

XXXV.—*Action of Nitrosyl Chloride on Unsaturated Compounds.*

By WILLIAM A. TILDEN, D.Sc., F.R.S., and MARTIN O. FORSTER,
Ph.D.

THE action of nitrosyl chloride on the olefines was found by Tilden and Sudborough to result in the formation of the dichloride only from ethylene, of a mixture of the dichloride and nitrosochloride from propylene and isobutylene, whilst trimethylethylene and phenylethylene yield a crystalline nitrosochloride unaccompanied by the dichloride (*Trans.*, 1893, **63**, 479). Recently, tetramethylethylene has been found by Thiele (*Ber.*, **27**, 455) to readily give a nitrosochloride in almost theoretical quantity; this compound is of interest because there can be no doubt about its constitution. As it contains only methyl groups and no hydrogen in connection with the ethylenic carbon atoms, combination can only take place in one way, namely, to form a true nitroso-compound, $\text{Cl}(\text{CH}_3)_2\text{C}\cdot\text{C}(\text{CH}_3)_2\text{NO}$. It is described as being of a blue colour, and giving solutions of the same tint. A vivid blue, or, in some cases, a green colour, appears to be characteristic of mononitroso-compounds. Those compounds which, though containing a nitroso-group, are colourless, belong either to the oximes or possess a different constitution at present unknown. The blue colour is shown when in the liquid state by nitrous anhydride and nitrous acid, as well as by the nitrosonitroparaffins (pseudonitrols), nitrosobenzene (Bamberger and Storch, *Ber.*, **26**, 473), nitrosoaniline, nitrosomethylaniline, nitroso-orthotolidine, and other compounds. This blue coloration is also produced during the action of nitrosyl chloride or of nitrous acid on many of the un-

saturated compounds experimented with, especially in the early stages of the process, although the crystalline compound ultimately obtained is colourless. This leads us to think that probably in such cases the formation of true nitroso-compounds is actually the first step in the process. We have now ascertained that the nitrosochlorides of propylene, butylene, and amylene (trimethylethylene), are in reality isonitroso-compounds or oximes, and that they yield hydroxylamine by spontaneous decomposition in the presence of moisture, or by boiling with solvents. The substance described as deposited after long standing from the propylene nitrosochloride (footnote, *Trans., loc. cit.*, 481) is, in fact, hydroxylamine hydrochloride itself, the nitrosochloride from which it is formed being a liquid. The supposed second nitrosochloride (m. p. 152°) from amylene is also hydroxylamine hydrochloride.

Amylene nitrosochloride (m. p. 74—75°), when distilled in a current of steam, was found to undergo partial decomposition, in this point resembling tetramethylethylene nitrosochloride described by Thiele (*loc. cit.*). The aqueous distillate, which had a pungent, camphor-like odour, was free from nitrous acid and did not reduce Fehling's solution, but the residual liquid in the distillation flask was odourless, and, though strongly acid to test paper, gave none of the reactions of nitrous acid, reducing Fehling's solution, however, immediately in the cold. Evaporated on a water bath, a crystalline residue was obtained (m. p. 152—153°) consisting of hydroxylamine hydrochloride. Recrystallised from water, and dried at 80°, it gave the following result on analysis.

0.1500 gave 0.3032 AgCl. Cl = 50.53.

Hydroxylamine hydrochloride requires Cl = 51.08 per cent.

8 grams of amylene nitrosochloride sealed up in a tube with 30 c.c. of water, and heated for two hours in a water bath, yielded 3.5 grams of hydroxylamine hydrochloride, the calculated amount being 4.1 grams. Associated with the hydroxylamine hydrochloride was a small quantity of a fragrant, volatile oil, but we have not accumulated enough of this substance to determine its constitution.

Amylene nitrosochloride, dissolved in alcohol and boiled with a slight excess of piperidine, yields a nitropiperidine, which crystallises slowly in small, colourless needles on adding water to the alcoholic solution. This compound melts at 96—97°. Determination of nitrogen gave the following results.

0.1297 gave 16.8 c.c. moist nitrogen at 12° and 751.0 mm. N = 15.20.

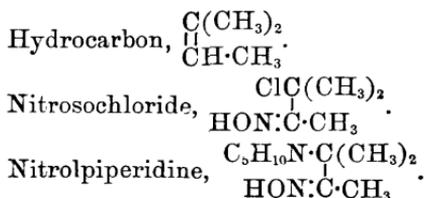
0.1193 „ 15.6 c.c. „ „ 16° „ 758.1 „ N = 15.20.

