

Novel Coupling of Dithioacetals with Grignard Reagents

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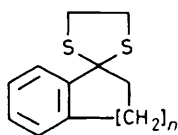
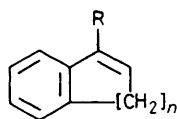
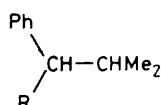
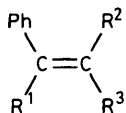
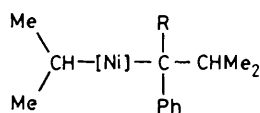
Dithioacetals react with Grignard reagents in the presence of a catalytic amount of $[\text{NiCl}_2(\text{PPh}_3)_2]$ to give the corresponding olefinic coupling products in good yields; a mechanism for the reaction is suggested.

The transition-metal-mediated transformation of thioethers into other functions has received much attention.¹⁻³ Vinyl, aryl,² and allyl sulphides³ can couple readily with Grignard reagents in the presence of a nickel catalyst. On the other hand, the chemistry of the dithioacetal functionality is relatively little explored.^{4,5} We recently reported that tung-

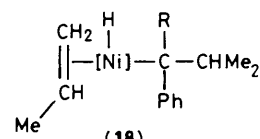
sten hexacarbonyls can promote desulphurisation-dimerisation of dithioacetals to give the corresponding dimeric alkenes.⁵ We now describe another synthetic use of dithioacetals, their reaction with Grignard reagents in the presence of a catalytic amount of $[\text{NiCl}_2(\text{PPh}_3)_2]$.

In a typical procedure, the dithioacetal was treated under

nitrogen with 3 equiv. of the Grignard reagent and $[\text{NiCl}_2(\text{PPh}_3)_2]$ (5 mol %) in ether-benzene at ambient temperature for 7–20 h. After work-up and chromatographic

(1) $n = 2$ (3) $n = 1$ (2) $n = 2, R = \text{Me}$ (4) $n = 1, R = \text{Me}$ (19) $n = 2, R = \text{Ph}$ (5) $R = \text{Ph}$ (9) $R = \text{PhCH}_2$ (13) $R = \text{Ph}$ (16) $R = \text{PhCH}_2$ (6) $R^1 = \text{Ph}, R^2 = R^3 = \text{H}$ (7) $R^1 = \text{Ph}, R^2 = \text{Me}, R^3 = \text{H}$ (8) $R^1 = \text{Ph}, R^2 = \text{Pr}^i, R^3 = \text{H}$ (10) $R^1 = \text{PhCH}_2, R^2 = R^3 = \text{H}$ (11) $R^1 = \text{H}, R^2 = \text{Me}, R^3 = \text{Ph}$ (12) $R^1 = \text{Ph}, R^2 = R^3 = \text{Me}$ (14) $R^1 = \text{H}, R^2 = \text{Pr}^i, R^3 = \text{Ph}$ (15) $R^1 = \text{PhCH}_2, R^2 = R^3 = \text{Me}$ 

(17)



(18)

separation the corresponding coupling products were obtained in good yields. The results are summarized in Table 1. Substrates containing β -hydrogen atoms normally afforded the corresponding cross-coupled alkenes in good yields. For example, tetralone dithioacetal (1) with methylmagnesium iodide gave 1-methyl-3,4-dihydronaphthalene (2) in 60% yield. In a similar manner, indanone dithioacetal (3) gave the corresponding methylated product (4) in 69% yield. Phenylmagnesium bromide behaved similarly to the methyl derivative.

