1. *Relations between Acidity and Tautomerism. Part III. The Nitro-group and the Nitronic Esters.*

By FRITZ ARNDT and JOHN D. ROSE.

THE methods, deductions, and terminology developed in the previous communications of this series (Part I, Arndt and Martius, *Annalen*, 1932, **499**, 228; Part II, Arndt and Scholz, *ibid.*, 1934, **510**, 62) are applied in this paper to the group CH·NO$_2$. The acidity-promoting action (acidification) of nitroxyl is stronger than that of the substituents hitherto studied, as is shown by its effect on hydroxyl in the simplest example (HO·NO$_2$). The degree of acidity produced in a hydrocarbon residue by the introduction of *one* nitro-group is, empirically speaking, sufficient to endow the substance with the property of solubility in aqueous alkalis, whereas *two* sulphonyl groups or *three* carbethoxy-groups are necessary to produce this effect.

The following questions arise : (1) Is this empirical acidity due only to the acidification of the CH by the nitro-group, or to a previous progressive transformation into a more acidic hydroxyl form? (2) What is the constitution of the hydroxyl form, if any? In the case of the SO$_2$ group, the answer to the first question has been shown (Arndt and Martius, *loc. cit.*) to be, that the action of sulphonyl is purely acidifying without tautomerism. This is in harmony with the electronic formula (I), in which there is no double bond. The electronic formula (II) of the nitro-group, however, shows one of its oxygen
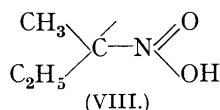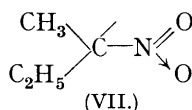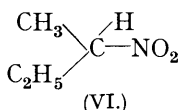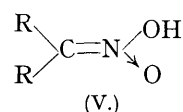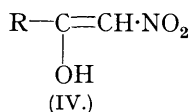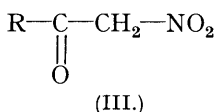

atoms to be bound by a double bond which makes the nitro-group analogous to carbonyl rather than to sulphonyl and it might therefore be capable of electromeric change and of acting as a partner in conjugation.

It is well known, thanks to Hantzsch, that certain arylnitromethanes yield, on acidification of their alkaline solutions, solid *aci*-forms (nitronic acid), which are much more acidic than the normal forms, and from which, furthermore, they are sharply distinguished by intense colour reactions with ferric chloride, and unsaturation towards bromine. Unlike the enolic modifications of many β-dicarbonyl compounds, these nitronic acids are unstable and soon revert entirely to the normal form. No spontaneous change of a normal nitro-compound to the free *aci*-form has been observed. The existence of the nitronic acids, therefore, gives no complete answer to question (1), although it is clear that the salts of the mononitrated hydrocarbons have the electronic system of the nitronic acids.

K. H. Meyer (*Ber.*, 1914, **47**, 2380) concludes that nitro-ketones of the type (III) enolise appreciably, although to a less extent than β-ketonic esters, and that this enolisation involves the carbonyl (IV) rather than the nitro-group. This suggests that the enolising tendency of the nitro-group is less than that of keto-carbonyl, but that the nitro-group is implicated in the full conjugated system. The acidifying action of the nitro-group cannot

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alone explain such enolisation of the keto-group because the disulphonyl ketones are non-enolising (Arndt and Martius, *loc. cit.*). The effect of the nitrogen–oxygen double bond is apparent here, although to a less extent than in the case of carbonyl, even ester carbonyl.

$$R-\underset{\underset{O}{\|}}{C}-CH_2-NO_2 \qquad R-\underset{\underset{OH}{|}}{C}=CH\cdot NO_2 \qquad \underset{R}{\overset{R}{>}}C=N\underset{O}{\overset{OH}{<}}$$

(III.)   (IV.)   (V.)

$$\underset{C_2H_5}{\overset{CH_3}{>}}C\overset{H}{\underset{NO_2}{-}} \qquad \underset{C_2H_5}{\overset{CH_3}{>}}C-N\underset{O}{\overset{O}{<}} \qquad \underset{C_2H_5}{\overset{CH_3}{>}}C-N\underset{OH}{\overset{O}{<}}$$

(VI.)   (VII.)   (VIII.)

With regard to the constitution of the nitronic acids and their salts, the three-membered ring formula tentatively suggested by Hantzsch (*Ber.*, 1896, **29**, 699, 702, 2251) was later abandoned by Hantzsch himself and for very good reasons (*Ber.*, 1912, **45**, 89, footnote 1). Since then the generally accepted formula has been (V), analogous to the enols of carbonyl compounds.

Kuhn and Albrecht (*Ber.*, 1927, **60**, 1297) found that on treating a methanol solution of the optically active *sec.*-nitrobutane (VI) with sodium methoxide, the optical activity was preserved. This was corroborated by Shriner and Young (*J. Amer. Chem. Soc.*, 1930, **52**, 3332) in the case of 2-nitro-*n*-octane. As (V) contains no centre of asymmetry, Kuhn and Albrecht ascribe the structure (VII) to the anion in which the unshared pair of electrons on the carbon atom is supposed to function as a fourth substituent, analogous to the optically active sulphoxides and sulphinic esters of Phillips. To the *aci*-form, the structure (VIII) is ascribed, *i.e.*, the proton which is added to the anion (VII) on acidification becomes temporarily attached to the singly bound oxygen atom, which is available in the nitro-group in any case, and from this unstable condition returns to the unshared carbon electrons. The Kuhn–Albrecht formula implies that salt formation in the mononitrated hydrocarbons consists exclusively in the removal of the proton from the carbon, without any electronic change (cf. Kuhn and Albrecht, *loc. cit.*, footnote 19) and that the tautomerism of the nitro-group is purely prototropic. This would suggest that the double bond of the nitroxyl is incapable of electromeric changes, leading to the conclusion that the nitro- and the sulphonyl group are practically analogous. One would, therefore, expect the behaviour of suitably constituted analogous nitro-sulphonyl compounds towards diazomethane to be comparable, *i.e.*, sufficiently acidic normal nitro-compounds containing no aldehydo- or keto-carbonyl should be capable of *C*-methylation. Our experiments, however, give evidence to the contrary.

