The Reactions of Silyl Nitronates with Organolithium Reagents

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Summary Silyl nitronates derived from primary and secondary nitroalkanes react with organolithium reagents to yield chain-extended oximes in modest to good yield.

CONTINUING our investigations[1–4] on the properties of silyl nitronates (silyl esters of *aci*-nitroalkanes), and seeking some parallel with the reactions of silyl enol ethers, we now report the effective α-alkylation (arylation) of such nitronates derived from primary nitroalkanes, and β-alkylation (arylation) of those derived from secondary nitroalkanes, with oximes being the isolated products in both cases.

Silyl nitronates derived[2] from primary nitroalkanes react with Grignard reagents with exclusive attack at silicon, to produce magnesium nitronates. In contrast, and unlike silyl enol ethers,[5] reaction of the same nitronates with organolithium reagents leads to the production of oximes. This is illustrated in Table 1 for the silyl nitronate from 1-nitrohexane.

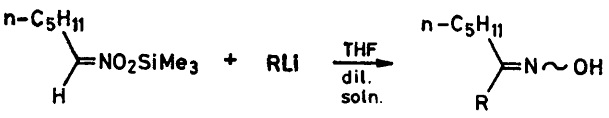
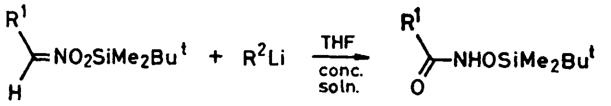


Table 1.

RLi	% Yield[a] of oxime[b]
MeLi·LiBr	58
Bu^{n}Li	51
Bu^{t}Li	30
PhLi	40

[a] Yields are based on starting silyl nitronate. All yields refer to pure distilled oximes. [b] All new compounds exhibited satisfactory i.r., ^{1}H n.m.r., and mass spectral properties, including exact mass data.

The general experimental procedure consists of treating a solution of the silyl nitronate in tetrahydrofuran (THF) (10 ml per mmol of silyl nitronate) with two equivalents of the appropriate organolithium reagent at −78 °C. The reaction mixture is allowed to warm up to room temperature, then poured on to saturated aqueous NH$_4$Cl solution. Normal isolation procedures and distillation (kugelrohr) afford the product oximes. If significantly more concentrated solutions are employed (2—3 ml THF per mmol of silyl nitronate), then the major product is the silyl ester of a hydroxamic acid (Scheme) isomeric with the starting silyl nitronate; this species can also occur as a minor by-product under the earlier, more dilute conditions.



Scheme

Such dichotomy in product formation could suggest the common intermediacy of a nitrile oxide, which would be formed by elimination of the elements of triorganosilanol from the starting silyl nitronate. Addition of either the second equivalent of organolithium reagent[6] or trialkylsilanoxide, followed by appropriate isomerization, would then lead to the alternative products. Nitrile oxide intermediates have also been proposed[7,8] in one mechanism for the Victor Meyer[9] reaction, in which primary nitroalkanes are transformed into the isomeric hydroxamic acids upon treatment of their *aci*-salts with warm mineral acids.

Silyl nitronates derived[2] from secondary nitroalkanes react under the same dilute conditions, again to afford oximes, as illustrated in Table 2 for the silyl nitronate from 2-nitroheptane.

Table 2.

RLi	% Yield[a] of oxime[b]
MeLi[c]	35
Bu^{n}Li	30
Bu^{s}Li	50
PhLi	25

[a] Yields are based on starting 2-nitroheptane. All yields refer to pure distilled products. [b] All new compounds exhibited satisfactory i.r., ^{1}H n.m.r., and mass spectral properties, including exact mass data. [c] Use of MeLi·LiBr resulted in a LiBr-catalysed Nef process, ultimately forming 2-methylheptan-2-ol.

A possible mechanism for this reaction could involve elimination of the elements of triorganosilanol to give a nitrosoalkene; conjugate addition of the second equivalent of organolithium reagent would then lead to the observed products. Both this and the earlier mechanistic possibility are under active investigation, with particular attention being given to attempted trapping of proposed intermediates. Attempts are also being made to enhance the yields and to define the scope of this potentially most useful process.

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