240. *Addition of Dinitrogen Tetroxide to Olefins. Part I. General Introduction.*

By Norman Levy and Charles W. Scaife.

By the addition of dinitrogen tetroxide to the lower olefins in the liquid phase, dinitroparaffins, nitro-alcohols, and nitroalkyl nitrates are produced in good total yield. The first products are a dinitroparaffin and a nitro-nitrite, of which the latter is unstable and requires conversion into nitro-alcohol by reaction with water or alcohol as an essential first stage in satisfactory recovery of pure products. The nitro-nitrate is formed by oxidation of the nitro-nitrite. Difficulties previously inherent in this field have been overcome by use of pure tetroxide, conversion of the nitro-nitrite into stable nitro-alcohol, and the use of ether or ester solvents for some of the lower olefins. Ethylene itself and the higher olefins may be satisfactorily nitrated without solvent. Control of the reaction at or below room temperature is a further essential, while interference by dinitrogen trioxide may be prevented by addition of oxygen.

Only two modes of addition of the tetroxide appear, *i.e.*, as two nitro-groups or as one nitro- and one nitrite group, the latter invariably being attached to the carbon with the fewer hydrogen atoms.

THE present series of papers describes research carried out on the addition of dinitrogen tetroxide (N_2O_4) to olefins, a systematic study of which has been made during the past six years in these laboratories. This has resulted in general methods for the preparation of dinitroparaffins, nitro-alcohols, and nitro-alkyl nitrates, applicable as far as can be seen to all olefins and affording many substances not previously reported. The literature on this subject, apart from the conflicting descriptions of products, is confused for a variety of reasons : (1) the use of impure tetroxide or " nitrous gases " consisting of mixtures of tri- and tetr-oxide and nitric and nitrous acids, (2) oxidative side reactions leading to formation and subsequent addition of the trioxide, (3) failure to note the influence of reaction medium, in certain cases decisive, on the course of reaction, and (4) difficulties in separating the products, arising in part from the instability of some of the primary products. Many products described by earlier workers are now known to be mixtures; in particular, it may be said that reasonably pure dinitro-paraffins have hitherto only been obtained from fully-substituted ethylenes, *e.g.*, tetrahaloethylenes (Biltz, *Ber.*, 1902, **35**, 1528) and tetramethylethylene (Michael and Carlson, *J. Org. Chem.*, 1940, **5**, 14). Dinitro-derivatives of simple olefins, *e.g.*, propylene, *iso*butylene, 1- and 2-butylene, have only now been satisfactorily prepared from the olefins and clearly characterised.
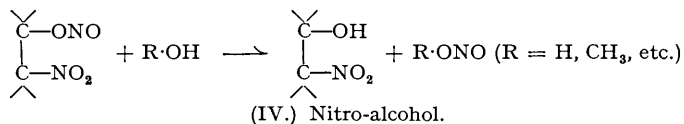
Compounds other than dinitroparaffins mentioned in the literature as arising from the reaction between nitrogen oxides and olefins include nitrosites (now generally regarded as bisnitronitroso-compounds), nitrosates, nitro-olefins in small amount, and oximes, but only in few cases have nitro-alcohols or nitroalkyl nitrates been isolated. Often the materials separated and defined have represented only a minor proportion of the reaction product, the major proportion having resisted identification because of spontaneous and vigorous decomposition during attempted isolation. In the work now described, the nitration procedure, together with the methods of separation devised, permits the isolation of the main products in amount substantially equivalent to the olefins consumed.

Nitration Reaction.—Ethylene and *iso*butylene were originally treated in the vapour phase with dinitrogen tetroxide at about 150°. Substantial oxidation also occurred, and the product was very difficult to separate, although a small quantity of solid 1 : 2-dinitroethane was isolated from the product from ethylene. Far better reaction control and recovery of nitro-compounds were obtained by liquid-phase methods now outlined.
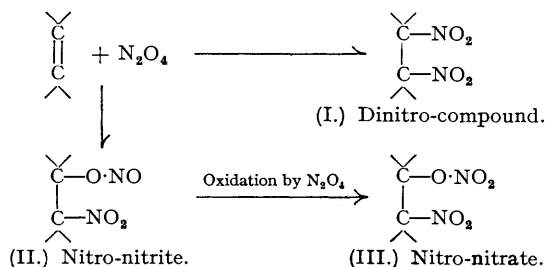
With gaseous olefins reaction is normally carried out by passing the gas into tetroxide either liquid (b. p. 20·7°) or dissolved in an ether or ester solvent, the reaction being kept at or below room temperature by means of a cooling bath. Similar cooling should be employed with non-gaseous olefins which are usually brought into reaction by dropwise addition to the tetroxide or *vice versa.* Under these liquid-phase conditions, addition of tetroxide occurs both as two nitro-groups and as one nitro- and one nitrite group (see foot of p. 1093).

