415. *The Reaction between Aromatic Compounds and Derivatives of Tertiary Acids. Part II. The Acylation of Benzene Derivatives by Tertiary Acid Chlorides.*

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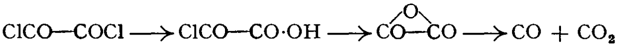
Derivatives of aliphatic tertiary acids usually alkylate benzene in the presence of aluminium chloride, but by the choice of a suitable aromatic compound it is possible to synthesise the ketone. p-*Methoxyphenyl* tert.-*butyl ketone* is obtained, for example, when pivaloyl chloride is condensed with anisole, and analogous products result from other tertiary acid halides and anhydrides. When the alkylbenzenes are used, mixtures of ketone and hydrocarbon are formed, the ratio of the two depending partly on the proportion of catalyst present and partly on the nature of the alkyl groups. The yield of ketone is greatest with toluene and ethylbenzene, and least with *tert.*-butylbenzene. It is believed that hyperconjugation involving the methyl and ethyl groups provides a reasonable explanation of these last results (Part V).

THE cyclisation, to cyclic ketones, of certain aryl-substituted tertiary acid chlorides shows that in favourable conditions the preferential reaction for this class of acid derivatives is acylation rather than alkylation. The main factor facilitating the first of these reactions is the contiguity of the end of the chain to the aromatic nucleus, one of minor importance being its activation (Part I, preceding paper). It is evident that the former condition is not available for straight-chain acylation, but by the employment of a suitably substituted aromatic compound it should be possible to overcome the difficulty. This has been realised, and experiments are now described leading to the successful preparation of ketones where in normal circumstances alkylation would be the expected result.

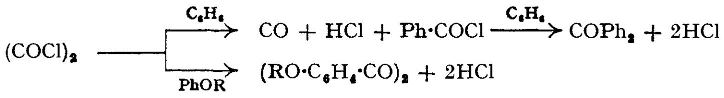
Pivaloyl chloride which has been used for the greater part of the work reacts similarly to the anhydride. There is, however, the difference, that whereas the latter requires the presence of more than one molecule of the catalyst, in the case of the acid halides only " catalytic " quantities are necessary. Neither derivative reacts in the absence of a catalyst; and the anhydride is unchanged when only 0·1 mol. aluminium chloride is used. Pivaloyl chloride on the contrary condenses with benzene in the presence of this molecular proportion of catalyst, and at least 66% of *tert.*-butylbenzene is formed though the speed of the reaction is noticeably less. This aspect is the main topic of Part III, but it should be remarked that in the case of ketone formation, as is generally known, the extent is dependent on the proportion of aluminium chloride initially used, quite irrespective of whether or not simultaneous alkylation takes place.

There are a few examples known where the type of product formed in a Friedel–Crafts reaction differs with the nature of the aromatic component, but the generality of, and the reason for, this phenomenon do not appear to have been recognised. It is not, in this paper, proposed to discuss the matter in detail, but it is appropriate to outline the relevant reactions of oxalyl chloride because of their importance to the present problem. A carbon disulphide solution of oxalyl chloride and benzene affords benzophenone when aluminium chloride is added. On the other hand, the addition of the halide to a cooled mixture of the other components yields benzoyl chloride and very little benzophenone (Staudinger, *Ber.*, 1908, **41**, 3558). By the use of anisole (*idem, ibid.*, 1912, **45**, 1594) and other phenolic ethers (Mitter and Mukherjee, *J. Indian Chem. Soc.*, 1939, **16**, 393; Staudinger, Schlenker, and Goldstein, *Helv. Chim. Acta*, 1921, **4**, 334) the substituted benzils are obtained. These authors do not mention the evolution of carbon monoxide in the course of their reactions, though Staudinger in his first paper did notice that a solution of oxalyl chloride in carbon disulphide eliminates the gas when treated with aluminium chloride. No mechanism was suggested beyond citing the decomposition of the acid chloride by water which he considered took place with the intermediate formation of oxalic anhydride :



$$\mathrm{ClCO{-}COCl} \longrightarrow \mathrm{ClCO{-}CO{\cdot}OH} \longrightarrow \overset{O}{\mathrm{CO{-}CO}} \longrightarrow \mathrm{CO} + \mathrm{CO_2}$$

