748. *The Fries Rearrangement of* p-*Tolyl Acetate Catalysed by Zirconium Tetrachloride and Stannic Chloride.*

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The rearrangement of *p*-tolyl acetate in homogeneous nitrobenzene solution, catalysed by zirconium tetrachloride and stannic chloride, has been studied. The reaction is fastest when two mol. of the former and one of the latter catalyst are used. The catalytic activities of titanic chloride, aluminium chloride, zirconium tetrachloride and stannic chloride have been compared for this isomerisation.

THE rearrangement of *p*-tolyl acetate to 2-hydroxy-5-methylacetophenone has been examined for nitrobenzene solutions under the catalytic influence of titanium tetrachloride [1] and aluminium chloride,[2] and now of zirconium tetrachloride and stannic chloride. The zirconium halide does not appear to have been previously used as a catalyst in the Fries

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[1] Cullinane and Edwards, *J.*, 1957, 3016.

[2] Cullinane, Edwards, and Bailey-Wood, *Rec. Trav. chim.*, 1960, **79**, 1174.

reaction; it has the advantage that it is readily soluble in organic solvents. This applies also to stannic chloride which has been used by D'Ans and Zimmer [3] to catalyse the rearrangement of 1-naphthyl acetate to 2-acetyl-1-naphthol.

The reaction is of approximately first order and is interpreted as being mainly intramolecular, the hydroxy-ketone being formed from the catalyst–ester complex (*a*) by a direct intramolecular shift and (*b*) by scission into an ion-pair composed of acetylium and phenoxymetal chloride ions which then react to form the ketone.[4] The claim by Zimmer and Eibeck [5] that an ion of the form $R{\cdot}CO^+$ cannot be involved in the Fries reaction is based on the results they obtained by treating 1-naphthyl pivalate with stannic chloride, which gave the normal rearrangement product, 2-pivaloyl-1-naphthol. They point out that the ion $Me_3C{\cdot}CO^+$ is known to decompose readily into Me_3C^+ and carbon monoxide. While experiments carried out by Rothstein and his co-workers [6] show that pivaloyl chloride (and other tertiary acid chlorides) with benzene gives, not a ketone, but a hydrocarbon produced by loss of carbon monoxide, the ion Me_3C^+ being obtained and not $Me_3C{\cdot}CO^+$, nevertheless they also note that when the aromatic component is an active one such as anisole (and therefore phenol also) the tertiary acid chloride yields almost exclusively the ketone, and not the hydrocarbon; hence the claim of Zimmer and Eibeck cannot be sustained.

The rearrangement goes to completion at all the temperatures studied, the rates increasing with the temperature. Yields of ketone of approximately 90% were obtained in all the runs (see Table 1). The effect of the amount of zirconium tetrachloride used on the reaction rate is shown in the Table; this increases with the catalyst–ester molar ratio to a maximum of 2, the results obtained with 2 and 3 mol. being very similar; this is also the case with titanic and aluminium chloride. Our results may be compared with the observations of Furka and Széll [7] who claim that the rate of disappearance of thymyl acetate in nitrobenzene, catalysed by aluminium chloride, is greater for a catalyst–ester ratio of 1·5 : 1 than for one of 3 : 1. However, in our experiments we find, as expected, that the rate of disappearance of *p*-tolyl acetate when 1·5 mol. of zirconium tetrachloride are used is intermediate between those observed when 1 and 2 (or 3) mol. are present. In the stannic chloride-catalysed reaction we find similar results when 1 and 2 mol. of the halide are used.

