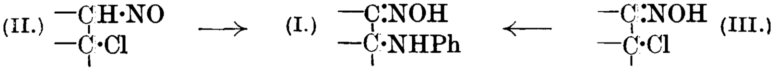
CLXXVI.—*The Recovery of Pinene from its Nitrosochloride.*

By JOHN CAMPBELL EARL and JAMES KENNER.

THE observation by Wallach (*Annalen*, 1889, **252**, 132; 1890, **258**, 343), that pinene can be regenerated from its nitrosochloride by heating this with aniline, has remained unique until the present time. All other nitrosochlorides which have been examined in this respect furnish nitrolanilides (I) :—

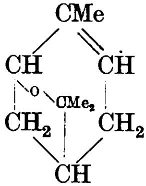


$$\text{(II.)}\ \begin{array}{l}-\text{CH}\cdot\text{NO}\\ -\text{C}\cdot\text{Cl}\end{array} \longrightarrow \text{(I.)}\ \begin{array}{l}-\text{C:NOH}\\ -\text{C}\cdot\text{NHPh}\end{array} \longleftarrow \begin{array}{l}-\text{C:NOH}\\ -\text{C}\cdot\text{Cl}\end{array}\ \text{(III.)}$$

This applies equally to the bisnitrosochlorides such as those of limonene and pinol, which dissociate to a greater or less extent in solution into the unimolecular, blue nitroso-compounds (II), and also to the *iso*nitrosochlorides (III) exemplified by pinol *iso*nitrosochloride (Wallach and Sieverts, *Annalen*, 1899, **306**, 278). The nitrosochloride of trimethylethylene also exists in the two forms (Schmidt, *Ber.*, 1902, **35**, 3727), and again from each of these we have obtained by reactions conducted at the ordinary temperature a nitrolanilide agreeing in properties with that prepared by Schmidt from the nitrosonitrate (*Ber.*, 1902, **35**, 2339; also Wallach, *Annalen*, 1887, **241**, 296). These results, together with the close structural relationship of both pinol (IV) and trimethylethylene (V) to pinene

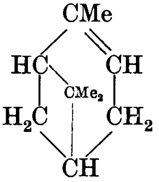
(VI), only serve to accentuate the exceptional nature of the reaction between aniline and pinene nitrosochloride.

(IV.)



(V.)

$$\begin{matrix}CMe_2\\ \| \\ CHMe\end{matrix}$$

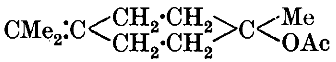


(VI.)

There is one class of nitrosochlorides the behaviour of which with aniline has not been investigated previously, namely, those which are constitutionally unable to pass into the *iso*nitroso-form. The derivatives of tetramethylethylene (VII) and γ-terpinyl acetate (VIII) were therefore examined in this respect, and both reproduced the behaviour of pinene.

(VII.)

$$\begin{matrix}CMe_2\\ \| \\ CMe_2\end{matrix}$$



$$CMe_2{:}C{<}\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}{>}C{<}\begin{matrix}Me\\ OAc\end{matrix}$$

(VIII.)

The parent unsaturated compounds were recovered and identified by reconversion into the characteristic nitrosochlorides, and diazoaminobenzene was the other product of the reaction. But the velocity of reaction is much less in these cases than in that of pinene nitrosochloride, a difference which must be ascribed in part to the readiness with which the latter compound loses hydrogen chloride. For, as we have found, it is converted into nitrosopinene by simply boiling its solution in carbon tetrachloride, whereas Schmidt and Leipprand (*Ber.*, 1904, **37**, 545) observed that the nitrosobromide of tetramethylethylene is only slowly acted upon by aqueous potassium hydroxide. It is known that acids assist the condensation of aniline with nitrosobenzene, and, correspondingly, a comparative experiment showed that the interaction of aniline and tetramethylethylene nitrosochloride is accelerated by the addition of aniline hydrochloride at the outset. Even then, however, the velocity of reaction is much less than in the case of the pinene derivative, a point which will be referred to in more detail later.

