773. *The Reaction between Aromatic Compounds and Derivatives of Tertiary Acids. Part XI.* Friedel–Crafts Reactions with Optically Active Acid Chlorides.*

By William Bleazard and Eugene Rothstein.

Friedel–Crafts reactions of optically active phenyl-*p*-tolyl- and *p*-chlorodiphenyl-acetyl chloride with anisole afford inactive ketones, but the active ketones are obtained from methylphenyl-*p*-tolyl- and ethylmethyl-*n*-propyl-acetyl chloride. An active ketone has not been isolated from (+)-*tert.*-butylmethyl*neo*pentylacetyl chloride because this substance expels carbon monoxide even in the above favourable conditions but with phenol in the presence of aluminium chloride the optically active phenyl ester is isolated. Inactive products are obtained from all the above acid chlorides if the reaction is carried out so as to eliminate carbon monoxide, *i.e.*, in benzene solution.

The synthesis of optically active ketones by means of the Friedel–Crafts reaction has not hitherto been described. The only record of an attempted preparation of this kind is that of McKenzie and Widdows[1] who condensed (+)-phenyl-*p*-tolylacetyl chloride with benzene but failed to obtain the expected ketone; instead, a mixture largely consisting of diphenyl- and triphenyl-methane and of triphenylmethanol was isolated.[2] The synthesis of a ketone from the inactive acid chloride by substituting anisole for benzene was carried out by Rothstein and Saville.[3] They showed that, in benzene solution, the non-production of a ketone resulted from the preferential elimination of carbon monoxide by the acid derivative. McKenzie and Widdows originally believed that they had isolated the inactive ketone but, although this was erroneous, they made the correct inference that the presence of an α-hydrogen atom leads to racemization and in analogy contrasted the optical stability of atrolactic acid towards alkali with that of its lower homologue mandelic acid which racemizes easily. This optical instability of secondary diarylacetyl chlorides has now been confirmed in the cases of (+)-phenyl-*p*-tolylacetyl chloride and (+)-α-*p*-chlorophenyl-α-phenylacetyl chloride, both of which yield inactive ketones when condensed with anisole. Racemization is of course due to the potential keto-enol system and is only indirectly connected with the Friedel–Crafts reaction itself because whereas *p*-tolyl is an activating group, *p*-chlorophenyl greatly decelerates both ketone formation and elimination of carbon monoxide.[4] A less effective enolizing agent might perhaps distinguish between the two acid halides since in somewhat analogous circumstances Conant and Carlson[5] observed a difference between, for example, (+)-αβ-diphenylpropionyl chloride which reacts with phenylzinc chloride to yield (+)-αβ-diphenylpropiophenone and (+)-phenyl-*p*-tolylacetyl chloride which as in the Friedel–Crafts reaction affords the inactive ketone only.

McKenzie and Widdows had, by implication, expected that a tertiary optically active acid should condense without recemization though they had not envisaged that under some conditions the loss of carbon monoxide might vitiate the experiment. This has been prevented by using anisole as the aromatic component and the first established case of an asymmetric synthesis using the Friedel–Crafts reaction is now recorded, (—)-*p*-methoxyphenyl 1-phenyl-1-*p*-tolylpropyl ketone having been prepared from (—)-α-phenyl-α-*p*-tolylpropionyl chloride:

$$\mathrm{CMePhTol{\cdot}COCl + MeOPh \longrightarrow CMePhTol{\cdot}CO{\cdot}C_6H_4{\cdot}OMe}$$

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* Part X, *J.*, 1958, 581.

[1] McKenzie and Widdows, *J.*, 1915, **107**, 702.

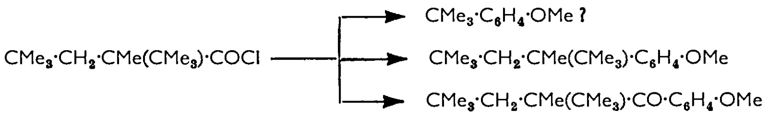
[2] McKenzie, Roger, and McKay, *J.*, 1932, 2597; Koelsch, *J. Amer. Chem. Soc.*, 1932, **54**, 4048.

[3] Rothstein and Saville, *J.*, 1949, 1961.

[4] Grundy, Hsü, and Rothstein, unpublished work.