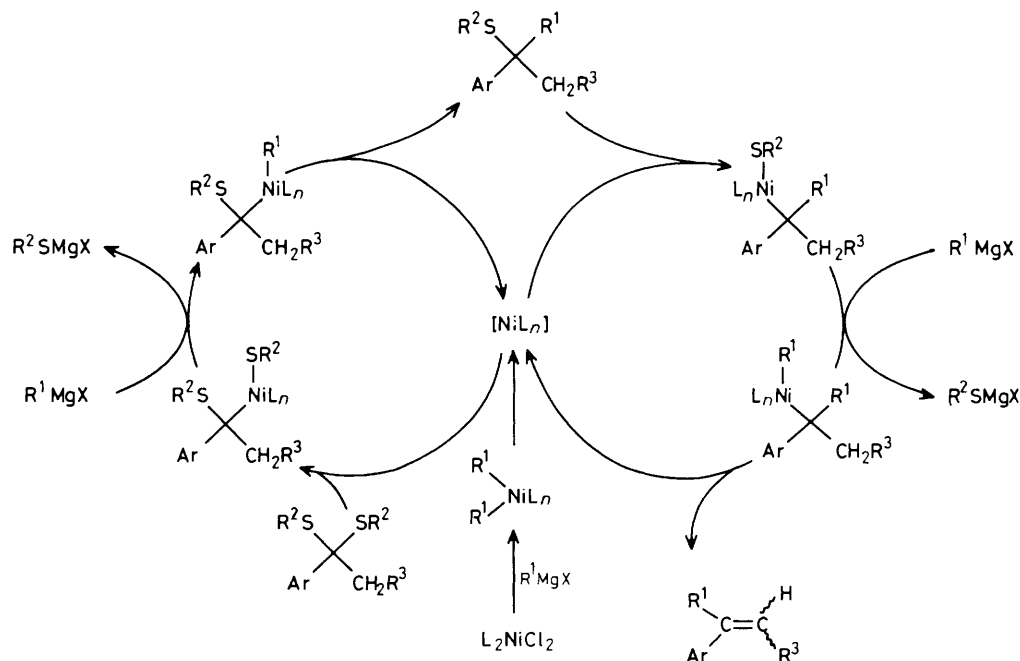
A suggested catalytic cycle for this reaction is outlined in Scheme 1. The two carbon-sulphur bonds in the substrate may not be cleaved at the same time. When the first carbon-sulphur bond is cleaved by nickel,⁶ the Grignard reagent may react immediately to give the corresponding alkylated intermediate. Nickel catalyst may then react with the second carbon-sulphur bond to give a sterically crowded alkylnickel intermediate which would readily undergo β -elimination to give an alkene.

The mechanism shown in Scheme 1 is supported by the reactions of substrates containing no β -hydrogen. Thus, the

Table 1. Coupling of dithioacetals with Grignard reagents.

Dithioacetal	RMgX	Product ^a	% Yield
(1)	MeMgI	(2)	60
(1)	PhMgBr	(19)	68
(3)	MeMgI	(4)	69
(5)	MeMgI	(6)	70
(5)	EtMgBr	(7)	78
(5)	BuMgBr	(8)	84
(9)	MeMgI	(10) and (11) (1:1)	83
(5)	Pr ⁱ MgBr	(12) and (13) (6.7:1)	76
(9)	Pr ⁱ MgBr	(14), (15) and (16) (1.6:1:1)	72

^a All compounds gave satisfactory spectroscopic data (n.m.r. and mass spectrometry).



Scheme 1

dithioacetal (**5**) of benzophenone reacted with MeMgI, EtMgBr, and BuMgBr under the usual conditions to afford in good yields 1,1-diphenylethene (**6**), 1,1-diphenylpropene (**7**), and 1,1-diphenylpent-1-ene (**8**), respectively. Furthermore, reaction of the dithioacetal (**9**) of benzyl phenyl ketone with MeMgI gave a 1:1 mixture of 1-benzyl-1-phenylethene (**10**) and 1-methylstilbene (**11**). These results indicate that C-C bond formation precedes β -elimination, as shown in Scheme 1.

The reaction of the dithioacetal (**5**) with PrⁱMgBr afforded a mixture of (**12**) and (**13**). In a similar manner, (**9**) gave a mixture of (**14**), (**15**) and (**16**), in 72% yield. In spite of the bulk of the isopropyl group, the reaction behaviour essentially follows the general pattern shown in Scheme 1. The formation of (**13**) and of (**16**) is striking. Presumably the intermediate (**17**), first formed according to Scheme 1, undergoes β -elimination to give the metal hydride (**18**), which then undergoes reductive elimination to afford the reduction products.

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