112. *Acylation Reactions catalysed by Strong Acids. Part IV. "Benzoyl and Substituted Benzoyl Perchlorates" as* C-*Aroylating Agents.*

By H. Burton and P. F. G. Praill.

"Benzoyl perchlorate," prepared *in situ* from silver perchlorate and benzoyl chloride, is an effective benzoylating agent and will convert anisole in nitromethane into *p*-methoxybenzophenone in at least 84% yield. Adding benzoic anhydride to the mixture markedly increases the yield of the ketone. A comparison is made of the yields of analogous ketones from three substituted "benzoyl perchlorates;" certain structural features of the substituted benzoyl cations are discussed.

Evidence for the adsorption of aroyl cations on silver chloride is discussed.

Note on Nomenclature.—The proposal (*J.*, 1950, 1203) to use the name acetylium for the acetyl cation (Ac^+) has been extended—with some reserve—to the designation of aroyl cations ($ArCO^+$) as aroylium (*e.g.*, benzoylium; *p*-nitrobenzoylium) (cf. *J.*, 1950, 2997).

In Part II (*J.*, 1950, 2034) we investigated in some detail the action of acetylium perchlorate on anisole both in the absence and presence of an inert solvent, and also of acetic acid and acetic anhydride. We expressed the view that acetylium perchlorate reacted as if it were the ion pair ($Ac^+ClO_4^-$) but we do realise that the evidence presented did not preclude the possibilities that the molecule was (*a*) ionically dissociated, (*b*) largely ionised, or (*c*) very easily ionising. We considered that our postulation, namely (*b*), did represent a reasonable working hypothesis which appeared to be fully substantiated by our experimental results. The increase in yield of ketone obtained by carrying out the reaction in a medium of increased dielectric constant was consistent with the view that the *rate* of the reaction

$$PhOMe + Ac^+ \longrightarrow OMe{\cdot}C_6H_4{\cdot}COMe + H^+$$

was affected (increased) and this appeared to us to be the only logical conclusion, since an *equilibrium* could not possibly be involved in this irreversible change. The only possibility of an equilibrium in the work discussed (*loc. cit.*) was in the reaction producing the acetylium perchlorate, *viz.* :

$$AgClO_4 + AcCl \rightleftharpoons AcClO_4 + AgCl$$

Although we did not make specific reference to this point we were sure from our results that the equilibrium in this reaction did lie entirely to the right; we have since confirmed this to some extent by showing that the yield of silver chloride was almost quantitative. We do however in the light of our further experience make this statement with some reserve and we discuss our reasons for this reservation on p. 531.

We assumed from our results with acetylium perchlorate that benzoylium perchlorate ("benzoyl perchlorate") should be capable of preparation from silver perchlorate and benzoyl chloride and should be an effective benzoylating agent. We did not study its action on hydroxy-compounds but investigated its properties as a benzoylating agent towards anisole both in the absence and in the presence of nitromethane as a solvent of relatively high dielectric constant. Under these different conditions we were able to isolate at least 0·68 and 0·84 mol. respectively of *p*-methoxybenzophenone by using 1 mol. of benzoylium perchlorate with 4 mols. of anisole, and it is interesting to note that under comparable conditions exactly the same yields of *p*-methoxyacetophenone were obtained (*loc. cit.*) when using acetylium perchlorate. The results showed clearly that the reaction

$$PhOMe + Bz^+ \longrightarrow OMe{\cdot}C_6H_4{\cdot}COPh + H^+$$

was taking place and we surmised that the liberated hydrogen ion would react with benzoic anhydride, if present in the reaction mixture, to regenerate benzoylium ions :

$$H^+ + Bz_2O \rightleftharpoons Bz_2OH^+ \rightleftharpoons Bz^+ + BzOH.$$

When the reaction between benzoylium perchlorate (1 mol.) and anisole (4 mols.) was carried out in the presence of benzoic anhydride (3 mols.) again in nitromethane as a solvent, the yield of isolable ketone was increased to 1·32 mols. and thus exceeded that stoicheiometrically possible from the benzoylium perchlorate used. The increase in the yield of ketone was not so marked as in the case of the acetylium perchlorate–acetic anhydride experiments (*loc. cit.*) but we ascribe this to the probable greater reactivity of acetic anhydride towards hydrogen ions. We think that this follows from the known fact that acetic anhydride is more readily hydrolysed by aqueous acid than is benzoic anhydride. In this connexion however we should like to make it quite clear that we do not believe that the acetylium (or benzoylium) ion has any separate existence in an aqueous medium. We did refer to this point in Part I (*J.*, 1950, 1203) but we should like to draw particular attention to our view since it is apparent from some of the newer textbooks discussing reaction mechanisms that a misleading representation of this (and similar) acid-catalysed hydrolysis is being advanced. Our view is that the reaction proceeds as follows :

$$Ac_2O + H_3O^+ \rightleftharpoons Ac_2O^+H + H_2O \longrightarrow 2AcOH + H^+$$