$$R\cdot CH_2\cdot NO_2 \qquad\qquad R\cdot CH{:}NO\cdot OH \qquad\qquad Ph\cdot\underset{\underset{O}{\|}}{C}\cdot CH_2\cdot NO_2$$

(IX.)   (X.)   (XI.)

$$NO_2\cdot CH_2\cdot\underset{\underset{O}{\|}}{C}\cdot OEt \qquad O{:}C(OMe)\cdot CH(NO_2)\cdot CO\cdot OMe \qquad C_6H_4Me\cdot\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}\cdot CH_2\cdot NO_2$$

(XII.)   (XIII.)   (XIV.)
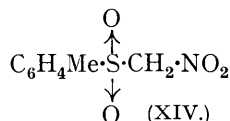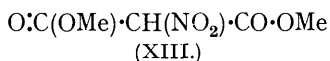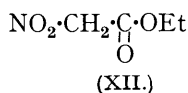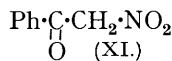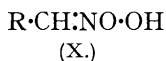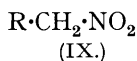
The following compounds have been investigated: Phenylnitromethane (IX, X; R = Ph), *p*-bromophenylnitromethane (IX, X; R = C₆H₄Br), ω-nitroacetophenone (XI), ethyl nitroacetate (XII), methyl nitromalonate (XIII), and p-*toluenesulphonylnitromethane* (XIV). The last compound has been prepared as an example of a type in which the methylene group carrying the nitro-group is very strongly acidified, but in which no conjugated system is possible. This sulphone nitromethane, a new type, was prepared by the introduction of the nitro-group into the sulphides C₆H₄Me·S·CH₂·CO·R (R = CH₃ or C₆H₅), by ethyl nitrate and sodium ethoxide, followed by oxidation with hydrogen peroxide ; the acyl group is eliminated during the reactions.

The two nitronic acids (X), as expected, react vigorously with diazomethane to give the

nitronic esters. The corresponding normal nitro-compounds (IX), the solutions of which give none of the reactions of the nitronic acids, show no visible reaction with diazomethane, but are nevertheless slowly transformed into the same nitronic esters as obtained from the *aci*-forms.   In these cases it would be possible to assume that during the long duration of the reaction the whole of the starting material has gradually undergone spontaneous isomerisation into the *aci*-form, the equilibrium amount of which is too small to be detected by ferric chloride, etc., but which, on account of its strong acidity, can react with diazomethane.   Such an assumption, however, becomes untenable in the cases of (XII) and (XIV).   These compounds, too, give no enolic reactions, but they react vigorously with diazomethane, yielding also nitronic esters.   Considering the difference between the sulphonyl ketones (which do not enolise) and the β-ketonic esters (which enolise considerably), then, if the reaction of (XIV) were due to spontaneous desmotropy, the equilibrium amount of nitronic acid in (XII) ought to be detectable by ferric chloride.   The authors, therefore, consider the formation of nitronic esters from (XII) and (XIV) to be analogous to the formation of enolic esters from sulphonyl ketones, *i.e.*, due to the mechanism described in Part I of this series as "indirect methylation."   It also seems probable that the same mechanism applies in the case of (IX).   The electronic conditions for this mechanism, which, in the case of a keto-carbonyl, are fulfilled only by the presence of a sulphonyl group in the β-position, are fulfilled by the nitro-group as such, with regard both to the polarity of the double bond and to the necessary mobility of a neighbouring proton.   Nitromalonic ester (XIII) shows, in alcoholic solution, a feeble enolic reaction which, after the experience with toluenesulphonylmalonic ester and methanetricarboxylic ester (Part I), is probably due to a small enolisation of the ester carbonyl.   Nevertheless diazomethane, reacting vigorously, yields almost quantitatively and under all conditions the nitronic ester; the indirect methylation of the nitro-group prevails.   ω-Nitroaceto-phenone (XI) shows a much stronger enolic reaction due to the enolisation of the carbonyl (see above); the reaction product with diazomethane is an oil which contains much nitronic ester, and is probably a mixture of about $\frac{2}{3}$ nitronic ester and $\frac{1}{3}$ enolic ester.   This result would be easily explained by the competition between the indirect methylation of the nitro-group and the methylation of the enol.

It follows that the behaviour of the nitro-group is entirely different from that of the sulphonyl group, and is similar to that of carbonyl under corresponding conditions of polarity.   It shows either tautomerism or indirect methylation.   The latter implies an addition reaction of the nitrogen–oxygen double bond, which, in its turn, depends on a tendency for electromeric changes.   In both cases there is a disagreement with the deductions from the Kuhn–Albrecht formulæ (VII) and (VIII).   Tertiary and aromatic nitro-compounds do not exhibit addition reactions with diazomethane, but it can be assumed that the addition is reversible, and therefore does not lead to a permanent change unless a mobile proton interferes.   Aromatic polynitro-compounds react with diazomethane (Heinke, *Ber.*, 1898, **31**, 1399) and it is noteworthy that the same compounds give addition reactions with many other reagents.

