The Elimination of Carbon Monoxide from Acid Derivatives.   Part IV.[1] Friedel–Crafts Reactions of Some Primary (Alkylphenyl)acetyl Chlorides

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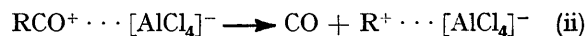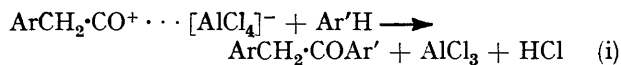
When primary (alkylphenyl)acetyl chlorides react with aluminium chloride they tend to eliminate carbon monoxide to an extent which is partly determined by the substituent groups, by the reactivity of the aromatic component, and by the temperature.   Displacement of alkyl groups may also occur.

PHENYLACETYL CHLORIDE and its derivatives have frequently been utilised for the Friedel–Crafts synthesis of deoxybenzoins [reaction (i)][2] but concurrent elimination of carbon monoxide [reaction (ii)] appears not to have been reported.   Decarbonylation of carboxylic acid derivatives by aluminium chloride is however, not uncommon and is displayed by the acid chlorides of tertiary acids,[3a] of diarylacetic acids,[4] and, to a much lesser degree, of the derivatives of primary and secondary aliphatic acids.[3b]   Secondary and tertiary aryloxyacetyl chlorides have also been reported to undergo this reaction.[5]   In this paper we indicate that primary arylacetyl chlorides are very prone to undergo similar decompositions when conditions are suitable.

The extent of decarbonylation is often limited by a competitive acylation reaction (i), which in turn is

$$\text{ArCH}_2\text{·CO}^+ \cdots [\text{AlCl}_4]^- + \text{Ar'H} \longrightarrow$$
$$\text{ArCH}_2\text{·COAr'} + \text{AlCl}_3 + \text{HCl} \quad \text{(i)}$$

$$\text{RCO}^+ \cdots [\text{AlCl}_4]^- \longrightarrow \text{CO} + \text{R}^+ \cdots [\text{AlCl}_4]^- \quad \text{(ii)}$$

dependent on the reactivity of the other component (usually the solvent) of the reaction.   On the other hand solvents have comparatively little influence on the rate at which carbon monoxide is eliminated.[6]   In consequence the yields of carbon monoxide for the following solvents are diminished in the order: inert solvent > chlorobenzene > benzene > alkylbenzene > anisole (see

[1] Part III, D. G. Pratt and E. Rothstein, *J. Chem. Soc. (C)*, 1968, 2548.

[2] See, for instance, (a) A. Fischer, B. A. Grigos, and J. Packer, *J. Amer. Chem. Soc.*, 1961, **83**, 4206; (b) D. M. Curtin and M. C. Crew, *ibid.*, 1954, **76**, 3719; (c) D. J. Cooper and L. N. Owen, *J. Chem. Soc. (C)*, 1966, 353.

[3] E. Rothstein and R. W. Saville, *J. Chem. Soc.*, 1949, (a) p. 1950; (b) p. 1961.

[4] M. E. Grundy, W. H. Hsü, and E. Rothstein, *J. Chem. Soc.*, 1960, 371.

[5] M. H. Palmer and G. J. McVie, *J. Chem. Soc. (B)*, 1968, 745, 856.

[6] E. Rothstein and R. W. Saville, *J. Chem. Soc.*, 1949, 1954.

Table 2). An interesting example is isobutyryl chloride from which the yield of carbon monoxide is 8—10% in benzene but 90% in 1,2,4-trichlorobenzene.[7]

The ease of decarbonylation must to some extent reflect the relative stabilities of the two cations RCO^+ and R^+. Furthermore there is a similarity between the loss of carbon monoxide from benzoyl and phenylacetyl chlorides and the separation of chloride ion from chlorobenzene and benzyl chloride, since identical pairs of ions, Ph^+ and $PhCH_2^+$, are produced. The implication, therefore, is that in contrast to phenylacetyl chloride, benzoyl chloride should resist decomposition.*

Only the 4-t-butyl derivative afforded a detectable amount ($<5\%$) of carbon monoxide (Table 1), from