According to circumstances and subject to a degree of control, part of the nitro-nitrite is oxidised to nitro-nitrate. In the subsequent working up, which necessarily includes treatment of the crude oily product with water or alcohol, the unstable nitro-nitrite is converted into nitro-alcohol :
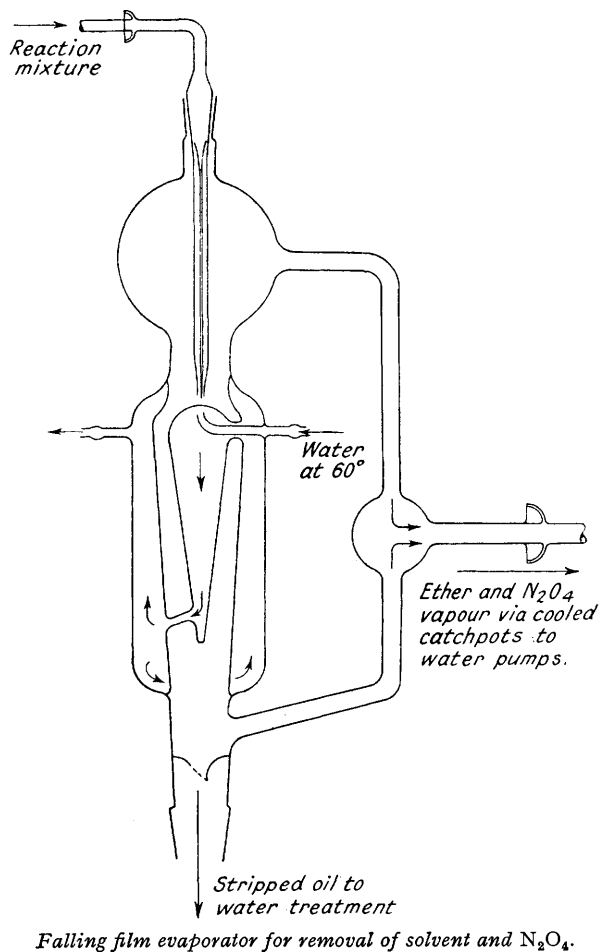
$$\begin{array}{c} \overset{|}{\underset{\wedge}{C}}-ONO \\ \overset{|}{\underset{\wedge}{C}}-NO_2 \end{array} + R \cdot OH \longrightarrow \begin{array}{c} \overset{|}{\underset{\wedge}{C}}-OH \\ \overset{|}{\underset{\wedge}{C}}-NO_2 \end{array} + R \cdot ONO \ (R = H, CH_3, \text{etc.})$$

(IV.) Nitro-alcohol.

Effect of Solvent.—It has been found that, although ethylene and olefins such as the octylenes and *cyclo*hexene may be suitably nitrated in the absence of solvent, *i.e.*, by addition to liquid tetroxide, yet propylene and the butylenes give rise to partly oxidised substances containing little or no dinitroparaffin unless an ether- or ester-type solvent is used. Thus, passage of propylene or *iso*butylene into liquid dinitrogen tetroxide yields a product from which only the nitrate ester of the 2-hydroxy-carboxylic acid has been isolated, formed presumably from the nitro-nitrate :

$$NO_2 \cdot O \cdot \overset{|}{\underset{|}{C}} \cdot CH_2 \cdot NO_2 \longrightarrow NO_2 \cdot O \cdot \overset{|}{\underset{|}{C}} \cdot CO_2 H.$$
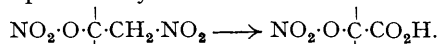
In these cases, the ether or ester solvent, *e.g.*, ethyl ether, dioxan, ethyl acetate, etc., is thought to moderate the oxidising action of dinitrogen tetroxide through molecular complex formation; with dioxan a white solid complex $(C_4H_8O_2,2NO_2)$ can in fact be separated when the solvent and liquid tetroxide are mixed. Some support for this view arises from the fact that ethers with electron-attracting substituents, *i.e.*, with reduced electron availability at the oxygen atom, are unsuitable reaction media, *e.g.*, 2 : 2′-dichlorodiethyl ether and ethyl 2-nitroethyl ether. Benzyl methyl ether does, on the other hand, yield dinitroparaffins, while formic esters, *e.g.*, ethyl formate, act as intermediate types, giving rise both to dinitroparaffins, etc., and to oxidation products.

