CCCXXIX.—*Reactions of ω-Substituted Acetophenone Derivatives. Part I. ω-Halogeno-derivatives of ωm- and ωp-Dinitroacetophenone.*

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THE development and the experimental verification of electronic theories of substitution in the benzene nucleus have also thrown considerable light on various subsidiary problems, notably that of side-chain activity, and have rendered possible the classification of such side-chain reactions into four main categories (Ingold and Rothstein, J., 1928, 1219; compare Ingold and Patel, *J. Indian Chem. Soc.*, 1930, **7**, 97). In the present series of investigations it is proposed to study certain side-chain reactions of ω-substituted acetophenone derivatives, more especially side-chain nitration and the replacement of halogens and ψ-halogens in derivatives of the type Ar·CO·CHRX. The present communication deals with the action of acetyl nitrate on various ω-halogeno-derivatives of *m*- and *p*-nitroacetophenones and the properties of the resulting ω-halogeno-ω*m*- and -ω*p*-dinitroacetophenones.*

When a solution of ω-*iodo*-m-*nitroacetophenone* (prepared by the action of alcoholic potassium iodide on the corresponding ω-bromo-derivative) in a mixture of acetic anhydride and nitric acid

* The initial action of acetyl nitrate on *m*- and *p*-nitroacetophenone themselves also appears to be side-chain nitration, but the ω-nitro-compounds are further converted into substances $(C_4H_2O_2N)_x$, the nature of which is under investigation.

(*d* 1·52) is evaporated in a vacuum at the ordinary temperature, no iodine is liberated but a colourless crystalline compound separates from the solution. Although apparently quite stable under such conditions, this compound immediately decomposes, with liberation of iodine, on exposure to air. Its constitution is, however, clearly indicated by its decomposition products. It was first shown that the effective reagent is the nitric acid, since the brown solution formed when ω-iodo-*m*-nitroacetophenone is added to absolute nitric acid at 0°, is decomposed either by ice and potassium hydrogen carbonate or by evaporation in a vacuum at the ordinary temperature, iodine being liberated. On the other hand, only a very slight liberation of iodine occurs when the ω-iodo-compound is boiled with acetic anhydride, and most of the material may be recovered unchanged.

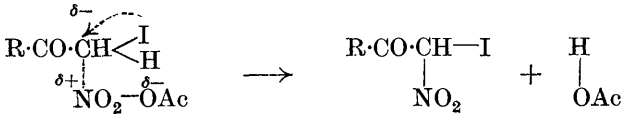
When the unstable compound, obtained by the action of acetyl nitrate, is decomposed with water, the main product is *m*-nitrophenylglyoxal. A small amount of *m*-nitrophenacyl acetate can also be isolated (see below). The constitution of the latter product was proved by direct comparison with a synthetic specimen (Evans and Brooks, *J. Amer. Chem. Soc.*, 1908, **30**, 407). The identity of the *m*-nitrophenylglyoxal was established by the similarity of its properties with those described by Evans and Witzemann (*ibid.*, 1911, **33**, 1772), by conversion into its osazone and a semicarbazone identical with that of a specimen obtained by oxidation of *m*-nitrophenacyl alcohol (*loc. cit.*). All the oxidising agents investigated by Evans and Witzemann convert *m*-nitrophenylglyoxal directly into *m*-nitrobenzoic acid, but with nitric acid its conversion into *m*-nitrobenzoylformic acid, identical with a specimen synthesised by Claisen and Thompson's method (*Ber.*, 1879, **12**, 1943), was effected. The glyoxal readily reduces warm ammoniacal silver nitrate solution.

