

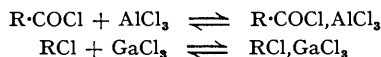
416. *The Reaction between Aromatic Compounds and Derivatives of Tertiary Acids. Part III. A Kinetic Investigation of the Alkylation of Benzene by Pivaloyl Chloride.*

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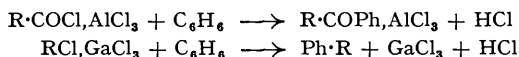
The kinetics of the reaction between pivaloyl chloride and benzene in the presence of aluminium chloride has been investigated. There is a straight-line relation between time and the logarithm of the concentration of the acid chloride, and the first-order constant deduced therefrom is independent of the concentrations of both the halide and the hydrocarbon but varies with the square of that of the aluminium chloride. Thus the rate-determining stage of hydrocarbon formation is either that of formation of the complex between pivaloyl chloride and the catalyst or of the decomposition thereof. These observations are contrasted with those of Olivier (references below) for the acylation of benzene with benzoyl chloride and of Ulich and Heyne for the corresponding alkylation with *n*-propyl chloride. These authors find that in these cases the rates of reaction are dependent on the concentrations of both the benzene and the complex formed by the halide with the catalyst.

THE qualitative results so far recorded throw little light on the factors influencing the alkylation of benzene by *tertiary* acid derivatives. In order to obtain a greater insight into the mechanism of the reaction and in view of the general considerations to be discussed in Part V, some preliminary kinetic investigations have been carried out. The kinetics of the *acylation* of benzene by acyl halides have been studied by Olivier (*Rec. Trav. chim.*, 1914, **33**, 91, 344; 1915, **35**, 109; 1918, **37**, 205), who found that, as a result of complex formation with the ketone, the loss of catalytic efficiency of the aluminium halide influences the velocity of the reaction. This is not the case for alkylation. We have commented on this point already (Part II) and we return to it later.

Alkylation by *alkyl* halides in presence of gallium chloride has been carried out by Ulich and his collaborators (Ulich and Heyne, *Z. Elektrochem.*, 1935, **41**, 509; Ulich and Fragstein, *Ber.*, 1939, **72**, B, 291; Ulich, *Z. Elektrochem.*, 1943, **49**, 291) who followed the reaction between propyl chloride and benzene by measuring the hydrogen chloride evolved. In each case these authors considered the initial stage to be the formation of a complex between the acid or alkyl halide and the catalyst:



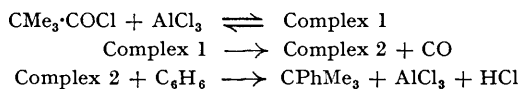
The second stages differ slightly for the reason stated above:



Olivier calculated his second-order constants for the reaction on the basis of a bimolecular reaction between the complex and benzene, Ulich on the basis of a termolecular reaction in-

volution of the concentrations of the catalyst, the alkyl chloride, and benzene. For values not less than that of the halide, changes in the initial concentration of the catalyst were without effect on the rate of reaction. Thus, both the acylation and alkylation reactions were of the second-order, dependent on the concentrations of the halide and of the benzene. It may be remarked that the catalytic efficiency of the gallium chloride decreased with the progress of the reaction and this seems characteristic of our alkylation reactions also, even though in theory the concentration remains constant. It is possibly due to traces of moisture or to some other cause not directly attributable to the reaction studied.

The reaction of pivaloyl chloride differs markedly from those described above. One obvious difference makes it necessary to predicate at least three stages which, without making any new assumptions, can be set down in the following reactions :



The first of these may be identified with the initial stages of Olivier's and Ulich's reactions. The formation of a complex is well established by inference (Olivier, *loc. cit.*; Rothstein and Saboor, *J.*, 1943, 425), by experiment with radioactive isotopes (Fairbrother, *J.*, 1937, 503), and by actual isolation (Saboor, *J.*, 1945, 922). It is not of course necessarily true that the identical complex is present in each type of reaction. The third equation may provisionally be assumed to correspond with the second of Ulich though only indirect evidence and analogy are available at present. As is evident from the results described later in this paper, the present work concerns the first two stages only, these including any intermediate reaction coming before the final production of hydrocarbon.

