

TRIMETHYLSILYLDIAZOMETHANE: A USEFUL REAGENT FOR THE PREPARATION OF (Z)-1-TRIMETHYLSILYL-1-ALKENES¹⁾

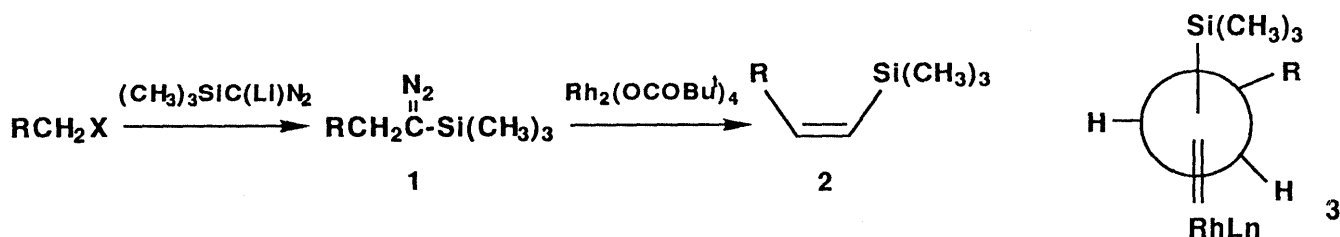
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The rhodium(II) pivalate-catalyzed decomposition of α -trimethylsilyldiazoalkanes stereoselectively affords (Z)-1-trimethylsilyl-1-alkenes in good yields.

KEYWORDS trimethylsilyldiazomethane; α -trimethylsilyldiazoalkane; (Z)-1-trimethylsilyl-1-alkene; rhodium(II) pivalate; catalytic decomposition

We have already reported²⁾ a stereoselective preparation of (E)-1-trimethylsilyl-1-alkenes by cuprous chloride-catalyzed decomposition of α -trimethylsilyldiazoalkanes (1), easily prepared from the lithium salt of trimethylsilyldiazomethane (TMSCHN₂) and alkyl halides.³⁾ As an extension of this work, we now wish to report that (Z)-1-trimethylsilyl-1-alkenes (2) can also be prepared from α -trimethylsilyldiazoalkanes (1) by decomposition with rhodium(II) pivalate in place of cuprous chloride.



A typical experimental procedure is as follows: A solution of 1³⁾ (1 mmol) in dry benzene (3 ml) was added dropwise over 3 min to a solution of rhodium(II) pivalate⁴⁾ (6 mg, 1 mol%) in dry benzene (7 ml) under argon. The mixture was stirred at reflux for 30 min, and the catalyst was removed by short column chromatography on silica gel (BW-820MH, Fuji Davison, hexane : benzene=2:1). The eluate was concentrated, and the residual oil was purified by distillation to give 2.

The results are summarized in the Table. Decomposition of various α -trimethylsilyldiazoalkanes (1) with rhodium(II) pivalate smoothly proceeds to give vinylsilanes (2) in good yields with moderate to high (Z)-stereoselectivity. Rhodium(II) pivalate seems to be the catalyst of choice. The use of rhodium(II) acetate⁵⁾ shows a remarkable decrease in the selectivity (Run 2). The high (Z)-stereoselectivity of the reaction may be explained by the intermediacy of the rhodium carbenoids (3)⁵⁾ in which the bulky pivalate ligand (Ln) will push away alkyl or aryl residues.

The present method using commercially available TMSCHN₂ makes possible the conversion of alkyl halides to homologous (Z)-1-trimethylsilyl-1-alkenes in two steps and will provide a useful methodology for the (Z)-vinylsilane synthesis.⁶⁾ Furthermore, combined with a preceding observation,²⁾ TMSCHN₂ can be efficiently used for the selective preparation of (E)- and (Z)-1-trimethylsilyl-1-alkenes from alkyl halides via α -trimethylsilyldiazoalkanes.

Table. a) Preparation of (Z)-1-Trimethylsilyl-1-alkenes (2)

Run	R	Yield(%)	Z/E	bp(°C)/mmHg ^{b)}	¹ H-NMR, δ in CDCl ₃ =CHSi(CH ₃) ₃ (J _{HZ})
1	Benzyl	84	78/22 ^{c)}	80~85/5	5.58 (d, 14)
2	Benzyl ^{d)}	78	56/44 ^{c)}		
3	Nonyl	93	80/20 ^{c)}	70~75/0.5	5.46 (d, 14)
4	9-Decenyl	84	83/17 ^{c)}	65~70/0.1	5.40 (d, 14)
5	4- <i>tert</i> -Butyl- α -methylphenethyl	95	95/5 ^{c)}	75~80/0.07	5.36 (d, 14)
6	Phenyl	81	96/4 ^{e, f)}	70~75/5	5.80 (d, 15)
7	4-Methylphenyl	96	96/4 ^{e, f)}	70~75/4	5.73 (d, 15)
8	4-Chlorophenyl	91	94/6 ^{e)}	55~60/0.05	5.82 (d, 15)
9	4-Methoxyphenyl	93	96/4 ^{e)}	70~75/0.7	5.67 (d, 15)
10	1-Naphthyl	94	97/3 ^{e)}	85~90/0.25	6.08 (d, 14)
11	2-Thienyl	80	95/5 ^{e)}	60~65/0.4	5.75 (d, 15)

a) All products gave satisfactory spectral data and elemental analysis. b) By Kugelrohr distillation. c) Determined by ¹H-NMR. d) The reaction was carried out at 50~55°C for 1 h in dry benzene using rhodium(II) acetate. e) Determined by GLC. f) When the distillation was carried out at 110~115°C/22~25 mmHg, Z to E slight isomerization occurred.

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