It would thus appear that the action of acetyl nitrate on ω-iodo-*m*-nitroacetophenone involves side-chain nitration, the unstable compound being ω-*iodo*-mω-*dinitroacetophenone*. This is decomposed by water in accordance with the following scheme, similar to that previously suggested for the decomposition of phenylbromocyanonitromethane and α-bromo-α-nitro-α-phenylethane into benzoyl cyanide and acetophenone, respectively (Baker and Ingold, J., 1929, 434): $R{\cdot}CO{\cdot}CH_2I \xrightarrow[Ac_2O]{HNO_3} R{\cdot}CO{\cdot}CHI{\cdot}NO_2 \xrightarrow{H_2O}$ $[R{\cdot}CO{\cdot}CH(OH){\cdot}NO_2] \longrightarrow R{\cdot}CO{\cdot}CHO + HNO_2$ ($R = m\text{-}NO_2{\cdot}C_6H_4{\cdot}$), the iodine being formed by interaction of the liberated nitrous and hydriodic acids: $2HNO_2 + 2HI = I_2 + 2H_2O + 2NO$. The iodine so formed was determined quantitatively, and the formation

of nitric oxide qualitatively demonstrated, by isolation of the unstable ω-iodo-compound with exclusion of air and moisture in a manner described on p. 2423.

Somewhat less conclusive results were obtained in the case of ω-*iodo*-p-*nitroacetophenone*. The initial product of the action of acetyl nitrate is an unstable compound which similarly liberates iodine on exposure to air and is most probably ω-iodo-ω*p*-dinitroacetophenone. Decomposition with water affords a solid product, which appears from the analysis figures to consist mainly of *p*-nitrophenacyl acetate and is oxidised by nitric acid to p-*nitrobenzoylformic acid*, giving the same colour reaction (with thiophen and concentrated sulphuric acid) as does the corresponding *m*-derivative. The mechanism of the formation of *m*- and *p*-nitrophenacyl acetates from the unstable intermediates, which undoubtedly contain very labile iodine, is not yet clear. *A priori* it seems reasonable to assume that the initial unstable compound has a similar constitution to that established for the *m*-nitro-derivative, but further investigation of the reaction is intended.

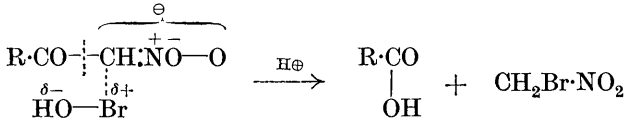
Further light is thrown on the mechanism of the initial side-chain nitration of ω-iodo-*m*- or -*p*-nitroacetophenone by the observations that, under identical conditions, ω-chloro- and ω-bromo-*m*- and ω-bromo-*p*-nitroacetophenone are all unattacked by acetyl nitrate. In each series only the halogen atom is varied and hence the nature of this substituent would seem to be an important factor in the mechanism of the nitration involved. The inductive ($-I$) effects of chlorine, bromine and iodine are in the order Cl>Br>I, whilst their tautomeric ($+T$) effects are in the reverse order I>Br>Cl, and hence, since only the iodine derivatives undergo side-chain nitration, this reaction must require an accession of electrons to the ω-carbon atom :



It would appear that whilst the tautomeric effect of chlorine or bromine is insufficient to outweigh the contrary polar effect of the carbonyl group (which will tend to render the ω-carbon atom incipiently positive) and so initiate the attachment of the positively polarised portion of the reagent molecule, the greater tautomeric effect of iodine is capable of so doing, side-chain nitration thus belonging to the category A_2 as predicted by Ingold and Rothstein (*loc. cit.*).

In order to compare the relative stability of the ω-halogeno-ω*m*- and -ω*p*-dinitroacetophenones the corresponding bromo-derivatives

were prepared indirectly by the action of bromine on the potassium salts of ω*m*- and ω*p*-dinitroacetophenone. When an ice-cold aqueous solution of the *potassium* salt of ω*p*-dinitroacetophenone is treated with 1 mol. of bromine water, *p*-nitrobenzoic acid, and not the ω-bromo-compound, is precipitated, and the presence of bromonitromethane can be detected in the filtrate by its characteristic lachrymatory odour. Under these conditions the reaction which occurs is evidently between hypobromous acid and the anion of the *aci*- form of ω*p*-dinitroacetophenone;