In following the kinetics of the condensation, advantage was taken of the possibility of titrating the unchanged acid halide (compare Olivier, *loc. cit.*), thereby eliminating the uncertainties that are inherent when the volume of hydrogen halide is measured. This latter method, first adopted by Steele (*J.*, 1903, 1470) and later with modification by Martin (*J. Amer. Chem. Soc.*, 1935, 57, 2584) and by Ulich (*loc. cit.*), does not afford very consistent results and for that reason was criticised by Olivier, but obviously the titration method was not applicable to alkylations by alkyl halides.

Apart from other considerations, the use of a titration method necessitates a homogeneous medium, and a search had to be made for a solvent in which the catalyst would remain in solution when it was mixed with the other reactants. Nitromethane was found to be excellent in many respects, but decomposition occurred in certain cases, and because of its interaction with alkali it would have to be removed completely before the unchanged acid chloride could be titrated. With the concentrations used it was found that a solution of aluminium chloride in nitrobenzene fulfilled the requirements mentioned above, a constant concentration of it being used throughout the determinations. The possibility of following the reaction by the quantitative absorption of the evolved carbon monoxide was considered, but the difficulties arising from varying pressures and from the absence of reagents for absorbing the gas suitably for accurate work made it desirable to employ an alternative method.

The quantities of the various reagents used were very similar to those used by Ulich and Heyne, though these authors provide very scanty details of their experiments. Therefore conclusions based on our work are comparable with theirs. Except in one case (experiment 10), the concentration of the catalyst was less than that of the acid chloride, and a straight line relation between the logarithm of the concentration of the latter and the time was observed. There was a short period at the beginning of most of the runs (nos. 1, 2, 3, 5, 6, and 9) when the concentration changed rather rapidly, but this covered only a small portion of the curve which rapidly straightened out. Table I summarizes the results obtained. Nitrobenzene (20 ml.) was present in every case, the concentration being 1.08 g.-mols./l.

From Table I it is evident that up to concentrations of 0.13 g.-mol./l. of aluminium chloride, the reaction gives a first-order constant which is not affected by changes in the initial concentrations of the acid chloride (compare expts. nos. 1 and 5), nor by the presence or absence of benzene (expts. nos. 5 and 8). On the other hand, the velocity constant is proportional to the square of the concentration of the catalyst; there is a straight-line relation between the two quantities, the curve being displaced somewhat along the axis of the velocity constant. The latter can be fairly accurately calculated from the equation, $k_1^{20} = 0.43 \times [\text{AlCl}_3]^2 + 0.0002$, which would imply that in the absence of catalyst there is a small residual velocity. This is not

the case however (see Part II). The decrease in the value of the velocity constant when the medium is changed to carbon disulphide is in accordance with the commonly observed experimental fact that a change of solvent affects the speed of the Friedel-Crafts reaction.

TABLE I.

The reaction between pivaloyl chloride and benzene.

Expt.	Concn. of :		G.-mols./l. of benzene	Solvent	$10^2 \times k_1^{20}$	$k_1^{20}/[\text{AlCl}_3]^2$
	AlCl_3	$\text{CMe}_3\text{-COCl}$				
1	0.063	0.630	Solvent	Benzene	0.184	0.46
2	0.063	0.630	"	"	0.187	0.47
3	0.063	0.630	"	"	0.189	0.48
4	0.127	0.630	"	"	0.719	0.45
5	0.063	0.315	"	"	0.186	0.47
6	0.087	0.318	"	"	0.342	0.45
7	0.063	0.319	0.0	CS_2	0.149	—
8	0.063	0.315	0.315	CS_2	0.151	—
9	0.105	0.540	Solvent	Benzene	0.485	0.44
10	0.322	0.315	"	"	—	—

The last experiment is the only one attempted where the ratio of the concentration of aluminium chloride to that of the acid chloride is greater than unity. The reaction was extremely rapid, being about 40% completed between the times of mixing and the first titration. Less than 20% of unchanged acid chloride remained after 45 minutes, compared with 40% after 480 minutes in experiment 1 for instance. We do not, however, consider that the circumstance of the acid chloride concentration being rather less than that of the catalyst is of great significance; it is noticeable that some of the curves tend to flatten out towards the time axis at the end of the reaction, *i.e.*, as the relative concentration of the aluminium chloride increases. This is very marked in the tenth determination also. The calculated value for $10^2 \times k_1^{20}$ is about 4.5, which gives 18 seconds as the calculated time for the 39% change which occurs between the first and the second titration, the experimental value being 19 seconds. The validity of this agreement should be qualified because the initial reaction is too rapid for accurate measurement, but it may be noted that the general shape of the curve resembles the earlier curves but is much more convex towards the time axis.