TABLE 1

Friedel–Crafts reactions of substituted benzoyl chlorides

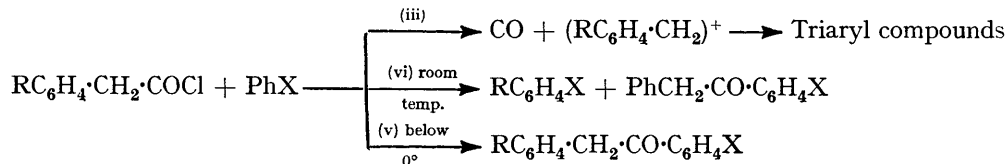| Expt.	Subst.	B.p. (°C) [mmHg]	Reaction temp. (°C)	Solvent	Benzophenone g	%
1	2-Me	105 [15]	17·5	Benzene	49	68
2	4-Me	109 [20]	18·0	Benzene	29	73
3a	2,6-Me$_2$	91 [12]	20·0	Benzene	23	0 a
3b	2,5-Me$_2$		80·0	Benzene	19	0 a
3c	2,6-Me$_2$		Room	Benzene b	9	0
3d	2,6-Me$_2$		Room	Anisole	50	71
4a	4-Bu^t	65 [0·08]	13·2	Benzene	15	77 cd
4b	4-Bu^t		16·5	CCl$_4$	47·5	0

a A complex was formed but there was no further reaction. b Light petroleum (b.p. 40—60°; 15 g) was also added. c Carbon monoxide (5%) was evolved. d There was no emission of carbon monoxide.

which it could be inferred that there was virtually no tendency for elimination to occur even as an alternative to ketone formation. This conclusion was supported by the failure of 2,6-dimethylbenzoyl chloride to react. There must have been complex formation with the catalyst since the reaction in anisole furnished 4'-methoxy-2,6-dimethylbenzophenone.

The principal products from the reactions of primary arylacetyl chlorides are summarised in Table 2. Side-reactions were minimised by employing approximately equimolecular amounts of acid chloride and catalyst. This usually restricted the maximum yield of carbon monoxide to 70—80% or less if the complexes were insoluble in the reaction mixtures (Table 2, nos. 5 and 6). Three principal reaction types [(iii)—(v)] could be distin-

TABLE 2

Friedel–Crafts reactions of primary arylacetyl chlorides

Expt.	Subst.	Reaction temp. (°C)	Wt. solvent (g)	CO (%)	Dexoybenzoin formed	Yield (%)
		In cyclohexane				
5	None	19	39	30·6		
		In chloroform				
6	4-Me	18	74	44		
		In benzene				
7	2-Me	19	29	0	2-Me	76
8	3-Me	Room	30	0	3-Me	74
9	4-Me	16	23	4	4-Me	68
10	4-Et	20	18	0	Unsubst. a	64
11	4-Et	-10	34	0	4-Et	73
12	4-Pr^i	21·5	18	0	Unsubst. a	66
13	4-Pr^i	-10	15	0	4-Pr^i	67
14	4-Bu^t	17	38	2	Unsubst. 4-Bu^t	42 32
15	4-Bu^t	-10	30	0	None isolated b	0
16	2,4,6-Me$_3$	22	139	30	2,4,6-Me$_3$ a	22
17	2,4,6-Pr$^i_3$	22	17	18	None isolated a	0
		In chlorobenzene				
18	None	18	55	7	4'-Cl	55
19	2-Me	20·5	55	28	4'-Cl-2-Me (?) c	16
20	2-Me	0	55	1	None isolated	0
21	3-Me	23—25	55	11	4'-Cl-3-Me	Small
22	3-Me	0	55	1	4'-Cl-3-Me	29
23	4-Me	19	55	34	4'-Cl-4-Me	29
24	4-Me	0	55	14·5	4'-Cl-4-Me	39
25	4-Et	18	55	37	4'-Cl d	23
26	4-Et	0	55	13·8	4'-Cl-4-Et	47
27	4-Pr^i	21	55	34·5	4'-Cl d	27
28	4-Pr^i	0	55	14·2	4'-Cl-4-Pr^i	41
29	4-Bu^t	18·5	55	11	4'-Cl d	54
30	4-Bu^t	0	55	5·3	4'-Cl d	66
31	2,4,6-Me$_3$	21	55	64	None isolated e	0
32	2,4,6-Pr$^i_3$	22	55	31	None isolated d	0
		In anisole				
33	4-Et	14	11 f	0	4-Et-4'-MeO	51
34	4-Pr^i	16	11 f	0	4-Pr^i-4'-MeO	62
35	4-Bu^t	19	25	0	4-Bu^t-4'-MeO	70
36	2,4,6-Pr$^i_3$	16·5	11 g	0	2,4,6-Pr$^i_3$-4'-MeO	68

a The corresponding alkylbenzenes were also isolated (see Experimental section). b Benzoin and 4-t-butylbenzoic acids were among the products. c The deoxybenzoin formed ca. 75% of the principal product. d The corresponding alkylchlorobenzenes were included in the product. e The yield comprised mesitylene and a mixture of chlorohydrocarbons. The anisole was diluted with light petroleum (b.p. 40—60°; 50 ml). g The anisole was diluted with light petroleum (b.p. 40—60°, 10 mol).

