111. *Acylation Reactions catalysed by Strong Acids. Part III. The Acetylium Ion as a Debenzylating Agent.*

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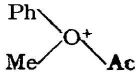
Benzyl phenyl ether forms an oxonium salt with the acetylium ion and the subsequent reactions of the benzyl cation arising by decomposition of the oxonium ion are followed by investigating the products formed in various solvents. Suitably constituted aryl benzyl ethers are shown to be largely debenzylated by treatment with a little 72% perchloric acid in acetic anhydride. The benzyl group is removed as benzyl acetate and the acetate of the phenol results. Sulphuric acid is less effective than perchloric acid for the same purpose.

In view of the well-known tendency for ethers to undergo oxonium salt formation, it was necessary in Part I (*J.*, 1950, 1203) to point out that in the reaction between anisole and acetylium perchlorate the experimental results indicated that formation of the ion, 

could have occurred only to a very limited extent. We expressed the view that this ion could not be expected to undergo a Friedel–Crafts type of reaction with the acetylium ion (Ac^+), but we did consider that an oxonium ion of this type might be expected to undergo an " acetolysis " in the presence of acetic anhydride, namely :

$$PhO^+MeAc + Ac_2O \longrightarrow PhOAc + MeOAc + Ac^+$$

This reaction would clearly result in the regeneration of acetylium ion, and if realisable should consequently give valuable evidence of the catalytic nature of the acetylium ion in such processes. The only evidence adduced (*loc. cit.*) for such an acetolysis was that extraction of the reaction product from anisole and acetylium perchlorate with cold aqueous sodium hydroxide gave small but definite amounts of phenol, undoubtedly formed by hydrolysis of a little phenyl acetate.

We did not wish to imply in Part I (*loc. cit.*) that addition of the acetylium ion to the ethereal oxygen was a limited process but rather that the overall reaction resulted in the setting up of an equilibrium, $PhOMe + Ac^+ \rightleftharpoons PhO^+MeAc$, lying well to the left. We consider that such an oxonium ion once formed could equally readily eliminate the acetylium ion to regenerate the original reactants. In our view both processes would be of comparable facility and consequently the final nature of any subsequent reaction would not be affected to any appreciable extent.

In order to see if we could increase the stability of the ion, or, in other words, displace the above equilibrium from the left towards the right for a similarly constituted oxonium ion we investigated the reaction between acetylium perchlorate and benzyl phenyl ether. The greater electron-donating property of the benzyl group (as compared with methyl), which is apparent from the well-known fact that debenzylation is a much more facile process than demethylation of the corresponding aryl ethers, should facilitate the decomposition of the oxonium ion, $CH_2Ph{\cdot}O^+PhAc$, which we should expect, if formed to any appreciable extent, to undergo characteristic fission. We surmised that benzyl phenyl ether would add acetylium much more readily than anisole and that once formed, it would give, *inter alia*, more positive evidence of an acetolysis reaction of the type discussed above. To avoid the possible complications of acetic acid in the reaction mixtures we decided in the first place not to use an acetic anhydride–perchloric acid mixture but to apply our technique (*J.*, 1950, 2034) of using acetyl chloride and silver perchlorate in an inert solvent of relatively high dielectric constant, namely, nitromethane. We found that, with equimolecular amounts of the reagents and generation of the acetylium perchlorate in the presence of all the ether, the reaction product was a mixture containing (as indicated by normal qualitative tests) only a trace of benzyl ether, and also small amounts of ketonic material (since treatment of the reaction product with Brady's reagent resulted in a marked, red coloration). At first we were of the opinion that these observations indicated that the reaction

$$CH_2Ph{\cdot}OPh + Ac^+ \longrightarrow CH_2Ph{\cdot}O{\cdot}C_6H_4{\cdot}COMe + H^+$$

might possibly be occurring to a very minor degree, although we could not reconcile this view with the fact that the reaction product gave an almost negative test for the benzyl ether grouping with hot concentrated hydriodic acid. We were compelled therefore to consider that any ketone formed could not be *p*-benzyloxyacetophenone, which we found (see Experimental) gave a very characteristic, insoluble 2 : 4-dinitrophenylhydrazone and which, even in small amount, also gave the characteristic smell of benzyl iodide when treated with hydriodic acid. We were fortunate in one experiment (of several carried out in nitromethane as solvent) to isolate a small but definite amount of a crystalline 2 : 4-dinitrophenylhydrazone which from its composition and physical and chemical properties was almost certainly *p*-hydroxyacetophenone 2 : 4-dinitrophenylhydrazone. The formation of very small amounts of ketone, irrespective of the structure of the product, was in marked contrast to the results obtained with anisole and acetylium perchlorate, which under identical conditions gave at least 84% of *p*-methoxyacetophenone, and indicated quite clearly that the reaction mechanism for the benzyl ether was taking a different course.

