

Studies on Alcoholysis III. The Alcoholysis of Aromatic Esters
and the inhibiting influence of Ortho-substituents.

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INTRODUCTION.

Purdie (J. C. S., Trans., 1885, 47, 859) has shown that the ethyl esters of fumaric, oxalic and cinnamic acids are transformed into the corresponding methyl esters when warmed with methyl alcohol and a small amount of sodium methoxide. In a later paper (*ibid.*, 1887, 51, 627) it is stated that the reaction is probably due to the formation of an additive compound between the original ester and the methoxide. It is pointed out that potassium carbonate or barium hydroxide may be used in place of sodium methoxide, but that sodium carbonate or borate acts less readily, and that oxides of lead and zinc are extremely slow in bringing about the transformation. In a third paper, (Purdie and Marshall, *ibid.*, 1888, 53, 391) a resumé is given of previous work conducted by Friedel and Crafts, Rose, Bachmann and Bertoni on the action of alcohols on esters without the use of an alkali. The general conclusions drawn by Purdie and Marshall are:—(1.) The reaction does not depend merely on the relative amounts of ester and alcohol, but also on the specific affinities of the alkyl groups concerned. (2.) The reaction represented by the equation, $XCO_2R + R^1OH = XCO_2R^1 + ROH$, occurs most readily when R is simple compared with R¹.

Conrad and Epstein (Ber., 1887, 20, 3057) and Th. Peters (*ibid.*, 3325) have shown that esters of acetoacetic acid may be transformed in a similar manner and analogous phenomena have been observed by Kremann (Monatsh., 1905, 26, 783) between triacetin, ethyl alcohol and alkalis.

Claisen (Ber., 1887, 20, 648) has shown that alcoholysis may also be effected in the aromatic series. Thus benzyl benzoate and sodium methoxide yield methyl benzoate and benzyl alcohol on the addition of acetic acid. The same author obtained a solid

additive compound, $C\text{ Ph} \begin{cases} \text{ONa} \\ \text{OMe} \\ \text{OC}_7\text{H}_7 \end{cases}$, from methyl benzoate, benzyl

alcohol and sodium. Numerous other additive compounds of the same type were prepared, and the correctness of Purdie's conclusion that the transformation is preceded by the formation of such additive compounds, may be regarded as established.

In 1898 Pechmann (Ber., 31, 501) was able to show, that the esters of di-ortho-substituted benzoic acids do not yield additive compounds with sodium ethoxide.

The only inference to be drawn from Purdie's conclusion and Pechmann's statement, is that the methyl esters of di-ortho-substituted benzoic acids should not be transformed into the corresponding ethyl esters when warmed with sodium ethoxide and similarly for the conversion Of ethyl into methyl esters.

Some of the experiments described in this paper were undertaken with the object of testing this inference. The results obtained prove, beyond doubt, that the conclusion is correct. We have been able to transform the following methyl esters into ethyl esters by means of sodium ethoxide and ethyl alcohol.

1. Methyl 3:5-dibromobenzoate
2. Methyl 3:5-dibromo-4-aminobenzoate .
3. Methyl *p*-nitrobenzoate
4. Methyl *m*-nitrobenzoate
5. Methyl 3:5-dinitrobenzoate

and the following ethyl esters into methyl esters by means of sodium methoxide and methyl alcohol.

1. Ethyl *p*-toluate
2. Ethyl *p*-bromobenzoate
3. Ethyl 3:5-dibromo-4-aminobenzoate
4. Ethyl 3:4:5-tribromobenzoate
5. Ethyl *p*-nitrobenzoate
6. Ethyl *m*-nitrobenzoate
7. Ethyl 3:5-dinitrobenzoate
8. Ethyl 2:4-dinitrobenzoate

Also the following methyl into the corresponding isobutyl esters by means of isobutyl alcohol and sodium isobutyl oxide.

1. Methyl *p*-nitrobenzoate
2. Methyl 3:5-dinitrobenzoate

and the ethyl esters mentioned below into the corresponding *n*-propyl esters by means of *n*-propyl alcohol and sodium *n*-propyl oxide.

