Formation of Amines from Aromatic Hydrocarbons in Molecular Nitrogen Fixation Reactions

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Summary Reaction of molecular nitrogen with sodium and naphthalene in tetrahydrofuran gives amines plus ammonia in the presence of $TiCl_4$; a similar reaction occurs using lithium even in the absence of $TiCl_4$.

IT has been shown that aromatic amines can be formed in reactions of molecular nitrogen with systems based on organo-lithium and -titanium compounds. These reactions seem to proceed *via* insertion of N_2 into the Ti–C bond.†[1]

It was of interest to attempt a synthesis of amines directly from molecular nitrogen and hydrocarbons; for this purpose reactions of hydrocarbons with transition metal compounds which result in formation of σ-carbon–metal bonds were thought likely to be effective.

Some transition-metal compounds, by reaction with aromatic anion-radical solutions, are capable of forming complexes containing transition-metal–aryl σ-bonds.[4,5] Similar systems may also reduce molecular nitrogen to ammonia (after hydrolysis).[5–7]

We have found that reactions of molecular nitrogen with a mixture of naphthalene and sodium in tetrahydrofuran in the presence of $TiCl_4$ give after hydrolysis ammonia, together with aromatic amines: α-naphthylamine, 5,8-dihydro-α-naphthylamine, 5,6,7,8-tetrahydro-α-naphthylamine, and β-naphthylamine (formation of hydrogenated derivatives of β-naphthylamine was not studied).‡ The yield of amines and their relative amounts depend upon the ratio of components: the higher the sodium : naphthalene ratio, the higher the yield of amines (see Table). In the absence of the titanium compound, neither naphthylamines nor ammonia were found.

Metallic lithium can be used instead of sodium as the reducing agent, producing the same amines, but in higher yields (*cf.* ref. 8). It is noteworthy that in this case formation of ammonia and amines occurs in the absence of $TiCl_4$, also.§ The addition of the titanium salt to a mixture of naphthalene and lithium causes some increase in the yield of amines (particularly for relatively high quantities of titanium compound) (see Table).

Some other aromatic hydrocarbons also undergo these reactions to give the corresponding aromatic amines (along with ammonia). Thus, in the case of biphenyl *o*- and *p*-aminobiphenyls were found.

Formation of amines from naphthalene and N_2[a]

System	Molar ratio of the components	Total yield of amines mol. % calc. on $TiCl_4$	calc. on $C_{10}H_8$	Content of amines in mixture in %[b] A	B	C	D
$TiCl_4 + C_{10}H_8 + Na$	1 : 6 : 6	0·1	*ca.* 0·02	70	30	—	—
	1 : 6 : 24	0·25	*ca.* 0·04	24	12	—	64
	1 : 6 : 100	0·5	*ca.* 0·08	17	—	37	46
$C_{10}H_8 + Na$	6 : 100	none					
$TiCl_4 + C_{10}H_8 + Li$	1 : 6 : 6	0·06	0·01	83	17	—	—
	1 : 6 : 24	0·9	0·15	60	—	35	5
	1 : 6 : 100	2·7	*ca.* 0·5	47	—	53	—
	3 : 6 : 100	2·3	*ca.* 1·2	70	—	19	11
$C_{10}H_8 + Li$	6 : 6		0				
	6 : 24		0·08	23	—	70	7
	6 : 100		0·3	26	—	26	48

[a] THF solution, room temperature, pressure of N_2 80—100 at., reaction time 6 h.
[b] A α-naphthylamine; B β-naphthylamine; C 5,8-dihydro-α-naphthylamine; D 5,6,7,8-tetrahydro-α-naphthylamine.

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† Recently van Tamelen *et al.*[2] described an indirect two-step operation leading to amines: reduction of N_2 by the system $(C_5H_5)_2TiCl_2$ + Mg with formation of nitride-like products and subsequent treatment of these nitrides by aldehydes or ketones. Concerning fixation of nitrogen as ammonia by systems including Mg as a reducing agent, see ref. 3.

‡ This and all other reactions carried out under argon showed neither ammonia nor amines.

§ Ammonia yield (in the absence of $TiCl_4$) at molar ratio naphthalene : lithium 6 : 100 is 30 mol. % based on naphthalene (THF, room temperature, nitrogen pressure 80—100 atm. reaction time 6 h). In the absence of naphthalene there is no significant reaction between metallic lithium and N_2. Some other aromatic hydrocarbons also can activate lithium for reaction with N_2. Yields of NH_3 in the case of biphenyl is 21 mol. %; anthracene 2 mol. % (molar ratio ArH : Li = 6 : 100).

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