326. *Acylation and Allied Reactions Catalysed by Strong Acids. Part XVI.* The Reactions of Some ω-Phenylalkanoyl Perchlorates.*

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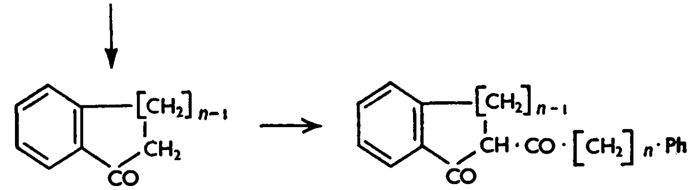
The ω-phenylalkanoyl perchlorates when suitably constituted exhibit both inter- and intra-molecular acylating activity as well as concurrent β-diketone formation in nitromethane solution. The reactions proceed less well in methyl, phenyl, or benzyl cyanide and this is ascribed to solvation of the perchlorates. The acetylation of some cyclic ketones is also described.

THE insoluble nature of the ketone–catalyst complex produced in Friedel–Crafts acylations with catalysts such as aluminium chloride generally prevents further attack on the ketone by the acylating agent. However, in the simplified Friedel–Crafts-type reaction in which silver perchlorate and an acyl halide are used to produce silver chloride and acyl perchlorate, the latter acting as a source of carbonium ions,[1-4] this is not so, and it should be possible for the product first formed to undergo further acylation. In experiments with phenylalkanoyl perchlorates, $\mathrm{Ph{\cdot}[CH_2]_n{\cdot}CO{\cdot}ClO_4}$ ($n = 2$—4), we have found this to be the case.[5] Cyclic ketones and diketones, as well as open-chain ketones formed by competitive reaction with a reagent such as toluene or anisole, are obtained:

$$\mathrm{Ph{\cdot}[CH_2]_n{\cdot}COCl + AgClO_4 \longrightarrow Ph{\cdot}[CH_2]_n{\cdot}CO^{+}ClO_4^{-} + AgCl}$$

$$\mathrm{Ph{\cdot}[CH_2]_n{\cdot}CO^{+}ClO_4^{-} \xrightarrow{ArH} Ph{\cdot}[CH_2]_n{\cdot}COAr + HClO_4}$$



Indan-1-one (0·30 mole) and 2-β-phenylpropionylindan-1-one (0·23 mole) are produced readily at 0° from β-phenylpropionyl perchlorate (1 mole) in nitromethane solution. In toluene alone, 0·55 mole of *p*-β-phenylpropionyltoluene is produced together with 0·09 mole of indan-1-one, whereas in a mixture of nitromethane and toluene (2 moles) the higher dielectric constant favours cyclisation and 0·20 mole of indan-1-one, 0·06 mole of diketone, and only 0·40 mole of the open-chain ketone are formed. In the presence of the more reactive anisole the product is exclusively *p*-β-phenylpropionylanisole.

When $n = 4$ similar results are obtained, but only 0·10 mole of 1 : 2-benzosuberone is produced even with a longer reaction time. This is in accordance with the 4 : 1 ratio for yields of indan-1-one and 1 : 2-benzosuberone obtained by the action of aluminium chloride on the corresponding halides.[6] Some diketone material is also formed, as is indicated by the violet colour produced when an alcoholic solution of the reaction product is treated with aqueous ferric chloride, and also by the formation of a viscous copper derivative; but so far we have been unable to isolate the pure diketone. In toluene no cyclisation was observed at all and only 0·01 mole of the straight-chain ketone was formed, indicating the diminishing reactivity of the carbonium ion as n increases. However, with the markedly more nucleophilic anisole a quantitative yield of *p*-δ-phenylvalerylanisole confirmed the

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[*] Part XV, *J.*, 1956, 3933.

[1] Mackenzie and Winter, *Trans. Faraday Soc.*, 1948, **44**, 159, 171, 243.

[2] Barrera i Costa, *Ann. Chim. (France)*, 1949, **4**, 84.

[3] Cauquil and Barrera, *Bull. Soc. chim. France*, 1949, **16**, 689, 837.

[4] Burton and Praill, *J.*, (*a*) 1950, 2034; (*b*) 1951, 522, 529; (*c*) 1953, 827.

[5] Burton, *J. Roy. Inst. Chem.*, 1954, 242.

[6] Braun and Rath, *Ber.*, 1927, **60**, 1182.

presence of the cation. The results for $n = 2$ are in a sense complementary to those of Rothstein[7] who found that increasing proportions of open-chain ketone are produced when β-phenylpropionyl chloride is treated with aluminium chloride in the presence of increasingly active aromatic compounds; formation of diketone does not occur, of course, under his experimental conditions.

When $n = 3$, the ease of cyclisation, as expected, is much greater than that of substitution in the α-methylene group, so that no diketone is produced; in fact it is so great that some cyclisation (0·05 mole) occurs even in competitive reaction with anisole, 0·74 mole of open-chain ketone being produced at the same time.

The phenylacetyl cation has also been investigated for comparison and was found to be the most active of the series. Toluene was attacked at 0° to form *p*-phenylacetyltoluene in 59% yield, whilst with anisole in nitromethane the cation gave *p*-phenylacetylanisole (94%).

The formation of the diketones may, as expected, be carried out in two successive stages. Indan-1-one (1 mole) in nitromethane yields, on treatment with β-phenylpropionyl perchlorate (1 mole), in the very short time of ten minutes, 0·26 mole of the diketone. Indan-1-one (0·50 mole) and 0·20 mole of β-phenylpropionic acid may also be recovered from the reaction product together with a quantity of intractable tar (which is formed to some extent in most of the reactions described and may arise by self-condensation of the cyclic ketones under the influence of the perchloric acid formed in all these acylations).