We proved that the reaction product did in fact contain a fair amount (at least 0·22 mol.) of phenyl acetate together with a larger quantity of a higher-boiling product, the composition and molecular weight of which approximated to those of a benzylphenyl acetate and which on this formulation resulted to the extent of at least 0·38 mole. In addition, an appreciable amount of a still more complex product was also found but this was not investigated further owing to its intractable nature. The possibility that this last product was formed by the condensation of *p*-benzyloxyacetophenone produced (as above) appeared to us to be excluded by the fact that no appreciable reaction for the benzyl ether group was observed.

We concluded from the experiments carried out under these conditions that the following reactions had occurred :

$$CH_2Ph{\cdot}OPh + Ac^+ \rightleftharpoons CH_2Ph{\cdot}O^+PhAc \quad . . . . (1)$$

$$CH_2Ph{\cdot}O^+PhAc \longrightarrow PhOAc + {}^+CH_2Ph \quad . . . . (2)$$

$$PhOAc + {}^+CH_2Ph \longrightarrow CH_2Ph{\cdot}C_6H_4{\cdot}OAc + H^+ \quad . . . . . . (3)$$

$$PhOAc + Ac^+ \longrightarrow COMe{\cdot}C_6H_4{\cdot}OAc + H^+ \quad . . . . (4)$$

In addition it may be that further reaction of the benzylphenyl acetate with benzyl cations had also taken place. Alternatively, it might be possible that " polymerisation " of some of the benzyl cations had occurred in the manner suggested by Monicelli and Hennion (*J. Amer. Chem. Soc.*, 1941, **63**, 1722), *viz.* :

$$n^+CH_2Ph \longrightarrow (CHPh)_n + nH^+$$

but we put forward this suggestion with considerable reserve.

We showed that the properties of the " benzylphenyl acetate " were in accordance with our formulation but we did not think it worth while or necessary to see if it was a mixture of *o*- and *p*-isomerides. It is also clear that the almost negative test for the benzyloxy-group also excludes the unlikely possibility that the decomposition

$$CH_2Ph{\cdot}O^+PhAc \longrightarrow CH_2Ph{\cdot}OAc + Ph^+$$

had taken place.

We have formulated reaction (3) in the above manner because we do not wish to imply that the benzylphenyl acetate arises as a result of an intramolecular reaction

$$CH_2Ph{\cdot}O^+PhAc \longrightarrow CH_2Ph{\cdot}C_6H_4{\cdot}OAc + H^+$$

which would involve a migration of the benzyl group. We show in our subsequent discussion that such a rearrangement is excluded.

The above results are in some respects similar to those obtained by Monicelli and Hennion (*loc. cit.*) on the decomposition of, *e.g.*, benzyl propyl ether by boron trifluoride. In the latter case, however, the reaction mechanism is clearly different since the neutral ether and boron trifluoride give a benzyl cation and a complex anion :

$$CH_2Ph{\cdot}OPr + BF_3 \longrightarrow {}^+CH_2Ph + [BF_3{\cdot}OPr]^-$$

Proof of the formation of the benzyl cation was given (*loc. cit.*) by carrying out the decomposition in presence of various solvents, but we wish to mention two in particular, benzene and acetic anhydride, since the results obtained by Monicelli and Hennion are pertinent to our subsequent work. The formation of diphenylmethane in benzene as a solvent clearly establishes the production of the benzyl cation and its high reactivity. On the other hand, we are extremely surprised that in the presence of acetic anhydride as a solvent no benzyl acetate was produced : we should predict that this would have been formed to the same extent as propyl acetate by the reaction :

$${}^+CH_2Ph\,[BF_3{\cdot}OPr]^- + Ac_2O \longrightarrow CH_2Ph{\cdot}OAc + PrOAc + BF_3$$

It is possible that the reaction does take this course and that the regenerated boron trifluoride reacts preferentially with the benzyl acetate to give the so-called polymerised product (*loc. cit.*).

Our reasons for postulating reaction (4) are supported by the behaviour of *p*-benzyloxyacetophenone towards acetylium perchlorate in nitromethane. The ketone is not debenzylated to any appreciable extent but does undergo partial conversion into an orange compound exhibiting a marked green fluorescence in alcoholic solution. This compound is clearly of the same type as that produced from *p*-methoxyacetophenone under similar conditions (see Parts I and II). We surmise that the method used for isolation of the reaction product in our first series of experiments, together with the use of alcoholic sulphuric acid for the preparation of the 2 : 4-dinitrophenylhydrazone, did in fact lead to hydrolysis of the original acetoxy-group.

