STUDIES ON ALCOHOLYSIS.

Part II. Alcoholysis in the absence of a Catalyst.

(By J. J. Sudborough, N. B. Bhagvat and V. K. Bhagvat.)

The processes of catalytic esterification and of hydrolysis of esters by means of mineral acids appear to resemble one another in many respects (Williams and Sudborough *J. C. S.*, 1912, *101*, 412), one of the most noticeable of which is that any substituent introduced into the molecule in a position in close proximity to the carboxylic group in the case of esterification, or of the alkylated carboxylic group in the case of esters, tends to diminish the velocity of either esterification or hydrolysis when mineral acids are used as catalysts. The retarding action is observed whether the substituents are of a positive or negative character and is most pronounced when the substituting groups are in the α position in open chain compounds and in the ortho position in aromatic compounds. The relative strengths of the organic acids are factors of very little importance in either process.

When the method of direct esterification, *i. e.* esterification in the absence of a catalyst is used, the relative strengths of the organic acids are of primary importance, and can completely mask any retarding effects due to the presence of substituents. This is extremely well shown in the case of the chloro-substituted acetic acids (Lichty, *Amer. Chem. J.*, 1895 *17*, 27 ; 1896, *18*, 590). In the hydrolysis of esters by means of water or dilute alkalis the rate of hydrolysis depends to a large extent on the relative strengths of the acids from which the esters are derived (Sudborough and Feilmann, Proc. Chem. Soc., 1897, *13*, 241; Williams and Sudborough *loc cit.* p 417).

A reaction which is to be regarded as analagous to the esterification of an organic acid and to the hydrolysis of an ester is the one usually termed alcoholysis, *viz*, the conversion of the ester derived from one alcohol into that derived from a homologue by treating the ester with the requisite alcohol in the presence of a catalyst.

Esterification $R.CO.OH + R'.OH = R.CO.OR' + H_2O$

Hydrolysis $R.CO.OR' + H.OH = R.CO.OH + R'OH$

Alcoholysis $R.CO.OR' + R''.OH = R.CO.OR'' + R'.OH$

These three reactions may be compared with the three corresponding reactions where monovalent metallic radicals replace the alkyl groups.

The process of esterification is then analagous to the neutralisation of a carboxylic acid by means of a metallic hydroxide, the process of hydrolysis is analagous to the hydrolytic dissociation of metallic salts and the process of alcoholysis analogous to double decomposition between a salt and a metallic hydroxide.

The catalysts usually employed to induce alcoholysis are small amounts of the following:—

(a) Mineral acids such as hydrogen chloride or sulphuric acid (Patterson and Dickenson, J. C. S., 1901, *79*, 280)

(b) Alkali hydroxides or alkyl-oxides *e. g.*, sodium methoxide or ethoxide (Purdie, J. C. S., 1885, *47*, 862; 1887, *51*, 627; 1888, *53*, 391; Claisen, *Ber.*, 1887, *20*, 646; Conrad and Epstein, *ibid* 3057; Peters *ibid* 3323; Kremann, *Monatsh.*, 1905, *26*, 783; 1908, *29*, 23.)

(c) Ammonia (Leuchs and Theodorsen, *Ber.*, 1910, *43*, 1239.

The results of Kolhatkar's investigations on the velocities of typical cases of alcoholysis (This Journal Vol. 1 p 107 and *J. C. S.*, 1915, *107*, 921) establish still more clearly the relationships between catalytic esterification and catalytic alcoholysis with hydrogen chloride.

Direct alcoholysis, or alcoholysis in the absence of a catalyst, can apparently take place. In his researches on the action of traces of alkali hydroxides and alkyloxides on mixtures of esters and alcohols, (Purdie J. C. S., 1887, *51*, 631) carried out a number of blank experiments by fractionally distilling mixtures of an ester and an alcohol without the addition of a catalyst. Among the mixtures distilled were the following:—(a) ethyl oxalate and amyl alcohol (b) amyl oxalate and ethyl alcohol (c) amyl oxalate and methyl alcohol (d) ethyl acetate and amyl alcohol (e) amyl acetate and ethyl alcohol. Purdie states that in all cases the transformation of the ester was small when compared with the amount transformed under similar conditions but in the presence of a small amount of an alkali hydroxide. In the case of ethyl acetate and amyl alcohol the amount of ester transformed is stated to be 6·7 per cent.