These experiments do not in themselves enable a decision to be made as to which of the first two reactions is rate-determining. It may well be that, whilst at low concentrations of the catalyst the first is the slower, the rate of formation of complex 1 may exceed that of its decomposition to complex 2 as the concentrations of catalyst are increased. It is convenient to defer to later papers any further discussion on this point and on the role of the aluminium chloride for which there is not yet sufficient evidence.

EXPERIMENTAL.

Preparation of Starting Materials.—Pivalic acid, prepared from pure pinacol hydrate (*Org. Synth.*, Coll. Vol. 1, 459, 512), was dried by distillation with benzene and fractionated twice, the product having m. p. 34–35° and b. p. 77–78°/20 mm. Freshly distilled, purified thionyl chloride was used for preparing the acid chloride. This after careful fractionation had b. p. 104–107°, and was then fractionally distilled using an electrically heated column, packed with glass helices. A very high initial reflux ratio was used, otherwise dissolved hydrogen chloride tended to carry over a considerable amount of the acid chloride below its true boiling point. The pivaloyl chloride (b. p. 106.5°) was stored in a glass-stoppered flask over phosphoric oxide.

The benzene (B.D.H. sulphur-free, of "molecular-weight quality") was dried (Na) and distilled. The carbon disulphide and the nitrobenzene were of AnalaR standard and were purified and distilled.

The catalyst was prepared by passing dry hydrogen chloride over pure aluminium foil at a dull red heat, and was then resublimed in a current of the same gas. The aluminium chloride, practically white, was stored over phosphoric oxide in a desiccator. It was resublimed immediately before use, otherwise the small lumps made dissolution in nitrobenzene difficult.

Calibration Curve for Pivaloyl Chloride.—2N-Aqueous sodium hydroxide (20 ml.) was pipetted into each of four 100-ml. stoppered flasks. Various quantities of pure pivaloyl chloride were weighed into each flask from a weight-burette, and set aside overnight. The hydrolyses were then completed by heating the liquids under reflux for 1 hour on the steam-bath. After cooling and acidification with dilute hydrochloric acid, the liquid was extracted six times with ether. Each of the extracts was washed with a little water, the aqueous layer being returned to the main bulk, and the extraction continued. The ethereal layers were united, the solvent was removed by distillation, and the residue dissolved in 95% alcohol (50 ml.). Titration with sodium hydroxide (0.102N.) with phenolphthalein as indicator gave the results shown in Table II (the alcohol gave a blank titration of 0.2 ml. which was subtracted from the main titration, the corrected figures being shown in the table).

TABLE II.

Calibration curve for titrations of pivaloyl chloride.

G. of acid chloride taken	0.1271	0.2880	0.5101	0.7759
Ml. of NaOH required	10.3	22.8	40.7	61.0

The two quantities, when plotted, gave a straight-line graph, the weight of pivaloyl chloride at each point corresponding to 97.2% of the actual weight taken. Identical results were obtained by repeating the calibration in the presence of small amounts of nitrobenzene and of the reaction product, namely *tert.*-butylbenzene.

Preliminary Measurements.—Since certain Friedel-Crafts reactions may occur without the use of aluminium chloride, it was necessary to ascertain that no uncatalysed reaction took place under the conditions of the experiment. Pure pivaloyl chloride (1.880 g.) was weighed into pure dry benzene, and the solution made up to 50 ml. in a thermostat at 20°. At intervals, 10-ml. samples were withdrawn and the weight of acid chloride determined. The results are shown in Table III.

TABLE III.

Reaction of pivaloyl chloride with benzene in absence of catalyst.

Time (minutes)	0	450	1220
Pivaloyl chloride (g.-mol./l.)	0.3120	0.3119	0.3114

Similar experiments with solutions containing small quantities of nitrobenzene and *tert.*-butylbenzene showed the virtual absence of uncatalysed reaction over the normal experimental period.