Not only does hydrogen chloride accelerate, but it actually determines the course of the reaction in the case of pinene nitrosochloride. The formation of " nitrolamines " by the action of piperidine and the aliphatic amines (Wallach, *Annalen*, 1887, **241**, 296; 1888, **245**, 253; 1889, **252**, 107; 1891, **262**, 327) may be attributed to the greater efficiency of these bases, compared with aniline, in neutralising the hydrogen chloride which is necessarily liberated. For, as has now been found, *pinene nitrolanilide* is obtainable by allowing the interaction of the nitrosochloride and aniline to take place in the presence of either pyridine or sodium acetate. It is, however, essential that these reagents should be employed in a homogeneous solution. For when the reaction was allowed to proceed in chloroform solution in presence of either anhydrous sodium acetate or crystalline lead acetate, diazoaminobenzene was formed. This observation was, however, of value in that diazoaminobenzene had apparently not previously been isolated as such from this reaction, but only after conversion into aminoazobenzene.*

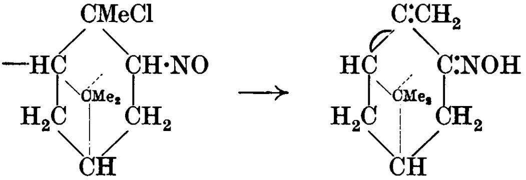
It would therefore seem that, whereas in nitrolanilide formation the chlorine is the first point of attack by the base, Wallach's reaction is due to the preferential reactivity of the nitroso-group, aided by a small proportion of hydrogen chloride derived from the chlorine atom :

$$C_7H_{12}<\begin{array}{l}\text{CMeCl}\\ \text{CH·NO}\end{array} \longrightarrow C_7H_{12}<\begin{array}{l}\text{CMeCl}\\ \text{CH·N:NPh}\end{array} \longrightarrow C_7H_{12}<\begin{array}{l}\text{CMe·NHPh}\\ \text{CH·N:NPh}\end{array}$$

(IX.) (X.)

The question whether the diazoaminobenzene originates in the reaction by the coupling of aniline with benzenediazonium chloride eliminated from the preliminary condensation product (IX), or from an anilide (X) derived from the latter, is for the present left in abeyance.

It remains to be explained why pinene nitrosochloride, in its usual behaviour towards aniline, ranges itself with the nitrosochlorides of tetramethylethylene and γ-terpinyl acetate rather than with those compounds to which its formula shows it to be more closely related, and which are capable of transition into the *iso*nitroso-form. It seems obvious that the reason for this peculiarity must be sought in the strained condition of the bonds uniting the central atom of the *gem*-dimethyl group with the rest of the pinene molecule. This produces a state of unsaturation which asserts itself in the conversion of pinene into sobrerol, and is very possibly responsible for the readiness, already mentioned, with which pinene nitrosochloride is converted into nitrosopinene :



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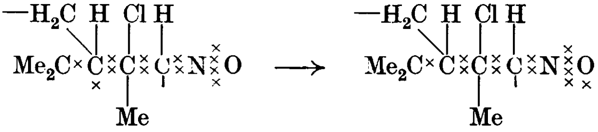
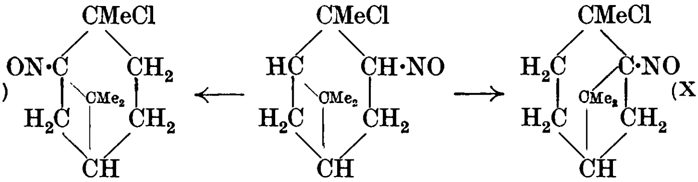
* In quite another direction also, this matter is one requiring further attention, since, in each of the experiments made, the diazoaminobenzene was first isolated in the labile form described by Walther (*J. pr. Chem.*, 1897, **55**, 551).

If, now, this unsaturation be transmitted as a general polar effect along the chain to the nitroso-group, the conditions are such as to enhance the unsaturation of the nitroso-group, as indicated by the following scheme (compare Robinson, *J. Soc. Chem. Ind.*, 1925, 456T) :



It is therefore conceivable that the nitroso-group may be so reactive as to condense with aniline before passing into the *iso*nitroso-condition. At the same time, it must be emphasised that in the cases of pinol nitrosochloride and trimethylethylene nitrosochloride, already mentioned, where both forms are known, the nitroso- as well as the *iso*nitroso-isomerides are converted by aniline into nitrolanilides. Further, it is agreed that transmission of electronic displacement does not occur so readily through a saturated as through an unsaturated chain. For these reasons, it seems more plausible to assume that the condensation with aniline is preceded by a molecular rearrangement of the nitrosochloride such as to render it formally analogous to those compounds which it resembles in behaviour, and to confer the condition of unsaturation, already mentioned, on the carbon atom directly attached to the nitroso-group. These results would be achieved by the change of the nitrosochloride into (XI), involving migration of the nitroso-group and a hydrogen atom, or into (XII) by interchange of hydrogen and the *gem*-dimethyl group :



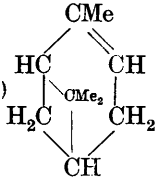
(XI.) (XII.)

