418. *The Reaction between Aromatic Compounds and Derivatives of Tertiary Acids. Part V. The Stability of the Carbonyl Group in Certain Acid Halides and Anhydrides.*

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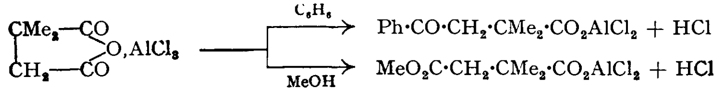
The factors influencing the acylation or alkylation of aromatic compounds by derivatives of acids in the Friedel–Crafts synthesis are discussed. It is suggested that the stability of the acyl cation $CR_3{\cdot}\overset{\oplus}{C}O$ determines the relative rates of the two processes. Loss of carbon monoxide results in the formation of an electrophilic carbonium ion, $R_3C^{\oplus}$, which can be substituted in the nucleus, yield an olefin, or undergo rearrangement. The effect of substituents on the relative ease of elimination of carbon monoxide is also examined and it is shown that the decomposition may be used for the determination of the course of the reaction. Thus condensation of diarylacetyl chlorides with benzene is attended by the simultaneous liberation of this gas; this was not detected by previous workers in this field and in consequence an explanation advanced by McKenzie, Roger, and McKay (*J.*, 1932, 2597) of the formation of diphenyl- and triphenyl-methane from phenyl-*p*-tolylacetyl chloride is untenable. These diarylacetic acid derivatives provide the first instance of an unstable *secondary* acyl ion, $Ar_2CH{\cdot}\overset{\oplus}{C}O$.

THE experiments described in the foregoing papers enable the discussion of the hypotheses outlined by one of us and Saboor (*J.*, 1943, 425; see also Saboor, *J.*, 1945, 922) to be elaborated.

We now wish to restate the portion dealing with the Friedel–Crafts reactions of *tertiary* acid derivatives so as to include the new results, making the incidental modifications, foreshadowed in Part I, necessitated by the replacement of the acid anhydride by the chloride. Rothstein and Saboor made no attempt to distinguish between the intermediate stages that must intervene before the final products are formed, and it is essential to what follows in the latter part of this paper to extend the comments we made in Part III on this question.

The formation of a complex which may be written $\mathrm{R{\cdot}\overset{\oplus}{C}O}$, $[\mathrm{AlCl_4}]^{\ominus}$ has already been mentioned as constituting the initial reaction in the synthesis of ketones from acid chlorides, and Saboor (*loc. cit.*) isolated a product of this kind from *as*-dimethylsuccinic anhydride which decomposed in the expected manner when the appropriate reagents were added:



Notwithstanding the differences between the reactions of acid halides and anhydrides it seems reasonable to assume that the reactions are equivalent in the first stage for both classes of compounds. On the other hand, because of the dependence of the velocity constant on the square of the catalyst concentration we cannot be sure that the intermediate involved in alkylation is precisely the same as in acylation. They *may* be identical but, if they are not, then the two must be in equilibrium with one another since variation in the aromatic component alters the ratio of hydrocarbon to ketone (Part II). Olivier (*Rec. Trav. chim.*, 1914, **33**, 91) did in fact suggest that the initial complex reacted only slowly, but that a second and more reactive complex was formed when the concentration of the catalyst was increased. Modifying his structures somewhat to suit our present symbolism, these were:

$$\mathrm{O{=}CRCl + AlCl_3 \rightleftharpoons O{=}\overset{\oplus}{C}R{-}[\overset{\ominus}{Al}Cl_4] \rightleftharpoons \overset{\ominus}{Al}Cl_3O{-}\overset{\oplus\oplus}{C}R{-}[\overset{\ominus}{Al}Cl_4]}$$

but it must be emphasized that this explanation requires the use of an excess of aluminium chloride and is not altogether applicable to our own experiments where reaction occurs rapidly in the presence of quite low concentrations thereof. Although the first complex might be expected to eliminate carbon monoxide, it is difficult to accept this for the second.

