XXIX.—*The Triazo-group. Part XVII. Nitrosoazides of Pinene and Terpeneol.*

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DURING the thirty-five years which have elapsed since pinene nitrosochloride was characterised by Tilden, the substance itself, and the reaction upon which it is based, have continued to furnish data of interest and importance to the chemistry of the terpene

series. Early in the history of the nitrosochlorides, it was found that whilst the action of sodium ethoxide withdraws the elements of hydrogen chloride, treatment with a primary aliphatic amine involves an exchange of chlorine for the substituted ammonia residue, the products being called nitrolamines. Variations of this reaction have been described by Tilden and Burrows (Trans., 1905, **87**, 344), Tilden and Leach (Trans., 1904, **85**, 931), Leach (Trans., 1907, **91**, 1), and Cusmano (*Gazzetta*, 1910, **40**, ii, 122), as the results of which pinene nitrosocyanide, the limonene nitrosocyanides, pinene nitrolamine, and pinene hydroxylamineoxime, respectively, have been brought to light. The general applicability of this reaction suggested the possibility of introducing the triazo-group into the pinene nucleus by the action of sodium azide on the nitrosochloride, and we find that this change may be brought about very easily, the yield of nitrosoazide leaving little to be desired.

Pinene nitrosoazide is a unimolecular substance, melting at 120° , dissolving readily in organic media, and distilling slowly in steam. Alcoholic sodium ethoxide quickly removes the elements of hydrazoic acid, forming nitrosopinene, but the analogy to the nitrosochloride does not extend to the action of piperidine, for this base also produces nitrosopinene instead of the nitrolpiperidide, behaving, in fact, like diethylamine with the nitrosochloride. This indication of the presence of an *isonitroso*-group is confirmed by the production of an acetyl derivative (m. p. 64°), but on attempting to convert the nitrosoazide into the triazoketone, as prescribed by Wallach (*Annalen*, 1906, **346**, 220) for the isolation of carvopinone from nitrosopinene, namely, hydrolysis with aqueous oxalic acid, it was found that hot water alone gives rise to an isomeric pinene nitrosoazide, melting at 126° , and yielding an acetyl derivative which melts at 71° . Two possibilities present themselves as an explanation of this change, either inversion of the carbon atom which carries the methyl and triazo-groups, or transference of the latter to a neighbouring atom, similar to the rearrangement which takes place when hydrogen chloride converts pinene into bornyl chloride. We believe that the latter alternative underlies the transformation in question. Although it is true that sodium ethoxide withdraws hydrazoic acid from the isomeric pinene nitrosoazide (m. p. 126°), thereby producing nitrosopinene, the following formulæ made it clear that the latter might arise from an isomeride differing in structure from the original pinene nitrosoazide (m. p. 120°). As, moreover, the action of hot water on the isomeride involves disruption of the tetramethylene ring, and leads to the oxime of hydroxydihydrocarvone with elimination of hydrazoic acid, it is natural to conclude that

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it is one of the carbon atoms involved in this disruption which carries the azoimide nucleus; interchange of the latter with a methyl group being precluded, the representation we suggest seems the most probable:

The terpineol nitrosoazide represented above was prepared from inactive terpineol, melting at 35° , by converting it into the nitrosochloride, and acting on this with alcoholic-aqueous sodium azide. Thus the hydroxydihydrocarboxime obtained from it by the action of sodium ethoxide is inactive also, and is identical with the specimen produced from the isomeric pinene nitrosoazide (m. p. 126°).

Progress has been made in the extension of this reaction to other nitrosochlorides, including those of limonene, and the results will be described later.

EXPERIMENTAL.

Pinene Nitrosoazide, $C_{10}H_{15}(\cdot NOH) \cdot N_3$.