This does not appear to be a very satisfactory formulation and for reasons given in Part V it is suggested that the mechanism for the production of the acid chloride and ketone, and the benzil, respectively, involves two different routes :



$$(\mathrm{COCl})_2 \begin{cases} \xrightarrow{C_6H_6} \mathrm{CO + HCl + Ph{\cdot}COCl} \xrightarrow{C_6H_6} \mathrm{COPh_2 + 2HCl} \\ \xrightarrow[PhOR]{} \mathrm{(RO{\cdot}C_6H_4{\cdot}CO)_2 + 2HCl} \end{cases}$$

It is now found that all the *tertiary* acid chlorides so far examined yield the corresponding ketone when condensed with anisole; it is necessary in these cases to use more than one molecule of aluminium chloride :

$$CR_3\cdot COCl + PhOMe \longrightarrow CR_3\cdot CO\cdot C_6H_4\cdot OMe + HCl$$

Table I summarizes the results of the reactions of anisole with various acid halides. In each case the ketone was the only product.

TABLE I.

Condensation of Acid Halides with Anisole.

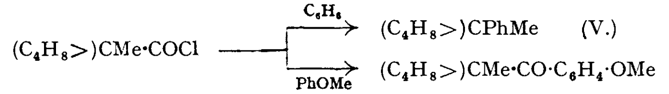
Acid.	Solvent.	Product.	Yield, %.
Pivalic	Ligroin	p-*Methoxyphenyl* tert.-*butyl ketone*	79·6
Pivalic	CS_2	,, ,, ,,	45
Tetramethylsuccinic (anhydride)	CS_2	*β*-p-*Anisoyl-ααβ-trimethylbutyric acid*	**54**
α-Phenyl*iso*butyric	Ligroin	*p*-Methoxyphenyl 2-phenyl-2-propyl ketone	71
αα-Diphenylpropionic	CS_2	p-*Methoxyphenyl* 1 : 1-*diphenylethyl ketone*	**64**
1-Methyl*cyclo*pentanecarboxylic (IV)	Ligroin	p-*Methoxyphenyl* 1-*methyl*cyclo*pentyl ketone* (VI)	60·5

It may be remembered that α-phenyl*iso*butyryl and αα-diphenylpropionyl chloride yield hydrocarbons with benzene (Part I), whilst tetramethylsuccinic anhydride affords β-phenyl-ααβ-trimethylbutyric acid (Rothstein and Saboor, *J.*, 1943, 425).

We have re-examined the reactions of *cyclo*pentane derivatives because Saboor (*J.*, 1945, 922) claimed to have isolated both methyl 1-phenyl*cyclo*pentylacetate (II) (yield, 95%) and methyl 1-benzoyl*cyclo*pentylacetate (III) (yield not stated) from the acid chloride of methyl 1-carboxy*cyclo*pentylacetate (I) :

$$\underset{\text{(I.)}}{ClOC\cdot C(<C_4H_8)\cdot CH_2\cdot CO_2Me} \longrightarrow \underset{\text{(II.)}}{Ph\cdot C(<C_4H_8)\cdot CH_2\cdot CO_2Me} + \underset{\text{(III.)}}{Ph\cdot CO\cdot C(<C_4H_8)\cdot CH_2\cdot CO_2Me}$$

