Journal of Organometallic Chemistry, 443 (1993) C41–C43

JOM 23114PC

Preliminary Communication

Exclusive β-hydrosilylation of acrylates catalyzed by copper-tetramethylethylenediamine

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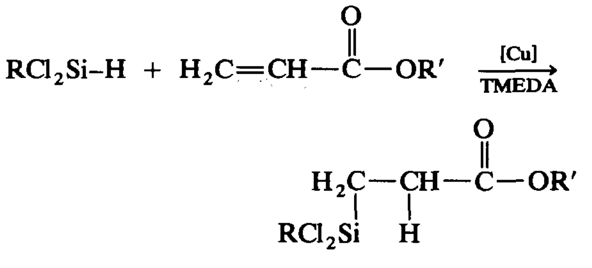
(Received May 8, 1992; in revised form July 6, 1992)

Abstract

Trichlorosilane and methyldichlorosilane react with methyl and ethyl acrylate to give high yields of only the β adduct in the presence of copper salts and tetramethylethylenediamine.

Hydrosilylation of acrylates using chlorosilanes gives valuable silicon-functionalized monomers that are easily transformed into alkoxysilanes or silicones [1]. However, no catalyst has been reported that gives exclusive β-adduct formation from Si–H addition of a chlorosilane to the olefinic bond of an unsubstituted acrylate. As examples, platinum catalysts give mixtures of α- and β-products [2], nickel complexes generally favor α-isomer formation [3], and Wilkinson's catalyst produces α-products exclusively [4]. As part of our studies of the hydrosilylation of functionalized olefins [5–7], we investigated acrylates using a binary catalyst system composed of a copper salt and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) and obtained high yields of only β-hydrosilylation products (eqn. (1)).



$$\mathrm{RCl_2Si{-}H} + \mathrm{H_2C{=}CH{-}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{{-}OR'} \xrightarrow[\text{TMEDA}]{[\text{Cu}]} \underset{\mathrm{RCl_2Si}}{\mathrm{H_2C}}{-}\underset{\mathrm{H}}{\mathrm{CH}}{-}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{{-}OR'} \quad (1)$$

$(\mathrm{R} = \mathrm{Cl}, \mathrm{Me}, \mathrm{Ph};\ \mathrm{R'} = \mathrm{Me}, \mathrm{Et})$

In a typical reaction, 2.0 g (14 mmol) of Cu_2O and 6.0 ml (40 mmol) of TMEDA were placed in a 50 ml round bottom flask equipped with a dry-ice condenser and a nitrogen inlet. The flask was cooled to 0°C, and a mixture of 7.20 ml (80 mmol) of methyl acrylate and 12.4 ml (120 mmol) of methyldichlorosilane was added dropwise to the mixture. After addition, the reaction mixture was refluxed for 5 h at a pot temperature of 80°C. Following removal of TMEDA by evacuation at room temperature, 15.44 g (96%; 45°C/0.6 torr) of methyl-3-(methyldichlorosilyl)propionate was isolated by distillation in > 95% purity as determined by NMR spectroscopy. The catalyst is recyclable. When the reaction flask containing the catalytic residue was recharged with 6.0 ml of TMEDA, the above reaction sequence could be repeated to give a yield of ~ 95%. The residue from the reaction is not catalytic but requires TMEDA. In separate experiments it was determined that the combination of copper (or its salts) and TMEDA is required for useful rates of hydrosilylation. Our results are summarized in Table 1 [8].

Other copper compounds catalyze the addition of chlorosilanes to acrylates. All of the copper(0), copper(I), and copper(II) compounds we used with TMEDA did promote the addition to some degree. Exclusive β-hydrosilylation was observed in all cases (Table 2). Triethylamine gave very low yields, < 1%, under the reaction conditions suggesting that TMEDA is playing a role unique to its structure, such as coordination of the copper [9] and/or the silicon [10], in promoting this reaction. When the hydrosilylation of methyl acrylate was performed under an oxygen environment the yield for the trichlorosilane addition was unchanged, while that for methyl dichlorosilane decreased to 80% after 5 h of refluxing.

A 7.0 : 10 : 20 : 30 mole ratio of copper/TMEDA/acrylate/silane was found to be effective, giving reaction times of less than 1 h for trichlorosilane, and 5 h for methyldichlorosilane. When the amount of TMEDA was decreased, the reaction proceeded at a much slower rate (Table 3).

In non-functionalized alkenes, the electropositive silicon adds preferentially to the terminal position. However, when vinyl groups having an electron-withdrawing group (such as acrylonitrile or acrylates) are used, silicon hydrides prefer α or internal addition to match the polarization of the Si–H bond with the

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0022-328X/93/$6.00

TABLE 1. Hydrosilylation of acrylates catalyzed by Cu_2O/tetramethylethylenediamine [a]

Acrylate	Silane	Yield [b] (%)
Methyl	$HSiCl_3$	95
Methyl	$HSiPhCl_2$	93
Methyl	$HSiMeCl_2$	95
Ethyl	$HSiCl_3$	99
Ethyl	$HSiMeCl_2$	99
Methyl Meth [c]	$HSiCl_3$	50
Methyl Meth [c]	$HSiMeCl_2$	10
Methyl	$HSiMe_2Cl$	0
Methyl	$HSiEt_3$	0
Methyl	$HSi(OEt)_3$	0

[a] Reactions were refluxed from 1 to 7 h.