We have also shown that, when sufficient benzoic anhydride was treated with 72% perchloric acid (1 mol.) in nitromethane (which was necessary to give a homogeneous mixture) in the presence of anisole (4 mols.), so that the resulting solution contained benzoic acid (4·4 mols.) and benzoic anhydride (4 mols.), there was a fairly rapid production of at least 1·08 mols. of *p*-methoxybenzophenone. The reaction did not occur as readily as the corresponding one with acetic anhydride and perchloric acid (Part I, *loc. cit.*) and again indicated the lower reactivity of benzoic anhydride.

We should point out that the yields of *p*-methoxybenzophenone quoted in the experiments involving the use of benzoic anhydride are strictly *minimal* since we had, of necessity, to adopt an alkaline hydrolysis to remove unchanged anhydride. We showed that the ketone was not cleaved by aqueous-alcoholic potassium hydroxide but the necessity of submitting the reaction product to this treatment must have involved some loss in the isolation processs.

Our proof that benzoic anhydride and hydrogen ion react in the manner we have indicated has also been confirmed recently by Gillespie (*J.*, 1950, 2997) who showed, by a cryoscopic method, that in an excess of sulphuric acid as the solvent, benzoic anhydride reacts thus :

$$\mathrm{Bz_2O + 2H_2SO_4 \longrightarrow Bz^+ + BzOH_2^+ + 2HSO_4^-}$$

Gillespie's results are in a sense complementary to those of Treffers and Hammett (*J. Amer. Chem. Soc.*, 1937, **59**, 1708) who proved by a similar method that benzoic acid and 2 : 4 : 6-trimethylbenzoic acid behave differently in sulphuric acid. The former adds a proton to give the benzoic acidium ion, $\mathrm{BzOH_2^+}$, whereas the latter affords the 2 : 4 : 6-trimethylbenzoylium ion, $\mathrm{C_6H_2Me_3{\cdot}CO^+}$.

It was clearly of interest to study the reaction between " 2 : 4 : 6-trimethylbenzoyl perchlorate " and anisole. We found as expected that the addition of 2 : 4 : 6-trimethylbenzoyl chloride (1 mol.) to silver perchlorate (1 mol.) in anisole (4 mols.) and nitromethane resulted in the production of at least 0·92 mol. of 4-methoxy-2′ : 4′ : 6′-trimethylbenzophenone when the reaction was carried out at 0—5° for 45 minutes. This result appeared to us to be capable of interpretation in two ways, namely, (i) that the 2 : 4 : 6-trimethylbenzoylium ion was more reactive, that is, reacted faster, than the benzoylium ion, or (ii) that in the reaction

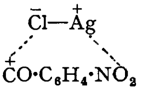
$$\mathrm{ArCOCl + AgClO_4 \rightleftharpoons ArCO^+ClO_4^- + AgCl}$$

the equilibrium lies more to the right for the 2 : 4 : 6-trimethylbenzoyl than for the benzoyl compound. It will be apparent that the combined electron-repelling effects of the three methyl groups in the acid chloride would tend to help the separation of the chlorine in the sense $\mathrm{Me_3C_6H_2{\rightarrow}CO{\rightarrow}Cl}$, but we should also expect that once the cation had been formed, the same electronic effects would tend to neutralise the positive charge, *i.e.*, $\mathrm{Me_3C_6H_2{\rightarrow}CO^+}$. We found in these experiments that the yield of silver chloride was almost quantitative in both cases and we feel justified for this reason in assuming that (i) is the correct premise. It should be emphasised however that a final decision regarding reactivities cannot be made on the basis of yields alone.