This reaction may also account for the diminution in yield noticed when the reaction mixtures were left for longer times; *e.g.*, the yield of benzosuberone decreased from 10% to 1·3% when the reaction time was increased from 3 to 18 hours.

These experiments led us to attempt the acetylation of some cyclic ketones, generating the acetylium perchlorate by both the previous methods used, *i.e.*, by the use of equimolecular quantities of silver perchlorate and acetyl chloride, method (A), which was more efficient than acetic anhydride–perchloric acid mixtures, method (B). Indan-1-one, *cyclo*pentanone, 1-tetralone, and *cyclo*hexanone gave the 2-acetyl derivatives in yields of 88, 52, 30, and 13% respectively by method A, and 14, 9, 7, and 5% respectively by method B. The low yields with *cyclo*hexanone are due to its proneness to self-condensation. *cyclo*Hexylidene*cyclo*hexanone may be obtained in 25—30% yields by treatment of *cyclo*hexanone with a few drops of aqueous 70% perchloric acid in nitromethane, together with further condensed products, whilst from anhydrous systems containing acetic anhydride and perchloric acid dodecahydrotriphenylene has been isolated in 5% yield from the viscous residues.

Barrera i Costa[2] in his discussion of the mechanism of the cyclisation of arylaliphatic acids attributed the power of silver perchlorate to cyclise suitably constituted acyl halides solely to its ability to act in a manner similar to stannic chloride, anhydrous zinc chloride, etc., *i.e.*, as a Lewis acid.

To prove that it was the "Lewis acid" nature of the silver perchlorate that was causing cyclisation and not just its power to generate by metathesis a silver halide and an acyl perchlorate, $R\cdot CO\cdot ClO_4$, which incidentally he regarded as a mixed anhydride cyclising either spontaneously or under the influence of more silver perchlorate, he carried out experiments using methyl cyanide as solvent in place of benzene or toluene.

He suggested that methyl cyanide, acting as a base according to the Lewis theory, would neutralise the Lewis acid nature of the silver perchlorate and no cyclisation would result; he found this to be so. We cannot agree with this view and we have therefore investigated the cyclisation in methyl cyanide, of the above series of phenylalkanoyl perchlorates.

We have found that acylation still takes place but only where a highly nucleophilic centre exists, *i.e.*, when $n = 3$ (60% of 1-tetralone formed) or when anisole is present

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[7] Rothstein, *J.*, 1951, 1459.

(86% of *p*-β-phenylpropionylanisole formed from the perchlorate; $n = 2$). In other cases most of the original acid chloride is recovered as the acid, *e.g.*, with the perchlorate, $n = 2$ or $n = 4$, alone, 79 and 91%, respectively, of the corresponding acids were isolated, together with small amounts of products such as *N*-acetyl-β-phenylpropionamide (2%) which had arisen by interaction with the solvent. The formation of these products will be discussed more fully below.

Similar results were obtained when phenyl or benzyl cyanide was used as the solvent. In the former, the perchlorate, $n = 2$, reacted with anisole to give the straight-chain ketone in 70% yield, and, in the latter, the perchlorate, $n = 3$, gave 1-tetralone in 82% yield.

Our interpretation of these partly successful acylations in cyanide solutions is that the metathesis occurs as before but that the perchlorate is now solvated, *e.g.*, $(\mathrm{MeCN})_n\cdots\mathrm{RCO^+ClO_4^-}$. This solvation diminishes the electron demand of the perchlorate and hence its acylating activity.[8] Consequently, the reactions which occurred most readily in nitromethane have still taken place in methyl cyanide, etc., but with smaller yields, whilst those which occurred less readily in nitromethane have been completely inhibited, *e.g.*, the intramolecular acylation with β-phenylpropionyl perchlorate does not take place in any of the cyanides. But as acylation depends both on the electrophilic activity of one component and the nucleophilic activity of the other it should be possible for the lowered reactivity of the β-phenylpropionyl cation to be still sufficiently high for a reaction to occur with a more highly reactive nucleophile. This is so: anisole is acylated in good yields by the perchlorate, $n = 2$, in all three cyanides.

On filtration of the reaction mixture it was noticed that quantitative yields of silver chloride were not now obtained as had been the case when hydrocarbons or nitromethane was used as the solvent, but that the deficiency was made up on hydrolysis of the reaction product with water. The amount of the deficiency was, in the case of methyl or benzyl cyanide, approximately equivalent to the amount of organic acid recovered by alkaline extraction of the reaction product; with phenyl cyanide the deficiency was approximately equivalent to half of the acid recovered (see Table). (We must stress here that these results are from semiquantitative experiments designed to explore the general reactions of these perchlorates and whilst the usual precautions were taken to exclude moisture, etc., the rigorous conditions necessary in work of a " kinetic " standard were not employed.)

