

**Nickel-induced Conversion of Carbon–Sulphur into Carbon–Carbon Bonds.
One-step Transformations of Enol Sulphides into Olefins and
Benzenethiol Derivatives into Alkylarenes and Biaryls**

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Summary The reactions of alkenyl sulphides, benzenethiols, and aryl sulphides with methylmagnesium and arylmagnesium bromides, mediated by bis(triphenylphosphine)nickel dichloride, in benzene solution have been shown to lead to olefins (predominantly with retention of configuration), toluenes, and biphenyls in medium to high yields.

RECENTLY a new carbon–carbon bond-forming reaction was introduced, which showed that MeMgBr and PhMgBr react under the influence of phosphine-ligated nickel dichloride with enol ethers to furnish olefins, and that PhMgBr also reacts with aryl ethers to yield biaryls.¹ The observation of the formation of *p*-methylbiphenyl from a nickel-induced reaction between an aryl toluene-*p*-sulphonate and

TABLE. The reactions of thioenol ethers and benzenethiol derivatives with methyl-, phenyl-, and *p*-tolyl-magnesium bromides.^{a, b}

	Products	% Yield
1-Methylthio-oct-1-ene (4:1) ^c	{ Non-2-ene (5:1) ^e	71
	{ 1-Phenyloct-1-ene (4:1) ^c	80
Thiophen	{ 1,4-Diphenylbuta-1,3-diene ^d	85
Thianaphthene	{ <i>o</i> -Propenyltoluene (1:3) ^c	48
	{ <i>o</i> -Phenylstilbene (1:1) ^c	61
Dibenzothiophen	{ <i>o,o'</i> -Dimethylbiphenyl	73
	{ <i>o,o'</i> -Quaterphenyl	52
Benzenethiol ^e	{ Toluene	64 ^f
	{ <i>p</i> -Methylbiphenyl	62
<i>p</i> - <i>t</i> -Butylbenzethiol	{ <i>p</i> - <i>t</i> -Butyltoluene ^g	50
	{ <i>p</i> - <i>t</i> -Butylbiphenyl ^g	30
Thioanisole	{ Toluene	97 ^f
	{ <i>p</i> -Methylbiphenyl	74
<i>p</i> - <i>t</i> -Butylthioanisole	{ <i>p</i> - <i>t</i> -Butyltoluene ^g	55
	{ <i>p</i> - <i>t</i> -Butylbiphenyl ^g	53
Diphenyl sulphide	{ Toluene	74 ^f
	{ <i>p</i> -Methylbiphenyl	74
<i>p</i> - <i>t</i> -Butylthioanisole oxide	{ <i>p</i> - <i>t</i> -Butyltoluene	50
Diphenyl sulphoxide	{ Toluene	77 ^f
	{ <i>p</i> -Methylbiphenyl	57
Methyl phenyl sulphone	{ Toluene	97 ^f
	{ <i>p</i> -Methylbiphenyl	45
Diphenyl sulphone	{ Toluene	70 ^f
	{ <i>p</i> -Methylbiphenyl	53
Sodium toluene- <i>p</i> -sulphinat ^e	{ <i>p</i> -Methylbiphenyl	27

^a All starting materials and end products are known substances and were available commercially or prepared by standard means.
^b A benzene solution of ca. 2–5 mol of Grignard reagent and 0.1 mol of bis(triphenylphosphine)nickel dichloride per mol of sulphur compound was refluxed for 1–30 h. ^c *trans*:*cis* Ratio. ^d 1:1 Mixture of stereoisomers. ^e Refluxing for 48–72 h. ^f Based on g.l.c. analysis. ^g The by-product (8–15% yield) was *t*-butylbenzene.

PhMgBr² led to this study of nickel-mediated reactions of organomagnesium compounds with alkenyl sulphides and various aromatic sulphur compounds.

