Rearrangement of Ketones. Part 3.[1] Kinetic Study and Intermediate Complexes in the Reaction of t-Butyl Phenyl Ketone with Aluminium Chloride

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A kinetic study of the rearrangement of t-butyl phenyl ketone to 3-methyl-3-phenylbutan-2-one with aluminium chloride is reported. In addition, a study by ^1H and ^{13}C n.m.r. of the system t-butyl phenyl ketone–aluminium chloride in benzene shows the consecutive formation of a 1:1 complex and a later complex species, which according to the kinetic scheme proposed may have 2:5 stoicheiometry. This is the reactive intermediate in the rearrangement process.

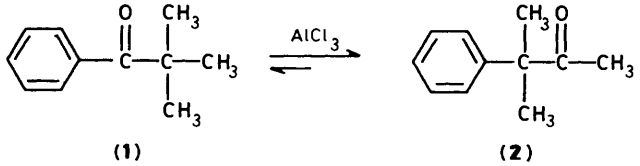
The role of charge-transfer complexes in organic reactions is well established and the correlation between the chemical structure of these complexes and the reaction mechanism is of interest.[2,3] Molecular complexes from oxygen-containing organic compounds and Lewis acids usually have 1:1 stoicheiometry,[4–7] although 2:1[8,9] and 2:5[10] complexes have also been reported. In this sense, the rearrangement of ketones catalysed by Lewis acids is a typical example of an intermediate donor–acceptor complex. There are several reports[11] dealing with the rearrangement of carbonyl compounds catalysed by Lewis or mineral acids, and different mechanisms have been proposed for this reaction. All suggest that the conjugated acid of the substrate (*i.e.* the adduct with stoicheiometry 1:1) is the reactive intermediate. However, several authors[12–14] have indicated that an excess of Lewis acid is necessary for the reaction to take place. From our point of view, this behaviour suggests that the 1:1 complex might not be the true reactive intermediate in the rearrangement.

Since kinetic studies for this process are scarce in the literature and we have not found any reference to the structure and nature of reactive intermediate complexes, the study of both aspects is interesting. This work investigates the kinetics of the reaction of t-butyl phenyl ketone with aluminium chloride and the intermediate complexes involved in this process.

Results and Discussion

The reaction of t-butyl phenyl ketone (**1**) with aluminium chloride, in benzene as solvent, takes place without the formation of secondary products,[14] to give 3-methyl-3-phenylbutan-2-one (**2**) according to the reversible process shown in Scheme 1. The position of this equilibrium is shifted towards (**2**) in favourable experimental conditions.

The experiment carried out are summarized in Table 1. It is noteworthy that when the initial concentration of (**1**) is equal to that of $AlCl_3$ (experiments 1 and 2), the starting ketone (**1**) is quantitatively recovered after heating at 50 °C for 100 h.



(**1**) (**2**)

Scheme 1.

Equilibrium constants (K) at 50 and 70 °C were calculated [as the ratio between %(**2**) and %(**1**)] from experiments 6 and 9, which proceeded until equilibrium was reached. The results obtained are quoted in Table 2.

The rate of the transformation of ketone (**1**) into the corresponding isomer ketone (**2**) must follow the general equation (1). The fact that the concentration of $AlCl_3$ can be

$$v = k[\text{ketone}]^{\alpha}\,[AlCl_3]^{\beta} \quad (1)$$

considered constant (there is no consumption of the catalyst) allow equation (1) to be expressed as (2) where (3) holds. Figure

$$v = k_{exp}\,[\text{ketone}]^{\alpha} \quad (2)$$

$$k_{exp} = k\,[AlCl_3]^{\beta} \quad (3)$$

1 shows a plot of $\ln [x_e/(x_e - x)]$ *versus* time for experiments 6 and 9, where x_e is the percentage of ketone (**2**) at equilibrium and x is the percentage at any time. The linear relationship obtained for all kinetic experiments indicates that the reaction can be considered as a pseudo-first-order process with respect to ketone (**1**).

