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Acylation and Alkylation Reactions. Part III.¹ The Interaction of Aryloxyacetyl Chlorides with Aluminium Chloride in Aromatic Solvents

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The proportion of intermolecular acylation to both intramolecular acylation and decarbonylation, during the interaction of aryloxyacetyl chlorides with aluminium chloride in aromatic solvents, increases with the nucleophilic character of the solvent, thus showing the unimolecular nature of carbon monoxide loss. 4-Chlorophenoxy-propionyl and -isobutyryl chlorides undergo decarbonylation more readily than the corresponding acetyl chloride; the products of decarbonylation in some of these reactions are the diarylmethane or cumene rather than the expected diaryl-ethane or -propane.

IN Part II,¹ a study of the influence of substituents on the proportion of acylation (intramolecular and intermolecular) to decarbonylation led to the conclusion that the decarbonylation of aryloxyacetyl chlorides was unimolecular. A study of similar reactions in other aromatic solvents is now presented.

RESULTS

With (1; $R^1 = H$) (1 mole) in p-xylene (15 moles) containing aluminium chloride (1·1 moles as AlCl₃) at 5—10°, the products isolated (after alkali extraction and silica gel chromatography) were 2',5'-dimethyl-2-phenoxyacetophenone (2; $R^1 = H$, $R^2 = 2,5$ -Me₂) (65%), the cyclic ketone (3; $R^1 = H$) (5%), and di-(2,5-xylyl)methane (4; $R^2 = 2,5$ -Me₂) (1%). According to the previous mechanism (Part II¹), as well as the ketonic materials, (4; $R^2 = 2,5$ -Me₂) and (5; $R^1 = H$) should have been formed in equimolar amounts; although no phenol was detected it may well have been present in the 1% yield required. As in the previous work the ratio (2): (3): (4 + 6) was evident from the ¹H n.m.r. spectrum of the crude product where the CH₂ reactions the non-acidic product showed absorptions at $\tau 4.9$ and 4.8 (ratio 2:1); there were no absorptions near $\tau 5.5$, so (3; $R^1 = H$) was absent, and the absorptions at 6.25 and 6.15 (ratio 2:1) indicated the absence of decarbonylation products. This was confirmed by the overall aromatic: CH_2 : OMe ratio 9:2:3 respectively. Fractional crystallisation of the mixed products gave 4'-methoxy-2-phenoxyacetophenone (2; $R^1 = H$, $R^2 = 4'$ -MeO) as the major component, and although the minor component could not be separated in a pure state, it is reasonable to assign its structure as (2; $R^1 = H$, $R^2 = 2'$ -MeO) from the n.m.r. absorptions; this indicates a higher ortho/para ratio than is normally obtained with anisole and aliphatic acid chlorides,† although some other aryloxyacetyl chlorides behave similarly.²

The reaction of (1; $R^1 = H$) in [7; $R^2 = 1,3$ -(OMe)₂] gave a mixture of the phenoxy-ketone [2; $R^1 = H$, $R^2 = 2',4'$ -(OMe)₂] (A) (66%) and a second compound (B) (34%) which could not be obtained free from (A). The ¹H n.m.r. spectrum of (B) [after allowance for the presence of (A)] showed singlets ($\tau 2.2$ and 3.6) which are consistent with a *para*-substituted aromatic with one of the protons ortho

$$R^{1} \cdot C_{6}H_{4} \cdot O \cdot CH_{2} \cdot COCI \xrightarrow{A1C1_{3}} R^{1} \cdot C_{6}H_{4} \cdot O \cdot CH_{2} \cdot CO \cdot C_{6}H_{4} \cdot R^{2} + (R^{2}C_{6}H_{4})_{2}CH_{2} + R^{1} \cdot C_{6}H_{4} \cdot OH + (R^{2}C_{6}H_{4})_{2}CH_{2} + R^{1} \cdot C_{6}H_{4} \cdot OH + (H^{2}C_{6}H_{4})_{2}CH_{2} + (H^{2}C_{6}H_{4})_{2}CH_{$$

absorptions are near τ 5, 5.5, and 6.1 respectively. These n.m.r. percentages are calculated on the assumption that all of the reacted (1) is converted into (2)—(6). This is justified by the high percentages of isolated material and the failure to detect any other reaction products by n.m.r. and i.r. spectroscopy. As in Part II,¹ the ease of isolation of the products was (2) and (4) > (3) and (5) > (6); the agreement between the isolated and n.m.r. determined product ratios usually decreases in the same order.