We do not consider that the stability of the benzyloxy-group in *p*-benzyloxyacetophenone towards the acetylium ion vitiates any of our results, because it must be apparent that in the structure, $COMe{\cdot}C_6H_4{\cdot}O{\cdot}CH_2Ph$, the carbonyl oxgen atom would be expected to undergo more ready addition of acetylium than the ethereal oxygen and so lead, in the first place, to the formation of the ion, $CH_2Ph{\cdot}O{\cdot}C_6H_4{\cdot}C^+Me{\cdot}OAc$. We think it very probable that an ion of this type is involved in the production of the coloured compound exhibiting fluorescence. This and the similar compounds formed in the reaction between anisole and acetylium perchlorate, especially in the presence of acetic anhydride, are undoubtedly pyrylium salts of the type obtained by Dilthey (*J. pr. Chem.*, 1916, [ii], **94**, 75) from, for example, *p*-methoxyacetophenone, acetic anhydride, and various catalysts (all of which would be expected to produce acetylium ions). We have found in all our experiments with anisole and with benzyl phenyl ether that if *C*-acetylation does occur to any appreciable extent then the reaction mixture on treatment with water and ether generally shows a green fluorescence.

We have found when acetylium perchlorate and benzyl phenyl ether are allowed to react in benzene as the solvent that phenyl acetate, the fraction corresponding to benzylphenyl acetate, and diphenylmethane are all produced. The isolation of diphenylmethane indicates clearly that the possibility of an intramolecular reaction as discussed above (p. 524) is untenable since the benzyl cation produced in equation (2) reacts with both phenyl acetate and the benzene. In this experiment it is clear that reactions (1), (2), (3), possibly (4) (see Experimental) and also the reaction

$$^{+}CH_2Ph + C_6H_6 \longrightarrow CH_2Ph_2 + H^{+}$$

have occurred.

Our formulation of an " acetolysis " reaction of the type first mentioned (p. 523) in this paper should clearly be capable of proof if the reaction between acetylium perchlorate and benzyl phenyl ether were carried out in the presence of an excess of acetic anhydride, since the following reactions could occur in addition to (1), (2), (3), and (4) :

$$CH_2Ph{\cdot}O^{+}PhAc + Ac_2O \longrightarrow CH_2Ph{\cdot}OAc + PhOAc + Ac^{+} \quad . \quad . \quad . \quad . \quad (5)$$

$$\text{(or} \quad ^{+}CH_2Ph + Ac_2O \longrightarrow CH_2Ph{\cdot}OAc + Ac^{+}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5a)$$

$$\text{and} \quad CH_2Ph{\cdot}OPh + Ac^{+} \longrightarrow CH_2Ph{\cdot}O{\cdot}C_6H_4{\cdot}COMe + H^{+} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

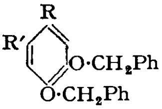
Since reaction (5) or (5*a*) regenerates acetylium ions, and reactions (3), (4), and (6) produce hydrogen ions which are known (Parts I and II) to give acetylium ions in the presence of acetic anhydride, it is clear that these conditions should all tend to maintain a high concentration of acetylium in the reaction mixture. If *C*-acetylation of the neutral benzyl phenyl ether can occur it must be apparent that reaction (6) is thus capable of being realised. We have shown that the ether (1 mol.) and acetylium perchlorate (0·5 mol.) in the presence of acetic anhydride (2 mols.) diluted with nitromethane give a complex reaction mixture containing *p*-benzyloxyacetophenone, phenyl acetate, benzyl acetate, and the benzylphenyl acetate fraction, all of which have been identified.

It is apparent from these results that reaction (1) clearly leads, as expected, to an equilibrium. Our initial experiments, *i.e.*, in nitromethane alone, and those in benzene, were so carried out that an excess of the benzyl phenyl ether was present in the first half of the reaction and our results are in accordance with this procedure. The constant regeneration of acetylium ions in the experiment using acetic anhydride–nitromethane as the solvent indicates that the free ether is necessary for the Friedel–Crafts type of reaction to take place. It must also be apparent that reactions (1) (*et seq.*) and (6) occur at markedly different rates and it would be expected that the latter would be the slower. All our results prove that such is the case. They also indicate quite definitely that the benzyl cation is an extremely reactive entity and far exceeds the reactivity of the acetylium ion. We attach considerable importance to this marked difference in reactivity since we feel that the alkylation and acylation of aromatic compounds by the Friedel–Crafts procedure are not strictly comparable. We propose to elaborate this thesis in a subsequent paper.

We did also carry out one experiment in which the benzyl phenyl ether was added to the pre-formed acetylium perchlorate. Under these conditions, *i.e.*, an excess of acetylium ion present in the first 50% of the reaction, a non-distillable reaction product resulted. This result was not unexpected since the intermediate phenyl acetate must be attacked by acetylium and benzyl cation.

It has been stated by Roberts and Hammett (*J. Amer. Chem. Soc.*, 1937, **59**, 1063; cf. Clark and Todd, *J.*, 1950, 2030) that the benzyl cation is probably yellow. It is true that in our experiments involving the benzyl cation a yellow colour usually developed in the first instance; we have also remarked (Parts I and II) on the development of a similar yellow colour in solutions containing acetylium perchlorate. We find, however, that in the presence of ethers in particular there is usually an intensification of the original yellow colour to sometimes intense shades of purple. It may well be that the benzyl and acetyl cations are both yellow but we would not attach undue importance to this, since the production of colour appears to us to depend partly on the medium in which the reaction is carried out and largely on the nature of the compound produced in the reaction.