Table 1 lists k_{exp} values calculated by the integral method for a reversible first-order reaction. From a kinetic point of view, there are some surprising and apparently anomalous results. First, we stress the absence of reaction when the initial concentrations of (**1**) and $AlCl_3$ are equal. Secondly, comparison of the results of experiments 3 and 4 or 6 and 7 seems to indicate a decrease of the reaction rate with increasing concentration of ketone (**1**) at constant $[AlCl_3]$, which is opposite to the expected normal trend. However, an increase of the initial concentration of the Lewis acid gives rise to an increase in the reaction rate as expected from equation (3). Moreover, according to equation (3), reactions with equal initial concentrations of $AlCl_3$ should give the same value of k_{exp} (experiments 3, 4 and 6, 7). This evidently does not occur (Table 1).

The fact that the reaction does not take place when $[AlCl_3]_0 = [\text{ketone}]_0$ indicates that a molar ratio $AlCl_3$:ketone higher than unity is necessary for the rearrangement to occur. Thus, an equimolecular amount of $AlCl_3$ and ketone does not have a catalytic role in the process.

We assume that equation (4) holds for the rearrangement where $[AlCl_3]_0$ and $[(\mathbf{1})]_0$ are the initial concentration of $AlCl_3$ and ketone (**1**), respectively. If this hypothesis is correct, a plot

Table 1. Reaction of t-butyl phenyl ketone (**1**) with $AlCl_3$ in benzene solution

Experiment	1[a]	2[a]	3[a]	4[a]	5[a]	6[a]	7[a]	8[a]	9[b]
$[(1)]_o$/M	0.50	1.00	0.50	0.25	0.75	1.00	0.50	0.75	1.00
$[AlCl_3]_o$/M	0.50	1.00	1.00	1.00	1.50	2.00	2.00	3.00	2.00
$10^5 k_{exp}/s^{-1}$			0.56	0.90	1.10	1.62	3.18	5.30	8.70

[a] 50 °C. [b] 70 °C.

Table 2. Equilibrium constants for the reaction of t-butyl phenyl ketone (**1**) with $AlCl_3$ in benzene as solvent

%(1)[a]	%(2)[a]	T/ °C	t/h[b]	K
6	94	50	98	15.6
2	98	70	24	49.0

[a] % at equilibrium. [b] Time necessary to reach equilibrium.

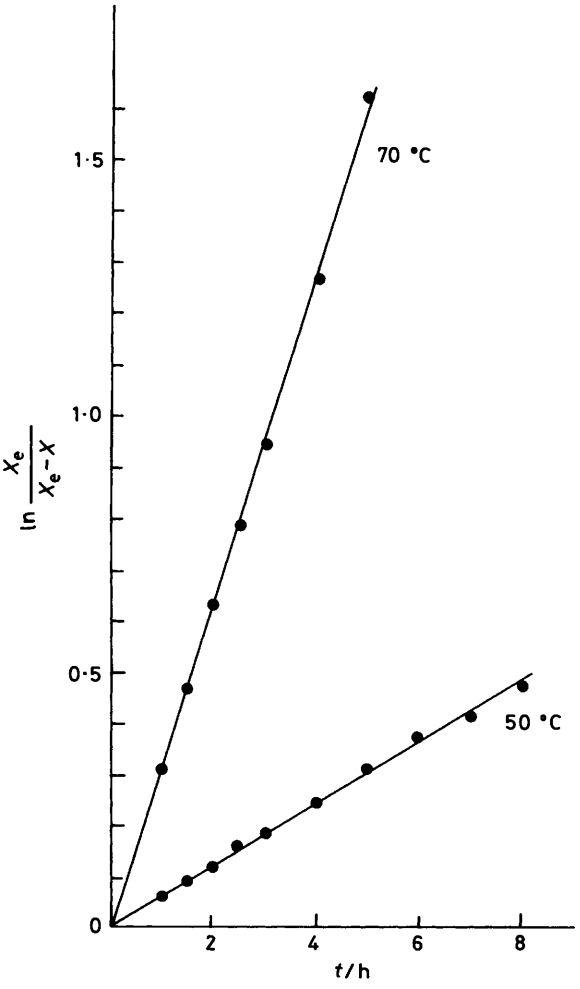


Figure 1. Plot of $\ln [x_e/(_e - x)]$ *versus* time of reaction for $[AlCl_3]_o$ (2.0M)