1. Ethyl *p*-nitrobenzoate
2. Ethyl 3:5-dinitrobenzoate

Also, the following *n*-propyl esters into the corresponding ethyl esters by means of ethyl alcohol and sodium ethoxide.

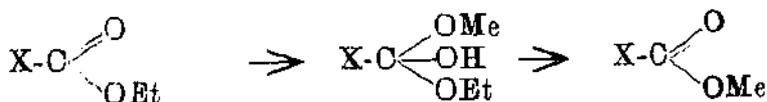
1. *n*-Propyl *p*-nitrobenzoate
2. *n*-Propyl 3:5-dinitrobenzoate

and the following isobutyl esters into the corresponding methyl esters by means of methyl alcohol and sodium methoxide.

1. Isobutyl *p*-nitrobenzoate
2. Isobutyl 3:5-dinitrobenzoate

All attempts to transform esters of the following di-ortho-substituted benzoic acids, proved fruitless:—2:6-dibromobenzoic; 2:4:6-tribromobenzoic; 2:4:6-tribromo-3-aminobenzoic; 2:3:4:6-tetrabromobenzoic; 2:6-dinitrobenzoic; 2:4:6-trinitrobenzoic.

Patterson and Dickinson (J. C. S., Trans., 1901, 79, 280) have proved that ethyl tartarate, when boiled with a four per cent solution of hydrogen chloride in methyl alcohol, is transformed into methyl tartarate. This process is exactly similar to E. Fischer and Speier's well known esterification method (Ber., 1895, 28, 3252) and it is probable that the mechanism of the two reactions is similar. It is now generally accepted that, in the conversion of an acid into its ester by the catalytic process, an additive compound of the acid and alcohol is first formed and then water is eliminated from this. (Wegscheider, Monatsh., 1895, 16, 137). If the conversion of ethyl tartarate into methyl tartarate by Patterson's method is analogous, we must assume the formation of an additive compound of the ethyl ester with methyl alcohol and subsequent elimination of ethyl alcohol.



It is certain that the esters of di-ortho-substituted benzoic acids would be incapable of forming such additive products and should therefore not be transformed by Patterson's method.

The experiments described in this paper clearly show that the ethyl or methyl esters of substituted benzoic acids, which contain no ortho-substituents are readily transformed when

boiled with methyl or ethyl alcohol, saturated at the boiling point with hydrogen chloride. Esters which contain two ortho-substituents cannot be transformed by such a method and esters with one ortho-substituent appear to be more difficult to transform than those which are not ortho-substituted.

The following esters have been transformed by the hydrogen chloride method :—

1. Methyl *p*-toluate \rightarrow Ethyl
2. Ethyl *p*-toluate \rightarrow Methyl
3. Methyl *m*-bromobenzoate \rightarrow Ethyl
4. Ethyl *m*-bromobenzoate \rightarrow Methyl
5. Methyl 3:5-dibromo-4-aminobenzoate \rightarrow Ethyl
6. Ethyl 3:5-dibromo-4-aminobenzoate \rightarrow Methyl
7. Methyl 3:4:5-tribromobenzoate \rightarrow Ethyl
8. Ethyl 3:4:5-tribromobenzoate \rightarrow Methyl
9. Methyl *p*-nitrobenzoate \rightarrow Ethyl
10. Methyl *p*-nitrobenzoate \rightarrow Isobutyl
11. Ethyl *p*-nitrobenzoate \rightarrow Methyl
12. Ethyl *p*-nitrobenzoate \rightarrow *n*-Propyl
13. *n*-Propyl *p*-nitrobenzoate \rightarrow Ethyl
14. Isobutyl *p*-nitrobenzoate \rightarrow Methyl
15. Methyl *m*-nitrobenzoate \rightarrow Ethyl
16. Ethyl *m*-nitrobenzoate \rightarrow Methyl
17. Methyl 3:5-dinitrobenzoate \rightarrow Ethyl
18. Methyl 3:5-dinitrobenzoate \rightarrow Isobutyl
19. Ethyl 3:5-dinitrobenzoate \rightarrow Methyl
20. Ethyl 3:5-dinitrobenzoate \rightarrow *n*-Propyl
21. *n*-Propyl 3:5-dinitrobenzoate \rightarrow Ethyl
22. Isobutyl 3:5-dinitrobenzoate \rightarrow Methyl
23. Methyl 2:4-dinitrobenzoate \rightarrow Ethyl
24. Ethyl 2:4-dinitrobenzoate \rightarrow Methyl