An $\alpha\gamma$-change of this type is most probably involved in the formation of β- from α-dichlorocamphane under the influence of phosphorus pentachloride below 0°, and of *iso*fenchyl from fenchyl alcohol (Meerwein and Wortmann, *Annalen*, 1923, **435**, 190), and perhaps also in the generation of inactive pinol from active sobrerol by hot dilute mineral acids.

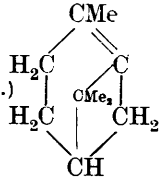
Of the alternatives (XI) and (XII), the latter is perhaps preferable, since lability of the *gem*-dimethyl group may, for the reasons already indicated, be expected to be greater than that of the nitroso-group.

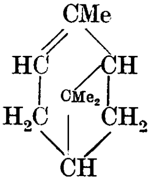
The product (XIII), derived from (XII) by elimination of the elements of nitrosyl chloride, must, according to Bredt's rule (*Ber.*, 1902, **35**, 1286), suffer a rearrangement, and this might lead either to α- or to β-pinene. But the easy conversion of β- into α-pinene by various means (Austerweil, *Bull. Soc. chim.*, 1926, **39**, 695; Delépine, *ibid.*, pp. 1475, 1479; Richter and Wolff, *Ber.*, 1926, **59**, 1733) makes it clear that the disturbed system arising from (XI) should settle down into an α-pinene. Lynn (*J. Amer. Chem. Soc.*, 1919, **41**, 361) has shown experimentally that the optically active nitrosochloride obtainable at low temperatures from active pinene reverts, on treatment with aniline, to a hydrocarbon having the same rotatory power as that originally used. The substance (XIII) can conform to this result only if interchange of the *gem*-dimethyl group and a hydrogen atom occurs. The simpler migration of a hydrogen atom would lead to the enantiomorph (XV) of the original pinene (XIV).

(XIV.)



(XIII.)





(XV.)

EXPERIMENTAL.

Action of Aniline on Trimethylethylene Nitrosochloride, m. p. 74—75°.—A solution of the nitrosochloride (3 g.) in chloroform (50 c.c.) was allowed to remain with aniline (7 g.) at the ordinary temperature for 17 hours. The resulting crystalline mass was dissolved by addition of water and more chloroform, and the anilide isolated from the chloroform solution by evaporation of the solvent at the ordinary temperature. After purification in the usual manner by solution in acetic acid and precipitation by ammonia, the crystalline product (3·7 g.) melted at 143° (Found, by micro-analysis: N, 14·3. $C_{11}H_{16}ON_2$ requires N, 14·5%).

Action of Aniline on Trimethylethylene iso*Nitrosochloride*, m. p. 48—49°.—The change of the nitrosochloride, m. p. 74—75°, to its *iso*nitroso-isomeride requires the closest adherence to the conditions prescribed by Schmidt (*Ber.*, 1902, **35**, 3734). For example, in one experiment in which stirring of the hot mass was momentarily neglected, a syrupy product insoluble in light petroleum was obtained in place of the crystalline *iso*nitroso-compound. Similar material is also gradually produced when the nitrosochloride is kept even at 0° in a stoppered bottle.

The *iso*nitrosochloride, m. p. 46—47° (0·45 g.), chloroform (5 c.c.), and aniline (0·62 g.) were allowed to react, and the product isolated, precisely in the manner just described for the nitroso-chloride. The crystalline product (0·48 g.) melted at 143° and did not depress the melting point of the above material.

Action of Aniline on the Nitrosochloride of Tetramethylethylene.—In place of the method described by Thiele (*Ber.*, 1894, **27**, 455) tetramethylethylene was prepared much more conveniently and economically by the conversion of amylene hydrate successively into trimethylethylene, its chlorohydrin, and dimethyl*iso*propylcarbinol, which was then dehydrated. Details of the procedure will be published elsewhere by one of us (J. C. E.).

(*a*) When a mixture of the nitrosochloride (2 g.), excess of aniline (6 c.c.), and alcohol (16 c.c.) was boiled under reflux, the green colour disappeared completely in 5 minutes. After a further 5 minutes, one half of the solution was cooled, treated with concentrated hydrochloric acid (6 c.c.), and kept at 0° for 2 hours. Aminoazobenzene hydrochloride (0·4 g.) was then collected and identified by liberation of the base, m. p. 119°. After crystallisation from alcohol, this, alone or mixed with authentic aminoazobenzene, melted at 124°.

An attempt to isolate the hydrocarbon from the other portion of the solution by distillation in steam was unsuccessful. Modified conditions of experiment were therefore devised for this purpose.

(*b*) A solution of the nitrosochloride (3 g.) and aniline (7 g.) in xylene (30 c.c.) was heated under reflux in boiling water for 40 minutes. By fractionation with a bead column a volatile fraction was obtained, from which, on redistillation, the hydrocarbon (1·3 c.c., b. p. 73—83°) was isolated. It was identified by conversion into the characteristic blue nitrosochloride (1·0 g.), m. p. 119—120°, which did not depress the melting point of the original material.

