[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ARMOUR AND COMPANY]

REARRANGEMENT OF PHENYL CAPRYLATE WITH FERRIC CHLORIDE, TITANIUM TETRACHLORIDE, STANNIC CHLORIDE, AND ZINC CHLORIDE

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When phenyl caprylate is rearranged in the presence of aluminum chloride it has been shown (1) that the ratio of para- to ortho-hydroxy ketones obtained is influenced by the amount of catalyst employed. Although metallic halides, other than aluminum chloride, have been somewhat extensively investigated as acylation catalysts very little work has been reported with regard to the effect of such catalysts upon the rearrangement of phenyl esters. Eijkman (2) studied the rearrangement of substituted phenyl esters in the presence of ferric and zinc chlorides. The rearrangement of phloroglucinol triacetate in the presence of ferric chloride and also of zinc chloride has been reported by Heller (3, 4). These catalysts were considered only slightly less active than aluminum chloride. Huber and Brunner (5) obtained a 25% yield of *p*-hydroxyacetophenone by the action of ferric chloride upon phenyl acetate, and a 16% yield of *p*-hydroxyisobutyrophenone from phenyl isobutyrate. They also reported a 28% yield of *p*-hydroxybenzophenone together with a small amount of *o*-hydroxybenzophenone by the action of ferric chloride upon phenyl benzoate. Sekera (6) has studied the transformation of aryl esters of carboxylic acids to hydroxyaryl ketones by the use of ferric chloride and also of zinc chloride, and considered neither as effective as aluminum chloride.

This previous work has indicated that both ferric and zinc chlorides produce less ester rearrangement than aluminum chloride. The quite recent work of Dermer and co-workers (7, 8) upon the acylation of toluene with acetyl chloride in the presence of various metallic halides has essentially confirmed the order of catalytic activity in acylation reactions as given by Calloway (9). The conclusions were that ferric chloride, titanium tetrachloride, stannic chloride, and zinc chloride are materially less active than aluminum chloride. Although these conclusions were drawn from acylation experiments, it seems likely that they would also apply to ester rearrangements. Since we have previously studied (1, 10) the rearrangement of phenyl caprylate with aluminum chloride under a variety of conditions, it appeared of interest to investigate this rearrangement further using several other metallic halides. Ferric chloride, titanium tetrachloride, stannic chloride, and zinc chloride were selected as the halides to be used in this investigation. The rearrangement of phenyl caprylate with various molecular ratios of these halides has, therefore, been studied and the results compared with those previously obtained with aluminum chloride under similar conditions.

Ferric chloride is a very active catalyst for the rearrangement of phenyl caprylate as can be seen from the data in Table I. For this particular rearrangement the activity of ferric chloride appears to be comparable to that of aluminum chloride.

Compared to aluminum chloride, ferric chloride gives a decidedly greater ratio of para- to ortho-hydroxy ketones for the same percentage of ester conversion. One very significant difference between ferric chloride and aluminum chloride is that when ferric chloride is used as the catalyst the p/o ratio of the product is less the greater the molecular amount of catalyst employed, while with aluminum chloride the reverse was found to be true (10). The reason for this is not apparent at the present time. In drawing conclusions from any comparisons of this nature it is necessary to establish the absence of any rearrangement of the products under the experimental conditions employed in the ester rearrangement. When ortho-hydroxycaprylophenone was heated for six hours at 70° in the presence of a molecular ratio of ferric chloride, an 84.5% recovery of the hydroxy ketone was obtained and no para isomer was found. A recovery of 94.5% of the para-hydroxy ketone was encountered under similar conditions. It is, therefore, apparent that these hydroxy ketones did not undergo rearrangement in our experiments.

TABLE I

REARRANGEMENT OF PHENYL CAPRYLATE BY FERRIC CHLORIDE: SOLVENT, TETRACHLOROETHANE

MOLECULAR RATIOS	TIME, AND TEMP., °C	% PARA	% ORTHO	% ESTER	RATIO P/O	REMARKS
Ester 1 $FeCl_3$ 0.5	6 hrs. 70	45.9	12.5	24.3	3.67	8.7% ortho residue
Ester 1 $FeCl_3$ 1	6 hrs. 70	52.3	18.6	9.1	2.81	15.0% ortho residue
Ester 1 $FeCl_3$ 1.3	6 hrs. 70	55.9	23.5	6.5	2.38	5.5% ortho residue
Ester 1 $FeCl_3$ 2	6 hrs. 70	44.5	28.7	6.7	1.55	3.2% ortho residue
Ester 1 $FeCl_3$ 2	3 days 40	57.7	27.4	4.4	2.10	4.1% ortho residue 4.2% para residue

That titanium tetrachloride is not as effective in promoting the rearrangement of phenyl caprylate as ferric chloride is apparent from a comparison of the results in Tables II and III with those in Table I. Several other significant differences between the action of these two catalysts are worthy of comment. The p/o ratio is much less when titanium tetrachloride is employed than when ferric chloride is used. Substantial amounts of caprylic acid and *p*-caprylylphenyl caprylate are present in the reaction products when titanium chloride is employed whereas these substances were not observed in rearrangements with ferric chloride. In similar rearrangements using aluminum chloride (1) caprylic acid was found to be one of the reaction products when less than molecular amounts of aluminum chloride were used or when aluminum chloride complexes were employed to effect the rearrangement. Its presence was ascribed to the slow rate of acylation of aluminum chloride complexes. *p*-Caprylylphenyl caprylate has been previously shown (1) to be one of the intermediate products in the rearrangement of phenyl caprylate with aluminum chloride and its presence is indicative of incomplete acylation.