TABLE

Expt. no.	Solvent	Perchlorate $\mathrm{Ph{\cdot}[CH_2]_n{\cdot}CO{\cdot}ClO_4}$	Reactant	AgCl on hydrol. (%)	Org. acid recovered (%)
a	MeCN	$n = 1$	—	93	91
b	,,	,, 2	—	76	79
c	,,	,, 2	—	68	67
d	,,	,, 3	—	19	18
e	,,	,, 4	—	82	91
f	,,	,, 2	Anisole	16	0
g	$\mathrm{Ph{\cdot}CH_2{\cdot}CN}$	,, 1	—	53	62
h	,,	,, 2	—	49	53
i	,,	,, 3	—	2	3
j	PhCN	,, 1	—	36	78
k	,,	,, 2	—	37	77
l	,,	,, 2	Anisole	0	23

We attribute the non-appearance of all of the silver chloride and the correlation between the " silver chloride on hydrolysis " and the " recovered organic acid " to the formation of a soluble complex between the silver chloride and equivalent amounts of organic perchlorate in methyl and benzyl cyanide, and twice the equivalent in phenyl cyanide. Cyanide molecules must also be involved in the complexes. We obtained evidence for the formation of soluble complexes containing silver salts in the following experiments.

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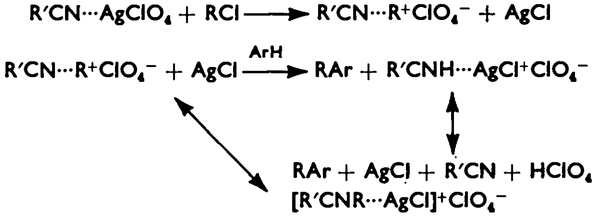
[8] Baddeley, *Quart. Rev.*, 1954, **4**, 369.

First, when a solution of phenylacetyl perchlorate in nitromethane was added to an equal volume of methyl cyanide containing a suspension of silver chloride and the mixture shaken, 19% of the silver chloride went into solution during 3½ hours at room temperature; when anhydrous perchloric acid was substituted for the phenylacetyl perchlorate, 17% went into solution in 3 hr. The effect of nitromethane in the latter experiment may be judged from the fact that only 58% of the theoretical amount of silver was obtained as silver chloride when equivalent amounts of hydrogen chloride and silver perchlorate each in methyl cyanide were mixed and left at room temperature for 21 hr. The presence of anisole did not upset the latter equilibrium greatly, whereas silver nitrate in place of the perchlorate gave rapid and quantitative yields of silver chloride. Silver chloride is not soluble in methyl cyanide alone.

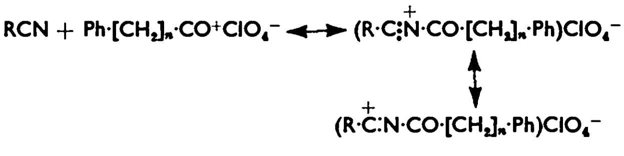
The reactions in methyl and benzyl cyanides may be summarised thus:



where $R' = Me$ or $Ph\cdot CH_2$, and $R = Ph\cdot[CH_2]_n\cdot CO$ or H, and ArH is an active benzene derivative. When $n = 3$, ArH may be considered to be contained in R.

The yields of *N*-substituted amides, referred to above, were always small, *e.g.*, 2% and 4% of *N*-acetyl- and *N*-benzoyl-propionamide were formed by the perchlorate ($n = 2$) in methyl and phenyl cyanide respectively. Generally, the reaction products from methyl cyanide solution were " cleaner " than those from the other cyanides; from the viscous gums formed in benzyl cyanide, phenylacetamide as well as acylated phenylacetamides were often isolated. The perchlorate ($n = 1$) gave rise to 7% each of phenylacetamide and diphenyldiacetylamine, whilst only 38% of the perchlorate was recovered as the acid, the rest being a viscous tar.

It seems probable that the small amounts of *N*-acylamides have been produced by the addition of the perchlorate to the solvent:



Subsequent hydrolysis of the carbonium ion would give rise to the *N*-acylamide:

$$R\cdot\overset{+}{C}{:}N\cdot CO\cdot[CH_2]_n\cdot Ph + OH^- \longrightarrow R\cdot CO\cdot NH\cdot CO\cdot[CH_2]_n\cdot Ph$$

We cannot find any references in the literature concerning the addition of acyl cations to ·C⁝N, but additions of alkyl cations to cyanides have been described recently by several authors. Ritter *et al.*[9] have reported the addition of olefins and tertiary and secondary alcohols to a wide variety of cyanides, the last-named addendum in concentrated sulphuric acid and the first two in acetic acid with an equivalent of sulphuric acid present. The addition of triphenylmethyl nitrate to methyl cyanide has been substantiated,[10,11] whilst Kornblum and his co-workers[12] quoting the work of Taub,[13] report the addition of the

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[9] See Plaut and Ritter, *J. Amer. Chem. Soc.*, 1951, **73**, 4076 for earlier references.

[10] Cheeseman, *Chem. and Ind.*, 1954, 281.

[11] Cristol and Leffler, *J. Amer. Chem. Soc.*, 1954, **76**, 4468.

[12] Kornblum, Smiley, Blackwood, and Iffland, *ibid.*, 1955, **77**, 6271.

[13] Taub, Ph.D. Thesis, Purdue, 1952.

tert.-butyl cation to methyl cyanide. Cast and Stevens [14] described the addition of the diphenylmethyl cation (derived from the sulphate) to methyl cyanide.