Determination of Velocity Constants.—The reaction vessel was a three-neck flask fitted with a mercury-sealed stirrer and an inlet tube for dry nitrogen. The third neck was normally closed by a calcium chloride guard-tube and was used for withdrawing the samples. The vessel was immersed in a thermostat at 20°. The reaction vessel and all the flasks used were dried at 110° and kept in a large desiccator.

A solution of the pure, freshly distilled acid chloride in the solvent was made up in a graduated flask, the volume of liquid being adjusted with the flask immersed in the thermostat. A solution of freshly sublimed aluminium chloride in nitrobenzene was similarly prepared. The concentration of nitrobenzene was maintained constant throughout the determinations. The catalyst solution was added to a measured volume of the solvent in the reaction vessel and, when it had reached the temperature of the bath, that of the acid chloride was added. A slow stream of nitrogen was passed through the apparatus during the determination. After reaction had begun, 10-ml. samples were withdrawn at suitable intervals, using pipettes fitted with drying tubes, and run directly into sodium hydroxide (20 ml.), the pivalic acid being determined by the standardised method. The process was modified somewhat when high concentrations of the catalyst were used. In this case it was added directly to the reaction flask containing the nitrobenzene and stirred until dissolution was complete.

Results.—For the first three experiments, benzene was used as solvent, the concentrations of the acid chloride and the aluminium chloride being 0.630 and 0.063 g.-mol./l., respectively. The figures obtained are given in Table IV. The values of $10^2 \times k_1^{20}$ were obtained by plotting the curves and reading off the slope.

TABLE IV.

Time (min.)	NaOH (ml.)	CMe ₃ COCl (g.)	CMe ₃ COCl (g.-mol./l.)	Log ₁₀ [CMe ₃ COCl]	Time (min.)	NaOH (ml.)	CMe ₃ COCl (g.)	CMe ₃ COCl (g.-mol./l.)	Log ₁₀ [CMe ₃ COCl]
Experiment 1.									
0	57.4	0.730	0.605	1.782	154	40.7	0.510	0.424	1.627
13.7	52.4	0.665	0.552	1.742	237	33.9	0.430	0.357	1.553
48.7	48.8	0.618	0.513	1.710	336	28.7	0.365	0.302	1.480
89.5	46.0	0.584	0.484	1.685	524	22.7	0.288	0.239	1.378
$10^2 \times k_1^{20} = 0.184.$									
Experiment 2.									
0	59.1	0.750	0.622	1.794	197	38.1	0.484	0.402	1.604
19.3	56.1	0.712	0.591	1.772	258	34.0	0.430	0.357	1.553
72.6	48.9	0.618	0.513	1.710	338	30.1	0.380	0.315	1.498
118	44.1	0.562	0.466	1.668	447	25.6	0.325	0.270	1.431
$10^2 \times k_1^{20} = 0.187.$									
Experiment 3.									
0	58.8	0.747	0.619	1.792	266	34.1	0.432	0.358	1.554
60	50.4	0.642	0.532	1.726	364	82.0	0.355	0.294	1.468
141	42.4	0.538	0.446	1.649	463	24.1	0.305	0.253	1.403
$10^2 \times k_1^{20} = 0.189.$									

Table V shows the effect of doubling the concentration of the catalyst (experiment 4), of halving the concentration of the acid chloride (experiment 5), and of halving the concentration of acid chloride and increasing that of aluminium chloride (experiment 6).

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TABLE V.

Time (min.)	NaOH (ml.)	CMe ₃ ·COCl (g.)	CMe ₃ ·COCl (g.-mol./l.)	Log ₁₀ [CMe ₃ ·COCl]	Time (min.)	NaOH (ml.)	CMe ₃ ·COCl (g.)	CMe ₃ ·COCl (g.-mol./l.)	Log ₁₀ [CMe ₃ ·COCl]
Experiment 4 : [CMe ₃ ·COCl] = 0.630 g.-mol./l. ; [AlCl ₃] = 0.127 g.-mol./l.									
0	55.0	0.700	0.581	I-764	167	16.0	0.202	0.168	I-225
16.5	49.1	0.623	0.517	I-713	239	10.3	0.127	0.105	I-021
46.5	38.5	0.489	0.406	I-608	327	6.5	0.082	0.068	I-832
82.2	29.2	0.370	0.307	I-485					

$$10^2 \times k_1^{20} = 0.719.$$

Experiment 5 : [CMe₃·COCl] = 0.315 g.-mol./l. ; [AlCl₃] = 0.063 g.-mol./l.

