stereochemical control than the more common trimethylsilyl unit. For example, the condensation of allylic zinc reagents with benzoyl triisopropylsilane produced the α-adduct exclusively.

The overall applicability of the process is quite broad.[10] Similar results were obtained using α,β-unsaturated or aliphatic aldehydes, with organozinc, magnesium, lithium,[10a,11] or potassium reagents. Some of our results are shown in Table II.

Noteworthy is the example that condensation of *cis*-2-pentenyl potassium[12,13] prepared from *cis*-2-pentene, po-

tassium *tert*-butoxide, TMEDA, and a solution of n-butyllithium in hexane with hexanoyltrimethylsilane in THF at −78 °C for 20 min followed by desilylation afforded the homoallylic alcohol in 72% yield with α/γ ratio of 20:1. The desired α-adduct exhibited high *Z* selectivity (*Z/E* = 99:1).[14,15]

The above example provides further evidence for the power of this new process and demonstrates that its use can lead to a profound simplification of the problem of synthesis of various derivatives from fatty acid cascades, an increasingly important class of biologically active molecules. The versatility of acylsilanes as electrophiles for the ambident nucleophiles has been demonstrated.[16]

(10) Other examples of the use of acylsilane in organic synthesis: (a) Wilson, S. R.; Hague, M. S.; Misra, R. N. *J. Org. Chem.* 1982, *47*, 747. (b) Nakada, M.; Urano, Y.; Kobayashi, S.; Ohno, M. *J. Am. Chem. Soc.* 1988, *110*, 4826.

(11) Similar regioselectivity was observed by Noyori in reactions between allenyltin/alkyllithium and acyl silanes: Suzuki, M.; Morita, Y.; Noyori, R. 56th Annual Meeting of the Chemical Society of Japan Abstract 3XIIA33, Tokyo, 1988.

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(13) Brandsma, L.; Verkruijsse, H. D. *Preparative Polar Organometallic Chemistry*; Springer-Verlag: New York, 1986.

(14) Recent example of *Z*-selective allylation of aldehydes: Guo, B.-S.; Doubleday, W.; Cohen, T. *J. Am. Chem. Soc.* 1987, *109*, 4710.

(15) The isomer ratio, *Z/E*, was determined by 500-MHz ¹H NMR assay.

(16) Satisfactory IR, ¹H NMR, and ¹³C NMR spectra as well as microanalytical data were obtained for all new compounds.

The Addition of the Highly Functionalized Zinc, Copper Reagents RCu(CN)ZnI to Nitro Olefins
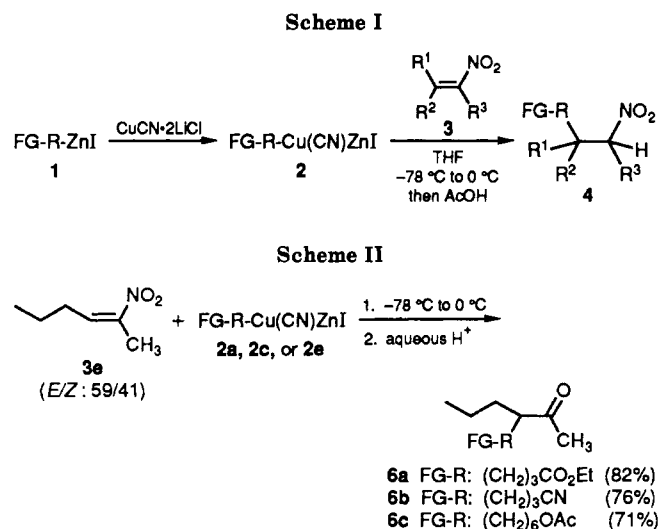
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Received July 18, 1989

Summary: The addition of the highly functionalized zinc and copper organometallics FG-RCu(CN)ZnI to nitro olefins furnishes polyfunctional nitroalkanes in good to excellent yields; with α-substituted nitro olefins, the Michael adducts can be directly converted into polyfunctional ketones.

Sir: The addition of carbon nucleophiles to nitro olefins represents an easy access to a variety of nitroalkanes which are versatile intermediates in organic synthesis.[1] Several classes of stabilized lithium nucleophiles such as enolates or sulfur stabilized anions[2] as well as nonstabilized lithium,[2-4] magnesium,[4,5] cadmium[6] organometallics, zincates,[7] allylic tin[8] and silicon[9] derivatives, and recently organoaluminum[10] compounds have been shown to add to nitro

Scheme I

Scheme II

6a FG-R: (CH₂)₃CO₂Et (82%)
6b FG-R: (CH₂)₃CN (76%)
6c FG-R: (CH₂)₆OAc (71%)

olefins in satisfactory yields. Surprisingly, the reports on the addition of organocopper derivatives[7,11] to nitro olefins are rare and the reactions proceed generally in moderate yields.