The formation of the benzoyl compound (III) is unusual when a *tertiary* acid halide reacts with benzene. The only instances which have been encountered by the present authors are the formation of trichloroacetophenone from trichloroacetyl chloride, and the small quantity of benzil reported to be isolated when oxalyl bromide is treated in benzene with aluminium bromide (Staudinger, *Ber.*, 1912, **45**, 1599). Repeating Saboor's condensation we have been unable to detect any ketone, though the yield of hydrocarbon was rather less than his (79%). On the other hand, the very high yield of carbon monoxide (89%) did not indicate appreciable ketone formation. It is possible that Saboor's ester contained a small quantity of the isomeric 1-carbomethoxy*cyclo*pentylacetyl chloride, $MeO_2C\cdot C(<C_4H_8)\cdot CH_2\cdot COCl$. Nevertheless, envisaging the possibility that the *cyclo*pentyl group might facilitate ketone formation, 1-methyl*cyclo*pentane-1-carboxyl chloride (IV) was condensed with benzene; here again no ketone was formed, the only product being 1-*phenyl*-1-*methyl*cyclo*pentane* (V) :



$$\text{(IV.)}\quad (C_4H_8>)CMe\cdot COCl \begin{cases} \xrightarrow{C_6H_6} (C_4H_8>)CPhMe & \text{(V.)} \\ \xrightarrow[PhOMe]{} (C_4H_8>)CMe\cdot CO\cdot C_6H_4\cdot OMe & \text{(VI.)} \end{cases}$$

With anisole the expected ketone (VI) was produced.

Since in the cyclisations mentioned in Part I, the activating groups is the side-chain itself, the next consideration was the possibility that the homologues of benzene might be sufficiently reactive for ketone formation to occur. It had previously been found (Rothstein and Saboor, *J.*, 1943, 425) that tetramethylsuccinic anhydride affords β-*p*-tolyl-ααβ-trimethylbutyric acid and no ketone. In the present work we describe the first examples where appreciable quantities of both ketone and hydrocarbon have been produced simultaneously: pivaloyl chloride is converted into a mixture of approximately equal parts of *p*-*tert.*-butyltoluene and of p-*tolyl* tert.-*butyl ketone*, together with a small quantity of impure material which appeared to be mainly the *ortho*-isomeride. Ethylbenzene and *tert.*-butylbenzene behaved similarly, but neither acetanilide nor diphenyl gave rise to ketonic products though the electromeric effect of the former is similar to that of anisole. The *tert.*-butyldiphenyl obtained from diphenyl was presumably the *para*-isomeride, but we were unable to isolate a crystalline substance, m. p. 53°, which Grosse, Mavity, and Ipatieff prepared in 5% yield from *p*-bromo-*tert.*-butylbenzene and phenyl-lithium (*J. Org. Chem.*, 1939, **3**, 448).

Table II and III show the proportions of ketone and hydrocarbon obtained with excess of hydrocarbon (or anisole) or of carbon disulphide, respectively, as solvent. In every case more than one molecule of aluminium chloride was used. When less than one molecule of the catalyst was used, the proportion of the ketone formed was considerably less; thus toluene afforded only 6·8% ketone when 0·1 mol. of catalyst was present.

TABLE II.

Condensations of Pivaloyl Chloride with Various Aromatic Derivatives in Excess.

Hydrocarbon.	Yield of products, %.	Proportion isolated of ketone, %.	Proportion isolated of hydrocarbon, %.	Yield of CO, %.
Benzene	67	0	100	87
Toluene	87 *	58·6	41·4	53
Ethylbenzene	78·5	62·9	37·1	50
tert.-Butylbenzene	—	26·3 †	—	65
Anisole	79·6	100	0	7

* Inclusive of 17% of *o*-tolyl *tert.*-butyl ketone.

† Percentage yield. The proportion of ketone could not be calculated (see Experimental section).

TABLE III.

Condensations of Pivaloyl Chloride with Various Hydrocarbons and Anisole in Carbon Disulphide.