It is generally agreed that the formation of a ketone is the consequence of the electrophilic attack by the positive ion, $\mathrm{R{\cdot}\overset{\oplus}{C}O}$ on the aromatic molecule, no different from, say, bromination or nitration:

$$\mathrm{R{\cdot}\overset{\oplus}{C}O + H{\cdot}Ph \longrightarrow R{\cdot}CO{\cdot}Ph + \overset{\oplus}{H}}$$

the function of the catalyst being to enhance the polarisation of the acid derivative. This mechanism is, however, inadequate in certain respects for Mentzner and Xuong (*Bull. Soc. chim.*, 1947, [iv], **14**, 885) have shown that diarylation can take place using aryl ethers, the suggested formulation being:

$$\mathrm{CHR_2{\cdot}CO{\cdot}Cl + ArH \longrightarrow CHR_2{\cdot}CArCl{\cdot}OH \longrightarrow CR_2{:}CAr{\cdot}OH \xrightarrow{ArH} CR_2Ar_2 + H_2O}$$
$$[\mathrm{R = Alk{\cdot}O{\cdot}C_6H_4{-}}]$$

Rothstein and Saboor (*loc. cit.*) suggested a course of reaction ("B") which in effect is somewhat similar, namely a transition complex, the structures of which when applied to acid halides could be written:

$$\mathrm{H{-}C{-}\overset{\oplus}{C}{=}O\ (AlCl_4)^{\ominus} \qquad \overset{\oplus}{H}\ C{=}C{=}O\ (AlCl_4)^{\ominus}\ etc.}$$

Mentzner and Xuong showed that this reaction only occurred during the original condensation; no diaryl compound resulted from heating the *ketone*, $\mathrm{CHR_2{\cdot}CO{\cdot}Ar}$ with an ether and aluminium chloride. They ignored the function of the latter, and at present there is very little experimental work to support the above mechanism.

Turning now to alkylation, at least two stages can be distinguished. The first involves the elimination of carbon monoxide and, whether this is a composite reaction or not, it leads to the formation of a carbonium ion:

$$\mathrm{R{\cdot}\overset{\oplus}{C}O[AlCl_4]^{\ominus} \longrightarrow \overset{\oplus}{R} + [AlCl_4]^{\ominus} + CO}$$

It is evident that this can take place in the complete absence of an aromatic compound or, alternatively, when the formation of ketone is the slower reaction. With very few exceptions, reference to which is made towards the end of this paper, these decompositions are exhibited exclusively by derivatives of *tertiary* acids; moreover, they occur independently of any subsequent transformation of the carbonium ion. This emerges from the kinetics of the reaction (Part III) and it may be recalled that, when ketone synthesis is absent or virtually so, the concentration of the aromatic component is without effect on the rate-determining stage of the reaction which in consequence must depend solely on the nature of the group R.

The reaction which succeeds the formation of the carbonium complex may follow alternative paths. When a suitable aromatic compound is present, a reaction analogous to ketone formation results, *i.e.*, there is an electrophilic attack by a cation, in this case the carbonium ion : $\overset{\oplus}{R} + H\cdot Ph \longrightarrow R\cdot Ph + \overset{\oplus}{H}$. Unless the nucleus is deactivated, as, *e.g.*, in nitrobenzene, this is the usual course and, like the ketonic reaction, is subject to the usual orientation rules for electrophilic substitution though in actual examples the effect of the aluminium chloride in modifying the influence of orienting groups may have to be taken into consideration. It is significant that, since alkylation is dependent on the primary formation of the carbonium ion, further activation of the nucleus, beyond that required for any reaction to take place at all, will not influence the proportion of hydrocarbon derivative obtained. On the contrary, it may reduce it by encouraging ketone production. This by contrast is a bimolecular reaction involving the aromatic reagent, and the presence of electron-releasing groups on the latter will facilitate it. There is of course the incidental effect, to which attention has already been directed (Part IV), of the reduction of the activity of the aluminium chloride arising from its combination with the product. Thus the velocities of the two reactions are altered in favour of ketone formation. A modification of this last statement must be applied to the case of alkylation by acid anhydrides because this entails salt formation which again renders the catalyst inactive :

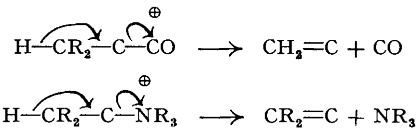
$$(R\cdot CO)_2\overset{\oplus}{O}\colon[AlCl_3]^{\ominus} \longrightarrow R\cdot\overset{\oplus}{C}O + AlCl_2\cdot O\cdot COR$$