All attempts to transform the following were without effect.

1. Methyl 2:6-dibromobenzoate
2. Methyl 2:4:6-tribromobenzoate
3. Ethyl 2:4:6-tribromobenzoate

4. Methyl 2:4:6-tribromo-3-aminobenzoate
5. Ethyl 2:4:6-tribromo-3-aminobenzoate
6. Methyl 2:6-dinitrobenzoate
7. Ethyl 2:6-dinitrobenzoate
8. Methyl 2:4:6-trinitrobenzoate

Several experiments were made by boiling an ester with a four per cent alcoholic solution of hydrogen chloride for several hours; but in no case was the alcoholysis complete.

The following list gives the boiling or melting points of the esters used for the experiments described in this paper:—

Name.	m. p.	b. p.	Authority.
1. Methyl <i>p</i> -toluate	31-35°	...	Fischli, Ber., 1879, 12, 615
2. Ethyl <i>p</i> -toluate	...	228°	Noad, Ann., 1845, 63, 289
3. Methyl <i>m</i> -bromobenzoate	31-32°	254-256°	Ador, Ann., 1871, 159, 14
4. Ethyl <i>m</i> -bromobenzoate	...	259°	Engler, Ber., 1862, 4, 707
5. Ethyl <i>p</i> -bromobenzoate	...	262°	Errera, Gaz. Chim. It., 1887, 17, 211
6. Methyl 2:6-dibromobenzoate	78°	...	Sudborough, J.C.S., 1895, 67, 595
7. Methyl 3:5-dibromobenzoate	63°	...	" ibid, 596
8. Ethyl 3:5-dibromobenzoate	51°	...	see page 6
9. Ethyl 3:5-dibromo-4-amino- benzoate	108°	...	see page 6
10. Methyl 3:5-dibromo-4-amino- benzoate	127-128°	...	see page 6
11. Methyl 2:4:6-tribromoben- zoate	67°	...	Sudborough, J.C.S., 1895, 67, 597
12. Ethyl 2:4:6-tribromobenzoate	79-80°	...	see page 7
13. Ethyl 3:4:5-tribromobenzoate	126°	...	Sudborough, J.C.S., 1895, 67, 596
14. Methyl 3:4:5-tribromoben- zoate	154°	...	" " "
15. Methyl 2:4:6-tribromo-3-ami- nobenzoate	96-97°	...	see page 7
16. Ethyl 2:4:6-tribromo-3-ami- nobenzoate	61-62°	...	see page 7
17. Methyl 2:3:4:6-tetrabromo- benzoate	77°	...	Sudborough, J.C.S., 1895, 67, 599
18. Ethyl 2:3:4:6-tetrabromo- benzoate	31°	...	see page 7
19. Methyl <i>m</i> -nitrobenzoate	78-5°	...	Chancel, Ann., 1849, 72.

