

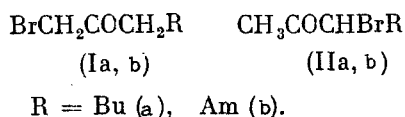
**Br₂-CO(NH₂)₂-AcOH SYSTEM FOR THE HIGHLY SELECTIVE
α-MONOBROMINATION OF KETONES**

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The search for convenient, selective methods for the halogenation of ketones is one of the important problems in organic chemistry [1-5].

We are the first to establish that the Br₂-CO(NH₂)₂-AcOH system may be used for the highly selective α-monobromination of ketones and the 1-bromination of 2-alkanones



A sample of 1.4 ml (27.5 mmoles) Br₂ was added with stirring and ice water cooling to a mixture of 4 ml (25.6 mmoles) 2-octanone and 2.5 g (41.7 mmoles) CO(NH₂)₂ in 10 ml acetic acid and stirred at 18-20°C until the bromine disappeared (~4 h). This mixture was diluted with water and extracted with CH₂Cl₂. The extract was washed with aqueous sodium carbonate, dried over MgSO₄, and evaporated to give 3.8 g (71%) 1-bromo-2-octanone (Ib), bp 117-120°C (19 mm), n_D¹⁸ 1.4660. PMR spectrum in CCl₄ (δ, ppm): 0.81 m (CH₃), 1.30 m (CH₂)₄, 2.56 t (CH₂CO, J = 7 Hz, 3.75 s (COCH₂Br). Gas-liquid chromatography indicated that the sample of bromoketone (Ib) contained 10% of the isomeric 3-bromoketone (IIb).

The analogous procedures for 2-heptanone (5 h at -18-20°C), acetophenone (24 h at -20°C and then 1 h at 45-50°C), and cyclohexanone (0.5 h at -20°C) correspondingly gave 1-bromo-2-heptanone (Ia), 7% of the isomeric 3-bromoketone (IIa), bp 105-109°C (20 mm), n_D²⁰ 1.4640, α-bromoacetophenone, mp 48-49°C, and 2-bromocyclohexanone, bp 108-111°C (19 mm), n_D²⁰ 1.5130. The yields of these products were 74, 80, and 69%, respectively.

The bromination of 2-heptanone and 2-octanone in acetic acid without CO(NH₂)₂ gave (IIa) and (IIb), while the reactions in methanol with CO(NH₂)₂ gave ~82:18 mixtures of (Ia) and (IIa) and of (Ib) and (IIb).

It is interesting to note that the combined use of CO(NH₂)₂ and acetic acid, which have opposite effects on the orientation of the bromination of 2-alkanones, enhances one of these effects. In light of its simplicity and high selectivity, the proposed method for the α-monobromination of ketones may be competitive with other methods [1-5].

LITERATURE CITED

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