As already suggested for the aluminium chloride-catalysed rearrangement of 1-naphthyl acetate,[4] the zirconium tetrachloride is here considered to form two complexes with the ester, $C_6H_4Me{\cdot}OAc,2ZrCl_4$ and $C_6H_4Me{\cdot}OAc,ZrCl_4$. In the stannic chloride-catalysed rearrangement the rate curves are typical of a first-order reaction and the reaction goes to completion with all the proportions of catalyst and ester studied. These facts could be explained in two ways: (*a*) the stannic chloride is a true catalyst and is regenerated during the course of the reaction; thus its concentration would not alter as the reaction proceeded and the rate would have a first-order dependence on the ester concentration alone: (*b*) the catalyst and ester form a complex, rearrangement of which follows first-order kinetics, and is rate-determining. If the former interpretation were true the reaction rate should increase regularly with increasing concentration of the stannic halide. It is true that the rate does increase as the catalyst : ester ratio increases from 0·5 : 1 to 1 : 1, but not on further increase in the ratio. Hence this explanation cannot be correct. Considering (*b*), we note that the maximum rate is achieved with a catalyst : ester ratio of 1 : 1. This suggests that the intermediate complex has the formula $C_6H_4Me{\cdot}OAc,SnCl_4$ (I). If this were the only possible intermediate we should expect that on halving the catalyst concentration the initial rate would also be halved since only half the initial amount of complex would be formed; and if the catalyst were not regenerated only half the total ester would

[3] D'Ans and Zimmer, *Chem. Ber.*, 1952, **85**, 585.

[4] Cf. Cullinane and Bailey-Wood, *Rec. Trav. chim.*, 1959, **78**, 440.

[5] Zimmer and Eibeck, *Naturwiss.*, 1958, **45**, 263.

[6] Cf. Grundy, Hsü, and Rothstein, *J.*, 1958, 581.

[7] Furka and Széll, *J.*, 1960, 2312.

react. In fact the initial rate is not halved and the reaction goes to completion. This must mean that another intermediate, $2C_6H_4Me{\cdot}OAc,SnCl_4$ (II), can be formed and that this rearranges more slowly than complex (I). That there is no appreciable increase in rate with a catalyst : ester ratio greater than 1 : 1 indicates that complexes such as $C_6H_4Me{\cdot}OAc,2SnCl_4$ are not possible. Moreover if the 0·5 : 1 catalyst : ester complex were the only possible one then increasing the stannic chloride : ester ratio above 0·5 : 1 would not affect the rate unless the stannic halide complex acted as a true catalyst, a possibility already excluded. Hence we conclude that, in nitrobenzene, stannic chloride and *p*-tolyl acetate give two complexes, (I) and (II), and that the difference in the reaction rates is due to the differing reactivities of these complexes.

Varying the volume of solvent is seen from the Table to have very little effect on the rate of reaction.

In our experience some phenol is always isolated; this was not taken into account by Furka and Széll. While it is true that very little phenol is left at the end of the reaction yields of up to 20% are obtained in the shorter runs.

The effect of the addition of acetyl chloride on the aluminium chloride-catalysed rearrangement of thymyl acetate has been shown by Furka and Széll to increase the rate of formation of the ketone; a similar effect has been observed in the isomerisation of *o*-tolyl acetate by titanic chloride.[8] This is due to the hydrogen chloride here liberated since it is known [9] to accelerate the reaction. Moreover, addition of acetyl chloride increases the concentration of acetylium ion and thereby influences the rate of formation of the ketone resulting from the combination of the acylium and phenoxide components; for instance, in the reaction between titanium tetrachloride and *o*-tolyl acetate addition of acetyl chloride increases the ketone formation while reducing the amount of phenol.[8] Further, as pointed out by Furka and Széll, acyl chloride, phenol, and hydroxy-ketone all form complexes with the catalyst, and so addition of acetyl chloride will alter the quantity of catalyst available for the rearrangement proper. It has also been suggested [8] that the acyl chloride introduced may cause direct acylation of the ester nucleus or react with the hydroxyl group of the ketone, forming a ketone ester; however, in all the reactions we have examined, not more than traces of ketone ester have been found.

When thymol is added in the thymyl acetate rearrangement it decreases the reaction rate. This could be caused by formation of a complex by the phenol and catalyst, diminishing the amount of the latter available for the rearrangement. The effect is very slight when 3 mol. of aluminium chloride are employed; here presumably there is sufficient catalyst for all purposes.

