Thermal and Metal-Catalyzed Rearrangements of Bis(stannyl)diazo Derivatives into Carbodiimides: Carbodiimide-Transfer Reactions

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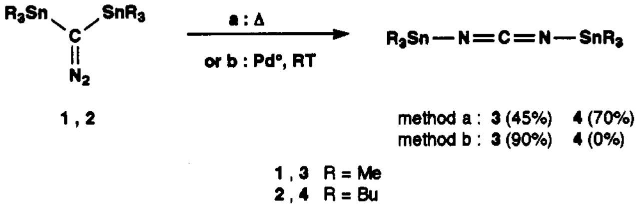
Summary: Thermolysis of bis(trimethylstannyl)diazomethane (1) or bis(tributylstannyl)diazomethane (2) affords the corresponding bis(stannyl)carbodiimides 3–4. Bis(trimethylstannyl)carbodiimide (3) is also obtained at room temperature by palladium-catalyzed isomerization of diazo derivative 1 and is a powerful precursor of elaborated carbodiimides.

Diazo derivatives are unique compounds, not only because of their wide utility in organic and inorganic synthesis as carbene precursors or as 1,3-dipoles[1] but also because they possess six known or suspected structural isomers. A few interconversions of one isomer into another have been reported,[2] but starting from the diazo compounds, only the reversible isomerization into diazirines has been extensively studied.[3] In this paper, we wish to report the unprecedented isomerization of diazo derivatives into carbodiimides. This rearrangement provides a straightforward entry to bis(stannyl)carbodiimides, which are powerful "carbodiimide transferring agents"; the preparation of (silyl)(stannyl)carbodiimide and bis(carbodiimide)phosphanes is described.

Heating neat bis(trimethylstannyl)diazomethane (1)[4] at 180 °C, or bis(tributylstannyl)diazomethane (2)[4] at 250 °C, affords the corresponding bis(stannyl)carbodiimides 3[5] (45% yield) and 4[6] (70% yield), respectively. Interestingly, bis(trimethylstannyl)carbodiimide (3) is also obtained in 90% yield when a THF solution of diazo derivative 1 is stirred overnight at room temperature in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium or bis(dibenzilydeneacetone)palladium (Scheme I). Note that the bis(tributylstannyl)carbodiimide (4) is not accessible under this experimental condition; furthermore no thermal or palladium-catalyzed isomerization is observed with bis(trimethylsilyl)diazomethane[7,8] or (trimethylsilyl)(trimethylstannyl)diazomethane.[8]

Scheme I



The isomerization of diazo derivatives (1, 2) into carbodiimides (3, 4) implies the migration of the two substituents from the carbon atom to the two nitrogen atoms, and also a rearrangement of the CNN skeleton. Since under such experimental conditions diazo derivatives usually lose dinitrogen,[1] this complicated process is very