$$k_{exp} = k\{[AlCl_3]_o - [(1)]_o\}^{\beta} \quad (4)$$

of $\log k_{exp}$ *versus* $\log \{[AlCl_3]_o - [(1)]_o\}$ should give a straight line. The resulting diagram for reactions at 50 °C (Figure 2) shows a straight line with a good correlation coefficient (0.996). According to equation (4), values of β (3/2) and k (1.59×10^{-5} $mol^{-1.5}$ $l^{1.5}$ s^{-1}) have been calculated from the slope and the intercept, respectively. This value of k is in fairly good agreement with the experimental value obtained from the experiment 6 in which the term $\{[AlCl_3]_o - [(1)]_o\}^{\beta} = 1$ (Table 1).

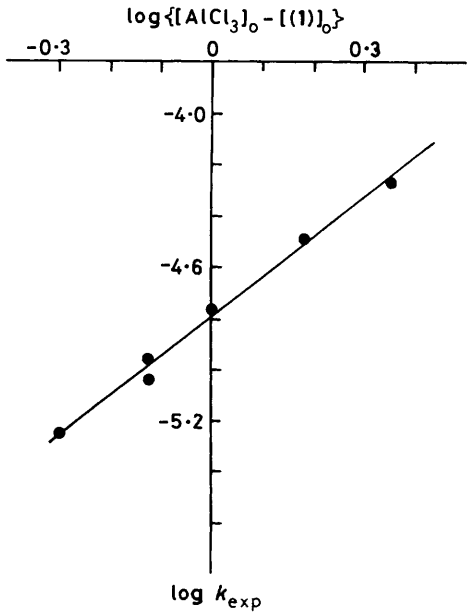


Figure 2. Plot of $\log k_{exp}$ *versus* $\log \{[AlCl_3]_o - [(1)]_o\}$ for reaction at 50 °C

As a result, the rate of reaction for the rearrangement of ketone (**1**) into (**2**) can be written as in equation (5) where

$$v = k\{[AlCl_3]_o - [(1)]_o\}^{\beta}[(1)]^{\alpha} \quad (5)$$

$\alpha = 1$, $\beta = 3/2$, $k(50\,°C) = 1.59 \times 10^{-5}$ $mol^{-1.5}$ $l^{1.5}$ s^{-1}, and $k(70\,°C) = 8.70 \times 10^{-5}$ $mol^{-1.5}$ $l^{1.5}$ s^{-1}. Equation (5) indicates that an excess of $AlCl_3$ with respect to ketone (**1**) is necessary for the reaction to take place, and thus the 1:1 complex is not truly the reactive intermediate. Therefore, other complex species must be formed for the rearrangement to occur.

A ^1H n.m.r. study of the formation of intermediate complexes has been carried out in benzene solutions using different $AlCl_3$–ketone ratios. Spectra recorded at room temperature present a set of peaks which correspond to the average of signals for the free and complexed ketone (**1**). Even when [ketone] > $[AlCl_3]$ we do not observe the appearance of resonance signals corresponding to free ketone, indicating rapid breaking and re-forming of the donor–acceptor bonds. The addition of aluminium chloride to a solution of ketone (**1**) in benzene gives rise to a clear downfield shift of the signals of protons in the vicinity of the carbonyl group, with effect being enhanced for the *ortho*-protons of the aromatic ring. The chemical shift of the *ortho*-protons changes linearly with the $[AlCl_3]$:[ketone] ratio as the relative proportion of $AlCl_3$ is increased up to a 1:1 ratio (Figure 3); this is a general trend reported for donor–acceptor systems in which the equilibrium position is independent of the concentration of the uncomplexed acceptor compound.[3] As shown in Figure 3 the linarity of the plot with a sharp break corresponding to a 1:1 ratio supports the formation of an equimolecular donor–acceptor complex with a relatively small degree of dissociation.[5] However, when the ratio $[AlCl_3]$: [ketone] is >1 we observed an increase in the multiplicity of the signals corresponding to the aromatic protons. Moreover, the change in shielding and multiplicity of the resonance signals corresponding to the methyls of the t-butyl group are negligible below a molar ratio $[AlCl_3]$:[(**1**)] = 1, but

