REACTION OF TRIMETHYLSILYLDIAZOMETHANE WITH OLEFINS[1]

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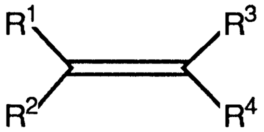
Most of the reactions of trimethylsilyldiazomethane with various olefins in the presence or absence of metal salt catalysts give silylcyclopropanes.

KEYWORDS —— trimethylsilyldiazomethane; olefin; cyclopropanation; 1,3-dipolar cycloaddition; silylcyclopropane; pyrazoline; pyrazole

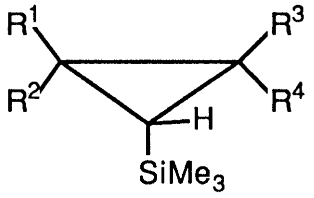
The cuprous chloride-catalyzed[2)] and photochemical[3)] reactions of trimethylsilyldiazomethane ($TMSCHN_2$) with olefins produce silylcyclopropanes, versatile synthetic reagents,[4)] via a silylcarbene or carbenoid. However, the olefins used in these reactions are limited to simple aliphatic and alicyclic ones. Furthermore, it has been reported that $TMSCHN_2$ undergoes the 1,3-dipolar cycloaddition to activated olefins, such as acrylonitrile[2a,b)] and metacrylonitrile,[5)] affording silylpyrazolines, but ethyl cinnamate, diethyl maleate, and maleic anhydride give no 1,3-dipolar cycloadducts.

We have already demonstrated that $TMSCHN_2$ is quite useful as a reagent for introducing a C_1-unit and as a [C-N-N] synthon for the preparation of azoles.[6)] Our continued interest in the use of $TMSCHN_2$ in organic synthesis has led us to reinvestigate the reaction with various olefins.

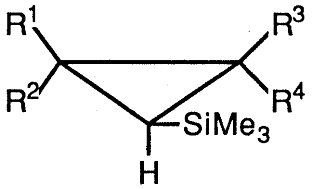
First, the cyclopropanation of olefins with $TMSCHN_2$ in the presence of metal catalysts was investigated. Treatment of (E)-ethyl cinnamate (**1a**) (3 mmol) with $TMSCHN_2$ (1 mmol)[7)] in the presence of palladium (II) chloride (5 mo1%) in dry benzene (1 ml) at 60°C for 1 h under argon gave two silylcyclopropanes (**2a**) and (**3a**) in 45 and 34% yields, respectively, after separation on a silica gel column.[8)] Since no reaction occurs without the catalyst,[9)] the actual reaction species is apparently the trimethylsilylcarbenoid, which inserts in (**1a**) affording (**2a**) and (**3a**). Although palladium (II) acetate could also catalyze this cyclopropanation in moderate yield, neither cuprous chloride, copper sulfate, nor rhodium (II) acetate is effective for the reaction. Under the palladium (II) chloride-catalyzed conditions as above, (E)-benzylideneacetone (**1b**) also underwent the cyclopropanation with $TMSCHN_2$ to give a mixture of (**2b**; 11%) and (**3b**; 21%). In contrast with (**1a**), the reaction of (**1b**) with $TMSCHN_2$ proceeded without the catalyst, affording the pyrazole (**4a**) in 38% yield. The pyrazole (**4a**) may be formed by 1,3-dipolar cycloaddition of $TMSCHN_2$ to (**1b**), followed by desilylation by work-up with water after the reaction, then by oxidation with air. Similarly, (E)-benzylideneacetophenone (**1c**) afforded a mixture of silylcyclopropanes (**2c**; 12%) and (**3c**; 9%) by the reaction with $TMSCHN_2$ in the presence of palladium (II) chloride, while the pyrazole (**4b**) was the major product (30% yield) without the catalyst. Treatment of (E)-ethyl 2-octenoate (**1d**) with $TMSCHN_2$ in the presence of palladium (II) chloride also gave a mixture of silylcyclopropanes (**2d**) and (**3d**) in 23% yield.