Aromatic derivative.	Yield of products, %.	Proportion isolated of: ketones, %.	Proportion isolated of: hydrocarbon, %.	Yield of CO, %.
Ethylbenzene	66	42·4	57·6	68
tert.-Butylbenzene	71	0	100	75
Anisole	45	100	0	0

In view of the liberation of carbon monoxide which occurs when pivalic acid or its chloride is heated with sulphuric acid at 135° (Bistrzycki, *Ber.*, 1907, **40**, 4370) or 100°, respectively (Boeseken, *Rec. Trav. chim.*, 1910, **29**, 85), a sulphuric-acid-catalysed reaction between pivalic acid and benzene was attempted. The greater part of the acid was recovered unchanged; the only other product was a very small quantity of an acid, m. p. 145°, which could not be identified. Campaigne and Suter (*J. Amer. Chem. Soc.*, 1946, **68**, 880) similarly found that in toluene the only reaction was sulphonation of the solvent.

EXPERIMENTAL.

Condensations of Pivalic Acid Derivatives.—(a) *With benzene.* (i) A stirred mixture of pivalic acid (20 g.), 75% sulphuric acid (30 c.c.), and benzene (31 g., 2 mols.) was boiled for 40 minutes. The yield of carbon monoxide was 41·5 c.c. (N.T.P.), corresponding to 0·95% of the acid used. About 93% of the acid was recovered, though it had the odour of *iso*butene polymers. After removal of the benzene, the original reaction mixture gradually deposited a colourless acid (0·4 g.), m. p. 145° (after crystallisation from benzene) (Found: C, 47·9; H, 7·9%; *M*, 396).

(ii) A stirred suspension of aluminium chloride (11·6 g., 1 mol.) in benzene (60 c.c.) was cooled in an ice-bath, and a solution of pivaloyl chloride (10 g.) in benzene added. The yield of carbon monoxide (1697 c.c.) was 86·9%. The main product, *tert.*-butylbenzene (67·2%), b. p. 63°/10 mm., was identified by conversion into the 2 : 4-dinitro-derivative (mixed m. p.) (Malherbe, *Ber.*, 1919, **52**, 321). 0·5 G. of a hydrocarbon, b. p. 105—110°/10 mm., possibly impure tri-*tert.*-butylbenzene was also isolated (Found: C, 87·2; H, 11·1. Calc. for $C_{18}H_{30}$: C, 87·8; H, 12·2%).

(iii) By use of 0·1 mol. of aluminium chloride, 66% of *tert.*-butylbenzene was obtained; the reaction was noticeably slower.

(iv) A mixture of pivalic anhydride (12 g.), benzene (50 c.c.), and aluminium chloride (0·86 g., 0·1 mol.) was warmed at 40° for 30 minutes. Approx. 31 c.c. of carbon monoxide were collected (5% yield); the product was a mixture of the anhydride and the acid, but no *tert.*-butylbenzene.

(b) *With toluene.* (i) The reaction was carried out at 0°, with pivaloyl chloride (7 g.), aluminium chloride (11·5 g., 1·5 mols.), and toluene (60 c.c.). It was completed over a period of 75 minutes, about half this time at room temperature. The yield of carbon monoxide was 53% (689 c.c. at N.T.P.). The liquid products were *p-tert.*-butyltoluene, b. p. 83°/15 mm. (3·1 g., 36%), identified by its dinitro-derivative, m. p. 96° (Auwers, *Ber.*, 1916, **49**, 2403), *p-tolyl* tert.*-butyl ketone*, a colourless liquid with a faint almond odour, b. p. 125°/17 mm. (3·0 g., 34·5%) (Found: C, 81·7; H, 9·1. $C_{12}H_{16}O$ requires C, 81·8; H, 9·1%) [the *semicarbazone*, prepared by heating the ketone (0·2 g.) for 10 minutes in a concentrated aqueous-alcoholic solution of semicarbazide hydrochloride (0·2 g.) and crystalline sodium acetate (0·3 g.), separated from alcohol in prisms, m. p. 185—186° (Found: C, 66·6; H, 7·8; N, 17·8. $C_{13}H_{19}ON_3$ requires C, 66·9; H, 8·1; N, 18·0%)], and *o-tolyl* tert.*-butyl ketone*, a colourless viscous liquid, b. p. 145—150°/14 mm. (17%) (Found: C, 82·7; H, 9·5. $C_{12}H_{16}O$ requires C, 81·8; H, 9·1%), from which no ketonic derivative could be obtained, whilst the analytical results indicated the presence of a small quantity of impurity.