This point appeared to be capable of further verification by studying the preparation and the action of " *p*-anisoyl perchlorate " on anisole, since the powerful electron-repelling effect of the methoxyl group should be comparable with the combined effects of the methyl groups discussed above. We realised that in the case of the 2 : 4 : 6-trimethylbenzoyl compound there might be present a steric hindrance factor which is completely lacking in the *p*-anisoyl derivative. With the same molecular ratio of reactants under comparable conditions we were able to isolate also 0·92 mol. of 4 : 4′-dimethoxybenzophenone and an almost quantitative yield of silver chloride. We thus find that the *p*-anisoylium ion, *p*-$\mathrm{MeO{\cdot}C_6H_4{\cdot}CO^+}$, in which the positive charge must to some extent again be neutralised by the electronic displacement of the methoxyl group, is as reactive as the 2 : 4 : 6-trimethylbenzoylium ion. It appears clear that a steric hindrance factor is not involved in the type of reaction we are investigating. In this sense the preparative value of such reactions might be of considerable value.

It appeared to us to be of considerable interest to study the preparation and reactivity of a cation in which the substituent in the benzene ring was of the opposite type to methoxyl and for this purpose we selected the *p*-nitrobenzoyl cation, *p*-$\mathrm{NO_2{\cdot}C_6H_4{\cdot}CO^+}$. In this case the electron-attracting nitro-group should clearly tend to retard the removal of the chlorine but should also stabilise the cation once it is formed. Consequently, we should have expected this cation to be the most reactive of those studied. When the reaction between " *p*-nitrobenzoyl perchlorate " and anisole was carried out under otherwise identical conditions we found that the yield of 4-methoxy-4′-nitrobenzophenone was only 0·70 mol. An increase in the reaction time from 45 minutes to 2 hours did not affect the yield and it was thus apparent that the reaction stopped for a reason which may not, at first sight, be apparent. In both these sets of reaction conditions the weight of the supposed silver chloride produced actually exceeded the theoretical amount and it was obvious that some adsorption of either unchanged *p*-nitrobenzoyl chloride or the actual *p*-nitrobenzoylium ion was taking place. In our experimental procedure we had always washed the filtered silver chloride with an organic solvent and finally, as a measure of safety, with water. We should have expected any adsorbed *p*-nitrobenzoyl chloride to have been largely removed by this procedure. Extraction of the supposed silver chloride with boiling alcohol removed an appreciable amount of *p*-nitrobenzoic acid leaving a residue of silver chloride which amounted to 95—100% of the theoretical amount. These results show definitely that the reaction

$$NO_2{\cdot}C_6H_4{\cdot}COCl + AgClO_4 \longrightarrow NO_2{\cdot}CH_4{\cdot}CO^+ClO_4^- + AgCl$$


(*A*.)

had in fact gone to completion since adsorption of any of the acid chloride on silver chloride would have resulted in the non-reaction of an appreciable amount of silver perchlorate, which would therefore have remained in solution. Under these conditions the yield of silver chloride could not possibly have reached the value of 95—100%. We are of the opinion that in this case, the nitro-group with its lone pairs of electrons on the oxygen atoms is acting as an electron-donor to the silver cations but we do not wish to exclude the possibility that the chloride ion is acting similarly towards the organic cation (see *A* *). It is possible, and indeed probable, that in the case of the benzoylium cation the latter type of adsorption also occurs to a limited extent, but that the resulting complex is much less stable than that produced from the *p*-nitrobenzoylium ion. In our method of treatment of the silver chloride, the washing with water would clearly result in its reaction with the adsorbed cation to give *p*-nitrobenzoic acid and hydroxonium ion :

$$NO_2{\cdot}C_6H_4{\cdot}CO^+ + 2H_2O \longrightarrow NO_2{\cdot}C_6H_4{\cdot}CO_2H + H_3O^+$$

Our findings appear to accord with this view.

The idea that an organic ion is capable of adsorption by a silver halide is not altogether novel. It has been postulated by Hughes, Ingold, *et al.* (*J.*, 1937, 1237, 1243) that a silver halide will adsorb an organic halide owing to a certain degree of electronic bonding between the silver cations and the (organic) halogen thus facilitating the separation of the organic radical as a cation. This view is not strictly comparable with our postulate but we feel that the two processes are closely allied.