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(6) **4**: Neat bis(tributylstannyl)diazomethane (5.0 g, 8.1 mmol) was heated for 3 h under insert atmosphere at 250 °C. Bis(tributylstannyl)carbodiimide (4) was obtained as a colorless oil by distillation with a Kugelrohr apparatus at 220–225 °C/5 × 10^{-2} mmHg (3.5 g, 70%): ^{1}H NMR (CDCl$_3$) δ 0.86 (t, J_{HH} = 7.2 Hz, 18 H, CH$_3$), 1.04 (m, 12 H, CH$_2$), 1.27 (m, 12 H, CH$_2$), 1.55 (m, 12 H, CH$_2$); ^{13}C NMR (CDCl$_3$) δ 13.28 (s, CH$_3$), 14.13 (s, $J_{C^{117}Sn}$ = 351.7 Hz, $J_{C^{119}Sn}$ = 366.4 Hz, SnCH$_2$), 26.72 (s, J_{CSn} = 61.0 Hz, CH$_2$), 27.76 (s, J_{CSn} = 22.0 Hz, CH$_2$), 137.51 (s, NCN); ^{119}Sn NMR (CDCl$_3$) +45.45; ^{14}N NMR (CDCl$_3$) δ −363.45 ($\nu_{1/2}$ = 428 Hz); IR (CDCl$_3$, ν (cm^{-1})) 2074 cm^{-1} (NCN); MS (*m/z*) 563 (M − Bu). Anal. Calcd for $C_{26}H_{54}N_2Sn_2$: C, 48.42; H, 8.77; N, 4.52. Found: C, 48.29; H, 8.70; N, 4.48. **5**: Triisopropylchlorosilane (0.988 mL, 4.62 mmol) was added dropwise at room temperature to a THF solution (10 mL) of **3** (1.70 g, 4.62 mmol). After the solution was stirred for 2 h, the solvent and trimethylstannyl chloride were removed under vacuum (overnight, room temperature, 10^{-2} mmHg). Carbodiimide **5** is purified by sublimation and obtained as white crystals (1.42 g, 85%); mp 37 °C: ^{1}H NMR (CDCl$_3$) δ 0.42 (s, $J_{H^{117}Sn}$ = 56.1 Hz, $J_{H^{119}Sn}$ = 58.6 Hz, 9 H, CH$_3$Sn), 1.03 (m, 21 H, C*H*$_3$C*H*Si); ^{13}C NMR (CDCl$_3$) δ −4.35 (s, $J_{C^{117}Sn}$ = 380.9 Hz, $J_{C^{119}Sn}$ = 398.4 Hz, SnCH$_3$), 12.52 (s, CH), 17.63 (s, CH$_3$), 131.01 (s, NCN); ^{119}Sn NMR (CDCl$_3$) δ +78.83 ($\nu_{1/2}$ = 295 Hz); ^{29}Si NMR (CDCl$_3$) δ +3.26; ^{14}N NMR (CDCl$_3$) δ −358.65 ($\nu_{1/2}$ = 295.15 Hz); IR (THF, ν (cm^{-1})) 2127 (NCN); MS (*m/z*) 362 (M$^+$). Anal. Calcd for $C_{13}H_{30}N_2SiSn$: C, 43.23; H, 8.37; N, 7.75. Found: C, 43.19; H, 8.34; N, 7.72. **7**: ^{31}P NMR (CDCl$_3$) δ 85.54; IR (THF, ν (cm^{-1})) 2160 (NCN). **9**: ^{1}H NMR (CDCl$_3$) δ 1.02 (m, 42 H, C*H*$_3$C*H*Si), 1.17 (d, J_{HH} = 6.8 Hz, 12 H, C*H*$_3$CHN), 3.58 (sept d, J_{HH} = 6.8 Hz, J_{PH} = 12.0 Hz, 2 H, CH$_3$C*H*N); ^{13}C NMR (CDCl$_3$) δ 11.99 (s, *C*HSi), 17.50 (s, *C*H$_3$CHSi), 24.03 (d, J_{PC} = 8.5 Hz, *C*H$_3$CHN), 44.64 (d, J_{PC} = 12.3 Hz, CH$_3$*C*HN), 126.21 (d, J_{PC} = 17.4 Hz, NCN); ^{31}P NMR (CDCl$_3$) δ +98.78; IR (THF, ν (cm^{-1})) 2137, 2192 (NCN). **10**: ^{1}H NMR (CDCl$_3$) δ 1.04 (m, 48 H, C*H*$_3$C*H*Si and CH$_2$C*H*$_3$), 3.08 (q d, J_{HH} = 7.1 Hz, J_{PH} = 11.0 Hz, 4 H, CH$_2$); ^{13}C NMR (CDCl$_3$) δ 12.02 (s, CHSi), 14.75 (d, J_{PC} = 4.2 Hz, CH$_2$*C*H$_3$), 17.61 (s, *C*H$_3$CHSi), 39.10 (d, J_{PC} = 20.6 Hz, CH$_2$), 126.69 (d, J_{PC} = 16.9 Hz, NCN); ^{31}P NMR (CDCl$_3$) δ +104.09; IR (THF, ν (cm^{-1})) 2135, 2193 (NCN). **11**: isolated as colorless oil; ^{1}H NMR (CDCl$_3$) δ 1.05 (m, 42 H, C*H*$_3$C*H*Si), 1.27 (d, J_{HH} = 6.9 Hz, 12 H, C*H*$_3$CHN), 3.81 (sept d, J_{HH} = 6.9 Hz, J_{PH} = 20.8 Hz, 2 H, NCH); ^{13}C NMR (CDCl$_3$) δ 11.77 (s, CHSi), 17.50 (s, *C*H$_3$CHSi), 22.28 (d, J_{PC} = 2.3 Hz, *C*H$_3$CHN), 47.15 (d, J_{PC} = 5.3 Hz, CHN), 124.64 (d, J_{PC} = 2.9 Hz, NCN); ^{31}P NMR (CDCl$_3$) δ +46.91; IR (THF, ν (cm^{-1})) 2184 (NCN); ^{29}Si NMR (CDCl$_3$) δ +10.25; MS (*m/z*) 558 (M + 1). Anal. Calcd for $C_{26}H_{56}N_5Si_2PS$: C, 55.97; H, 10.12; N, 12.55. Found: C, 55.29; H, 10.05; N, 12.41. **12**: isolated as a colorless oil; ^{1}H NMR (CDCl$_3$) δ 1.07 (m, 48 H, C*H*$_3$C*H*Si and CH$_2$C*H*$_3$), 3.24 (q d, 4 H, J_{HH} = 7.1 Hz, J_{PH} = 14.8 Hz, CH$_2$); ^{13}C NMR (CDCl$_3$) δ 11.76 (s, CHSi), 13.93 (d, J_{PC} = 3.9 Hz, CH$_2$*C*H$_3$), 17.49 (s, C*H*$_3$CHSi), 40.16 (d, J_{PC} = 4.3 Hz, CH$_2$), 124.76 (d, J_{PC} = 3.3 Hz, NCN); ^{31}P NMR (CDCl$_3$) δ +51.15; ^{29}Si NMR (CDCl$_3$) δ +10.49; IR (THF, ν (cm^{-1})) 2170 (NCN); MS (*m/z*) 530 (M + 1). Anal. Calcd for $C_{24}H_{52}N_5Si_2PS$: C, 54.40; H, 9.89; N, 13.22. Found: C, 54.20; H, 9.71; N, 13.08.