TABLE II

REARRANGEMENT OF PHENYL CAPRYLATE BY TITANIUM TETRACHLORIDE: SOLVENT, TETRACHLOROETHANE

MOLECULAR RATIO	TIME, AND TEMP. °C.	% PARA	% ORTHO	% ESTER	% ORTHO	REMARKS
Ester 1 $TiCl_4$ 1	1.5 hrs. 30	0.9	18.7	57.6	0.05	2.7% *p*-Caprylylphenyl caprylate 3.2% caprylic acid.
Ester 1 $TiCl_4$ 1	3 hrs. 70	13.5	11.5	44.6	1.17	8.2% *p*-Caprylylphenyl caprylate 10.0% caprylic acid.
Ester 1 $TiCl_4$ 1	3 hrs. 100	22.7	36.6	7.0	0.62	7.7% *p*-Caprylylphenyl caprylate 6.2% caprylic acid.
Ester 1 $TiCl_4$ 1	6 hrs. 70	19.1	22.1	19.7	0.86	10.0% *p*-Caprylylphenyl caprylate 5.2% caprylic acid.
Ester 1 $TiCl_4$ 2	2 hrs. 30	0.9	4.1	79.1	0.22	1.8% *p*-Caprylylphenyl caprylate 5.5% caprylic acid.

TABLE III

REARRANGEMENT OF PHENYL CAPRYLATE BY TITANIUM TETRACHLORIDE: SOLVENT, NITROBENZENE

MOLECULAR RATIO	TIME, AND TEMP. °C.	% PARA	% ORTHO	% ESTER	RATIO P/O	REMARKS
Ester 1 $TiCl_4$ 0.5	6 hrs. 70	29.5	11.6	19.3	2.54	5.4% Caprylic acid.
Ester 1 $TiCl_4$ 1	6 hrs. 70	35.0	18.4	2.0	1.90	17.4% Caprylic acid.
Ester 1 $TiCl_4$ 1.3	6 hrs. 70	29.5	26.3	1.9	1.12	10.5% Caprylic acid.

When nitrobenzene is employed as the solvent (Table III) the p/o ratio is decidedly greater than when tetrachloroethane is used. This is in agreement with previous observations (1) with aluminum chloride. The decrease in the value of p/o with increased amounts of titanium tetrachloride was also observed with ferric chloride.

When carbon disulfide was employed as the solvent, 2.3% of *p*-hydroxycaprylophenone and 0.9% of the ortho isomer were obtained after six hours at 30° in the presence of titanium tetrachloride. Since 85.4% of the ester was recovered unchanged, it is evident that this reaction does not proceed as rapidly as in either tetrachloroethane or nitrobenzene.

In order to exclude the possibility of a rearrangement of the hydroxy ketones themselves in the presence of titanium tetrachloride *o*-hydroxycaprylophenone and *p*-hydroxycaprylophenone were treated with one molecular equivalent of titanium tetrachloride in nitrobenzene for six hours at 70°. The recovery of the former was 91.4% and of the latter 94.5%, thus showing the absence of rearrangement.

Stannic chloride is a much weaker catalyst than either ferric chloride or titanium tetrachloride for the rearrangement of phenyl caprylate as shown by the results in Table IV. In spite of the higher temperatures employed, the yield of ortho- and para-hydroxy ketones is quite small and a large proportion of the original ester is recovered unchanged. The presence of significant amounts of *p*-caprylylphenyl caprylate in the reaction products is noteworthy.

TABLE IV

REARRANGEMENT OF PHENYL CAPRYLATE BY STANNIC CHLORIDE: SOLVENT, TETRACHLOROETHANE

MOLECULAR RATIO	TIME, AND TEMP. °C.	% PARA	% ORTHO	% ESTER	REMARKS
Ester 1 $SnCl_4$ 0.5	7 hrs. 150	1.8	6.9	70.8	5.0% *p*-Caprylylphenyl caprylate.
Ester 1 $SnCl_4$ 1	7 hrs. 150	1.8	6.7	71.5	2.7% *p*-Caprylylphenyl caprylate.
Ester 1 $SnCl_4$ 2	7 hrs. 150	4.5	6.3	70.1	5.0% *p*-Caprylylphenyl caprylate.

Runs made with phenyl caprylate and zinc chloride in both tetrachloroethane and nitrobenzene under conditions varying from six hours at 100° to twenty-four hours at 160°, showed this catalyst to be much less effective than stannic chloride. In all cases the phenyl caprylate was recovered essentially unchanged, showing that zinc chloride is only very slightly catalytic under these conditions. The order of activity of the catalysts investigated is, therefore: $FeCl_3 > TiCl_4 > SnCl_4 > ZnCl_2$.