With regard to question (1) (p. 1), the acid character of (XII) and (XIV) must be evinced at the methylene group, and the feeble enolisation of (XIII) is shown to contribute little towards the observed acidity.   The formation of salts of mononitrated hydrocarbons such as nitromethane and (IX) in aqueous alkaline solution need not be consequent on previous isomeric change to the *aci*-form, even if this were the case in the slow reaction with diazomethane.   Since the action of hydroxyl ion, unless it is an addition reaction, consists in the removal of a proton, and since the desmotropic changes in question are considered to be prototropic, it is difficult to conceive that the proton, after leaving the carbon through the influence of alkali, should become temporarily and loosely attached to the oxygen of the nitro-group before uniting with hydroxyl ion.   The slowness of the dissolution of such nitro-compounds (as compared with XII—XIV) in aqueous alkali need not be due to a slow tautomeric process, but can be attributed to the weakness of the acidity of the methylene.   This weakness does not show itself, as it usually does, in the incomplete formation of a salt (hydrolytic equilibrium), because the process is irreversible; as soon as the proton is removed from the carbon, the resulting electronic system changes to the

nitronic state (corresponding to V), which is far less prone to recapture the proton. The Kuhn formula (VII), on the contrary, does not account for this stability towards hydrolysis.

The anions of nitro-compounds containing carbonyl (XI—XIII, etc.) would be expected to be enolic, rather than nitronic, owing to the greater " enotropic effect " of carbonyl, or " in between the two " (cf. Arndt, *Ber.*, 1930, **63**, 2963). The salts of (XIII) are known to yield the *C*-methyl derivative with methyl iodide (Beilstein, IV edition, **2**, 597), as do enolic salts; the silver salt of (XII) gives with methyl iodide at least in part the *C*-methyl product (Steinkopf, *Annalen*, 1923, **434**, 21), whereas the alkaline solution of (IX) yields the nitronic ester with methyl sulphate (see below).

The nitronic esters from bromophenylnitromethane, and from nitromalonic ester (XIII) are crystalline solids in the pure state; the rest are liquids, diagnosed by means of alkoxyl estimations. All these nitronic methyl esters are characterised by the violent decomposition which occurs at 70—90° with evolution of formaldehyde in all cases except (XIV). This property has been ascribed to the whole class by Nef (*Annalen*, 1894, **280**, 286), who, however, did not isolate any of them. Bamberger (*Ber.*, 1901, **34**, 589) obtained from phenylazonitromethane with diazomethane a crystalline nitronic ester showing the same property. This seems to be the only authentic nitronic ester hitherto described. Hantzsch (*Ber.*, 1907, **40**, 1541) describes a " perfectly stable " nitronic ester obtained from the silver salt of phenylcyanonitromethane with methyl iodide, and attributes this stability to the presence of two negative radicals. In view of the instability of the nitronic ester from (XIII), and considering that Bamberger (*loc. cit.*, p. 590) obtained from the salt of phenylazonitromethane with methyl iodide an *N*-methyl derivative, the compound of Hantzsch, which has not been proved to contain methoxyl, may be an *N*-methyl derivative. Steinkopf (*Annalen*, 1923, **434**, 29) claims to have obtained the nitronic ester of (XIII) as the main product of the action of methyl iodide on the silver salt. This product is described as boiling at 84°/2·5 mm. and no decomposition with evolution of formaldehyde is mentioned. The product obtained from (XIII) with diazomethane, giving the correct alkoxyl value, has quite different properties. Auwers (*Ber.*, 1924, **57**, 456) described the nitronic ester of phenylnitromethane as being obtained from the alkaline solution of the latter on treatment with methyl sulphate, and as distilling at 117°/10 mm. On repeating this experiment, we found that the product was actually the nitronic ester, but we were unable to distil it unchanged; the fraction b. p. 117°/10 mm. contained no methoxyl and was a mixture of benzaldehyde and other products.

The nitronic ester from (XIV) also decomposes at 80—90°, but according to the equation $C_7H_7 \cdot SO_2 \cdot CH\text{:}NO \cdot O \cdot CH_3 = C_7H_7 \cdot SCN + CO_2 + 2H_2O$. It is remarkable in this case that not only the nitrogen but the sulphone group is reduced, in favour of a complete oxidation of the methyl.

The nitronic esters are more or less readily attacked by strong aqueous acids and by aqueous alkali. In this case, however, the methyl is not oxidised but is eliminated in the form of methanol. The original nitro-compound has never been recovered from a nitronic ester, as saponification is accompanied by a reduction of the nitronic group with corresponding oxidation of the reagent (hydriodic acid) or even of the carbon atom attached to nitrogen.

On treatment of the nitronic ester from (XIII) with cold concentrated hydrochloric acid, nitrogen trioxide and other products not yet identified were produced. The action of cold 2*N*-sodium hydroxide is comparatively slow, thereby excluding the possibility of the compound being a keten-acetal (compare the behaviour of the keten-acetal from the methane-tricarboxylic ester, Part I); the nitronic ester dissolves within about 5 minutes, to yield methanol, carbonate, and fulminate. The nitronic ester from (XII) is immediately attacked by concentrated hydrochloric acid, even at − 10°, and is transformed, with evolution of heat, into chloro-oximinoacetic ester (whereas Steinkopf, *loc. cit.*, had to evaporate his ester with concentrated hydrochloric acid, and states that it is transformed into *iso*nitrosoacetic acid); cold 2*N*-sodium hydroxide yields, also exothermically, the so-called " bis-anhydro-nitro-acetic ester " described by Scholl (*Ber.*, 1901, **34**, 868, 876), which is a dimerisation product of oxalic ester nitrile oxide, different from furoxandicarboxylic ester.