$C_{10}H_{20}N_2O$ requires N = 15.22 per cent.

It forms a platinum salt, which was found to contain 24.98 per

cent. of platinum, the calculated percentage for $(C_{10}H_{20}N_2O)_2, H_2PtCl_6$, being 25.01.

It may be remarked that, as there is but one atom of hydrogen united to the ethylenic carbon in trimethylethylene, and as the nitrosochloride yields hydroxylamine on hydrolysis, its constitution is fully established, and may be represented as follows.



The following compounds have been operated on in addition to the compounds referred to in the former paper (T. and S., *loc. cit.*).

Hexylene (Methylpropylethylene), $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH : CH \cdot CH_3$.

The liquid used in these experiments was obtained from mannito by the action of hydriodic acid, and the subsequent treatment with potash of the secondary iodide thus obtained. It was procured from Kahlbaum.

Hexylene mixed with chloroform was cooled by immersion in a mixture of ice and salt, and submitted to the action of gaseous nitrosyl chloride (NOCl). The products obtained were liquid; when dried air was blown over the surface in order to evaporate the solvent, the liquid became blue, and colourless needles separated. These when drained were deliquescent and soluble in water, giving an acid liquid which reduced Fehling's solution immediately in the cold. The solution also gave Angeli's reaction for hydroxylamine, which consists in adding a little sodium nitroprusside to the solution, then caustic soda, and boiling; a brilliant, magenta-red colour is developed (*Gaz.*, **23**, ii, 102; *Abstr.*, 1894, ii, 67). The crystals melt at 150—152°, disengagement of gas occurring almost immediately.

It will be seen, therefore, that hexylene nitrosochloride is very unstable, resembling the analogous compound derived from propylene.

Caprylene (Methylpentylethylene), $CH_3 \cdot CH : CH \cdot C_5H_{11}$, or normal octylene, $CH_2 \cdot CH \cdot C_6H_{13}$.

Caprylene (from castor oil) behaved in the same way as hexylene when submitted to a similar treatment. On standing for some time, the liquid deposited long, colourless needles of hydroxylamine hydrochloride.

NITROSYL CHLORIDE ON UNSATURATED COMPOUNDS. 327

Stilbene (Diphenylethylene), $C_6H_5 \cdot CH : CH \cdot C_6H_5$.

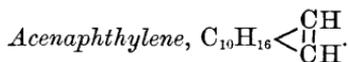
Stilbene, dissolved in the minimum quantity of chloroform, was submitted to the action of nitrosyl chloride at -10° ; the solution soon became dark red, and smelt strongly of nitrosyl chloride. On allowing the chloroform to evaporate spontaneously, a colourless, amorphous compound was obtained, which smelt strongly of benzoyl chloride. The product was washed with cold chloroform, and then with cold ether; after this treatment, it melted with evolution of gas at $138-139^\circ$. At this stage, an analysis gave the following numbers, from which it will be seen that partial chlorination has occurred.

	Found.		
	I.	II.	Calculated for $C_{14}H_{12}NOCl$.
Nitrogen.....	5.40	—	5.70
Chlorine.....	17.1	16.9	14.5

On boiling this compound with strong hydrochloric acid, hydroxylamine is not formed. In this respect, the stilbene compound resembles that obtained from cinnamene.



Phenanthrene dissolved in ten times its weight of chloroform was treated with nitrosyl chloride at the temperature of melting ice. The solution became red, and yielded, on fractional precipitation with alcohol, first a portion containing chlorine but no nitrogen, and afterwards unaltered phenanthrene. Nitrosyl chloride was also bubbled through a solution of phenanthrene in twice its weight of dry benzene. The liquid became warm and dark red, a brown resin separating; on standing for 12 hours in the dark, yellow needles (m. p. 209°) were deposited, containing 23.5 per cent. of chlorine, but no nitrogen. The substance slowly turned green on exposure to sunlight. It probably consists of dichlorphenanthraquinone, $C_{14}H_6Cl_2O_2$, which contains 25.6 per cent. of chlorine.



Acenaphthylene, prepared from acenaphthene, does not combine with nitrosyl chloride in chloroform solution, even when allowed to remain at the atmospheric temperature for several hours.