A comparison of the relative efficiencies of the four catalysts is shown in the Table: titanic chloride is more active than aluminium chloride, which possesses similar activity to zirconium tetrachloride; stannic chloride is the least active. Antimony trichloride and pentachloride are only very slightly active. (Titanic chloride has been observed to be more active than aluminium chloride also in the rearrangement of *o*-tolyl acetate.[2])

The velocity constants at 40°, 50°, and 60° and the activation energies for the overall reaction are given below. Values for titanic [1] and aluminium chloride [2] have already been published.

Isomerisation of p-*tolyl acetate* (0·1 *mole*) *by catalyst* (0·2 *mole*).
(*k in* 10^{-5} sec.$^{-1}$; *E in* kcal. mole^{-1}.)

$PhNO_2$ (c.c.)	Catalyst	k_{40}	k_{50}	k_{60}	E
150	$ZrCl_4$	1·5	5·0	13·5	22·5
100	$SnCl_4$	1·07	2·4	5·65	17·5

Experimental.—Materials were purified by standard methods; Johnson and Matthey's zirconium tetrachloride was used direct; the products obtained from Magnesium Elektron, Ltd., and Peter Spence and Sons, Ltd., were somewhat less effective.

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[8] Cullinane, Evans, and Lloyd, *J.*, 1956, 2222.
[9] Széll and Furka, *J.*, 1960, 2321.

The rearrangement was carried out and the products separated and analysed in a similar manner to the aluminium chloride-catalysed reaction.[2] Results are in Table 1.

TABLE 1. *Rearrangement of* p-*tolyl acetate.*

	Ketone (%)	*p*-Cresol (%)	Ester recovd. (%)	$PhNO_2$ (c.c.)
(*a*) Ester, 0·1 mole; catalyst, 0·2 mole.				
$TiCl_4$ (6 hr., 60°)	87·7	4·1	0·2	150
(13 hr., 50°)	91·5	3·2	0·0	150
$ZrCl_4$ (9·5 hr., 60°)	86·0	7·1	0·0	300
(26 hr., 50°)	81·3	12·4	0·0	300
$SnCl_4$ (18 hr., 60°)	78·4	9·5	2·5	100
(48 hr., 50°)	80·2	7·8	1·6	100
(*b*) Ester, 0·1 mole; catalyst, 0·2 mole; at 60°.				
$TiCl_4$ (6 hr.)	87·6	3·6	0·3	100
	87·7	4·1	0·2	150
	87·3	4·9	0·3	200
$ZrCl_4$ (4 hr.)	66·3	14·2	12·9	150
	68·8	15·3	13·7	300
$SnCl_4$ (18 hr.)	78·4	8·7	2·5	100
	74·8	9·1	2·3	150
	74·8	10·2	2·9	200

	Ketone (%)	*p*-Cresol (%)	Ester recovd. (%)	$PhNO_2$ (c.c.)
(*c*) Ester, 0·1 mole; at 60°.				
$TiCl_4$				
(0·1 mole, 6 hr.)	47·2	12·0	32·5	200
(0·2 mole, 6 hr.)	87·3	4·9	0·3	200
(0·3 mole, 6 hr.)	87·6	4·0	0·5	200
$ZrCl_4$				
(0·1 mole, 6 hr.)	41·1	13·4	42·9	300
(0·15 mole, 6 hr.)	59·9	17·9	18·0	300
(0·2 mole, 6 hr.)	75·4	13·5	5·1	300
(0·3 mole, 6 hr.)	75·1	13·8	5·8	300
$SnCl_4$				
(0·05 mole, 18 hr.)	52·7	14·8	16·9	100
(0·1 mole, 18 hr.)	74·6	9·5	2·6	100
(0·2 mole, 18 hr.)	78·4	8·7	2·5	100
(*d*) Ester, 0·1 mole; catalyst, 0·2 mole; 4 hr. at 60°.				
$TiCl_4$	81·3	5·5	4·5	150
$AlCl_3$	67·6	16·9	17·0	150
$ZrCl_4$	66·3	14·2	12·9	150
$SnCl_4$	33·4	14·0	44·3	150

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