If our view that the nitro-group is involved in an adsorption process is correct, then it would follow that an ion containing two nitro-groups might show, irrespective of its structure, an enhanced effect. It was noteworthy that when 3 : 5-dinitrobenzoyl chloride was added to a solution of silver perchlorate and anisole in nitromethane there was the obvious separation (after a short induction period) of silver chloride, but after 45 minutes at 0—5° there was no ketone in the reaction mixture. When the reaction mixture was kept for 2 hours we found that there was an uncontrollable and sudden rise in temperature from 0—5° to 75°, and we are of the opinion that the 3 : 5-dinitrobenzoylium ion had been largely adsorbed on the silver chloride and that, after a fairly long induction period, an extremely rapid reaction had occurred on the silver chloride surface. Extensive decomposition of any material formed during the reaction occurred, and we did not think it advisable to pursue this aspect of the investigation.

We had always been aware of the possibility that silver chloride might interfere in some way with the reaction of the " acyl perchlorate " prepared by the silver perchlorate technique, but we drew special attention in Part II (*loc. cit.*) to the fact that the results with acetylium perchlorate were the same irrespective of the method of its preparation. In this case the adsorption process may occur but is clearly of little consequence.

We also envisaged the possibility that the *p*-nitrobenzoylium (or similar) ion might react with the ethereal oxygen of anisole in the way we have discussed in Part III (preceding paper), thus leading to, for example, some phenyl *p*-nitrobenzoate :

$$PhOMe + NO_2{\cdot}C_6H_4{\cdot}CO^+ \rightleftharpoons NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}O^+PhMe \longrightarrow NO_2{\cdot}C_6H_4{\cdot}CO_2Ph + Me^+$$

We made a careful search for the presence of this ester in our reaction product but without success. We did find however that repeated fractionation gave a few crystals of a substance which was ketonic and was most probably 2-methoxy-4′-nitrobenzophenone.

EXPERIMENTAL.

Materials.—Benzoyl chloride was an AnalaR reagent. 2 : 4 : 6-Trimethylbenzoyl chloride was prepared by Barnes's method (*Org. Synth.*, 1941, **21**, 77). Commercial *p*-nitrobenzoyl chloride was treated with thionyl chloride and subsequently purified by repeated crystallisation from carbon tetrachloride. Commercial *p*-anisoyl chloride was purified by treatment with thionyl chloride and subsequent

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* Scheme (*A*) is not intended to be anything other than illustrative.

repeated vacuum-distillation. " Pure " 3 : 5-dinitrobenzoyl chloride (see Introduction) was crystallised first from carbon tetrachloride and then from a large volume of light petroleum (b. p. 40—60°) in which it was only sparingly soluble. Benzoic anhydride, m. p. 42°, was dried for at least 48 hours over phosphoric oxide. Anisole and nitromethane were dried and redistilled. Silver perchlorate was treated as in Part II (*loc. cit.*).

p-*Methoxybenzophenone*.—(*a*) Silver perchlorate (0·05 g.-mol.), dissolved in anisole (0·2 g.-mol.) and nitromethane (43·2 g.), was cooled to 0° and benzoyl chloride (0·05 g.-mol.) was added during 15—18 minutes, the temperature being kept at 0—5°. The initially yellow mixture slowly became more brown on being kept at 0—5° for 45 minutes. The mixture was poured on crushed ice (*ca.* 150 g.) and, after all the ice had melted, the silver chloride was filtered off and washed with water and with ether. The oily material in the filtrate was extracted twice with ether and the combined ethereal extracts were washed successively with water, 2N-sodium hydroxide (twice), and water (twice). The dried (Na_2SO_4) ethereal solution was evaporated and the residue fractionated; the fraction, b. p. 180—190°/7—8 mm., solidified on cooling (0·042 g.-mol.) and had m. p. 58°. It crystallised from light petroleum (b. p. 40—60°) in clusters of colourless needles, m. p. 61—62° (Found: C, 79·2; H, 5·6. Calc. for $C_{14}H_{12}O_2$: C, 79·2; H, 5·7%). The ketone was further characterised as the 2 : 4-*dinitrophenylhydrazone*, bright red needles (from ethyl acetate), m. p. 221—222° (Found: C, 61·2; H, 4·0. $C_{20}H_{16}O_5N_4$ requires C, 61·2; H, 4·1%). Preparation of this and other 2 : 4-dinitrophenylhydrazones of the substituted benzophenones required heat.

When the reaction mixture obtained as under (*a*) was kept for 2 hours the yield of ketone was unchanged.