(ii) The acid chloride (12·2 g.) was slowly added to the stirred mixture of the catalyst aluminium chloride (1·35 g., 0·1 mol.) and toluene (70 c.c.) at room temperature. After 2 hours, the reaction was completed by boiling the liquid for the same period of time. The products were *p-tert.*-butyltoluene (9·8 g., 65%), *p*-tolyl *tert.*-butyl ketone (0·6 g., 3·4%), and *o*-tolyl *tert.*-butyl ketone (0·2 g., 1·2%) (the quantity was too small for effective purification (Found : C, 81·9; H, 9·8. Calc. for $C_{12}H_{16}O$: C, 81·8; H, 9·1%). The total quantity of the mixed ketones before fractionation was 1·2 g.

(c) *With* tert.*-butylbenzene.* The yield of hydrocarbon is uncertain particularly when excess of *tert.*-butylbenzene is used because reaction of the catalyst with the former may lead to the formation of *p*-di-*tert.*-butylbenzene and benzene. For this reason, the proportion of non-ketonic substances is of little significance. (i) Pivaloyl chloride (8·8 g.), *tert.*-butylbenzene (50 c.c.), and aluminium chloride (12·3 g.) were stirred for 1 hour at room temperature. The yield of carbon monoxide was 1073 c.c. (65%). Together with unchanged *tert.*-butylbenzene and di-*tert.*-butylbenzene, there was obtained p-tert.*-butylphenyl* tert.*-butyl ketone*, a colourless liquid, b. p. 100—102°/1·2 mm. (26·3%) (Found : C, 82·7; H, 10·2. $C_{15}H_{22}O$ requires C, 82·6; H, 10·1%).

(ii) In carbon disulphide solution. This experiment was carried out in the same way as the first with pivaloyl chloride (7·7 g.), alumium chloride (13 g., 1·5 mols.), *tert.*-butylbenzene (12·3 g., 1·1 mols.), and carbon disulphide (80 c.c.). Carbon monoxide in 75% yield, *tert.*-butyl- and di-*tert.*-butyl-benzene were formed. The latter hydrocarbon was identified by its m. p. (76°) and by conversion into the dinitro-derivative (plates m. p. 190°, from alcohol) with fuming nitric acid at room temperature.

(d) *With ethylbenzene.* (i) By use of pivaloyl chloride (9·2 g.), ethylbenzene (12·2 g., 1·5 mols.), aluminium chloride (15·3 g., 1·5 mols.), and carbon disulphide (100 c.c.), 1157 c.c. of carbon monoxide (68%), *p*-ethyl-*tert.*-butylbenzene, b. p. 102—105°/17 mm. (4·7 g., 38%) (Found : C, 88·7; H, 11·0. Calc. for $C_{12}H_{18}$: C, 88·9; H, 11·1%), and p-*ethylphenyl* tert.*-butyl ketone*, b. p. 85°/0·2 mm. (4·1 g., 28%) (Found : C, 82·5; H, 9·5. $C_{13}H_{18}O$ requires C, 82·1; H, 9·5%), were obtained. Both benzene derivatives furnished terephthalic acid when oxidised by chromic acid (cf. *Org. Synth.*, 1946, **26**, 95).

(ii) Slow addition of pivaloyl chloride (6 g.) to a suspension of aluminium chloride (10 g.) in ethylbenzene (60 c.c.) afforded carbon monoxide (616 c.c., 50%), *p*-ethyl-*tert.*-butylbenzene (2·6 g., 32%), and the above ketone (46·5%).

