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Preliminary communication

OLEFIN METATHESIS OF ALKENYLTRIMETHYLSILANES

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Summary

WCl_6 has been used as a catalyst for the metathesis of various alkenylsilanes and the degree of conversion found to be dependent on the distance between the olefinic bond and the silyl group. The first observation of metathetical conversion of allyltrimethylsilane in the absence of a co-catalyst is reported.

Several studies of metathesis of functionalized olefins, e.g. esters [1], ethers [2], amines [3] have been described. By means of such metathesis these substrates can be converted into difunctionalized olefins or, via cross-reaction with other olefins, into shorter or longer homologues [4].

Only few reports have dealt with metathetical conversions of alkenylsilanes. Friedman et al. [5] reported that vinyl- and allyl-trimethylsilane could be disproportionated, with low conversion, on a heterogeneous alumina-supported molybdenum catalyst. Recently Marciniec et al. described the succesful metathetical conversion of vinyltriethoxysilane into 1,2-bis(triethoxy)-silylethene with phosphineruthenium complexes as catalysts [6]. We now report the first study of the use of WCl_6 as catalyst for disproportionation of vinyl-, allyl- and 3-butenyl-trimethylsilane, involving self-metathesis as well as co-metathesis. Reactions were carried out under nitrogen in a closed glass vessel at 25°C in chlorobenzene.

The following order of addition of the reactants was used. To the reaction vessel, filled with nitrogen, 1 ml of a stock solution of WCl_6 in chlorobenzene was added. Subsequently 10 ml of chlorobenzene, the cocatalyst and the substrate were added sequentially.

The cross-metathesis experiments were performed with *cis*-2-pentene as the second olefin. Two different alkenylsilanes are possible as a result of cross-reaction (C and D, Scheme 1); the self metathesis produces B. The cross-metathesis results are shown in Table 1.

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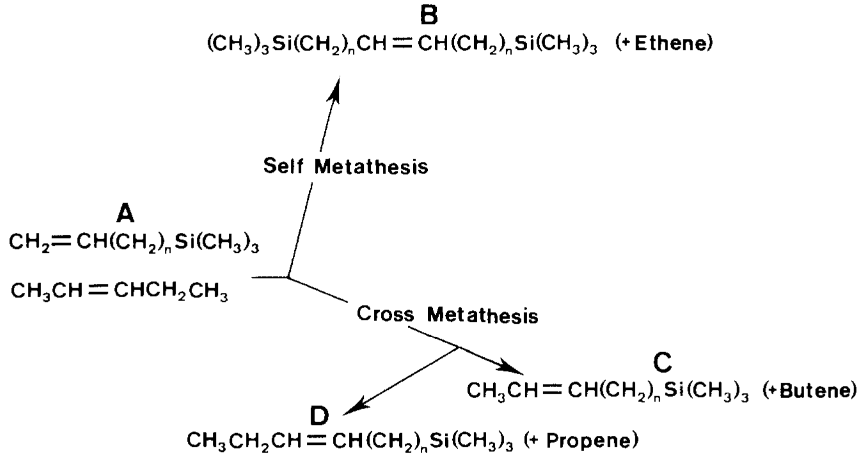

SCHEME 1. Products expected for the cross-metathesis of alkenyltrimethylsilanes (n = 0, 1, 2) and *cis*-2-pentene.

TABLE 1

CROSS-METATHESIS OF ALKENYLSILANES WITH 2-PENTENE

Entry	Catalytic [c] system	Sn/W	n	Conversion [a] of A (%)	Yield [b] C + D	C/D	Yield [b] B
1	$WCl_6/SnMe_4$	4	0	<1	—	—	—
2	WCl_6	—	0	4.3	0	—	0
3	$WCl_6/SnMe_4$	4	1	24.0	22.8	5.5	0.5
4	WCl_6	—	1	43.1	37.2	2.7	1.2
5	$WCl_6/SnMe_4$	4	2	44.1	35.3	4.9	3.9
6	WCl_6	—	2	8.0	5.1	—	0

[a] By GC. Column: 10% OV 17 on Chromosorb WHP. [b] In mol %. [c] $c_{WCl_6} = 1.05 \times 10^{-2}$ M, solvent: chlorobenzene; t 25°C; [A]/[Pentene] = 1, [A]/[WCl_6] = 50; reaction time: 20 h.

With vinyltrimethylsilane no metathetical conversion was observed (entry 1 and 2). Even addition of small amounts of vinyltrimethylsilane, e.g. 2 mole per mole WCl_6, totally inhibited the metathesis of *cis*-2-pentene with WCl_6/$SnMe_4$. This is in agreement with the results reported by Dolgoplosk et al. [7]. When, however, allyltrimethylsilane was used as a substrate reasonable yields of cross-products (C and D) were obtained with the usual $WCl_6/SnMe_4$ system as well as with the cocatalyst-free system. Apparently allyltrimethylsilane can itself activate WCl_6 to form an active catalyst. The first step in this activation is most probably an allylation of WCl_6, as indicated by the formation of 2.2—2.5 mol chlorotrimethylsilane per mole WCl_6. In contrast to allyltrimethylsilane, for which the most active system is the one without cocatalyst, 3-butenyltrimethylsilane reacts most effectively in the presence of $SnMe_4$ (entry 5 and 6); this is probably due to the weaker alkylating properties of 3-butenyltrimethylsilane compared to those of allyltrimethylsilane [8]. The self-metathesis results shown in Table 2 show that the distance between the double bond and the trimethylsilyl group is an important factor, the yield

TABLE 2

SELF-METATHESIS OF ALKENYLSILANES

Entry	Catalytic system	Sn/W	n	Yield of B [a] (%)	Selectivity (%)
7	WCl_6/4 EtAc/$SnBu_4$	4	0	0	—
8	WCl_6/4 EtAc/$SnBu_4$	4	1	2.2	96
9	WCl_6	—	1	4.2	95
10	WCl_6/4 EtAc/$SnBu_4$	4	2	20.0	94
11	WCl_6/$SnMe_4$	4	2	4.5	>95
12	WCl_6	—	2	<1.0	—

[a] In mol%.

of B increasing as this distance increases (entry 7, 8, 10). The same feature is also observed in the cross experiments for the WCl_6/$SnMe_4$ system (entry 1, 3 and 5, Table 1). The low overall conversion in the self-metathesis reaction is not surprising, since it is well known that WCl_6-based systems are not very effective for conversion of terminal olefins [9].

We also studied the synthetic utility of the cross-reaction by bringing allyltrimethylsilane into reaction with *cis*-2-butene; a yield of 76% (as indicated by GLC) of 2-butenyltrimethylsilane was achieved by passing a stream of *cis*-2-butene gas through the reaction vessel, so shifting the equilibrium by removal of the propene gas formed.

Contrary to earlier reports [1], our results indicate that the behaviour of silicon-containing olefins in the metathesis reaction is similar to that of other functionalized olefins. For instance, there is a dependence of the ease of reaction on the distance between the double bond and the functional group, just as in the case of ethers [2].

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