It will be apparent from the reactions postulated above leading to the regeneration of acetylium or hydrogen ions, that mixtures of perchloric acid and an excess of acetic anhydride should be capable of debenzylating suitably constituted benzyl ethers, and also that the process should be catalytic as far as the perchloric acid is concerned. We have shown that benzyl phenyl ether treated under these conditions gives the same simpler products as our last series of experiments. The qualitative differences can be ascribed to the rather different composition of the reaction mixture since the use of aqueous perchloric acid must lead to the formation of acetic acid. It is noteworthy that, under the conditions we have actually used, a little unchanged ether could be isolated; this was not observed in any of the other series of experiments. The formation of the more complex products was actually less. Encouraged by this result we decided to investigate this catalytic debenzylation process with three dibenzyl ethers of the general formula (I) which had been prepared in connection with another investigation. In each case the group R was nitro- or formyl whilst in two cases R′ was hydrogen and in the third methyl. We selected these structural conditions deliberately since there appeared to us to be no possibility of nuclear acetylation in these cases. We found that 3 : 4-dibenzyloxybenzaldehyde (protocatechualdehyde dibenzyl ether) (I; R = CHO, R′ = H) gave a good yield of 3 : 4-diacetoxybenzylidene diacetate which was also similarly obtained from protocatechualdehyde itself. Similarly, 3 : 4-dibenzyloxy-1-nitrobenzene (4-nitrocatechol dibenzyl ether). (I; R = NO_2, R′ = H) gave mainly 4-nitrocatechol diacetate, or the monoacetate monobenzyl ether according to the conditions used, but the analogous 4 : 5-dibenzyloxy-2-nitrotoluene (I; R = NO_2, R′ = Me) gave mainly 4(or 5)-acetoxy-5(or 4)-benzyloxy-2-nitrotoluene. This last result may be a consequence of the electron-repelling methyl group and we think it would be worth while to study this effect in due course. In the meantime we feel that our results give valuable support to the various reactions postulated in this communication.



(I.)

In Part I (*loc. cit.*) we also suggested that concentrated sulphuric acid in an excess of acetic anhydride should also give rise to acetylium ions :

$$Ac_2O + H_2SO_4 \rightleftharpoons Ac^+ + AcOH + HSO_4^-$$

A proof of the correctness of this suggestion has recently been supplied by Gillespie (*J*, 1950, 2997) who has shown, by cryoscopic measurements, that acetic (and benzoic) anhydride in an excess of sulphuric acid reacts completely as follows :

$$Ac_2O + 2H_2SO_4 \longrightarrow Ac^+ + AcOH_2^+ + 2HSO_4^-$$

The well-known fact that such mixtures undergo mutual interaction to produce sulphoacetic acid also appeared to be manifest in Gillespie's experiments. Our view that the sulphuric acid–acetic anhydride mixture would not be such an effective source of acetylium ions as the perchloric acid–acetic anhydride mixture appears to us to be well substantiated by our finding that 3 : 4-dibenzyloxy-1-nitrobenzene was converted under comparable reaction conditions, by a little sulphuric acid in acetic anhydride into a 4-nitrocatechol acetate monobenzyl ether without any trace of 4-nitrocatechol diacetate. Similarly 3 : 4-dibenzyloxybenzaldehyde gave a triacetate which was undoubtedly 3(or 4)-acetoxy-4(or 3)-benzyloxybenzylidene diacetate, $CH_2Ph{\cdot}O{\cdot}C_6H_3(OAc){\cdot}CH(OAc)_2$. These results show, however, in spite of the differences, that debenzylation with concentrated sulphuric acid in acetic anhydride does occur. We did not investigate the orientation of the acetoxy- and benzyloxy-groups in these mixed ether acetates.

Incidental to this investigation we have examined, in the first instance in collaboration with Dr. J. L. Stoves, the nitration of *o*-dibenzyloxybenzene (catechol dibenzyl ether) and find, as with veratrole, that this leads exclusively to substitution in the 4-position of the original benzene ring. The constitution of the resulting 3 : 4-dibenzyloxynitrobenzene (4-nitrocatechol dibenzyl ether) was proved by its ready debenzylation by hydrobromic acid to 4-nitrocatechol which was further identified as its diacetate and also as its dimethyl ether (4-nitroveratrole).

We have found dioxan to be a very convenient medium for the preparation of aryl benzyl ethers in spite of the reaction being generally slower than when alcohol is used as the solvent. The main advantage is that the resulting product is not contaminated with benzyl ethyl ether.

EXPERIMENTAL.

Materials.—Acetyl chloride and benzene were AnalaR reagents. Silver perchlorate was treated as described in Part II (*J.*, 1950, 2034).