Name.	m. p.	c. p.	Authority.
20. Ethyl <i>m</i> -nitrobenzoate	47°	...	Kopp. Jahresb. 1847, 48, 737
21. Methyl <i>p</i> -nitrobenzoate	96°	...	Wilbrand, Ann., 1863, 128, 257
22. <i>iso</i> -Butyl <i>p</i> -nitrobenzoate	64-65°	...	see page 8
23. Ethyl <i>p</i> -nitrobenzoate	57°	...	Wilbrand, Ann., 1863, 128, 257
24. <i>n</i> -Propyl <i>p</i> -nitrobenzoate	35°	...	Chem. Zent. 1909, [2], 1025
25. Methyl 2:4-dinitrobenzoate	70°	...	Teichmann, J. Pr., 1895, (2), 52, 428
26. Ethyl 2:4-dinitrobenzoate	41°	...	" " "
27. Methyl 2:6-dinitrobenzoate	147°	...	Sudborough, J.C.S., 1895, 67, 592
28. Ethyl 2:6-dinitrobenzoate	75·5°	...	see page 8
29. Methyl 3:5-dinitrobenzoate	112°	...	Hesse, Ber., 1895, 28, 596
30. Ethyl 3:5-dinitrobenzoate	91°	...	Kurbatow, Ann., 1880, 202, 223
31. <i>n</i> -Propyl 3:5-dinitrobenzoate	71°	...	see page 8
32. <i>iso</i> -Butyl 3:5-dinitrobenzoate	85°	...	see page 8
33. Methyl 2:4:6-trinitrobenzoate	157°	...	Sudborough, J.C.S., 1895, 67, 600
34. Ethyl 2:4:6-trinitrobenzoate	155°	...	" " "

EXPERIMENTAL.

A. *New Esters.*

The following new esters have been prepared during the course of the investigation.

1. *Ethyl 3:5-dibromobenzoate.*

The ester was prepared by eliminating the amino group from ethyl 3:5-dibromo-4-aminobenzoate (see below). It crystallises from alcohol in glistening white needles melting at 51°.

0·2888 gram gave 0·3531 AgBr. Br=52·02 per cent.

$C_9H_5O_2Br_2$ requires Br=51·93 per cent.

2. *Ethyl 3:5-dibromo-4-aminobenzoate* was prepared by dissolving ethyl *p*-aminobenzoate in dilute sulphuric acid and adding excess of bromine water, when the dibromo-amino ester is precipitated. It crystallises from light petroleum (60-90°) in long, snow-white needles, melting at 108°. The yield is very nearly quantitative.

0·3000 gram gave 0·3495 AgBr. Br=49·57 per cent.

$C_9H_6O_2NBr_2$ requires Br=49·54 per cent.

3. *Methyl 3:5-dibromo-4-aminobenzoate*, which is prepared in an exactly similar manner from methyl *p*-aminobenzoate, crystallises from a mixture of light petroleum and benzene in long snow-white, feathery needles melting at 127-128°.

0.2988 gram gave 0.3605 AgBr. Br=50.34 per cent.

$C_8H_7O_2N Br_2$ requires Br=51.77 per cent.

4. *Ethyl 2:4:6-tribromobenzoate*.

This ester was prepared from the silver salt and ethyl iodide, and crystallises from ethyl alcohol in colorless flat needles melting at 80°

0.2422 gram gave 0.3527 AgBr. Br=61.95 per cent

$C_9H_7O_2Br_3$ requires Br=62.02 per cent.

5. *Ethyl 2:4:6-tribromo-3-aminobenzoate*.

This ester was prepared as follows:—*m*-aminobenzoic acid was dissolved in dilute sulphuric acid and excess of bromine water was added. The precipitated tribromo-amino acid was filtered, washed and dried. It was then dissolved in the exact quantity of ammonia and the silver salt precipitated by the addition of a very slight excess of silver nitrate solution. The dry silver salt was then mixed with dry benzene and ethyl iodide and boiled under reflux for an hour. The precipitated silver iodide was filtered off and the solution evaporated to dryness. The residue crystallises from light petroleum in colorless compact prisms, melting at 61—62°. Yield very nearly quantitative.

0.2568 gram gave 0.3580 AgBr. Br=59.32 per cent,

$C_9H_8O_2N Br_3$ requires Br=59.7 per cent.

6. *Methyl 2:4:6-tribromo-3-aminobenzoate*.

