, but exposure to the

air involves gradual decomposition. The acids dissolve readily in ammonium carbonate or sodium hydrogen carbonate, but are not soluble in mineral acids or water; at the melting point, a vigorous disengagement of carbon dioxide occurs, and ammonia is also liberated in small quantities. The residue has a strong odour of carraway, and reduces Fehling's solution. It would therefore appear that besides loss of carbon dioxide, a partial elimination of the :NOH group takes place, yielding hydroxylamine and the ketone dihydrocarvone. These facts serve to account for the variety of products obtained on hydrolysing the cyanides.

In order to ascertain the proportion of carbon dioxide lost by the α -nitrosoacid, weighed quantities were heated to 130° .

0.5559 gave 0.1129 CO_2 . $\text{CO}_2 = 20.31$.

0.5335 „ 0.1082 CO_2 . $\text{CO}_2 = 20.28$.

$\text{C}_{11}\text{H}_{17}\text{O}_3\text{N}$ requires $\text{CO}_2 = 20.85$ per cent. for the loss of 1 molecule of carbon dioxide.

The solid residue was associated with a small proportion of dihydrocarvone, and by crystallisation from dilute alcohol the former was obtained in long needles, melting at 88.5° , Wallach (*Annalen*, 1894, 279, 381) giving the melting point $88-89^\circ$ for the oxime of dihydrocarvone. The identity of this substance was established by treating it with hydrogen bromide in glacial acetic acid; on pouring the solution into water, a white, crystalline hydrobromide was obtained melting and decomposing at $109-110^\circ$. According to Wallach, the normal oxime gives a hydrobromide melting at 109° , whilst the *isooxime* does not yield a corresponding derivative (*Annalen*, 1894, 279, 382).

0.1898 [*d*-] gave 14.5 c.c. nitrogen at 24° and 769 mm. $\text{N} = 8.67$.

0.1547 [*l*-] „ 11.0 c.c. „ at 16° „ 769.5 mm. $\text{N} = 8.41$.

$\text{C}_{10}\text{H}_{17}\text{ON}$ requires $\text{N} = 8.38$ per cent.

The following determinations were made of the rotatory powers of the *d*- and *l*-dihydrocarvoximes:

0.4738 gram of the *d*-oxime, dissolved in chloroform and made up to 25 c.c., gave a mean rotation of $+0^\circ 21.5'$ at 20° and in a 2-dcm. tube, whence $[\alpha]_D + 9.45^\circ$.

0.4068 gram of the *l*-oxime gave a mean rotation of $-0^\circ 18'$, whence $[\alpha]_D - 9.25^\circ$.

The Racemic Compounds.

The racemic α -nitrosocyanide was prepared by mixing 2.5 grams each of the *d*- and *l*- α -nitrosocyanides, dissolved in alcohol; water precipitated an oil, which soon crystallised and melted at 81° . The

product dissolves less readily in hot petroleum, and crystallises in small, hard, ill-defined prisms. As would be anticipated from the melting point, the racemic compound is more soluble in common media than the active compounds. Its solution is optically inactive.

0.1442 gave 18.6 c.c. nitrogen at 16° and 746.5 mm. $N = 14.75$.

$C_{11}H_{16}ON_2$ requires $N = 14.58$ per cent.

The *benzoyl* derivative crystallises from dilute alcohol in prisms which melt at 96°; it is more soluble than its active components, which melt at 108°.

0.1532 gave 13.4 c.c. nitrogen at 17° and 747.6 mm. $N = 9.98$.

$C_{18}H_{20}O_2N_2$ requires $N = 9.46$ per cent.

The racemic β -nitrosocyanide, prepared from 1 gram each of the active compounds dissolved in a little alcohol, crystallises in slender needles on dilution, and melts at 159—160° without decomposing. It is less soluble than the active compounds and is optically inactive.

0.1344 gave 17.2 c.c. nitrogen at 17° and 762.5 mm. $N = 14.89$.

$C_{11}H_{16}ON_2$ requires $N = 14.58$ per cent.

The *benzoyl* derivative crystallises from dilute alcohol in long, colourless needles with silky lustre and melts at 98°, softening at 96°.

0.1544 gave 13.0 c.c. nitrogen at 18° and 764 mm. $N = 9.77$.

$C_{18}H_{20}O_2N_2$ requires $N = 9.46$ per cent.