[5] Conant and Carlson, *J. Amer. Chem. Soc.*, 1932, **54**, 4048.

In Part V[3] and in subsequent papers of this series the hypothesis was adopted that elimination of carbon monoxide proceeds through an intermediate complex the decomposition of which is not affected by any subsequent reaction. The zero-order with respect to the aromatic component indicates, for instance, that transition complexes such as $\mathrm{ArH \ldots CR_3{\cdot}CO^+\}AlCl_4^-}$ are not intermediates. The formation of optically active ketones, on the other hand, makes it evident that only after separation of the carbonyl group will the asymmetric carbon atom become planar. The separation should occur provided that structural considerations do not preserve a tetrahedral structure since the known properties of a tertiary carbonium ion do not suggest that this configuration would be stabilised solely by the electrostatic attraction of the aluminium tetrachloride anion. It follows that in general an optically active tertiary acid chloride should yield an inactive hydrocarbon CRR'R''Ar, but in selecting an example which would illustrate this point care had to be taken that the carbonium ion $^+$CRR'R'' did not undergo rearrangement or disintegration. For this reason the phenyl-*p*-tolylpropionyl chloride used above was unsuitable because, as was shown by Rothstein and Saville,[6] the lower homologue, *i.e.*, αα-diphenylpropionyl chloride with benzene affords a mixture of diphenylethane and a polymer of triphenylmethane. It has not yet been possible to identify the products from (—)-phenyl-*p*-tolylpropionyl chloride, but an inactive mixture apparently containing diphenyl- and diphenyl-*p*-tolyl-ethane is obtained. In the aliphatic series, disruption of the carbonium ion may also occur, especially if highly ramified chains are present. The reaction between benzene and (+)-2 : 2 : 3 : 5 : 5-pentamethylhexane-3-carbonyl chloride (*tert.*-butylmethyl*neo*pentylacetyl chloride) afforded at least five fractions, whose boiling points covered a range of 80° at 9 mm. and which mostly contained oxygen. Fragmentation when anisole was used was less evident. The product was also inactive, the main portion appearing to contain *tert.*-butylanisole and the remainder a mixture of 3-methoxyphenyl-2 : 2 : 3 : 5 : 5-pentamethylhexane, a trace of the corresponding ketone, 1-*tert.*-butyl-1 : 3 : 3-trimethylbutyl methoxyphenyl ketone with possibly other fragments and rearrangement entities:



$$\mathrm{CMe_3{\cdot}CH_2{\cdot}CMe(CMe_3){\cdot}COCl} \longrightarrow \begin{cases} \mathrm{CMe_3{\cdot}C_6H_4{\cdot}OMe}\ ? \\ \mathrm{CMe_3{\cdot}CH_2{\cdot}CMe(CMe_3){\cdot}C_6H_4{\cdot}OMe} \\ \mathrm{CMe_3{\cdot}CH_2{\cdot}CMe(CMe_3){\cdot}CO{\cdot}C_6H_4{\cdot}OMe} \end{cases}$$

For both the above acid chlorides it was apparent that disruption of the molecule was consequent on the appearance of the carbonium ion; the retention of optical activity when (—)-phenyl-*p*-tolylpropionyl chloride was converted into the ketone demonstrated that the catalyst itself had no direct effect on the carbon skeleton. Furthermore, though it was not possible to obtain a ketone from (+)-*tert.*-butylmethyl*neo*pentylacetyl chloride, the reaction of the latter with phenol in the presence of aluminium chloride afforded an excellent yield of the (+)-phenyl ester, there being no racemization as far as could be judged.*

There remained the need to ascertain whether the carbonium ion formed by elimination of carbon monoxide was sufficiently free to assume a planar configuration. The simplest optically active aliphatic acid chloride which should yield a non-rearranging carbonium ion is 3-methylhexane-3-carbonyl chloride (ethylmethyl-*n*-propylacetyl chloride). Examination of the carbonium ion (i) derived from it shows that hyperconjugation

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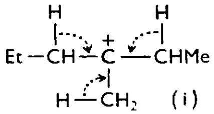
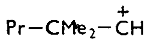
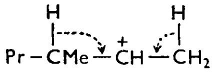
* It has been suggested that, in solution, aluminium chloride reacts with phenol to form phenoxyaluminium dichloride which is the esterifying agent. Even if this is the case this would not completely deactivate the compound as a catalyst in the Friedel–Crafts reaction since phenoxyaluminium dichloride can react with acetyl chloride, affording excellent yields of the hydroxyacetophenones (cf. Norris and Sturgis, *J. Amer. Chem. Soc.*, 1939, **61**, 1413).