This ester was prepared by dissolving methyl *m*-aminobenzoate in hydrochloric acid and aspirating bromine vapour through the solution until the red color of bromine persisted. It crystallises from light petroleum in colorless crystals melting at 96—97°.

0.3386 gram gave 0.4930 AgBr. Br=61.94 per cent.

$C_8H_6O_2NBr_3$ requires Br=61.85 per cent.

7. *Ethyl 2:3:4:6-tetrabromobenzoate.*

This ester, prepared from both the silver salt and ethyl iodide and also from the acid chloride and ethyl alcohol, separates as a slightly colored oil from solutions in benzene, ethyl alcohol and petrol (60-70°). When solidified by immersing in a freezing mixture, it then melts at 31°.

0.2292 grain gave 0.362 AgBr. Br=67.2 per cent
 $C_9H_6O_2Br_4$ requires Br=68.66 per cent.

8. *Isobutyl-nitrobenzoate.*

p-Nitrobenzoic acid was mixed with a slight excess of phosphorus pentachloride and gently warmed. The phosphorous oxychloride was then distilled off under reduced pressure, and the *p*-nitrobenzoyl chloride was boiled for a short time with isobutyl alcohol. The ester crystallises from alcohol in glistening yellow plates, melting at 64°-65°.

0.2178 gram gave 13.4 c. c. nitrogen at 27° and
677 mm. N=6.23 per cent.
 $C_{11}H_{13}O_4N$ requires N=6.27 per cent.

9. *n-Propyl 3:5-dinitrobenzoate.*

3:5-dinitrobenzoic acid was mixed with a slight excess of phosphorus pentachloride and gently warmed. The oxychloride was distilled off under reduced pressure and the 3:5-dinitrobenzoyl chloride was boiled for a short time with *n*-propyl alcohol. The ester crystallises from alcohol in flat yellowish parallelograms, melting at 71°.

0.1520 gram gave 17.15 c. c. nitrogen at 29° and
670 mm. N=11.20 per cent.
 $C_{10}H_{10}O_6N_2$ requires N=11.03 per cent.

10. *Isobutyl fr.b-dinitrobenzoate.*

This was prepared in the same manner as the *n*-propyl ester, using isobutyl alcohol instead of *n*-propyl alcohol. It crystallises from alcohol in long silky yellow needles melting at 85°.

0.1785 gram gave 18.35 c.c. nitrogen at 27° and
683 mm. N=10.5 per cent.
 $C_{11}H_{12}O_6N_2$ requires N=10.45 per cent.

11. *Ethyl 2:6-dinitrobenzoate.*

2:6-dinitrobenzoyl chloride was prepared from the acid and phosphorus pentachloride and was boiled with ethyl alcohol. The ester crystallises from alcohol in yellowish flat needles melting at 75.5° .

0.1258 gram gave 14.6 c.c. nitrogen at 27° and 675 mm.
N=11.73 per cent.

$C_{10}H_8O_6N_2$ requires N=11.67 per cent.

B. *Modified method for the preparation of 3:5-dibromobenzoic and 2:4:6-tribromobenzoic acids.*

The method used by Simonsen and Rau (J. C. S., Trans. 1917, III, 227) for eliminating the amino group from nitro-amino-methoxybenzoic acids was tried and also the method of passing nitrous fumes into an alcoholic solution of the brominated amino acids, but the results were not satisfactory.

The following process in which ethyl nitrite was used gave good results.

5 grams of the acid were dissolved in 50 c.c. of the ethyl alcohol and 5 grams of sulphuric acid were added. The solution was then poured into a wide mouthed flask fitted with a reflux condenser and a dropping funnel, with its tip below the surface of the liquid. A measured quantity of the 10 per cent. ethyl nitrite solution, containing about 5 per cent excess of ethyl nitrite, was then slowly run in with constant shaking. The solution was then boiled for one hour on the water bath and poured into cold water. The solid which separated weighed 4.5 grams and was soluble in benzene. When crystallised from benzene, it melted at $185-186^{\circ}$.