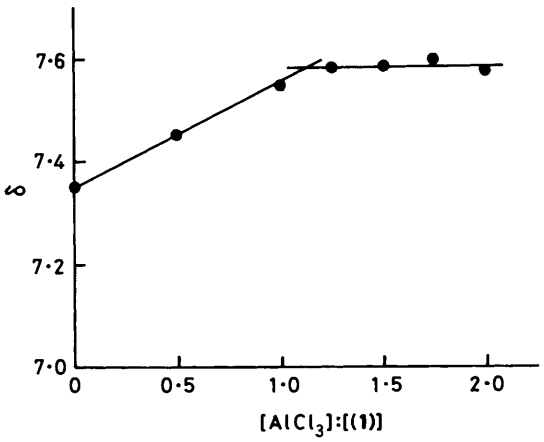


Figure 3. Variation of the chemical shift of the *ortho*-aromatic protons of ketone (**1**) with the $[AlCl_3]$:[(**1**)] ratio

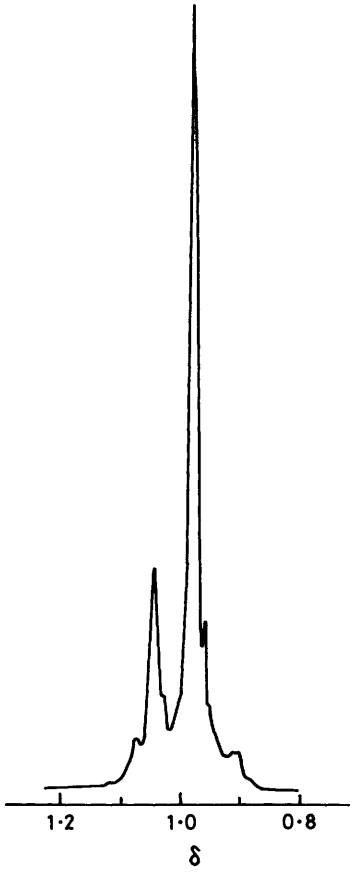


Figure 4. ^1H N.m.r. resonances (90 MHz) of methyl groups for $[AlCl_3]$:[(**1**)] 1.75

when this ratio is higher than unity the signal is converted into a set of peaks (Figure 4) whose relative intensities change with the ratio $[AlCl_3]$:[ketone].

^1H N.m.r. spectra at 300 MHz of samples with $[AlCl_3]$:[ketone] ratios > 1 have resonance signals for the methyl groups with nine different peaks (Figure 5), whose relative intensities change with the molar ratio mentioned above. The splitting of the resonance signal of the t-butyl group in the presence of an excess of aluminium chloride could be ascribed to a loss of free rotation of the t-butyl group which could give rise to the 'non-equivalence' of the methyl groups. Such loss of