Before leaving the subject of orientation, it is relevant to notice the influence of alkyl groups as set down in Table II of Part II. The high yields of ketone obtained from toluene and ethylbenzene are reduced to 26% for *tert.*-butylbenzene, when the hydrocarbons themselves are the solvents, and to zero in carbon disulphide solution (Table III, *loc. cit.*). This would appear to be the effect of hyperconjugation involving the methyl and ethyl groups, first postulated by Baker and Nathan (*J.*, 1935, 1844), which reverses the normal inductive effect ($Bu^t > Et > Me$). It agrees with our opinion of the validity of the usual orientation rules :

When an aromatic hydrocarbon is not present, a rearrangement of the carbonium ion may occur, *e.g.*, the formation of an olefin :

$$H—CR_2—\overset{\oplus}{C}\,[AlCl_4]^{\ominus} \longrightarrow CR_2{=}C + H^{\oplus} + Cl^{\ominus} + AlCl_3$$

This of course is the well known mechanism for olefinic decomposition, and written in a slightly different form is another example of this, corresponding to the reaction of quaternary ammonium salts (cf. Hughes and Ingold, *Trans. Faraday Soc.*, 1941, **37**, 657) :



$$H—CR_2—C—\overset{\oplus}{C}O \longrightarrow CH_2{=}C + CO$$

$$H—CR_2—C—\overset{\oplus}{N}R_3 \longrightarrow CR_2{=}C + NR_3$$

It is not a necessary condition for this reaction that the carbonium ion should be *tertiary* (although it may be so for its *formation* from an acid derivative). It is manifest that the first of these last three reactions can also represent the formation of an olefin from an alkyl halide, but direct evidence is not yet available that both reactions are identical at this point.

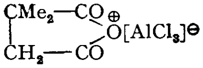
It is clear that the prerequisite for the elimination of carbon monoxide in the compounds under discussion is the electron-releasing power of the group to which it is attached, that is the stability of the ion $CR_3\cdot\overset{\oplus}{CO}$. It so happens that when R is alkyl, the decomposition of the ion is comparatively rapid, but if it is halogen the $-I$ effect of the latter reduces the speed considerably, so that *tert.*-butylbenzene is obtained from pivaloyl chloride but trichloroacetyl chloride affords trichloroacetophenone (see below). We find it necessary therefore to modify in certain respects the conclusion reached by Rothstein and Saboor (*loc. cit.*) that *tertiary* acid derivatives never yield ketones and the converse that *primary* and *secondary* ones always do so. It remains generally true for aliphatic acids when the substituent groups are alkyl and for condensations with benzene. The formation of methoxyphenyl *tert.*-butylphenyl ketone demonstrates that it is possible to compensate for the lack of stability of the carbonyl compound by electron accession to the reactive point of the aromatic molecule. On the other hand, an unreactive nucleus does not *as a rule* lead to the expulsion of carbon monoxide in the case of *primary* and *secondary* acids but, as is shown later in this paper, the aryl-substituted acetic acids form an exception.

Past work in the Friedel–Crafts reaction provides a number of examples where " anomalous " results have been recorded. The case of oxalyl chloride to which reference was made in Part II is one of a number of instances where a carbonium ion unites with a chlorine atom to yield a chloro-acid chloride (carbonyl chloride) which in the absence of an aromatic compound can be isolated. Dialkylmalonyl chlorides, on the contrary, do not, apparently, form a carbonium ion in spite of their reactions resembling superficially those of oxalyl chloride. The three products obtained are 2 : 2-dialkylindane-1 : 3-dione, dialkyldibenzoylmethane, and dialkylacetophenone, but the last of these products is not the result of elimination of carbon monoxide; we find, in fact, that hardly any of the gas is evolved either in benzene or in carbon disulphide, and the volume is certainly much less than would be expected from the amount of this ketone isolated. It is possible that its presence arises from the decomposition of the β-keto-acid formed by the condensation of one molecule of benzene :

$$ClCO\cdot CR_2\cdot COCl + HPh \longrightarrow Ph\cdot CO\cdot CR_2\cdot CO_2H \longrightarrow Ph\cdot CO\cdot CHR_2 + CO_2$$

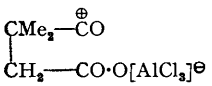
The di- and tri-chlorocarbonium ions derived from the corresponding acetyl chloride are formed only in the absence of benzene (Böeseken, *Rec. Trav. chim.*, 1910, **29**, 85); otherwise the corresponding ketones result. Hence the acyl ions are comparatively stable. Our own experiments, carried out to determine the amount of carbon monoxide liberated, have furnished only trichloroacetophenone, when anhydrous catalyst was used with trichloro- and tribromoacetyl chloride or trichloroacetic anhydride. Other workers in this field have isolated also triphenylvinyl alcohol.