This affords confirmatory evidence of the distribution of the anionic charge in such ψ-acidic systems (Baker, J., 1929, 2257). By the action of an ethereal solution of bromine on a suspension of the appropriate, finely divided, potassium salt in the same solvent, however, the required ω-*bromo*-ωp- and -ωm-*dinitroacetophenones* were readily prepared. In contrast to the marked instability of the corresponding ω-iodo-derivatives, the bromo-compounds are stable crystalline substances. They are unattacked by cold water, but are decomposed by boiling water, yielding the corresponding nitrobenzoic acid (and, presumably, bromonitromethane). The stability of the corresponding nitrophenylglyoxal under these conditions precludes the assumption that this compound is an intermediate in the decomposition, the necessary corollary being that in the bromo-compounds fission of the molecule $R{\cdot}CO{\cdot}CHBr{\cdot}NO_2 \xrightarrow{H_2O} RCO_2H + CH_2Br{\cdot}NO_2$ occurs in preference to replacement of the halogen by hydroxyl, which appears to be the main reaction in the case of the ω-iodo-compounds.

In considering the mechanism of such hydrolysis of α-halogenoketones two salient factors emerge. First, the polar effect of a carbonyl group, and, in the cases considered in this communication, the even greater effect of the dipolar nitro-group, attached to the α-carbon atom must induce on this atom an incipient positive charge. Hence, whatever may be the mechanism of reactions resulting in the replacement of the halogen atom, it probably includes a stage which involves the electrostriction of a basic (positive-centre seeking) reagent to this α-carbon atom.

Secondly, the same effects which render the α-carbon atom incipiently positive will also tend to inhibit the separation of the halogen as a halide ion. Moreover, were such anionisation of the halogen a rate-determining factor in the mechanism, the order of

electron affinity Cl>Br>I would predict a reversal of the observed order of stabilities, the iodine derivative then being the most stable. Again, then, it would appear that the mechanism involves a stage which is facilitated by the positive character of the halogen atom (compare Bennett and Berry, J., 1927, 1676). In this connexion the greater tendency of iodine, relative to bromine, to co-ordinate a proton (greater stability of iodinium salts) may well be an important factor when attack by a reagent polarised in the direction $\overset{\delta+}{H}\overset{\delta-}{X}$ is involved.

EXPERIMENTAL.

Preparation of Materials.—ω-*Chloro*-m-*nitroacetophenone*. The claim of Dale and Nierenstein (*Ber.*, 1927, **60**, 1026) to have obtained this compound by the action of diazomethane on *m*-nitrobenzoyl chloride has been challenged by Bradley and Robinson (J., 1928, 1310); it was therefore prepared by passing the theoretical amount of chlorine gas into molten *m*-nitroacetophenone. It crystallised from ether in stout short prisms, m. p. 103° (Dale and Nierenstein, *loc. cit.*, gave m. p. 97°) (Found: C, 48·3; H, 3·2. Calc. for $C_8H_6O_3NCl$: C, 48·1; H, 3·0%).

ω-*Bromo*-m-*nitroacetophenone*. This was prepared by the method of Evans and Brooks (*J. Amer. Chem. Soc.*, 1908, **30**, 406) by the action of bromine in chloroform on *m*-nitroacetophenone. After most of the solvent had been distilled off, the product crystallised. Recrystallised from ethyl acetate–ligroin, it had m. p. 96°. The same compound was obtained by the action of aqueous-alcoholic potassium bromide on the ω-chloro-derivative.

ω-*Iodo*-m-*nitroacetophenone*. The ω-bromo-compound (24 g.) was warmed for a few minutes with a solution of 18 g. of potassium iodide in 100 c.c. of 90% alcohol, just sufficient water added to dissolve the separated potassium bromide, and the warm solution filtered. The ω-*iodo*-compound crystallised, and was purified by recrystallisation from ether–ligroin, from which it separated in rhombic prisms, m. p. 96° (mixed m. p. with the ω-bromo-derivative depressed to 84°). A further quantity was obtained by concentration of the mother-liquor (Found: C, 33·2; H, 2·1. $C_8H_6O_3NI$ requires C, 33·0; H, 2·1%).