It is interesting that the *N*-acylamide obtained by the formation of β-phenylpropionyl perchlorate in benzyl cyanide is diphenyldiacetylamine and not the asymmetrical *N*-acylamide. This has probably arisen from the further addition of $(\mathrm{R'{\cdot}\overset{+}{C}{:}N{\cdot}CO{\cdot}[CH_2]_2{\cdot}Ph)ClO_4^-}$ across a molecule of the solvent :

$$(\mathrm{R'{\cdot}\overset{+}{C}{:}N{\cdot}CO{\cdot}[CH_2]_2{\cdot}Ph)ClO_4^-} + \mathrm{R'CN} \longrightarrow \mathrm{R'{\cdot}\overset{+}{C}{:}N{\cdot}C(R'){:}N{\cdot}CO{\cdot}[CH_2]_2Ph}$$

hydrolysis of the product would give diphenyldiacetamide.

Particular care has been taken to use cyanides free from amides as these are readily acylated by the perchlorates.

Experimental

Materials.—Silver perchlorate [4a] was dried as previously described. Nitromethane, anisole, toluene, *cyclo*pentanone, *cyclo*hexanone, and 1-tetralone were dried and redistilled. Acetic anhydride and perchloric acid (72%) were " AnalaR " reagents. Methyl, phenyl, and benzyl cyanide were repeatedly distilled from phosphoric oxide.

Procedure.—The general procedure used in experiments involving silver perchlorate was to add, at a controlled temperature, a solution of the acid chloride in the appropriate solvent to a solution of silver perchlorate in a mixture of the same solvent and the reactant, if any. After a variable period the silver chloride was filtered off, the filtrate being allowed to fall on crushed ice. The silver chloride was then washed with water and ether. Any further silver chloride which separated in the combined filtrate and washings was subsequently filtered off before these were washed free from acids with sodium hydrogen carbonate solution. Any acid derived from unchanged organic perchlorate was then recovered by extraction of the acidified washings with ether. It was frequently identified by m. p. and mixed m. p. Treatment of the reaction product after removal of the dried (Na_2SO_4) solvents varied from experiment to experiment.

Reaction of β-Phenylpropionyl Perchlorate.—(a) *In nitromethane.* β-Phenylpropionyl chloride (0·05 mole) in nitromethane (30 c.c.) was added during 10 min. to a cold (0—2°) solution of silver perchlorate in nitromethane (70 c.c.). After a further 50 min. the reaction was stopped. β-Phenylpropionic acid (0·7 g.) was recovered and the product (6·2 g.) was treated with a saturated solution of copper acetate in ethyl alcohol until no more of the copper salt (m. p. after recrystallisation from benzene, 218°) of the diketone was precipitated. The 2-β-*phenylpropionylindan*-1-*one* (3·0 g.), m. p. 64°, was obtained by treatment of the salt with 2N-sulphuric acid. Recrystallisations from ethyl alcohol raised the m. p. of the white plates to 71° (Found : C, 81·6; H, 6·5. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·1%). The *dioxime*, recrystallised from ethyl alcohol, had m. p. 187° (decomp.) (Found : C, 72·8; H, 6·2; N, 9·7. $C_{18}H_{18}O_2N_2$ requires C, 73·4; H, 6·1; N, 9·5%).

Steam-distillation of the residue gave indan-1-one, m. p. 39°, identified by the m. p. and mixed m. p. of the 2 : 4-dinitrophenylhydrazone (254—255°).

(b) *In toluene.* β-Phenylpropionyl chloride (0·05 mole) in toluene (30 c.c.) was added during 90 min. to a solution of silver perchlorate (0·05 mole) in toluene (70 c.c.) at 24°. After 3 hr. the reaction was stopped. β-Phenylpropionic acid (1·0 g.) was recovered. The reaction product (9·2 g.) gave, on crystallisation from ethyl alcohol, *p*-β-phenylpropionyltoluene (4·3 g.), m. p. 69°; distillation of the residue at 0·7 mm. gave (i) 0·6 g., b. p. 80—86°, (ii) 1·8 g., b. p. 150—170°, mainly 160—162°. Fraction (i) was indan-1-one, identified as before, and (ii) was the tolyl ketone, m. p. 69° (Burton and Ingold [15] give m. p. 70—71°).

(c) *With toluene in nitromethane.* β-Phenylpropionyl chloride (0·05 mole) in nitromethane (30 c.c.) was added in 20 min. to a cold (0—2°) solution of silver perchlorate in toluene (0·1 mole) and nitromethane (60 c.c.), and the reaction allowed to proceed for 3 hr. β-Phenylpropionic acid (0·6 g.) was recovered. The product was distilled at 1·5 mm., yielding fractions (i) 1·3 g., b. p. 88—94°, (ii) 0·7 g., b. p. 106—162°, (iii) 4·5 g., b. p. 162—174° (mainly 168°),

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[14] Cast and Stevens, *J.*, 1953, 4180.

[15] Burton and Ingold, *J.*, 1928, 916.

and (iv) residue, 1·7 g. Fraction (ii) was a mixture of fraction (i) which was indan-1-one, identified as before, and fraction (iii) which was the tolyl ketone, m. p. 69—70°. The residue gave a copper salt, m. p. and mixed m. p. with that obtained in (a), 217°.

(d) *With anisole in nitromethane.* Repetition of expt. (c) with anisole (0·05 mole) in place of toluene and at 25° during 45 min. gave a crystalline product (10·7 g.), m. p. 95—96°. Rothstein [7] gives the m. p. of *p*-β-phenylpropionylanisole as 102°.