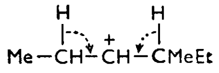
[6] Rothstein and Saville, *J.*, 1949, 1946.

(indicated by dotted arrows) stabilises it in comparison with other rearranged structures (ii—iv):


$\mathrm{Et{-}CH{-}\overset{+}{C}{-}CHMe}$, $\mathrm{H{-}CH_2}$ (i)


$\mathrm{Pr{-}CMe_2{-}\overset{+}{C}H_2}$ (ii)


$\mathrm{Pr{-}CMe{-}\overset{+}{C}H{-}CH_2}$ (iii)


$\mathrm{Me{-}CH{-}\overset{+}{C}H{-}CMeEt}$ (iv)

The experimental results showed that the (+)-acid chloride which yielded a (+)-ketone when condensed with anisole, probably afforded inactive 3-methyl-3-phenylhexane with benzene. The Table below summarizes the optical properties of the acids and ketones derived from them.

Optical activity of acids and their related ketones.

	$RR'R''C{\cdot}CO_2H$		Alkaloid used for resolution	Optical activity of: acid	ketone
R	R′	R″	—	$[\alpha]_D^{18}$ solvent	$[\alpha]_D^{18}$ solvent
H	Ph	*p*-Tol	Cinchonidine	+14·4° $CHCl_3$	Inactive
H	Ph	*p*-C_6H_4Cl	Cinchonidine	+15·3° EtOH	Inactive
Me	Ph	*p*-Tol	Quinine	−11·0° $CHCl_3$	−12·1° $CHCl_3$
Me	CMe_3	$CH_2{\cdot}CMe_3$	Cinchonine	+23·8° EtOH	+24·5° * EtOH
Me	Et	Pr^n	Brucine	+19·7° EtOH	+14·5° $CHCl_3$

* Phenyl ester of original acid.

EXPERIMENTAL

Optical rotations were measured with $l = \frac{1}{2}$ or 1, and $c = 2 - 10$.

Preparation of Materials.—(+)-*Phenyl*-p-*tolylacetic acid.* The *cinchonidine salt* [1] (Found: C, 78·2; H, 7·0; N, 5·2. $C_{34}H_{36}O_3N_2$ requires C, 78·4; H, 7·0; N, 5·4%) yielded (+)-phenyl-*p*-tolylacetic acid, m. p. 82°, $[\alpha]_D^{18}$ 14·4° (in chloroform) (Found: C, 79·4; H, 6·1. Calc. for $C_{15}H_{14}O_2$: C, 79·6; H, 6·2%). McKenzie and Widdows found m. p. 83—84°, $[\alpha]_D$ +14·6° (in acetone). The *acid chloride* (formed by use of thionyl chloride, 75%) had b. p. 136°/0·1 mm. (Found: C, 73·7; H, 5·0; Cl, 14·7. $C_{15}H_{13}OCl$ requires C, 73·6; H, 5·3; Cl, 14·5%). It was optically active but precise measurements were not made.

(+)-α-p-*Chlorophenyl*-α-*phenylacetic acid.* Cinchonidine (98 g.) was gradually added to a boiling ethanolic solution (1·5 l.) of inactive α-*p*-chlorophenyl-α-phenylacetic acid [4] (82 g.). The liquid was boiled under reflux for 30 min. and sufficient water was added to produce cloudiness. The cooled solution deposited *cinchonidine* α-p-*chlorophenyl*-α-*phenylacetate*, m. p. 160° (74 g.) (Found: C, 73·7; H, 6·3; N, 5·1; Cl, 6·7. $C_{33}H_{33}O_3N_2Cl$ requires C, 73·3; H, 6·1; N, 5·2; Cl, 6·7%). Eight recrystallisations of the cinchonidine salt from 60% aqueous acetone afforded the optically pure salt (12 g.). This was decomposed by dilute sulphuric acid, and the precipitated (+)-α-*p*-chlorophenyl-α-phenylacetic acid recrystallised from dilute acetic acid. It had m. p. 112° and $[\alpha]_D^{18}$ 15·3° (in ethanol).