Various substituted compounds (1) were then treated with aluminium chloride in p-xylene and other aromatic solvents, the product ratios determined, and the mixtures separated. The results are in Table 1. With (1; $\mathbb{R}^1 = \mathbb{H}$) in anisole, according to the above conditions, hydrolysis of the reaction mixture gave a high recovery of phenoxyacetic acid, but the conversion into products was higher when the ratio of aluminium chloride to solvent was increased (this is commented upon further below). In these to a carbonyl group, a multiplet (5 protons, $\tau 2 \cdot 5 - 3 \cdot 5$) as in (A), a CH₂ group ($\tau 4 \cdot 8$), a methyl group attached to an aromatic ring ($\tau 7 \cdot 9$), and a methoxy-group degenerate with that of (A). The structure (2; R¹ = H, R² = 4'-OH, 5'-Me, 2'-OMe) is assigned to (B), since the alternative (2; R¹ = H, R² = 2'-OH, 4'-OMe, 5'-Me) should show a lower carbonyl absorption than (A) (intramolecular hydrogen bonding), whereas both (A) and (B) absorb at 1660 cm.⁻¹. Whether demethylation occurred before or after acylation has not been ascertained.

In the halogenated solvents, (7; $R^1 = Cl$, $R^2 = 1,2-Cl_2$), extensive formation of intractable tars occurred; this is probably a result of the greater nucleophilic character of the aromatic ring in the acid chloride and the acylation product (3; $R^1 = H$) than that of the solvent, and hence polymer formation (for this reason reactions in nitrobenzene were not attempted).

Electron-releasing substituents (R^1) in (1) increase the rate of decarbonylation relative to acylation (Part II and

¹ Part II, M. H. Palmer and G. J. McVie, *J. Chem. Soc.* (*B*), 1968, 745.

² M. H. Palmer and N. H. Scollick, to be published.

 $[\]dagger$ The alkylation of anisole also gives a high o/p ratio (P. Kovacic and J. J. Hiller, J. Org. Chem., 1965, **30**, 1581), and this has been attributed to complex formation between the carbonium ion and the ether oxygen atom.

ref. 3), and the effect of methyl substitution in the sidechain was next determined; in order to suppress the rate of cyclisation and thus allow a direct comparison of decarbonylation and intermolecular acylation, (9a) ($R^1 =$ 2-Cl, $R^2 = H$, $R^3 = Me$), (9b) ($R^1 = 4$ -Cl, $R^2 = H$, $R^3 =$ Me), and (9c) $(R^1 = 4$ -Cl, $R^2 = R^3 = Me)$ were treated with aluminium chloride in benzene under the previous conditions. With (9a) and (9b) there was no evidence of intermolecular acylation and the products were 1,1diphenylethane (10; $R^2 = H$, $R^3 = Me$) and the corresponding phenol (5; $R^1 = 2$ - and 4-Cl); with (9c) again no acylation products were observed, and (5; $\mathrm{R^{1}=4\text{-}Cl})$ was the sole phenolic product; the alkali-insoluble material together with the solvent benzene formed a complex mixture (g.l.c.), and although (10) (a, $R^2 = R^3 = H$; b, $R^2 = H$, $\mathrm{R}^3=\mathrm{Me};\,$ and c, $\mathrm{R}^2=\mathrm{R}^3=\mathrm{Me})$ were all absent, cumene was identified. In p-xylene, the decarbonylation of (9a) and (9b) was again complete (absence of carbonyl absorption