For reasons that will become evident, we were led to examine the reactions of camphoric anhydride with aluminium chloride. It is pertinent to this subject to refer to reactions of dimethylsuccinic anhydride which it was noted (p. 1962) forms a particularly stable complex with the catalyst, the stability probably being due to the resonance energy contributed by structures such as (I), (II), and (III) :



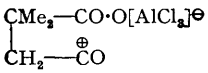
$$\begin{array}{l}\text{CMe}_2\text{—}\overset{\oplus}{\text{CO}}\\ \quad\quad\quad\quad >\text{O[AlCl}_3]^{\ominus}\\ \text{CH}_2\text{—CO}\end{array}$$

(I.)



$$\begin{array}{l}\text{CMe}_2\text{—}\overset{\oplus}{\text{CO}}\\ |\\ \text{CH}_2\text{—CO}\cdot\text{O[AlCl}_3]^{\ominus}\end{array}$$

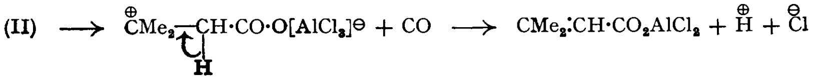
(II.)



$$\begin{array}{l}\text{CMe}_2\text{—CO}\cdot\text{O[AlCl}_3]^{\ominus}\\ |\\ \text{CH}_2\text{—}\overset{\oplus}{\text{CO}}\end{array}$$

(III.)

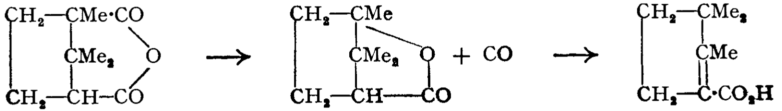
Of these, only (II) can lead to the direct elimination of carbon monoxide; (I) and (III) must revert to the acid. In fact, Desfontaines (*Compt. rend.*, 1902, **134**, 295) obtained a mixture of *as*-dimethylsuccinic and ββ-dimethylacrylic acid. The dimethylacrylic acid is obviously the result of the decomposition of (II) :



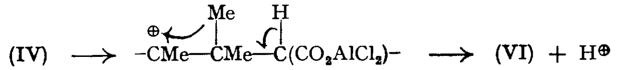
$$\text{(II)} \longrightarrow \overset{\oplus}{\text{C}}\text{Me}_2\text{—}\underset{\text{H}}{\text{CH}}\cdot\text{CO}\cdot\text{O[AlCl}_3]^{\ominus} + \text{CO} \longrightarrow \text{CMe}_2\text{:CH}\cdot\text{CO}_2\text{AlCl}_2 + \overset{\oplus}{\text{H}} + \overset{\ominus}{\text{Cl}}$$

The production of the ketone from benzene suggests that (III) is the predominating structure and that this is a faster reaction than the expulsion of carbon monoxide.

A chloroform solution of camphoric anhydride, similarly treated, affords *iso*lauronolic acid together with certain lactones derived therefrom (Lees and Perkin, *J.*, 1901, **79**, 356; Perkin and Yates, *ibid.*, p. 1373); it was suggested (*loc. cit.*) that the reaction took place through the intermediate " *ψ*-campholactone " (α-campholytolactone) (V) :


(IV.) (V.) (VI.)

the second stage (V ⟶ VI) was considered to be a pinacolic displacement. The lactone (V) was not isolated in this reaction but was later prepared by a different method and does afford *iso*lauronolic acid (VI), but only by fission of the lactone ring with hydrogen bromide, removal of the bromine with alkali, and finally by an acid isomerisation of the resulting β-campolytic acid (Perkin and Thorpe, *J.*, 1904, **85**, 143). The reaction of campholytolactone with aluminium chloride has not been recorded, but in view of the known reactions of lactones would probably afford (VI). It is clear, however, in the light of the arguments put forward in the preceding pages, that *iso*lauronolic acid is the result of a pinacolic displacement, not of campholytolactone, but of the carbonium ion (VII) derived from the camphoric anhydride :

