Br_2—$B(OMe)_3$—MeOH SYSTEM FOR THE α-MONOBROMINATION OF KETONES

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The α-monobromination of ketones by molecular bromine is frequently complicated by the formation of dibromo derivatives and structural isomers [1, 2]. Thus, the search for selective methods for the bromination of ketones remains an important problem in organic synthesis [3-6].

In the framework of these studies, we are the first to show that trimethyl borate has a positive effect on the α-monobromination of ketones. For example, the reaction of Br_2 with acetone, cyclohexanone, acetophenone, or p-bromoacetophenone in methanol in the presence of $B(OMe)_3$ gives the corresponding α-bromo derivatives with 60-80% yields. The α-bromoketones obtained were identified by comparison with authentic samples and conversion to α-phthalimidoketones by the action of potassium phthalimide in DMF.

A sample of 1.2 ml Br_2 was added with stirring and cooling to a solution of 4 g p-bromoacetophenone in a mixture of 15 ml methanol and 3 ml $B(OMe)_3$ and stirred until the bromine disappeared, which took about 1 h at ∿20°C. The precipitate formed was filtered off, washed with methanol, and dried in the air to give 3.6 g p, α-dibromoacetophenone, mp 108-109°C. PMR spectrum in CCl_4 (δ, ppm): 4.01 s (CH_2), 7.30 q (4H, arom. ring). The partial evaporation of the mother liquor gave an additional 0.88 g bromination product. The total yield of this product was 80%. The yield of p, α-dibromoacetophenone was only 40% in the reaction of p-bromoacetophenone with Br_2 in methanol in the absence of $B(OMe)_3$.

Analogously, the bromination of acetone (∿10 min), cyclohexanone (∿10 min), acetophenone (∿30 min) with subsequent treatment of the reaction mixtures with water and chloroform extraction gave bromoacetone, bp 77-80°C (100 mm), PMR spectrum in CCl_4 (δ, ppm): 2.25 s (CH_3), 3.91 s (CH_2), 2-bromocyclohexanone, bp 110-113°C (20 mm), PMR spectrum in CCl_4 (δ, ppm): 2.03 m (—$(CH_2)_3$—), 2.85 m (CH_2CO), 4.56 m (CHBr), and α-bromoacetophenone, bp 138-141°C (12 mm), mp 49-50°C, PMR spectrum in CCl_4: 4.20 s (CH_2), 7.30 m, 7.76 m (arom. ring protons) in 60, 70, and 73% yield, respectively.

The selective α-bromination of ketones by the Br_2—$B(OMe)_3$—MeOH system may compete with previously described procedures [3-6] due to its high yields and simplicity.

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