We reported previously,[12] that the polyfunctionalized zinc organometallics FG-R-ZnI **1** could be readily trans-

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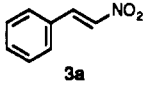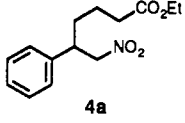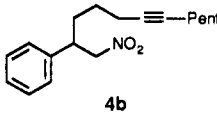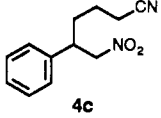(8) Uno, H.; Watanabe, N.; Fujiki, S.; Suzuki, H. *Synthesis* 1987, 471.
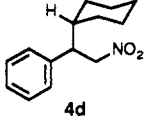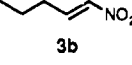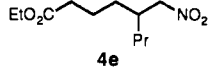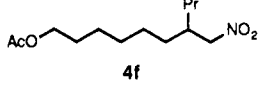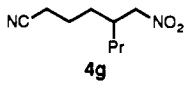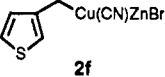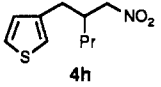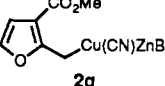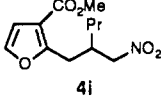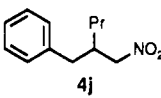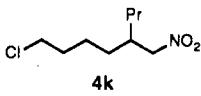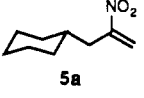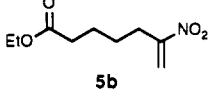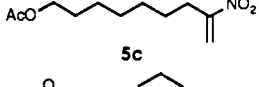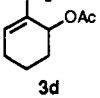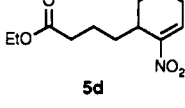
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Table I. Nitroalkanes 4a–k, 5a–d Obtained by the Addition of the Copper Organometallics 2 to the Nitro Olefins 3a–d

entry	copper organometallic	nitro olefin	product	yield,[a] %
1	EtO$_2$C(CH$_2$)$_3$Cu(CN)ZnI, 2a	3a	4a	90
2	Pent-≡-(CH$_2$)$_3$Cu(CN)ZnI, 2b	3a	4b	77
3	NC(CH$_2$)$_3$Cu(CN)ZnI, 2c	3a	4c	84
4	c-HexCu(CN)ZnI, 2d	3a	4d	71
5	EtO$_2$C(CH$_2$)$_3$Cu(CN)ZnI, 2a	3b	4e	94
6	AcO(CH$_2$)$_6$Cu(CN)ZnI, 2e	3b	4f	76
7	NC(CH$_2$)$_3$Cu(CN)ZnI, 2c	3b	4g	94
8	2f	3b	4h	81
9	2g	3b	4i	75
10	PhCH$_2$Cu(CN)ZnI, 2h	3b	4j	96
11	Cl(CH$_2$)$_4$Cu(CN)ZnI, 2i	3b	4k	90
12	c-HexCu(CN)ZnI, 2d	3c	5a	94
13	EtO$_2$C(CH$_2$)$_3$Cu(CN)ZnI, 2a	3c	5b	92
14	AcO(CH$_2$)$_6$Cu(CN)ZnI, 2e	3c	5c	88
15	EtO$_2$C(CH$_2$)$_3$Cu(CN)ZnI, 2a	3d	5d	72

[a] All yields refer to isolated yields of analytical pure products. Satisfactory spectral data (IR, ^{1}H and ^{13}C NMR, mass spectra and high-resolution mass spectra) were obtained for all new compounds (supplementary material).

metalated to the corresponding copper derivatives FG-R-Cu(CN)ZnI 2 by the addition of the THF soluble copper salt CuCN·2LiCl. These copper reagents react with various organic electrophiles such as acid chlorides, enones, allylic halides, acetylenic esters, 1-haloalkynes, and aldehydes to furnish a variety of polyfunctional molecules. We found now that the reagents FG-R-Cu(CN)ZnI 2 add in excellent yields (71–96%) to different types of nitro olefins 3, leading to highly functionalized nitroalkanes of type 4 and to newly substituted nitro olefins of type 5 (Scheme I and Table I).

The nitro olefin **3** is typically[13] added at –78 °C to a THF solution of the copper organometallic **2** (1.3 equiv) and is then allowed to warm up. In the case of nitro olefins **3a,b,d** the reaction is complete after a few hours at 0 °C (0.5–4 h). For the more reactive 3-acetoxy-2-nitro-1-propene[4a] (**3c**), the reaction is performed in the presence of 1 equiv of Me₃SiCl (in order to avoid the polymerization of the β-unsubstituted nitro olefins formed **5a–c**), and is completed at –55 °C after 10 min. The reaction is quenched at this temperature with aqueous NH₄Cl (entries 12–14). These additions to 3-acetoxy-2-nitro-1-propene (**3c**) and to 3-acetoxy-2-nitro-1-cyclohexene (**3d**) occur with excellent chemoselectivity, since the nitro olefins of type **5** formed (entries 12–15) do not react at the reaction temperature (–55 °C to –60 °C for **3c** and 0 °C for **3d**) with the excess copper reagent to afford an undesired diadduct.[4a,b] Various functionalized copper organometallics **2** containing a functional group such as an ester, a nitrile, a chloride, or an alkyne undergo the addition reaction efficiently, as shown in Table I. We noticed also that nitrogen-containing copper reagents like the organocopper compound **2c**[14] derived from (3-cyanopropyl)zinc iodide