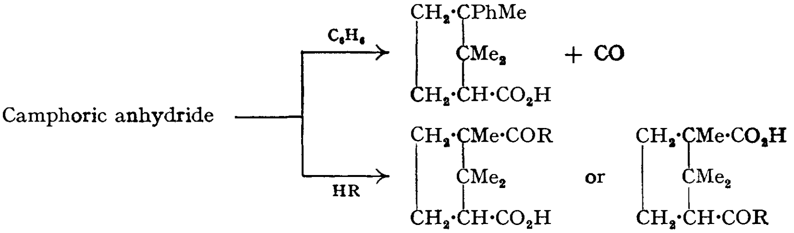


$$\text{(IV)} \longrightarrow \text{-}\overset{\oplus}{\text{C}}\text{Me—}\overset{\text{Me}}{\text{C}}\text{Me—}\overset{\text{H}}{\text{C}}(\text{CO}_2\text{AlCl}_2)\text{-} \longrightarrow \text{(VI)} + \text{H}^{\oplus}$$

(VII.)

and we regard, indeed, the rearrangement as a confirmation of our view that a kinetically free carbonium ion is actually formed.

The reaction of camphoric anhydride with benzene is rather unusual in that carbon monoxide is eliminated and 2-phenyl-1 : 1 : 2-trimethyl*cyclo*pentane-5-carboxylic acid is produced (Burcker, *Bull. Soc. chim.*, 1890, [iii], **4**, 112; Burcker and Stabil, *Compt. rend.*, 1894, **119**, 426). Subsequently Eykman (*Chem. Zentr.*, 1907, II, 2046) obtained a ketone by use of toluene or anisole, the position of the acyl group being undetermined :



(R = anisole or toluene)

Most dicarboxylic anhydrides with at least one *non-tertiary* carboxyl group, *e.g.*, *as*-dimethylsuccinic or trimethylsuccinic anhydride, yield ketones with benzene and it would thus appear that the accumulation of methylene and alkyl groups promotes decomposition to such an extent that it is faster than the usually very rapid synthesis of the ketone. Thus the stability of the carbonyl group is rather less than in the trialkylated succinic derivatives but greater than in those of tetramethylsuccinic acid which even with toluene yields only the hydrocarbon. We found it desirable to repeat some of the experiments with camphoric anhydride because the yields of neither the main products nor the carbon monoxide were available. Likewise, in order to complete the comparison with the other alkylated acids, the condensations with *tert.*-butylbenzene (in carbon disulphide) and with acetanilide were carried out. In the former case, 3-p-tert.-*butylphenyl*-1 : 1 : 2-*trimethyl*cyclo*pentane*-5-*carboxylic acid*, purified by its conversion into the *methyl* ester, was the only product. With acetanilide the condensation is evidently slower than the rearrangement, the reaction affording *iso*lauronolic acid.

It has already been remarked that it is most unusual for a primary or secondary acid halide to produce a hydrocarbon with loss of carbon monoxide, and even when condensation to a ketone cannot take place as with γ-4-methoxy-3-diphenylylbutyryl or β-*p*-nitrophenylpropionyl chloride, the original substance is recovered unchanged (Part I). The ketone was obtained from the acid chlorides of diethylacetic and aceturic acid where it was thought there might be sufficient electron-releasing groups present. It was noticed, however, that, when phenyl-

p-tolylacetyl chloride is condensed with benzene, diphenylmethane alone or with triphenylmethane and triphenylcarbinol is produced according to the purity of the thionyl chloride used for the preparation of the acid chloride (McKenzie and Widdows, *J.*, 1915, **107**, 702; McKenzie, Roger, and McKay, *J.*, 1932, 2597; Koelsch, *J. Amer. Chem. Soc.*, 1932, **54**, 2049). A possible mechanism, suggested by McKenzie, Roger, and McKay, was one involving three molecules of benzene in the first instance :

$$C_6H_4Me{\cdot}CHPh{\cdot}COCl + 3C_6H_6 \longrightarrow H_2O + HCl + C_6H_4Me{\cdot}CHPh{\cdot}CHPh_3$$
$$C_6H_4Me{\cdot}CHPh{\cdot}CPh_3 \longrightarrow C_6H_4Me{\cdot}CH_2Ph + CHPh_3$$

In the process the tolyl group was exchanged for phenyl, and the triphenylmethane oxidised to the carbinol. It was presumed that the tetraphenyltolylethane was dissociated into triphenylmethyl and phenyltolylmethyl radicals which then gave the above products.