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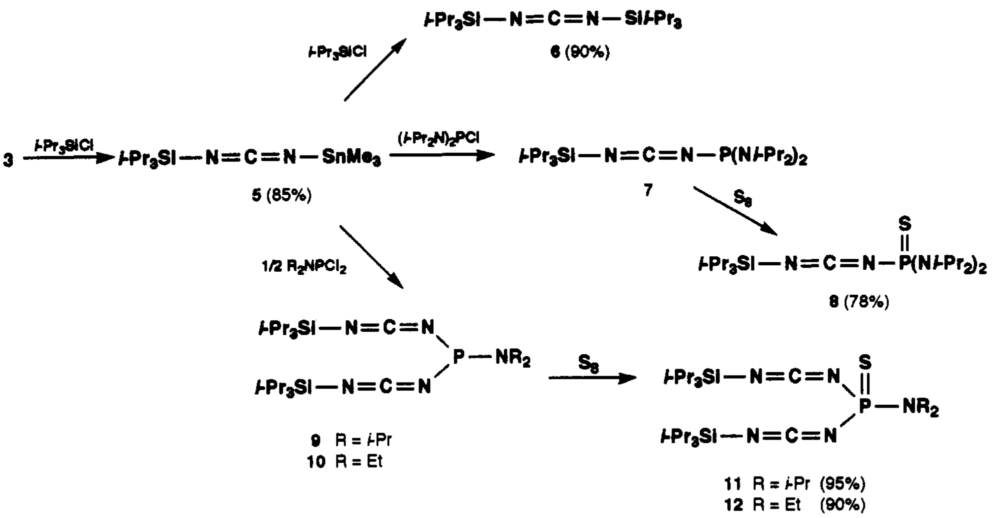
Scheme II



surprising. One can easily anticipate that the migrating aptitude of the stannyl substituents is a key point of the process. All attempts to demonstrate the intra- or intermolecular nature of the rearrangement failed, since, even at room temperature, exchange reactions of stannyl groups are observed between diazo derivatives 1 and 2. However, a mechanism involving the formation of a transient 1*H*-diazirine, a diazo isomer which is known to rearrange into carbodiimide via an imidoyl-nitrene,[2a] seems likely.

In contrast to the well-known bis(trimethylsilyl)carbodiimide,[9] the two nitrogen-heteroatom bonds of the bis(trimethylstannyl)carbodiimide (3) are reactive toward electrophiles. As examples, addition at room temperature of 2 equiv of trimethylchlorosilane or even tributylchlorostannane to carbodiimide 3 affords bis(trimethylsilyl)- and bis(tributylstannyl)carbodiimide in 85 and 90% yields, respectively, along with trimethylchlorostannane. However, using bulky electrophiles such as triisopropylchlorosilane, the reaction can be controlled and stopped at the first substitution, giving unsymmetrical carbodiimide 5, which was isolated by sublimation in 85% yield.[6] This new mixed substituted carbodiimide 5 is still reactive toward electrophiles: it reacts at room temperature with triisopropylchlorosilane and bis(diisopropylamino)chlorophosphane affording bis(triisopropylsilyl)carbodiimide (6)[10] (90% yield) and [bis(diisopropylamino)phosphanyl]-(triisopropylsilyl)carbodiimide (7),[6] which was isolated after treatment with elemental sulfur as 8[11] in 78% yield. More interestingly, carbodiimide 5 reacts in THF solution with 0.5 equiv of (diisopropylamino)dichlorophosphine or (diethylamino)dichlorophosphine to give bis(carbodiimido)phosphines 9[6] and 10,[6] which were isolated after sulfuration as thioxophosphoranyl derivatives 11[6] (95% yield) and 12[6] (90% yield (Scheme II).

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