Isoxazoles as Latent Siloxybutadienes: An Easy Entry to Polyfunctionalized Benzene Systems via Diels–Alder Reaction with Acetylenes

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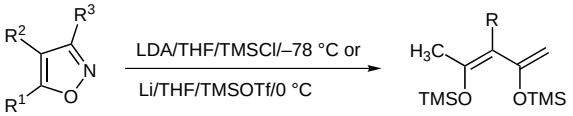
Abstract: Base-induced or reductive cleavage of isoxazole rings followed by silylation of the resulting open-chain products affords bis(siloxy)butadienes in high yields. Their synthetic usefulness in the construction of multifunctionalized aromatic systems, via Diels–Alder reactions, is shown. The ability of bis(siloxy)butadienes to undergo deprotonation and reaction with electrophiles is also studied.

Key words: isoxazoles, siloxybutadienes, silyl dienol ethers, Diels–Alder cycloaddition, β-diketones

Some time ago we reported a general method for the synthesis of β-cyano silyl enol ethers from 3-unsubstituted isoxazoles.[1] They are masked β-enaminoketones[2] of wide application as intermediates in the synthesis of nitrogen-containing natural products.[3] We also noted their ability to undergo inverse electron demand hetero-Diels–Alder reactions when treated with heterodienes (enones, azabutadienes),[1,4] thus providing new pathways for heterocyclic synthesis. Isoxazoles[5] bearing no substituents at C-3 are readily attacked by bases leading to (*Z*)-β-cyanoenolates, which are trapped by chlorosilanes giving β-cyano silyl enol ethers in high yield.[1–3]

In the past years, our effort has been directed to the development of new synthetic methodologies using silicon compounds.[6] As part of this work, we now report an efficient synthesis of bis(siloxy)butadienes from isoxazole precursors and their usefulness in the construction of polyfunctionalized benzene systems. Siloxybutadienes[7] are masked β-diketones and useful intermediates in Diels–Alder reactions.[8]

Treatment of 4-acetyl-5-methylisoxazole (**1a**) with LDA at –78 °C followed by reaction with an excess of TMSCl and gentle warming to room temperature, in the presence of a catalytic amount of zinc chloride, gives the cyano-bis(siloxy)butadiene **2a**. The cleavage of the ring by attack of LDA to H-3 and the capture of the resulting intermediate enolate with TMSCl are accompanied with further silyl enol ether formation from the remaining 4-acetyl group, leading to the silyl dienol ether **2a** as the temperature increases (Scheme 1). On the other hand, metal-acid reductive cleavage of isoxazoles **1b**,**c** with lithium granulated in wet THF (1%) at room temperature for several hours, followed by slow addition of an excess of triethylamine/trimethylsilyl triflate at 0 °C and warming to room temperature gives the bis(siloxy)butadienes **2b**,**c** (Scheme 1). Compounds **2a**–**c** are obtained as mixtures of *Z*/*E*-isomers, which were used directly without separation. As shown below, this is not a limitation for the reported procedure since both stereoisomers undergo Diels–Alder cycloaddition with acetylenes leading to the same product.



1a: R^1 = Me, R^2 = Ac, R^3 = H
1b: R^1 = R^3 = Me, R^2 = H
1c: R^1 = R^2 = R^3 = Me

2a: R = CN (93%)
2b: R = H (91%)
2c: R = Me (87%)

Scheme 1

Siloxybutadienes **2a**–**c** react with methyl propiolate and diethyl acetylenedicarboxylate giving the phenols **3a**–**c** and **4a**–**c** in good yields (Scheme 2). The reaction takes place in a closed flask, without solvent, at temperatures between 120–140 °C. After stirring the mixture for three hours, the crude is poured into saturated ammonium chloride and extracted with diethyl ether. Apparently, the intermediate Diels–Alder adduct undergoes elimination of silanol leading to the aromatic nucleus (Scheme 3). NMR analysis of the crude showed that the benzene ring was present before the final hydrolysis. Protodesilylation of the resulting silyl phenol ether affords **3** and **4** (Scheme 3).

The high regioselectivity of the cycloaddition is to be noted. Reactions with methyl propiolate lead to **3a**–**c** as the only products; we were not able to detect other isomeric compounds. Thus, the procedure provides a facile and regioselective entry to polyfunctionalized benzene rings.