Now in Part I we described a very similar reaction, in which diphenylethane is obtained from αα-diphenylpropionyl chloride : $CPh_2Me{\cdot}COCl \longrightarrow CHPh_2Me$, but the above mechanism could not possibly apply in our case because carbon monoxide was evolved in 86% yield. We therefore doubted whether phenyl-*p*-tolylacetyl chloride did actually undergo the transformations suggested. The crucial point was of course the liberation of carbon monoxide which has no place in the proposed scheme. Repetition of the experiment, following the procedure of the three authors, afforded a large volume of carbon monoxide representing a yield of at least 70%. The crystalline products were those previously described, except that a better yield of triphenylcarbinol separated from the reaction mixture.

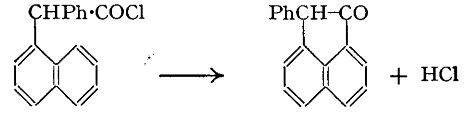
Thus this was the first case that we had encountered where a secondary acid derivative decomposed in this way and the logical deduction is that, whatever be the subsequent changes of the phenyl-*p*-tolylcarbonium ion, the initial step of the reaction is its formation :

$$C_6H_4Me{\cdot}CHPh{\cdot}COCl + AlCl_3 \longrightarrow C_6H_4Me{\cdot}CHPh{\cdot}\overset{\oplus}{C}O[AlCl_4]^{\ominus} \longrightarrow C_6H_4Me{\cdot}\overset{\oplus}{C}HPh + CO + \overset{\ominus}{Cl} + AlCl_3$$

To test the matter further, the acid chloride was next condensed with anisole. Ketone should not be formed according to the original mechanism; in fact the substitution of the more reactive aromatic compound might be expected to facilitate complete condensation. Actually, as was expected, very little carbon monoxide was collected and the main product was *methoxyphenyl α-*p*-tolylbenzyl ketone*, m. p. 107—108°.

The electron-releasing effect of the methyl group in the *p*-tolyl group is just sufficient to prevent formation of ketone (where benzene is the solvent); substitution of *p*-tolyl by phenyl is accompanied by partial retention of the carbonyl group. The Friedel–Crafts reaction with diphenylacetyl chloride is known to yield mainly benzoyldiphenylmethane (or the enol form, triphenylvinyl alcohol), triphenyl- and diphenyl-methane (compare, *inter al.* Klingemann, *Annalen*, 1893, **275**, 88; Biltz, *Ber.*, 1899, **32**, 650; Ramart-Lucas, *Ann. Chim.*, 1913, [viii], **30**, 349), but as in the case of the tolyl homologue, the elimination of carbon monoxide was not recorded. We again find that a considerable quantity of the gas is evolved.

The diaryl compounds resemble the tertiary alkylated acids in that cyclisation takes precedence over decomposition. For example, phenyl-α-naphthylacetyl chloride cyclises to 7-phenylacenaphthenone when treated in benzene solution with aluminium chloride (McKenzie and Tattersall, *J.*, 1925, **127**, 2522; Koelsch and Richter, *J. Amer. Chem. Soc.*, 1937, **59**, 2165), and neither the open-chain ketone nor a hydrocarbon is formed :



This is consistent with the conclusion arrived at in Part I that cyclisation occurs preferentially in these cases.

EXPERIMENTAL.

Dialkylmalonyl Chloride Condensations.—(i) *In benzene* (Freund and Fleischer, *Annalen*, 1910, **373**, 291; 1913, **399**, 182). The product from dimethylmalonyl chloride (13·5 g.), aluminium chloride (22 g., 2 mols.), and benzene (140 c.c.) was dibenzoyldimethylmethane (10·5 g., 52%) and a negligible volume of carbon monoxide.

(ii) *In carbon disulphide.* By use of benzene (6·5 g.), dimethylmalonyl chloride (14 g.), and aluminium chloride (23 g., 2 mols.), in carbon disulphide (120 c.c.) solution, there were produced carbon monoxide (37 c.c., 8·1%), phenyl *iso*propyl ketone, b. p. 110—112°/15 mm. (yield, 23%) [identified by its oxime (plates, m. p. 94°, from ligroin) and semicarbazone (needles, m. p. 181°, from ethyl alcohol) (cf. Lapworth and Steel, *J.*, 1911, **99**, 1885)], dibenzoyldimethylmethane (1·7 g., 8·1%), and a substance (0·5 g.) which crystallised from ligroin in plates, m. p. 99° (0·5 g.) (Found : C, 74·6; H, 5·6. Calc. for $C_{11}H_{10}O_2$: C, 75·8; H, 5·7%) and may have been 2 : 2-dimethylindanedione although repeated crystallisations failed to raise the m. p. to that recorded (103—105°; Gabriel and Neumann, *Ber.*, 1893, **26**, 954).