A solution of cinnamic acid in five parts of dry boiling benzene was allowed to cool, and then saturated with nitric peroxide obtained by heating dry lead nitrate. Heat was developed, and the acid which

had crystallised out redissolved. The dinitrocinnamic acid (m. p. 72°), which separated on allowing the liquid to cool, was quickly washed with benzene, then dried, and finally treated with cold water, which converts it into *o*-nitrocinnamene with evolution of carbon dioxide. When recrystallised from dilute alcohol it forms long, yellow needles, melting at 58° (Gabriel, *Ber.*, **18**, 2438). When the pure nitro-compound was dissolved in chloroform and treated with nitrosyl chloride at a low temperature, the solution became red, but no combination took place, the unaltered compound crystallising out on evaporation of the solvent. The introduction of the nitro-group therefore prevents the formation of an addition compound with nitrosyl chloride, though not with chlorine or bromine.

Crotonic acid, $\text{CH}_3\cdot\text{CH}\cdot\text{CH}\cdot\text{COOH}$.

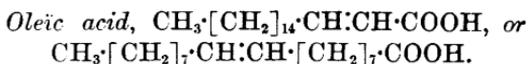
Solutions of crotonic acid in chloroform have failed to yield an addition compound when submitted to the action of nitrosyl chloride at various temperatures, the unaltered acid (m. p. 72°) crystallising out in each case on evaporating the solvent.

Dry crotonic acid was soon dissolved by liquid nitrosyl chloride when sealed up with it, and on opening the tube after it had remained at the ordinary temperature for some time, a considerable quantity of gas, containing carbon dioxide, was evolved. On allowing the excess of nitrosyl chloride to evaporate, a green oil was obtained, which, on standing for some time in a desiccator, became blue, and ultimately colourless. It had a pungent smell, recalling that of the substance obtained from propylene. It did not decolorise bromine. After remaining in a desiccator over lime for some days, the oil was found to contain 28·18 per cent. of chlorine. This approaches the figure for monochlorobutyric acid, which contains 28·9 per cent. of chlorine. When distilled under a pressure of 40 m.m. a liquid passed over which after some weeks deposited a few crystals of hydroxylamine hydrochloride.

It seems probable that an unstable addition compound is formed in the first instance by crotonic acid, but that this is resolved into carbon dioxide and propylene nitrosochloride, which in its turn gives hydroxylamine hydrochloride in the presence of moisture.

Isocrotonic or Allocrotonic acid, $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{COOH}$.

When liquid nitrosyl chloride is mixed with isocrotonic acid there is no sign of action, and the unaltered acid is left on allowing the chloride to evaporate, retaining its property of decolorising bromine. When isocrotonic acid is sealed up in a tube with liquid nitrosyl chloride, and allowed to remain for some time at the ordinary temperature, carbon dioxide is eliminated, and a product similar to that derived from crotonic acid is obtained.



On passing nitrosyl chloride into oleic acid dissolved in chloroform and kept at a temperature below -15° , the solution becomes red, and no rise of temperature is observed. If, however, the solution be allowed to remain at the ordinary temperature during the operation, the liquid assumes a green tint, and a considerable rise in temperature, amounting to about 20° , is observed. If now the chloroform be rapidly evaporated by passing a current of air over the surface of the liquid, the residue consists of a mixture of a crystalline substance with unchanged oleic acid. It is dissolved in warm spirit, from which waxy scales separate, melting, after repeated crystallisation from spirit, at $98-99^\circ$. Another preparation, made under similar conditions, melted at 102° . The appearance of the crystals, and the proximity of their melting point to that of elaidic acid nitrosochloride ($99-100^\circ$), renders it probable that these two compounds are identical. Neither compound yields hydroxylamine hydrochloride on boiling with hydrochloric acid. On analysis, numbers were obtained which correspond with the formula $\text{C}_{18}\text{H}_{34}\text{O}_2\text{NOCl}$.

Elaidic acid.

Five grams of elaidic acid were dissolved in about 50 c.c. of dry chloroform and submitted to the action of a current of gaseous nitrosyl chloride. The solution became red, and the temperature rose to about 35° , the colour finally changing to green. By means of a current of dried air, the chloroform was evaporated as quickly as possible, a pale blue oil remaining, which solidified to a crystalline paste when left in a desiccator for 12 hours. It was redissolved in warm alcohol, which deposited white, waxy, crystalline plates on standing. It is difficult to obtain the compound quite free from oil, the latter lowering the melting point to a remarkable degree, even when the analytical results give no evidence of impurity. By repeated recrystallisation from alcohol, however, the substance was obtained in small nodules of colourless crystals (m. p. $99-100^\circ$). The following results were obtained on analysis.