(e) *With anisole.* (i) The acid chloride (11·2 g.) in dry light petroleum (b. p. 60—80°; 20 c.c.) was added slowly to a stirred mixture of the catalyst (18·6 g., 1·5 mols.), anisole (20 g., 2 mols.), and light petroleum (100 c.c.) cooled in an ice-bath. After a further 45 minutes, the mixture was very gently warmed (to minimise the danger of any cleavage of the ether), and the resulting pink complex decomposed by acid. No more than 35 c.c. of carbon monoxide were collected (6·7%), and the p-*methoxyphenyl* tert.*-butyl ketone*, b. p. 138—140°/8 mm., was obtained in 79·6% yield (14·2 g.) (Found : C, 74·7; H, 8·2. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·3%). The *semicarbazone* crystallised from absolute alcohol in plates, m. p. 150—151° (Found : C, 62·5; H, 7·5; N, 16·8. $C_{13}H_{19}O_2N_3$ requires C, 62·6; H, 7·6; N, 16·9%).

(ii) Condensation in carbon disulphide gave rather smaller yields (45%) of the ketone which in this case was coloured pink in spite of repeated distillations. Anisole, however, is known to yield products such as *p*-dithiocarbomethoxyphenol with carbon disulphide when aluminium chloride is present (Jorg, *Ber.*, 1927, **60**, 1466). This substance was not actually isolated, though traces of a liquid, b. p. 110—120°/15 mm., were present (Found : C, 66·1; H, 7·1%).

(f) *With acetanilide.* Aluminium chloride (12·3 g., 1·5 mols.) was added in small portions over a period of 30 minutes to a vigorously stirred mixture of pivaloyl chloride (7·4 g.), acetanilide (8·3 g.), and chloroform (60 c.c.) cooled in ice. The liquid was then boiled under reflux for 30 minutes. The carbon monoxide content of the liberated gases was 1397 c.c. (75·2%), whilst decomposition of the complex gave a liquid which solidified to a mixture of unchanged acetanilide and *p-tert.*-butylacetanilide. The latter being only sparingly soluble in boiling water was separated and crystallised from aqueous alcohol in shining white plates, m. p. 171—172° (55%) (Found : C, 75·7; H, 8·9; N, 6·9. Calc. for $C_{12}H_{17}ON$: C, 75·4; H, 8·9; N, 7·3%). No ketonic product could be detected.

(g) *With diphenyl.* The reaction was accomplished in carbon disulphide solution using 1·1 mols. of the catalyst. There was the usual immediate evolution of carbon monoxide, and a 62% yield of 4-*tert.*-butyldiphenyl, b. p. 110—115°/0·2 mm., which was separated from traces of unchanged diphenyl by fractional distillation, was obtained (Found : C, 90·9; H, 8·7. Calc. for $C_{16}H_{18}$: C, 91·4; H, 8·6%). Owing possibly to traces of isomerides it could not be induced to crystallise.

Condensations of cyclo*Pentane Derivatives.—The acid chloride* (I) *of methyl* 1-*carboxy*cyclo*pentylacetate.* The acid chloride (10 g.), prepared essentially by the method of Vogel (*J.*, 1928, 2010), was added to aluminium chloride (14 g., 2·1 mols.) and benzene (100 c.c.), the temperature being maintained below 10°. The products were carbon monoxide (89·2%) and methyl 1-phenyl*cyclo*pentylacetate (II), b. p. 118—120°/9 mm. (78·9%) (Found : C, 76·9; H, 8·5. Calc. for $C_{14}H_{18}O_2$: C, 77·4; H, 8·3%). No ketonic fraction, b. p. 190°/11 mm. (Saboor, *loc. cit.*), was present. There was a trace of residual oil, b. p. >230°/0·2 mm., which was not examined.

1-*Methyl*cyclo*pentane*-1-*carboxyl chloride* (IV). 1-Methyl*cyclo*pentane-1-carboxylic acid (Meerwein, *Annalen*, 1914, **405**, 171; 1918, **417**, 263) was converted into the acid chloride by keeping it overnight with thionyl chloride (1·5 mols.), warming it for 15 minutes, and then distilling it. B. p. 61°/15 mm. Yield, 85%. The substitution of thionyl chloride for the phosphorus trichloride used by previous workers affords a much purer specimen of the acid chloride.