This method was also successfully used for the preparation of ethyl 3:5-dibromobenzoate from ethyl 3:5-dibromo-4-aminobenzoate. 2 grms. of the latter, when treated as above, gave 1.8 grms. of the former i. e. the yield was 95 per cent.

C. *Transformation of esters.*

I. With sodium alkyl oxides.

The following experiments are fairly typical of the results obtained.

1. 1.0 gm. of ethyl 3:5-dinitrobenzoate (m. p. 91°) was dissolved in 10 c. c. of 99 per cent methyl alcohol by warming on the water bath. 1 c. c. of a solution of sodium in methyl

alcohol (1 grm. in 20 c. c.) was then added and the ester allowed to crystallise. The first crop of crystals weighed 0.795 grm. and melted at 111°. (The m. p. of the pure methyl ester is 112°.) The mother liquor gave 0.101 grm. more crystals melting at 108°.

2. 2.0 grms. of ethyl 3:5-dibromo-4-aminobenzoate (m. p. 108°) were dissolved in 10 c. c. methyl alcohol by warming on the water bath and 1 c.c. of the sodium solution added. The solution was then kept boiling for 10 minutes and then allowed to crystallise. The following was the result of the crystallisation.

		wt.	m. p.
1st.	fraction	0.82	127.5-128°
2nd.	fraction	0.94	127°
3rd.	fraction	0.12	122°
	Total	1.88	

The m. p. of the pure methyl ester is 127-128°.

3. 1.0 grm. of methyl *p*-nitrobenzoate (m. p. 96°) was dissolved in 10 c. c. of isobutyl alcohol by warming on a sand bath and then 1 c. c. of a solution of sodium in iso-butyl alcohol (1 grm. in 20 c. c.) was added. The solution was then evaporated down to dryness and the residue weighed 0.98 grm. and melted at 63°. It was recrystallised from ethyl alcohol with the following result:—

		wt	m. p.
1st.	fraction	0.79	63.5°
2nd.	fraction	0.14	61-62°
	Total	0.93	

The m. p. of the pure isobutyl ester is 64°.

Table I gives the results of experiments with methyl esters.

TABLE I.

Names of ester	weight	m. p.	wt. of product	m. p.	m. p. of ethyl ester
Methyl 3:5-dibromobenzoate	1.5	63°	1.02	51°	51°
Methyl 3:5-dibromo-4-aminobenzoate	0.8	123°	0.68	104.5°	108°
Methyl <i>m</i> -nitrobenzoate	1.0	78.5°	0.87	46°	47°
Methyl <i>p</i> nitrobenzoate	1.5	96°	1.18	56°	57°
Methyl 3:5-dinitrobenzoate	2.0	112.5°	1.74	90.5°	91°

Table II gives the results of experiments with ethyl esters.

TABLE II.

Names of ester	weight	m. p.	wt. of product	m. p.	m. p. of methyl ester
Ethyl <i>p</i> -toluate	12.0	228° (b. p.)	10.5	235° (b. p.)	236° (b.p.)
Ethyl <i>p</i> -bromobenzoate	8.4	262° (b. p.)	7.3	73°	78°
Ethyl 3:5-dibromo-4-amino-benzoate	2.0	108°	1.76	127-128°	127-128°
Ethyl 3:4:5-tribromobenzoate	0.63	126°	0.5	153°	154°
Ethyl <i>m</i> -nitrobenzoate	3.0	47°	1.85	65-70°	78.5°
Ethyl <i>p</i> -nitrobenzoate	0.52	57°	0.31	94.5-95°	96°
Ethyl 3:5-dinitrobenzoate	1.0	91°	0.80	111°	112°
Ethyl 2:4-dinitrobenzoate	5.0	41°	4.25	67°	70°

Table III gives the results of the conversions of methyl into the corresponding isobutyl esters.

TABLE III.

