

which should take at least two hours, the reaction mixture is diluted with 200 ml of methanol and precipitated with 2 l of ether.

After a night in the icebox the solvents are decanted from the oily precipitate, which is washed with ether and dissolved in 50 ml of anhydrous ethanol. This solution is evaporated to half its volume *in vacuo* keeping a bath temperature of no more than 30° C. Upon cooling, and addition of a small amount of ether, a crystalline precipitate starts to settle, which is removed, washed with ether and dried over conc. sulphuric acid and paraffin.

The prisms melted at 60° C (Barbière finds 63° C). Yield 22 g = 50 % of the theoretical.

We have prepared other similar compounds without difficulty according to Barbière's directions.

1. Barbière, J. *Bull. Soc. Chim.* [5] 11 (1944) 473.

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## The Structure of Pauly's Dibromo-diethyl Ketone

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A dibromo-diethyl ketone with the bromine atoms in the  $\alpha$ -position of the keto group has been prepared by Pauly<sup>1</sup>, and he assumed the substance to be symmetrically substituted. No structure proof is given, however, and he made his conclusions from the attributed similarity to 1,3-dichloroacetone.

When a ketone is brominated, it is well known that the first bromine atom will substitute at the  $\alpha$ -carbon atom and the

second one, if possible, in most cases at the same  $\alpha$ -position.<sup>2</sup> Acetone and methyl ethyl ketone are thus brominated according to the given rule, and it is surprising to find that diethyl ketone gives a symmetrical dibromide. This substance was needed in connection with other work, and a structure proof and an examination of the dibromide of diethyl ketone was therefore performed.

The usual way to get evidence about the structure of a dibromo substituted ketone is to hydrolyze the substance.<sup>3</sup> The dibromide was thus hydrolyzed in an alkaline medium, and from the products acetylpropionyl could be isolated. The hydrolysis is very rapid and has been performed with potassium hydroxide in cooled alcohol as well as with potassium carbonate in water solution. Acetylpropionyl was easily identified by the dioxime and the orange-coloured nickel precipitate, formed from the dioxime, a well known reagent of aliphatic  $\alpha$ -diketones. Duroquinone was also obtained from acetylpropionyl and dilute alkali hydroxide,<sup>3</sup> and if a mixture of the dibromide and potassium carbonate in water solution is refluxed, until the dibromide is dissolved, duroquinone can be isolated from the reaction products. A similar investigation has once been performed by Faworsky on  $\alpha,\alpha$ -dichloropropyl methyl ketone.<sup>4</sup>

From the results it is obvious that the dibromide must be unsymmetrically substituted, as the hydrolysis gives an  $\alpha$ -diketone and not  $\alpha,\alpha'$ -dioxi-diethyl ketone. The author is conscious, however, of the possibility of a rearrangement of the dibromo ketone from  $\alpha,\alpha'$ - to  $\alpha,\alpha$ -substitution during the hydrolysis, but it must be emphasized that such an isomerisation is not very probable in an alkaline medium and not found in analogous reactions; the Faworsky rearrangement<sup>2</sup> only results in other products of hydrolysis and is specially studied for  $\alpha,\alpha'$ -dibromo ketones. *The dibromide is thus  $\alpha,\alpha$ -dibromo-diethyl ketone.*

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  $\alpha$ -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.*  $\alpha,\alpha$ -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.<sup>1</sup>

$C_6H_8OBr_2$  (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-yellow coloured. Yield: 5.9 g (59 %).

A qualitative test showed the substance to be an  $\alpha$ -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  $\alpha$ -diketone was treated with hot dilute sodium hydroxide for a few minutes a product, crystallizing in yellow needles with the melting point, 108–110°, identified as duroquinone, was obtained.<sup>3</sup>

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

1. Pauly, H. *Ber.* 34 (1901) 1771.
2. Faworsky, A. J. *Pract. Chem.* (II) 88 (1913) 645.
3. von Fechmann, H. *Ber.* 21 (1888) 1420.
4. Faworsky, A. J. *Pract. Chem.* (II) 51 (1895) 538.

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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<sup>1</sup>. Under the same conditions phloroglucinol and  $\beta$ -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<sup>2</sup>), 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-

\* All melting points uncorrected.