(*c*) A solution of the nitrosochloride (1 g.) and aniline (1·24 g.) in alcohol (15 c.c.) was divided into two equal portions. After the addition of aniline hydrochloride (0·5 g.) to one portion, both were left at the ordinary temperature for 3½ hours. Each portion then still retained a green colour, but that to which the hydrochloride had been added was perceptibly tinged with yellow. The difference in colour of the two became very much more marked when they were immersed side by side in a bath at 56—60°; after 10 minutes, the one containing the hydrochloride was orange brown, whilst the other still retained a green shade.

Action of Aniline on the Nitrosochloride of γ-Terpinyl Acetate.—The melting point of this nitrosochloride was given by Baeyer (*Ber.*, 1894, **27**, 445) as 82°, but material which had been repeatedly purified by precipitation from alcoholic solution by addition of water as recommended by Baeyer usually melted at about 77°. The discrepancy is perhaps attributable to polymerisation, since a sample which had been preserved for several weeks and again recrystallised was almost colourless and melted at 95° (Found, by micro-analysis : N, 5·2. Calc. for $C_{12}H_{20}O_3NCl$: N, 5·3%).

A mixture of the nitrosochloride (1 g.), aniline (0·36 g.), and alcohol (25 c.c.) became deep red when boiled under reflux for 35 minutes. By distillation in steam, a yellowish oil (0·5 c.c.) was isolated from which a blue nitrosochloride (0·12 g.) was obtained. This melted at 76° after precipitation from alcoholic solution by means of water, and did not depress the melting point of the original nitrosochloride.

Formation of Nitrosopinene from Pinene Nitrosochloride.—When a solution of the nitrosochloride (2 g.) in carbon tetrachloride (40 c.c.) was heated, depolymerisation was indicated by the development of a blue colour. This, however, disappeared almost immediately, presumably owing to formation of the *iso*nitroso-isomeride, and at the same time evolution of hydrogen chloride set in. After boiling for 2 minutes, the solution was cooled, and the solvent was allowed to evaporate at the ordinary temperature. By maceration of the sticky residue with ice-water, hydrochloric acid was removed. After further purification by crystallisation from light petroleum, nitrosopinene (0·38 g.), m. p. 131°, was obtained.

Pinene Nitrolanilide.—(*a*) A mixture of pinene nitrosochloride with a solution of crystallised sodium acetate (10 g.) and aniline (2·3 g.) in alcohol (150 c.c.) was boiled for 5 minutes and cooled, and excess of ice-water added. A sticky mass separated and gradually solidified. After reprecipitation by addition of ammonia to a diluted and filtered solution of the material in glacial acetic acid, it was further purified by crystallisation from light petroleum. The *anilide* was thus obtained in small, yellowish, hexagonal prisms (1·95 g.), m. p. 122° (Found, by micro-analysis : N, 10·6. $C_{16}H_{22}ON_2$ requires N, 10·8%).

(*b*) A solution of the nitrosochloride (1 g.) in chloroform (15 c.c.) was added to a mixture of aniline (0·46 g.) and pyridine (2 g.) in chloroform (5 c.c.) at 20°. After 16 hours, the solution was washed with water, dried over sodium sulphate, and allowed to evaporate at the ordinary temperature. After purification in the manner just described, the anilide (0·2 g.) was obtained crystalline, m. p. 121°, and did not depress the melting point of material prepared by the preceding method.

Diazoaminobenzene from Pinene Nitrosochloride.—As an alternative to the procedures just described, a solution of the nitrosochloride (2 g.) in chloroform (30 c.c.) was shaken with aniline

(0·92 g.) in presence of finely powdered, crystalline lead acetate (3·8 g.) at the ordinary temperature for 2½ hours. After filtering from lead chloride, the solution was allowed to evaporate at the ordinary temperature. Unchanged nitrosochloride (0·92 g.), m. p. 109—110°, remained after extraction of the residue with alcohol. The cooled alcoholic solution deposited yellow needles (0·5 g.), m. p. 79—80°, on careful dilution with water.

This material represented the labile form of diazoaminobenzene, to which Walther ascribed the melting point 79—81° (*J. pr. Chem.*, 1897, **55**, 551). The material melted at 91—92° (Found : N, 21·2. Calc. : N, 21·3%) after crystallisation from alcohol, and at 98° after further crystallisation from ligroin.

Exactly similar phenomena resulted from the use of anhydrous sodium acetate in place of lead acetate.

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