References and Notes

(1) Abstracted from the Ph.D. Dissertation of R. G. Posey, University of Florida, Dec 1975.

(2) S. W. Tobey and R. West, *J. Am. Chem. Soc.*, **88**, 2481 (1966).

(3) Initial attempts in our laboratory to directly generate **1a** from **1b** by reductive debromination have not met with success. Most surprising was the failure of tri-*n*-butyltin hydride to produce any volatile products on reaction with **1b** in mineral oil.

(4) (a) D. C. Law and S. W. Tobey, *J. Am. Chem. Soc.*, **90**, 2376 (1968); (b) related work described in ref 1.

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(7) (a) With exception of the broad triplet for the $-CF_2H$ proton the pattern of the proton spectrum and the coupling constants for the bridgehead protons H_a, H_b were almost identical with that observed for the model system 7-chlorodibenzobicyclo[2.2.2]octa-2,5,7-triene[7b] in deuteriobenzene [δ (C_6D_6, 60 MHz) 7.17–6.56 (m, 8, aromatic), 6.40 (dd, $J = 2.3, 6.5$ Hz, 1, vinyl), 4.82 (d, $J = 2.3$ Hz, 1, bridgehead), 4.50 (d, $J = 6.5$ Hz, 1, bridgehead); δ ($CDCl_3$) 7.38–6.75 (m, 8, aromatic), 6.68 (dd, $J = 2.2, 6.4$ Hz, 1, vinyl), 4.94 (overlapping doublets, 2, bridgeheads)]. (b) Prepared by the method of S. J. Cristol, R. Caple, R. M. Sequeira, and L. O. Smith, Jr., *J. Am. Chem. Soc.*, **87**, 5679 (1965).

(8) As pointed out by a referee, an alternative ionic pathway for rearrangement of **2** involving carbon–bromine ionization with simulaneous electrocyclic cleavage of a peripheral cyclopropane ring bond cannot be excluded on the basis of the limited data. While this mechanistic possibility should not be ignored, the lack of literature precedent for cyclopropyl to allyl conversions of bridgehead halides and the energetically unfavorable accumulation of positive charge at the $-CF_2$ carbon render it suspect in comparison with the postulated diradical mode of ring opening.

Carbonyl Insertion Reactions of Ethyl α-Trimethylsilyldiazoacetate. An Improved Route to Diazoacetate Aldol Products

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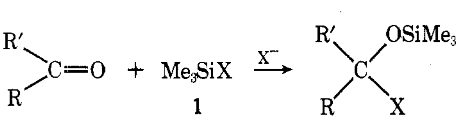
Received April 20, 1976

Interest in the carbonyl insertion[1] chemistry of organosilicon compounds has only recently developed in spite of the central role the carbonyl function plays in organic synthesis.[2–4] Of particular interest to us has been the generality of the anion-initiated carbonyl insertion process illustrated below (eq 1). To date we have demonstrated that the reaction of

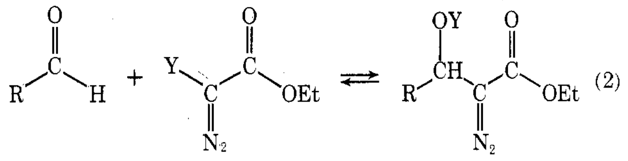


$$R'RC{=}O + Me_3SiX \xrightarrow{X^-} R'RC(OSiMe_3)X \quad (1)$$

1 2

trimethylsilyl cyanide (1, X = CN) with an extensive variety of aldehydes and ketones is readily initiated by both cyanide and fluoride ion.[2a,b] The only other silicon pseudohalide which has been found to react in an analogous fashion has been trimethylsilyl azide (1, X = N_3) which forms aldehyde adducts 2 (X = N_3; R′ = H) in excellent yields.[2b] Recently, we have found that thiosilanes 1 (X = SR), in the presence of anionic initiators, will also form aldehyde adducts 2 (X = SR) in excellent yields.[4a] As has recently been demonstrated, these organosilane–carbonyl adducts are valuable intermediates in chemical synthesis.[5,6]

