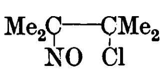
CCLXXXIV.—*The Action of Hydrogen Iodide on Nitroso-compounds.*

By JOHN CAMPBELL EARL and JAMES KENNER.

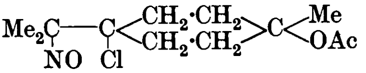
THE observation of the ortho-para directive influence of the nitroso-group in aromatic substitution was considered by Ingold (J., 1925, **127**, 513) to be in conflict with the theory of induced alternate polarity, but a theoretical discussion of the nitroso-group by Robinson (*Chem. and Industry*, 1925, **44**, 456) showed this to be at least not necessarily the case. In addition, it was pointed out (Kenner, Tod, and Witham, J., 1925, **127**, 2343) that, quite apart from any purely theoretical considerations, the well-known liberation of iodine from hydrogen iodide by nitrous acid, by hypochlorous acid, and by hydrogen peroxide is a simple experimental indication of possible similarity in polar properties of the nitroso-group, the chlorine atom, and the hydroxyl group. The analogy is not perfect, since in the case of nitrous acid the primary nitrogenous product undergoes a further reaction with formation of nitric oxide, but a parallelism also exists between the behaviours of the nitroso-group and chlorine, in that each is readily displaced from *N*-nitroso- or -chloro-amines and -acetanilides (von Pechmann and Frobenius, *Ber.*, 1894, **27**, 651).

It seemed that further evidence in regard to the nature of the nitroso-group might be obtained from a study of the action of hydrogen iodide on nitroso-compounds in general. Reference to the literature showed that among aliphatic compounds, iodine is liberated from hydrogen iodide by the nitrosochlorides of tetramethylethylene (I) (Thiele, *Ber.*, 1894, **27**, 456) and $\Delta^{4(8)}$-menthen-1-ol (γ-terpineol) acetate (II) (Baeyer, *ibid.*, p. 446). Later, Baeyer showed the nitrosobromide of 1-bromo-$\Delta^{4(8)}$-menthene to be converted into the hydroxylamino-derivative (III) by hydrogen bromide, in the presence of red phosphorus as an absorbent of the bromine liberated, and concluded that the reaction with hydrogen iodide follows a similar course. Baeyer observed (*loc. cit.*) that the nitrosochlorides of tetramethylethylene and menthenol acetate behaved differently towards hydrogen bromide in acetic acid. There is, however, no essential difference between the two reactions. The product derived from tetramethylethylene nitrosochloride is a basic substance, which, like the compounds examined by Baeyer, loses the elements of hydrogen chloride when it is liberated in the presence of alkali. The colourless *hydrochloride* of the resulting unsaturated base exhibits reducing properties and its composition corresponds with the formula (IV). In further support of the constitution assigned to this compound, it was shown to furnish a *condensation product* with salicylic aldehyde, the composition of which was in accord with the formula (V) (compare Bamberger, *Ber.*, 1894, **27**, 2556).

(I.)



$$\underset{NO}{Me_2C}-\underset{Cl}{CMe_2}$$

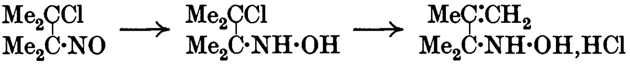


$$\underset{NO}{Me_2C}-\underset{Cl}{C}{<}\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}{>}C{<}\begin{matrix}Me\\ OAc\end{matrix}$$

(II.)

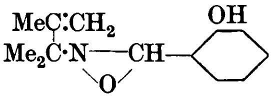
$$\underset{NH\cdot OH}{Me_2C}-\underset{Br}{C}{<}\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}{>}C{<}\begin{matrix}Me\\ Br\end{matrix}$$

(III.)



$$\begin{matrix}Me_2CCl\\ Me_2C\cdot NO\end{matrix} \longrightarrow \begin{matrix}Me_2CCl\\ Me_2C\cdot NH\cdot OH\end{matrix} \longrightarrow \begin{matrix}MeC{:}CH_2\\ Me_2C\cdot NH\cdot OH,HCl\end{matrix}$$

(IV.)