The synthetic versatility of siloxybutadienes of type **2** is also shown in their ability to generate carbanionic species, which are synthetically equivalent to β-diketone anions, by deprotonation of the 5-methyl group (Figure 1). Allylic deprotonation in electron rich systems as the silyl dienol ethers **2a**–**c** is known to proceed with difficulty and little work has been reported in this area.[9] We wondered if this possibility could be taken into account. Effectively, metalation of **2a**,**c** with BuLi in THF at low temperature for half an hour, followed by reaction with simple electro-

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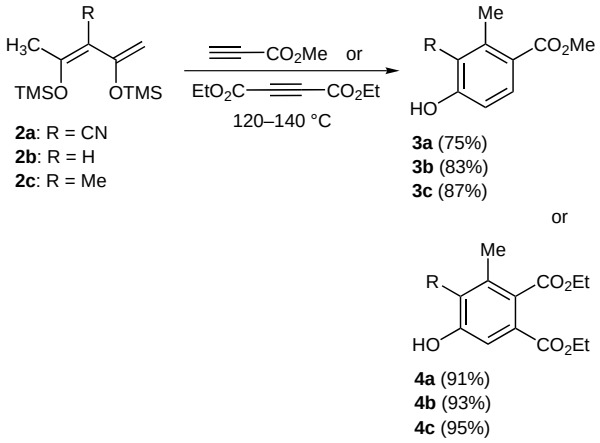
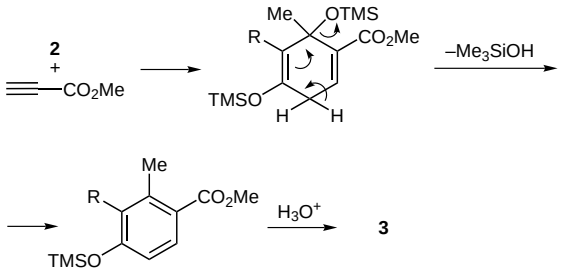


2a: R = CN
2b: R = H
2c: R = Me

3a (75%)
3b (83%)
3c (87%)

4a (91%)
4b (93%)
4c (95%)

Scheme 2



Scheme 3

philes (bromine, methyl iodide or ethyl bromide) and final workup of the mixture gives the β-diketones **5**, **6**, and **7** (Scheme 4). IR and NMR spectra of **5**–**7** show that they are predominantly in enolic form. Since alkylation of penta-1,3-dienones under basic conditions occurs, in general, at the C-3 'meso' position, this procedure introduces a new aspect of the reactivity pattern of penta-1,3-dienones, thus providing an easy method for the regioselective alkylation of the less common C-1 position, via silyl dienol ethers.

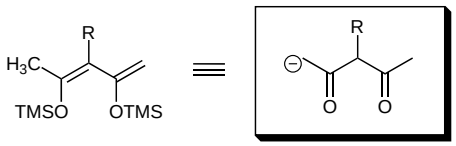
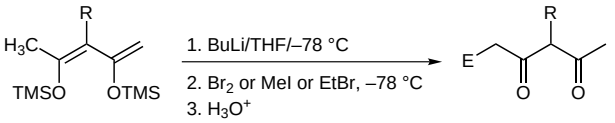


Figure 1 Siloxybutadienes as synthetic equivalents of β-diketone anions

In conclusion, isoxazoles are efficient precursors of bis(siloxy)butadienes by ring cleavage and subsequent silylation. The latter are versatile intermediates of wide synthetic scope. They behave as highly reactive dienes in Diels–Alder reactions that allows the construction of multifunctionalized aromatic rings. Furthermore, they are masked β-diketones, which upon deprotonation and reaction with electrophiles can be alkylated at C-1, thus enlarging their synthetic applicability.