The nitration of ethylene is slow at atmospheric pressure and absorption should not be carried beyond 0·4 mol. of C_2H_4 per mol. of N_2O_4 for good yields. For propylene and the butylenes, which react rapidly, the concentration of tetroxide in the solvent is of importance, and for the higher olefins the proportion of tetroxide (molar or excess) may affect the proportions of the main products.

Effect of Oxygen.—A further variable is introduced through reduction of some of the tetroxide to trioxide which can give rise to undesirable or unstable side products. The introduction of oxygen into the reaction prevents or limits this tendency and yields a much more stable crude product. Addition of oxygen is not always desirable, however; in the nitration of

Reaction mixture

Water at 60°

Ether and N_2O_4 vapour via cooled catchpots to water pumps.

Stripped oil to water treatment

Falling film evaporator for removal of solvent and N_2O_4.

*iso*butylene, the proportion of nitro-nitrate is increased by oxygen addition and the separation of 1 : 2-dinitro-*iso*butane by crystallisation made more difficult.

Separation of Products.—After completion of the reaction, excess of dinitrogen tetroxide and solvent, if used, are taken off as vapour under reduced pressure and condensed for re-use. Care must be taken in the final stage of solvent removal since the nitro-nitrites appear to be least stable when free from solvent or tetroxide. This is especially important with the lower members, where it is best to remove solvent and tetroxide by evaporation at water-pump vacuum from a falling film, allowing the solvent-free product to drip into water or alcohol for immediate conversion of the nitro-nitrite component into nitro-alcohol. A convenient and simple form of evaporator is provided in the ordinary double-surface condenser by passing warm water through

the jacket. An improved type with a conical inner element is shown in the figure (see also British Patent Application No. 17,160/45).

The crude product now consists mainly of a mixture of dinitroparaffin, nitro-alcohol, and nitroalkyl nitrate. Ethylene, propylene, the butylenes, and *cyclo*hexene give rise to nitro-alcohols soluble in water, whereas the dinitroparaffins and nitro-nitrates are insoluble. Thus, for these olefins, the nitro-alcohols are removed by water washing and later extracted with an organic solvent or fractionally distilled. The water-insoluble oil, after drying, is fractionally distilled to separate the dinitroparaffin and nitro-nitrate. Variations of this procedure are desirable with particular olefins. For instance, 1 : 2-dinitro*iso*butane is best recovered by freezing a methanol solution of the water-insoluble oil. Similarly, 1 : 2-dinitroethane is crystallised from the methanol solution of the three main products, but subsequent separation of the remaining mixture of nitroethanol and nitroethyl nitrate is made by extraction with a benzene–water mixture, the nitroethyl nitrate passing into the benzene and the nitroethanol into the aqueous layer. Further, the trimethylpentenes give rise to nitro-alcohols insoluble in water, and here the mixed product must be separated by fractional distillation. All distillations in this series must be conducted with care behind non-shatter screens, and means of rapid cooling, *e.g.*, a solid carbon dioxide–methanol bath, used if gas evolution becomes visible.

Nitration Products.—The main products of nitration of the olefins mentioned are tabulated below. Total yields on olefin vary between 65% and 85% of pure isolated products. In the absence of oxygen the amount

Olefin.	Dinitrohydrocarbon.	Nitro-alcohol.	Nitroalkyl nitrate.
Ethylene	1 : 2-Dinitroethane	2-Nitroethanol	2-Nitroethyl nitrate
Propylene	1 : 2-Dinitropropane	1-Nitropropan-2-ol	β-Nitro*iso*propyl nitrate
*iso*Butylene	1 : 2-Dinitro*iso*butane	Nitro-*tert.*-butanol	Nitro-*tert.*-butyl nitrate
1-Butylene	1 : 2-Dinitro-*n*-butane	1-Nitrobutan-2-ol	——
2-Butylene	2 : 3-Dinitro-*n*-butane	2-Nitrobutan-3-ol	——
2 : 4 : 4-Trimethylpent-1-ene	1 : 2-Dinitro-2 : 4 : 4-tri-methylpentane	1-Nitro-2 : 4 : 4-trimethyl-pentan-2-ol	——
2 : 4 : 4-Trimethylpent-2-ene	2 : 3-Dinitro-2 : 4 : 4-tri-methylpentane	3-Nitro-2 : 4 : 4-trimethyl-pentan-2-ol	——
*cyclo*Hexene	1 : 2-Dinitro*cyclo*hexane	2-Nitro*cyclo*hexanol	2-Nitro*cyclo*hexyl nitrate