Reactions of δ*-Phenylvaleryl Perchlorate.*—(a) *In nitromethane.* δ-Phenylvaleryl chloride (0·05 mole) in nitromethane (30 c.c.) was added in 25 min. to a cold (0°) solution of silver perchlorate (0·05 mole) in nitromethane (70 c.c.), and reaction allowed to proceed at 2° for 3 hr.: δ-phenylvaleric acid (1·6 g.) was recovered. The product was separated into parts soluble (2·2 g.) and insoluble (3·5 g.) in sodium hydroxide. The latter part yielded on treatment with 2 : 4-dinitrophenylhydrazone (4·5 g.) in ethanolic sulphuric acid a tacky derivative (5·5 g.), which on recrystallisation from ethyl acetate gave 2 : 3-benzosuberone 2 : 4-dinitrophenylhydrazone (1·9 g.), m. p. and mixed m. p. 204°. The other portion, which gave an intense violet colour with aqueous-alcoholic ferric chloride, yielded a viscous copper salt (4·3 g.) when treated as described in (a) above.

In a second experiment (18 hr. at 3°) only 0·22 g. of the 2 : 4-dinitrophenylhydrazone of 2 : 3-benzosuberone was isolated.

(b) *In toluene.* δ-Phenylvaleryl chloride (0·025 mole) in toluene (20 c.c.) was added during 15 min. to a solution of silver perchlorate (0·025 mole) in toluene (40 c.c.) at 2°. The reaction was stopped after 3½ hr.: δ-phenylvaleric acid (3·2 g.) was recovered and the product, a dark oil (2·0 g.), yielded by the usual procedure *p*-δ-phenylvaleryltoluene 2 : 4-dinitrophenylhydrazone (220 mg.), m. p. and mixed m. p. 156°.

(c) *With anisole in nitromethane.* δ-Phenylvaleryl chloride (0·025 mole) in nitromethane (20 c.c.) was added in 10 min. to a cold (2°) solution of silver perchlorate (0·025 mole) in anisole (3·0 g.) and nitromethane (40 c.c.); the reaction was stopped after 30 min. The product (6·7 g.) crystallised as plates from ethyl alcohol; the m. p. 38° was increased to 39° by recrystallisation of the p-δ-*phenylvalerylanisole* twice more from ethyl alcohol (Found: C, 80·0; H, 7·3. $C_{18}H_{20}O_2$ requires C, 80·6; H, 7·4%). A 2 : 4-*dinitrophenylhydrazone* crystallised as bright red prisms, m. p. 140°, from ethyl acetate, and an *oxime* was obtained as thick rods, m. p. 85°, from ethyl alcohol–light petroleum (Found: C, 75·7; H, 7·6; N, 5·1. $C_{18}H_{21}O_2N$ requires C, 76·3; H, 7·4; N, 4·9%).

Reactions of γ*-Phenylbutyryl Perchlorate.*—(a) *In nitromethane.* γ-Phenylbutyryl chloride (0·05 mole) in nitromethane (20 c.c.) was added at 24° in 20 min. to a solution of silver perchlorate (0·05 mole) in nitromethane (70 c.c.). After 30 min. more the reaction was stopped: γ-phenylbutyric acid (0·5 g.) was recovered. The product was distilled at 1 mm., yielding the fractions: (i) 4·8 g., b. p. 92—95°, (ii) 0·5 g., b. p. 96—116°, (iii) 0·4 g., b. p. 116—180°, and (iv) 1 g. of viscous residue. Fractions (i) and (ii) were 1-tetralone, identified by the m. p. and mixed m. p. 256° of the 2 : 4-dinitrophenylhydrazone. Fraction (iii) also contained tetralone, but like the residue, did not give a colour with aqueous-alcoholic ferric chloride.

(b) *With anisole in nitromethane.* γ-Phenylbutyryl chloride (0·05 mole) in nitromethane (25 c.c.) was added in 30 min. to a solution of silver perchlorate (0·05 mole) in anisole (5·8 g.) and nitromethane (70 c.c.) at 23°. The reaction was stopped after 1 hr. and γ-phenylbutyric acid (0·5 g.) was recovered. The product crystallised from ethyl alcohol, yielding p-γ-*phenylbutyrylanisole* (4·6 g.), m. p. 56°. Recrystallisation from ethyl alcohol raised the m. p. of the plates to 59°. Fractionation of the remainder of the product (6·3 g.) gave (i) 0·4 g., b. p. 120°/2—3 mm., (ii) 4·8 g., b. p. 226—232°/2 mm., and (iii) 1·1 g. of residue. Fraction (i) was 1-tetralone, identified as above, and fraction (ii) which crystallised from ethyl alcohol had m. p. 56—57°, and was identical with the *p*-γ-phenylbutyrylanisole which crystallised from the reaction product (Found: C, 80·2; H, 7·5. $C_{17}H_{18}O_2$ requires C, 80·3; H, 7·1%).

Reactions of Phenylacetyl Perchlorate.—(a) *In toluene.* Phenylacetyl chloride (0·05 mole) in toluene (25 c.c.) was added in 20 min. to a solution of silver perchlorate (0·05 mole) in toluene (70 c.c.) at −2°. After 3 hr. at +7° the reaction was stopped. After the recovery of phenylacetic acid (1·3 g.), the semi-solid product (8·7 g.) crystallised from alcohol to yield *p*-phenylacetyltoluene (5·0 g.), m. p. 108°; a further 1·2 g., m. p. 104°, were obtained on concentration of the mother-liquors.