These vigorous reactions with acids are exhibited only by the nitronic esters containing carbonyl. The same esters on treatment with cold azeotropic hydriodic acid release iodine :

the ester from (XII) gives two atoms of iodine, the ester from (XIII) between four and five atoms, which is explained by the entire fission of the nitronic group with strong acids. The fact that the product from (XI) (which also contains one carbonyl) and diazomethane releases only 1·3 atoms of iodine instead of two, with partial recovery of the original nitro-ketone, leads us to the assumption that it contains about $\frac{1}{3}$ of enolic and $\frac{2}{3}$ of nitronic ester.

The nitronic esters from (IX) to (X) do not release appreciable amounts of iodine from cold azeotropic hydrogen iodide; they are attacked by concentrated hydrochloric acid only on warming and are transformed into the corresponding diaryl oxdiazoles. The nitronic ester from (XIV) gave with hot acids and alkali, tarry products which could not be purified.

The original nitro-compounds are far more stable towards acids, alkali and reduction by hydriodic acid under the same conditions. This difference leads again to the conclusion that the electronic structure of the nitronic group is different from that of the nitro-group, as expressed by formulæ (II) and (V). It seems desirable to ascertain whether the conditions of experiment used by Kuhn and Shriner and their collaborators lead to the removal of a proton; this investigation is being carried out, independently of the present authors, by Dr. Weissberger in this laboratory.

<center>EXPERIMENTAL.</center>

p-Bromophenylnitromethane (IX, R = C_6H_4Br).—This was prepared according to Wislicenus and Elvert (*Ber.*, 1908, **41**, 4121) and Scholtze (*Ber.*, 1896, **29**, 2253); m. p. 60°. It was converted into the *aci-p*-bromophenylnitromethane by dissolution in 2*N*-sodium hydroxide, and acidification of the filtered ice-cold solution with 2*N*-sulphuric acid. The *aci*-form may be recrystallised from a large volume of light petroleum, forming white needles, m. p. 90°, but even the crude precipitated compound has m. p. 89—90°.

The Methyl Ether of aci-p-*Bromophenylnitromethane.*—(a) *Methylation of* aci-p-*bromophenyl-nitromethane.* A solution of dried precipitated *aci-p*-bromophenylnitromethane (1 g.) in anhydrous ether (50 c.c.) was treated with an ethereal solution of diazomethane (from 5 g. of nitrosomethylurea), and 15 minutes after the vigorous reaction and gas evolution had ceased the solution was filtered, and the solvent removed under diminished pressure at 15°. The viscous yellow residue, which solidified on cooling and scratching, was crystallised from the minimum of methanol at − 20°, and again from light petroleum, forming white needles, m. p. 65° (Found : C, 42·0; H, 3·6; MeO, 12·9.* $C_8H_8O_2NBr$ requires C, 41·7; H, 3·5; 1MeO, 13·5%).

(b) *Methylation of* p-*bromophenylnitromethane.* *p*-Bromophenylnitromethane (20 g.) was treated in anhydrous ethereal solution with diazomethane (from 40 g. of nitrosomethylurea). Evolution of gas was not more rapid than that which normally occurs in diazomethane solutions, and the reaction mixture was kept for 3 days. The solvent was removed under diminished pressure, and the oily product was seeded with the nitronic ester produced by method (a); it then solidified, and after crystallisation from methanol, and later from light petroleum, yielded white needles (7 g.), m. p. and mixed m. p. with the ester produced by method (a), 65°.

Decomposition of the Nitronic Ester.—(a) When plunged into a bath at 80°, the ester underwent almost explosive decomposition and evolved formaldehyde, which was recognised by passage into a solution of *o*-nitrophenylhydrazine in *N*-hydrochloric acid, a thick orange precipitate of formaldehyde-*o*-nitrophenylhydrazone being produced : long orange needles from methanol, m. p. and mixed m. p. with an authentic specimen, 84°. This method was used throughout for the detection and proof of the presence of formaldehyde in decomposition products of the nitronic esters.

The residues, after decomposition of the nitronic ester, were dissolved in dilute caustic soda solution, filtered, and acidified, yielding a white solid which crystallised from petroleum (b. p. 100—120°) in needles, m. p. 110°. This substance contained nitrogen, and showed the m. p. 110° given in the literature for *p*-bromobenzaldoxime (*Ber.*, 1897, **30**, 1899). (b) The nitronic ester was boiled for 5 minutes with a large excess of hydrochloric acid (*ca.* 15%) and the semi-solid residue obtained on cooling was collected, dried, and crystallised from *n*-butyl alcohol and then from ethyl acetate, forming white needles, m. p. 181°. This substance is considered to be 3 : 5-*di*-p-*bromophenyl*-1 : 2 : 4-*oxadiazole*, the structure being supported by the analogous formation of 3 : 5-diphenyl-1 : 2 : 4-oxadiazole from the nitronic ester related to phenylnitromethane (q.v.) (Found : C, 44·7; H, 2·3; N, 7·3; *M*, cryoscopic in camphor, 383. $C_{14}H_8ON_2Br_2$

* All alkoxyl determinations were carried out by the method of Viebock (*Ber.*, 1930, **63**, 2818).

requires C, 44·2; H, 2·1; N, 7·4%; *M*, 380). On prolonged heating with hydrochloric acid, the nitronic ester yields *p*-bromobenzoic acid, m. p. and mixed m. p. with an authentic specimen, 251°, also characterised by the preparation of the methyl ester, m. p. and mixed m. p. 79°.

The nitronic ester yields no iodine when treated with cold colourless azeotropic hydriodic acid.