Fifty grams of freshly prepared pinene nitrosochloride were suspended in 250 c.c. of 84 per cent. alcohol containing 24 grams of sodium azide, and gently warmed; at the first sign of action, the flask was withdrawn from the steam-bath, and allowed to remain at about 40° during one hour. This treatment was repeated throughout the day, when it was found that the nitrosochloride had passed into solution, leaving a suspension of sodium chloride; the liquid was then diluted with water until crystallisation began. At no time was a blue or green colour noticed, and an occasional test for free hydrazoic acid gave only the faintest indication of that substance. The filtered product, which weighed 40 grams, was recrystallised from hot alcohol, then from a mixture of benzene and petroleum, and finally from benzene alone, 4 grams requiring about 15 c.c. of the hot solvent, which deposited brilliant, colourless, transparent prisms, melting to a colourless liquid at 120° :

0.2122 gave 0.4474 CO_2 and 0.1490 H_2O . $C=57.50$; $H=7.87$.

0.0950 „, 22.0 c.c. N_2 at 18° and 767 mm. $N=27.13$.

$C_{10}H_{16}ON_4$ requires $C=57.63$; $H=7.74$; $N=26.92$ per cent.

The substance is freely soluble in cold ethyl acetate, chloroform, acetone, and hot benzene or alcohol, less readily in boiling petroleum. It is insoluble in 15 per cent. potassium hydroxide, and the solution in concentrated sulphuric acid effervesces only slowly on being stirred vigorously; with stannous chloride in hydrochloric acid, however, liberation of nitrogen takes place more actively. In steam the nitrosoazide is somewhat volatile, the vapour having a terpenoid and pungent odour, producing the disagreeable throbbing effect in the head which is so characteristic of the aliphatic azoimides. A determination of molecular weight by depression of the freezing point of benzene gave the mean value 227, $C_{10}H_{16}ON_4$ requiring 208.

Conversion into Nitrosopinene.—The nitrosoazide was heated under reflux with alcohol in which one atomic proportion of sodium

had been dissolved, precipitation of sodium azide taking place very rapidly. After three hours the liquid was poured into water, which precipitated nitrosopinene, identified with a specimen prepared from the nitrosochloride. The same substance, melting at 131° , was obtained by the action of piperidine in hot alcohol, this base failing to yield the nitrolpiperidide, which melts at $118-119^{\circ}$.

The Acetyl Derivative.—On heating pinene nitrosoazide with acetic anhydride during a few hours on the steam-bath, water precipitated a material which was recrystallised twice by diluting a solution in warm acetic acid:

0.1212 gave 23.2 c.c. N_2 at 20° and 774 mm. $N=22.23$.

$C_{12}H_{18}O_2N_4$ requires $N=22.41$ per cent.

The substance is very freely soluble in organic media, even petroleum, from which it separates in aggregates of tough, transparent, rectangular prisms, melting at 64° .

The Isomeric Pinene Nitrosoazide (m. p. 126°).

On subjecting a considerable quantity of the nitrosoazide (m. p. 120°) to steam distillation, it was noticed that the solid distillate, even after recrystallisation, melted very indefinitely at $80-100^{\circ}$, whilst the residual liquid deposited lustrous, colourless needles, melting at 133.5° , and no longer containing the triazo-group. Accordingly, 10 grams were heated under reflux during six hours on the steam-bath with about 100 c.c. of water and sufficient alcohol to ensure the return of the volatile nitrosoazide to the flask; a current of steam then carried over 3.5 grams of a colourless solid, accompanied by a considerable proportion of hydrazoic acid, whilst the hot aqueous residue yielded about 3 grams of the substance melting at 133.5° . The distillate was recrystallised three times from hot petroleum, in which it is more readily soluble than the original nitrosoazide, forming lustrous, transparent, six-sided prisms, melting at 126° :

0.1818 gave 0.3838 CO_2 and 0.1284 H_2O . $C=57.57$; $H=7.90$.

0.1361 „ 31.3 c.c. N_2 at 17° and 764 mm. $N=26.84$.

$C_{10}H_{16}ON_4$ requires $C=57.63$; $H=7.74$; $N=26.92$ per cent.

Thus the product appears to be isomeric with the original material, the melting point of which was depressed to about 100° by admixture. The presence of the triazo-group was revealed by effervescence with concentrated sulphuric acid and a hydrochloric acid solution of stannous chloride. The cold substance has a distinct, terpenoid colour, which becomes very pronounced in steam. A determination of molecular weight by depression of the freezing point of benzene gave the mean value 224, $C_{10}H_{16}ON_4$ requiring 208.

