A Stereospecific Route to Olefins through Sequential Coupling Reactions of Grignard Reagents with 1-Bromo-2-phenylthioethene in the Presence of Nickel or Palladium Catalysts

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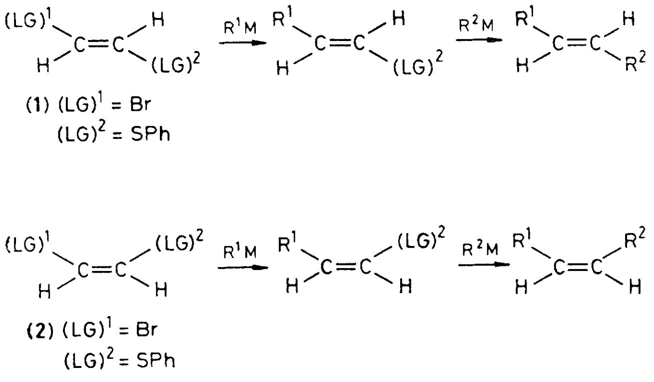
The room temperature sequential formation of two C–C bonds by reaction of aromatic or aliphatic Grignard reagents with (*E*)- or (*Z*)-1-bromo-2-phenylthioethene in the presence of nickel(II) or palladium(II) catalysts provides a novel stereospecific route to a variety of (*E*)- or (*Z*)-olefins of the R–CH=CH–R and R^1–CH=CH–R^2 type, with a stereoselectivity higher than 99% for the (*E*) isomers and in the range 95—98% for the (*Z*) isomers.

Many methods exist for the synthesis of symmetric and non-symmetric 1,2-disubstituted ethenes. However, when stereoselectivity is required, the synthetic task becomes much more difficult, and procedures of various degrees of complexity and validity have been proposed.[1] In recent years, significant progress in this field has been achieved[2] by the use of copper(I) reagents which permit the synthesis of the (*Z*) isomers with a stereoselectivity higher than 99%. We reasoned that a very simple synthesis of *both* (*Z*) and (*E*) isomers of dialkyl- and diaryl-ethenes could be based on sequential formation of two C–C bonds which should occur when ethenes bearing two different leaving groups were allowed to react with suitable



Scheme 1

organometallic reagents according to Scheme 1 [$(LG)^1$ being a better leaving group than $(LG)^2$ and RM being an organometallic species able to undergo cross-coupling]. Kumada and coworkers have reported that (*Z*)- and (*E*)-1,2-dichloroethenes couple with Grignard reagents in the presence of Ni^{II} complexes to give symmetrical dialkyl- or diaryl-ethenes in a non-stereospecific manner.[3] The substitution of a methoxy-[4a] or methylthio-[4b] group has been carried out by Wenkert and coworkers and further relevant work has been performed by others.[5] We now report two sequential stereospecific cross-coupling reactions of readily available (*E*)- and (*Z*)-1-bromo-2-phenylthioethene, (**1**) and (**2**),[6] using Ni^{II} or Pd^{II} complexes as catalysts.

When the (*E*) isomer (**1**) was allowed to react with a Grignard reagent in the presence of an Ni^{II} complex, substitution of the bromine was found to occur readily. Furthermore, when an excess of Grignard reagent and longer reaction times were used, the cross-coupling was followed by formation of the second C–C bond. Both aromatic and aliphatic reagents could be used. Retention of configuration (higher than 99% isomeric purity of the final olefin) was found to be maintained (see Table 1).

In order to prepare the non-symmetrical olefins, it was only necessary to use a different Grignard reagent after completion of the first reaction. Indeed, the leaving group ability of the bromine was so much higher than that of the phenylthio-group that formation of the symmetric final product (*i.e.* R^1–CH=CH–R^1) was completely avoided. Also, it is worth noting that the second reaction was performed by adding the Grignard reagent (*i.e.* R^2MgX) to the mixture containing the catalyst and the intermediate vinyl sulphide without isolation of the latter.

The same procedure was extended to the (*Z*)-isomer (**2**), but unsatisfactory results were obtained when the Ni^{II} catalyst was used in the first step (runs 7 and 9). Nevertheless, a change to a Pd^{II} catalyst brought about a significant improvement in the stereoselectivity, the isomeric purity of the final product increasing to values in the range of 95—98%.

Even when two different catalysts were used in the two reactions (runs 8, 10, 11, and 12) there was no need to isolate the vinyl sulphide intermediate. Isolation was required, however, for the other (*Z*)-isomers (runs 13 and 14).