Similar results were obtained for diethylmalonyl chloride.

Condensations of Chloroacetyl Chlorides with Benzene.—(i) *Chloroacetyl chloride.* Phenacyl chloride (87%) and carbon monoxide (1%), but no benzyl chloride, were formed. (ii) *Dichloroacetyl chloride.* ωω-Dichloroacetophenone (79%) and carbon monoxide (3·6%) were formed. (iii) *Trichloroacetyl chloride.* ωωω-Trichloroacetophenone (56%), carbon monoxide (3·1%), and a tar of high b. p. were produced.

Condensations of Other Halogenated Compounds.—These were carried out in benzene. Trichloroacetic anhydride (Swartz, *Bull. Soc. chim.*, 1895, [iii], **13**, 992; Fichter, Fritsch, and Müller, *Helv. Chim. Acta*, 1923, **6**, 503) afforded carbon monoxide (7%) and trichloroacetophenone (57%); similar results were obtained with trichloroacetyl bromide. α-Bromo*iso*butyryl chloride and bromide gave substantially the products described in the literature, *i.e.*, α-bromo*iso*butyrophenone and 2-methyl-1-indanone.

Condensations of Camphoric Anhydride.—(i) *With benzene.* Aluminium chloride (15 g., 2·1 mols.) was added in small portions to a vigorously stirred solution of the anhydride (10 g.) in benzene (160 c.c.). The volume of carbon monoxide was 1095 c.c. (89%). 2-Phenyl-1 : 1 : 2-trimethyl*cyclo*pentane-5-carboxylic acid crystallised from aqueous alcohol as a powder, m. p. 139° (67%) (Found : C, 77·4; H, 8·6. Calc. for $C_{15}H_{20}O_2$: C, 77·6; H, 8·6%). The diphenyl condensation product (Burcher, *loc. cit.*) was not found, but there was a small quantity of hydrocarbon of undetermined structure which separated from benzene as a crystalline powder, m. p. 80—81° (Found : C, 93·1; H, 6·6%).

(ii) *With anisole.* Substituting anisole for benzene, but otherwise using the same conditions, gave 3·4% of carbon monoxide, and the chief product was 5-(or 2-)anisoyl-1 : 1 : 2-trimethyl*cyclo*pentane-2-(or 5)-carboxylic acid (8 g., 89%), m. p. 165° (from benzene) (Found : C, 70·5; H, 7·5. Calc. for $C_{17}H_{22}O_4$: C, 70·3; H, 7·6%).

(iii) *With toluene.* Conditions were as before. The toluoyl derivative separated from benzene in plates, m. p. 187° (82%). The yield of carbon moxoxide was 3%.

(iv) *With* tert.-*butylbenzene.* A stirred mixture of camphoric anhydride (7 g.), aluminium chloride (10·5 g., 2·1 mols.), and carbon disulphide (70 c.c.) was cooled to 0° and to it was added a solution of *tert.*-butylbenzene (10·5 g., 2 mols.) in carbon disulphide (10 c.c.). There was only slight reaction at this temperature, but after warming there was a vigorous evolution of carbon monoxide (639 c.c., 74·2%). Approx. one quarter of unchanged *tert.*-butylbenzene (2·7 g.) with a rather smaller amount of di-*p*-*tert.*-butylbenzene, in addition to an acid, were obtained. The silver salt of the acid, when boiled with methyl iodide, yielded *methyl* 2-p-*tert-butylphenyl*-1 : 1 : 2-*trimethyl*cyclo*pentane*-5-*carboxylate*, b. p. 110—115°/0·2 mm. (Found : C, 79·2; H, 9·7. $C_{20}H_{30}O_2$ requires C, 79·5; H, 9·9%).

(v) *With acetanilide.* Aluminium chloride was added in small portions (10 g. in all, 2 mols.) to a chloroform solution of camphoric anhydride (5 g.) and acetanilide (3·6 g.), and the mixture boiled for 1 hour and decomposed with ice. The acid portion was converted into the methyl ester, b. p. 93—95°/17 mm., which appeared to be mainly methyl *iso*lauronolate (Found : C, 70·6; H, 9·7. Calc. for $C_{10}H_{16}O_2$: C, 71·4; H, 9·6%).