α-*Phenyl*-α-p-*tolylpropionic acid.* (i) Anhydrous stannic chloride (60 g.) was gradually added to a stirred boiling solution of atrolactic acid [7] (12 g.) in toluene (250 c.c.) and the whole was heated until no more hydrogen chloride was evolved. The liquid was mixed with water, and the toluene layer extracted with dilute sodium carbonate solution. The alkaline layer yielded a yellow oil when acidified, which on drying and admixture with benzene afforded a crystalline acid, m. p. 185—190°. This was shaken with concentrated hydrochloric acid. Crystallisation from dilute ethanol afforded isotropic acid (1-phenyltetralin-1 : 4-dicarboxylic acid), m. p. 238°, formed by the condensation of two molecules of atrolactic acid (Found: C, 72·9; H, 5·8. Calc. for $C_{18}H_{16}O_4$: C, 73·0; H, 5·4%).

A second method of preparation using aluminium chloride as the condensing agent [8] yielded only the starting material.

(ii) The synthesis finally adopted was that of Ramart and Amagat [9] who however did not record any yields. Benzyl phenyl-*p*-tolylacetate, b. p. 205—206°/0·05 mm. (130 g., 80%), was

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[7] *Org. Synth.*, 1953, **33**, 7.

[8] Wegmann and Dahn, *Helv. Chim. Acta*, 1946, **29**, 426.

[9] Ramart and Amagat, *Ann. Chim.* (*France*), 1927, **8**, 276.

obtained by boiling the acid chloride (135 g.) with benzyl alcohol (500 c.c.) under reflux for 12 hr. Dibenzyl ether, b. p. 110°/0·2 mm. (80 g.), was also isolated. The benzyl ester (126 g.) was then boiled for 2 hr. under reflux with a suspension of sodamide (from 9 g. of sodium) in benzene (500 c.c.) and then for a further 12 hr. with methyl iodide (60 g.). The product, b. p. 195—200°/0·05 mm. (81 g., 60%), was hydrolysed with ethanolic potassium hydroxide, affording a yellow syrupy acid (52 g., 93%). The quinine salt was recrystallised eleven times from 50% aqueous acetone and on decomposition afforded (−)-*α-phenyl-α-*p*-tolylpropionic acid*, m. p. 96°, $[\alpha]_D^{18}$ −11·0° (7%) (Found: C, 80·2; H, 6·7. $C_{16}H_{16}O_2$ requires C, 80·0; H, 6·7%).

(+)-2 : 2 : 3 : 5 : *5-Pentamethylhexane-*3*-carboxylic Acid*. Ten recrystallisations of the brucine salt (m. p. 116—118°) from 75% aqueous acetone yielded a product which on decomposition afforded an optically inactive acid. The cinchonidine salt, m. p. 153°, was recrystallised four times from dilute alcohol and then decomposed with mineral acid, to yield a partially resolved acid, m. p. 135°, $[\alpha]_D^{18}$ +2·7°. The cinchonine salt, on the other hand, afforded an acid of $[\alpha]_D^{18}$ +3·1° after only three recrystallisations. Accordingly, cinchonine (112 g.) was gradually added to a boiling solution of the acid (75 g.) in ethanol (1 l.), and the liquid diluted with more ethanol until dissolution was complete, the total volume then being 4 l. On cooling, unchanged cinchonine (35 g.) was deposited. After filtration the solution was boiled and water added until crystallisation commenced. When cold, the liquid afforded a salt, m. p. 220—225°, $[\alpha]_D^{18}$ +143°. Eleven more recrystallisations from 50% aqueous ethanol yielded the pure *cinchonine* 2 : 2 : 3 : 5 : *5-pentamethylhexane-*3*-carboxylate*, m. p. 215° (10 g.) (Found: C, 74·9; H, 9·3; N, 6·0. $C_{31}H_{46}O_3N_2$ requires C, 75·3; H, 9·4; N, 5·7%), whence was obtained a (+)-acid, m. p. 130°, $[\alpha]_D^{18}$ +23·8° (in ethanol).