In conclusion, although more work is needed to elucidate the scope and limitations of the present procedure, it appears to be a promising, conceptually straightforward, and useful route to olefins. The procedure has as a main feature a stereo-

Table 1. Sequential cross-coupling of (*E*)- or (*Z*)-1-bromo-2-phenylthioethene with Grignard reagents in the presence of nickel- or palladium-phosphine complexes as catalysts.[a]

$$\text{Br–CH=CH–SPh} \xrightarrow{\text{i, } R^1MgX/\text{catalyst}} R^1\text{–CH=CH–SPh} \xrightarrow{\text{ii, } R^2MgX/\text{catalyst}} R^1\text{–CH=CH–}R^2$$

	Substrate	Step i		Step ii				Overall	% Product	
Run	configuration	R^1MgX[b]	Catalyst[c]	R^2MgX[d]	Catalyst[c]	Time/h[e]	Final olefin[f]	yield (%)[g]	configuration (*E*)	(*Z*)
1[h,i]	(*E*)	PhMgBr	A	PhMgBr	A	30	Ph–CH=CH–Ph	100	>99	<1
2[l]	(*E*)	PhMgBr	A	MeMgI	A	14	Ph–CH=CH–Me	100	>99	<1
3[h,j]	(*E*)	Bu^nMgBr	A	Bu^nMgBr	A	14	Bu^n–CH=CH–Bu^n	90	>99	<1
4[h,k]	(*E*)	NpMgBr	A	NpMgBr	A	15	Np–CH=CH–Np	100	>99	<1
5[j]	(*E*)	Ph(Me)CHMgCl	A	Bu^nMgBr	A	22	Ph(Me)CH–CH=CH–Bu^n[l]	91	>99	<1
6[l]	(*E*)	Ph(Me)CHMgCl	A	PhMgBr	A	36	Ph(Me)CH–CH=CH–Ph	85	>99	<1
7[h,i]	(*Z*)	PhMgBr	A	PhMgBr	A	20	Ph–CH=CH–Ph	95	23	77
8[l]	(*Z*)	PhMgBr	C	PhMgBr	A	8	Ph–CH=CH–Ph	91	3	97
9[l]	(*Z*)	PhMgBr	A	MeMgI	A	14	Ph–CH=CH–Me	80	10	90
10[l]	(*Z*)	PhMgBr	C	MeMgI	A	8	Ph–CH=CH–Me	93	3	97
11[j]	(*Z*)	Bu^nMgBr	C	Bu^nMgBr	A	24	Bu^n–CH=CH–Bu^n	72	2	98
12[k]	(*Z*)	NpMgBr	C	NpMgBr	A	12	Np–CH=CH–Np	85	5	95
13[j]	(*Z*)	Ph(Me)CHMgCl	C	Bu^nMgBr	B	7	Ph(Me)CH–CH=CH–Bu^n	53	3	97
14[l]	(*Z*)	Ph(Me)CHMgCl	C	PhMgBr	B	30	Ph(Me)CH–CH=CH–Ph	70	4	96

[a] All reactions were carried out at room temperature in ether in the presence of catalyst (3 mol %). The concentrations of reagents ranged between 7.0×10^{-2} and 9.0×10^{-2} M. [b] 1.1 equiv. [c] A: $NiCl_2(Ph_2PCH_2CH_2PPh_2)$, B: $NiCl_2(Ph_2PCH_2CH_2CH_2PPh_2)$, C: $PdCl_2(PPh_3)_2$. [d] 2.2 equiv. [e] Times required for step ii. Step i was completed in less than 1 h. [f] The structure of the products, unless otherwise indicated, was confirmed by comparison with authentic samples. [g] The yields were determined by g.l.c. [h] In this run all Grignard reagent (3.3 equiv.) was added at the same time. [i] As reported in similar cases biphenyl was present in this run (ref. 5a). [j] Toward the end of the reaction butylbenzene was formed, very likely through the reaction of the organometallic compound with PhS^- (or derived species). Indeed, PhSH has been found to undergo cross-coupling with Grignard reagents in the presence of Ni^{II} catalysts (ref. 4b). [k] Np = 1-naphthyl. Binaphthyl and 1-phenylnaphthalene were present in this run (*cf.* footnotes i and j). [l] A new compound which gave consistent ^1H n.m.r. and i.r. spectral characteristics.

selectivity ranging from excellent [(*E*)-isomers] to good [(*Z*)-isomers].†

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† In a recent paper (*Tetrahedron Lett.*, 1981, **21**, 315) Ratovelomanana and Linstrumelle, starting with a large excess of (*Z*) or (*E*)-1,2-dichloroethene, were able to obtain stereospecifically the substitution of one chlorine atom with alkyl Grignard reagents. In one case the resulting alkenyl chloride was isolated in 33% yield and coupled with a different Grignard reagent in the presence of a Pd^0 catalyst. However, in all the reactions involving the substitution of one halogen atom of the 1,2-dichloroethene system, a very sensitive catalyst, namely $Ni(PPh_3)_4$, was used rather than the readily available (ref. 3) or commercial catalysts of the present investigation. Furthermore, in preliminary experiments we have found that the reactions of (*Z*)- or (*E*)-1,2-dichloroethene with PhMgBr in the presence of $Ni(PPh_3)_4$ prepared according to a reported procedure (J. F. Fauvarque and A. Jutand, *J. Organomet. Chem.*, 1979, **177**, 273) give unsatisfactory results. Indeed, mono- and bis-coupling products are formed (in a 1:2.5 ratio), and the degree of retention of configuration in the production of stilbenes is low [(*Z*)-1,2-dichloroethene: 50% retention; (*E*)-1,2-dichloroethene: 80% retention]. Similar results were obtained with NpMgBr.