$NaBO_2\cdot 4H_2O$–KBr–$Bu_4\overset{+}{N}\overset{-}{I}$–DMF SYSTEM FOR THE N-ALKYLATION OF IMIDES BY α-BROMOKETONES

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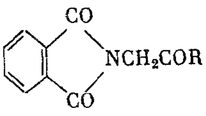
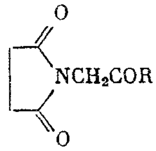
α-Phthalimidoketones obtained by the reaction of α-bromoketones and potassium phthalimide are used in the Gabrial synthesis of α-aminoketones. We are the first to establish that α-bromoketones may be employed in N-alkylation reactions with free imides (phthalimide and succinimide) in the presence of the $NaBO_2\cdot 4H_2O$–KBr–$Bu_4\overset{+}{N}\overset{-}{I}$ system in DMF at 20°C,


(Ia—c)


(IIa—b)

R = Et (Ia), $(CH_2)_5CH_3$ (Ib), Ph (Ic), (IIa), C_6H_4Br-*n* (IIb)

A mixture of 0.74 g (5.02 mmoles) phthalimide, 1 g (5.02 mmoles) α-bromoacetophenone, 1.2 g (8.70 mmoles) ground $NaBO_2\cdot 4H_2O$, 1 g (8.40 mmoles) KBr, and 0.2 g (0.54 mmole) $Bu_4\overset{+}{N}\overset{-}{I}$ in 8 ml DMF was stirred for 10 h at about 20°C and diluted with water. The precipitate was filtered off, washed with water and ether, and dried in the air to give 1.1 g (82%) N-phenacylphthalimide (Ic), mp 165-167°C (from ethanol). PMR spectrum in $CDCl_3$ relative to HMDS (δ, ppm): 5.05 s (CH_2), 7.63 m (aromatic ring).

Analogously, the corresponding imides and α-bromoketones gave N-(2-oxobutyl)phthalimide (Ia), mp 106-108°C (from ether at −70°C), N-(2-oxooctyl)phthalimide (Ib), mp 56-58°C (from ether at −70°C), N-phenacylsuccinimide (IIa), mp 143-144°C (from ethanol), and N-(p-bromophenacyl)succinimide (IIb), mp 173-175°C (from ethanol). The yields of these products were 78, 73, 80, and 86%, respectively.

The use of $Bu_4\overset{+}{N}\overset{-}{I}$ as a phase transfer catalyst and a solution of KBr in DMF as a highly polar medium facilitates a smooth course for this alkylation reaction. The proposed method for the N-alkylation of cyclic imides permits us to bypass the prior preparation of their metal derivatives and obtain pure imidoketones in high yield.

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