of dinitro-compound is of the same order as the combined amounts of nitro-alcohol and nitro-nitrate (both derived from nitro-nitrite). Oxygen addition tends to favour the last component to a marked extent.

Discussion.—Under the reaction conditions employed, addition of tetroxide takes only two forms : (i) as two nitro-groups, giving dinitro-compounds, and (ii) as one nitro- and one nitrite group, giving nitro-nitrites which ultimately yield the corresponding nitro-alcohols and nitro-nitrates. Ordinarily, the two forms of addition occur to a similar extent and only the use of relatively large quantities of oxygen effects any drastic change in their proportion. For unsymmetrical olefins, the second mode of addition always results in attachment of the nitro-group to the carbon with the greater number of hydrogen atoms and the nitrite group to that with the smaller number. No evidence has been obtained in any case for the reverse mode of addition or for the addition of two nitrite groups. The formation of minor, if troublesome, amounts of nitro-nitroso-compounds (nitrosites) has been shown to occur only when dinitrogen trioxide is present or allowed to form in the course of uncontrolled oxidation reactions. Nitroso-nitrates have not been found and, since it is usually possible to account for the reagents almost quantitatively by (i) and (ii) above, together with experimentally verified extraction losses, it is reasonable to conclude that these other modes of addition do not occur to a significant degree. The main reaction may therefore be regarded as one between the activated double bond

>C=C< and forms of the tetroxide expressed for the time being as $(^-NO_2)(^-NO_2)$ and $(^-NO_2)(^-ONO)$. It is suggested that both additions are polar and involve the same initial attack by the electropositive nitrogen of the nitro-group.

The structure of the active tetroxide molecule is still uncertain, chemical evidence suggesting both forms (A) and (B). Although the X-ray evidence is said to support (A) and to indicate an abnormally long N–N
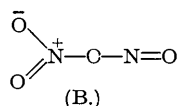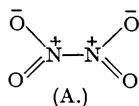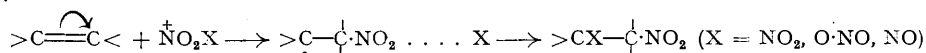
distance, yet the balance of past chemical evidence is thought to favour (B), which can give rise by appropriate fission to nitro-, nitrite, nitroso-, and nitrate groups and therefore to a variety of modes of action of the tetroxide. Since the present series of investigations establishes that only nitro- and nitrite groups are involved, they cannot be said to favour either of the two possible structures. Formation of nitro-nitrate is relatively small in the absence of oxygen and cannot therefore be regarded as indicating (B). The directive influence noted with unsymmetrical olefins, the specific solvent effect with the intermediate olefins in the series, and perhaps also the effect of oxygen, all suggest a polar mechanism for the addition reactions, the first step in which appears to be the attachment of the electropositive nitrogen to the activated carbon atom, the second nitro-group being attached either by C–N or C–O linkage to the other side of the double bond. Propylene, for example, would
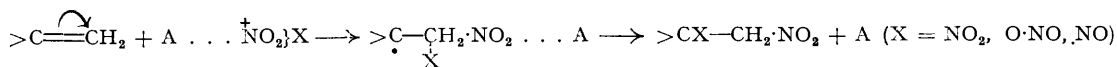
give the required nitro-nitrite as shown in (C), whereas the dinitro-compound may similarly be supposed to be formed as in (D).

