The substance is found to oxidize the iodide ion in a water solution of potassium iodide to iodine on heating, and on the other hand it reduces Fehling's solution and Tollen's reagent. However, these two reductions might be caused by acetylpropionyl, formed to some extent in a rapid hydrolysis of the dibromide, as both the reagents are alkaline. The aliphatic α-diketones diacetyl and acetylpropionyl reduce namely Fehling's solution easily. An oxidation of the dibromide with potassium permanganate gives propionic acid and acetic acid.

Experimental. *α,α-Dibromo-diethyl ketone.* 320 g (2 moles) of bromine was added dropwise to 86 g (1 mole) of diethyl ketone in the presence of red phosphorus. Nitrogen gas was bubbled through the solution in order to remove hydrogen bromide. After half the bromine was added, the mixture was warmed to 80° and maintained at that temperature for one hour after the addition. The product was washed with water and some 5 % sodium carbonate and distilled with benzene, then fractionated *in vacuo*. B. p. 75—77°/ 10 mm. Yield: 180 g (74 %). The density as well as the boiling point is in agreement with the values found by Pauly.[1]

$C_5H_8OBr_2$ (243.94) Calc. Br 65.52
Found » 65.56

The hydrolysis and some derivatives. 24.4 g (0.1 mole) of the dibromide of diethyl ketone was dropped into an ice-cooled solution of 16.8 g (0.3 moles) of potassium hydroxide in 80 ml of alcohol. The mixture was stirred and allowed to stand overnight. Potassium bromide was separated, and the solution neutralized with concentrated hydrochloric acid and then distilled in order to remove the alcohol and some water. The residue was dissolved in ether, dried over anhydrous potassium carbonate and, after removal of the ether by distillation, fractionated and a middle fraction, b. p. 109—112°/ 752 mm, taken. The liquid was dark-yiellow coloured. Yield: 5.9 g (59 %).

A qualitative test showed the substance to be an α-diketone, and the dioxime could be prepared from the liquid and hydroxylamine hydrochloride in alcoholic solution in the presence of sodium acetate, according to the general process. M. p. 172—173°. From an alcoholic solution of the dioxime and a water solution of nickel chloride the typical nickel salt could be obtained. M. p. 276—280°. — When a water solution of the α-diketone was treated with hot dilute sodium hydroxide for a few minutes a product, crystallizing in yiellow needles with the melting point, 108—110°, identified as duroquinone, was obtained.[3]

The three above-mentioned derivatives give full evidence for the identification of the hydrolysis product as acetylpropionyl.

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A Synthesis of *dl*-2-Methyl-5,7-dihydroxyflavanone

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5,7-Dihydroxyflavanone (dihydrochrysin) has been synthesised from phloroglucinol and cinnamoyl chloride by the Friedel-Crafts method[1]. Under the same conditions phloroglucinol and β-methylcinnamoyl chloride gave a mixture of two colourless substances. The main product, m. p. 154—156° *, had the composition $C_{16}H_{14}O_4$, gave a yellow colour when reduced with magnesium and hydrochloric acid and a reddish brown colour with ferric chloride, and thus must be the expected *dl*-2-methyl-5,7-dihydroxyflavanone (I). On the paper chromatogram, its R_F value is about 0.55 (benzene-ligroin solvent[2], and the substance gives a red spot with diazotised benzidine. The R_F value of 5,7-dihydroxyflavanone in the same solvent is 0.44, so that, as expected, the in-

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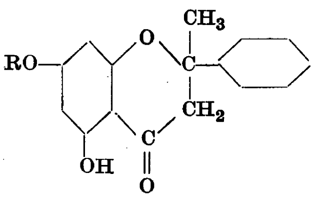
* All melting points uncorrected.

troduction of the C-methyl group causes an increase in R_F.



I: $R = H$
II: $R = CH_3$

Methylation of 2-methyl-5,7-dihydroxyflavanone with diazomethane yields a monomethyl ether, m. p. 92–93°. Since the hydroxyl group in the 7-position is always much more readily methylated than that in the 5-position, this compound must be 2-methyl-5-hydroxy-7-methoxyflavanone (II).

A second product formed during the synthesis of 2-methyl-5,7-dihydroxyflavanone was isolated from the mother liquors. It melted at 233–234° and had the same composition, $C_{16}H_{14}O_4$, and is thus isomeric with the main product. It gave no colour reactions either with magnesium-hydrochloric acid or with ferric chloride. The R_F value was very low (0.05), and diazotised benzidine gave a reddish-brown colour. Methylation with diazomethane did not lead to any crystalline product. A possible structure for this compound would be phloroglucinol mono-β-methylcinnamate: a chalkone structure is less probable owing to the absence of colour.