Action of Alcoholic Sodium Ethoxide.—Two grams were heated

under reflux with 15 c.c. of alcohol, in which 0.3 gram of sodium had been dissolved, and having been poured into water after two hours, rendered faintly acid with acetic acid. The precipitate was crystallised first from alcohol, then from petroleum, when it melted at 131° , and did not depress the melting point of nitrosopinene when mixed with it.

The Acetyl Derivative.—Three grams of the isomeride of pinene nitrosoazide (m. p. 126°) were heated with 10 c.c. of acetic anhydride during three hours on the steam-bath; the solid obtained on dilution was crystallised twice from dilute acetic acid, and finally from hot petroleum, which deposited aggregates of brittle, transparent plates, melting at 71° ; a mixture of this product with the isomeric acetyl derivative (m. p. 64°) became liquid at about 50° :

0.1284 gave 24.0 c.c. N_2 at 18° and 781 mm. $N=22.20$.

$C_{12}H_{18}O_2N_4$ requires $N=22.41$ per cent.

The substance is very freely soluble in organic media.

Action of Hot Water.—Two grams of the nitrosoazide (m. p. 126°) were heated under reflux with water and a small quantity of alcohol during six hours, when a current of steam was passed through the liquid; 1.1 gram of unchanged material was carried over, along with hydrazoic acid, whilst the residual liquid deposited lustrous needles identical with the above-mentioned by-product melting at 133.5° . This was found on analysis to have the composition $C_{10}H_{17}O_2N$:

0.1649 gave 0.3976 CO_2 and 0.1431 H_2O . $C=65.77$; $H=9.70$.

0.2273 „, 15.4 c.c. N_2 at 17° and 759 mm. $N=7.85$.

$C_{10}H_{17}O_2N$ requires $C=65.57$; $H=9.37$; $N=7.65$ per cent.

We were thus led to suspect identity with the oxime of hydroxy-dihydrocarvone, stated by Wallach to melt at $133-134^{\circ}$, and on preparing the diacetyl derivative from our product, this melted at 107° , the temperature recorded by Wallach for that substance. The presence of the oximino-group was further indicated by the action of hot dilute sulphuric acid, which eliminated hydroxylamine.

The Benzoyl Derivative.—By the action of benzoyl chloride in 10 per cent. sodium hydroxide, a monobenzoyl derivative was produced:

0.2194 gave 9.8 c.c. N_2 at 17° and 764 mm. $N=5.12$.

$C_{17}H_{21}O_3N$ requires $N=4.88$ per cent.

It melts at $83-84^{\circ}$ after crystallisation from a mixture of benzene and petroleum.

Terpineol Nitrosoazide, $C_{10}H_{16}(OH)(:NOH) \cdot N_3$.

Thirteen grams of nitrosochloride, prepared from inactive terpineol (m. p. 35°), were suspended in 100 c.c. of 84 per cent. alcohol, and allowed to remain with 6 grams of sodium azide at about 40° until the suspended material consisted of sodium chloride. This occupied a few hours, and did not involve change of colour or liberation of hydrazoic acid. On pouring the product into water, terpineol nitrosoazide separated as an oil which solidified very slowly, the first crop weighing 5 grams; a further quantity separated from the mother liquor in the course of another week. The product was moistened with cold petroleum, drained on earthenware, and recrystallised twice from the minimum quantity of hot benzene, which deposited clusters of small, transparent, six-sided plates, melting at 111° :

0.1717 gave 0.3337 CO_2 and 0.1244 H_2O . $C=53.01$; $H=8.11$.

0.0952 „ 20.2 c.c. N_2 at 19° and 779 mm. $N=25.01$.

$C_{10}H_{16}O_2N_4$ requires $C=53.05$; $H=8.02$; $N=24.80$ per cent.

The substance is freely soluble in organic media, excepting petroleum, which dissolves it sparingly on boiling; it is also somewhat soluble in cold water, crystallising slowly in long, six-sided prisms. The nitrosoazide is odourless, even in boiling water, but the azidic character is revealed by effervescence with concentrated sulphuric acid and a hydrochloric acid solution of stannous chloride. When heated with alcoholic sodium ethoxide, sodium azide is precipitated, and hydroxydihydrocarboxime is formed (m. p. 133.5°).

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