As the Table indicates, methylmagnesium and arylmagnesium bromides react in the presence of bis(triphenylphosphine)nickel dichloride catalyst with alkenyl sulphides, aryl thiols, and aryl sulphides and their sulphoxides and sulphones in medium to high yields.³ This efficient replacement of a carbon–sulphur bond by a carbon–carbon linkage requires the nickel catalyst⁴ and is limited to substances containing unsaturated carbon–sulphur bonds, as shown by the inertness of di-*n*-octyl sulphide to MeMgBr as well as PhMgBr in the presence of the nickel salt. The sulphur displacement process is faster for alkenyl sulphides (*i.e.* the first three entries in the Table) than for aryl sulphides and leads predominantly to retention of the olefin configuration. These properties are similar to those observed for enol and aryl ethers¹ and alkenyl and aryl halides.⁵ The sulphur replacement is duplicated also by selenium compounds. Thus the nickel-catalysed reaction of phenyl vinyl selenide with *p*-tolylmagnesium bromide yielded *p*-methylbiphenyl (60%) and *p*-methylstyrene (25%).

In general, sulphur compounds undergo the catalysed

reaction with Grignard reagents more readily than the corresponding oxy compounds,¹ remarkable contrasts being the ready interaction of aryl sulphides with MeMgBr compared with the inertness of anisoles towards this reagent¹ as well as the ease of replacement of an aromatic sulphydryl group *vs.* the strong resistance of phenolic hydroxy groups towards substitution by aryl groups.¹

No reaction took place between several of the thio compounds (*cf.* the Table) and EtMgBr in the presence of the nickel species, even though such reaction had occurred with an enol ether.¹ However, the use of bis(1,3-diphenylphosphino)propanenickel dichloride as catalyst with EtMgBr caused the fast transformation of *p*-*t*-butylthioanisole into *p*-*t*-butylethylbenzene (36%). In contrast to the observation of both ethylation and reduction products in the reaction of the enol ether with the Grignard reagent¹ no reduction product resulted from reaction with the thioanisole.⁶

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¹ E. Wenkert, E. L. Michelotti, and C. S. Swindell, *J. Amer. Chem. Soc.*, 1979, **101**, 2246.

² Footnote 5 of ref. 1.

³ All reactions yield biphenyl as a minor by-product. In the reactions involving phenylmagnesium bromide it originates in the preparation of the Grignard reagent, whereas in the reactions with methylmagnesium and *p*-tolylmagnesium bromides it arises from the interaction of the Grignard reagent with the triphenylphosphine ligand of the catalyst (M. L. H. Green, M. J. Smith, H. Felkin, and G. Swierczewski, *Chem. Comm.*, 1971, 158).

⁴ Grignard reagents leave sulphides unaffected, act as bases towards thiols, alkyl sulphoxides, and alkyl sulphones, and behave as nucleophiles toward sulphoxides (M. S. Kharasch and O. Reinmuth, 'Grignard Reactions of Nonmetallic Substances,' Prentice-Hall, New York, 1954, p. 1296). None of these activities interfere with the nickel-induced reaction.

⁵ K. Tamao, K. Sumitani, Y. Kato, M. Zembayashi, A. Fujioka, S. Kodama, I. Nakajima, A. Minato, and M. Kumada, *Bull. Chem. Soc. Japan*, 1976, **49**, 1958, and references therein.

⁶ Towards the end of this investigation there appeared a study of the nickel-catalysed reactions of alkenyl phenyl (or alkyl) sulphides in ether solvents (H. Okamura, M. Miura, and H. Takei, *Tetrahedron Letters*, 1979, 43) and we became aware of a report on nickel-catalysed reactions of alkenyl *t*-butyl sulphones with methylmagnesium halides in ether solvents (M. Julia, 'Organic Synthesis with Sulphones,' Plenary Lectures of the 8th International Symposium on Organic Sulphur Chemistry, Portoroz, Yugoslavia, June 1978, pp. 121–146). We thank Professor Julia for drawing our attention to the latter work.