ω-Bromo-*p*-nitroacetophenone was prepared by the action of bromine in acetic acid (Engler and Zielke, *Ber.*, 1889, **22**, 209) on *p*-nitroacetophenone (prepared from ethyl *p*-nitrocinnamate by Drewson's method; *Annalen*, 1882, **212**, 160; compare Perkin and Ballenot, J., 1886, **49**, 441). Crystallised from ethyl acetate–ligroin, it had m. p. 98°.

ω-*Iodo*-p-*nitroacetophenone* was obtained from the ω-bromo-

compound in a similar manner to the *m*-derivative. It crystallised from ethyl acetate–ligroin in compact masses of feathery needles, m. p. 97—98° (Found : C, 33·2; H, 2·2%).

ω*p*-Dinitroacetophenone was prepared in accordance with the scheme : $NO_2 \cdot C_6H_4 \cdot CH{:}CH \cdot NO_2 \longrightarrow NO_2 \cdot C_6H_4 \cdot CHBr \cdot CHBr \cdot NO_2 \longrightarrow NO_2 \cdot C_6H_4 \cdot CH{:}CBr \cdot NO_2 \longrightarrow NO_2 \cdot C_6H_4 \cdot C(OMe)_2 \cdot CH_2 \cdot NO_2 \longrightarrow NO_2 \cdot C_6H_4 \cdot CO \cdot CH_2 \cdot NO_2$ (Thiele and Haeckel, *Annalen*, 1902, **325**, 1). The *potassium* salt was obtained by the action of cold alcoholic potassium ethoxide (1 mol.) on a solution of the ω*p*-dinitro-compound in the same solvent. The precipitated salt was washed with cold absolute alcohol and then with dry ether (Found : K, 16·2. $C_8H_5N_2K$ requires K, 15·7%). It exploded when gently heated or on addition of one drop of concentrated sulphuric acid.

Action of bromine on the potassium salt. (a) *In water.* An aqueous solution of the theoretical quantity (1 mol.) of bromine was slowly added to an aqueous solution of the potassium salt at 0°. A white precipitate formed and slowly flocculated. Crystallised from ethyl acetate–ligroin, it was identified as *p*-nitrobenzoic acid (m. p. and mixed m. p. 238°). Extraction of the acidified filtrate with ether afforded a small amount of a very lachrymatory oil, probably bromonitromethane.

(b) *In ether. Formation of* ω-*bromo*-ω*p*-*dinitroacetophenone.* The theoretical quantity of dry bromine in anhydrous ether was slowly added to a fine suspension of the dry potassium salt in ether at 0°. After removal of potassium bromide by filtration, evaporation of the ethereal solution under reduced pressure at the ordinary temperature afforded ω-*bromo*-ω*p*-*dinitroacetophenone*, which crystallised from ether in stout prisms, m. p. 89—90° (Found : C, 33·4; H, 1·8; Br,* 26·9. $C_8H_5O_5N_2Br$ requires C, 33·2; H, 1·7; Br, 27·7%). Boiled with water, the ω-bromo-compound slowly passed into solution and, on cooling, *p*-nitrobenzoic acid (m. p. and mixed m. p. 239°) crystallised. The ω-bromo-compound immediately liberated iodine from aqueous or alcoholic potassium iodide, but attempts to isolate *p*-nitrophenylglyoxal by the action of exactly 1 mol. of alcoholic potassium iodide gave only *p*-nitrobenzoic acid.

ωm-*Dinitroacetophenone.* *m*ω-Dinitrostyrene (Friedländer and Lazarus, *Annalen*, 1885, **229**, 233) was boiled with bromine (1 mol.) in chloroform, the solvent evaporated, and the residue drained on porous porcelain. Crystallised from acetic acid, αβ-*dibromo*-α-*nitro*-β-m-*nitrophenylethane* had m. p. 158° (Found : Br, 44·6. $C_8H_6O_4N_2Br_2$ requires Br, 45·2%). This was converted by the action of alcoholic sodium acetate into ω-*bromo*-m ω-*dinitrostyrene*, which crystallised from ethyl acetate in slender needles, m. p. 114—115° (Found :

* Control analysis of a less pure sample.