dicated that acylation was probably preceded by separation of alkyl (R^+). Reaction (iii) resulted in

$$\text{RC}_6\text{H}_4\cdot\text{CH}_2\cdot\text{COCl} + \text{PhX}$$

(iii) → $CO + (RC_6H_4\cdot CH_2)^+$ → Triaryl compounds

(vi) room temp. → $RC_6H_4X + PhCH_2\cdot CO\cdot C_6H_4X$

(v) below 0° → $RC_6H_4\cdot CH_2\cdot CO\cdot C_6H_4X$

R = H, Et, Pr^i, or Bu^t; X = H, Cl, or OMe

guished (Table 2, nos. 7—14, and 18—30). Reactions (iv) and (v) refer more particularly to those of the 4-ethyl and 4-isopropyl compounds (Table 2, nos. 10, 12, 26, and 28). Formation of an alkylchlorobenzene and 4'-chlorodeoxybenzoin [reaction (iv) X = Cl] in-

* Aryl halides have been prepared by decarbonylation of benzoyl halides with heated rhodium catalysts.[8] It is evident that this is not a reaction of the Friedel–Crafts type.

mixtures of two or more triaryl derivatives. Other possibilities, however, could not be precluded.

Migration of methyl from the aromatic nucleus was

[7] V. F. Tavern, Z. K. Kiro, and B. J. Stepanov, J. Org. Chem. (U.S.S.R.), 1966, 2, 371.

[8] J. Tsuji and K. Ohno, Tetrahedron Letters, 1965, 4565; J. Blum, ibid., 1966, 1605; J. Blum, E. Oppenheimer, and E. A. Bergmann, J. Amer. Chem. Soc., 1967, 89, 2338.

not observed. Fuson and his co-workers [9] obtained the corresponding deoxybenzoin and diphenylmethane when 2,4,6-trimethylphenylacetyl chloride reacted with benzene. Evidently the complete mesityl group was replaced by phenyl; we have now isolated the mesitylene which was formed. The reaction in chlorobenzene (Table 2, no. 31) also yielded mesitylene but the principal products afforded by this reaction were chlorohydrocarbons.

No deoxybenzoin was formed from 2,4,6-tri-isopropylphenylacetyl chloride either in benzene or in chlorobenzene and the yields of carbon monoxide were smaller than might have been expected from such highly alkylated compounds. It appears that a rapid separation of isopropyl preceded any further reaction since 40% of the group was isolated as isopropylbenzene or 4-chloroisopropylbenzene from the reactions in benzene and chlorobenzene, respectively.

4-t-Butylphenylacetyl chloride behaved atypically. In benzene at 17° a mixture of deoxybenzoin and 4-t-butyldeoxybenzoin was formed, but at −10° there appeared to have been an intermolecular transfer of carbonyl to benzene and to t-butylbenzene thus yielding benzoic and 4-t-butylbenzoic acids, respectively. There were no corresponding reactions in chlorobenzene; the principal products were 4'-chlorodeoxybenzoin and 1-chloro-4-t-butylbenzene.

Condensations in anisole (Table 2, nos. 33—35) gave the normal 4'-methoxydeoxybenzoins. Carbon monoxide was not evolved and no by-products were isolated.

EXPERIMENTAL

Details of starting acids and acid chlorides are given in Table 3; purified [10] thionyl chloride at room temperature was used. Tables 1 and 2 summarise the reaction conditions and the principal products: more detailed descriptions of the experiments are given below, their numbers corresponding to those in the Tables. Structures of the deoxybenzoins were confirmed by their [1]H n.m.r. spectra (Varian A60A instrument). For example, 4'-chloro-4-methyldeoxybenzoin showed τ 2·90 (4H, s, aromatic), 7·75 (s, Me), 5·88 (s, CH_2), 2·16 (d, $2H_o$), and 2·70 (d, $2H_m$) (J 8·6 Hz). The other deoxybenzoins had closely similar spectra.