3-*Methylhexane*-3-*carboxylic acid*. Attempted syntheses of this acid employing published methods [10] were unsuccessful; consequently Doering and Wilberg's procedure starting from substituted acetoacetic esters [11] was adopted. Ethyl propylacetoacetate was best methylated by using potassium *tert.*-butoxide as catalyst. Ethyl α-methylvalerate, b. p. 108—112°/13 mm. (53%) (Found: C, 65·0; H, 10·2. Calc. for $C_{10}H_{18}O_3$: C, 64·5; H, 9·7%), so obtained was reduced with Raney nickel in ethanol, affording ethyl α-(1-hydroxyethyl)-α-methylvalerate, b. p. 104—106°/12 mm. (65%), and unchanged keto-ester. The hydroxy-ester (50 g.) was dehydrated by phosphoric oxide (50 g.) yielding impure ethyl 3-methylhex-1-ene-3-carboxylate, b. p. 83—85°/19 mm. (60%) (Found: C, 69·0; H, 11·1. Calc. for $C_{10}H_{18}O_2$: C, 70·5; H, 10·7%). Hydrogenation of the unsaturated compound (250 g.) with Raney nickel at 5 atm. furnished ethyl 3-methylhexane-3-carboxylate, b. p. 73—75°/13 mm. (227 g., 85%). The corresponding acid, b. p. 114—117°/11 mm., was obtained (yield, 80%) by hydrolysis with concentrated methanolic potassium hydroxide (Found: C, 66·7; H, 11·1. Calc. for $C_8H_{16}O_2$: C, 66·6; H, 11·2%). A mixture of the acid (22 g.) and thionyl chloride (30 g.) was kept at room temperature for 12 hr.: distillation yielded the acid chloride, b. p. 68—69°/17 mm. (22 g., 90%).

Resolution: Brucine was used but later experience suggested that it was probably not the best choice. The acid (151 g.) was boiled for 30 min. under reflux with brucine (412 g.) and acetone (500 c.c.), and the product (532 g.) then precipitated with light petroleum (b. p. 60—80°). The salt was very soluble in ethyl acetate, forming viscous solutions when concentrated. In the first instance methanol was used for recrystallising it but after 19 recrystallisations the acid recovered from the sample had a specific rotation of only 6° and consequently a 1 : 2 mixture of ethyl acetate and light petroleum (b. p. 60—80°) was employed, about two-thirds of the salt separating after each operation. Owing to the relatively low yield of salt and the large number of recrystallisations required (about 40 in all), a systematic procedure such as is described in " Organic Reactions " [12] was followed, the progress of the resolution being followed by measuring the rotation of the free acid. The final brucine salt, m. p. 70—71°, yielded optically pure (+)-3-methylhexane-3-carboxylic acid, $[\alpha]_D^{18}$ +19·7° (in 95% ethanol).

Friedel–Crafts Reactions.—In these reactions, the benzene and aluminium chloride were of the quality employed in the kinetic work.[13] " AnalaR " anisole was dried over anhydrous sodium sulphate and redistilled.

(i) Inactive phenyl-*p*-tolylacetyl chloride (from 2 g. of acid) in anisole (5 c.c.) was added

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[10] Haller and Bauer, *Compt. rend.*, 1909, **148**, 130; Hauser and Breslow, *J. Amer. Chem. Soc.*, 1940, **62**, 2457; Lester and Proffitt, *ibid.*, 1949, **71**, 1877.

[11] Doering and Wilberg, *ibid.*, 1950, **72**, 2608.

[12] *Org. Reactions*, Vol. 2, p. 400.

[13] Grundy, Hsü, and Rothstein, *J.*, 1956, 4558.

slowly to a stirred suspension of aluminium chloride (2 g.) in the same solvent (25 c.c.) at 0°. The mixture was stirred for 1 hr. at room temperature and for 1 hr. at 50—60°. The resulting *p*-methoxyphenyl 4-methyl-α-phenylbenzyl ketone (2·3 g.) crystallised from dilute ethanol in a form of m. p. 134° (Found: C, 83·6; H, 6·3. Calc. for $C_{22}H_{20}O_2$: C, 83·5; H, 6·4%). This ketone, as previously prepared by Rothstein and Saville,[3] had m. p. 107—108° but the two did not depress each other's melting points on admixture and their infrared spectra (in KCl) were identical. Repeated crystallisations from various solvents left their respective m. p. unchanged.

