241. Synthesis of Unbranched 4-Alkylbenzaldehydes

by **Maged A. Osman**

Brown Boveri Research Center, CH-5405 Baden

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Summary

The preparation of unbranched 4-alkylbenzaldehydes free of positional and branched-chain isomers by different methods is described. A one-step preparation of the aldehydes is reported which involves the direct hydrogenation of a *Friedel-Craft's* complex in the presence of Pd/C catalyst.

Introduction. – The unbranched 4-alkylbenzaldehydes are useful intermediates in the synthesis of a number of liquid crystals [1-3]. However, exceptionally pure aldehydes completely free of positional and branched-chain isomers are required, since these impurities can form non-liquid crystalline products the presence of which, in even very small quantities, lowers the clearing point of the liquid crystal. An elegant direct method for the preparation of substituted benzaldehydes was reported by *Rieche et al.* [4]. In this method the reaction of dichloromethyl alkyl ether with alkylbenzenes in presence of $TiCl_4$ is described. In case of toluene a mixture of *o*- and *p*-tolualdehyde was obtained.

Results. – The higher homologues (alkyl = C_3–C_{10}) which are the most interesting for the synthesis of liquid crystals were prepared by *Rieche's* method. The yields could be increased and the amount of side products decreased by reducing the reaction temperature to –20°. The ratio of *o*- to *p*-isomers was 1:4. Separation of the two isomers by destillation under reduced pressure was possible on a spinning band but was time-consuming and the yield of pure *p*-alkylbenzaldehyde was poor. The high temperatures needed for the destillation destroyed a quantity of the product. Low-temperature crystallization was found to be an efficient method to separate the *p*-aldehydes from their *o*-isomers since the latter do not freeze down to –80° while the former possess melting points between –43° and +8°. This method has also the advantage of using low temperatures which avoids any decomposition of the product. The melting points of the unbranched 4-alkylbenzaldehydes are given in the *Table*.

The aldehydes were also obtained by the hydrogenation of the corresponding aroyl chlorides. The acid chlorides were prepared with a slight modification,

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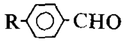
Table. *Melting points of the unbranched 4-alkylbenzaldehydes*



R	C_3H_7	C_4H_9	C_5H_{11}	C_6H_{13}	C_7H_{15}	C_8H_{17}	C_9H_{19}	$C_{10}H_{21}$
M.p. [°C][a])	19	43	-33	-27	-4	-6	-5	8

[a]) Determined by differential thermal analysis.

according to a method of *Neubert* [5], by the action of oxalyl chloride on the corresponding alkylbenzene in presence of anhydrous $AlCl_3$. In a variation of this method the *Friedel-Craft's* complex was directly hydrogenated in the presence of Pd/C as catalyst. Although the overall yields were lower using this method, the isolation and purification of the acid chlorides was avoided, and the aldehydes were directly obtained.

Experimental Part

Unbranched 4-alkylbenzaldehydes from 4-alkylbenzenes. $TiCl_4$ (0.18 mol) was added to a cooled ($-20°$) solution of the 4-alkylbenzene (0.12 mol) in 50 ml of $CHCl_3$. $CHCl_2-O-CH_3$ (0.1 mol) was added dropwise to the solution under stirring within 20 min. The mixture was stirred at $-20°$ for another 45 min before it was thrown on ice. An antioxidant was added to the organic phase which was separated and washed with water. The product (80% yield) was separated from the residual alkylbenzene by flash destillation under reduced pressure. The *o-/p*-aldehyde mixture was dissolved in 5 ml of petrol ether and cooled to $-50°$. The product which crystallized out was filtered off and washed with cooled petrol ether. The purity was checked by GC. on an *OV25* column and the crystallization repeated if necessary.

Unbranched 4-alkylbenzoyl chlorides. $AlCl_3$ (0.1 mol) was added portionwise to a solution of the 4-alkylbenzene (0.1 mol) and oxalyl chloride (0.1 mol) in 130 ml trichloroethylene under stirring. The mixture was kept below r.t. during the addition and stirred at this temp. for another 30 min, then thrown on ice. The organic phase was separated, washed (H_2O) and dried ($MgSO_4$). The acid chloride was purified by destillation under reduced pressure (yield: 80-90%).

Aldehydes from acid chlorides. The acid chloride (0.1 mol) was dissolved in benzene and hydrogenated at r.t. under normal pressure in the presence of 10% Pd/C and tributylamine (0.1 mol). The hydrogenation was completed within 6 h.

Hydrogenation of the Friedel-Craft's *complex.* A mixture of $AlCl_3$, alkylbenzene and oxalyl chloride in tetrachloroethane was allowed to react at r.t. for 30 min as described above. Pd/C 10% was added to the mixture and hydrogenated for 2 h either at 100° under normal pressure or at 50° under 30 atm. AcONa can be added to absorb the HCl evolved.

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