The racemic α -amide, prepared from solutions in chloroform of 2 grams of each of the *d*- and *l*-amides, separates quickly, whilst light petroleum precipitates it as a fine, crystalline powder. It crystallises from alcohol on addition of water in prisms or prismatic needles melting at 155° with slight evolution of gas.

The solution in chloroform was optically inactive.

0.1402 gave 16.2 c.c. nitrogen at 18° and 764 mm. $N = 13.43$.

$C_{11}H_{18}O_2N_2$ requires $N = 13.33$ per cent.

The active compounds are extremely soluble in alcohol and are not readily precipitated by addition of water.

The *benzoyl* derivative crystallises from dilute alcohol in hard prisms which melt at 150° without decomposition. The active compounds melt at 152°.

0.1747 gave 13.5 c.c. nitrogen at 16° and 769 mm. $N = 9.12$.

$C_{18}H_{22}O_3N_2$ requires $N = 8.91$ per cent.

The racemic α -acid separates almost immediately on mixing alcoholic solutions of 3 grams each of the *d*- and *l*- α -acids; it melts at 116° with vigorous evolution of carbon dioxide.

0.2004 gave 11.8 c.c. nitrogen at 18° and 770 mm. $N = 6.89$.

$C_{11}H_{17}O_3N$ requires $N = 6.63$ per cent.

The *ammonium* salt separates as a fine, crystalline powder on passing ammonia into the dried ethereal solution of the acid.

The *silver* salt, prepared from an aqueous solution of the ammonium salt and slight excess of silver nitrate, is precipitated in the amorphous condition.

0.3236 gave 0.1088 Ag. $Ag = 33.62$.

$C_{11}H_{16}O_3NAg$ requires $Ag = 33.93$ per cent.

The racemic acid resembles the *d*- and *l*-acids in losing carbon dioxide, the racemic oxime of dihydrocarvone being formed; this melts at 115° and crystallises from dilute alcohol in prismatic needles. Wallach (*Annalen*, 1893, **275**, 117) gives 115 — 116° for the melting point of this oxime.

0.1170 gave 8.7 c.c. nitrogen at 17° and 763 mm. $N = 8.66$.

$C_{10}H_{17}ON$ requires $N = 8.38$ per cent.

The Oily By-products.

The yellow oil, which forms some 50—60 per cent. of the total product when the preparation of the nitrosocyanides is conducted at 25 — 30° , constitutes almost the sole product at higher temperatures; it decomposes when distilled under reduced pressure, and is only very slightly volatile in steam. Dilute alkalis dissolve it sparingly, but it is insoluble in dilute acids, which eliminate hydroxylamine on heating. A solution of bromine in chloroform is immediately decolorised, from which only oily products could be obtained.

When heated with 25 per cent. aqueous potassium hydroxide, the oil gradually dissolves, much ammonia being liberated, and there separates an oil which slowly deposits carvoxime, and on removing this with ether and acidifying the aqueous liquid with hydrochloric acid a colourless specimen of the acid was obtained, identical with that derived from the α -nitrosocyanide; 30 grams of the original oil yielded 5.3 grams of acid and 4.2 grams of carvoxime.

Ten grams of the yellow oil were next dissolved in methyl alcohol and saturated with dry hydrogen chloride; on adding the solution to crushed ice, a semi-solid was precipitated, and on crystallising this from dilute alcohol a small quantity of a compound which melts and evolves gas at 165° was obtained. It becomes discoloured at about 161° , and the crystals possess a peculiar stickiness, which is not removed by recrystallisation. Analysis showed that the substance contains approximately 10 per cent. of nitrogen and 16 per cent. of chlorine, but

these results do not agree with the requirements of any unimolecular compound likely to arise from the foregoing reaction. Molecular weight determinations by the depression of the freezing point of benzene gave the following results:

Weight of benzene.	Weight of substance.	Depression Δ .	Molecular weight.
20.0	0.0792	0.060	323.4
20.0	0.1670	0.125	327.3

The substance is therefore probably bimolecular.

0.5688 gram of the substance, dissolved and made up to 25 c.c. with chloroform gave a mean rotation of $+9^{\circ}52.6'$ at 19° and in a 2-dm. tube, whence $[\alpha]_D +217^{\circ}$.

The corresponding *lævo*-compound has not yet been prepared.

The investigation of these compounds, and of the oils obtained from the α - and β -nitrosochlorides will be continued.

I desire to express my indebtedness to Professor Tilden for the valuable advice which I have received from him during the progress of this work.

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