(C.)   (D.)
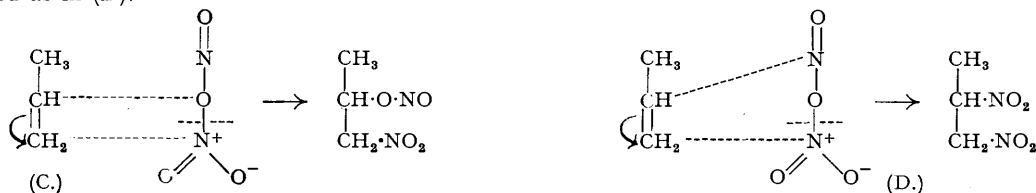
In this connection, it is noteworthy that dinitrogen trioxide in ether yields both nitro-nitroso-compounds and the normal products of tetroxide addition in substantial amount. The nitro-nitroso-compounds formed from propylene and *iso*butylene follow a rule similar to that shown by nitro-nitrites, the nitroso-group, like the nitrite group, becoming attached to the carbon with fewer hydrogen atoms. Whatever the constitution of the trioxide in these circumstances, these results suggest an equilibrium between dissolved and combined NO, in turn giving rise to structures of the type $\overset{+}{N}O_2\}X$, where X is either form of NO_2 or NO. Addition of all these assemblies appears to be polar and to proceed by the same initial step. The general reaction can thus be written :

$$>C\!=\!\!=\!\!C< \; + \; \overset{+}{N}O_2X \longrightarrow \; >\!\!\underset{\bullet}{C}\!-\!\overset{|}{\underset{|}{C}}\!\cdot NO_2 \; \ldots . \; X \longrightarrow \; >CX\!-\!\overset{|}{\underset{|}{C}}\!\cdot NO_2 \quad (X = NO_2, \; O\cdot NO, \; NO)$$

That dinitrogen tetroxide can also act as an oxidising agent and thus give rise to the trioxide is of course to be expected, though this tendency should be limited at the low temperatures employed ($-10°$ to $+25°$). The interfering effects of the trioxide can be eliminated by one or more of the following : (*a*) excess of tetroxide, (*b*) high concentrations of tetroxide, (*c*) use of oxygen, through which the concentration of the trioxide becomes unimportant. The tendency to oxidise varies with the olefin; thus, ethylene, the trimethylpentenes, and *cyclo*hexene are little oxidised, even when reacting with pure liquid tetroxide, whereas propylene and *iso*butylene in these circumstances give rise to aqueous nitric acid, water-soluble oxidation products and the nitrate of the α-hydroxycarboxylic acid, $CHMe(O\cdot NO_2)\cdot CO_2H$ and $CMe_2(O\cdot NO_2)\cdot CO_2H$. Dinitroparaffin is apparently not formed, although the survival of the carboxyl group suggests a single C–N linkage initially, followed by hydrolysis of the primary $CH_2\cdot NO_2$ group. With ether- or ester-type solvents, depending on electron availability at the oxygen bridge, the oxidation reactions are largely prevented, even in very concentrated solutions (*e.g.*, 50% tetroxide by weight in diethyl ether), thus permitting formation and survival of the normal addition products. The isolation of the dioxan–dinitrogen tetroxide complex, and the gradation of solvent effect with the nature of the side groups about the oxygen bridge, seem to establish that these solvents act by molecular association with the tetroxide, increasing its polarity and facilitating initial attack by the $\overset{+}{N}O_2$ group. The balance between the two normal modes of addition does not appear to be affected by the solvent, from which it may be suggested that solvent–tetroxide association takes the form of $A \ldots \overset{+}{N}O_2X$ where A is solvent and X the second group :

$$>C\!=\!\!=\!\!CH_2 \; + \; A \ldots \overset{+}{N}O_2\}X \longrightarrow \; >\!\!\underset{\bullet}{C}\!-\!\underset{X}{CH_2}\!\cdot NO_2 \ldots A \longrightarrow \; >CX\!-\!CH_2\cdot NO_2 \; + \; A \quad (X = NO_2, \; O\cdot NO, \; NO)$$

Oxygen was originally fed to the reaction in minor quantities to reduce trioxide formation and hence provide a product more stable to distillation. Two further effects have, however, been found : (i) it increases the formation of nitro-nitrate, by assisting the oxidation of nitro-nitrite; with ethylene, the amount of oxygen absorbed corresponds closely to the amount of nitroethyl nitrate formed, (ii) at least in the case of *iso*butylene, it increases the total yield of products derived from nitro-nitrite at the expense of the dinitro-compound. No satisfactory explanation of the latter effect can yet be offered.

More detailed description of the procedures with individual olefins is given in later papers, together with an account of the characterisation, properties, and chief reactions of the main products, many of which are new and have proved to be of unusual interest. For some of the compounds made, special analytical methods were necessary, and these will be described subsequently.