$$\begin{array}{c} \operatorname{R}^{1} \cdot \operatorname{C}_{6}\operatorname{H}_{4} \cdot \operatorname{O} \cdot \operatorname{CR}^{2}\operatorname{R}^{3} \cdot \operatorname{COCl} \xrightarrow{\operatorname{C}_{6}\operatorname{H}_{4} + \operatorname{AlCl}_{3}} \operatorname{R}^{1} \cdot \operatorname{C}_{6}\operatorname{H}_{4} \cdot \operatorname{O} \cdot \operatorname{CR}^{2}\operatorname{R}^{3} \cdot \operatorname{COPh} \\ (9a, b, c) & (11) \\ & & \\ & & \\ & & \\ \left[\operatorname{R}^{1} \cdot \operatorname{C}_{6}\operatorname{H}_{4} \cdot \operatorname{O} \cdot \operatorname{CR}^{2}\operatorname{R}^{3}\operatorname{Ph}\right] \xrightarrow{} \operatorname{Ph}_{2}\operatorname{CR}^{2}\operatorname{R}^{3} + \operatorname{R}^{1} \cdot \operatorname{C}_{6}\operatorname{H}_{4} \cdot \operatorname{OH} \\ & (12) & (10) & (5) \end{array}$$

and no ¹H n.m.r. absorptions corresponding to -O-CHMe-CO). Although the phenolic material was solely (5; $R^1 = 2$ - and 4-Cl), the hydrocarbon fraction was shown to be di-(2,5-xylyl)methane rather than the corresponding ethane in each reaction.

The behaviour of the benzyl ethers (12) with aluminium chloride in benzene and p-xylene was studied with (12; $R^1 = 4$ -Cl, $R^2 = H$, $R^3 = Me$). In the former reaction an equimolecular mixture of (5; $R^1 = 4$ -Cl) and (10; $R^2 = H$, $R^3 = Me$) was the major product but a small quantity of this com-4-chloro-2-(1-phenylethyl)phenol was isolated; pound was not detected in the reaction of (9; $R^1 = 4$ -Cl, $R^2 = H$, $R^3 = Me$), but this may reflect the difference in molar concentrations of benzyl ether and benzene in the two reactions. In p-xylene, the phenolic product was (5; $R^1 = 4$ -Cl) while the hydrocarbon mixture was complex (g.l.c.) and contained p-xylene, 1,2,4-trimethylbenzene, and di-(2,5-xylyl)methane as well as unidentified products. Di-(2,5-xylyl)ethane was not present (see below).

Spectra of the Products.—Apart from [2; $R^1 = H$, $R^2 =$ 2,4-(MeO)₂], the carbonyl stretching frequencies (1690 \pm 10 cm.⁻¹) of the intermolecular ketones are consistent with those of Part II,¹ as are the chemical shifts of the methylene group ($\tau 5.0 \pm 0.1$, in dilute solution in deuteriochloroform or carbon tetrachloride). The 2',6'-protons absorb at $\tau 2.0 \pm 0.1$ (as in Part II) except in the cases where R' = 2',5'-Me₂, where the 6'-absorption is at 2.5 ± 0.1 . This shift is greater than expected from the upfield shift (0.24)p.p.m.) of the ring protons of p-xylene with respect to benzene; 4 a study of molecular models suggests that interaction between the side-chain and the 2'-methyl leads to

1,1-Diphenylethane has also been prepared from $\alpha\alpha$ -diphenylpropionyl chloride with aluminium chloride in benzene at room temperature (ref. 7a).

out-of-plane twisting of the carbonyl group and hence a reduction in the amount of deshielding at the 6'-proton.

DISCUSSION

The high recovery of the starting acid from reactions in [7; $R^2 = OMe$, $R^2 = 1,3-(OMe)_2$] is indicative of a slow reaction between the acyl halide and the aluminium chloride, and probably results from a competing equilibrium in which the latter co-ordinates with the solvent.* Similarly, (1; $R^1 = 2$ - or 4-MeO) is largely recovered unchanged after a reaction with aluminium chloride (1 mol.) in benzene, but is rapidly converted into acylation and alkylation products when a second molecule of the catalyst is present.³