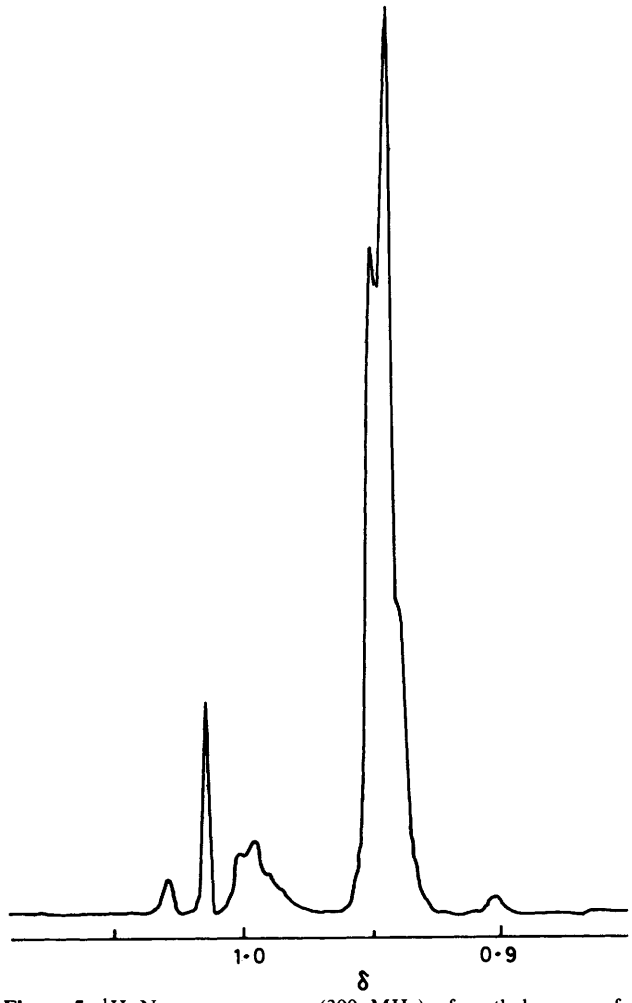


Figure 5. ^1H N.m.r. resonances (300 MHz) of methyl groups for $[AlCl_3]$:[(**1**)] 2.0

freedom of rotation might be produced by the formation of a new complex which co-ordinates more molecules of $AlCl_3$ through a chlorine bridge. If the new complex has stoicheiometry $1:n$, there would be a maximum of three signals due to the loss of free rotation of the t-butyl group;[15] the appearance of more peaks would indicate the formation of a new complex with stoicheiometry at least $2:n$, including the possibility of different stereoisomers. On the other hand, we cannot observe changes in the shape of resonance signals with temperature, since the ketone (**1**) is converted into 3-methyl-3-phenylbutan-2-one (**2**) at 50 °C in the presence of an excess of $AlCl_3$. All samples studied by n.m.r. were hydrolysed and analysed by g.l.c. after recording the spectrum, verifying that ketone (**1**) was unaltered, so that the rearrangement of (**1**) in the experimental conditions used can be disregarded and therefore the splitting observed can only be ascribed to the presence of different complexed species.

Changes in the chemical shift induced by the complexation are higher in ^{13}C that in ^1H n.m.r., which makes the study of adducts easier. Proton-decoupled ^{13}C n.m.r. spectra show that an increase of the $[AlCl_3]$:[ketone] ratio gives rise to a downfield shift of the resonance signals corresponding to the carbonyl group, the *para*-carbon, the quaternary carbon, and the methyl carbons of the t-butyl group, whereas an upfield shift of the resonance signal is observed corresponding to the aromatic carbon directly linked to the carbonyl group. It is clear from the n.m.r. spectra that the signal of the carbonyl group is most affected, whereas that of the t-butyl group is less affected

Table 3. ^{13}C N.m.r. chemical shifts (δ) for samples with different $[AlCl_3]:[(1)]$ ratios

	$[AlCl_3]:[(1)]$								
Signal	0.00	0.25	0.50	0.75	1.00	1.25	1.50	1.75	2.00
>C=O	207.10	214.73	220.60	225.29	229.05	230.06	230.96	231.28	231.48
para-C	130.57	132.65	134.60	136.38	137.60	137.90	138.13	138.27	138.38
ipso-C	138.93	137.20	135.44	134.20	133.30	133.08	132.93	132.79	132.73

Table 4. Complex formation parameters according to different treatments

		Equation (6)		Equation (7)	
Signal	δ_D (p.p.m.)	K	δ_{AD} (p.p.m.)	K	δ_{AD} (p.p.m.)
>C=O	207.10	4.23	234.38	1.34	234.73
para-C	130.57	4.02	139.37		
ipso-C	138.90	4.20	131.98		