Experiments of a somewhat similar nature have been made by others. Friedel and Crafts (*Annalen,* 1864, *130,* 198; 1864, *131,* 55; 1865, *133,* 207) show that ethyl iodide and ethyl silicate react with amyl alcohol at 160—180° yielding appreciable amounts of the corresponding amyl esters. They also state that ethyl acetate and amyl alcohol behave in a similar manner but give no details. With ethyl oxalate and amyl alcohol at 250-259° the products are carbon monoxide and dioxide, ethyl alcohol, unaltered ethyl oxalate, amyl oxalate and probably ethyl amyl oxalate. Ethyl chloride and ethyl benzoate do not react with amyl alcohol to any appreciable extent. These authors state that no free acid exists in the mixtures of esters and alcohols after heating, so that presumably the reaction is a direct replacement of one alkyl group by another. In their later experiments it is shown that alcoholysis can occur between ethyl benzoate and amyl alcohol at temperatures of 210-240° and similarly for ethyl acetate and amyl alcohol. In nearly all their experiments Friedel and Crafts isolated and analysed the ester obtained by exchange of alkyl groups, whereas Purdie determined the amounts of ester present in the different fractions by saponification with standard alkali.

According to Friedel and Crafts ethers do not exchange radicals when heated with alcohols at 200-250° during 75 hours, whereas Bachman (*Annalen,* 1883, *218,* 38), states that an acetal $\mathrm{CH_3.CH_2}{<}\genfrac{}{}{0pt}{}{\mathrm{OR}}{\mathrm{OR}}$ readily reacts with an alcohol R′OH at 120° yielding the homologue $\mathrm{CH_3.CH}{<}\genfrac{}{}{0pt}{}{\mathrm{OR'}}{\mathrm{OR'}}$. Bachmann (p. 50) also states that mixtures of alkyl acetates and alcohols when heated to the boiling point of the mixture undergo no change.

Rose (*Annalen,* 1880, *205,* 240), claims that in the case of alkyl carbonates a complex radical like propyl is capable of replacing a simple group like methyl when a suitable mixture is heated with the requisite alcohol for two days at 100°.

The action of menthol on various esters has been studied polarimetrically by Bruni and Contardi (*Atti R. Accad. Lincei,* 1906, [v], *15,* (*i*), 637; Abstr. J. C. S., 1906, (*i*), 621.) They find that after several hours at 80° or 100° menthol has no action on ethyl acetate or ethyl benzoate, but that double decomposition proceeds at an appreciable velocity when ethyl exalate, ethyl malonate or ethyl acetoacetate is heated at 100° with menthol; in the later case equilibrium is attained after 24 hours.

The general conclusion to be drawn from all these experiments is that in the absence of a catalyst alcoholysis can take place in the case of most esters provided a sufficiently high temperature is used, and Friedel and Crafts make the statement that esters which are rapidly decomposed by water undergo alcoholysis most readily. The conflicting statements with regard to the alcoholysis of alkyl acetates is mainly due to the fact that the change is largely dependent upon temperature and length of time of heating and that different workers have used different temperatures.

In order to ascertain whether the process of alcoholysis without a catalyst is comparable with direct esterification or with hydrolysis of esters by means of water, we have carried out a series of experiments with certain pairs of esters. If the three processes are analagous it should follow that alcoholysis proceeds more readily with esters of strong acids than with those derived from feeble acids.

For purposes of comparison we selected the methyl or ethyl esters of the following three pairs of acids :—

(a) Oxalic and succinic
(b) Formic and acetic
(c) Pyruvic and laevulic.

The dissociation constants of these six acids are :—

Oxalic	10·0	Formic	0·0214	Pyruvic	0·560
Succinic	0·0066	Acetic	0·0018	Laevulic	0·0025

so that in each pair one ester was derived from a relative strong and one from a relatively weak acid, although in each pair the acids were of the same type *viz.*, first pair dibasic acids, the 2nd pair monobasic fatty acid and the 3rd pair monobasic ketonic acids.