Benzyl Phenyl Ether.—Potassium hydroxide (0·67 g.-mol.) in water (38 c.c.) was added to phenol (0·67 g.-mol.) in dioxan (500 c.c.), and the resulting solution was heated on a steam-bath. Benzyl chloride (0·67 g.-mol.) was added during 30 minutes and the resulting heterogeneous mixture was heated and stirred for 36 hours. About two-thirds of the solvent was removed in a vacuum and the residue poured into water (*ca.* 1·2 l.). After extraction with ether the combined ethereal extracts were washed with 2N-sodium hydroxide until the washings no longer became opaque on acidification. The residue from the dried (Na_2SO_4) ethereal extract gave a fraction (*ca.* 50%), b. p. 160—165°/12 mm., which solidified on cooling. Crystallisation from alcohol gave colourless flakes, m. p. 38—39°.

p-*Benzyloxyacetophenone*.—The spongy mass of yellow solid precipitated on addition of potassium hydroxide (4·5 g.) in water (4·5 c.c.) to a solution of *p*-hydroxyacetophenone (9·6 g.) in dioxan (100 c.c.) was heated on a steam-bath and benzyl chloride (10·1 g.) was added. After refluxing gently for 15—16 hours the mixture was added to water (750—800 c.c.). The light-brown waxy solid which precipitated was dissolved in ether, and the solution washed thrice with 2N-sodium hydroxide and then with water. The dried (Na_2SO_4) ethereal solution was evaporated, excess of dioxan being removed in a vacuum. The *ketone* crystallised from methyl alcohol in pale cream-coloured needles (9·1 g.), m. p. 88°. Recrystallisation from benzene gave almost colourless prisms, m. p. 91—92° (Found : C, 79·6; H, 6·3. $C_{15}H_{14}O_2$ requires C, 79·6; H, 6·2%). *p*-Hydroxyacetophenone (1·6 g.) was recovered from the alkaline washings.

The 2 : 4-*dinitrophenylhydrazone* separated in deep crimson flakes, m. p. 188—190°, from ethyl acetate (Found : C, 62·1; H, 4·5; N, 13·8. $C_{21}H_{18}O_5N_4$ requires C, 62·1; H, 4·4; N, 13·8%).

Fission of Benzyl Phenyl Ether with Acetylium Perchlorate.—*In nitromethane.* (*a*) Acetyl chloride (0·05 g.-mol.) was added during 15 minutes to a cold (0—5°) solution of benzyl phenyl ether (0·05 g.-mol.) and silver perchlorate (0·05 g.-mol.) in nitromethane (104 g.). The mixture was kept for a further 30 minutes at 0—5°, and the silver chloride was filtered off from the mauve solution, the filtrate being allowed to drop on crushed ice. After washing of the silver chloride with ether, the combined ethereal nitromethane solution was separated and washed repeatedly with water until the washings were no longer acid (Congo-red). After evaporation of the dried (Na_2SO_4) solution, the residue was separated by distillation in a vacuum into the fractions : (i) b. p. 77—80°/8 mm. (1·7 g.), which redistilled at 190—194° under atmospheric pressure ; (ii) b. p. 160—180°/6—8 mm. (4·3—4·4 g.) ; (iii) b. p. 200—250°/4 mm. (1·4—1·8 g.) ; and (iv) a residue (2—3 g.).

Fraction (i) consisted of phenyl acetate, confirmed by hydrolysis with boiling 2N-sodium hydroxide to phenol which was liberated by carbon dioxide (general procedure) and identified (standard procedure) as 2 : 4 : 6-tribromophenol, m. p. and mixed m. p. 91°. No evidence for the presence of benzyl acetate (see p. 528) was obtained.

Fraction (ii) (Found : C, 81·1 ; H, 6·2% ; *M*, 255. Calc. for $C_{15}H_{14}O$: C, 79·6; H, 6·2% ; *M*, 226), a viscous pale yellow oil, did not yield any crystalline material when kept. It gave an intense red colour with cold, alcoholic 2 : 4-dinitrophenylhydrazine sulphate but on one occasion only was crystalline material (0·3 g.) deposited. This crystallised from ethyl acetate in dark red needles, m. p. 255° (decomp.) (Found : C, 53·4; H, 4·1; N, 17·7. Calc. for $C_{14}H_{12}O_5N_4$: C, 53·2; H, 3·8; N, 17·7%), which did not depress the m. p. of genuine *p*-hydroxyacetophenone 2 : 4-dinitrophenylhydrazone, m. p. 254° (decomp.), and was readily soluble in cold, dilute sodium hydroxide. Vogel (" Practical Organic Chemistry," Longmans, Green & Co., 1948, p. 706) gives m. p. 261° for this 2 : 4-dinitrophenylhydrazone.

Hydrolysis of fraction (ii) with boiling 2N-sodium hydroxide for 2 hours gave a little insoluble, dark-coloured oil together with mainly phenolic material which could not be induced to crystallise.