C, 35·1; H, 2·1. $C_8H_5O_4N_2Br$ requires C, 35·2; H, 1·8%). This was converted by methyl-alcoholic potassium hydroxide, in a manner similar to that used in the case of the *p*-compound, into the dimethylacetal, which was obtained as a gum on acidification of the reaction mixture. After dissolution in ether a small amount of insoluble material was removed. The residue from the dried ethereal solution partly crystallised. Recrystallised from ethyl acetate-ligroin, this portion had m. p. 103—104°. It contained bromine and appeared to be, not the acetal, but the initial methyl alcohol addition product, *α-bromo-α-nitro-β-methoxy-β-m-nitrophenylethane* (Found: C, 35·7; H, 3·0. $C_9H_9O_5N_2Br$ requires C, 35·4; H, 2·9%). The non-crystalline product was hydrolysed by addition of an equal volume of concentrated hydrochloric acid to its solution in boiling glacial acetic acid. The ketone was precipitated as a thick red oil; this, since it could not readily be induced to crystallise, was converted by alcoholic potassium ethoxide directly into the potassium salt, which was purified by washing with cold alcohol and ether.

ω-*Bromo*-mω-*dinitroacetophenone* was prepared from the above potassium salt in the same manner as that used for the corresponding *p*-derivative. It crystallised from ether–ligroin in compact clusters of tiny needles, m. p. 87° (Found: Br, 27·1. $C_8H_5O_5N_2Br$ requires Br, 27·7%). Like the *p*-derivative, it liberated iodine from potassium iodide and was converted by boiling water into *m*-nitrobenzoic acid (m. p. and mixed m. p. 141°).

m-*Nitrobenzoylformic acid.* The nitrile (Claisen and Thompson, *loc. cit.*) is rapidly (2 hrs.) hydrolysed to the amide by cold aqueous hydrogen chloride saturated at 0°. The reaction may become vigorous after about 1·5 hrs. and should be conducted in a large, loosely stoppered vessel. The purified amide was hydrolysed by 15—20% potassium hydroxide at 100° for 0·5 hr., and the solution acidified with dilute hydrochloric acid and extracted with ether. The residue from the dried ethereal solution crystallised. Recrystallised from benzene, the acid afforded clusters of small prisms, m. p. 105° (*loc. cit.*, m. p. 78—79°) (Found: C, 49·2; H, 2·6. Calc.: C, 49·2; H, 2·6%).

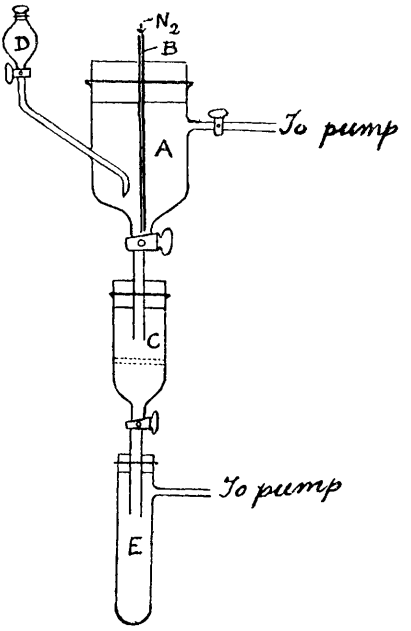
m-*Nitrophenacyl alcohol.* The acetate, m. p. 53°, was prepared from ω-bromo-*m*-nitroacetophenone and hydrolysed to the alcohol, m. p. 91—92°, as described by Evans and Brooks (*loc. cit.*). It formed a semicarbazone, m. p. 214° after crystallisation from absolute alcohol.

m-*Nitrophenylglyoxal.* The alcohol was oxidised by aqueous copper acetate as described by Evans and Witzemann (*loc. cit.*). The glyoxal was obtained as a pale yellow gum which rapidly

reduced ammoniacal silver nitrate but could not be induced to crystallise. With semicarbazide acetate it afforded a semicarbazone, which crystallised with difficulty from absolute alcohol (in which it was only sparingly soluble). With the quantity of material available the m. p. could not be raised above 198° (decomp.), which, however, was not depressed by admixture with the semicarbazone (m. p. 203°) of the decomposition product of ω-iodo-ω*m*-dinitroacetophenone (below).