The Methyl Ether of aci-*Phenylnitromethane.*—(a) *aci*-Phenylnitromethane (2·5 g.) in dry ether (50 c.c.) was cautiously treated with a dry ethereal solution of diazomethane (from 10 g. of nitrosomethylurea). There was a vigorous reaction and gas evolution, and the solution was kept for 15 minutes, and the ether then removed under diminished pressure; the residual yellow oil would not crystallise and methoxyl was therefore estimated after prolonged drying in a vacuum desiccator (Found : MeO, 17·3. $C_8H_9O_2N$ requires 1MeO, 20·5%); the low value was expected, as the ester slowly decomposes even in the cold. (b) Phenylnitromethane (2 g.), methylated during 3 days with diazomethane (from 10 g. of nitrosomethylurea), yielded a yellow oil identical in properties with that produced by method (a) (Found in dried material : MeO, 17·1%). The nitronic ester is insoluble in hot alkalis, gives no ferric reaction, absorbs only a little bromine in alcoholic solution, and does not oxidise hydriodic acid.

Decomposition of the nitronic ester. (a) When plunged into a bath at 85°, the ester decomposed suddenly with evolution of formaldehyde. When the ester was heated slowly from room temperature to 100°, the decomposition was slow and benzaldehyde was recognised in the gaseous products (*o*-nitrophenylhydrazone, m. p. and mixed m. p. 185°). The decomposition also took place at room temperature, and the benzaldehyde formed in 3—4 hours was again recognised as its *o*-nitrophenylhydrazone. (b) The nitronic ester was boiled for 5 minutes with hydrochloric acid (*ca.* 15%); the semi-solid product crystallised from methanol in long white needles, m. p. 108°, undepressed in admixture with authentic 3 : 5-diphenyl-1 : 2 : 4-oxadiazole prepared from benzamideoxime according to Schulz (*Ber.*, 1885, **18**, 1081) (Found : C, 75·2; H, 4·6; N, 12·7. Calc. for $C_{14}H_{10}ON_2$: C, 75·6; H, 4·5; N, 12·6%).

Repetition of an Experiment of von Auwers (*Ber.*, 1924, **57**, 456).—Methyl sulphate (12 g.) was added to a cold solution of phenylnitromethane (10 g.) in the minimum of aqueous 2*N*-sodium hydroxide and the whole was shaken vigorously for 30 minutes; a little more caustic soda was then added to preserve an alkaline reaction, and the shaking was continued for a further 30 minutes. The excess of methyl sulphate was then decomposed with ammonia, the heavy oil taken up in ether, washed with dilute acid and with water, and dried, and the solvent removed at a low temperature. The residual oil exhibited the properties of the nitronic ester described above; it decomposed suddenly when heated quickly to 85°, formaldehyde being evolved. The whole product was decomposed in this way, and the residue distilled under reduced pressure. A small fraction was collected, b. p. 115°/10 mm., which is the b.p. given by von Auwers (*loc. cit.*), but this was not homogeneous, had no methoxyl content, and consisted largely of benzaldehyde (recognised as the *o*-nitrophenylhydrazone). After the distillation, a considerable quantity of non-volatile semi-solid remained, which crystallised from a little methanol as white needles of 2 : 5-diphenyl-1 : 2 : 4-oxadiazole, m. p. and mixed m. p. with the authentic specimen, and with a specimen produced by the action of hydrochloric acid on the nitronic ester, 108°.

Ethyl Nitroacetate (XII).—This was prepared by a modification of the method of Bouveault and Wahl (*Bull. Soc. chim.*, 1904, **31**, 851) as follows. An ice-cold mixture of fuming nitric acid (60 g., *d* 1·5) and acetic anhydride (54 g.) was added dropwise to a mixture of ethyl acetoacetate (100 g.) and acetic anhydride (54 g.) at 30°. The temperature was kept between 30° and 35°, great care being taken not to exceed the upper limit. The mixture was added to ice-water (1000 c.c.) and stirred rapidly for 1 hour to remove nitric acid. The precipitated oil was then isolated by means of ether, mixed with an equal volume of absolute alcohol and boiled for 2 hours to decompose any remaining traces of acetic anhydride (failing this, the subsequent alkali extraction is rendered very inconvenient). The alcoholic solution was poured into water, extracted with ether, and the ether washed with dilute aqueous sodium carbonate until the alkaline layer was no longer yellow. The combined alkaline solutions were acidified; the precipitated oil, isolated by means of ether, distilled as a colourless oil, b. p. 89—91°/12 mm. (yield, 30%).

The ethereal solution, from which the nitro-ester had been extracted with alkali, was dried and distilled, yielding 10 g. of the substance described by Bouveault and Wahl (*loc. cit.*) as " Bis anhydro nitroacetate d'ethyle," b. p. 154°/13 mm. This substance is actually ethyl furoxandicarboxylate, as on shaking with concentrated aqueous ammonia, it yields a colourless solid, which after crystallisation from boiling water has the m. p. 223° attributed by Wieland to the diamide of furoxandicarboxylic acid (*Annalen*, 1909, **367**, 52). The formation of the furoxan derivative in this reaction is doubtless due to a decomposition of ethyl nitro-oximidoacetate

(cf. Bouveault and Wahl, *Bull. Soc. chim.*, 1907, **31**, 679; Wieland, *loc. cit.*) and not to a decomposition of dinitroacetic ester.

Ethyl nitroacetate is readily soluble in sodium carbonate solution. Its alcoholic solution is coloured by a drop of a dilute solution of bromine in methanol; after 1—2 minutes the colour disappears. Decoloration of further bromine occurs very slowly, and in chloroform solution the ester does not decolorise bromine at all. The alcoholic solution gives no reaction with ferric chloride, even on standing.