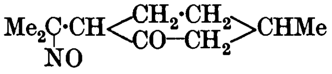
(V.)

There seemed also a possibility that the negative character of the nitroso-group might induce positive polarity in the chlorine atom, which, in the presence of hydrogen iodide, would render it liable to displacement by hydrogen. It was, however, shown that this does not occur in either of the above instances, since the quantity of iodine liberated in the reaction was found to correspond approximately with the decrease in the amount of halogen ion present in solution. The slight discrepancy was shown to be attributable to formation of chlorine ions by hydrolytic action, which occurred in absence of hydrogen iodide under otherwise similar experimental conditions.

Since the conditions for the transmission of the influence of the nitroso-group to the chlorine atom should be more favourable in the aromatic nucleus than in the above compounds, the behaviour of *p*-chloronitrosobenzene towards hydrogen iodide was investigated. Here also reduction occurred, being immediately followed by condensation of the hydroxylamine with the nitroso-derivative, so that 4 : 4′-dichloroazoxybenzene was produced in excellent yield. No elimination of halogen occurred from *p*-chloronitrosobenzene or from its meta-isomeride under the conditions employed. The nitroso-group itself is therefore the sole point of attack by hydrogen iodide in such cases. Doubtless its reactivity in the aromatic compounds is affected by the position of the chlorine atom, but our hopes of demonstrating this relationship could not be realised owing to the uncertainty as to the relative proportions of polymerised and unpolymerised material present in solution, and to the condensation of nitroso- with hydroxylamino-derivatives just mentioned.

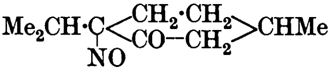
In order further to demonstrate the general character of the reaction here discussed, δ-nitroso-δ-methylpentan-β-one (VI) (Harries, *Ber.*, 1898, **31**, 1379), 8-nitrosomenthone (VII) (Harries and Rolder, *Ber.*, 1899, **32**, 3365), and 4-nitrosomenthone (VIII) (Baeyer, *Ber.*, 1894, **27**, 1912; 1895, **28**, 1586) were examined qualitatively in respect of their behaviour towards hydrogen iodide.

(VI.) $\mathrm{CMe_2(NO)\cdot CH_2\cdot COMe}$



$$\mathrm{Me_2\underset{NO}{C}\cdot CH{<}\begin{matrix}CH_2\cdot CH_2\\ CO-CH_2\end{matrix}{>}CHMe}$$

(VII.)



$$\mathrm{Me_2CH\cdot \underset{NO}{C}{<}\begin{matrix}CH_2\cdot CH_2\\ CO-CH_2\end{matrix}{>}CHMe}$$

(VIII.)

In each case, iodine was liberated, but the rate of reaction, as in other cases, was affected by the degree of polymerisation of the nitroso-compounds.

It may therefore be concluded that nitroso-compounds, in general, are reduced by hydrogen iodide to the corresponding hydroxylamines. The facility with which this occurs is in remarkable contrast to the behaviour of carbonyl compounds, with which nitroso-compounds are in some respects comparable. The significance of this contrast will be dealt with in a subsequent paper discussing the chemistry of nitroso-compounds. Meanwhile, the possibility must be entertained in the case of nitrous acid, also, that

$$\mathrm{HO\cdot NO \longrightarrow HO\cdot NH\cdot OH}\ \text{(IX.)} \qquad \mathrm{H\cdot NO}\ \text{(X.)}$$

the primary action leads to the formation of dihydroxyammonia (IX) rather than of nitroxyl (X), as might be anticipated from the analogy between the nitroso- and hydroxyl groups or the chlorine atom mentioned at the outset of this paper. This possibility must also be regarded as the more probable, when it is recalled that the ultimate nitrogenous product of the reaction is nitric oxide, the formation of which could be represented by the equation $NH(OH)_2 + HO{\cdot}NO \longrightarrow 2NO + 2H_2O$ (compare Raschig, " Schwefel und Stickstoffstudien," Leipzig, 1925, p. 19; Angeli and Angelico, *Gazzetta*, 1900, **30**, i, 593; *Ber.*, 1904, **37**, 2390).

