The action of Methyl and Ethyl alcohols on Esters of 2 : 6-Dinitro-and 2 : 4 : 6-Trinitro-benzoic acids.

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Introduction.

Rosanoff and Prager (J. Amer. Chem. Soc., 1908, *30* 1895) have observed that when 2 : 4 : 6-tribromo- or 2 : 4 : 6-trichloro-benzoic acid is heated in a sealed tube with ethyl alcohol for 100 to 110 hours at 180—200° an almost quantitative yield of the corresponding ethyl ester in obtained, although the yield of ester at the ordinary temperature or at the boiling point of the alcohol is practically nil when mineral acids are used as catalysts.

The experiments of Sudborough and Karvé (This Journal, 1919, *3*, 1) have proved that when the methyl ester of a di-ortho-substituted benzoic acid is heated with ethyl alcohol and a catalyst such as hydrogen chloride or sodium ethoxide alcoholysis does not occur. As the processes of alcoholysis and esterification are so similar we decided to study the action of ethyl alcohol on the methyl esters of 2 : 6-dinitro- and 2 : 4 : 6-trinitro-benzoic acids at about 180° in the absence of a catalyst.

Our results show that a reaction takes place, but that it is not a simple process of alcoholysis. The chief product obtained from methyl 2 : 6-dinitro-benzoate was *m*-dinitrobenzene and from methyl 2 : 4 : 6-trinitrobenzoate, *s*-trinitrobenzene. The method of identifying these products was by means of their characteristic additive compounds with bases such as *α*-naphthylamine, benzidene and *p*-tolyl-*β*-naphthylamine.

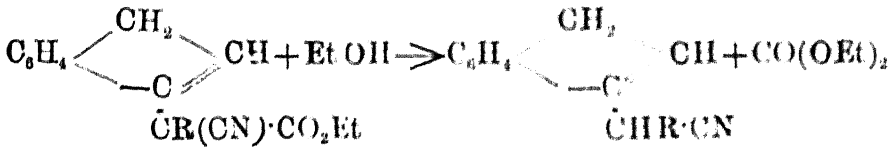
It is thus clear that when the methyl and also ethyl esters of the di-ortho-nitro substituted benzoic acids are heated with alcohols at about 180° the carbmethoxy or carbethoxy group is eliminated and replaced by hydrogen.

$$(NO_2)_2C_6H_3\cdot COOCH_3 \rightarrow C_6H_4(NO_2)_2.$$

$$(NO_2)_3C_6H_2\cdot COOCH_3 \rightarrow C_6H_3(NO_2)_3$$

$$(NO_2)_3C_6H_2\cdot COOC_2H_5 \rightarrow C_6H_3(NO_2)_3$$

This elimination of the carbmethoxy or carbethoxy group from esters is not a common phenomenon, although the removal of the carboxylic group from a free acid at moderate temperatures is quite common (Raikow and Tischkow, Int. Congress Appl. Chem., 1909, IV. A. 1. p. 91). The same authors (Chem. Zeit., 1905, *29*, 1268) have also shown that certain esters of substituted benzoic esters lose carbon dioxide when heated with phosphoric acid at 100—200°. Ingold and Thorpe (J. Chem. Soc., 1919, *115*, 143) give an example of the elimination of the carbethoxy group from the ethyl ester of a substituted indene acid, when it is heated with alcohol and a trace of sodium. This reaction may be represented by the equation.



the carbethoxy group of the ester forming ethyl carbonate, $CO(OEt)_2$, with the ethyl alcohol.

A reaction of a similar type is also observed with esters of certain substituted unsaturated acids (Thole and Thorpe, *ibid* 1911, *99*, 2187. $(CO_2Et)_2CR{\cdot}CH : C(CO_2Et) + EtOH \rightarrow CO_2Et{\cdot}CHR{\cdot}CH : C(CO_2Et)_2 + CO(OEt)_2$
a reaction which is of value for the preparation of alkylated glutacome esters; and Rogerson and Thorpe (*ibid.* 1905, *85*, 1702) have shown that ethyl γ-cyano-$\alpha\beta\gamma$-trimethylglutaconate readily forms ethyl carbonate and ethyl γ-cyano-$\alpha\beta\gamma$-tri-methyl-crotonate $CO_2Et{\cdot}CMe(CN){\cdot}CMe : CMe{\cdot}CO_2Et + EtOH \rightarrow CHMe(CN){\cdot}CMe : CMe{\cdot}CO_2Et + CO(OEt)_2$

In the reactions studied by us carbon dioxide was one of the products formed, so that in all probability they must be represented by an equation of the type:

$(NO_2)_2C_6H_3{\cdot}COOCH_3 + C_2H_5OH \rightarrow C_6H_4(NO_2)_2 + CO_2 + CH_3{\cdot}O\,C_2H_5$
the third product being methyl ethyl ether, or, if an ethyl ester is used, ordinary ether.