(ii) Reaction (i) was repeated with (+)-phenyl-*p*-tolylacetyl chloride. In two experiments the yield of *inactive* ketone, m. p. 134°, was 2·3 g. and 2·1 g. The products were identical with that described above.

(iii) Reaction (i) was repeated both with inactive and with (+)-α-*p*-chlorophenyl-α-phenylacetyl chloride. In both cases the inactive ketone was obtained. 3-*Chloro-α-phenylbenzyl* p-*methoxyphenyl ketone* crystallised from dilute alcohol in needles, m. p. 141° (2·1 g., 77%) (Found: C, 75·4; H, 5·3; Cl, 10·4. $C_{21}H_{17}O_2Cl$ requires C, 75·0; H, 5·1; Cl, 10·6%).

(iv) Inactive α-phenyl-α-*p*-tolylpropionyl chloride was prepared from the acid (2 g.) and excess of thionyl chloride, the unchanged reagent being removed in a vacuum. The reaction with anisole afforded p-*methoxyphenyl* 1-*phenyl*-1-p-*tolylpropyl ketone*, m. p. 105° (1 g.) (from ethanol) (Found: C, 83·8; H, 6·3. $C_{23}H_{22}O_2$ requires C, 83·6; H, 6·7%).

(v) Similarly (—)-α-phenyl-α-*p*-tolylpropionyl chloride (2 g.) yielded (—)-*p*-methoxyphenyl α-phenyl-α-*p*-tolylpropyl ketone, m. p. 105°, $[\alpha]_D^{18}$ —12·1° (in chloroform) (1·1 g.).

(vi) The above (—)-acid chloride (from 1·2 g. of acid), dissolved in benzene (5 c.c.), was added to a stirred suspension of aluminium chloride (1·8 g.) in benzene (25 g.). The product had a yellow-blue fluorescence in ethyl acetate and on fractionation yielded two liquids: Fraction (*a*), b. p. 100—102°/0·05 mm. (0·30 g.), was mainly hydrocarbon. The b. p. was considerably higher than that of phenyl-*p*-tolylmethane (b. p. 85—86°/0·04 mm.) and of diphenylethane (b. p. 97—98°/0·2 mm.), indicating the possible presence of 1 : 1-diphenyl-1-*p*-tolylethane (Found: C, 91·6; H, 7·1. Calc. for $C_{21}H_{20}$: C, 92·6; H, 7·4%). The infrared spectrum differed considerably from that of diphenylmethane, diphenylethane, and phenyl-*p*-tolylethane. The substance was optically inactive. Fraction (*b*) was an optically inactive ketone of indefinite b. p. (160—175°/0·05 mm.), having strong CO absorptions at 1730 and 1718 cm.$^{-1}$ (Found: C, 86·9; H, 6·8%).

Condensations of 2 : 2 : 3 : 5 : 5-*pentamethylhexane*-3-*carbonyl chloride* (vii—x). (vii) A solution of the acid chloride (10 g., 0·046 mole) in anisole (50 c.c.) was cooled to 0° and aluminium chloride (10 g., 0·075 mole) was gradually added by means of a hopper. Carbon monoxide was vigorously evolved (1010 c.c., 95%). The mixture afforded three products all of which contained a methoxyphenyl group, *viz.*: (*a*) possibly *p*-*tert.*-butylanisole, b. p. 52—53°/0·1 mm. (5·2 g.) (Found: C, 80·1; H, 10·2. Calc. for $C_{11}H_{16}O$: C, 80·4; H, 9·8%), (*b*) possibly 3-p-*methoxyphenyl*-2 : 2 : 3 : 5 : 5-*pentamethylhexane*, b. p. 67—68°/0·1 mm. (2·9 g.) (Found: C, 81·8; H, 11·1. $C_{18}H_{30}O$ requires C, 82·4; H, 11·5%) (no infrared CO absorption), and (*c*) a low-melting solid, b. p. 108°/0·1 mm. (0·30 g.) (strong CO absorption at 1684 cm.$^{-1}$), analysis corresponding to 1-tert.-*butyl*-1 : 3 : 3-*trimethylbutyl methoxyphenyl ketone* (Found: C, 79·0; H, 10·2. $C_{19}H_{30}O_2$ requires C, 78·6; H, 10·4%).

(viii) The above experiment was repeated with 2 g. of the (+)-acid chloride. All the products obtained were inactive, but the trace of ketone obtained was in any case too small for reliable optical measurements.