Oxidation of the original material (fraction ii) with chromic oxide in warm glacial acetic acid gave an ether-soluble product which with hot alcoholic 2 : 4-dinitrophenylhydrazine sulphate—the condition necessary for 2 : 4-dinitrophenylhydrazone formation from benzophenone and substituted benzophenones—afforded a deep-red solution smelling strongly of ethyl acetate (ethanolysis of the acetoxy-group), from which solid matter separated slowly. This was obviously a mixture and may have consisted of at least *o*- and *p*-acetoxy- and *o*- and *p*-hydroxy-benzophenone 2 : 4-dinitrophenylhydrazones.

Fraction (iii) was a very viscous yellow oil which did not crystallise on being kept.

The residue was a viscous brown gum.

None of the fractions gave more than the merest trace of benzyl iodide when treated with boiling hydriodic acid (*d* 1·7) in acetic acid.

(*b*) When the reaction was carried out by adding the solution of benzyl phenyl ether in nitromethane to the prepared acetylium perchlorate also in nitromethane the main product was a non-distillable gum. No ketonic material could be isolated.

(*c*) *In benzene.* The reaction described under (*a*) was repeated, but in benzene (260 c.c.) instead of nitromethane as the solvent and at 5°. The following fractions were obtained : (i) B. p. 192—194° (2·2 g.), which was shown (as above) to be phenyl acetate. (ii) B. p. 68—95° (mainly 92—95°)/3·5—4·5 mm. (4·0 g.), a mixture of phenyl acetate and diphenylmethane in the ratio of 1 : 3. The diphenylmethane was separated from the phenyl acetate by treatment of the mixture with boiling 2N-sodium hydroxide and subsequent extraction of the alkaline mixture with ether ; it crystallised in long colourless needles, m. p. 25°, and was readily oxidised by chromic oxide in warm acetic acid to benzophenone which was identified as its 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 229°. (iii) B. p. 95—120°/3—4 mm. (0·9 g.). (iv) B. p. 120—150° (mostly 135—140°)/4 mm. (3·0 g.). The residue (1·2 g.) was a dark gum.

None of the fractions nor the residue gave more than a trace of benzyl iodide with boiling hydriodic acid. Only fraction (iv) gave an indication that a trace of ketonic material might be present.

(*d*) *In acetic anhydride.* A solution of silver perchlorate (0·025 g.-mol.) and benzyl phenyl ether (0·05 g.-mol.) in acetic anhydride (0·1 g.-mol.) and nitromethane (57·2 g.) was cooled to 0—5°. Acetyl chloride (0·025 g.-mol.) was added with shaking to the cooled solution during 15 minutes and the resultant mixture kept at 0—5° for 45 minutes. The product was isolated as described in (*a*) : in this case the ethereal extracts had a strong green fluorescence. Fractionation gave : (i) A liquid, b. p. 195—198°

(3·6 g.), a mixture of phenyl acetate and benzyl acetate in the approximate ratio of 7 : 1. Hydrolysis of the mixed product with boiling 2N-sodium hydroxide and extraction of the alkaline mixture with ether gave a little oil which was identified as benzyl alcohol by oxidation with boiling aqueous potassium permanganate to benzoic acid, m. p. and mixed m. p. 121°. The alkali-soluble material gave phenol. (ii) A small (1·1 g.) fraction, b. p. 100—180°/7·5—8 mm., which was not further investigated. (iii) A fraction, b. p. 190—205°/8—9 mm. (2·6 g.), which solidified on cooling and consisted mainly of *p*-benzyloxyacetophenone, m. p. 86—87°, which did not depress the m. p. of the synthetic ketone. (iv) Material, b. p. 205—260°/8—9 mm. (2·4 g.), consisting of an oil from which a little crystalline material slowly separated. The residue from the fractional distillation amounted to 1·0 g.

3 : 4-*Dibenzyloxybenzaldehyde* (*Protocatechualdehyde Dibenzyl Ether*).—Potassium hydroxide (0·2 g.-mol.) in water (12 c.c.) was cautiously added to a solution of protocatechualdehyde (0·1 g.-mol.) and benzyl chloride (0·2 g.-mol.) in ethyl alcohol (100 c.c.). The mixture was then refluxed until neutral to litmus and then poured into water. The crude *aldehyde*, which separated as a pale yellow solid, crystallised from ethyl alcohol in clusters of almost colourless needles, m. p. 91° (Found : C, 79·3; H, 5·6. $C_{21}H_{18}O_3$ requires C, 79·2; H, 5·7%).