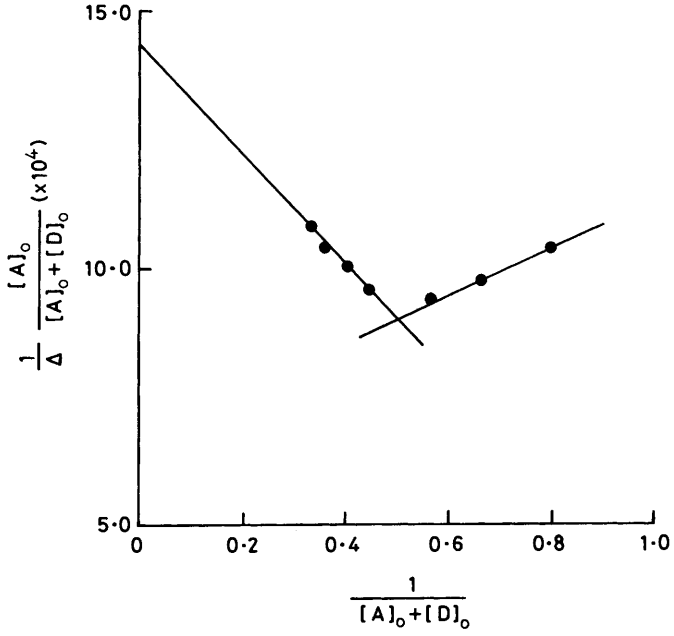


Figure 6. Application of equation (7) to the carbonyl carbon chemical shift increments for different $[AlCl_3]:[(1)]$ ratios

by the complexation process. In all cases the changes of the chemical shift are higher for $[AlCl_3]:[ketone]$ ratios < 1. However, small variations of chemical shifts for $[AlCl_3]:[ketone] > 1$ (Table 3), not apparent in the ^1H n.m.r. spectra, are also present. This can be accounted for by taking into consideration the different scale of both techniques. On the other hand, the resonance signal of methyl carbons of the t-butyl group splits into several peaks as in the ^1H n.m.r. spectra for ratios higher than unity.

From a theoretical point of view, the interactions between a donor (D) and an acceptor (A) can be estimated from n.m.r. data by the use of equation (6) (written here for $[A]_o \gg [D]_o$)

$$\frac{1}{\Delta} = \frac{1}{K\Delta_o^{AD}[A]_o} + \frac{1}{\Delta_o^{AD}} \qquad (6)$$

derived by Foster and Fyfe[16] for 1:1 molecular complexes. $[A]_o$ and $[D]_o$ are the initial concentrations of acceptor and donor, Δ is the difference between the measured chemical shift for the solution and the chemical shift of the donor in the absence of acceptor, Δ_o^{AD} is the difference between the chemical shift of the pure complex and the chemical shift of the donor, and K is the association constant of the donor–acceptor complex. Plots of $1/\Delta$ *versus* $1/[A]_o$ in the range $[A]_o > [D]_o$ for the resonance signals of the carbonyl group, *para*-carbon, and aromatic carbon directly linked to the carbonyl group give straight lines with fairly good correlation coefficients. Equation (6) gives the association constant of the donor–acceptor complex, K, as well as the parameter Δ_o^{AD}. The values are in Table 4.

Park and Herndon[17] have derived a more generalized equation which is not based on the assumption $[A]_o \gg [D]_o$ as in equation (6), although these authors eliminate a term of the equation that in some cases could produce an error in the results. When the active species in n.m.r. is the donor, equation (7) can be written. Equation (7) is applicable for $[A]_o > [D]_o$

$$\frac{1}{\Delta}\frac{1}{[A]_o + [D]_o} = \frac{1}{K\Delta_o^{AD}}\frac{1}{[A]_o + [D]_o} + \frac{1}{\Delta_o^{AD}} \qquad (7)$$

as well as $[A]_o < [D]_o$. Figure 6 shows the variation of the left-hand side of equation (7) as a function of $1/([A]_o + [D]_o)$ for the resonance signal of the carbonyl group. Two straight lines are obtained with fairly good correlation coefficients (0.9970 and 0.9998 respectively) and a sharp break which corresponds to $[A]_o = [D]_o$. The values of K and Δ_o^{AD} obtained from the straight line in the range $[A]_o > [D]_o$, are quoted in Table 4. It is clear that the values obtained for the chemical shift of the complex (δ_{AD}) from the two different equations are in excellent agreement, althought the correlation is not so good for the association constant K. However, the application of these mathematical treatments to n.m.r. data leads to relative errors that can reach 20%.[18]

It is noteworthy that the chemical shift of the signal corresponding to the carbonyl group reaches δ 231.2 p.p.m. for $[A]_o:[D]_o$ 2 and the chemical shift of the pure complex is δ 234.38 p.p.m. (Table 4); the magnitude of these values is comparable to that observed for carbocations generated from the corresponding carbinols.[19] Resonance contributions from dipolar structures such as $\overset{+}{C}–\overset{-}{O}$ could account for the extensive deshielding of this carbon nucleus.