The general method of procedure was as follows :—A mixture of the methyl or ethyl ester and alcohol, usually amyl alcohol, in the proportion of about four molecules of alcohol to one of ester, was heated to a given temperature either in sealed tubes or, with high boiling esters, in open vessels attached to a reflux apparatus, during 40—60 hours, and afterwards the mixture was carefully fractionated. A blank experiment was always made by taking a mixture of ester and alcohol in the same proportions as in the actual experiment and submitting the mixture to fractional distillation without any previous heating. It was hoped that a comparison of the fractions obtained from the actual experiment and the blank would give a clear indication as to the amount of change produced by the prolonged heating.

The results obtained (see sections I—VI. in experimental part) indicate that the prolonged heating of a mixture of ethyl acetate and amyl alcohol, ethyl succinate and amyl alcohol or of ethyl laevulate and amyl alcohol produce but little change, as the fractions obtained closely resemble those isolated in the blank experiments.

In the case of ethyl acetate and amyl alcohol the fraction with a boiling point corresponding with amyl alcohol contained a small amounts of ester *viz.*, 0·24 per cent. calculated as ethyl acetate. In the actual experiment a small amount of amyl acetate appears to have been formed and also a small amount of ethyl alcohol, but the amounts were exceedingly small and it was not possible to isolate either in a pure state.

With the esters derived from formic, oxalic and pyruvic acids the fractions obtained in the actual experiments differed appreciably from those obtained in the blank. Small amounts of methyl or ethyl alcohol were obtained and their presence proved by conversion into *p*-nitrobenzoates or by other methods and the high boiling fractions contained appreciable amounts of esters presumably the amyl ester corresponding with the methyl or ethyl ester taken.

Our results, in combination with those of Friedel and Crafts and of Bruni and Contardi, appear to prove conclusively that the esters derived from relatively strong organic acids enter into double decomposition with monohydric alcohols much more rapidly than do the corresponding esters of feeble acids. The esters which according to Bruni and Contradi are reactive towards menthol at 100° are derived from the relatively strong acids—oxalic, $K=10·0$; malonic, $K=0·163$ and acetoacetic K=unknown—and those which are indifferent are derived from the feeble acids—acetic $K=0·0018$ and benzonic $K=0·0060$.

As the chloroacetic acids are much stronger acids than acetic acid *e. g.*, dichloracetic acid $K=5·14$ and trichloracetic acid $K=121$, the idea of using the esters of these acids for comparison with ethyl acetate naturally suggested itself. A few experiments were made with methyl dichloroacetate and *n*-propyl alcohol by boiling for 30 hours and then distilling. The higher fractions contained much smaller percentages of chlorine than are required for propyl dichloroacetate indicating the presence in the fractions boiling at 170—180° and 193—194° of compounds of the type $C_3H_7.\ CHCl.\ CO_2C_3H_7$ and $CH\ (C_3H_7)_2.\ CO_2C_3H_7$.

EXPERIMENTAL.

Methyl oxalate and isobutyl alcohol.

A. Blank. A mixture of 6 grams of pure methyl oxalate melting at 54° and boiling at 163° under 682 mm. pressure and 29 grams of *iso*-butyl alcohol boiling at 103·6 was distilled. A rod and disc fractionating column was first used and 27 grams boiling at 103—105° were collected, after the removal of the column 2·5 grams boiling at 105—163° passed over and finally 4·5 grams at 163—167°, the greater part of which solidified on cooling and then melted at 54°.

B. A similar mixture consisting of 30 grams of methyl oxalate and 135 grams of *iso*-butyl alcohol was boiled for 38 hours in a reflux apparatus protected with a calcium chloride tube and the mixture was afterwards fractionated. The following fractions were collected :—

No of fraction.	Boiling point in degrees centigrade.	Weight in grams.
1	70—80	3·0
2	81—103	18·0
3	103—105	101·5
The rod and disc column was removed.		
4	105—163	2·5
5	163—192	9·5
6	192—195	9·1
7	195—208	5·5
8	208—215	4·0
9	215—221	3·0
10	221—224	3·5
11		
Residue	—	1·0
Total		160·6

Fraction No. 1 boiling at 70—80° was warmed with *p*-nitrobenzoyl chloride and the product crystallised from alcohol. Colourless needles melting at 95° were obtained. The correct melting point of methyl *p*-nitrobenzoate is 96°.