(i) The condensation was carried out at room temperature with the acid chloride (6 g.), aluminium chloride (8·1 g.), and benzene (50 c.c.). Carbon monoxide (322 c.c., 70·3%) and 1-*phenyl*-1-*methyl*cyclo*pentane* (V), b. p. 97°/10 mm. (67·4%) (Found : C, 89·9; H, 9·8. $C_{12}H_{16}$ requires C, 90·0; H, 10·0%), were the products.

(ii) Slow addition of the acid chloride (2·7 g.) in ligroin (10 c.c.) to a stirred mixture of anisole (6 g.), aluminium chloride (3 g., 1·2 mols.), and ligroin (50 c.c.) furnished 1-*methyl*cyclo*pentyl methoxyphenyl ketone* (VI), a thick colourless liquid, b. p. 145—150°/0·3 mm. (60·5%) (no ketonic derivative could be prepared) (Found : C, 77·2; H, 8·1. $C_{14}H_{18}O_2$ requires C, 77·1; H, 8·2%).

Other Condensations with Anisole.—(i) *Tetramethylsuccinic anhydride.* Anisole (7 g. 2 mols.) was added to a carbon disulphide solution of aluminium chloride (8·8 g., 2·1 mols.) and tetramethylsuccinic anhydride (5 g.) at 0°, the temperature being raised gradually to the b. p. After 30 minutes the complex was decomposed in the usual manner affording *β-anisoyl-ααβ-trimethylbutyric acid* which crystallised from ethyl alcohol in plates, m. p. 185° (54%) (Found : C, 67·9; H, 7·5. $C_{15}H_{20}O_4$ requires C, 68·2; H, 7·6%). The *methyl* ester, prepared from the silver salt was an unusually sweet-smelling liquid, b. p. 135—140°/0·6 mm.; it solidified in a freezing mixture to a milky-white solid, m. p. 26°, which resisted all attempts at recrystallisation (Found : C, 68·6; H, 7·9. $C_{16}H_{22}O_4$ requires C, 69·0; H, 7·9%). β-Methoxyphenyl-ααβ-trimethylbutyric acid was not detected and the quantity of carbon monoxide eliminated was negligibly small. Tetramethylsuccinic anhydride was recovered unchanged from a similar condensation where the anisole was replaced by *tert.*-butylbenzene, but some di-*p*-*tert.*-butylbenzene was formed.

(ii) *α-Phenyl*iso*butyryl chloride.* A ligroin solution of this chloride (4 g.) was allowed to react with aluminium chloride (4 g.), anisole (3·6 g.), and ligroin (60 c.c.). The product was *p*-methoxyphenyl 2-phenyl-2-propyl ketone, which crystallised from light petroleum (b. p. 60—80°) in small crystals, m. p. 99° (71%) (Found : C, 80·4; H, 7·0. Calc. for $C_{17}H_{18}O_2$: C, 80·3; H, 7·1%). The melting point, and those of the oxime (m. p. 194°) and the semicarbazone (m. p. 210°), agree with those obtained by Bruzau (*Compt. rend.*, 1932, **194**, 1662; *Ann. Chim.*, 1934, [ii], **1**, 257) who synthesised the ketone from *p*-methoxyphenylmagnesium bromide and α-phenyl*iso*butyramide.

(iii) *αα-Diphenylpropionyl chloride.* The reagents used were the acid chloride (7 g.), aluminium chloride (7 g., 2 mols.), and anisole (6·2 g., 2 mols.) in carbon disulphide. The resultant p-*methoxyphenyl* 1 : 1-*diphenylethyl ketone* (5·8 g., 64%) was sparingly soluble in ethyl alcohol, from which it crystallised in feathery needles, m. p. 136° (Found : C, 83·7; H, 6·6. $C_{22}H_{20}O_2$ requires C, 83·5; H, 6·4%).

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