Nitronic Methyl Ester from Ethyl Nitroacetate.—Dry ethereal diazomethane (from 20 g. of nitrosomethylurea) was cautiously added to ethyl nitroacetate (10 g.), dissolved in anhydrous ether (40 c.c.). When the vigorous reaction was complete, the solution was kept for 2 hours, filtered, and concentrated under diminished pressure; attempts to distil the resulting oil were fruitless (see below). A fresh specimen of the nitronic ester was estimated for alkoxyl content after drying for 24 hours in a vacuum (Found : RO, 21·3. $C_5H_9O_4N$ requires 2RO, 21·8%). This nitronic ester should be handled with extreme care, as in contact with the skin it produces extremely persistent and painful blisters, which often take a long time to heal.

Decomposition of the Nitronic Ester.—(a) When heated quickly to 90°, the nitronic ester decomposes explosively with evolution of formaldehyde (detected). On attempted distillation, an explosion occurred at 0·1 mm. (bath temperature, 90°) and at 0·01 mm. the decomposition occurred at 65° (bath temperature). The products of this decomposition were distilled : (i) b. p. 98—105°/15 mm., (ii) b. p. 105—108°/15 mm., and (iii) 108—109°/15 mm. Fractions (ii) and (iii), when cooled and scratched, solidified and yielded *iso*nitrosoacetic ester, white crystals from ether–light petroleum, m. p. 30° (Found : EtO, 38·4. Calc. for $C_4H_7O_3N$: 1EtO, 38·4%).

(b) The nitronic ester (0·1180 g.) was added to cold colourless azeotropic hydriodic acid (4 c.c., freshly distilled) in an atmosphere of carbon dioxide. There was an immediate formation of iodine, and the mixture was agitated for 30 seconds, and then diluted with water (30 c.c.) and titrated with $N/10$-thiosulphate (Found : 1·93 atoms of iodine per molecule of ester).

(c) When the nitronic ester (10 g.) was treated with concentrated hydrochloric acid, the temperature rose almost to the boiling point; nitrous fumes were not evolved (cf. the action of hydrochloric acid on the nitronic methyl ester from methyl nitromalonate). The solution was diluted with water (50 c.c.), and the oil isolated by means of ether and eventually solidified and crystallised from chloroform and from light petroleum (b. p. 60—80°), forming long white needles, m. p. 80°, of chloro-oximinoacetic ester (Found : EtO, 30·3. Calc. for $C_4H_6O_3NCl$: 1EtO, 29·6%). The same result was obtained by the action of concentrated hydrochloric acid on the nitronic ester at − 10°, the temperature being allowed to rise to room temperature when the reaction was over. The chloro-oximinoacetic ester was identified by its reaction (Wieland, *Ber.*, 1907, **40**, 1675) : the cold aqueous solution of the ester was treated with dilute aqueous sodium carbonate; an oil then separated, which was identified as furoxandicarboxylic ester by its transformation into the diamide with concentrated aqueous ammonia, m. p. and mixed m. p. with the specimen obtained from the by-product of Bouveault and Wahl, 223°. The aqueous solution of chloro-oximinoacetic ester, on warming, also affords furoxandicarboxylic ester, a fact not mentioned by Wieland. It is stated in the literature (Beilstein) that chloro-oximino-acetic ester is transformed by water into oxalic acid and hydroxylamine hydrochloride.

(d) The nitronic ester was shaken with aqueous $2N$-sodium hydroxide (2 vols.); heat was spontaneously developed and a yellow solution with an oil in suspension was produced. After neutralisation with hydrochloric acid, the mixture was shaken with concentrated aqueous ammonia; the oil then disappeared, but no solid separated. On cooling to − 10°, however, a white solid separated, which after crystallisation from water, softened at 119° and decomposed vigorously at 120—121° to a dark red-brown oil. This is the behaviour of the diamide of " bis anhydro nitroacetic acid " described by Scholl (*Ber.*, 1901, **34**, 868, 876), who obtained the ester, and other products, by the action of silver nitrite on bromoacetic ester. There is no doubt that this ester differs from furoxandicarboxylic ester, but the authors doubt the formula ascribed to the ester by Scholl. It is remarkable that the action of hydrochloric acid on the nitronic ester ultimately leads to furoxandicarboxylic ester, whereas the action of alkali gives its isomeride (Scholl). The latter compound has hitherto been obtained *only* by Scholl; all other references in the literature concerning " bis anhydro nitroacetic ester " refer to furoxandicarboxylic ester, and the references in Richter's " Lexicon " under $C_8H_{10}O_6N_2$ are to be corrected accordingly.

Methyl Nitromalonate (compare Franchimont and Klobbie, *Rec. trav. chim.*, 1889, **8**, 283; Willstätter and Hottenroth, *Ber.*, 1904, **37**, 1779; Wahl, *Bull. Soc. chim.*, 1901, **25**, 926).—The literature relating to the preparation of this compound is very unsatisfactory, and the following

method is therefore recorded.   Fuming nitric acid (300 c.c., d 1·5) was added slowly at 0° to methyl malonate (100 g.).   The mixture was kept at 0° for $\frac{1}{2}$ hour and then removed from the cooling mixture for a further $\frac{1}{2}$ hour, the temperature rising slowly to 30°.   The whole was then kept at 0° for $2\frac{1}{2}$ hours and poured into water (1500 c.c.).   A heavy oil which separated was extracted with ether, and the extract shaken with successive volumes of aqueous sodium carbonate until the alkaline layer was no longer yellow.   The combined alkaline extracts were acidified with hydrochloric acid, and the oil which separated was collected by means of ether and distilled, b. p. 124°/16 mm., 100°/1 mm. (yield, 80 g.) (Found : MeO, 34·6.   Calc. for $C_5H_7O_6N$: 2MeO, 35·0%).