The alkylation products (4)—(6) arise from the benzyl ether (see Parts I and II), formed either by (a) unimolecular loss of carbon monoxide from the acylium ion (or other reactive intermediate) followed by rapid reaction with the solvent, or (b) bimolecular displacement of carbon monoxide by the solvent. In this latter case the ratio of acylation to alkylation products for a given acid chloride (1) should be independent of the aromatic solvent; the data of Tables 1 and 3 show that this is not the case, and that the carbon monoxide loss (8a) is therefore unimolecular. Thus, there is a close analogy with the decarbonylation of α -hydroxy-acids (8b) in concentrated sulphuric acid,⁵ and with the unimolecular hydrolysis of methoxymethyl chloride.⁶

$$\begin{pmatrix} R^{1}-O-CHR^{2}-CO \\ R^{1}-O-CHR^{2}-CO_{2}H \end{pmatrix} \xrightarrow{\qquad Products} \\ (a) R^{1}=Ph, R^{2}=H \\ (b) R^{1}=H, R^{2}=CH_{2}CO_{2}H \end{pmatrix}$$

The facile decarbonylation of the secondary and tertiary acylium ions was expected by analogy with the behaviour of trialkyl-, diaryl-, and triaryl-acetyl chlorides.7 The formation of diaryl-methane rather than the corresponding -ethane or -propane from the propionyl and isobutyryl compounds respectively, in p-xylene but not in benzene, † was unexpected.

Although proof, probably requiring the use of ¹³C- or ¹⁴C-labelled aryloxy-acids, is lacking, one possibility is hydride ion transfer from xylene to the phenoxypropyl carbonium ion (13) giving cumene (cf. above) and a xylyl carbonium ion. Attack of the latter on the solvent and aryl exchange would lead to the observed products. We have confirmed that exchange of aryl groups occurs readily under our reaction conditions; thus, diphenylmethane, aluminium chloride, and p-xylene at 15°

³ M. H. Palmer and A. C. Brodie, to be published.

⁴ P. Diehl, Helv. Chim. Acta, 1961, **44**, 829.

 ⁵ R. J. Gillespie and J. A. Leisten, Quart. Rev., 1954, 8, 40.
 ⁶ T. T. Tidwell and T. G. Traylor, J. Amer. Chem. Soc., 1966, 88, 3442; J. Hine and R. J. Rosscup, *ibid.*, 1960, 82, 6115; P. Ballinger, P. B. D. de la Mare, G. Kohnstam, and B. M. Prestt. J. Chem. Soc. 1055, 2641 Prestt, J. Chem. Soc., 1955, 3641. ? (a) E. Rothstein and R. W. Saville, J. Chem. Soc., 1949,

1946; (b) M. E. Grundy, ibid., 1958, 581; 1960, 372. (b) M. E. Grundy, E. Rothstein, and Wei-Hwa Hsü,

^{*} The rate of reaction of pivaloyl chloride with aluminium chloride is slower in anisole than in benzene or toluene (E. Rothstein and R. W. Saville, J. Chem. Soc., 1949, 1959), and this is not associated with changes in dielectric constant for the reaction (M. E. Grundy, E. Rothstein, and Wei-Hwa Hsü, J. Chem. Soc., 1965, 4561).

Acid chloride (1;	Solvent	Recovered acid of	2-Aryloxyacetophen- one (2) (%)		Benzof (3)	furanone (%)	Phenol (5) (%)	Diaryl- methane	2-Benzylphenol		
$R^1 =)$	$(7; R^2 =)$	yield	n.m.r.	isolated	n.m.r.	isolated	isolated	isolated	n.m.r.	isolated	
н	H										
н	$1,4-Me_2$	5	79	65	6	5	0	1	9	0	
\mathbf{H}	OMe a	56	44	39 d	0	0	0	0	0	0	
\mathbf{H}	OMe b	20	80	64 ^d	0	0	0	0	0	0	
\mathbf{H}	OMe °	26	74	64 d	0	0	0	0	0	0	
H	1,3-(OMe) ₂	48	50 °	17	0	0	0	0	0	0	
н	CI	9	0	0	f	10	1	10 f	f	0	
н	$1, 2 - Cl_2$	11	0	0	Í0	4	0	11	í8	0	
4-Me	1,4-Me ₂	6	64	58	13	9	4	5	17	5	
4-C1	$1,4-Me_2$	4	90	83	2	0	0	1	4	0	
4-F	1,4-Me ₂	0	90	70	1	0	7	7	9	0	
2-C1	$1,4-Me_2$	0	100	93	0	0	0.	0	0	0	