Fraction No. 3 was practically pure *iso*-butyl alcohol. Fraction No. 5 when cold deposited 1·05 grams of colourless crystals of dimethyl oxalate melting at 53·6°

Fraction No. 6 was saponified with 0·1253 N. barium hydroxide solution with the following results :—

(a) 0·3494 gram required 35·43 c.c. of the standard barium hydroxide.

(b) 0·2516 gram required of 25·70 c.c. do.

The theoretical values for methyl *iso*-butyl oxalate, $CO_2Me.CO_2C_4H_9$, are (a) 34·9 and (b) 25·1.

Fraction No. 10 boiling at 221—224° was also saponified with the same barium hydroxide solution.

(a) 0·2850 gram required 22·08 c.c. of barium hydroxide.

(b) 0·2808 „ „ 22·80 do. do.

The theoretical values for di-*iso*-butyl oxalate are (a) 22·51 and (b) 22·28. The results show that when the mixture which had not been heated previously was fractionated little change took place, the highest boiling point was only a degree or two above that of methyl oxalate; when, however, the mixture was boiled for 38 hours appreciable change occurred ; methyl alcohol could be detected in the lowest fraction and di-butyl oxalate in the highest, and an appreciable amount of what appears to be methyl *iso*-butyl oxalate in the intermediate fraction.

2. *Ethyl Succinate* and *iso-Amyl Alcohol.* The ester used was quite neutral and boiled at 209—209.5°. The alcohol was dehydrated with potassim hydrogen sulphate and distilled at 127.5—128°.

A. *Blank.*

10 grams of ester and 48 grams of *iso*-amyl alcohol were fractioned with the following results :—

Fraction.	Boiling point. in degrees centigrade	Weight in grams.
1	126—128	36
2	128—209	6
3	209—210	6
Residue	...	1
Total		49 grams.

The first fraction was not absolutely free from ester and when saponified with standard barium hydroxide the amount of alkali used indicated the presence of 0·21 per cent. of ethyl succinate. In a similar manner fraction No. 2 was found to contain 50 per cent. of ester calculated as ethyl succinate and fraction 3 showed the presence of 99 per cent. of ethyl succinate.

B. Thirty grams of ethyl succinate and 120 grams of *iso*-amyl alcohol were boiled for 36 hours in a flask attached to a reflux condenser and the mixture then fractioned, using a rod and disc column until the temperature reached 128°.

Fraction.	Boiling point in degrees centiegrade.	Weight in grams.
1	126—128	115·5
2	128—209	10·5
3	209—211	18·5
4	211—214	3·5
Residue	...	1·5
Total		149·5 grams.

The saponification value of each fraction was determined.

No. 1 5·475 grams required 0·98 c.c. of 0.1252 N. baryta, thus indicating the presence 0·19 per cent. of ester (calculated as ethyl succinate) in the fraction.

No. 2. 0·3160 required 14·2 c.c. of the same baryta, indicating the presence of 49·05 per cent. of ester.

No. 3. 0·3592 required 32·64 c.c. equivalent to 99·0 per cent. of ester.

No. 4. 0·3796 required 34·50 c.c. equivalent to 99·1 per cent. of ester.

It will be noticed that 3·5 grams of ester boiling 2 or 3 degrees higher than the original ethyl succinate were obtained, but the saponification value for the fraction was identical with that of the fraction boiling at 209—211°.

Ethyl Acetate and *iso-amyl alcohol.*

The ethyl acetate was treated with calcium chloride, dehydrated with potassium hydrogen sulphate and the fraction boiling at 74—75° used for the experiments.

A. Blank.

A mixture of 45·2 grams of ethyl acetate and 136·1 grams of *iso*-amyl alcohol was fractionated using a fractionating column.

The following fractions were collected :—

Fraction.	Boiling point in degrees centigrade.	Weight in grams.
1	70— 80	33·5
2	80—110	12·7
3	110—127	1·8
4	127—129	121·4
Residue	...	8·3
Total		177·7 grams.

The fourth fraction when saponified showed the presence 0·24 per cent. of ethyl acetate whereas the 8·3 gram of residue were free from ester, thus proving the absence of amyl acetate 138·5° which boils at 760mm.