Condensations of Diarylacetyl Chlorides.—(i) Phenyl-*p*-tolylacetic acid was prepared from mandelic acid and toluene by the action of anhydrous stannic chloride (McKenzie and Widdows, *loc. cit.*). The recrystallised substance had m. p. 115° (Found : C, 79·8; H, 6·6. Calc. for $C_{15}H_{14}O_2$: C, 79·6; H, 6·2%). A solution of the acid chloride was prepared by warming the acid (22·6 g.) with B.D.H. " redistilled " thionyl chloride (18 c.c.), removing the excess in a vacuum, and dissolving the residue in carbon disulphide (25 c.c.). This was then added to a stirred mixture of aluminium chloride (20 g.), benzene (114 c.c.), and carbon disulphide (31 c.c.) (McKenzie, Roger, and McKay, *loc. cit.*), the evolved gases being collected. The volume of carbon monoxide was approx. 1890 c.c. (70%). The yield of triphenylcarbinol was nearly 33%, more than double that obtained by the above authors. The carbinol was recrystallised from benzene and petrol (b. p. 60—80°) and was identified by comparison (m. p. 159—160°, and mixed m. p.) with an authentic specimen.

(ii) *Diphenylacetyl chloride and benzene.* The acid chloride (prepared from 10·6 g. of acid and excess of thionyl chloride) was dissolved in carbon disulphide (12 c.c.) and added to the stirred mixture of the catalyst (10 g.), carbon disulphide (15 c.c.), and benzene (60 c.c.). The volume of carbon monoxide was 760 c.c. (68%). The oily product on distillation furnished diphenylbenzophenone, b. p. 160°/0·2 mm. which solidified and was recrystallised from light petroleum (b. p. 80—100°). It had m. p. 136° (Found : C, 88·0; H, 5·8. Calc. for $C_{20}H_{16}O$: C, 88·2; H, 5·9%). Yield, 4 g.

(iii) *Phenyl*-p-*tolylacetyl chloride and anisole.* The acid chloride (from 11·3 g. of acid) in carbon disulphide (12 c.c.) was added to aluminium chloride (10 g.), carbon disulphide (15·5 g.), and anisole (50 g.). Scarcely any carbon monoxide was liberated and from the solution was isolated *methoxyphenyl* α-p-*tolylbenzyl ketone*, separating from light petroleum (b. p. 80—100°) in colourless needles, m. p. 107—108° (14 g., 88·6%) (Found : C, 83·7; H, 6·5. $C_{22}H_{20}O_2$ requires C, 83·5; H, 6·3%). Fission with alcoholic potash afforded anisic acid, recrystallised from very dilute alcohol to m. p. 184° (Found : C, 63·3; H, 5·4. Calc. for $C_8H_8O_3$: C, 63·2; H, 5·3%).

Condensation of Diethylacetyl Chloride with Benzene.—The acid chloride (5·7 g.), prepared in 72% yield from the acid and thionyl chloride, was mixed with aluminium chloride (11·4 g.) and benzene (60 c.c.). The yields of carbon monoxide and of α-ethylbutyrophenone were 7% and 81%, respectively. The ketone furnished the 2 : 4-*dinitrophenylhydrazone* crystallising from alcohol in needles, m. p. 115—116° (Found : C, 60·2; H, 5·5; N, 15·4. $C_{18}H_{20}O_4N_4$ requires C, 60·5; H, 5·6; N, 15·7%). The oxime (Haller and Bauer, *Compt. rend.*, 1910, **150**, 1477) was unsuitable for the characterisation of the ketone owing to its indefinite m. p.

Condensation of Aceturyl Chloride with Benzene.—This was carried out with aceturyl chloride (9 g.) (Max, *Annalen*, 1909, **369**, 286), aluminium chloride (12 g.), and benzene (60 c.c.), yielding carbon monoxide (8%) and ω-acetamidoacetophenone, crystallising from benzene in feathery plates, m. p.

86—87° (51·5%) (Found : C, 67·5; H, 5·8; N, 7·5. Calc. for $C_{10}H_{11}O_2N$: C, 67·8; H, 6·2; N, 7·9%). Aceturyl chloride can be obtained in 50% yield by rapidly stirring a mixture of acetylglycine, phosphorus pentachloride, and acetyl chloride cooled to 0° with the usual precautions, and the method affords a convenient synthesis of ω-acetamidoacetophenone. No acetobenzylamide is formed.

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