TABLE 1

Molar ratio (1; $\mathbb{R}^1 = H$): (7; $\mathbb{R}^2 = OMe$): $AlCl_3$: (a) 1:14:1:1; (b) 1:14:2; (c) 1:7:1. ⁴ A mixture of 2'- and 4'-methoxy-2-phenoxyacetophenones (in ratio 34:66) (see text). ⁴ A mixture of two compounds (ratio 2:1 approximately) consisting of 2-phenoxy-2',4'-dimethoxyacetophenone and another 2-phenoxyacetophenone, probably the 4'-hydroxy-2'-methoxy-5'-methyl-isomer (see text). ⁴ Insoluble solid (50%) (*i.e.*, 5 g. from 9.5 g. of acid chloride) formed, which gave no interpretable spectra.

TABLE 2

Physical constants of 2-aryloxyacetophenones

¹H N.m.r. spectra ^a (τ)

					-								
\mathbb{R}^2	M.p. ^{<i>b</i>}	ν (C=O) (cm. ⁻¹)	CH_2	2'-	3′-	4'-	5'-	6′-	2-	3-	4-	5-	6-
4'-MeO	64-65° (A) ^{c,d}	1690	$5 \cdot 0$	2.05	3.16	$6 \cdot 2$	3.16	2.05	multi	olet 2.5	$5 - 3 \cdot 2$		
$2', 4' - (MeO)_2$	115 (A) °	1660	4.8	6·1 ^f	$3 \cdot 5$	6.15^{f}	3.45	$2 \cdot 0$	multi	blet 2.5	$5 - 3 \cdot 25$		
$2', 5' - (MeO)_2$	70 (A) g	1700	4.9	7.551	2.83	2.83	7·65 f	2.55	multi	blet 2.6	$55 - 3 \cdot 2$	5	
2′,5′-Me ₂	80 (A) h	1680	$5 \cdot 1$	7.65	2.92	2.92	7.7 f	2.6	3.32	3.02	7.78	3.02	3.32
$2', 5' - Me_2$	107 (B) i	1690	4.9	7.51	2.85	2.85	7.61	2.55	3.23	2.85		2.85	3.23
$2',5'-Me_2$	86 (B) ^j	1700	$5 \cdot 1$	7.61	2.88	2.88	7.75	2.63	multi	olet 3.0)53-4	5	
$2', 5' - Me_2$	76 (B) k	1680	4 ·9	7.65	obsc	ured	7.75	$2 \cdot 45$	multi	blet 2.6	33∙4		
	R ² 4'-MeO 2',4'-(MeO) ₂ 2',5'-(MeO) ₂ 2',5'-Me ₂ 2',5'-Me ₂ 2',5'-Me ₂	$\begin{array}{ccccc} {\rm R}^2 & {\rm M.p.}^b \\ {\rm 4'-MeO} & {\rm 6465^{\circ}~(A)} \ {}^{e,d} \\ {\rm 2',4'-(MeO)_2} & {\rm 115~(A)}^e \\ {\rm 2',5'-Me_2} & {\rm 70~(A)}^g \\ {\rm 2',5'-Me_2} & {\rm 80~(A)}^h \\ {\rm 2',5'-Me_2} & {\rm 107~(B)}^i \\ {\rm 2',5'-Me_2} & {\rm 86~(B)}^j \\ {\rm 2',5'-Me_2} & {\rm 76~(B)}^k \end{array}$	$\begin{array}{c ccccc} & & & & & & & & & \\ R^2 & M.p.^{b} & (cm.^{-1}) \\ 4'-MeO & 64-65^{\circ} (A) & ^{e,d} & 1690 \\ 2',4'-(MeO)_2 & 115 (A) & ^{e} & 1660 \\ 2',5'-(MeO)_2 & 70 (A) & ^{g} & 1700 \\ 2',5'-Me_2 & 80 (A) & ^{h} & 1680 \\ 2',5'-Me_2 & 107 (B) & ^{i} & 1690 \\ 2',5'-Me_2 & 86 (B) & ^{j} & 1700 \\ 2',5'-Me_2 & 76 (B) & ^{k} & 1680 \\ \end{array}$	$\begin{array}{c cccc} & & \nu(C=O) \\ R^2 & M.p.^{b} & (cm.^{-1}) & CH_2 \\ 4'-MeO & 6465^{\circ} (A) & ^{\epsilon,d} & 1690 & 5 \cdot 0 \\ 2',4'-(MeO)_2 & 115 (A) & 6 & 1660 & 4 \cdot 8 \\ 2',5'-(MeO)_2 & 70 (A) & 1700 & 4 \cdot 9 \\ 2',5'-Me_2 & 80 (A) & 1680 & 5 \cdot 1 \\ 2',5'-Me_2 & 107 (B) & 1690 & 4 \cdot 9 \\ 2',5'-Me_2 & 86 (B) & 1700 & 5 \cdot 1 \\ 2',5'-Me_2 & 76 (B) & 1680 & 4 \cdot 9 \end{array}$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$							