0.1530 gave 6 c.c. moist nitrogen at 20° and 751 m.m. $\text{N} = 4.43$.

0.2534 „ 0.1034 AgCl (Carius). $\text{Cl} = 10.09$.

$\text{C}_{18}\text{H}_{34}\text{O}_2\text{NOCl}$ requires $\text{N} = 4.03$; $\text{Cl} = 10.18$ per cent.

Elaidic acid nitrosochloride is readily soluble in ether, chloroform, benzene, and alcohol, but is insoluble in water.

Cinnamic acid, } \text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{COOH.}

Hitherto all attempts to obtain an addition compound of cinnamic acid with nitrosyl chloride have failed. Below -15° the gas is

altogether without action, unaltered cinnamic acid (m. p. 133°) crystallising out on removing the solvent by evaporation; an experiment in which the acid remained in contact with the chloride for a considerable time at the ordinary temperature gave the same result. Another attempt was made under conditions similar to those adopted by Gabriel (*Ber.*, 18, 2438) for the preparation of dinitrocinnamene. The acid was dissolved in 5 parts of dry boiling benzene, nitrosyl chloride being passed through the paste of crystals obtained by cooling the solution. Much heat was developed, and the solution became dark red, but after remaining for 48 hours in the dark no solid matter separated, and on evaporating the solvent, unaltered cinnamic acid, free from nitrogen, and melting at 130°, was deposited.

2 grams of cinnamic acid were then sealed up in a tube with about 10 c.c. of liquid nitrosyl chloride, and allowed to remain for several hours at the ordinary temperature. The acid, which was at first in a state of suspension, soon became dissolved, and on opening the tube there was evidence of very considerable pressure, the escaping gas containing a large proportion of carbon dioxide. On allowing the excess of nitrosyl chloride to evaporate, a green oil remained, from which colourless crystals were deposited. The oil possessed a pungent odour reminiscent of hyacinths (characteristic of the halogen derivatives of cinnamene), its vapour acting as a powerful irritant on the mucous membrane of the eyes and nose. The solid substance which separates after recrystallisation from alcohol is obtained in colourless scales melting at 158—160°, evolution of gas taking place at a higher temperature. When dissolved in cold potash, and reprecipitated by cold dilute hydrochloric acid, it is completely converted into cinnamic acid. It does not contain nitrogen, and, when heated with dry lime, it yields cinnamene. If the product be repeatedly crystallised from dilute alcohol, it is obtained in brilliant, white scales which melt without decomposition at 167°, and contain 28·02 per cent. of chlorine. Dichlorohydrocinnamic acid is described as melting at 162—164°, and contains 32·42 per cent. of chlorine.

Although it separates from boiling water in lustrous scales which melt at 165°, the difference in the percentage of chlorine is so great as to point to some chemical change having taken place; it was now found to contain only 12·83 per cent. of the halogen.

The original compound (m. p. 167°) dissolved readily in chloroform, and the solution does not decolorise bromine. It is always associated with a green oil, but neither it nor the oil loses hydroxylamine when boiled with hydrochloric acid.



Anethoïl obtained from oil of anise, and boiling between 228° and 236°, was dissolved in chloroform and kept at a temperature of -10°,

while a current of gaseous nitrosyl chloride was passed through the liquid; the contents of the vessel soon became converted into a pasty mass of crystals, which were quickly collected by means of the filter pump, and washed with cold chloroform until free from unaltered anethoïl. Owing to the difficulty of obtaining a suitable solvent from which to recrystallise the compound, it was repeatedly extracted with hot alcohol until the melting point was constant. It was then redissolved in chloroform, which, after the addition of alcohol, was allowed to evaporate, and the specimen obtained in this way was dried in a vacuum, and analysed.

0.2757 gave 15.6 c.c. moist nitrogen at 16° and 756.5 mm. N = 6.34.

0.2036 „, 0.1326 AgCl (Carius). Cl = 16.28.

$C_{10}H_{12}O \cdot NOCl$ requires N = 6.57; Cl = 16.57 per cent.

Anethoïl nitrosochloride melts at 127°, decomposing at this temperature with the formation of a brown tar. If a few grams of the substance be placed in a flask and fusion be started at one point, the heat evolved by the decomposition spreads through the mass, the whole of which melts without further application of heat. Hydroxylamine is not obtained when anethoïl is boiled with hydrochloric acid, either in aqueous or alcoholic solution. It is easily soluble in chloroform and benzene, less readily in ether, and practically insoluble in alcohol.