Friedel–Crafts Reactions.—The apparatus was similar to that previously described.[11] Free-flowing anhydrous aluminium chloride was used. A slow stream of nitrogen was passed through the reaction mixtures. At room temperature solutions of the acid chloride were added to suspensions of the catalyst (in the molecular ratio 1 : 1·25) in the aromatic component (or unreactive solvent) and the liquids were kept overnight. At low temperatures the catalyst was added to solutions containing equimolecular quantities of the acid chlorides and the products were isolated 1 h after completion of the addition. Except in experiment 3b, no external heat was applied to the reaction mixtures. Identification and measurement of carbon monoxide were carried out in the usual way with ammoniacal cuprous chloride [11] and also by i.r. spectroscopy.

[9] R. C. Fuson, D. H. Chadwick, and M. C. Ward, *J. Amer. Chem. Soc.*, 1946, **68**, 389.

[10] D. L. Cottle, *J. Amer. Chem. Soc.*, 1946, **68**, 1300.

Details of acids and of acid chlorides

Benzoic acids	M.p. (°C)	Acid chloride b.p. (°C) [mmHg]
2-Me		103 [15]
4-Me		109 [20]
2,6-Me₂	115	91 [12]
4-Buᵗ ᵃ	164—165 ᵇ	65 [0·08]
Phenylacetic acids		
Unsubst.	77	
2-Me ᶜ	88—89	134 [25]
3-Me ᵈ	64—65	115 [20]
4-Me ᶠ	94	100 [11]
4-Et ᵍ	91—92	136 [25]
4-Prⁱ ᵍ	52	139—140 [20]
4-Buᵗ ᵍ	79—80	140 [15]
2,4,6-Me₃ ʰ	166 ⁱ	140 [17]
2,4,6-Prⁱ₃ ʲ	141	106—107 [0·1] ᵏ (m.p. 79°)

ᵃ J. B. Shoesmith and A. Mackie, *J. Chem. Soc.*, 1936, 300. ᵇ M.p. 164° (A. Verley, *Bull. Soc. chim. France*, 1898, **19**, 67). ᶜ B. Radiziszewki and P. Wispek, *Ber.*, 1895, **18**, 1281. ᵈ A. F. Titley, *J. Chem. Soc.*, 1926, 514. ᵉ Lit.,³ m.p. 61°. ᶠ H. Rupe and F. Wiedekehr, *Helv. Chim. Acta*, 1924, **7**, 654. ᵍ J. W. Baker, J. F. J. Dippy, and J. E. Page, *J. Chem. Soc.*, 1937, 1778. ʰ R. C. Fuson and N. Rabjohn, *Org. Synth.*, Coll. Vol. III, 1955, p. 557. ⁱ Lit. m.p. 167—168° (R. E. Lutz, *J. Amer. Chem. Soc.*, 1950, **72**, 4091). ʲ R. C. Fuson, D. H. Chadwick, and M. C. Ward, *J. Amer. Chem. Soc.*, 1946, **68**, 389. ᵏ Lit. b.p. 107—110 at 5 mmHg (W. H. Miller, A. M. Dessert, and G. W. Anderson, *J. Amer. Chem. Soc.*, 1948, **70**, 500).

Products of Friedel–Crafts Reactions with Substituted Benzoyl Chlorides.—*Expt.* 1: 2-*methylbenzoyl chloride at* 18°. 2-Methylbenzophenone had b.p. 97—98° at 0·12 mmHg (lit.,¹² 168° at 12 mmHg).

Expt. 2: 4-*methylbenzoyl chloride at* 18°. 4-Methylbenzophenone crystallised from ethanol as needles, m.p. 59—60° (lit.,¹³ 59—60°).

Expt. 3d: 2,6-*dimethylbenzoyl chloride in anisole at room temperature.* 4'-*Methoxy*-2,6-*dimethylbenzophenone* had b.p. 163° at 0·3 mmHg (Found: C, 79·9; H, 6·8. $C_{16}H_{16}O_2$ requires C, 80·0; H, 6·7%), τ 7·87 (s, 2Me), 6·18 (s, OMe), 2·24 (d, $2H_o$), 3·91 (d, $2H_m$) (J 7·10 Hz), and 2·90 (m, $2H_m$ and H_p).