^a In CDCl₃ unless otherwise stated. ^b Solvent for recrystallisation: A = light petroleum (b.p. 60-80°); B = ethanol. ^c In Nujol. ⁴ R. Stoermer and P. Atenstadt (*Ber.*, 1902, **35**, 3562) give m.p. 65°. ^c A. Sonn (*Ber.*, 1919, **52**, 927) gives m.p. 115°; R. Stoermer and P. Atenstadt (*loc. cit.*) give m.p. 118°. ^f These columns may be interchanged. ^e Found: C, 79·9; H, 6·9. $C_{16}H_{16}O_4$ requires C, 80·0; H, 6·7%. ^k Found: C, 80·6; H, 6·9. $C_{17}H_{18}O_2$ requires C, 80·3; H, 7·1%. ⁱ Found: C, 69·8; H, 5·8; Cl, 12·7. $C_{16}H_{15}CO_2$ requires C, 69·8; H, 5·5; Cl, 12·8%. ^j Found: C, 73·8; H, 5·7. $C_{16}H_{15}FO_2$ requires C, 74·3; H, 5·8%. ^k Found: C, 69·9; H, 5·2; Cl, 12·6. $C_{16}H_{15}CO_2$ requires C, 69·8; H, 5·5; Cl, 12·8%.

TABLE 3

Ratio of intermolecular acylation to decarbonylation of aryloxyacetyl chloride in benzene and p-xylene

	(1, 4)	11)								
	(2; (4+6;		(1; $R^1 = 4$ -Me)		(1; $R^1 = 4$ -Cl)		$(1; R^1 = F)$		(1; $R^1 = 2$ -Cl)	
	$R^1 = H$	$\dot{\mathbf{R}^1} = \dot{\mathbf{H}}$	(2)	(4 + 6)	(2)	(4 + 6)	(2)	(4 + 6)	(2)	(4 + 6)
$C_6H_6 (R^1 = H)$	13 a,b	32	5	39	44	44	39	55	72	11
p-C ₆ H ₄ Me ₂ (R ¹ =	79	9	64	17	90	4	90	9	100	0

 $^{2,5-}Me_2$

^a Percentage composition of crude product as determined by n.m.r. absorptions at τ 5.0 \pm 0.2 (2), and 6.1 \pm 0.1 (4 + 6). ^b Data from Part II.¹

for 2 hours gave a mixture of diphenylmethane, phenyl-(p-xylyl)methane, and di-(p-xylyl)methane in the molar ratio 1:4:3.

 $(1 \cdot R1 - H)$

EXPERIMENTAL

Reaction of Aryloxyacetyl Chlorides with Aluminium Chloride in Aromatic Solvents.—A typical procedure is shown (below) for the reaction of phenoxyacetyl chloride in p-xylene; the other reactions were carried out under similar conditions, the molar ratio of acid chloride to aluminium chloride to solvent being $1: 1\cdot 1: 17 \sim 18$ in all

cases. The spectral and other properties of the products are shown in Table 2.