EXPERIMENTAL.

Reduction of Tetramethylethylene Nitrosochloride by Hydrogen Bromide.—A concentrated glacial acetic acid solution of hydrogen bromide (42 c.c.) was mixed with red phosphorus (1·4 g.) and cooled in ice-water until crystallisation commenced (12°); tetramethylethylene nitrosochloride (7 g.) was then added with thorough stirring. The reaction was completed by passing a stream of hydrogen bromide into the ice-cooled mixture during a period of 1 hour, and stirring for another 2 hours. The liquid was then added to a mixture of ice (60 g.) and water (60 g.), and the undissolved material filtered off. Benzene (50 c.c.) was added, together with sufficient sodium hydroxide solution to render the aqueous layer strongly alkaline. The liberated base passed into solution in the benzene, and after further extraction of the alkaline solution with benzene, the united extracts were shaken four times with hydrochloric acid (25 c.c.) diluted with an equal volume of water. The solid residue obtained by evaporating the united acid extracts to dryness under reduced pressure was purified by filtering its solution in alcohol, and again evaporating to dryness. The *hydrochloride* of *β-hydroxylamino-βγ-dimethyl-Δ^{γ}-butene* so obtained (4·5 g.) was further purified by recrystallisation from alcohol (Found: N, 9·5; Cl, 23·1. $C_6H_{13}ON,HCl$ requires N, 9·2; Cl, 23·2%). The base reduced Fehling's solution in the cold.

When the hydrochloride (0·8 g.) was dissolved in water (5 c.c.) with the addition of crystalline sodium acetate (1·2 g.), salicylic aldehyde (0·65 g.), and alcohol (5 c.c.), condensation readily occurred at the ordinary temperature. After 19 hours, the mixture was poured into ice water, and an oil separated which soon crystallised. The solid (0·55 g.) was filtered off, and a further quantity (0·2 g.) separated on saturating the filtrate with salt and cooling in ice. After one crystallisation from alcohol, the *condensation product* melted sharply at 53° (Found, by micro-analysis: N, 6·4. $C_{13}H_{17}O_2N$ requires N, 6·4%).

Reduction of Tetramethylethylene Nitrosochloride by Hydrogen Iodide.—A solution of the nitrosochloride (0·1355 g.) in pure benzene

(10 c.c.) was shaken with a mixture of an approximately $N/5$-solution of potassium iodide (corresponding to 19·94 c.c. of accurately $N/5$-solution) and an approximately $N/2$-solution of sulphuric acid (20 c.c.). After 3½ hours, the benzene layer, which contained the bulk of the liberated iodine, was separated, and the aqueous layer extracted with benzene until practically colourless. The halogen ion in the aqueous solution was then titrated with silver nitrate and potassium thiocyanate in the usual way, and found equivalent to 13·12 c.c. of $N/5$-solution. The united benzene solutions were shaken with excess of standard sodium thiosulphate, the excess being titrated with standard iodine. The iodine thus determined corresponded to 7·43 c.c. of $N/5$-solution.

It would thus appear that halogen corresponding to 0·61 c.c. of $N/5$-solution had been furnished by elimination of chlorine from the nitrosochloride. This occurred by hydrolysis, for when a similar benzene solution of the nitrosochloride was shaken for 3½ hours with dilute sulphuric acid under very similar conditions, the aqueous layer contained halogen corresponding to 2·0 c.c. of $N/5$-solution. In this case, of course, there was no decrease in the concentration of the nitrosochloride solution owing to reduction during the experiment, so that the amount of hydrolysis is higher than in the reduction experiments.

Reduction of γ-Terpinyl Acetate Nitrosochloride by Hydrogen Iodide.—The reaction was slower than in the case of the tetramethylethylene derivative so that a higher concentration of the nitrosochloride (0·2466 g. in 10 c.c. of benzene) was employed, and the shaking was continued for 5 hours. In other respects, the experimental conditions were similar to those described above.