(ix) The fractions obtained when the acid chloride (10·5 g.) in benzene (50 c.c.) was mixed with aluminium chloride at room temperature were as follows:

		Found (%)				Found (%)	
Fraction	B. p./mm.	C	H	Fraction	B. p./mm.	C	H
1	51°/12	83·8	12·3	2	55°/12	86·7	12·2
3	72°/12	85·2	11·7	4	93°/12	81·7	12·6
5	115°/12	80·1	11·5				

The last three fractions had appreciable CO absorptions, at: 1759 and 1715 cm.$^{-1}$; 1786 and 1695 cm.$^{-1}$; and 1783 and 1698 cm.$^{-1}$ respectively. The first peak was relatively more intense than the second except in the last case where the reverse was true.

(x) Aluminium chloride (2 g., 0·015 mole) was stirred with phenol (5 g., 0·05 mole) in benzene

(10 c.c.) at room temperature until the liquid was homogeneous. The acid chloride (2 g., 0·009 mole) in benzene (3 c.c.) was then added and stirring continued for 2 hr. Little gas was evolved and the principal product was *phenyl* 2 : 2 : 3 : 5 : 5-*pentamethylhexane*-3-*carboxylate*, b. p. 110°/0·2 mm. (2 g., 85%) (Found: C, 78·1; H, 10·1. $C_{18}H_{28}O_2$ requires C, 78·2; H, 10·2%) [no OH bands; ester-CO at 1742 (s) cm.$^{-1}$]. The (+)-acid chloride similarly furnished (+)-phenyl 2 : 2 : 3 : 5 : 5-pentamethylhexane-3-carboxylate (80%), b. p. 99—100°/0·05 mm., $[\alpha]_D^{18}$ +24·3°, +24 8° (in ethanol) (separate experiments).

Condensations of 3-*methylhexane*-3-*carbonyl chloride* (xi—xiii). (xi) The inactive acid chloride (4 g., 0·025 mole) in anisole (5 c.c.) was added slowly to a stirred suspension of aluminium chloride (4 g., 0·03 mole) in the same solvent (10 c.c.) cooled in an ice-bath. The liquid was then stirred for 1 hr. at room temperature and for a further hour at 50—60°. This mixture afforded inactive 3-p-*methoxybenzoyl*-3-*methylhexane*, b. p. 120—122°/0·6 mm. (4·6 g., 74%) (Found: C, 77·1; H, 9·6. $C_{15}H_{22}O_2$ requires C, 76·9; H, 9·5%).

(xii) (+)-3-Methylhexane-3-carboxylic acid (2 g.) was converted into the acid chloride by leaving it for 12 hr. at room temperature with excess of thionyl chloride. The residual product after removal of unchanged reagent yielded (+)-3-*p*-methoxybenzoyl-3-methylhexane, b. p. 118°/0·5 (yields 31% and 34% in two similar experiments), $[\alpha]_D^{18}$ +14·3°, 14·7°. Fission of the ketone with ethanolic potassium hydroxide afforded *p*-anisic acid, m. p. 184° (Found. C, 63·1; H, 5·4. Calc. for $C_8H_8O_3$: C, 63·2; H, 5·3%).

(xiii) The inactive acid chloride (2 g.) was similarly condensed with benzene, yielding a hydrocarbon, b. p. 95°/10 mm. (1·5 g.). Analysis corresponded to di-(1-ethyl-1-methylbutyl)-benzene rather than to 3-methyl-3-phenylhexane (Found: C, 87·2; H, 12·5. Calc. for $C_{20}H_{34}$: C, 87·6; H, 12·4%), but the b. p. was only slightly higher than that found for the latter prepared from 3-methylheptan-3-ol,[14] b. p. 93—95°/8 mm. (Found: C, 89·0; H, 11·3. Calc. for $C_{13}H_{20}$: C, 88·6; H, 11·4%). There was a vigorous liberation of carbon monoxide during this reaction. Two similar experiments with the (+)-acid chloride prepared from the (+)-acid (2 g.) afforded the same inactive hydrocarbon (45%, 37%). These experiments were carried out at room temperature and heat was not used to complete the reaction.

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[14] Huston and Hsiu, *J. Amer. Chem. Soc.*, 1936, **58**, 439.