Phenoxyacetyl Chloride and Aluminium Chloride in p-Xylene.—Phenoxyacetyl chloride [prepared from the acid (10 g., 0.0587 mole) with thionyl chloride] in p-xylene (60 ml.) was added to a stirred suspension of aluminium chloride (9.5 g., 0.07 mole) in p-xylene (60 ml.) at 10°. After stirring the mixture at 10—15° for 1.5 hr., and then with dilute hydrochloric acid for 1 hr., the layers were separated, and the aqueous phase extracted with ether (3×50 ml.). The combined organic solutions were extracted with aqueous sodium hydrogen carbonate, to give phenoxyacetic acid (0.4 g., 4%). The oil obtained by evaporation of the solvents showed strong absorption at 1700—1720 cm.⁻¹, and singlets at τ 4.9, 5.5, and 6.2, indicative of 2-phenoxy-2',5'-dimethylacetophenone, benzofuran-3(2H)-one, and di-(2,5-xylyl)methane respectively. Extraction of the oil

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with 2M-sodium hydroxide gave (after acidification) benzofuran-3(2H)one (0.4 g., 5%), m.p. 99°, whose 1H n.m.r. spectrum had complex multiplets at $\tau 2.4$ —2.7 (2 protons) and $2 \cdot 9 - 3 \cdot 3$ (2 protons), and a singlet (5.5) (2 protons). Treatment of the alkali-insoluble material with light petroleum (b.p. 40-60°) gave 2-phenoxy-2',5'-dimethylacetophenone (8.1 g., 55%), m.p. 70°, whose n.m.r. spectrum showed a complex multiplet between τ 2.6 and 3.25 (9 protons), a singlet at 4.9 (2 protons), and further singlets at 7.5 and 7.65 (each 3 protons) (Found: C, 79.9; H, 6.7. $C_{16}H_{16}O_2$ requires C, 80.0; H, 6.9%). Chromatography of the filtrate above on silica gel gave: (a) on elution with benzene, di-(2,5-xylyl)methane (50 mg., 1%), m.p. 62°, whose spectra (and absence of mixed m.p. depression) were identical with an authentic sample; (b) on elution with 50% benzene-ether, a further 1.4 g. (10%) of 2-phenoxy-2',5'-dimethylacetophenone.

2-Bromo-2',5'-dimethylacetophenone.—Acetyl chloride (20 g., 0.25 mole) in carbon disulphide (260 ml.) was added to a mixture of p-xylene (26 g., 0.25 mole) and aluminium chloride (33 g., 0.25 mole) in carbon disulphide (260 ml.) at a temperature between -10 and -4° , to give, after hydrolysis, 2',5'-dimethylacetophenone, b.p. $104^{\circ}/11$ mm. (30 g., 81%).⁸ This compound (11.5 g.) in acetic acid (15 ml.) was treated with bromine (12·8 g., 0·08 mole) in acetic acid (15 ml.) at 50°; after pouring into water, a green oil was obtained which was recrystallised from light petroleum (b.p. 40—60°) at -20° , to give the product (12 g., 67%), m.p. $< 20^{\circ}$, ν (C=O) 1680 cm.⁻¹, and n.m.r. spectrum (in CCl₄) τ 2·6 (6′-H), 2·9 (3′-H, 4′-H as singlet), 5·75 (2-CH₂, singlet), 7·6, 7·7 (2′-CH₃ and 5′-CH₃); cf. phenacyl bromide τ 5·7 (2-CH₂, singlet) (in CCl₄).

2-Phenoxy-2',5'-dimethylacetophenone. 2-Bromo-2',5'dimethylacetophenone (7 g., 0.03 mole) in methanol (25 ml.) was added to sodium phenoxide (from phenol 4.7 g., 0.05 mole) in methanol (75 ml.). After 3 hr. at 65°, 2-phenoxy-2',5'-dimethylacetophenone, m.p. 70° (from light petroleum, b.p. 60-80°) was obtained (6.0 g., 83%); it was identical with the product obtained from phenoxyacetyl chloride and p-xylene.

2-(2-Chlorophenoxy)- and 2-(4-Chlorophenoxy)-2',5'-dimethylacetophenone.—These compounds, m.p. 75° (EtOH) and m.p. 107° (EtOH), were prepared from 2-bromo-2',5'dimethylacetophenone in a similar manner.

[8/394 Received, March 19th, 1968]

⁸ D. V. Nightingale and H. B. Hucker, J. Org. Chem., 1953, 18, 1529.