We now wish to report that the carbonyl insertion reactions of ethyl α-trimethylsilyldiazoacetate (**3a**) can be effected (eq 2), and that the reaction is subject to specific anion initiation. Wenkert and McPherson have shown[7] that ethyl diazoacetate adds to aldehydes in the presence of a catalytic amount of sodium hydroxide. Unfortunately, the reaction affords an equilibrium mixture of the aldol product **4b** and starting materials where adduct formation is quite unfavorable for some aldehydes and most ketones. Based upon crude thermodynamic approximations, it was predicted that the silyldiazoacetate addition reactions (**3a** → **4a**) should be *more* exothermic than the analogous diazoacetate addition processes (**3b** → **4b**). These predictions have now been verified. The addition of **3a**[8] to both aromatic and aliphatic aldehydes occurs exothermically at room temperature in nearly quantitative yield when catalyzed by the potassium cyanide–18-crown-6 complex.[2b] For sensitive substrates (i.e., the isobutyraldehyde adduct), which were unstable to the heat generated by the reaction, solvents such as chloroform were used to moderate the temperature. Removal of the solvent at room temperature afforded essentially pure aldol adduct **4a**. Analytical samples were obtained by column chromatography on Florisil, *but partial hydrolysis of* **4a** *to the corresponding alcohol* **4b** *was usually observed.* Table I compares the chromatographed yields of the silyldiazo ester insertions with Wenkert's protiodiazo ester reactions where possible. Not only are the yields consistently higher, but the reaction conditions are nonaqueous and essentially neutral. Preliminary results indicate that even tigaldehyde survives the reaction to afford a moderate yield of the 1,2 adduct; no 1,4 adduct could be detected.



(2)

3 4

a, Y = $SiMe_3$; **b**, Y = H; **c**, Y = $SnMe_3$

Less reactive carbonyl systems such as acetophenone, cyclohexanone, 3-pentanone, and 3-methyl-3-penten-2-one all failed to produce detectable adducts (by NMR). In hope of achieving a still more favorable equilibrium, the analogous reactions of ethyl α-trimethylstannyldiazoacetate[9] (**3c**) were examined, but 3-pentanone was inert to the reagent and hexanal was slowly polymerized.[10] Since the completion of our work, Schollkopf has shown that **3** (Y = Li, MgX) will add to both aldehydes and ketones under very carefully controlled conditions to afford the corresponding aldol-type products in high and moderate yields, respectively.[11] Both thermal and Lewis acid catalyzed reaction conditions failed to generate the aldol adducts **4** from either the silyl or stannyldiazo esters **3a** or **3c**. This is in marked contrast to related carbonyl insertions by other organosilanes.[2–4]

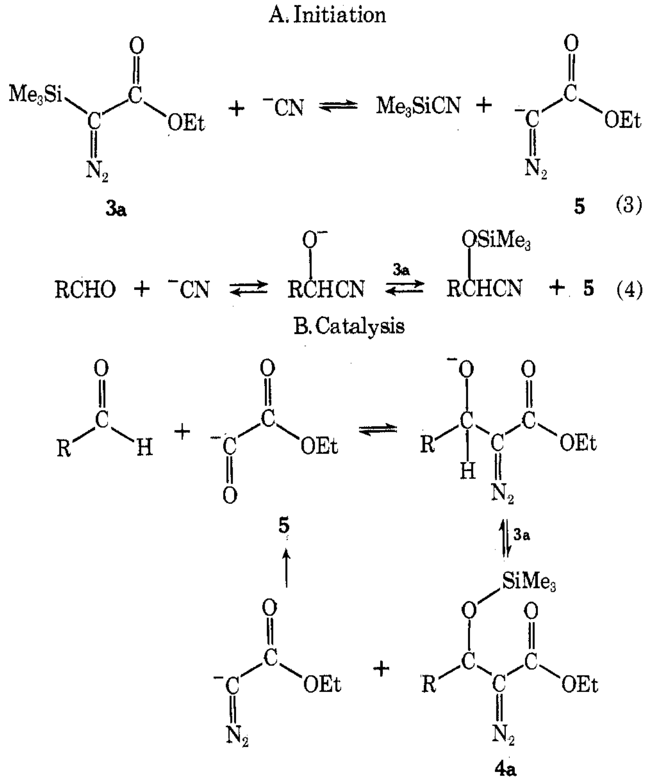
The presumed mode of catalysis by anionic initiators such as cyanide ion (Scheme I) involves the generation of catalytic amount of diazo ester enolate **5** via either of the processes illustrated in eq 3 and 4 followed by carbonyl addition and subsequent silicon transfer steps to regenerate **5**. It is pre-