react significantly slower than the other organocopper compounds. Besides alkylcopper derivatives, the benzylic reagent **2h** and the heterocyclic organocopper compounds[15] **2f** and **2g** were found to react in a satisfactory way with 1-nitropentene **3b** (75–96%). All these reactions were quenched with acetic acid at –30 °C and furnished exclusively the nitro compounds **4**. In the case of α-substituted nitro olefins such as **3e** (Scheme II) a mixture of nitroalkanes and ketones (Nef reaction) is formed after quenching with acetic acid; however, by stirring the reaction mixture after the Michael addition in aqueous acidic medium or simply with aqueous NH₄Cl (in the case of **6a** and **6c**),[16] we were able to convert the intermediate nitronate into the corresponding methyl ketone in good yields; see Scheme II.

Further extensions and synthetic applications are currently underway in our laboratories.

(13) **Typical Procedure for the Michael Addition to a Nitro Olefin.** The addition of the (4-chlorobutyl)copper derivative **2i** to 1-nitropentene **3b** (entry 11 of Table I). 1-Nitropentene **3b** (7.5 mmol, 0.86 g) was added dropwise at –78 °C to a THF solution of the (4-chlorobutyl)copper derivative **2i** (10 mmol) prepared as previously reported.[12] The reaction mixture was warmed up to 0 °C and allowed to react for 4 h. The reaction was monitored by GLPC analysis of aliquots. After completion, the reaction mixture was then cooled to –78 °C, quenched by the addition of an acetic acid solution (2 mL in 5 mL of THF), warmed up to 0 °C, and worked up as usual. The crude oil obtained after evaporation of the solvents was purified by SiO₂ flash chromatography (20:1 hexane/Et₂O) giving 1.40 g of 1-chloro-5-(nitromethyl)octane (**4k**) (90% yield). Analytical data for the product is included in the supplementary material.

(14) Due to its low reactivity, NCCH₂CH₂CH₂Cu(CN)ZnI (**2c**) does not react cleanly with the sensitive 3-acetoxy-2-nitropropene (**3c**); the rate of the Michael addition is obviously very similar to the polymerization rate of the product.

(15) A report on the preparation and reactivities of new heterocyclic "benzylic" zinc and copper organometallics is in preparation: Chen, H. G.; Knochel, P., Ann Arbor, 1989.

(16) **Typical Procedure for the One-Pot Michael Addition–Nef Reaction.** The addition of the (3-cyanopropyl)copper derivative **2c** to 2-nitro-2-hexene (**3e**). 2-Nitro-2-hexene (**3e**) (7.5 mmol, 0.97 g) was allowed to react with a THF solution of the (3-cyanopropyl)copper derivative **2c** (10 mmol) as previously described.[13] Under these conditions, a mixture of ketone and oxime was obtained. The mixture was further stirred overnight in a 10% HCl solution (20 mL) and worked up. The desired ketone **6b** was obtained as the exclusive product (0.95 g, 76% yield) after flash chromatography (4:1 to 2:1 hexane/ethyl acetate). Analytical data for the product is included in the supplementary material.

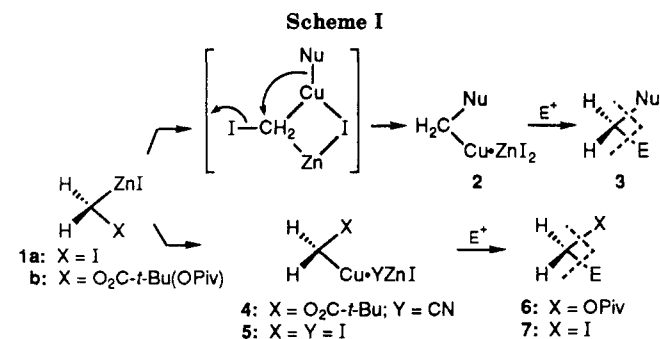# Nucleophilic Reactivity of Zinc and Copper Carbenoids. 2

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Received July 18, 1989

Summary: The reactivity of the new zinc and copper carbenoids PivOCH₂Cu(CN)ZnI (**4**) and ICH₂Cu·ZnI₂ (**5**) toward various electrophiles has been investigated. Of special interest is the direct and highly stereoselective conversion of allylic bromides to the corresponding homoallylic iodides by using the reagent ICH₂Cu·ZnI₂ (**5**).

Sir: The zinc carbenoids of type **1** are excellent carbene precursors and as such have found several synthetic applications.[1] We found recently that the reagent **1a** (X = I) undergoes a rapid 1,2-rearrangement in the presence of

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Scheme I

copper nucleophiles NuCu (Nu = CN, SR, NR₂, CH(R)CN, heteroaryl) leading to the methylene homologated organocopper **2**, which after reaction with various electrophiles E affords products of type **3** (Scheme I).[2]

(2) Knochel, P.; Jeong, N.; Rozema, M. J.; Yeh, M. C. P. *J. Am. Chem. Soc.* **1989,** *111,* 6474.