Name	weight	m. p.	wt. of product	m. p.	m. p. of isobutyl ester
Methyl <i>p</i> -nitrobenzoate	1.0	96°	0.79	63.5°	64°
Methyl 3:5-dinitrobenzoate	1.0	112°	0.65	83°	85°

Table IV gives the results of the transformation of ethyl esters into the corresponding *n*-propyl esters.

TABLE IV.

Name	wt.	m. p.	wt. of product	m. p.	m. p. of <i>n</i> -propyl ester
Ethyl <i>p</i> -nitrobenzoate	1.0	57°	0.6	35°	35°
Ethyl 3:5-dinitrobenzoate	1.0	92°	0.72	70-70.5°	71°

Table V gives the results of the conversion of *n*-propyl into the corresponding ethyl esters.

Table V.

Name	wt.	m. p.	wt. of product.	m. p.	m. p. of methyl ester.
<i>n</i> -Propyl <i>p</i> -nitrobenzoate	1.0	35°	0.69	55.5-56°	57°
<i>n</i> -Propyl 3:5-dinitrobenzoate	1.0	71°	0.71	89-90°	91°

Table VI gives the results of the transformation of isobutyl into the corresponding methyl esters.

Table VI.

Name.	wt.	m. p.	wt. of product.	m. p.	m. p. of methyl ester.
Isobutyl <i>p</i> -nitrobenzoate	1.0	64°	0.61	94°	96°
Isobutyl 3:5-dinitrobenzoate	1.0	85°	0.71	110-111°	112°

II. With hydrogen chloride.

The following experiments indicate the effect of boiling ethyl esters with a four per cent solution of hydrogen chloride in methyl alcohol.

1. 4.5 grams of ethyl 3:5-dinitrobenzoate were heated up on the water bath with 18 grms of a four per cent solution of hydrogen chloride in a flask fitted with a reflux condenser for five hours, and then allowed to cool and crystallise. The following is the result of the crystallisation.

	wt.	m. p.
1st. fraction	2.0	90-91°
2nd. fraction	0.71	80°
3rd. fraction	0.68	75°
4th. fraction	0.81	72°
Total	4.20	

The m. p. of the ethyl ester was 91° and m. p. of the methyl ester is 112°

2. 5 grams of ethyl 3:5-dibromo-4-aminobenzoate (m. p. 108°) were boiled with 60 c. c. of a four per cent solution of hydrogen chloride in methyl alcohol for 5 hours. The crystals which separated on cooling weighed 2.3 grams and melted at 103°.

3. 3.21 grams of ethyl *p*-nitrobenzoate (m. p. 57°) were boiled with 5.2 c. c. of a 4.5 per cent hydrogen chloride solution in methyl alcohol for six hours. The following is the result of crystallising the solution :—

wt.	m. p.
2.11	92-93°
0.53	85-88°

These two lots were then mixed and heated for 12 hours with a 4.5 per cent hydrogen chloride solution. When crystallised it gave the following result.

wt.	m. p.
2.0	94.5°
0.4	91°

Table VII gives the results of the experiments on transformation of esters when boiled with a solution of an alcohol saturated with hydrogen chloride for several hours.

Table VII.