Methyl nitromalonate is a colourless oil which forms a yellow alcoholic solution, exhibiting a feeble reddish-yellow ferric reaction.   The alcoholic solution decolorises a solution of bromine in methanol instantaneously at room temperature.   At − 15° the absorption is slower, and in chloroform at room temperature and at − 15° the absorption is very much slower than in alcohol at the same temperature.

The Nitronic Ester from Methyl Nitromalonate.—Methyl nitromalonate (5 g.) in anhydrous ether (30 c.c.) was cautiously treated with an anhydrous ethereal solution of diazomethane (from 10 g. of nitrosomethylurea).   A very vigorous reaction ensued, accompanied by brisk evolution of gas.   The solution was kept for 20 minutes and the ether was then removed, leaving a mass of white crystals contaminated with a little yellow oil (5·1 g.), which was absorbed on porous earthenware.   The residual solid (4·5 g.) crystallised from ether as white plates, m. p. 68° (Found : C, 38·0; H, 4·7; N, 7·5; MeO, 48·1, 48·4. $C_6H_9O_6N$ requires C, 37·7; H, 4·7; N, 7·3; 3MeO, 48·2%).   The *nitronic* ester is very soluble in the common organic solvents with the exception of light petroleum.   The alcoholic solution does not absorb bromine, and the ester is insoluble in aqueous sodium carbonate.

Decomposition of the nitronic ester.   (a) When plunged into a bath at 80°, the ester decomposes suddenly, with evolution of formaldehyde (detected), but the residues after such a decomposition could not be distilled.

(b) A weighed amount of the nitronic ester was added in an atmosphere of carbon dioxide to freshly distilled, colourless, azeotropic hydriodic acid (*ca.* 4 c.c.); there was an immediate production of iodine, and in successive determinations this was estimated as 4·38 and 4·36 atoms of iodine per molecule of ester.

(c) The nitronic ester, when shaken with cold 2N-sodium hydroxide, was not immediately attacked, but dissolved during about 5 minutes, and on acidification with 2N-nitric acid, nothing was precipitated, but there was a slight effervescence and a strong odour of fulminic acid.   The addition of aqueous silver nitrate precipitated silver fulminate, which detonated violently.

(d) The nitronic ester (10 g.) was shaken at room temperature with concentrated hydrochloric acid (20 c.c.).   After a short time the white solid vanished, and a dark greenish-blue oil separated (methyl nitromalonate itself is not attacked by cold concentrated hydrochloric acid in 24 hours).   The shaking was continued until there was no more solid present ($\frac{1}{2}$ hour) and the solution was then diluted with ice-water and shaken with ether, and the extract dried.   On standing overnight, the dark blue colour of the ethereal extract vanished, being apparently due to dissolved oxides of nitrogen.   The residue after the removal of the ether was separated into three fractions : (i) b. p. 57—97°/16 mm., (ii) b. p. 97—117°/16 mm., and (iii) b. p. 150°/16 mm.   Fraction (iii) contained nitrogen, gave a green-brown ferric reaction, was soluble in aqueous sodium carbonate to a yellow solution, from which it was precipitated by acid, and contained 36·5% of methoxyl.   It would not crystallise and was not identified.

p-Toluenesulphonylnitromethane (XIV).—(A) *p*-Thiotolylacetone (*Annalen*, 1890, **260**, 268) (3·5 g.) was dissolved in alcoholic sodium ethoxide (5 g. of sodium in 20 c.c. of absolute alcohol), ethyl nitrate (2 g.) added, and the mixture heated on the steam-bath for 4 hours.   A colourless sodium salt separated, which was collected, dissolved in water, in which it was readily soluble, and extracted with ether to remove tarry impurities.   The aqueous layer was acidified, and the resulting oil collected by ether and oxidised with perhydrol (5 c.c.) in glacial acetic acid (5 c.c.) at room temperature for 3 days.   A small quantity of white crystals which separated was recrystallised from alcohol, forming plates, m. p. 116°.   This substance was proved by analysis, and by the identity with the product obtained from thiotolylacetophenone, to be p-*toluenesulphonylnitromethane* (XIV) (Found : C, 44·8; H, 4·4; N, 6·5; S, 14·9. $C_8H_9O_4NS$ requires C, 44·7; H, 4·4; N, 6·5; S, 14·8%).

(B) ω-(*p*-Thiotolyl)acetophenone (*J. Amer. Chem. Soc.*, 1925, **47**, 1136) (20 g.) was dissolved in alcoholic sodium ethoxide (2 g. of sodium in absolute alcohol, 25 c.c.), and ethyl nitrate (8 g.) added.   The mixture was refluxed vigorously on the steam-bath for 3 hours, the solution was

then dark red and a white crystalline sodium salt had separated. This was collected, washed with alcohol and ether, and dried (6 g.). The solid was dissolved in water, filtered, and acidified, and the precipitated mixture of oil and solid was collected by means of ether, affording a mixture of a dark oil and white crystals of benzoic acid. The whole of the residue was dissolved in acetic acid (6 c.c.), perhydrol (8 c.c.) added, and the whole warmed on the steam-bath until a pale yellow homogeneous liquid was produced, which evolved gas freely. On cooling, the contents of the flask solidified to a crystalline mass, which was collected and crystallised from a little alcohol. The crystals were then heated to boiling with water (20 c.c.), filtered hot, and the insoluble residue crystallised again from alcohol, forming shining plates, m. p. and mixed m. p. with the product obtained by method (A), 116°.

The colourless sodium salt obtained by methods (A) and (B) evidently consists of the sodium salt of tolylnitromethane, *i.e.*, the acyl group is eliminated during the introduction of the nitro-group.