(b) *With anisole in nitromethane.* Phenylacetyl chloride (0·05 mole) in nitromethane (20 c.c.) was added in 15 min. to a solution of silver perchlorate (0·05 mole) in anisole (6 g.) and nitromethane (70 c.c.) at −2°. After an hour at +2° the reaction was stopped, and phenylacetic acid (0·4 g.) was recovered. The product, a solid mass (11·3 g.), gave, on crystallisation from ethyl alcohol–light petroleum (b. p. 60—80°), *p*-phenylacetylanisole (9·5 g.), m. p. 77°; a further 1·1 g., m. p. 75—76°, were obtained from the mother-liquor.

Reaction of β-*Phenylpropionyl Perchlorate with Indan*-1-*one*.—β-Phenylpropionyl chloride (0·05 mole) in nitromethane (30 c.c.) was added in 2 min. to a solution of silver perchlorate (0·05 mole) and indan-1-one (0·05 mole) in nitromethane (70 c.c.) at 0°. The reaction was stopped after 10 min. The product (10·9 g.), after removal of β-phenylpropionic acid (1·5 g.), was fractionally distilled, giving (i) 1·2 g., b. p. 130°/2 mm., (ii) 2·1 g., b. p. 130—140°/2 mm., (iii) 3·5 g., b. p. 226—232°/2 mm., (iv) 4·0 g., of a viscous mixture. Fractions (i) and (ii) were indan-1-one, and fraction (iii) crystallised to give pale yellow plates of 2-β-phenylpropionylindan-1-one, m. p. 68—69°. Both products were identified as above.

Acetylation of Some Cyclic Ketones.—(a) *Using silver perchlorate and acetyl chloride*. (i) Indan-1-one. Indan-1-one (0·05 mole) and silver perchlorate (0·05 mole) were dissolved in nitromethane (70 c.c.) and treated with acetyl chloride (0·05 mole) in nitromethane (30 c.c.) during 25 min. at 18°. After a further hour the silver chloride was filtered off from the intensely red solution which was allowed to fall on crushed ice. The silver chloride was washed with ether and water. Adding the ether washings to the filtrate gave an orange solid (0·4 g.), which exploded quietly on being heated. This was filtered off and the filtrate washed until alkaline with sodium hydrogen carbonate solution. The dried (Na_2SO_4) solution yielded, after the removal of the solvents, 2-acetylindan-1-one (7·7 g.), which after recrystallisation from methyl alcohol melted at 77°. A *dioxime* crystallised as fine white needles (from ethyl acetate), m. p. 175° (Found: C, 64·6; H, 6·0. $C_{11}H_{12}O_2N_2$ requires C, 64·7; H, 5·9%).

(ii) *cyclo*Pentanone. Acetyl chloride (0·05 mole) in nitromethane (20 c.c.) was added during 15 min. at 4—8° to a solution of silver perchlorate in nitromethane (70 c.c.) and *cyclo*pentanone (5 g.). After a further 90 min. at 5° the silver chloride was filtered off from the orange solution, and the filtrate allowed to fall on crushed ice. The product treated in the usual way gave, on distillation at 18 mm., 3·5 g. of diketonic material, b. p. 88°. A viscous black residue (4·7 g.) remained. The *disemicarbazone* crystallised as white needles (from ethanol), m. p. 215° (Found: C, 45·1; H, 6·6; N, 35·6. $C_9H_{16}O_2N_6$ requires C, 45·0; H, 6·7; N, 35·0%).

(iii) 1-Tetralone. Acetyl chloride (0·05 mole) in nitromethane (70 c.c.) was added during 15 min. at 0° to a solution of silver perchlorate (0·05 mole) in nitromethane (70 c.c.) and 1-tetralone (8·0 g.). The silver chloride was filtered off from the fluorescent solution after a further hour. The product obtained in the usual way was dissolved in ether and separated into sodium hydroxide-soluble and -insoluble parts. The former (2·8 g.) was diketonic and yielded a *semicarbazone* as fine white needles, m. p. 179° (Found: C, 62·9; H, 5·9; N, 18·0. $C_{13}H_{15}O_2N_3$ requires C, 63·6; H, 6·1; N, 17·1%). Attempts to make an oxime or dioxime gave an *oxazole* as yellow prisms, m. p. 59° (Found: C, 77·0; H, 5·8; N, 7·6. $C_{12}H_{11}ON$ requires C, 77·8; H, 5·9; N, 7·6%). From the sodium hydroxide-insoluble part (5·6 g.) 1-tetralone (4·8 g.), b. p. 150—160°/2 mm., 256—257°/758 mm., was recovered.

(iv) *cyclo*Hexanone. Acetyl chloride (0·05 mole) in nitromethane (20 c.c.) was added in 25 min. at 6° to a solution of silver perchlorate (0·05 mole) and *cyclo*hexanone (6·0 g.). After a further 3½ hr. the mixture was treated as above. The sodium hydroxide-soluble part (3·1 g.) gave on distillation 2-acetyl*cyclo*hexanone (0·9 g.), b. p. 102—111°/2 mm., identified as the semicarbazone, m. p. 161°.

(b) *Using acetic anhydride and perchloric acid*. (i) Indan-1-one. Indan-1-one (0·05 mole) in acetic anhydride (13 g.) was treated with 70% perchloric acid (0·0125 mole) and the reaction allowed to proceed at 15° for 90 min. The addition of water and ether caused the separation of an unstable orange perchlorate (0·98 g.). The sodium hydroxide-soluble part of the product crystallised as off-white needles (1·2 g.), m. p. 71°, mixed m. p. with 2-acetylindan-1-one, 74°. Recrystallisation from methyl alcohol raised the m. p. to 77°.