Tönnies (*Ber.*, 12, 169) describes the preparation of a nitrosochloride from anethoïl, but no analysis or melting point is given, and no mention is made of any of its properties.

Eugenol, $C_8H_3(OH)(O \cdot CH_3) \cdot CH_2 \cdot CH : CH_2$ [= 4 : 3 : 1].

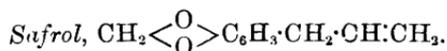
Eugenol was prepared by decomposing with hydrochloric acid the potassium salt obtained from oil of cloves, the eugenol being thrown out as an oil, which was collected, dried by means of calcium chloride, and distilled, passing over at 250—252°. Attempts to combine eugenol with nitrosyl chloride were unsuccessful. A solution of the oil in chloroform, when cooled to a temperature below -10° , became dark red, but, on allowing the solvent to evaporate, the substance was left unaltered. A similar result was obtained at the ordinary temperature.

Eugenol Ethylic Ether.

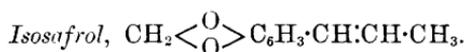
The ethylic ether of eugenol was obtained from eugenol by boiling it with aqueous potash and ethylic bromide until the latter was completely dissolved, the ether being precipitated as an oil on the addition of water.

A solution of the ether in chloroform became dark red on treatment with nitrosyl chloride at various temperatures; it does not, however,

unite with it, and in no case was evidence of the formation of a addition compound obtained.



Sassafras oil was freed from phenolic constituents by treatment with aqueous potash. After being washed several times with water, and dried by means of calcium chloride, a specimen of safrol was obtained which distilled between 231° and 233°. The safrol was dissolved in chloroform, the solution becoming dark red on treatment with nitrosyl chloride, but in this case, as in that of the two preceding compounds, no nitrosochloride was formed.



Isosafrol was prepared according to the method described by Polek (*Ber.*, 17, 1940). Safrol was heated with sodium formate and caustic potash for three hours at 250°. The isosafrol, obtained by submitting the crude product to steam distillation, was dried by calcium chloride and distilled, boiling at 239—243°

If a solution of isosafrol in chloroform be mixed with nitrosyl chloride in the same solvent, the dark red colour of the latter is destroyed, and the liquid becomes warm, depositing colourless crystals on cooling. The product is more conveniently obtained by passing a current of gaseous nitrosyl chloride through a mixture of equal parts of chloroform and isosafrol, the temperature of the liquid being kept between -10° and 0°. The crystals which separate, having been freed from mother liquor, are extracted successively with alcohol, glacial acetic acid, benzene, and, finally, once more with alcohol. Having been dried in a vacuum, it gave the following numbers on analysis.

0.2074 gave 11.6 c.c. moist nitrogen at 22° and 748 mm. N = 6.23.

0.1720 „ 0.1060 AgCl (Carius). Cl = 15.41.

$\text{C}_{10}\text{H}_{10}\text{O}_2 \cdot \text{NOCl}$ requires N = 6.16; Cl = 15.57 per cent.

Isosafrol nitrosochloride melts with decomposition at 150°, darkening somewhat, shortly before this temperature is reached. In a paper recently published by Angeli (*Gazzetta*, 22, ii, 445; *Abstr.*, 1893, i, 263), since our experiments with this compound were brought to a close, the melting point of isosafrol nitrosochloride is said to be 132°. Our crude product melted at 135°, but a substance of constant melting point was only obtained after repeated extraction with various solvents.

It is insoluble in cold alcohol, cold benzene, ether, and hot glacial acetic acid, and only sparingly soluble in chloroform, from which

it is thrown down on the addition of spirit. It dissolves to some extent in boiling benzene, from which it separates in minute crystals; but the solution appears to undergo decomposition on evaporation, so that this method cannot be made use of for purification. When heated with strong hydrochloric acid, isosafrol nitrosochloride does not yield hydroxylamine.

Fumaric and Maleic acids.

We have made several attempts to obtain addition compounds of these acids with nitrosyl chloride. The experiments in this direction, however, which have been carried out on the same lines as those described above, have in each case led to a negative result.

The following synopsis indicates the general result of the action of nitrosyl chloride on the unsaturated compounds which have been brought into contact with it under various conditions.

