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REACTION OF TRIMETHYL-(2-NITROVINYL)SILANE WITH ORGANOMETALLIC COMPOUNDS. AN EXAMPLE OF REACTIVITY UMPOLUNG OF 1-ALKENYLSILANE

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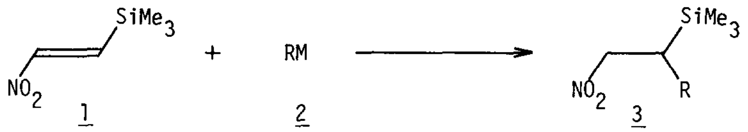
Summary: The first example of reactivity umpolung of 1-alkenylsilanes has been described. The reaction of trimethyl-(2-nitrovinyl)silane with organometallic compounds regioselectively provided trimethyl-(1-nitromethylalkyl)silanes in excellent yields.

While the concept of reactivity umpolung of carbonyl compounds has recently emerged as an extremely useful tool in organic synthesis, reversal of olefin reactivity has been a relatively unexplored area of study1) except for transition metal-promoted reactions2). Vinylsilanes, or more commonly 1-alkenylsilanes, are important synthetic intermediates for carbon-carbon bond forming reactions3), which typically involve regioselective attack of electrophiles at the olefinic carbon bearing a silyl substituent. We now wish to show that the reactivity of olefinic bond can be completely altered by introduction of a nitro group in the olefinic carbon atom.

The vinylsilane we have chosen to illustrate its reactivity umpolung is trimethyl-(2-nitrovinyl)silane (1). This compound has been prepared from trimethylvinylsilane4) employing the nitroselenenylation-oxidation sequence5) recently developed by us. Unlike ordinary vinylsilanes, compound 1 reacted with a variety of organometallic compounds 2 to give the products 3 in excellent yields (Table 1).



A typical procedure is as follows: To a tetrahydrofuran (THF) solution of organometallic reagent (2, 1.4–3.2 eq.) was dropwise added a THF solution of 1 at -78°C over 10 min under an argon atmosphere. After having been stirred for 5 min at -78°C, the reaction mixture was quenched with saturated aqueous ammonium chloride at -78°C and the temperature was raised slowly to room temperature. The usual extractive workup with diethyl ether provided an yellow oil, which was purified by silica-gel column chromatography to afford nitrosilane 36). The yields are presented in Table 1.

Some significant features of the reaction are to be mentioned. With one notable exception (entry 7, compound 3g)7), the yields are invariably high (67–94%). To our surprise, the nitrovinylsilane 1 was exceedingly reactive even at -78°C; at higher temperatures (e.g. -20°C) the reaction was too vigorous to afford detectable amount of the adduct 3. This is in sharp contrast to the behavior of ordinary conjugated nitroalkenes towards the Grignard reagent8). The high reactivity of 1 toward such nucleophiles is not only abnormal as a vinylsilane, but quite amazing as a conjugated nitroalkene since it carries trimethylsilyl substituent at the reaction site; the bulky electropositive substituent would reduce the reactivity of 1 as an electrophile in comparison with that of nitroethylene9).

The present reactions are intriguing not only because they represent the first examples of reactivity umpolung of 1-alkenylsilanes, but also because they are equally applicable to the unsaturated organometallic reagents (Entries 4, 5 and 7). The reaction with vinylmagnesium bromide (2e) suggests the possibility of stereoselective synthesis of functionalized allylsilanes10), whereas the reaction with alkynyllithium provides a convenient route to the triple bond analogues of allylsilane (propargylsilanes), which have attracted attention in view of electronic resemblance to allylsilanes, but have been only difficultly accessible11).

Further extension as well as exploitation of the synthetic potential of these reactions will be reported in due course.

Table 1. Synthesis and properties of 3

Entry	Compd. number suffix	2 RM	2 Mole eq.	3 Yields[a] / %	3 IR[b](NO_2), ν / cm^{-1}	
1	a	MeMgBr	2.7	94	1555,	1375
2	b	PrMgBr	3.2	78	1552,	1378
3	c	BuMgCl	1.4	88	1552,	1378
4	d	PhMgBr	2.9	75	1550,	1375
5	e	CH_2=CHMgBr	2.0	81	1555,	1375
6	f	BuLi	2.6	67	1552,	1378
7	g	BuC≡CLi	2.6	39	1552,	1373

[a] Isolated yield. [b] Measured as a neat liquid film.

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