(ii) *cyclo*Pentanone. *cyclo*Pentanone (0·10 mole) in acetic anhydride (20 g.) was treated with a solution of 70% perchloric acid (0·025 mole) in nitromethane (20 c.c.) in 10 min. at 20°. The reaction was allowed to proceed for a further 2 hr. at 18° before the solution was poured into water and ether. The sodium hydroxide-soluble part of the product (2·1 g.) gave on distillation, 1·1 g. of material, b. p. 102—104°/33 mm., which gave a disemicarbazone identical with that previously obtained.

(iii) 1-Tetralone. 1-Tetralone (0·10 mole) in acetic anhydride (26 g.) and nitromethane

(40 c.c.) was treated with 70% perchloric acid (0·025 mole) in nitromethane (20 c.c.) at 5° during 5 min. The reaction was stopped after a further 3½ hr. at 5° and the mixture worked up as above to give 2-acetyl-1-tetralone (1·3 g.). 1-Tetralone (12 g.) was recovered.

(iv) *cyclo*Hexanone. *cyclo*Hexanone (0·20 mole) in acetic anhydride (40 g.) and nitromethane (15 c.c.) was treated at 2° during 30 min. with 70% perchloric acid (0·05 mole) in nitromethane (25 c.c.). After 3 hr. at 22—24° the red solution was poured into water and ether and worked up as above. 2-Acetyl*cyclo*hexanone (1·3 g.) was distilled from the sodium hydroxide-soluble part. It had b. p. 108—110°/16 mm. The sodium hydroxide-insoluble part contained unchanged *cyclo*hexanone (8 g.) and other products of b. p. >182°/16 mm. Dodecahydrotriphenylene (0·8 g.), m. p. 227°, crystallised from the residue.

Treatment of cyclo*Hexanone with* 70% *Perchloric Acid.*—*cyclo*Hexanone (0·20 mole) was treated with 70% perchloric acid (0·05 mole) at 18°. The reaction was stopped after 30 min. by addition of water and ether. The ethereal layer, washed free from acid, gave on distillation unchanged *cyclo*hexanone and 2-*cyclo*hexylidene*cyclo*hexanone (5·1 g.), b. p. 144—146°/18 mm. A semicarbazone, m. p. 178°, was prepared.

Reactions of the Perchlorates Alone in Methyl Cyanides.—(a) *γ-Phenylbutyryl perchlorate.* γ-Phenylbutyryl chloride (0·05 mole) in methyl cyanide (20 c.c.) was added during 15 min. to a solution of silver perchlorate (0·05 mole) in methyl cyanide (70 c.c.) at 6°. The reaction was stopped after a further 3½ hr., the insoluble silver chloride (5·8 g.) was collected and the filtrate allowed to fall on crushed ice. More silver chloride precipitated by this treatment was then collected. The product (7·2 g.), an orange oil, gave, after the removal from it of γ-phenylbutyric acid, 1-tetralone (4·5 g.), b. p. 104—111°/2—3 mm., identified as before.

(b) *δ-Phenylvaleryl perchlorate.* δ-Phenylvaleryl chloride was used in the place of the γ-phenylbutyryl chloride in an experiment similar to the above; δ-phenylvaleric acid (7·9 g.) was recovered from the product by extraction with sodium carbonate solution. Treatment of the remainder (1·8 g.) with aqueous ethanol resulted in the separation of δ-phenylvaleramide (0·3 g.), identified by the m. p. and mixed m. p. 107°, with an authentic sample of m. p. 108°.

(c) *β-Phenylpropionyl perchlorate.* β-Phenylpropionyl chloride, when treated as above, gave, after the removal of β-phenylpropionic acid (6·0 g.), a brown oil (2·6 g.) which on extraction with hot water gave *N*-acetyl-β-phenylpropionamide (190 mg.), m. p. and mixed m. p. 107°.

Reactions of the Perchlorates Alone in Phenyl Cyanide.—(a) *β-Phenylpropionyl perchlorate.* β-Phenylpropionyl chloride (0·05 mole) was added during 15 min. at 0° to a solution of silver perchlorate (0·05 mole) in phenyl cyanide (70 c.c.). After 3½ hr. the mixture was worked up in the usual way, to give β-phenylpropionic acid (5·4 g.) and a brown oil (3·1 g.) which partially crystallised, to give *N*-benzoyl-β-phenylpropionamide (460 mg.), m. p. 105° (Johnson and Chernoff [16] give the m. p. as 104—105°) (Found: C, 75·5; H, 6·2; N, 5·3. Calc. for $C_{16}H_{15}O_2N$: C, 75·9; H, 5·9; N, 5·5%).

(b) *Phenylacetyl perchlorate.* Phenylacetyl chloride (0·05 mole) was added during 10 min. at 0° to silver perchlorate (0·05 mole) in phenyl cyanide (60 c.c.). After 4 hr. the reaction was stopped and the mixture treated in the usual way. The phenyl cyanide was then removed in steam, leaving a brown oil (4·3 g.) which partially crystallised, to give *N*-benzoylphenylacetamide (260 mg.), m. p. and mixed m. p. 135°. The authentic sample of *N*-benzoylphenylacetamide was made by an analogous method to that described by Johnson and Chernoff [16] for the preparation of *N*-benzoylphenylpropionamide. Wheeler, Johnson, and MacFarland [17] give m. p. 129—130°.

