SNN'-Substituted Diimidosulphur Compounds from Alkylation or Arylation of Diimidosulphur Compounds: A Simple Method for Quantitative Determination of Grignard, Lithiumalkyl and Lithiumaryl Reagents

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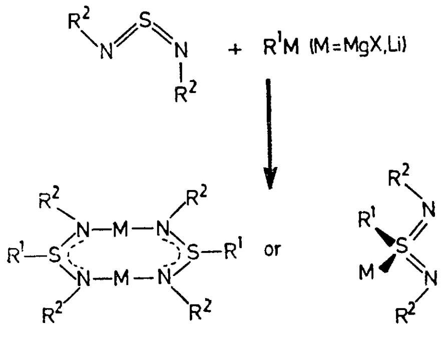
Summary *S*-alkyl- or aryl-substituted *NN'*-dialkyl-or diaryldiimidosulphur compounds are obtained in the reactions of R^1MgX, R^1_2Mg and R^1Li with R^2–N=S=N–R^2 (R^1 and R^2 = alkyl or aryl); the reactions are quantitative and can be used in titrations of solutions of these reagents.

IN the course of our work on the co-ordination properties of diimidosulphur[1,2] we have found that similar to the reactions[3] of sulphonamides with Grignards, lithiumalkyls or lithiumaryls, *NN'*-dialkyl- and diaryldiimidosulphur compounds react quantitatively with these reagents in dry ether under nitrogen and *S*-substituted, *NN'*-dialkyl- or diaryldiimidosulphur compounds of Mg or Li are obtained.

On the basis of n.m.r. spectroscopy (equivalent R^2 groups) either structure (I) (the most likely) or (II) is proposed. In the case of diaryldiimidosulphur compounds the orange-red ethereal solutions (R^2 = *e.g.* phenyl, tolyl, *p*-chlorophenyl, 3,5-xylyl, 2,4,6-mesityl; 1·00 mmol in 5—10 ml ether) become colourless (in some cases very light yellow) just at the equivalence point when R^1M is added under argon or nitrogen, and remain colourless if excess R^1M is added. Using the easily[2,4] and cheaply[4] accessible di-*p*-tolyl- (preferably) or di-*p*-chlorophenyldiimidosulphur this reaction is very suitable for titration purposes as no alkoxide, oxide or metallic impurities of R^1MgX, R^1_2Mg and R^1Li react with the diimidosulphur compounds. Since it is simple, rapid, requires no special equipment and is reproducible within volumetric analysis error, it is superior to the normal procedures which involve spectroscopic,[5] gas chromatographic,[6] thermal,[7] high-frequency titration[8] or two-step titration methods[9] (except for the 'alcohol' titration method[10] which is also simple and general).

The Grignard solution (R^1 = Me, Et, Pr^i, Bu^t, Ph, tolyl) is added dropwise under nitrogen to the orange-red solution



(I) (II)

of di-*p*-tolyldiimidosulphur in ether until the colour disappears completely in one drop. If R^1 = 2,4,6-mesityl or methallyl the diimidosulphur solution should be added to the Grignard (at about 0 °C). The reactions with $R^1{}_2Mg$ and R^1Li are analogous although in the latter case the temperature should be kept at 0 °C (preferably −20 °C) and for R^1 = Pr^i or Bu^t at −40 °C.

Most of the reactions could be followed by n.m.r. spectroscopy and at low temperatures very moisture sensitive white products could be isolated {*e.g.* *SNN'*-tris-t-butyl- [δ (C_6D_6) 1·34(2x) and 1·20]; *S*-phenyl-*NN'*-di-t-butyl- [δ (C_6D_6) 1·33]; *S*-methyl-*NN'*-di-*p*-tolyl- [δ (C_6D_6) 2·60 (Me) 2·16, 6·85, 6·90, (tolyl)] and *S*-phenyl-*NN'*-di-*p*-tolyl diimidosulphur-lithium [δ(C_6D_6) 2·21 and 6·95 (tolyl)]} for which satisfactory analyses were obtained.

Hydrolysis of the compounds obtained from diaryldiimidosulphur compounds gave mainly the corresponding arylamine.

These novel diimidosulphur ligands form a new class of compounds with transition metals *e.g.* [Ag(*S*-t-butyl-*NN'*-di-*p*-tolyldiimidosulphur)]$_2$ [δ ($CDCl_3$) 1·34 (Bu^t), 2·21, 6·94, 7·00 (tolyl)] and the corresponding Cu-compound [δ ($CDCl_3$) 1·40 (Bu^t), 2·22, 6·93, 7·08(tolyl)]. The dimeric structures (molecular weight) clearly indicate that the diimidosulphur group is bridging.

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