Expt. 4a: 4-*t*-*butylbenzoyl chloride and benzene at* 13·2°. Carbon monoxide (4·8%) was evolved. The other product was 4-t-butylbenzophenone, b.p. 137—138° at 0·2 mmHg, n_D^{25} 1·5775 (lit.,¹⁴ 1·5725); 2,4-*dinitrophenylhydrazone*, m.p. 210° (from ethanol) (Found: C, 66·2; H, 5·4; N, 13·4. $C_{23}H_{22}N_4O_4$ requires C, 66·0; H, 5·3; N, 13·4%).

Friedel–Crafts Reactions of Phenylacetyl Chlorides in Unreactive Solvents.—*Expt.* 5: *phenylacetyl chloride in cyclohexane at* 19°. Carbon monoxide was liberated from the pasty mass formed by the addition of the acid chloride to a suspension of aluminium chloride in cyclohexane. When the reaction was complete, benzene was added and the mixture boiled under reflux for 20 min; hydrogen chloride was then evolved. Decomposition by ice and acid yielded a yellow pasty material which was soluble in chloroform; it was not identified. There was no similar reaction in nitrobenzene, benzoyl chloride, or benzoyl chloride–cyclohexane.

Expt. 6: 4-*methylphenylacetyl chloride in chloroform at* 18°. In addition to carbon monoxide, an unidentified substance

[11] E. Rothstein and R. W. Saville, *J. Chem. Soc.*, 1949, 1946.

[12] A. W. Smith, *Ber.*, 1891, **24**, 4047.

[13] J. Marshall, *J. Chem. Soc.*, 1915, **107**, 516.

[14] E. Bergmann and J. Szmuszkowicz, *J. Amer. Chem. Soc.*, 1948, **70**, 2750.

insoluble in the usual solvents was isolated (Found: C, 65·6; H, 5·7; Cl, 9·0; Ash, 5·3%).

Friedel–Crafts Reactions of Phenylacetyl Chlorides in Benzene.—4-Ethylphenylacetyl chloride. (a) *At* 20° (*expt.* 10). The reaction afforded ethylbenzene (18%), identified by its i.r. spectrum, and deoxybenzoin, b.p. 117—125° at 0·07 mmHg, m.p. 55—56° (from aqueous ethanol) identified (m.p. and mixed m.p.) by comparison with an authentic specimen.

(b) *At* −10° (*expt.* 11). This gave 4-*ethyldeoxybenzoin*, b.p. 140° at 0·15 mmHg, separating from n-hexane as needles, m.p. 90—91° (Found: C, 85·4; H, 7·0. $C_{16}H_{16}O$ requires C, 85·7; H, 7·1%). The compound was unchanged when its solution in benzene was kept for 18 h with a 10% excess of aluminium chloride.

4-Isopropylphenylacetyl chloride. (a) *At* 21·5° (*expt.* 12). The products were (i) isopropylbenzene (1 g., 36%), identified by its i.r. and ^{1}H n.m.r. spectra; (ii) deoxybenzoin.

At −10° (*expt.* 13). The product was 4-*isopropyldeoxybenzoin*, b.p. 155—158° at 0·02 mmHg, separating from n-hexane as needles, m.p. 70° (Found: C, 85·4; H, 7·7. $C_{17}H_{18}O$ requires C, 85·7; H, 7·6%).

4-t-Butylphenylacetyl chloride. (a) *At* 17° (*expt.* 14). First, the mixed gases which were evolved were freed from carbon monoxide, and then the residual gases were kept over concentrated sulphuric acid for 18 h. The final residue was identified as isobutane by its i.r. spectrum. The other products of the reaction were (i) t-butylbenzene (1·5 g, 15%); (ii) deoxybenzoin; and (iii) 4-*t-butyldeoxybenzoin*, b.p. 145—155° at 0·05 mmHg, m.p. 42° (from ethanol) (Found: C, 85·9; H, 8·1. $C_{18}H_{20}O$ requires C, 85·7; H, 7·9%) [2,4-*dinitrophenylhydrazone*, m.p. 182—183° (from ethanol) (Found: C, 66·3; H, 5·7; N, 13·3. $C_{24}H_{24}N_4O_4$ requires C, 66·7; H, 5·6; N, 13·0%)].