2a: R = CN
2c: R = Me

5a: R = CN, E = Br (77%)
6a: R = CN, E = Me (75%)
7a: R = CN, E = Et (81%)
5c: R = Me, E = Br (70%)
6c: R = Me, E = Me (76%)

Scheme 4

All reactions involving silyl dienol ethers and air or moisture sensitive reagents were carried out under dry N_2. Reagents and anhyd solvents were handled by using standard syringe techniques. Flash column chromatography was carried out on Merck silica gel 60 (230–400) and TLC analysis using silica gel 60 F-254 thin layer plates (Merck). Diels–Alder reactions were performed in a thermostatic bath, in the absence of solvent, using a round-bottomed flask fitted with a plastic screw cap having an inner teflon seal. $CDCl_3$ was used as solvent for NMR spectra. Melting points are uncorrected. Isoxazoles **1a**–**c** were prepared according to literature procedures.[10,11]

3-Cyano-2,4-bis(trimethylsiloxy)penta-1,3-diene (2a)

To a cooled solution (–78 °C) of LDA (20 mmol) in THF (30 mL) was slowly added the isoxazole **1a** (2.5 g, 20 mmol) under vigorous stirring. The resulting cloudy solution was stirred for 1 h at this temperature, then TMSCl (60 mmol) was added at –78 °C and the mixture was allowed to warm to r.t. (45 min). When the mixture had reached the r.t., anhyd $ZnCl_2$ (0.27 g, 2 mmol) was added and the mixture was stirred overnight. Separation of the lithium salts using a sintered glass filter funnel under N_2 followed by rotoevaporation of the solvent and vacuum distillation (110–115 °C /2.5 mbar) gave **2a** as a yellowish oil (5 g, 93%). ^{1}H NMR of the distillate showed that **2a** was obtained as an equimolar mixture of *E*/*Z*-isomers.

IR (neat): 2220, 1622 cm^{-1}.

^{1}H NMR: δ = 0.23 (s, 18 H, *E* or Z), 0.34 (s, 18 H, *E* or *Z*), 2.13 (s, 3 H, *E* or *Z*), 2.27 (s, 3 H, *E* or *Z*), 4.35–4.58 (4 d, *J* = 1.8, 2.2 Hz, 4 H, *E* and *Z*).

^{13}C NMR: δ = 0.13, 1.02, 21.31, 22.54, 96.07 (br), 98.87 (br), 118.20, 118.93, 148.35, 149.91, 165.41, 166.32. The duplication of some signals was a consequence of the presence of a mixture of *E*- and *Z*-isomers.

MS: *m*/*z* (%) = 269 (M^+, 3), 180 (60), 165 (45), 137 (100), 109 (53).

Silyl Dienol Ethers 2b,c; General Procedure

The corresponding isoxazole **1b** or **1c** (20 mmol) was dissolved in wet THF (50 mL, 1% H_2O) and excess of granulated Li (1 g) was added at 0 °C. The suspension was stirred at r.t. for 4 h, then the remaining Li was removed from the solution. After cooling again to 0 °C, Et_3N (40 mmol, 4 g) was added followed by slow addition (15 min) of trimethylsilyl triflate (50 mmol, 11.1 g) dissolved in THF (20 mL). The mixture was stirred at 0 °C for 15 min, then the bath was removed and the stirring was continued at r.t. for 1 h. After the reaction was complete, most of the THF was rotoevaporated (around 50 mL) and anhyd Et_2O was added (50 mL). On standing two phases appeared. The upper ethereal layer was separated from the dense phase containing the triflate salts. Rotoevaporation of the upper layer and vacuum distillation of the residue gave **2b** (4.4 g, 91%); bp 85–90 °C/10 mbar (Lit.[12] bp 93 °C/11 mbar) and **2c** (4.5 g, 87%). NMR spectra of **2b**,**c** show mixtures of *E*/*Z*-isomers.

3-Methyl-2,4-bis(trimethylsiloxy)penta-1,3-diene (2c)
Colorless oil; yield: 87%; bp 95–100 °C/5 mbar.

IR (neat): 1622 cm^{-1}.

^1H NMR: δ = 0.25 (s, 18 H), 1.62 (br s, 3 H,), 2.07 (br s, 3 H), 4.13 (s, 1 H), 4.27 (br s, 1 H).

^{13}C NMR: δ = 0.19, 0.95, 14.38, 15.87, 20.11, 22.16, 92.60, 113.17, 115.01, 145.21, 158.39, 160.03. Duplication of some signals results from the presence of mixtures of *E*/Z-isomers.