In the absence of nitromethane the yield of ketone was 0·034 g.-mol.

(*b*) A solution of silver perchlorate (0·05 g.-mol.) and benzoic anhydride (0·15 g.-mol.) in anisole (0·2 g.-mol.) and nitromethane (111 g.) was cooled to 0°, and benzoyl chloride (0·05 g.-mol.) added during 15 minutes at 0—5°. After being kept for 45 minutes at 0—5° the deep-orange mixture was poured on crushed ice (*ca.* 200 g.). The silver chloride was filtered off and washed repeatedly with ether, and the oily product extracted with ether. The ethereal solution was washed with water and then evaporated, the last stage being carried out under reduced pressure. The solid residue was dissolved in 96% alcohol (70 c.c.), and a solution of potassium hydroxide (17·5 g.) in water (15 c.c.) added cautiously. The mixture was then refluxed for 1 hour, as much of the alcohol as possible was distilled off, and the residue diluted with water and re-extracted with ether. The ethereal extract was treated as previously. The yield of *p*-methoxybenzophenone was 0·066 g.-mol., and the m. p. 58—60° before recrystallisation.

(*c*) Benzoic anhydride (0·155 g.-mol.) was dissolved in a mixture of nitromethane (114·5 g.) and anisole (0·1 g.-mol.), and the solution was cooled to 0°. 72% Perchloric acid (3·5 g. ≡ 0·025 g.-mol.) was cautiously added during 15—16 minutes. After addition of the first few drops of acid the mixture became bright yellow, solid material separated, and in spite of strong cooling the temperature rose to 10°. The mixture was cooled rapidly to 5° and then kept between 0° and 5° for the rest of the addition. After being kept at 0—5° for a further 45 minutes, the mixture was poured on crushed ice (150—200 g.), a reddish-violet colour being produced. The ketone (0·027 g.-mol.), m. p. 58—60°, was isolated as described under (*b*).

4-*Methoxy*-2′ : 4′ : 6′-*trimethylbenzophenone*.—(*a*) A solution of 2 : 4 : 6-trimethylbenzoyl chloride (mesitoyl chloride) (0·025 g.-mol.) in nitromethane (4·6 g.) was added during 15 minutes to a cooled (0—5°) solution of silver perchlorate (0·025 g.-mol.) in anisole (0·025 g.-mol.) and nitromethane (13·5 g.). The bright yellow mixture was kept at 0—5° for 45 minutes and then filtered. The solid was washed repeatedly with chloroform and finally with water. The filtrate which was collected directly on crushed ice became almost colourless. After extraction of the filtrate twice with chloroform, the combined extracts were washed twice with 2N-aqueous ammonia and then with water. Evaporation of the solution gave a residue of *ketone* which solidified on trituration with a little light petroleum (b. p. 60—80°) to colourless needles (0·023 g.-mol.). Crystallisation from alcohol gave colourless needles, m. p. 76—77° (Found: C, 79·9; H, 7·1. $C_{17}H_{18}O_2$ requires C, 80·3; H, 7·1%).

(*b*) A mixture of *p*-anisoyl chloride (0·05 g.-mol.), mesitylene (0·05 g.-mol.), 95% zinc chloride (0·028 g.-mol.), and nitromethane (14·5 g.) was refluxed (*ca.* 3½ hours) until all the zinc chloride had dissolved. The crude ketone (0·03 g.-mol.) obtained by pouring the mixture on crushed ice, extracting the product with ether, and washing the ethereal extract with 2N-sodium hydroxide and water crystallised from alcohol in colourless needles, m. p. and mixed m. p. 76—77°.

The ketone did not give a 2 : 4-dinitrophenylhydrazone.

A solution of the ketone in an excess of concentrated sulphuric acid was heated on the steam-bath for 1—2 minutes. The intense yellow colour which developed disappeared on treatment of the solution with cold water, and the oily droplets then slowly crystallised. The solid melted almost completely at 75—76° but the melt did not become absolutely clear until 125—130°. A mixed m. p. with the original ketone was also 75—76° but a faint opalescence persisted until a little above 80°. When the crude product was shaken with dilute sodium hydrogen carbonate solution, the filtered solution gave on acidification a trace of solid material which redissolved on the addition of alkali.