[b] GC yield based on conversion of the acrylate to the β-adduct.

[c] Methyl methacrylate, $CH_2{=}C(Me)CO_2Me$.

olefin. To achieve effective β-hydrosilylation of acrylates, the silicon–hydrogen bond must be reversely polarized (eqn. (1)) [11].

Our observations can be explained by amine complexation of the silicon hydride in a manner similar to that proposed for the triisopropylamine/trichlorosilane adduct by Benkeser [10]. We have found that using TMEDA gives much higher yields than monoamines suggesting that the TMEDA-silane adduct is better suited to promoting the polarization required for this regioselectivity (eqn. (2)). The role of copper, essential to the hydrosilylation of acrylates, is under study.

TABLE 2. Effect of copper salts on the hydrosilylation of methyl acrylate [a]

Silane	Copper	Yield [b] (%)
$HSiCl_3$	CuCl	> 95
$HSiCl_3$	CuBr	> 95
$HSiCl_3$	$CuCl_2$	> 95
$HSiCl_3$	$CuBr_2$	> 95
$HSiCl_3$	CuCN	> 95
$HSiCl_3$	CuO	> 95
$HSiCl_3$	$2CuO{*}Cr_2O_3$ [c]	> 95
$HSiCl_3$	$Cu(acac)_2$	5
$HSiCl_3$	$CuSO_4$	30
$HSiCl_3$	Cu [d]	35–83
$HSiMeCl_2$	CuCl	> 95
$HSiMeCl_2$	CuBr	> 95
$HSiMeCl_2$	$CuCl_2$	> 95
$HSiMeCl_2$	$CuBr_2$	> 95
$HSiMeCl_2$	CuCN	57
$HSiMeCl_2$	CuO	84
$HSiMeCl_2$	$2CuO{*}Cr_2O_3$ [c]	82
$HSiMeCl_2$	$Cu(acac)_2$	5
$HSiMeCl_2$	$CuSO_4$	trace
$HSiMeCl_2$	Cu [d]	2–6

[a] A 7:10:20:30 mole ratio of copper/TMEDA/acrylate/silane was used. Trichlorosilane reactions were refluxed for 3 h, methyldichlorosilane reactions for 5 h. 6 ml of benzene was added to trichlorosilane reactions to facilitate stirring.

[b] GC or NMR yield based on conversion to β-adducts.

[c] Copper chromite, barium promoted (Aldrich).

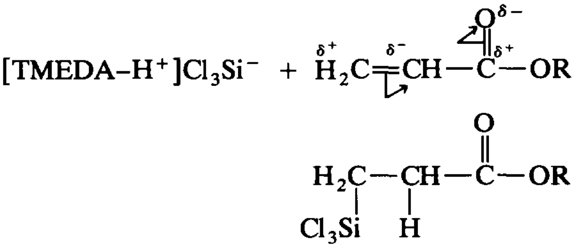
[d] Formed by passing H_2 over Cu_2O at 250°C for 2.5 h.

TABLE 3. Effect of catalyst load on yield [a,b]

Cu_2O (mmol)	TMEDA (mmol)	Yield (%) (1 h reflux)	Yield (%) (3 h reflux)	Yield (%) (5 h reflux)
7	20	> 95	> 95	> 95
3.5	20	> 95	> 95	> 95
1.75	20	> 95	> 95	> 95
0.7	20	> 95	> 95	> 95
0.07	20	15	60	80
0	20	0	0	0
7	10	30	50	70
7	5	15	17	17
7	0	0	0	0
3.5	10	18	70	75
1.75	5	10	14	16

[a] For the reaction of 60 mmol of trichlorosilane with 40 mmol of methyl acrylate and 6 ml of benzene solvent.

[b] NMR yield based on conversion to β-adducts. Determined by monitoring the appearance of the methoxy protons on the product and the disappearance of the methoxy signal from the acrylate.



$$[\text{TMEDA-H}^+]\text{Cl}_3\text{Si}^- + \overset{\delta+}{\text{H}_2\text{C}}{=}\overset{\delta-}{\text{CH}}-\overset{\overset{\text{O}^{\delta-}}{\|}}{\underset{\delta+}{\text{C}}}-\text{OR} \xrightarrow{[\text{Cu}]} \underset{\text{Cl}_3\text{Si}}{\text{H}_2\text{C}}-\underset{\text{H}}{\text{CH}}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{OR} \quad (2)$$

Acknowledgments

Financial support from Air Force Office of Scientific Research through Grant No. 91-0197, Dow Corning Corporation and the North Dakota Space Grant Program is gratefully acknowledged.

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