Synthesis of *NN'*-Disubstituted Ureas from Nitro-compounds using Bromomagnesium Alkyl- or Aryl-amides and Pentacarbonyliron

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Summary *NN'*-Disubstituted ureas were prepared under mild conditions in high yields from nitro-compounds using bromomagnesium alkyl- or aryl-amides and pentacarbonyliron.

ALTHOUGH several syntheses of substituted ureas have been reported,[1] only a few have described their derivation from nitro-compounds.[2] These reactions are restricted to aromatic nitro-compounds and are of no use in syntheses because of the poor selectivity and drastic reaction conditions.

TABLE. Synthesis of substituted ureas.

Amide $R^1NHMgBr$ R^1	Nitro-compound R^2NO_2 R^2	% Yield of urea[a] $R^1NHCONHR^2$
Ph	Ph	99
Ph	p-MeC_6H_4	71
Ph	p-$MeOC_6H_4$	80
Ph	p-ClC_6H_4	92
$Me[CH_2]_{11}$	Ph	42
p-MeC_6H_4	$Me[CH_2]_2$	50
Ph	C_6H_{11}	60
C_6H_{11}[b]	Ph	72
C_6H_{11}	C_6H_{11}	55

[a] Isolated yields based on the amount of nitro-compound. All compounds gave satisfactory analytical and spectroscopic data.
[b] C_6H_{11} = cyclohexyl.

We now report a synthesis of *NN'*-disubstituted ureas from aromatic and also aliphatic nitro-compounds using bromomagnesium alkyl- or aryl-amides, RNHMgBr, and pentacarbonyliron [equation (1)].

$$R^1NHMgBr + Fe(CO)_5 \xrightarrow{R^2NO_2} \xrightarrow{H^+} R^1NHCONHR^2 \quad (1)$$

The synthesis of *NN'*-diphenylurea is typical. A solution in tetrahydrofuran (40 ml) of bromomagnesium anilide (22 mmol)† and pentacarbonyliron (11 mmol) was stirred for 30 min at 0 °C under argon, and nitrobenzene (11 mmol) was then injected. CO_2 was evolved in a vigorous reaction. After 1 h, 10% H_2SO_4 (50 ml) was added and the mixture was extracted with diethyl ether (50 ml). The extract was dried (Na_2SO_4) overnight, solvent was removed, and recrystallization from ethanol of the resulting white solid gave pure *NN'*-diphenylurea (2·32 g, 99% based on nitrobenzene). The product was identified by its i.r. and n.m.r. spectra, and elemental analysis. Further results are shown in the Table.

In these reactions, we assume that carbamoyl tetracarbonylferrates are formed as intermediates from the bromomagnesium amides and pentacarbonyliron [equation

$$RNHMg + Fe(CO)_5 \longrightarrow [RNHCOFe(CO)_4]^-[MgBr]^+ \quad (2)$$

(2)], which react with the nitro-compounds in a similar manner to acyl carbonylferrates,[3] although the mechanism is obscure. Treatment of a mixture of bromomagnesium anilide and pentacarbonyliron with excess of methyl iodide gave acetanilide [60% yield based on an amount of $Fe(CO)_5$], strongly suggesting the formation of phenylcarbamoylferrate as an intermediate.[4]

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† Bromomagnesium alkyl- or aryl-amides were prepared *in situ* by the reaction of amines with n-butylmagnesium bromide in tetrahydrofuran.

[1] S. R. Sandler and W. Karo, 'Organic Functional Group Preparations,' Vol. II, Academic Press, New York, 1971, p. 134.

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[3] M. Yamashita, Y. Watanabe, T. Mitsudo, and Y. Takegami, *Tetrahedron Letters*, 1976, 1585.

[4] Treatment of acyl tetracarbonylferrates with alkyl iodides gives the corresponding ketones (J. P. Collman, S. R. Winter, and D. R. Clark, *J. Amer. Chem. Soc.*, 1972, **94**, 1788.