(b) *At* −10° (*expt.* 15). Apart from hydrogen chloride, traces only of other gases were evolved. Distillation afforded (i) benzoic acid (1 g, 21%), m.p. 120°; (ii) 4-t-butylbenzoic acid, b.p. 130° at 0·1 mmHg, m.p. 164—165° (from ethanol) (Found: C, 74·3; H, 7·9. Calc. for $C_{11}H_{14}O_2$: C, 74·2; H, 7·9%), τ 8·64 (s, 3Me), 1·95 (d, 2H_m), and 2·58 (d, 2H_o) (*J* 8·8 Hz); (iii) a residual mixture (g.l.c.) probably containing more 4-t-butylbenzoic acid (Found: C, 74·5; H, 7·8%).

Expt. 16: 2,4,6-*trimethylphenylacetyl chloride at* 22°. Products: (i) mesitylene (0·3 g, 14%), b.p. 140° at 17 mmHg, i.r. spectrum identical with that published; [15] (ii) mainly diphenylmethane containing traces of mesitylene and an unidentified substance (g.l.c. on silicone grease at 202°); (iii) 2,4,6-trimethyldeoxybenzoin (1 g, 21%) separating from ethanol as long needles, m.p. 160° (lit.,[9] 161—162°); (iv) a resinous syrup, b.p. 220—230° at 0·07 mmHg, which when washed with ethanol yielded a substance which separated from acetic acid as small, white crystals, m.p. 168° (Found: C, 83·8; H, 7·4. Calc. for $C_{28}H_{30}O_2$: C, 84·4; H, 7·5%) having a ^{1}H n.m.r. spectrum resembling that of trimethyldeoxybenzoin but with additional absorptions.

Expt. 17: 2,4,6-*tri-isopropylphenylacetyl chloride at* 22°. Non-gaseous products were isopropylbenzene (35%) and three unidentified substances with b.p.s 100° at 16 mmHg, 152° at 16 mmHg, and 165° at 0·3 mmHg (lit.,[9] 176—178° at 3 mmHg).

* The reaction between *p*-chlorobenzoyl chloride and benzyl magnesium chloride was reported [17] to yield the ketone as *cream* scales, m.p. 107·5°.

Friedel–Crafts Reactions of Phenylacetyl Chlorides in Chlorobenzene.—Expt. 18: *phenylacetyl chloride at* 18°. 4′-Chlorodeoxybenzoin separated from ethanol as pure white needles,* m.p. 104—105° (lit.,[16] 102°) (Found: C, 73·0; H, 4·8; Cl, 15·6. Calc. for $C_{14}H_{11}ClO$: C, 72·9; H, 4·8; Cl, 15·4%).

2-Methylphenylacetyl chloride. (a) *At* 20·5° (*expt.* 19). An orange complex yielded a ketonic product (i), b.p. 130—150° at 0·05 mmHg, m.p. 73° (from ethanol) (Found: C, 77·2; H, 5·6; Cl, 12·8. Calc. for $C_{15}H_{13}ClO$: C, 73·6; H, 5·3; Cl, 14·5%). Analysis and ^{1}H n.m.r. indicated a mixture containing ca. 75% of 4′-chloro-2-methyldeoxybenzoin. An extra methyl signal at τ 7·67 (s, 0·25Me) and additional minor ones in the methylene and aromatic regions of the spectrum indicated that the remaining 25% was a chlorine-free substance. The second product (ii) (2 g), b.p. 205—215° at 0·05 mmHg, may also have been a mixture (Found: C, 78·5; H, 6·0; Cl, 10·5. Calc. for $C_{22}H_{19}ClO$: C, 78·9; H, 5·7; Cl, 10·6%).

(b) *At* 0° (*expt.* 20). A complex substance (8 g), m.p. 218°, insoluble in most solvents was isolated (Found: C, 76·6; H, 5·8; Cl, 3·3; Ash, 0·4%), τ 7·58 (s, nuclear Me), 5·33 (2CH), and multiplets in the aromatic region (4H).

3-Methylphenylacetyl chloride. (a) *At* 23—25° (*expt.* 21). The three non-gaseous products were an oil (i) (4·1 g), b.p. 145—146° at 0·13 mmHg, which partly crystallised. Filtration afforded 4′-*chloro-3-methyldeoxybenzoin*, separating from ethanol as needles, m.p. 52·5° (Found: C, 74·1; H, 5·3; Cl, 14·4. $C_{15}H_{13}ClO$ requires C, 73·6; H, 5·3; Cl, 14·5%). Alumina (grade I) removed some fluorescence from a benzene solution of the second fraction (ii) (2·8 g), b.p. 210—220° at 0·13 mmHg, which then separated into two bands. The first of these was eluted with benzene, yielding an oil (Found: C, 78·7; H, 6·1; Cl, 10·8%). The other band was eluted with ethanol yielding an amorphous yellow paste which by treatment with light petroleum (b.p. 40—60°)–acetone (1 : 1) furnished a substance, m.p. 132° (long needles from the same solvent mixture) (Found: C, 80·0; H, 5·3; Cl, 9·9. Calc. for $C_{24}H_{19}ClO$: C, 80·3; H, 5·3; Cl, 9·9%), $\nu_{max.}$ 3540 (OH) and 1631w cm^{-1} (CO).