Reactions of the Perchlorates Alone in Benzyl Cyanide.—(a) *Phenylacetyl perchlorate.* Phenylacetyl chloride (0·05 mole) in benzyl cyanide (20 c.c.) was added at 0° during 15 min. to a solution of silver perchlorate (0·05 mole) in benzyl cyanide (50 c.c.). After 1½ hr. more the reaction was stopped. Phenylacetic acid (2·6 g.) was recovered, and the benzyl cyanide removed by steam-distillation. The crude product (6·8 g.) partially crystallised from ethanol, to give yellowish plates (1·1 g.), m. p. 184°, which, recrystallised from ethanol, had m. p. 190° and mixed m. p. 192° with diphenylacetamide (m. p. 194°) made by the method of Colby and Dodge.[18] Hot-water extracts of the residue gave brown plates (0·79 g.), m. p. *ca.* 120°. Recrystallisation of these from benzene gave phenylacetamide (0·50 g.), m. p. 156°.

(b) *β-Phenylpropionyl perchlorate.* β-Phenylpropionyl chloride (0·05 mole) in benzyl

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[16] Johnson and Chernoff, *J. Amer. Chem. Soc.*, 1911, **33**, 520.

[17] Wheeler, Johnson, and MacFarland, *ibid.*, 1903, **25**, 795.

[18] Colby and Dodge, *Amer. Chem. J.*, 1891, **13**, 3.

cyanide (20 c.c.) was added in 10 min. at 2° to a solution of silver perchlorate (0·05 mole) in benzyl cyanide (70 c.c.). After 2½ hr. the reaction was stopped. Diphenyldiacetylamine (0·55 g.) and phenylacetamide (140 mg.) were obtained and identified as in the preceding experiment. The crude product (5·4 g.) did not contain any phenylpropionamide.

(c) *γ-Phenylbutyryl perchlorate.* γ-Phenylbutyryl chloride (0·05 mole) in benzyl cyanide (20 c.c.) was added to a cold (4°) solution of silver perchlorate (0·05 mole) in benzyl cyanide during 10 min. After 2½ hr. at 5° the reaction was stopped, and phenylbutyric acid (0·3 g.) was recovered. The amount of 1-tetralone in the steam-volatile part of the product was determined by treating part of it with Brady's reagent. A one-tenth part yielded 1·33 g. of 1-tetralone 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 256°. The non-steam-volatile part (1·1 g.) partially crystallised, to give phenylacetamide (48 mg.), m. p. and mixed m. p. 155—157°.

Reactions with Anisole in Alkyl Cyanide Solutions.—(a) *In methyl cyanide.* β-Phenylpropionyl chloride (0·025 mole) in methyl cyanide (15 c.c.) was added in 15 min. to a solution of silver perchlorate (0·025 mole) in methyl cyanide (35 c.c.) at 20°. The reaction was stopped after 35 min. more and a trace of the acid recovered. The product, a pasty mass (7·2 g.), gave *p*-β-phenylpropionylanisole (5·4 g.), identified as before.

(b) *In phenyl cyanide.* In an experiment similar to the above but with phenyl cyanide in place of methyl cyanide, β-phenylpropionic acid (0·9 g.) was recovered and the yield of *p*-β-phenylpropionylanisole was reduced to 4·2 g.

Solubility of Silver Chloride in the Presence of Alkyl Cyanides and Some Perchlorate.—(a) *In the presence of methyl cyanide and phenylacetyl perchlorate.* A solution of phenylacetyl perchlorate was made by mixing equimolecular amounts of phenylacetyl chloride (0·025 mole) in nitromethane (5 c.c.) and silver perchlorate in nitromethane (40 c.c.). The silver chloride was filtered off and washed with nitromethane (5 c.c.), and the washings were added to the solution. Silver chloride (6·195 g.) was then added, followed by methyl cyanide (50 c.c.), and the mixture shaken for 3½ hr. at room temperature. The silver chloride was then filtered off; it amounted to only 5·032 g.

(b) *In the presence of methyl cyanide and anhydrous perchloric acid.* In an experiment similar to the above but with hydrogen chloride in the place of the acid chloride, only 2·087 g. of silver chloride were filtered off out of a total of 2·518 g. after 3½ hr. at room temperature.

p-δ-*Phenylvaleryltoluene.*—Aluminium chloride (2 g.) was added to a cooled (ice–salt) mixture of δ-phenylvaleryl chloride (4 g.), toluene (20 c.c.), and light petroleum (b. p. 60—80°; 50 c.c.); the mixture was then allowed to warm to room temperature and heated on a water-bath until the evolution of hydrogen chloride had ceased. After 4 hr. more at room temperature it was worked up in the usual way. Distillation of the product gave the *ketone* (2·4 g.), b. p. 228—230°/2 mm. A 2 : 4-*dinitrophenylhydrazone* crystallised as orange needles (from ethyl acetate), m. p. 156° (Found: C, 66·1; H, 5·6; N, 13·3. $C_{24}H_{24}O_4N_4$ requires C, 66·6; H, 5·5; N, 13·0%).

N-*Acetyl*-β-*phenylpropionamide.*—β-Phenylpropionyl chloride (8·5 g.) was added to acetamide (3·0 g.) dissolved in pyridine (30 c.c.), and the solution heated on a water-bath for 6 hr. It was then poured into water and ether. The ether-soluble part yielded a pasty mass on removal of the solvents, and this on subsequent recrystallisations from light petroleum gave the N-*acylamide*, m. p. 105° (Found: C, 68·9; H, 6·8; N, 7·0. $C_{11}H_{13}O_2N$ requires C, 69·1; H, 6·8; N, 7·3%).

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