3 : 4-*Diacetoxybenzylidene Diacetate*.—A solution of protocatechualdehyde (10 g.) in warm acetic anhydride (100 c.c.) was cooled to room temperature and then treated with 72% perchloric acid (0·25 c.c.), the mixture becoming warm. After 30 minutes the solution was poured into ice-water, and the crude product filtered off and recrystallised from ethyl alcohol (96%), giving the tetra-acetate (18·8 g.), m. p. 131° (Found : C, 55·7; H, 5·3. Calc. for $C_{15}H_{16}O_8$: C, 55·6; H, 5·0%).

o-*Dibenzyloxybenzene* (*Catechol Dibenzyl Ether*).—A solution of sodium hydroxide (20 g.) in water (150 c.c.) was gradually added to a boiling solution of catechol (27·5 g.) and benzyl chloride (70 c.c.) in ethyl alcohol (300 c.c.), and the mixture then refluxed for 8 hours. The oil which separated solidified when kept overnight. The ether crystallised from light petroleum (b. p. 40—60°) in colourless prisms (32·5 g.), m. p. 61·5°.

3 : 4-*Dibenzyloxy*-1-*nitrobenzene* (4-*Nitrocatechol Dibenzyl Ether*).—*o*-Dibenzyloxybenzene (10 g.) was dissolved in warm glacial acetic acid (100 c.c.) and the solution cooled to 20—25°. Nitric acid (*d* 1·4; 10 c.c.) was then added gradually with stirring so that the temperature did not exceed 25°; a yellow solid separated during the reaction. The mixture was diluted with water and the crude nitro-ether crystallised from a large volume of ethyl alcohol from which it separated in needles (yield, 96—100%), m. p. 97·5° (Found : N, 4·2. Calc. for $C_{20}H_{17}O_4N$: N, 4·2%). Balaban (*J.*, 1929, 1092) gives m. p. 97° for this ether prepared from 4-nitrocatechol.

A mixture of the nitro-ether (10·1 g.), 50% hydrobromic acid (50 c.c.), and acetic acid (75 c.c.) was boiled under reflux for 6—7 hours. The mixture, from which a dark oil separated, was evaporated to dryness in a vacuum and the residue was extracted with boiling water (100 c.c.), in the presence of charcoal. Evaporation of the filtered extract to *ca.* 20 c.c. gave, on cooling, yellow needles (2·4 g.) which when recrystallised from water separated in long yellow needles, m. p. 174—175° (decomp.). 4-Nitrocatechol has m. p. 176° (decomp.) (Cardwell and Robinson, *J.*, 1915, **107**, 258).

4-Nitrocatechol (1·6 g.), dissolved in acetic anhydride (16 c.c.), was treated with 72% perchloric acid (2 drops). The mixture, which became warm (35—40°), was left for 30 minutes and then poured on crushed ice. The crude diacetate crystallised from ethyl alcohol in colourless needles, m. p. 84° (Found : C, 50·4; H, 4·1. Calc. for $C_{10}H_9O_6N$: C, 50·2; H, 3·8%).

The diacetate is reported (Balaban, *loc. cit.*) to have m. p. 98° when prepared from 4-nitrocatechol by the action of acetic anhydride–sulphuric acid. We have not been able to attain this m. p. (see also p. 529) even after repeated crystallisation.

Methylation of the nitrocatechol with methyl sulphate and aqueous sodium hydroxide gave 4-nitroveratrole, m. p. and mixed m. p. 96°.

Debenzylations with a Small Amount of 72% Perchloric Acid in Acetic Anhydride.—(*a*) Benzyl phenyl ether (4·6 g.) in acetic anhydride (10·2 g.) was treated with 72% perchloric acid (2 drops), the resultant deep orange-red mixture being kept below 27° by cooling. After 30 minutes the reaction mixture was poured on crushed ice (*ca.* 40 g.). Most of the colour then slowly disappeared but a strong green fluorescence was evident. During extraction of the oily product with ether a small amount of a light brown solid material separated; this was sparingly soluble in alcohol, giving a yellow solution with an intense green fluorescence. The combined ethereal extracts were washed with 5% sodium hydrogen carbonate solution and with water. Evaporation of the dried (Na_2SO_4) ethereal solution gave an oil which was separated by vacuum distillation into the following fractions : (i) b. p. 70—80°/8 mm. (1·0 g.), an 8 : 1 mixture of phenyl acetate and benzyl acetate; (ii) b. p. 120—140°/9 mm. (0·9 g.), containing some phenyl acetate, some benzyl acetate, and some unchanged ether, since redistillation at atmospheric pressure gave approximately equal amounts of the mixed acetates, b. p. *ca.* 210°, and a residue of unchanged ether; (iii) b. p. 140—150°/9 mm. (1·0 g.), which solidified on cooling and was unchanged ether (m. p. and mixed m. p.); (iv) b. p. 150—200° (mainly 180—190°)/6—7 mm. (1·0 g.), which also solidified on cooling and was *p*-benzyloxyacetophenone (m. p. and mixed m. p.). The residue from the distillation amounted to 1·1 g.