Action of Acetyl Nitrate on ω-*Iodo*-mω- *and* -pω-*dinitroacetophenones.*—An almost saturated solution of ω-iodo-*m*ω-dinitroacetophenone in a mixture of 4 c.c. of acetic anhydride and 2 c.c. of nitric acid (*d* 1·52) was evaporated in a vacuum at the ordinary temperature. After 12—24 hours, colourless crystals began to separate until finally the whole solution was filled with a crystalline mass. When an attempt was made to drain these on porous porcelain, even in a desiccator, they immediately decomposed, iodine being liberated. Analysis of the unstable compound was effected in the apparatus shown diagrammatically in Fig. 1. The solution of ω-iodo-*m*-nitroacetophenone in acetyl nitrate was evaporated at 18 mm. in the vessel A, a very slow stream of dry nitrogen being bubbled through the liquid by means of the fine capillary tube B. After the unstable compound had crystallised, the crystals were transferred under suction, by suitable manipulation of the taps, to the sintered glass disc fused into C, the whole filter tube C having previously been weighed filled with nitrogen and closed with a stopper. By means of the tap funnel D the crystals were washed with a little acetic anhydride (in which they are readily soluble) and then with sodium-dried ligroin (b. p. 40—60°). The filter tube E was then replaced by one containing potassium hydroxide and the last traces of nitric acid and acetic anhydride were removed in a vacuum (24 hrs.). After the apparatus had again been filled

FIG. 1.



with dry nitrogen, C was removed, quickly stoppered, and again weighed. The filter tube C was then washed with a large volume of water containing a little potassium hydrogen carbonate to neutralise any trace of nitric acid which may have remained, the solution acidified with acetic acid, and the liberated iodine titrated with thiosulphate solution (Found: 0·3045 g. of ω-iodo-*m*ω-dinitroacetophenone required 9·2 c.c. of 0·1030*N*-sodium thiosulphate; whence the amount of iodine in the compound is 39·5%. $C_8H_5O_4N_2I$ requires I, 39·4%).

Subsequent addition of potassium iodide caused a further slow liberation of iodine, and in another determination, where potassium iodide was added in the initial decomposition, 0·1634 g. of the unstable compound required 15·1 c.c. of 0·1030*N*-thiosulphate, equivalent to 0·1975 g. of iodine (approx. 3 atoms per mol. of the ω-iodo-compound). The mechanism of this further liberation of iodine has not been elucidated. After titration the solution was extracted with ether. The residue from the dried ethereal extract gave a small amount of crystalline material which, after draining on porous porcelain, crystallised from ether in clusters of slender prisms, m. p. 53°, not depressed by admixture with a synthetic specimen of *m*-nitrophenacyl acetate (above) (Found: C, 53·7; H, 4·1. Calc.: C, 53·8; H, 4·0%).

When the decomposition of the unstable iodine compound was effected by boiling with a dilute solution of sodium thiosulphate in boiled-out distilled water in a flask attached to a small eudiometer (the whole apparatus being filled with the solution), a small volume of nitric oxide (brown fumes on admission of oxygen) was obtained.

Similar evaporation of a solution of ω-iodo-*p*-nitroacetophenone in acetic anhydride–nitric acid (*d* 1·52) afforded a brownish compound containing iodine which could rapidly be drained on porous porcelain but was similarly decomposed with liberation of iodine on further exposure to air.

Hydrolysis of ω-*Iodo*-mω- and -pω-*dinitroacetophenones.*—A solution of ω-iodo-*m*-nitroacetophenone in acetic anhydride–nitric acid was evaporated in a vacuum until most of the solvent had been removed. The whole product was then decomposed with water, extracted with ether, and the ethereal extract washed successively with sodium thiosulphate and sodium carbonate solutions and finally with water. The residue from the dried ethereal extract of the neutral products was a pale yellow gum which reduced ammoniacal silver nitrate but could not be induced to crystallise. With semicarbazide acetate in the usual manner, it afforded the *semicarbazone*, m. p. 203° (decomp.) after crystallisation from hot alcohol (in which it was only sparingly soluble), of *m*-nitrophenyl-

glyoxal, not depressed by admixture with the semicarbazone obtained from the synthetic specimen prepared as described above (Found : C, 46·3; H, 3·6; N, 23·8. $C_9H_8O_4N_4$ requires C, 45·9; H, 3·4; N, 23·8%). It was converted, as described by Evans and Witzemann, into its osazone, m. p. 233° after crystallisation from benzene (*loc. cit.*, m. p. 223°) (Found : N, 18·8. Calc. : N, 19·5%).