Unsaturated compound employed.	Nitrosochloride formed.	Constitution.	Accompanied by chlorination.
Ethylene.....	No.....	—	Yes
Propylene.....	Yes.....	Oxime.....	Yes
Isobutylene (unsymmetrical dimethylethylene)	Yes.....	Oxime.....	Yes
Trimethylethylene.....	Yes.....	Oxime	
Tetramethylethylene.....	Yes (Thiele)....	Nitroso	
Hexylene (methylpropylethylene)	Yes.....	Oxime	
Octylene (hexylethylene).....	Yes.....	Oxime	
Phenylethylene (cinnamene)....	Yes.....	Not an oxime?	
Diphenylethylene (stilbene).....	Yes.....	Not an oxime?.	Yes
Phenylnitroethylene (<i>w</i> -nitrocinnamene)	No.....	—	
Phenanthrene.....	No.....	—	Yes
Acenaphthylene.....	No.....	—	
Crotonic acid.....	Carbon dioxide evolved; small quantity of a doubtful oxime formed	—	Yes
Allo-(iso)crotonic acid.....		—	Yes
Phenylacrylic (cinnamic) acid....		—	Yes
Ethyl cinnamate.....	No.....		
Oleic acid.....	Yes.....	Not an oxime?	
Elaïdic acid.....	Yes.....	Not an oxime?	
Erucic acid.....	Yes (Sudborough)		
Fumaric acid.....	No.....		
Eugenol.....	No.....		
Ethyl eugenol.....	No.....		
Safrol.....	No.....		
Isosafrol.....	Yes.....	Not an oxime?	
Anethoil.....	Yes.....	Not an oxime?	
Pinene.....	Yes.....	Not an oxime	
Limonene.....	Yes.....	Oxime	

In considering these results, it is worthy of remark that the proximity of a nitro- or carboxyl-group to the ethylenic carbon atoms appears to prevent the addition of nitrosyl chloride. This, so far as it goes, seems to be evidence in favour of the symmetrical formula for oleic acid, $\text{CH}_3\cdot[\text{CH}_2]_7\cdot\text{CH}:\text{CH}\cdot[\text{CH}_2]_7\cdot\text{COOH}$, advocated by Saytzev (*J. per Chem.*, 1887, [2], 35, 389) and Benedikt (*Monatshefte*, 1890, 11, 83), and supported by Wagner, in his discussion of the oxidation of unsaturated compounds (*Ber.*, 21, 3353). The probability of this being the true constitution of oleic acid is also indicated by Baruch (*Ber.*, 27, 173). In the case of the crotonic acids and of cinnamic acid, contact with nitrosyl chloride appears to give rise to the destruction of the adjacent carboxyl group. But the fact that phenathrene and acenaphthylene do not unite with nitrosyl chloride whilst cinamene and stilbene do, although all four readily unite with bromine, seems to open up a wider question. The explanation of this is probably connected with peculiarities in the structure of unsaturated compounds not hitherto recognised in existing formulæ.

Another fact of equal significance is the difference, already pointed out by Angeli (*Ber.*, 24, 3994), between the behaviour of compounds which contain the allyl group, $-\text{CH}_2\cdot\text{CH}:\text{CH}_2$, and that of the isomeric compounds containing the propenyl group, $-\text{CH}:\text{CH}\cdot\text{CH}_3$. The latter unite with nitrous anhydride and with nitrosyl chloride, whilst the former do not, although both classes of compounds readily combine with two atoms of bromine.

A few qualitative experiments to illustrate the comparative behaviour of unsaturated compounds with bromine and with nitrosyl chloride have been made with some of the substances referred to in the preceding pages, with the following results

Compound employed.	Bromine.	Nitrosyl chloride.
Cinnamene	Immediately decolorised..	Very slowly decolorised
Cinnamic acid	Slowly decolorised	Not decolorised
Ethyl cinnamate	Slowly decolorised.....	Not decolorised
Eugenol	Immediately decolorised..	Not decolorised
Ethyl eugenol	Immediately decolorised..	Not decolorised
Oleic acid	Immediately decolorised..	Very slowly decolorised
Safrol	Immediately decolorised..	Not decolorised
Isosafrol	Immediately decolorised..	Immediately decolorised

These experiments were performed in chloroform solution, and it will be seen from the results that the property of not immediately decolorising a solution of nitrosyl chloride is not peculiar to those unsaturated compounds which do not form addition compounds with this reagent.

Finally, in order to ascertain whether an intermediary, such as a

NITROSYL CHLORIDE AND UNSATURATED COMPOUNDS. 335

chloride, would induce combination between nitrosyl chloride and some of those substances which had been experimented with unsuccessfully, we have tried the effect of bringing the substances together in the presence of zinc chloride, or aluminium chloride, but in each case without the desired result.

*Mason College,
Birmingham.*
