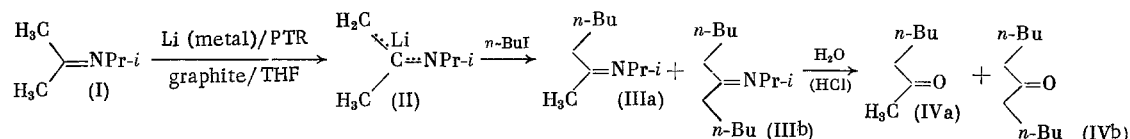


GRAPHITE AS A HYDROGEN ACCEPTOR IN DIRECT LITHIATION REACTIONS

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Graphite may be used as an acceptor in direct lithiation reactions by metallic lithium in the presence of a phase-transfer reagent (PTR)



This method does not require prior preparation of the inclusion complex. 5-Crown-15 was used as the PTR. A mixture of 4.25 ml (0.03 mole) imine (I), 0.21 g lithium foil (0.03 g-atom), 0.5 g graphite, 0.2 ml 5-crown-15, and 20 ml tetrahydrofuran was stirred rapidly in an argon atmosphere at 20°C. The lithium was almost completely dissolved after about 2 h. Then, 3.4 ml (0.03 mole) butyl iodide was added, and after 15 min the mixture was treated with hydrochloric acid or aqueous ammonia in order separate imine (III). After the completion of hydrolysis, the mixture was filtered and reaction product (IV) was extracted with ether and distilled. The yield of ketones (IV) was 65%. The (IVa)/(IVb) ratio was 4.6:1.

Methyl amyl ketone (IVa), bp 37-39°C (9 mm); semicarbazone, mp 120°C. PMR spectrum (CCl₄, δ, ppm): 0.86 t (3H, CH₃), 1.26 br.s (6H, CH₂), 1.97 t (3H, CH₃CO-). Mass spectrum: m/z 114.

Diamyl ketone (IVb), bp 100-104°C (9 mm). PMR spectrum (CCl₄, δ, ppm): 0.86 t (6H, CH₃), 1.26 br.s (12H, CH₂), 2.22 t (4H, CH₂CO-). Mass spectrum: m/z 170.

Air-dried graphite from the reaction upon heating increases its volume by a factor of 8-10.