The mother-liquor from the initial semicarbazone formation slowly deposited the more soluble *semicarbazone*, m. p. 177° after crystallisation from alcohol, of *m*-nitrophenacyl acetate, not depressed by admixture with the semicarbazone prepared from a genuine synthetic specimen (Found : C, 47·1; H, 4·4; N, 20·3. $C_{11}H_{12}O_5N_4$ requires C, 47·2; H, 4·3; N, 20·0%).

The acid fraction obtained in the initial hydrolysis of ω-iodo-*m*ω-dinitroacetophenone consisted essentially of *m*-nitrobenzoic acid, which, before purification, gave the characteristic colour reaction of *m*-nitrobenzoylformic acid.

Oxidation of the *m*-nitrophenylglyoxal obtained in the above decomposition to *m*-nitrobenzoylformic acid was effected by nitric acid (2 : 1), but unless the conditions are carefully controlled the sole product is *m*-nitrobenzoic acid, which was the only product obtained with all the oxidising agents used by Evans and Witzemann (*loc. cit.*). The best result was obtained by gently warming the aldehyde with nitric acid (2 : 1) until the reaction started and then allowing it to proceed without external heating for 5—10 minutes. The solution was then heated gently to incipient ebullition until the brown fumes began to clear (5 mins.), poured into cold water, extracted with ether, and the extract well washed with cold water. After evaporation of the ether from the dried solution at the ordinary temperature in a vacuum, the residue crystallised completely on keeping. It crystallised from benzene in clusters of small prisms, m. p. 105°, either alone or mixed with a genuine specimen of *m*-nitrobenzoylformic acid obtained by Claisen and Thompson's method (*loc. cit.*). With semicarbazide acetate, the acid forms a derivative, decomp. 285—290°, which is soluble in water but insoluble in alcohol, and contains sodium. It is probably the sodium salt of the semicarbazido-acid (compare the similar formation of such a sodium salt with *cyclo*heptane-1-acetic-1-glyoxylic acid; Baker, J., 1926, **127**, 1680).

Similar hydrolysis of the product obtained by the action of acetyl nitrate on the unstable ω-iodo-ω*p*-dinitroacetophenone gave a solid, which was filtered off and dissolved in ether. The filtrate was extracted with ether and the combined ethereal solutions were washed successively with dilute sodium thiosulphate solution, water, sodium carbonate solution, and water Concentration of

the dried ethereal solution gave a crystalline product which after successive crystallisation from ethyl acetate–ligroin and ether gave (?) p-*nitrophenacyl acetate*,* m. p. 124° (Found : C, 54·0; H, 4·3; N, 6·55. $C_{10}H_9O_5N$ requires C, 53·8; H, 4·0; N, 6·3%). Boiled with water and phenylhydrazine, it was converted into (?) the *phenylhydrazone* of *p*-nitrophenacyl alcohol, which crystallised from benzene in fine needles, m. p. 178° (Found : N, 15·2. $C_{14}H_{13}O_3N_3$ requires N, 15·5%). Oxidised with nitric acid as described above it was converted into p-*nitrobenzoylformic acid*, m. p. 150° (previous softening) after crystallisation from benzene (Found : N, 7·3. $C_8H_5O_5N$ requires N, 7·2%).

Action of Acetyl Nitrate on ω-*Bromo*-m- *and* -p- *and* ω-*Chloro*-m-*nitroacetophenones*.—Evaporation of solutions of any of these derivatives in acetic anhydride–nitric acid in a vacuum at the ordinary temperature gave only the original material (m. p. and mixed m. p.).

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