4 : 4′-*Dimethoxybenzophenone*.—*p*-Anisoyl chloride (0·05 g.-mol.) in nitromethane (4·2 g.) was added during 15 minutes to a solution of silver perchlorate (0·05 g.-mol.) in nitromethane (27·0 g.) and anisole (0·05 g.-mol.) at 0—5°. After a further 45 minutes at 0—5° the silver chloride was filtered off from the yellow-brown mixture and the filtrate collected directly on crushed ice (*ca.* 150 g.). The silver chloride was washed repeatedly with chloroform which was then used to extract the aqueous phase. The combined extracts were washed thrice with 2N-sodium hydroxide and then with water. The residue from the evaporated extract solidified to a crystalline mass which after being washed with light petroleum (b. p. 40—60°) had m. p. 140° (yield, 0·046 g.-mol.). The ketone crystallised from alcohol in colourless

needles (or flakes), m. p. 143° (Found : C, 75·0; H, 5·8. Calc. for $C_{15}H_{14}O_3$: C, 75·0; H, 5·8%). The ketone was further characterised as the 2 : 4-*dinitrophenylhydrazone*, bright red needles, m. p. 198°, from chloroform–alcohol (3 : 1) or from ethyl acetate (Found : C, 59·9; H, 4·1; N, 13·2. $C_{21}H_{18}O_6N_4$ requires C, 59·7; H, 4·3; N, 13·3%).

A similar experiment in which the reaction mixture was kept for 2 hours gave the same results.

A trace only of *p*-anisic acid was obtained by acidification of the alkaline extracts of the reaction product.

4-*Methoxy*-4′-*nitrobenzophenone*.—Silver perchlorate (0·05 g.-mol.) was dissolved in anisole (0·05 g.-mol.) and nitromethane (27·0 g.) and treated at 0° with a solution of *p*-nitrobenzoyl chloride (0·05 g.-mol.) in nitromethane (23·3 g.) during 15 minutes. The mixture was kept for 45 minutes at 0—5° and then filtered (sintered-glass filter), the filtrate being allowed to drop directly on crushed ice (*ca.* 150 g.). The solid was washed repeatedly with chloroform, until all the pink colour was removed. The bright red semi-solid mass which separated from the filtrate was extracted repeatedly with more chloroform, and the combined extracts were washed with 2N-aqueous ammonia until the washings no longer gave a precipitate on acidification with 2N-sulphuric acid. After being washed with water the chloroform extracts were dried and evaporated, the excess of nitromethane and anisole being removed in a vacuum. The solid residue, after being washed with a little ether, consisted of pale pink or yellow needles (0·035 g.-mol.) which crystallised from alcohol in almost colourless needles, m. p. 121° (Found : C, 66·0; H, 4·5; N, 5·2. Calc. for $C_{14}H_{11}O_4N$: C, 65·4; H, 4·3; N, 5·4%).

The ketone was characterised as its 2 : 4-*dinitrophenylhydrazone*, scarlet plates (from chloroform), m. p. 265° (decomp.) (Found : C, 54·8; H, 3·4; N, 15·6. $C_{20}H_{15}O_7N_5$ requires C, 54·9; H, 3·4; N, 16·0%).

Evaporation of the various mother-liquors from the crystallisations gave variable amounts of a solid which melted at about 93°. When this was fractionated from methanol two types of crystal were obtained : (*a*) fine needles, m. p. 121°, identical (m. p. and mixed m. p.) with the above ketone, and (*b*) a small amount of stout prisms, m. p. 117° (Found : C, 65·6; H, 4·3; N, 5·6. $C_{14}H_{11}O_4N$ requires C, 65·4; H, 4·3; N, 5·4%), which depressed the m. p. of the above ketone and of phenyl *p*-nitrobenzoate (m. p. 126°) and appeared to be (?) 2-*methoxy*-4′-*nitrobenzophenone*. The prisms gave a bright yellow 2 : 4-dinitrophenylhydrazone, m. p. 210° (decomp.), which from its nitrogen content (Found : N, 16·8%) appeared to be contaminated with a little 2 : 4-dinitrophenylhydrazine.

Extraction of the original filter containing the silver chloride with boiling 96% ethyl alcohol and subsequent evaporation of the extracts gave *p*-nitrobenzoic acid (1·2 g.), identified by m. p. and mixed m. p. The residual silver chloride amounted to 95—100% of the theoretical amount.

We thank Imperial Chemical Industries Limited for a grant towards the cost of this investigation.

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[*Received, November* 16*th*, 1950.]