EXPERIMENTAL

The following procedures are typical examples of runs reported in this article.

Fries rearrangement of phenyl caprylate with ferric chloride. Anhydrous ferric chloride (16.2 g., 0.1 mole) was placed in a 200-cc. three-necked flask equipped with a mechanical stirrer, thermometer, and dropping-funnel. Tetrachloroethane (25 cc.) was then added, and phenyl caprylate (22 g., 0.1 mole) dissolved in 25 cc. of tetrachloroethane was admitted through the dropping-funnel (10 min.). The dropping-funnel was then replaced by a condenser and the reaction mixture heated for six hours at 70°. It was allowed to cool and hydrolyzed by pouring into 200 cc. of 5% hydrochloric acid. The tetrachloroethane was removed by steam distillation, the product cooled and extracted with ether. The ether solution was dried over anhydrous sodium sulfate. Unless this solution is dried, emulsions are obtained upon extraction of the para isomer. The ether solution was then extracted with four 25-cc. portions of 3% sodium hydroxide. The ether solution was then washed with water and these washings added to the alkaline extract.

The alkaline extract was acidified with hydrochloric acid, the excess ether removed by boiling, and the mixture cooled in order to solidify the *p*-hydroxy ketone. The mixture was then filtered and the product air dried. This product was weighed, recrystallized from petroleum ether, and identified as *p*-hydroxycaprylophenone by mixed melting point (yield 11.5 g., 52.3%).

The ether extract was dried with anhydrous sodium sulfate, filtered, and the ether removed in a Claisen flask in a water-bath. The product was distilled under reduced pressure and that boiling below 165° was retained. The percentage of phenyl caprylate in the mixture was then determined as previously described (10) (yields: 2.0 g. phenyl caprylate, 9.1%; 4.1 g. *o*-hydroxycaprylophenone, 18.6%).

Fries rearrangement of phenyl caprylate with titanium tetrachloride. Phenyl caprylate (22 g., 0.1 mole) was weighed into a 200-cc. three-necked flask and 25 cc. of tetrachloroethane added. Freshly distilled titanium tetrachloride (19.0 g., 0.1 mole) dissolved in 25 cc. of tetrachloroethane was added dropwise over a period of fifteen minutes. The reaction mixture was heated for six hours at 70°, after which it was cooled and hydrolyzed as previously described. The tetrachloroethane solution was washed several times with 5% hydrochloric acid in order to remove titanium salts. The omission of this step leads to the formation of emulsions during the separation of the isomers. The tetrachloroethane was removed by steam distillation and the separation and identification of the isomers carried out as previously described.

In the distillation of the *o*-hydroxy ketone-ester fraction a product boiling above 165° was obtained which, after purification, was identified as *p*-caprylylphenyl caprylate. Identification was made by mixed melting point. Caprylic acid in the para fraction was determined by titration. The yields were as follows: *p*-hydroxycaprylophenone, 4.2 g., 19.1%; *o*-hydroxycaprylophenone, 4.9 g., 22.3%; *p*-caprylylphenyl caprylate, 2.2 g., 10%; caprylic acid, 1.5 g., 6.8%.

Fries rearrangements of phenyl caprylate in the presence of stannic chloride and of zinc chloride. These arrangements and the separation of the products were conducted in a manner similar to that described above. When stannic chloride is employed it is advisable to remove the tin salts by washing with hydrochloric acid prior to steam distillation of the solvent. Failure to do this results in the formation of emulsions from which the product separates with great difficulty.

Attempted rearrangement of p-*hydroxycaprylophenone.* *p*-Hydroxycaprylophenone (22.0 g., 0.1 mole) was dissolved in 25 cc. of tetrachloroethane, and ferric chloride (16.2 g., 0.1 mole) added. The mixture was heated for six hours at 70° and steam distilled to remove the tetrachloroethane; alkaline extraction of the product gave 20.6 g., 94.5%, of *p*-hydroxycaprylophenone. No *o*-hydroxycaprylophenone was present.

Under similar conditions *o*-hydroxycaprylophenone was recovered unchanged (18.6 g., 84.5%).

Similar reactions using titanium tetrachloride as the catalyst and nitrobenzene as the solvent resulted in a recovery of 20.8 g., 94.5%, of *p*-hydroxycaprylophenone and 20.1 g., 91.4%, of *o*-hydroxycaprylophenone.

SUMMARY

1. A study of the rearrangement of phenyl caprylate in the presence of ferric chloride, titanium tetrachloride, stannic chloride, and zinc chloride has been made.

2. The activity of ferric chloride is comparable to that of aluminum chloride for this rearrangement; titanium tetrachloride is appreciably less active and both stannic and zinc chlorides are only weakly catalytic.

3. Ferric chloride produces a much higher ratio of para-hydroxy ketones to ortho-hydroxy ketones than aluminum chloride or titanium tetrachloride.

4. Caprylic acid and *p*-caprylylphenyl caprylate are among the products formed during the rearrangement of phenyl caprylate with either titanium tetrachloride or stannic chloride.

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