With the quantities of material used in our experiments we have not been able to isolate an ether although an odour of ether was noticeable.

Experimental.

The esters were prepared from the respective acids by first preparing the acid chlorides and then boiling these for a short

time with the requisite alcohol. They were then recrystallised until they gave a sharp melting point.

The ethyl alcohol used was Kahlbaum's absolute alcohol and was 99·1 per cent and the methyl alcohol was 99·15 per cent pure.

The following experiments are fairly typical of the whole investigation :—

(1) 1·0 gram of methyl 2 : 6-dinitrobenzoate and 10 grams of ethyl alcohol were heated in a hard glass sealed tube for 100 hours at 180°. When the tube was opened only a slight pressure was observed. The liquid was removed and the following crystalline fractions obtained on evaporation.

	Weight in grams	M. P.	
1st fraction	0·60	80-82°	yellow flat needles
2nd fraction	0·35	65-67°	yellowish crystals

The melting point of the ethyl ester is 75·5°, that of the methyl ester is 147° and that of *m*-dinitrobenzene is 90°. The first fraction was then recrystallised and crystals melting at 87° were obtained. Half of this was mixed with an alcoholic solution of the theoretical quantity of benzidene (m. p. 122°) and gave shining black needles (m. p. 125-126°) of the additive compound, the yield being very nearly quantitative. Romburg gives 128° as the melting point of the additive compound. The other half was similarly treated with *a*-naphthylamine when the additive compound was obtained in the form of red needles melting at 55-56° (Romburg gives m. p. as 57°) The product was therefore unquestionably *m*-dinitrobenzene.

(2) One gram of ethyl 2 : 6-dinitrobenzoate was treated with 10 c.c. of absolute ethyl alcohol for 100 hours at 180°. The tube was then opened by wiring on a stout piece of rubber tubing to the drawn out end of the tube and then breaking the tip by means of a pair of pliers (Bunsen, Gasometrische Methoden, 2nd. Edition, p. 10.) and the gases were led through a tube immersed in liquid air. When the tube was removed from the liquid air a white solid was seen to have accumulated in it, and a distinct smell of ether was noticeable. The gases evolved, when the tube was brought back to the atmospheric temperature, were collected in a nitrometer over saturated common salt solution, and it was seen that out of the 50 c.c. collected, 8·3 c.c. were absorbed by a concentrated potassium hydroxide solution.

The result of crystallising the solution from the tube was as follows :—

	Weight in grams	m. p.	
1st fraction	0·42	87-88°	yellow needles
2nd „	0·31	72°	yellowish crystals
3rd „	0·14	62°	„ „

The first fraction gave quantitative yields of the additive compounds with benzidene and naphthylamine, as in the first experiment.

(3) 1·0 gram of methyl 2 : 4 : 6-trinitrobenzoate was dissolved in 10 c.c. ethyl alcohol and the solution heated in a hard glass sealed tube for 100 hours at 180°. The tube was opened as above and 9·2 c.c. of the 50 c.c. of gas collected were seen to be absorbed by potassium hydroxide solution.

The following crystalline fractions were obtained from the solution in the tube :—

	weight in grams	m. p.	
1st fraction	0·61	118-118·5°	yellowish brown plates
2nd „	0·15	113-115°	faintly yellow crystals
3rd „	0·07	103°	do.

The melting point of the ester is 155°, that of the methyl ester is 157° and that of *s*-trinitrobenzene is 120°.

The 1st fraction was dissolved in alcohol and portions of the alcoholic solution mixed respectively with *α*-napthylamine and *p*-tolyl-*β*-naphthylamine. Both solutions gave additive products, the former deep red crystals melting at 212° and the latter dark red flat prisms melting at 110° (Sudborough, J. Chem. Soc., 1901, *79*, 522 gives the melting points as 214° (corr.) and 111° (corr.)).

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