the ashes are brought into solution with 5 ml 1 N HCl, cautiously added in small portions with stirring. The tubes are centrifuged. To 2 ml of the clear supernatant are added 2 ml 0.1 N arsenite and the test tubes are held for at least 15 min in a water bath at 25°C for temperature equilibration. 1 ml 0.04 N ceric ammonium sulphate solution of the same temperature is then thoroughly mixed with the contents of the tubes at a noted time and the mixture is kept in the water bath for exactly 30 min when they are read in a (Beckman B) photometer at 440 mμ against distilled water as a blank. The content of iodine is calculated from a calibration curve, plotted from readings of standard solutions.

Urine contains considerably less organic material than serum, but the basic acetate formed when $Zn(Ac)_2$ is precipitated with alkali brings up the total combustible carbon to the same values as those in serum.

Table 1. Apparent iodine content in duplicates from the same urine.

$ZnSO_4$	$Zn(Ac)_2$
3.2	4.2
4.0	4.3
3.9	4.2
4.2	4.2
3.1	

As shown in Table 1 the recovery of iodine in a series of duplicates, of the same urine is improved when $ZnSO_4$ is replaced with $Zn(Ac)_2$.

In a previous publication [3] we have shown, that the substitution of K_2CO_3 for Na_2CO_3 in the incineration mixture will result in considerably smaller losses of iodide in the determination of protein-bound iodine, probably because of the lower vapour pressure of KI.

In Table 2 are given the results of two parallel series where urine samples with added $K^{131}I$ have been incinerated with K_2CO_3 and Na_2CO_3, respectively. The average recovery in the Na_2CO_3 series was 83 % against 96 % in the K_2CO_3 series.

Naturally several types of medication can invalidate the analysis of iodine in urine. Besides iodine compounds, which of course can give very high iodine values, mercurial diuretics can give falsely low values, sulfur-containing drugs, such as sulfonamides, chlorothiazide *etc.* falsely high values, because of their influence on the ceric ammonium sulfate reaction. Urines with high values of calcium must first be treated with ammonium oxalate in order to remove calcium to avoid loss of iodine as CaI_2 during the incineration [3].

Table 2. Recovery of added ^{131}I.

K_2CO_3	Na_2CO_3
Recovery %	Recovery %
87	86
100.5	78
97.4	86
97.6	82
97.0	82
Mean: 96 %	Mean: 83 %

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Sodium Hydroxide in Alcohol as a Base for the Alkylation of Ethyl Acetoacetate

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In the alkylation of ethyl acetoacetate by means of an alkyl bromide and an alcoholic solution of sodium ethoxide it is usually stated that the quality of the absolute alcohol is important [1]. Most handbooks recommend the use of »superdry» alcohol, *i.e.* alcohol dried with magnesium or by similar methods.

Table 1.

Alkylhalide	*Yield* %	*B. p.*
C_2H_5Br	73	76— 80°/10 mm Hg
n-C_3H_7Br	56	86— 92°/10 » »
n-C_4H_9Br	45	100—105°/10 » »
$CH_2=CH—CH_2Br$	74	90— 95°/10 » »
$C_6H_5CH_2Cl$	59	145—150°/10 » »

In a kinetic investigation of the methylation of ethyl acetoacetate Brändström [2] has recently shown that the hydrolysis of ethyl acetoacetate is slow if the amount of water present in the sodium ethoxide solution is small. This suggests that it is not so important to dry the alcohol which is to be used as a solvent in alkylation of ethyl acetoacetate. In order to test this, some alkylations of ethyl acetoacetate have been undertaken where sodium hydroxide dissolved in 99.5 % alcohol was used as a base. With alkyl halides of an intermediate reactivity such as ethyl bromide the yields obtained were only slightly lower than those obtainable with "superdry" alcohol and sodium.

The use of sodium hydroxide in alcohol is thus strongly recommended as a base in alkylations of ethyl acetoacetate with alkyl halides of an intermediate or high reactivity.

It should be noted that the same base cannot be used in the alkylations of diethyl malonate or other esters which have a much lower acidity than ethyl acetoacetate.

Experimental. 40 g (1 mole) of sodium hydroxide is dissolved in 500 ml of technical absolute alcohol (containing about 0.5 % of water) in a 1 litre three-necked flask, fitted with a stirrer, a reflux condenser and a dropping funnel. 130 g (1 mole) of ethyl acetoacetate is added followed by 1.2 moles of an alkyl halide. The mixture is refluxed for several hours until it has a neutral reaction.

About 300 ml of alcohol is then distilled off. The residue is cooled and 500 ml of water is added. The layers are separated and the aqueous layer is extracted with benzene. The combined organic layers are dried with anhydrous magnesium sulphate, and then fractionated under reduced pressure. The yields and boiling points obtained are given in Table 1.

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A Method for the Preparation of *tert*-Alkylacetic Acids

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tert-Alkylacetic acids are very seldom referred to in chemical literature. The reason for this is that they are not readily available by the standard methods for the preparation of aliphatic acids. For instance, the malonic ester method has been used [1] but it gives a very low yield. The halides R-CH_2X where R is a *tert*-alkyl group are not readily available, and they do not react with cyanide ion to the corresponding nitrile. The only general method which has been used is that starting with the corresponding *tert*-alkylcyanoacetic ester which in turn can be prepared from an unsaturated cyanosubstituted ester and a Grignard reagent [2-4]. This method is, however, not very convenient for a large scale synthesis of *tert*-alkylacetic acids.

The following method is however, very useful (see p. 609).

The starting materials RCH_2CH_2Cl where R represents a tertiary alkyl group are readily available from the reaction of a tertiary chloride RCl with ethylene or by other methods [5]. All chlorides used in the following preparations are, *e.g.*, obtained from the reaction of *tert*-butyl chloride with ethylene [6].

The conversion of the chloride into the alcohol is conveniently carried out without isolating the intermediate ester by using polyethylene glycol as a solvent. The overall yield for the preparations of alcohols from the chlorides are 70—80 %.

The oxidation of the alcohols to the corresponding acids are the standard procedures using potassium permanganate or chromic acid.

Experimental. Preparation of 3,3-dimethylbutanol-1. 132 g (2 moles) of potassium hydroxide are dissolved in 600 ml of polyethylene glycole-300 in a 2 litres three-necked flask fitted with a strong stirrer, a reflux condenser, a thermometer and a dropping funnel. 120 g (2 moles) of conc. acetic acid are added with stirring. The water formed in the neutralisation is removed by distillation under reduced pressure. When the mixture starts foaming the distillation is discontinued. 241 g (2 moles)