(C) ω-(*p*-Thiotolyl)acetophenone (12·5 g.) was dissolved in sodium ethoxide solution (1·3 g. of sodium in 40 c.c. of absolute alcohol), and ethyl nitrate (6 c.c.) added. The flask was placed on a cold water-bath, which was warmed slowly, so that the mixture boiled very gently after about $\frac{3}{4}$ hour; boiling was allowed to continue for a further $1\frac{1}{2}$ hours. A voluminous yellow solid had then separated and, on cooling, the contents of the flask solidified. The yellow mass was collected, washed with alcohol and ether, and dried (9 g.). This yellow powder was crystallised from water (30 c.c.), affording long yellow needles of the sodium salt of ω-nitro-ω-(*p*-thiotolyl)-acetophenone (3 g.). This sodium salt was dissolved in water and acidified, yielding a pale yellow powder, which was crystallised from a little methanol. The ω-*nitro*-ω-(p-*thiotolyl*)*aceto-phenone* separated as pale yellow needles, m. p. 78° (Found : C, 62·7; H, 4·6; N, 4·9. $C_{15}H_{13}O_3NS$ requires C, 62·7; H, 4·5; N, 4·9%). The compound gives an intense brown-red colour with ferric chloride. Attempts to oxidise it by perhydrol in acetic acid solution did not lead to the corresponding sulphone, but to oxidised fission products which could not be separated.

The mother-liquors of the crystallisation of the sodium salt were acidified, and the resulting mixture of oil and solid was isolated by means of ether and oxidised with perhydrol (5 c.c.) in acetic acid (5 c.c.). The resulting white crystalline mass was recrystallised from alcohol, extracted with boiling water, and again crystallised from alcohol, yielding *p*-toluenesulphonyl-nitromethane in shining plates, m. p. and mixed m. p. with the substances obtained by methods (A) and (B), 116°.

In alcoholic solution the compound gives no ferric reaction and it does not immediately decolorise bromine; after some seconds, however, decolorisation takes place, as in the case of other similar sulphones (Part I).

Nitronic Methyl Ester from p-*Toluenesulphonylnitromethane.*—*p*-Toluenesulphonylnitro-methane (1 g.) was treated with diazomethane (from 2 g. of nitrosomethylurea) in ethereal solution; there was a brisk reaction and evolution of gas. The solution was kept for 1 hour, and the ether removed at a low temperature. The residue was a pungent viscous yellow oil which would not crystallise and therefore was examined in the crude state (Found in material dried in a vacuum : MeO, 11·9. $C_9H_{11}O_4NS$ requires 1MeO, 13·5%).

Decomposition of the nitronic ester. (a) When plunged into a bath at 95°, the yellow oil decomposed suddenly; the gases evolved contained no formaldehyde, but carbon dioxide was present in large relative amount. The dark brown, oily residue had the characteristic odour of *p*-tolylthiocarbimide. It was boiled with alcoholic potassium hydroxide, diluted, and acidified, the odour of *p*-tolylthiol then becoming apparent; on addition of more acid and zinc dust and steam-distillation, *p*-tolylthiol, m. p. and mixed m. p. 43°, was found in the distillate.

(b) The nitronic ester, when treated with colourless azeotropic hydriodic acid, liberated only a very small quantity of iodine.

ω-*Nitroacetophenone.*—This was prepared according to Thiele and Haeckel (*Annalen*, 1902, **325**, 8). The alcoholic solution gives with ferric chloride a red coloration which, however, appears only after a second or two and is completely developed after about 1 minute. The ketone is slowly soluble in dilute alkali solutions, and is thrown out by acids, whilst the alcoholic solution absorbs bromine instantaneously at room temperature in large quantities. The chloro-form solution shows a similar behaviour to bromine.

Methylation of ω-Nitroacetophenone.—Dry ethereal diazomethane (from 5 g. of nitroso-methylurea) was added slowly to the nitro-ketone (1 g.) in anhydrous ether (60 c.c.). A vigorous reaction and gas evolution ensued; the solution was kept for 20 minutes, and the ether then removed under diminished pressure. The residual viscous yellow oil would not crystallise and was therefore thoroughly dried (Found : MeO, 14·3. $C_9H_9O_3N$ requires 1MeO, 17·9%).

Decomposition of the methylated product.   (a) When plunged into a bath at 90°, the compound decomposed suddenly, formaldehyde was evolved, and a dark tarry residue was obtained.   This should have contained *iso*nitrosoacetophenone, but since attempts to isolate this substance were fruitless, the residue was submitted to a degradative reaction of *iso*nitrosoacetophenone described by Claisen (*Ber.*, 1897, **20**, 656).   The tarry material was boiled for a few minutes with aqueous caustic soda ; a clear solution was then formed and on acidification benzoic acid and hydrocyanic acid were produced and recognised.

(b) On warming for 1 minute with concentrated hydrochloric acid the original ketone was produced, m. p. and mixed m. p. 106°.

(c) The partial regeneration of the starting material from the methylated product by the action of hydrochloric acid gave rise to the suspicion that the latter might be a mixture of the nitronic ester with some nitro-α-methoxy-α-phenylethylene, that is, the enol ether.   An attempt was therefore made to estimate roughly the amount of nitronic ester present, by assuming that two atoms of iodine per molecule of the nitronic ester are liberated when the mixture is treated with colourless azeotropic hydriodic acid.   This was carried out in the manner described under nitroacetic ester, and the result was the formation of 1·3 atoms of iodine per molecule of $C_9H_9O_3N$, which, on the above assumption, indicates a mixture of about 65% of nitronic ester and 35% of enol ether.

The methylation was repeated by adding the powdered ketone to a solution of diazomethane, but the results differed in no way from those already described.