(**1**)

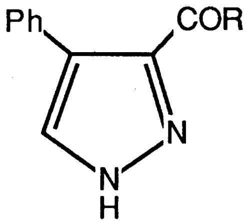


(**2**)

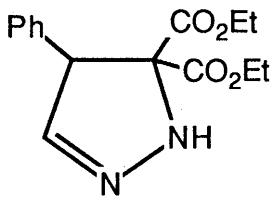


(**3**)

a : R^1 = Ph, R^2 = R^3 = H, R^4 = CO_2Et
b : R^1 = Ph, R^2 = R^3 = H, R^4 = MeCO
c : R^1 = Ph, R^2 = R^3 = H, R^4 = PhCO
d : R^1 = $Me(CH_2)_4$, R^2 = R^3 = H, R^4 = CO_2Et
e : R^1 = Ph, R^2 = R^3 = R^4 = H
f : R^1 = R^2 = Ph, R^3 = R^4 = H
g : R^1 = R^4 = Ph, R^2 = R^3 = H
h : R^1 = Ph, R^2 = H, R^3 = R^4 = CO_2Et
i : R^1 = Ph, R^2 = H, R^3 = CN, R^4 = CO_2Me
j : R^1 = Ph, R^2 = H, R^3 = R^4 = CN
k : R^1 = R^2 = R^3 = R^4 = CN



(**4a**) : R = Me
(**4b**) : R = Ph



(**5**)

Interestingly, the reaction of styrene (**1e**) with $TMSCHN_2$ in the presence of palladium (II) chloride gave no silylcyclopropanes, though nitrogen gas was evolved. However, cuprous chloride was effective as a catalyst at room temperature giving a mixture of silylcyclopropanes

(**2e**) and (**3e**) in 46% yield (**2e**/**3e**=4.8). 1,1-Diphenylethylene (**1f**) and (E)-1,2-diphenylethylene (**1g**) also underwent the cuprous chloride-catalyzed cyclopropanation with $TMSCHN_2$ though less efficiently (20 and 11% yields, respectively). Indene and 1,2-dihydronaphthalene gave the corresponding silylcyclopropanes in ca. 20% yields under similar reaction conditions in preference of the exo isomer (exo: endo=2.5 : 1 and 8 : 1, respectively). The results are similar to those of the cyclopropanation of aliphatic and alicyclic olefins.2) Surprisingly, however, representative electron-rich olefins such as 4-tert-butyl-1-trimethylsilyloxyhexene and 1-morpholinohexene were completely unreactive to $TMSCHN_2$ under metal salt-catalyzed reaction conditions.

Finally, we investigated the reaction of $TMSCHN_2$ with more electron-deficient olefins bearing two geminal electron-withdrawing groups. Diethyl benzylidenemalonate (**1h**) (1 mmol) easily reacted with $TMSCHN_2$ (1.2 mmol) at 60°C for 1 h, then at room temperature for 13 h in benzene to give the 1,3-dipolar cycloadduct (silylpyrazoline), which was hydrolyzed during column chromatography on silica gel affording the pyrazoline (**5**) in 85% yield. However, the metal-catalyzed reaction described above did not yield any identifiable products. The reaction of (E)-methyl benzylidenecyanoacetate (**1i**) with $TMSCHN_2$ also proceeded at room temperature, but the product was the silylcyclopropane (**2i**; 56% yield) as a sole identified product. In contrast with the result using $TMSCHN_2$, the reaction of (E)-ethyl benzylidenecyanoacetate with diazomethane has been reported to give (E)-ethyl 2-cyano-3-methylcinnamate quantitatively.10) Benzylidenemalononitrile (**1j**) and tetracyanoethylene (**1k**), more electron-deficient olefins than (**1i**), smoothly underwent the reaction with $TMSCHN_2$ to give the corresponding silylcyclopropanes (**2j**; 33%) and (**2k**; 97%), respectively. Possibly, the silylcyclopropanes are produced by the 1,3-dipolar cycloaddition of $TMSCHN_2$ followed by expulsion of nitrogen.

In conclusion, $TMSCHN_2$ reacts with various olefins in the presence or absence of metal salt catalysts, giving mainly silylcyclopropanes.

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8) All products gave satisfactory spectral data and elemental analysis (or high resolution mass spectrum). The stereochemistry of the silylcyclopropanes was determined by ^{1}H-NMR.

9) $TMSCHN_2$ has been reported to react with (**1a**) during several weeks in the dark to give polymeric solid, see ref. 1b.

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