B. A mixture of 53·6 grams of ethyl acetate and 155·2 grams of *iso*-amyl alcohol was heated in sealed tubes for 44 hours at 110—120° and then carefully fractionated. The results are given in table I.

4. *Ethyl Formate* and *iso-amyl alcohol*.

The ethyl formate was a sample of Kahlbaum's ester and was freshly distilled before use, its boiling point was 52°.

A. Blank. A mixture of 15 grams of ester and 47 grams of *iso*-amyl alcohol was fractionated with the following results :—

Fraction	Boiling point in degrees centigrade.	Weight in grams.
1	50-60	13 grams
2	60-126·6	3 ,,
3	126·6	41 ,,
Residue	...	Nil

The first and third fractions were saponified with the following results :—

No. 1. 0·2058 required 20·93 c.c. of 0·1253 N. barium hydroxide indicating the presence of 94·2 per cent. of ethyl formate.

No. 3. 5·45 grams required 3·8 c.c. of the same baryta indicating the presence of 0·64 per cent. of ester calculated as ethyl formate.

TABLE I.

ETHYL ACETATE AND AMYL ALCOHOL.

I. Fractionation with Hempel's fractionating column.			II. Fractionation (without column.)			III. Fractionation (without column.)			
Fraction No.	Boiling point in degrees cent.	Weight in grams.	Fraction No.	Boiling point in degrees cent.	Weight in grams.	Fraction No.	Boiling point in degrees cent	Weight in grams.	% of ester.
1	70— 73	0·58	1	69— 72	3·68	1	68— 72	5·02	94·45 as ethyl acetate
2	73— 80	15·65	2	72— 82	27·72	2	72— 75	18·87	97·12 do.
3	80—100	31·45	3	82— 92	9·14	3	75— 80	12·95	
4	100—125	19·60	4	92—102	5·00	4	80— 90	6·69	
5	125—128	122·00	5	102—125	5·63	5	90—127	7·45	
Residue	—	9·00	6	125—130	140·20	6	127—129	140·50	0·67 as amyl acetate.
			Residue	—	2·71	Residue	—	0·82	3·58 do.
Total		... 198·28	Total		... 194·08	Total		... 192·30	

B. A mixture of 25 grams of the same ester and 85 grams of *iso*-amyl alcohol was heated in a sealed tube for 36 hours at 110-120° and the mixture then fractionated when the following fractions were collected :—

Fraction	1	2	3	4	5	6	7	8	9
Boiling point	50-60	61-75	75-77	77-118	118-120	120-121	121	121-126·6	126·6
Weight	3·0	4·5	7·0	2·0	9·5	6·0	19·0	15·0	26·0

Residue 9·0 Total 101 grams.

The following fractions were hydrolysed using 0·1253 N· baryta.

No. 1 0·1798 gram required 15·55 c.c. of baryta corresponding with an 80·1 per cent. content of ethyl formate.

No. 3. 0·3276 gram required 4·04 c.c. of baryta indicating the presence of only 11·44 per cent. of ethyl formate.

No. 5. 0·2754 gram required 10·73 c.c. of baryta indicating the presence of 56·7 per cent. of ester calculated as *iso*-amyl formate the boiling point of which is 123·3 under 760 mm pressure.

No. 7. 0·3544 gram required 11·82 c.c. of baryta indicating the presence of 48·5 per cent. of *iso*-amyl formate.

No. 9. 5·1584 grams required 19·95 c.c. of baryta corresponding with 5·34 per cent. of amyl formate.

As fraction No. 3 boiling at 75-77° contained only 11·42 per cent of ethyl formate and as it was obvious that the remainder could not be *iso*-amyl alcohol the amount of free alcohol was determined by Dupré's method.

The mixture was first hydrolysed with baryta and the total alcohol oxidised to acetic acid by means of chromic acid mixture. The acetic acid was distilled over and titrated with standard alkali. From the acid thus obtained the total ethyl alcohol after saponification was calculated and this less the amount due to the ethyl formate gave the amount of free alcohol in the fraction. This was found to be 85·2 per cent, thus indicating that an appreciable amount of ethyl alcohol had been liberated.