Halogen originally present in aqueous solution = 19·94 c.c.
„ finally „ „ „ „ = 18·75 c.c.
Iodine liberated = 1·37 c.c.

Here, again, there is evidence of slight hydrolysis.

Reduction of Chloronitrosobenzenes by Hydrogen Iodide.—Both the *m*- and *p*-isomerides were examined in the usual way, 0·5 g. of the substance in benzene (10 c.c.) being used, and the shaking being continued for 4 hours.

	m-.	*p*-.
Halogen originally present in aqueous solution (c.c. of $N/5$)	19·94	19·94
„ finally „ „ „ „	17·82	18·72
Iodine liberated (c.c. of $N/5$)..	2·08	1·57

These results indicate a similarity in behaviour to the two nitrosochlorides, but in neither case was there any evidence of the removal of chlorine by hydrolysis.

An attempt was made to modify the reduction in such a way that the isolation of the reduction products would be possible. For this purpose, it was necessary to introduce some substance to remove the iodine as formed. Red phosphorus, mercury, and sodium thiosulphate were all successfully employed. Thus a mixture of *p*-chloronitrosobenzene (1 g.) red phosphorus (1 g.), and glacial acetic acid (25 c.c.) was well stirred at room temperature, and hydriodic acid (*d* 1·7; 5 c.c.) added drop by drop during 5 minutes. The mixture became warm and a mass of crystalline material separated. After a further 5 minutes, water was added, and the precipitated material was filtered off and washed thoroughly with water. The *pp'*-dichloroazoxybenzene was extracted from the residue by repeated maceration with ether, and the solvent allowed to evaporate at room temperature. The product so obtained (0·83 g.) melted at 153—154°, and at 154° after one recrystallisation from alcohol (Found, by micro-analysis: N, 10·7. Calc. for $C_{12}H_8ON_2Cl_2$: N, 10·5%). In another experiment the azoxy-compound (0·7 g., m. p. 153°) was obtained from the nitroso-derivative (0·85 g.), glacial acetic acid (25 c.c.), mercury (9·5 g.), and hydriodic acid (*d* 1·7; 3 c.c.).

From *m*-chloronitrosobenzene by means of phosphorus, *mm'*-dichloroazoxybenzene, m. p. 96°, was obtained (Found: N, 10·1%).

Action of Hydriodic Acid on the Nitroso-derivatives.—δ-Nitroso-δ-methylpentan-β-one yielded a colourless solution in acetone, which only reacted very slowly at the ordinary temperature with hydriodic acid, but when the solution was first warmed until a definite blue colour had developed, and then cooled, liberation of iodine occurred much more rapidly. 8-Nitrosomenthone, though blue when first prepared, slowly polymerises and therefore also reacts comparatively slowly with hydriodic acid in acetone solution. 4-Nitrosomenthone was definitely recognised by Baeyer (*loc. cit.*) to be a bis-compound, but nevertheless has some tendency towards dissociation since its solution in xylene became blue when heated. Although no similar development of colour occurred in boiling acetone solution, yet iodine was slowly liberated when a cold solution in acetone was treated with hydriodic acid.

Note on the Action of Hydriodic Acid on Ether.—Whilst it is well known that hydrogen iodide reacts with ethyl ether to form ethyl iodide, it is not recorded in the standard work of reference that they react in some way at the ordinary temperature with formation of iodine. This was observed in connexion with the experiments now described, and prevented the use of ether as solvent in cases where it would otherwise have been very desirable. The only reference to this reaction which we have been able to find is a statement by Hantzsch, who experienced the same difficulty and stated that " Jodwasserstoff in diesem Medium schon durch unvermeidliche Spuren von Sauerstoff zum Trijodwasserstoff oxydiert wird " (*Z. Elektrochem.*, 1923, **29**, 232). In a quantitative experiment with ether purified in the usual manner (20 c.c.), aqueous potassium iodide solution (*N*/5, 20 c.c.), and dilute sulphuric acid (*N*/2, 20 c.c.), the iodine liberated after some days at the ordinary temperature required 8·5 c.c. of *N*/10-thiosulphate.

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