Table I. Carbonyl Addition Reactions of 3a (Eq 1)

RCH═O	Registry no.	% yield of 4a[a,b]	% yield of 4b[c]
$CH_3(CH_2)_4CHO$	66-25-1	86 (63:37)	68 (R = C_6H_{13})
$(CH_3)_2CHCHO$	78-84-2	93 (76:24)	80
C_6H_5CHO	100-52-7	86 (84:16)	60
p-ClC_6H_4CHO	104-88-1	93 (78:22)	25
p-$CH_3OC_6H_4CHO$	123-11-5	83 (100:0)	
$CH_3CH{=}\overset{\overset{CH_3}{\vert}}{C}CHO$	497-05-0	44 (100:0)	

[a] Calculated on isolated yields of adduct. [b] Values in parentheses refer to the ration of **4a**:**4b** isolated from chromatography. Prior to chromatography only **4a** was present. [c] Yields for the base-catalyzed addition of **3b** to illustrated aldehydes (ref 7).

Scheme I



A. Initiation

B. Catalysis

sumed that fluoride ion would also serve as an efficient initiation catalyst.

In conclusion, the use of silyldiazo ester **3b** as a masked carbon nucleophile in carbonyl addition reactions establishes a valuable precedent for the design of related masked carbon nucleophiles. The extremely mild catalytic conditions under which these insertions occur make them particularly valuable in organic synthesis. In the present case not only is a carbon–carbon bond formed, but the β-hydroxy-α-diazocarbonyl function created is of practical interest.[7,11,12]

Experimental Section

Ethyl 2-Diazo-3-trimethylsiloxy-3-phenylpropionate (4a, R = C_6H_5). To a nitrogen-blanketed solution of 0.176 g (1.66 mmol) of freshly distilled benzaldehyde and 0.308 g (1.66 mmol) of ethyl 2-trimethylsilyl-2-diazoacetate (**3a**)[8] in 2 ml of chloroform was added 0.005 g (a catalytic amount) of 18-crown-6–potassium cyanide complex.[2b] The solution warmed instantly upon the addition of the catalyst. The yellow solution was stirred at ambient temperature for 1.75 h whereupon the solvent was removed at reduced pressure and the yellow oil was chromatographed on 50 g of Florisil eluting with 1% ether in hexane. This eluent afforded 0.348 g (72%) of product **4a** (R = C_6H_5) as a clear yellow oil. The eluting solvent was changed to 1:1 ether–hexane and 0.0955 g (14%) of the clear yellow alcohol **4b** (R = C_6H_5) was obtained. The trimethylsiloxy adduct had the following properties: ir (neat) 2100 ($C{=}N_2$), 1695 ($-CO_2Et$), and 1255 cm^{-1} ($SiGH_3$); NMR (CCl_4) 7.33 (s, 5, aryl H), 5.38 (s, 1, $OCHC_6H_5$), 4.28 (q, 2, J = 7.0 Hz, OCH_2), 1.33 (t, 3, J = 7.0 Hz, CH_2CH_3), 0.18 ppm (s, 9, $SiCH_3$).

Anal. Calcd for $C_{14}H_{20}N_2O_3Si$: C, 57.51; H, 6.89. Found: C, 57.31; H, 6.71.

Ethyl 2-Diazo-3-trimethylsiloxy-3-(4-methoxyphenyl)propionate (4a, R = p-$CH_3OC_6H_4$). The addition was carried out in 83% by the general method described above: ir (neat) 2090 ($C{=}N_2$), 1685 (CO_2Et), and 1245 cm^{-1} ($SiCH_3$); NMR (CCl_4) δ 7.31 (d, 2, J = 9 Hz, OC=C–CH), 6.84 (d, 2, J = 9 Hz, OC=CH), 5.78 (s, 1, CHOSi), 4.25 (q, 2, J = 7 Hz, OCH_2), 3.77 (s, 3, OCH_3), 1.30 (t, 3, J = 7 Hz, CH_2CH_3), 0.15 (s, 9, $SiCH_3$).