The structure (I) was once considered for strobopinin, a flavanone from the heartwood of *Pinus strobus* L.[3] However, strobopinin has recently been proved to be 6- or 8-methyl-5,7-dihydroxyflavanone [4].

Experimental. A suspension of phloroglucinol (4.8 g) in nitrobenzene (45 ml) was mixed with a solution of β-methylcinnamoyl chloride (6.7 g) in nitrobenzene (50 ml). The mixture was cooled in ice water, and a solution of aluminium chloride (7.1 g) and a few drops of thionyl chloride in nitrobenzene (120 ml) was added in small portions. After two days, the mixture was heated to 50–60° for one hour and then poured into a mixture of ice (100 g) and conc. hydrochloric acid (10 ml). The nitrobenzene was removed by steam distillation, and the remaining resinous product extracted three times with boiling water. The aqueous extracts were cooled and extracted with ether, and the ether solution dried over anhydrous sodium sulphate, decolourised by filtration through aluminium oxide and concentrated to a yellow oil, which soon crystallised. Recrystallisation from 50 % acetic acid gave colourless crystals, m. p. 153–154° (1.7 g). Further recrystallisation raised the m. p. to 154–156°. Colour reactions: magnesium-hydrochloric acid, yellow; ferric chloride, reddish-brown; diazotised benzidine, red.

$C_{16}H_{14}O_4$ (270.3) Calc. C 71.1 H 5.22
Found » 70.8 » 5.13

The monomethyl ether was obtained by treatment of the flavanone with diazomethane in ether solution. After recrystallisation from methanol, it formed colourless crystals, m. p. 92–93°. Colour reactions: Magnesium-hydrochloric acid, pale yellow; ferric chloride, reddish brown.

$C_{17}H_{16}O_4$ (284.3) Calc. OCH_3 10.9
Found » 10.8

The acetic acid mother liquors from the recrystallisation of 2-methyl-5,7-dihydroxyflavanone were diluted by water, and the precipitate thus formed recrystallised from toluene and then from methanol, yielding 0.3 g of colourless crystals, m. p. 233–234°. Colour reactions: Magnesium-hydrochloric acid, nil; ferric chloride, nil; diazotised benzidine, reddish brown.

$C_{16}H_{14}O_4$ (270.3) Calc. C 71.1 H 5.22
Found » 71.2 » 5.36

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The Acyl Exchange in Acidolysis of Diethyl Acylmalonates with Organic Acids

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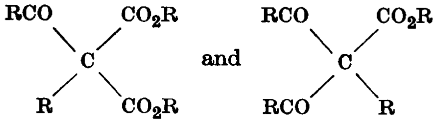
The present author has recently shown that diethyl acylmalonates are very valuable substances in the synthesis of β-ketoesters [1]. The diethyl acylmalonates were acidolysed with the organic acid containing the *same* acyl group thus giving excellent yields of the corresponding ethyl acylacetate according to the reaction:

$$RCOCH(CO_2C_2H_5)_2 + RCO_2H \longrightarrow RCOCH_2CO_2C_2H_5 + RCO_2C_2H_5 + CO_2$$

However, if the acid and the diethyl acylmalonate have *different* acyl groups a mixture of the two possible β-ketoesters, corresponding to the two different acyl groups is obtained. This indicates that the acyl group in the diethyl acylmalonate is not hold so firmly by the rest of the molecule.

A similar mobility of the acyl group has been observed by Dickmann and Wittmann [2] who studied the catalytic cleavage of compounds of the types:



with an alcoholic solution of sodium ethoxide. This reaction was found to proceed easily even when cold.

As the mobility of the acyl group is of great interest from both theoretical and preparative points of view a preliminary result of the investigation will be given here.

Equimolecular amounts of diethyl acetylmalonate and an organic acid were heated, using a little magnesium oxide and copper acetate as catalyst [1], for 5—8 hours, and the resulting product was fractionated in vacuo through a 30 cm Widmer column. In this way *ethyl* n-*butyrylacetate* b. p. 84—88°/10 mm (yield 38 %) and *ethyl* iso*butyrylacetate* b. p. 78—82°/10 mm (yield 35 %) were obtained. The actual amounts of these β-ketoesters in the mixtures are probably still higher, since there were losses in the isolation of the products. It seems to me very probable that this exchange is the result of a "redistribution reaction" [3] and that the yields hence would be 50 %.

From preparative point of view this method of preparing β-ketoesters has the advantage that the corresponding diethyl acylmalonate is not required as a starting material.

The reaction will be studied further to see if the acyl group exchange will be effected by other reagents, and if the reaction might be forced in a desired direction to give high yields of β-ketoesters.

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