(*b*) 3 : 4-Dibenzyloxybenzaldehyde (1·0 g.) in acetic anhydride (3 c.c.) was treated with 72% perchloric acid (2 drops), whereupon a dark green solution resulted. After 30 minutes the mixture was added to water (25 c.c.) and left for 18 hours at 0°. The aqueous layer was decanted from the semi-solid material, which smelled strongly of benzyl acetate. Dissolution of the paste in the minimum amount of boiling 96% alcohol and keeping at 0° gave crystalline material (0·64 g.), m. p. *ca.* 116°, which when recrystallised from alcohol and benzene gave colourless needles, m. p. 131°, unaltered by admixture with 3 : 4-diacetoxybenzylidene diacetate.

A small amount of material, m. p. 157—159°, was obtained from the crystallisation liquors which was identical with the compound obtained from the debenzylation with sulphuric acid (see below).

(*c*) 3 : 4-Dibenzyloxy-1-nitrobenzene (1·0 g.) in acetic anhydride (3 c.c.) was treated with 72% perchloric acid (2 drops). After 30 minutes the pale green mixture was added to water (25 c.c.) and left at 0° for 18 hours. The aqueous layer was decanted from the resulting pasty mass, which on dissolution in the minimum amount of hot ethyl alcohol and cooling gave colourless needles (0·52 g.), m. p. *ca.* 99°. Recrystallisation from alcohol or benzene–light petroleum gave colourless needles, m. p. 105—106° (Found : C, 62·9; H, 4·3. $C_{15}H_{13}O_5N$ requires C, 62·9; H, 4·5%), of presumably 4-*nitrocatechol acetate benzyl ether*.

In another experiment 3 : 4-dibenzyloxy-1-nitrobenzene (6·7 g.) in acetic anhydride (40 c.c.) was kept below 20° whilst 72% perchloric acid (1·4 g. ≡0·01 mol.) was added cautiously. The mixture was kept at room temperature for 17—18 hours and was then poured into ice-water (*ca.* 250 c.c.), whereupon most of the original deep orange colour disappeared. The oily material was washed once with water and was then dissolved in a small quantity of ethyl alcohol. On this solution being kept, solid material (3·0 g.) separated. This consisted of two types of crystal : (i) a major fraction of large diamond-shaped plates which crystallised well from benzene–light petroleum, had m. p. 85°, and were identical with 4-nitrocatechol diacetate (see p. 528) ; (ii) small needles, which on recrystallisation from benzene–light petroleum proved to be identical with the monoacetate obtained previously (m. p. and mixed m. p. 105—106°).

Distillation of the oily material recovered from the mother-liquors gave benzyl acetate (2·5 g.), b. p. 214—216°, and some tarry residue.

(*d*) 72% Perchloric acid (2 drops) was added to 4 : 5-dibenzyloxy-2-nitrotoluene (1·0 g.) in acetic anhydride (3 c.c.). After 30 minutes the orange-brown mixture was treated with water (25 c.c.) ; a strong smell of benzyl acetate was apparent. The mixture was kept at 0° for 18 hours and the semi-solid material which separated then dissolved in the minimum amount of hot ethyl alcohol. On this solution being kept, light brown needles (0·65 g.), m. p. *ca.* 126°, separated. Recrystallisation from alcohol gave colourless needles of the *monoacetate monobenzyl ether*, m. p. 133° (Found : C, 63·7; H, 4·9. $C_{16}H_{15}O_5N$ requires C, 63·8; H, 5·0%).

Debenzylations with a Small Amount of Concentrated Sulphuric Acid in Acetic Anhydride.—(*a*) 3 : 4-Dibenzyloxybenzaldehyde (0·5 g.) in acetic anhydride (1·5 c.c.) was treated with concentrated sulphuric acid (2 drops) and after 30 minutes the mixture was decomposed with water. The crude product (0·2 g.), isolated as above, crystallised from alcohol or benzene–light petroleum in colourless needles, m. p. and mixed m. p. 157—159° (Found : C, 65·1; H, 5·4. $C_{20}H_{20}O_7$ requires C, 64·5; H, 5·4%).

In another experiment only the merest trace of sulphuric acid was used and the mixture was kept for 1—2 minutes. The product (0·2 g.) was the almost pure triacetate, m. p. and mixed m. p. 157—159°.

(*b*) Sulphuric acid (2 drops) was added to 3 : 4-dibenzyloxy-1-nitrobenzene (1·0 g.) in acetic anhydride (3 c.c.) and after 30 minutes the pale green solution was decomposed with water (25 c.c.). The crude product (0·7 g.) gave a clear melt at 91°, and was separated by fractional crystallisation into the monoacetate, m. p. and mixed m. p. 103—105°, and a little unchanged starting material.

(*c*) Sulphuric acid (1 drop) was added to 4 : 5-dibenzyloxy-2-nitrotoluene (0·5 g.) in acetic anhydride (1·5 c.c.) and after 30 minutes the brown mixture was worked up as above. The crude product (0·33 g.), m. p. 110°, was separated by fractional crystallisation from benzene–light petroleum into a major fraction of colourless needles, m. p. 133°, identical with the monoacetate monobenzyl ether obtained by using perchloric acid, and a small amount of unchanged starting material.

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