0	30.0	0.380	0.315	I-499	224	19.2	0.243	0.202	I-305
31	28.1	0.356	0.295	I-470	293	16.7	0.210	0.174	I-241
78.5	25.3	0.324	0.269	I-430	364	14.2	0.179	0.149	I-172
156	22.0	0.279	0.232	I-365	480	12.6	0.159	0.132	I-120

$$10^2 \times k_1^{20} = 0.186.$$

Experiment 6 : [CMe₃·COCl] = 0.318 g.-mol./l. ; [AlCl₃] = 0.087 g.-mol./l.

0	30.3	0.384	0.319	I-503	191	15.1	0.192	0.159	I-202
21.5	27.0	0.342	0.284	I-453	218	13.7	0.172	0.143	I-155
83.5	21.3	0.270	0.224	I-351	288	10.8	0.136	0.113	I-053
128	17.4	0.223	0.185	I-267	317	9.7	0.121	0.100	I-002

$$10^2 \times k_1^{20} = 0.342.$$

The determinations shown in Table VI were carried out in carbon disulphide. They show the effect of varying the hydrocarbon concentration; that of aluminium chloride was 0.063 g.-mol./l. in both cases.

TABLE VI.

Time (min.)	NaOH (ml.)	CMe ₃ ·COCl (g.)	CMe ₃ ·COCl (g.-mol./l.)	Log ₁₀ [CMe ₃ ·COCl]	Time (min.)	NaOH (ml.)	CMe ₃ ·COCl (g.)	CMe ₃ ·COCl (g.-mol./l.)	Log ₁₀ [CMe ₃ ·COCl]
Experiment 7 : [CMe·COCl] = 0.319 g.-mol./l. ; [benzene] = zero.									
0	30.7	0.386	0.320	I-505	248	21.2	0.270	0.224	I-350
28.5	28.0	0.355	0.295	I-470	316	19.7	0.242	0.201	I-303
72	27.6	0.350	0.290	I-462	391	17.2	0.217	0.180	I-256
112	26.0	0.330	0.274	I-438	455	14.9	0.189	0.157	I-196

$$10^2 \times k_1^{20} = 0.149.$$

Experiment 8 : [CMe₃·COCl] = 0.315 g.-mol./l. ; [benzene] = 0.315 g.-mol./l.

0	30.8	0.387	0.321	I-506	220	21.7	0.274	0.227	I-356
49	28.7	0.364	0.302	I-480	330	18.8	0.239	0.198	I-297
130	25.2	0.318	0.264	I-422	400	16.8	0.212	0.176	I-245

$$10^2 \times k_1^{20} = 0.151.$$

The last two determinations, Table VII, were carried out in benzene and again showed the effects of large increases in the catalyst concentration. The curve for experiment 10 does not fit any simple expression for the velocity constant.

TABLE VII.

Time (min.)	NaOH (ml.)	CMe ₃ ·COCl (g.)	CMe ₃ ·COCl (g.-mol./l.)	Log ₁₀ [CMe ₃ ·COCl]	Time (min.)	NaOH (ml.)	CMe ₃ ·COCl (g.)	CMe ₃ ·COCl (g.-mol./l.)	Log ₁₀ [CMe ₃ ·COCl]
Experiment 9 : [CMe ₃ ·COCl] = 0.540 g.-mol./l. ; [AlCl ₃] = 0.105 g.-mol./l.									
0	50.8	0.648	0.537	I-730	142	23.1	0.294	0.244	I-388
20	43.5	0.554	0.460	I-663	216	13.4	0.171	0.142	I-153
81.5	30.9	0.394	0.327	I-514	310	10.2	0.130	0.108	I-034

$$10^2 \times k_1^{20} = 0.485.$$

Experiment 10 : [CMe₃·COCl] = 0.315 g.-mol./l. ; [AlCl₃] = 0.322 g.-mol./l.

0	15.1	0.192	0.159	I-201	177	4.3	0.054	0.044	I-643
3	10.6	0.135	0.112	I-049	127	4.2	0.052	0.042	I-623
18	6.1	0.076	0.063	I-801	200	3.5	0.045	0.037	I-568
45	4.4	0.055	0.046	I-663					