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NITROSO COMPOUNDS II[1]. THE REACTIONS OF DIORGANO-*N*-NITROSAMINES WITH METALLIC LITHIUM AND MAGNESIUM

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Our interest in the reactions of *N*-nitrosamines with organometallic reagents[2] led us to study and now report here the action of lithium and magnesium metals on some nitrosamines. Metallic lithium or magnesium reacts with compounds containing $C{=}O$ bonds by one-electron transfer to produce radical anions which dimerise to 1,2-diols[3]. We have found that these metals react with the $N\text{-}N{=}O$ functions of *N*-nitrosamines to give the parent secondary amines as the main products, presumably by the cleavage of the N-N bonds

Table 1 gives the experimental details of the various reactions. The formation of the secondary amines may be explained by the following mechanism :

$$R_2N\text{-}N{=}O \xrightarrow{M} \underset{\underline{1}}{R_2N\text{-}\dot{N}\text{-}O^-} + M^+ \xrightarrow{M} R_2N^-M^+ + \underset{\underline{2}}{[MNO]}$$

$$R_2N^-M^+ \xrightarrow{H_2O} R_2NH \quad ; \quad \underset{\underline{2}}{[MNO]} \longrightarrow \tfrac{1}{2}\,M_2O + \tfrac{1}{2}\,N_2O$$

The radical anion 1 , probably formed by an electron-transfer process, may not be very free from the metal surface and would more likely react with another atom of the metal than dimerise or react otherwise. The species 2 which may be the monomer of the corresponding hyponitrite[8] was not isolated. If it was formed it probably would disproportionate[9,10] under the reaction conditions producing nitrous oxide. Although we did not positively identify nitrous oxide we did observe the evolution of a colourless gas during the reaction.

The cleavage reaction to produce the secondary amines seems to be faster with lithium than with magnesium (Table 1), probably reflecting the electropositive nature of these metals. Under similar conditions the yield of the secondary amine decreases along the following series :

$Ph_2N\text{-}NO$, $PhRN\text{-}NO$, $R_2N\text{-}NO$

Since the secondary amine is formed by the cleavage of the N-N bond, the above series may also represent the decreasing ease with which this bond is cleaved by the metals.

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This is feasible because a phenyl group would be expected to delocalize the lone electron pair of the amino nitrogen and as a result the double bond character[11] of the N-N bond would be lowered. This makes the N-N bonds in *N*-phenylated nitrosamines more vulnerable to cleavage than those in *N*-alkylated ones.

Table 1. Reactions[4,5] of *N*-nitrosamines with lithium and magnesium

Nitrosamine (mole)	Metal (gram-atom)	Ether ml	Temp °C	Time hr	Products[6] (% yield)	Unreacted nitrosamine (%)
Me_2NNO (0.10)	Li (0.30)	75	27	2	Me_2NH (some)[7]	Me_2NNO (a lot)
Me_2NNO (0.10)	Mg (0.30)	50	35	4	Me_2NH (trace)	Me_2NNO (a lot)
n-Bu_2NNO (0.05)	Li (0.15)	75	27	2	*n*-Bu_2NH (2)[7]	*n*-Bu_2NNO (89)
n-Bu_2NNO (0.05)	Mg (0.15)	50	35	4	*n*-Bu_2NH (0.5)	*n*-Bu_2NNO (96)
PhEtNNO (0.05)	Li (0.15)	75	27	2	PhEtNH (19)[7]	PhEtNNO (a lot)
PhEtNNO (0.10)	Mg (0.30)	75	35	4	PhEtNH (8)	PhEtNNO (88)
Ph_2NNO (0.05)	Li (0.15)	75	27	2	Ph_2NH (25)[7]	Ph_2NNO (65)
Ph_2NNO (0.05)	Mg (0.15)	75	35	4	Ph_2NH (6)	Ph_2NNO (90)

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4. For details of the general experimental conditions see M. T. Rahman, M. R. Smith Jr., A. F. Webb and H. Gilman, Organometal. Chem. Syn., 1970/1971, 1 , 105; M. T. Rahman and H. Gilman, J. Indian Chem. Soc., 1974, 51 , 1018.
5. These reactions were stopped deliberately after definite intervals to compare the yields. The yields of the secondary amines therefore are not necessarily the best obtainable.
6. The products were identified by TLC under at least three different solvent conditions, by b.p./m.p., and where possible also by mixed m.p. Dibutylamine was identified by b.p. and superimposable IR and estimated by GLC. All other products were estimated by weighing after separation by column chromatography.
7. There were also formed small amounts of nitrogen-containing substances, presumably polymeric in nature, but these were not identified.
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