ISSN 0012-5008, Doklady Chemistry, 2017, Vol. 476, Part 2, pp. 227–229. © Pleiades Publishing, Ltd., 2017.
Original Russian Text © M.B. Gazizov, S.Yu. Ivanova, Sh.N. Ibragimov, R.A. Khairullin, R.F. Karimova, K.S. Gazizova, I.S. Antipin, 2017, published in Doklady Akademii Nauk, 2017, Vol. 476, No. 5, pp. 527–529.

CHEMISTRY

Synthesis of Functionally Substituted Benzaldehydes

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Received June 22, 2017

Abstract—A new method of synthesis of functionally substituted benzaldehydes by catalytic debromometoxylation of dibromomethylarenes with benzaldehyde dimethyl acetal has been suggested. Anhydrous zinc chloride has been used as a catalyst. Being soft Lewis acid, it formed no strong complex with aldehyde group and other functional groups. The initial acetal has been readily recovered by the treatment of benzaldehyde isolated from the reaction mixture with trimethyl orthoformate.

DOI: 10.1134/S0012500817100019

We have recently shown [1, 2] that dihalomethylarenes react with methyl esters of P(IV) acids to form aromatic aldehydes and phosphorus acid anhydrides. However, the reaction requires high temperature (160–180°C) and expensive methyl esters of P(IV) acids. In recent decade, two promising methods have been proposed for the synthesis of aromatic monoaldehydes from dihalomethylarenes: heating of a mixture of the latter with a large excess of dimethyl sulfoxide [3] of pyridine [4] at 70–120°C for 1–18 h followed by treatment of reaction mixture with water. However, the isolation of individual aldehydes is a laborious process.

The aim of this work is to develop a new method for preparing functionally substituted aromatic aldehydes by the catalytic debromomethoxylation of dibromomethylarenes with benzaldehyde dimethyl acetal.

We propose for the first time to synthesize functionally substituted aromatic aldehydes by the catalytic debromometoxylation of dibromomethylarenes **I** with benzaldehyde dimethyl acetal **II** (Scheme 1).

Zinc chloride was used as a catalyst, it is a soft Lewis acid, which forms no strong complex with aldehyde and other functional groups. We found in preliminary experiments that the reaction of compounds **I** and **II** without a catalyst occurs only at 220°C. When 10 mol % of $ZnCl_2$ is used, the reaction completes after 2 h at 50°C and after 1 h at 80°C. The reaction was conducted in isooctane or benzene or in the absence of a solvent. The reaction does not affect methoxycarbonyl and carbonyl groups (Scheme 2).

Acetal groups in dibromide **Ib** and 4-(dimethoxymethyl)benzaldehyde **IIIb** participate in debromomethoxylation to give terephthalic aldehyde **IIIa** as the major reaction product. Compound **IIIb** was detected only by ^{1}H NMR and chromatography. Moreover, since compound **Ib** contains both dibromomethyl and acetal groups, we expected the presence of intermolecular interaction between them. Indeed, the addition of catalytic amounts of $ZnCl_2$ to compound **Ib** caused the formation of terephthalic aldehyde **IIIa** in 96% yield.

In general case (Scheme 3), the reaction of tetrabromide **Ie** with benzaldehyde dimethyl acetal **II** depending on reagent ratio can result in formation of three aldehydes: monoaldehyde **Ia**, dialdehyde **IIIa**, and benzaldehyde **IV**, while tetrabromide **Ie** could react incompletely.

At the reagent ratio **Ie** : **II** = 1.0 : 2.1, the ^{1}H NMR spectrum of the reaction mixture showed no resonance signal at 6.61 ppm corresponding to the proton of the dibromomethyl group. We isolated terephthalic aldehyde **IIIa** in 90% yield.

With the aim to use this reaction for the preparation of 4-(dibromomethyl)benzaldehyde **Ia**—a promising heterofunctional compound for organic synthesis—synthesized by us for the first time [5], we reacted compounds **Ie** and **II** in different ratios.

According to ^{1}H NMR, the reaction mixture contained no tetrabromide **Ie** at the 1.0 : 1.5 ratio. Compounds **Ia** and **IIIa** were isolated in individual state by column chromatography (benzene as an eluent, silica gel as a sorbent) in 11 and 64% yield, respectively.

Thus, in the absence of tetrabromide **Ie**, terephthalic aldehyde **IIIa** is the major reaction product; i.e., the second dibromomethyl group of compound **Ie** is involved in the reaction to give target compound **Ia** in

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