Results obtained from equations (6) and (7) (in the range $[A]_o > [D]_o$) are in agreement with the initial formation of a 1:1 complex. However, the splitting of the resonance signal of the methyl groups indicates the formation of a new complex with a stoicheiometry at least $2:n$. This apparent disagreement can be explained satisfactorily by taking into account that, in the presence of an excess of $AlCl_3$, the equilibrium between ketone (**1**) and the 1:1 complex is shifted to the complex (which has a small degree of dissociation). The equilibrium between the 1:1 complex and the $2:n$ complex must be displaced to the first compound since there is not a large excess of $AlCl_3$ and so the concentration of the second species must be low. Thus, the theoretical calculations are in agreement with the formation of the main species.

We can conclude that the t-butyl phenyl ketone (**1**) in the presence of an excess of $AlCl_3$ gives rise to the initial formation of a 1:1 donor–acceptor complex followed by the formation of

a new complex species containing more molecules of $AlCl_3$; the geometry of such species creates difficulties for the free rotation of the t-butyl group {the splitting of the resonance signal of the methyl groups is only observed when $[AlCl_3] > [(1)]$}. These results are in agreement with the fact that the rearrangement of t-butyl phenyl ketone (**1**) to 3-methyl-3-phenylbutan-2-one (**2**) only takes place in the presence of an excess of aluminium chloride. Therefore, it can be suggested that the second species formed is the true reactive intermediate.

Accordingly, we suggest the kinetic Scheme 2 where C_1 and

$$(1) + AlCl_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_1 \quad a$$

$$2\,C_1 + n\,AlCl_3 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C_2 \quad b$$

$$C_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} C'_2 \quad c$$

$$C'_2 \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} 2\,C'_1 + n\,AlCl_3 \quad d$$

$$C'_1 \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} (2) + AlCl_3 \quad e$$

Scheme 2.

C'_1 are 1:1 complexes of ketones (**1**) and (**2**) respectively, and C_2 and C'_2 are 2:*n* complexes of ketones (**1**) and (**2**), respectively.

Taking into consideration that (i) the equilibrium of step a is practically displaced to C_1 and therefore its initial concentration is equal to the initial concentation of ketone (**1**) (this is supported by the fact that C_1 has a small degree of dissociation and that C_2 is only formed in an excess of $AlCl_3$); (ii) the equilibrium of step b is reached quickly when there is an excess of $AlCl_3$; (iii) in the first steps of the reaction, the reverse process is negligible; the rearrangement is controlled by the step $C_2 \longrightarrow C'_2$ and the rate of reaction can be written as (8); (iv)

$$v = k_3[C_2] \quad (8)$$

since the rate of transformation of $C_2 \longrightarrow C_1$ ($k_{-2}[C_2]$) is much higher than the rate of transformation of $C_2 \longrightarrow C'_2$ ($k_3[C_2]$), C_2 is an Arrhenius complex, and so $[C_2]$ can be obtained from the equilibrium (9) of step b, the rate of the direct reaction is given by equation (10). However, the kinetic study fits a first-

$$[C_2] = \frac{k_2}{k_{-2}}[AlCl_3]^n[C_1]^2 \quad (9)$$

$$v = \frac{k_3k_2}{k_{-2}}[AlCl_3]^n[C_1]^2 \quad (10)$$

order process for ketone (**1**), *i.e.* in C_1. The apparent disagreement could be satisfactorily explained taking into account the fact that the reaction mixture is analysed by g.l.c. This method requires the hydrolysis of mixtures and therefore we measure concentrations of ketones (**1**) and (**2**), independently of the stoicheiometry of their complexes in the reaction medium. This is equivalent to considering only equilibrium (11) which is