Anal. Calcd for $C_{15}H_{22}N_2O_4Si$: C, 55.87; H, 6.88. Found: C, 56.08; H, 6.95.

Ethyl 2-Diazo-3-trimethylsiloxy-3-(4-chlorophenyl)propanoate (4a, R = p-ClC_6H_4). The addition was carried out according to the general method described above in 73% yield along with 20% of the corresponding alcohol **4b**: ir (neat) 2105 ($C{=}N_2$), 1695 (CO_2Et), and 1250 cm^{-1} ($SiCH_3$); NMR ($CDCl_3$) δ 7.32 (s, 4, aryl H), 5.82 (s, 1, $OCHC_6H_4Cl$), 4.25 (q, 2, J = 7.0 Hz, OCH_2), 1.27 (t, 3, J = 7.0 Hz, CH_2CH_3), and 0.12 (s, 9, $SiCH_3$).

Anal. Calcd for $C_{14}H_{19}ClN_2O_3Si$: C, 51.45; H, 5.86. Found: C, 52.05; H, 5.71.

Ethyl 2-Diazo-3-trimethylsiloxyoctanoate (4a, R = n-C_5H_{11}). Following the general procedure the adduct was obtained in 54% yield by the general method described above along with 32% of the corresponding alcohol **4b**: ir (neat) 2085 ($C{=}N_2$), 1690 ($-CO_2Et$), and 1254 cm^{-1} ($SiCH_3$); NMR (CCl_4) δ 4.54 (t, 1, J = 6 Hz, CHOSi), 4.18 (q, 2, J = 7 Hz, OCH_2), 0.06 (s, 9, $Si{=}CH_3$).

Anal. Calcd for $C_{13}H_{26}N_2O_3Si$: C, 54.51; H, 9.15. Found: C, 54.67; H, 9.22.

Ethyl 2-Diazo-3-trimethylsiloxy-4-methylpentanoate (4a, R = i-C_3H_7). Following the general procedure the adduct was obtained in 71% yield by the general method described above along with a 22% yield of the corresponding alcohol **4b**: ir (neat) 2100 ($C{=}N_2$), 1695 ($-CO_2Et$), and 1280 cm^{-1} ($SiCH_3$); NMR (CCl_4) δ 4.20 (d, 1, J = 7.0 Hz, CHOSi), 4.16 (q, 2, J = 7 Hz, OCH_2), 1.73 [m, 1, $CH(CH_3)_2$], 1.25 (t, 3, J = 7 Hz, CH_3CHCH_3), 0.07 (s, 9, $SiCH_3$).

Anal. Calcd for $C_{11}H_{22}N_2O_3Si$: C, 51.13; H, 8.58. Found: C, 51.16; H, 8.45.

Ethyl 2-Diazo-3-trimethylsiloxy-4-methyl-(*E*)-4-hexenoate [4a, R = $C(CH_3){=}CHCH_3$]. The adduct was prepared in 44% yield by the general method described above: ir (neat) 2100 ($C{=}N_2$), 1695 ($-CO_2Et$), and 1250 cm^{-1} ($SiCH_3$); NMR (CCl_4) δ 5.64 (q, 1, J = 7 Hz, $CH_3CH{=}C$), 4.93 (s, 1, CHOSi), 4.20 (q, 2, J = 7 Hz, OCH_2), 1.65 (d, 3, J = 7 Hz, $CH_3CH{=}C$), 1.58 (s, 3, $CH_3C{=}CH$), 1.28 (t, 3, J = 7 Hz, OCH_2CH_3), and 0.12 (s, 9, $SiCH_3$). Combustion analysis was not obtained owing to the unstable nature of the adduct.

Acknowledgment. Research support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Registry No.—**3a**, 17145-48-1; **4a** (R = C_6H_5), 59840-31-2; **4a** (R = p-$CH_3OC_6H_4$), 59840-32-3; **4a** (R = p-ClC_6H_4), 59840-33-4; **4a** (R = n-C_5H_{11}), 59840-34-5; **4a** (R = i-C_3H_7), 59840-35-6; **4a** [R = $C(CH_3){=}CHCH_3$], 59840-36-7.

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