5. *Ethyl laevulate and iso-Amyl Alcohol*

The ethyl laevulate was prepared from silver laevulate and ethyl iodide using benzene as a diluent. The yield was nearly theoretical and the product distilled at 111-112° under 34 mm. pressure; the purity determined from its saponification value was 99·5 per cent.

A. Blank.

A mixture of 12 grams of ester and 30 grams of *iso*-amyl alcohol was fractionated with the following results:—

Fraction.	Boiling point in degrees centigrade.	Weight in grams.
1	90—127·2	A few drops
2	127·2—129	27·5
3	129—199·6	3·5
4	199·6—201	9·5
Residue	...	1·0

The rod and disc column was removed after the first two fractions had been collected.

Fraction No. 4 gave the following result on saponification. 0·4184 gram required 23·43 c.c. of 0·1252 N. barium hydroxide solution corresponding with 101·1 per cent. of ethyl laevulate.

B. 1. A similar mixture of 25 grams of ester and 65 grams of *iso*-amyl alcohol was boiled gently during 36 hours and the mixture then distilled and the following fractions collected; the fractionating column was removed when a temperature of 129° was reached.

Fraction	Boiling point in degrees centigrade	Weight in grams.
1	80—127	a few drops.
2	127—129	60·5
3	129—199·6	5·0
5	199·6—202·6	15·5
5	202·6—209	5·0
Residue		1·5

In the experiment the last fraction collected boiled several degree higher than the original ester, and may have contained traces of *iso*-amyl laevulate.

The following saponification values were obtained.

Fraction 4. 0·4940 gram required 27·25 c.c. of 0·1252 N. barium hydroxide solution corresponding with 99·6 per cent.

Fraction 5. 0·4892 gram required 26·92 c.c. of the same baryta corresponding with 95·4 per cent of ethyl laevulate.

B 2. A second experiment was made in which after removal of the fractionating column at 130°, the residue was distilled under reduced pressure. The following fractions were obtained from a mixture of 16 grams of ester and 39·1 grams of *iso*-amyl alcohol after a period of 41 hours' gentle boiling.

Fraction.	Temperature in degrees centigrade	Pressure in mm.	Weight in grams.
1	110—125	684	1·33
2	125—127·5	„	3·21
3	127·5—128	„	20·0
4	128—130	„	7·0
5	60—108	31	7·02
6	108—110	„	10·45
Residue	...	...	3

Fraction No. 6 and the residue were redistilled under reduced pressure. Result of saponification.

Fraction.	Boiling point.	Pressure.	Weight.	Per cent of ester.
1	115—117	39	6·27	97 per cent. of ethyl laevulate
2	110—115	34·5	1·93	87·9 per cent. of ethyl laevulate or 12·5 per cent of amyl laevulate

6. *Ethyl Pyruvate and iso-Amyl Alcohol*

The ester used for these experiments was prepared by Simon's method (*Bull. Soc. Chim.*, 1895, [iii], *13*, 477). The yield of crude product was 60-70 per cent. of the theoretical, but the ester always contained free acid in some cases as much as 15-20 per cent. The acid was removed by dissolving the liquid in dry ether and leaving in contact with anhydrous sodium carbonate for 30 minutes, and the operation was repeated two or three times until the ester was neutral to litmus. Prolonged contact with the carbonate diminished the yield of ester. The boiling point of the ester was 72-73^{c}/34-35 mm and its purity was checked by saponification with standard barium hydroxide solution.

A. Blank.

A mixture of 10 grams of pure ester and 30·4 grams of *iso*-amyl alcohol was distilled in the same manner as the ethyl laevulate mixture and the following fractions were obtained :—

Fraction.	Boiling point in degrees sentigrade.	Pressure in mm	Weight in grams.
1	115—125	686	6·3
2	125—126	686	29·0
3	60—70	39	2·6
4	70—80	39	1·2
Residue	...	...	0·6

These fractions were again distilled and the following collected :—

Fraction.	Boiling point in degrees centigrade	Pressure in mm	Weight in grams.
1	70—125	683·4	1·72
2	125—126	683·4	3·34
3	126—127·5	683·4	22·1
4	40—64	33	1·5
5	64—67	33	9·5
Residue	...	...	0·85

Fraction number one gave the idoform reaction. Fractions 3, 4 and 5 were saponified with standard barium hydroide and gave the following values for ethyl pyruvate. No. 3, 21·3 per cent., No. 4, 31·60 per cent., and No. 5, 32·2 per cent.