(b) *At* 0° (*expt.* 22). Products were 4′-chloro-3-methyl-deoxybenzoin (Found: C, 73·7; H, 5·3; Cl, 14·6%), and an oil (1·6 g), b.p. 220—230° at 0·09 mmHg, with a single sharp i.r. absorption at 3500 cm^{-1} (OH) and several at 1670—1770 (CO).

4-Methylphenylacetyl chloride. (a) *At* 19° (*expt.* 23). The reaction gave (i) a mixture of which three quarters was 4′-chloro-4-methyldeoxybenzoin, b.p. 125—135° at 0·07 mmHg, m.p. 101° (unchanged by repeated recrystallisations from ethanol) (Found: C, 75·4; H, 5·5; Cl, 12·6%), ^{1}H n.m.r. spectrum nearly identical with that of the pure compound (the principal differences were small additional signals in the aromatic region); (ii) a substance (1·5 g), b.p. 205—210° at 0·1 mmHg from which a slight fluorescence was removed with alumina, $\nu_{max.}$ 1675s cm^{-1} (aryl CO) (Found: C, 79·3; H, 6·2; Cl, 10·4%; *M*, 331).

According to Szegö and Ostinelli,[18] when the reaction mixture is heated at 130° for 2 h, the m.p. of the resulting 4′-chloro-4-methyldeoxybenzoin is 125°. We have re-

[15] Amer. Petroleum Inst., Research Project 44; Infrared Spectra Data, No. 169.
[16] L. Szegö and P. Ostinelli, *Atti. III Congresso. Naz. Chim. Pura Applicata*, 1930, 395 (*Chem. Abs.*, 1931, **25**, 1524).
[17] S. S. Jenkins and E. M. Richardson, *J. Amer. Chem. Soc.*, 1933, **55**, 1618.
[18] L. Szegö and P. Ostinelli, *Gazzetta*, 1930, **60**, 673.

peated their experiment but were unable to isolate a crystalline product, nor have we succeeded in obtaining the compound with this m.p. under any other conditions. The synthesis at room temperature has been repeated using equimolecular quantities of the acid chloride and the catalyst; the product was not distilled; instead it was washed with light petroleum and then recrystallised with a minimum of heat treatment. The m.p. was again 101° but improved analytical figures were obtained (Found: C, 74·0; H, 5·3; Cl, 13·9%).

(b) *At* 0° (*expt.* 24). 4'-Chloro-4-methyldeoxybenzoin, free from by-products, separated from ethanol as thin, transparent plates, m.p. 103—104° (lit.,[19] 103·5°) (Found: C, 73·8; H, 5·5; Cl, 14·5. Calc. for $C_{15}H_{13}ClO$: C, 73·6; H, 5·3; Cl, 14·5%). About one third of the total product was a yellow viscous oil (3 g), b.p. 210—215° at 0·08 mmHg (Found: C, 78·4; H, 5·3; Cl, 10·1%).

4-*Ethylphenylacetyl chloride.* (a) *At* 18° (*expt.* 25). This yielded (i) *p*-chloroethylbenzene (*ca.* 5 ml, 12%), b.p. 78—85° at 20 mmHg (lit.,[20] 84·2—84·6° at 30 mmHg); (ii) 4'-chlorodeoxybenzoin (23%); (iii) a substance (1·5 g, 15%), b.p. 210—222° at 0·08 mmHg (Found: C, 79·0; H, 6·2; Cl, 10·2%; *M*, 341).

(b) *At* 0° (*expt.* 26). This gave (i) 4'-*chloro*-4-*ethyldeoxybenzoin*, b.p. 140—145° at 0·03 mmHg, m.p. 104—105° (from ethanol) (Found: C, 74·5; H, 5·8; Cl, 13·5. $C_{15}H_{16}ClO$ requires C, 74·3; H, 5·8; Cl, 13·7%); (ii) a substance (2 g, 26%), b.p. 225° at 0·03 mmHg (Found: C, 79·5; H, 6·8; Cl, 9·1%).