$$2\,C_1 + n\,AlCl_3 \rightleftharpoons 2\,C'_1 + n\,AlCl_3 \quad (11)$$

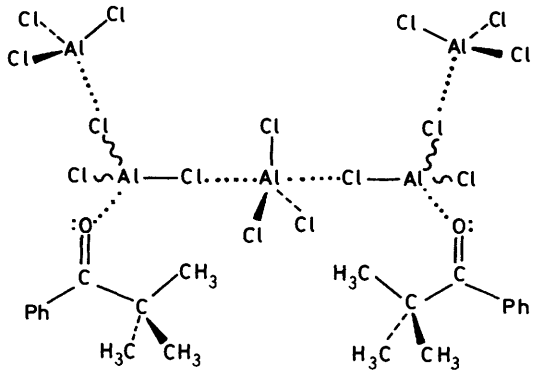
$$C_1 \rightleftharpoons C'_1 \quad (12)$$

similar to (12). We observed that the rate of reaction is first order in C_1 or in ketone (**1**) [equation (13)] where equation (14)

$$v = k_{exp}\,[C_1] \text{ or } v = k_{exp}\,[(1)] \quad (13)$$

$$k_{exp} = k([AlCl_3]_o - [(1)]_o)^{n/2} \quad (14)$$

holds. Taking into consideration equations (5) and (10) we have $n = 3$ and $k = (k_3k_2/k_{-2})^{\frac{1}{2}}$ with stoicheiometry for C_2 of 2:5,



Scheme 3.

similar to that suggested by Guyon and Villa[10] for complexes between epoxides and $ZnCl_2$ or $AlCl_3$. These have been proposed as intermediates in the opening and rearrangement of epoxides. As the mechanism of both process may be rather similar, we suggest a similar structure for C_2, which can be represented as in Scheme 3.

The geometry of such a species creates difficulties for the free rotation of the t-butyl group, allowing for the existence of different stereoisomers, which supports the appearance of the resonance signals of the methyl group.

Therefore, we conclude that an excess of $AlCl_3$ is necessary because the second species formed is the true intermediate on the rearrangement.

Experimental

A Perkin-Elmer Sigma 3 Chromatograph coupled to a Perkin-Elmer data-station was used. The column employed was 10% oxydiethylene succinate on 80—100 Chromosorb W-AW-DMCS (2 m × $\frac{1}{8}$ in at 150 °C; nitrogen as carrier gas at flow rates of 20 ml min^{-1}).

^1H N.m.r. spectra were recorded with Varian T-90 and XL-300 spectrometers, using dioxane as external reference. ^{13}C N.m.r. spectra were obtained at 25.2 MHz with a Varian XL-100 instrument using dioxane–D_2O as external reference.

Materials.—t-Butyl phenyl ketone (**1**) was prepared by the reaction of benzonitrile with t-butylmagnesium chloride[20] and purified by repeated fractional distillation under vacuum. Its purity (99.9%) was tested by g.l.c. $AlCl_3$ (Merck) was purified by vacuum sublimation and used shortly thereafter.

Kinetic Measurements.—All the reactions were carried out in a three-necked flask (50 ml) equipped with a calcium chloride-protected reflux condenser and a sealed stirrer. To the appropriate amount of $AlCl_3$, a solution (10 ml) of ketone (**1**) in dry benzene was added. The flask was placed in a thermostatted bath (±0.5 °C). Samples (0.5 ml) were taken periodically and poured into ice–hydrochloric acid (70:30). The aqueous layer was separated and extracted with three portions of ether. The combined organic layers were washed with water, saturated solutions of sodium hydrogencarbonate and water, and dried ($MgSO_4$). The composition of samples was analysed by g.l.c.

N.m.r. Measurements.—Samples were prepared by addition of $AlCl_3$ to a 1M solution of ketone (**1**) in benzene. The samples were stirred until total dissolution of $AlCl_3$, filtered, frozen, and stored at low temperature until spectra could be recorded. All spectra were recorded at room temperature.

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