It is thus clear that separation of ester and emyl alcohol was very incomplete.

B. A mixture of 12·5 grams of ethyl pyruvate and 37 grams of *iso*-amyl alcohol was heated in a sealed tube for 48 hours at 120—130° and then fractionated. As the result of the prolonged heating the liquid assumed a pale yellow colour.

The following fractions were obtained :—

Fraction.	Boiling point in degrees centigrade.	Pressure in mm.	Weight in grams.
1	70—110	689	2·0
2	110—126	689	8·7
3	126—128	689	15·4
4	50—67	32	9·3
5	67—75	32	5·7
6	75—110	32	4·5
Residue	—	—	1·6

The first two fractions were refractionated and the fraction boiling at 80—90 weighed 1·85 gram and gave the idoform reaction.

The 5th and 6th fractions were also refractionated and a fraction boiling at 102—104° under 35 mm. pressure collected. The saponification of the fraction with standard barium hydroxide indicated the presence of 74·6 per cent. of ester calculated as *iso*-amyl pyruvate. As this fraction still contained appreciable amounts of amyl alcohol attempts were made to remove this by means of calcium chloride but without success as the saponification value still indicated the presence of only 76 per cent. of amyl pyruvate.

The presence of ethyl alcohol in the lowest fraction and the formation of a high boiling fraction rich in esters support the view that an appreciable amount of alcoholysis had taken place although pure amyl pyruvate could not be isolated.

In a second experiment the mixture was boiled in a reflux apparatus for 36 hours and then fractionated. The first fraction boiling at 65—85° reacted with *p*-nitrobenzoyl chloride yielding an ester which crystallised in yellow prisms melting at 56—57°. The 6th fraction passed over at 90—107° under 32 mm. pressure, was free from acid and gave a saponification number corresponding with 95 per cent. of amyl pyruvate. The weight of the fraction was only 3 grams and a large quantity of residue was obtained which decomposed at temperatures above 110°/32 mm.

7. *Methyl o-nitrobenzoate and amyl alcohol.*

The ester boiled at 175° under 32 mm. pressure and when saponified 0.5322 grams required 23·65 c.c. of 0·1252 N. barium hydroxide the theoretical amount being 23·48 c.c.

In the blank experiment 7 grams ester were distilled with 59 grams of the amyl alcohol and 5·5 grams of pure ester were recovered boiling at 175°/32 mm. In the actual experiment the mixture, consisting of 15 grams of ester and 100 grams of amyl alcohol, was heated to gentle ebullition during 36 hours and then fractionated. 125 grams of ester boiling at 178—180°/29 mm. were recored and 0·5256 grams of the ester required 23·18 c.c. of the standard barium hydroxide of saponification as compared with the theoretical value 23·19 c.c., thus indicating that practically no alcoholysis had taken place.

8. *Alkyl Chloroacetates.*

(a) Ethyl trichloroacetate and methyl alcohol.

The ethyl ester prepared by the Fischer and Speier method boiled at 160—161°/680 mm. A mixture of 11 grams of the ester and 55 grams of methyl alcohol was boiled gently for 8 hours and then distilled. The boiling point of the last fraction was 159° whereas that of the pure ethyl ester is 160—161° and of the methyl ester 154°.

(b) Methyl dichloroacetate and *n*-propyl alcohol.

A mixture of 10 grams of the ester (b. p. 141-142°/680 mm) and 90 grams of *n*-propyl alcohol (b. p. 94-95°/680 mm) was boiled for 30 hours. The liquid was tested for free hydrochloric acid but none was found and was then distilled. The last fraction collected boiled at 170-180° and 0·2020 grams gave 0·3020 gram of silver chloride. The compound $CHCl_2{\cdot}CO_2C_3H_7$ requires 41·5 per cent. of chlorine and the compound $C_3H_7O{\cdot}CHCl{\cdot}CO_2Me$ requires 21·2 per cent of chlorine.

The small amount of residue contained only 11·5 per cent of chlorine.

DEPARTMENT OF GENERAL AND ORGANIC CHEMISTRY,
INDIAN INSTITUTE OF SCIENCE,
BANGALORE.