4-*Isopropylphenylacetyl chloride.* (a) *At* 21° (*expt.* 27). The products were (i) *p*-chloroisopropylbenzene (12%), b.p. 85° at 20 mmHg (lit.,[21] 81° at 15 mmHg), τ 8·77 (d, *gem*-Me₂), 7·95 (sept, Me_2CH) (*J* 6·9 Hz), and 2·02 (m, 4 ArH); (ii) 4'-chlorodeoxybenzoin; (iii) a substance (2 g, 20%), b.p. 195—205° at 0·09 mmHg (Found: C, 79·0; H, 6·3; Cl, 10·0%; *M*, 363).

(b) *At* 0° (*expt.* 28). Products were (i) 4'-*chloro*-4-*isopropyldeoxybenzoin*, b.p. 150—155° at 0·03 mmHg, m.p. 103° (from ethanol) (Found: C, 75·2; H, 6·2; Cl, 13·1. $C_{17}H_{17}ClO$ requires C, 74·8; H, 6·2; Cl, 13·0%); (ii) a ketone (1·5 g, 7%), b.p. 215° at 0·1 mmHg (Found: C, 79·6; H, 7·4; Cl, 9·1%).

4-*t*-*Butylphenylacetyl chloride.* (a) *At* 18·5° (*expt.* 29). In addition to carbon monoxide and a small quantity of

isobutane, (i) *p*-t-butylchlorobenzene (*ca.* 30%) and (ii) 4'-chlorodeoxybenzoin were isolated.

(b) *At* 0° (*expt.* 30). Isobutane was not detected; the principal products were (i) *p*-t-butylchlorobenzene (2·6 g, 32%), b.p. 102° at 35 mmHg (lit.,[22] 112° at 30 mmHg); τ 8·70 (s, 3Me) and 2·7 (m, 4 ArH); (ii) 4'-chlorodeoxybenzoin.

Expt. 31: 2,4,6-*trimethylphenylacetyl chloride at* 21°. Mesitylene and a mixture of chlorohydrocarbons (3 g), b.p. 190—195° at 20 mmHg were isolated. The slight carbonyl activity ($v_{max.}$ 1690 cm⁻¹) was not reflected by analysis (Found: C, 67·4; H, 4·9; Cl, 27·1%). The small proportion of methyl protons (¹H n.m.r.) suggested that 80—85% of the constituents were dichlorodiphenylmethanes; also, the absence of a methylene peak at τ 5·7 showed that a trimethyldeoxybenzoin was not formed.

Expt. 32: 2,4,6-*tri-isopropylphenylacetyl chloride at* 22°. Non-gaseous products were *p*-chloroisopropylbenzene (3·9 g, 41%) and a mixture of unidentified substances (2 g).

Friedel–Crafts Reactions of Phenylacetyl Chlorides in Anisole (*Table* 2).—¹H N.m.r. spectroscopy was not available at the time when the following 4'-methoxy-derivatives were prepared and could not be utilised for confirming the structures of the 4-ethyl and 2,4,6-isopropyl compounds owing to deterioration of the specimens.

Expt. 33: *at* 14°. 4-*Ethyl*-4'-*methoxydeoxybenzoin* separated from ethanol as plates, m.p. 60° (Found: C, 80·2; H, 7·0. $C_{17}H_{20}O_2$ requires C, 80·3; H, 7·1%).

Expt. 34: *at* 16°. 4-*Isopropyl*-4'-*methoxybenzoin* separated from light petroleum (b.p. 60—80°) as needles, m.p. 67° (Found: C, 80·7; H, 7·5. $C_{18}H_{20}O_2$ requires C, 80·6; H, 7·8%).

Expt. 35: *at* 19°. 4'-*Methoxy*-4-*t*-*butyldeoxybenzoin* crystallised from light petroleum (b.p. 40—60°) as long thin plates, m.p. 73° (Found: C, 80·7; H, 7·6. $C_{18}H_{20}O_2$ requires C, 80·6; H, 7·8%).

Expt. 36: *at* 16·5°. Initial crystallisation was slow. 2,4,6-*Tri-isopropyl*-4'-*methoxydeoxybenzoin* was deposited from ethanol as needles, m.p. 103° (Found: C, 81·8; H, 9·0. $C_{24}H_{32}O_2$ requires C, 81·8; H, 9·1%).

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