Ester.	Alcohol.	wt.	m. p.	wt. of recovered ester	m. p.
Methyl <i>p</i> -toluate	Ethyl	10.0	34°	9.2	236-236 5° (b.p)
Ethyl <i>p</i> -toluate	Methyl	12.0	228°(b.p.)	9.6	225.5°-770 (b.p)
Methyl <i>m</i> -bromobenzoate	Ethyl	13.0	31.32°	12.1	261-263° (b.p)
Ethyl <i>m</i> -bromobenzoate	Methyl	10.5	259(b.p)	8.0	254-255° (b.p)
Methyl 3:5-dibromo-4-amino-benzoate	Ethyl	0.95	128°	0.45	105°
Ethyl 3:5-dibromo-4-amino-benzoate	Methyl	2.0	108°	1.63	125-127°
Methyl 3:4:5-tribromobenzoate	Ethyl	1.35	154°	1.2	130-181°
Ethyl 3:4:5-tribromobenzoate	Methyl	1.45	126°	1.25	151°
Methyl <i>p</i> -nitrobenzoate	Ethyl	3.0	93°	2.23	55-56°
Ethyl <i>p</i> -nitrobenzoate	Methyl	5.0	57°	4.0	93°
Ethyl <i>p</i> -nitrobenzoate	<i>n</i> -Propyl	1.0	57°	0.8	35°
Methyl <i>p</i> -nitrobenzoate	Isobutyl	0.8	95°	0.45	64°
<i>n</i> -Propyl <i>p</i> -nitrobenzoate	Ethyl	1.0	34°	0.6	56°
Isobutyl <i>p</i> -nitrobenzoate	Methyl	1.0	64°	0.6	95°
Methyl <i>m</i> -nitrobenzoate	Ethyl	3.0	78.5°	1.8	38°
Ethyl <i>m</i> -nitrobenzoate	Methyl	3.5	41°	2.53	78°
Methyl 3:5-dinitrobenzoate	Isobutyl	1.0	111°	0.72	83-84°
Ethyl 3:5-dinitrobenzoate	Methyl	2.0	91°	1.48	109-111°
Ethyl 3:5-dinitrobenzoate	<i>n</i> -Propyl	1.0	91°	0.8	69°
<i>n</i> -Propyl 3:5-dinitrobenzoate	Ethyl	1.0	71°	0.8	91°
Isobutyl 3:5-dinitrobenzoate	Methyl	1.0	85°	0.72	110°
Methyl 2:4-dinitrobenzoate	Ethyl	3.2	70°	1.95	40°
Ethyl 2:4-dinitrobenzoate	Methyl	1.0	41°	0.65	68-69°

D. *Non-transformations.*

Table No. VIII gives the results of the experiments made with di-ortho-substituted esters, when no alcoholysis could be

Table VIII.

Name of ester	weight	m. p.	cataly-	wt. of product	m. p.
Methyl 2:6-dibromobenzoate	1.0	80-81°	HCl	0.63	80-81°
Methyl 2:4:6-tribromobenzoate	1.0	67°	HCl	0.67	66°
Methyl 2:4:6-tribromobenzoate	0.74	66.5°	Na	0.65	63.5-65°
Ethyl 2:4:6-tribromobenzoate	1.5	79.5-80°	HCl	1.3	80°
Methyl 2:4:6-tribromo-3-aminobenzoate	0.7	94-95	HCl	0.6	94-96°
Ethyl 2:4:6-tribromo-3-aminobenzoate	1.6	57°	Na	1.3	57°
Ethyl 2:4:6-tribromo-3-aminobenzoate	1.0	62°	HCl	0.56	61°
Methyl 2:3:4:6-tetrabromobenzoate	0.45	77°	Na	0.31	77°
Methyl 2:6-dinitrobenzoate	1.0	147°	Na	0.62	146°
Methyl 2:6-dinitrobenzoate	0.45	146°	HCl	0.41	146°
Ethyl 2:6-dinitrobenzoate	0.7	75.5°	HCl	0.695	75-76° ;
Ethyl 2:6-dinitrobenzoate	10	75°	Na	0.94	72-75°
Methyl 2:4:6-trinitrobenzoate	0.6	157°	HCl	0.45	157°
Ethyl 2:4:6-trinitrobenzoate	0.6	152°	HCl	0.5	152-153°

CONCLUSIONS.

1. It is clear that the majority of esters of aromatic acids undergo alcoholysis quite readily under the influence of small amounts of sodium alkyl oxides or larger quantities of hydrogen chloride.

2. The sodium alkyl oxide process is an extremely convenient one for transforming a solid ethyl into a methyl ester or for bringing about the reverse change. It is only necessary to dissolve the ester in about 10 times its weight of the requisite alcohol, to add a small piece of metallic sodium and then to warm for 10 minutes; on cooling the required ester separates in a crystalline form.

3. Two substituents in ortho positions to the alkylated carboxylic group completely inhibit the change.

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