MS: *m*/*z* (%) = 258 (M^+, 13), 243 (100), 229 (33), 147 (90), 73 (85).

Diels–Alder Reactions of Silyl Dienol Ethers 2a–c; General Procedure
In a sealed flask, a mixture of **2** (5 mmol) and methyl propiolate or diethyl acetylenedicarboxylate (5 mmol) was heated at 120 °C or 140 °C, respectively for 4 h. The crude mixture was poured into sat. aq NH_4Cl solution (30 mL), slightly acidified with HCl, and stirred for a 15 min. After extraction with Et_2O, drying and removal of the solvent, the residue was chromatographed (CH_2Cl_2) to give **3a–c** and **4a–c**, respectively.

Methyl 3-Cyano-4-hydroxy-2-methylbenzoate (3a)
Yellowish solid; yield: 75%; mp 208–210 °C (EtOH).

IR (Nujol): 3450–3150, 2227, 1698, 1580, 1462 cm^{-1}.

^1H NMR: δ = 2.65 (s, 3 H), 3.4 (very br s, 1 H, OH), 3.92 (s, 3 H), 6.86 (d, *J* = 8.8 Hz, 1 H), 7.88 (d, *J* = 8.8 Hz, 1 H).

^{13}C NMR: δ = 18.11, 50.23, 101.31, 112.50, 114.89, 120.17, 135.42, 144.08, 162.73, 165.91.

MS: *m*/*z* (%) = 191 (M^+, 35), 160 (100), 132 (19), 104 (25).

Anal. Calcd for $C_{10}H_9O_3N$: C, 62.82; H, 4.74. Found: C, 63.1; H, 4.9.

Methyl 4-Hydroxy-2-methylbenzoate (3b)
Colorless solid; yield: 83%; mp 102–104 °C (EtOH).

IR (Nujol): 3505–3420, 1717, 1602, 1587, 1500, 850 cm^{-1}.

^1H NMR: δ = 2.32 (s, 3 H), 3.52 (s, 3 H), 6.42 (s, 1 H), 6.51 (d, *J* = 9.0 Hz, 1 H), 7.58 (d, *J* = 9.0 Hz, 1 H). The OH signal is missing.

^{13}C NMR: δ = 21.31, 51.67, 112.88, 116.34, 119.92, 131.12, 141.17, 159.33, 165.91.

MS: *m*/*z* (%) = 166 (M^+, 63), 134 (100), 106 (51), 77 (41).

Methyl 4-Hydroxy-2,3-dimethylbenzoate (3c)
Colorless solid; yield: 87%; mp 140–142 °C (EtOH).

IR (Nujol): 3450–3150, 1720, 1581, 1464, 840 cm^{-1}.

^1H NMR: δ = 2.21 (s, 3 H), 2.65 (s, 3 H), 3.75 (s, 3 H), 6.54 (d, *J* = 9.2 Hz, 1 H), 7.58 (d, *J* = 9.2 Hz, 1 H). The OH signal is missing.

^{13}C NMR: δ = 21.48, 23.94, 52.76, 111.93, 120.55, 126.13, 128.29, 140.63, 160.21, 164.16.

MS: *m*/*z* (%) = 180 (M^+, 52), 149 (100), 121 (19), 91 (30).

Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 67.0; H, 6.9.

Diethyl 4-Cyano-5-hydroxy-3-methylphthalate (4a)
Colorless solid; yield: 91%; mp 93–95 °C (EtOH).

IR (Nujol): 3650–3100, 2213, 1715, 1580, 1458 cm^{-1}.

^1H NMR: δ = 1.37 (t, *J* = 7.2 Hz, 3 H), 1.46 (t, *J* = 7.6 Hz, 3 H), 2.56 (s, 3 H), 4.36 (q, *J* = 7.2 Hz, 2 H), 4.53 (q, *J* = 7.6 Hz, 2 H), 7.58 (s, 1 H). The OH signal is missing.

^{13}C NMR: δ = 13.86, 14.01, 17.79, 60.91, 61.35, 104.22, 114.46, 114.68, 125.29, 133.08, 140.61, 160.35, 165.17, 167.70.

MS: *m*/*z* (%) = 277 (M^+, 9), 231 (32), 204 (100), 175 (11), 159 (23).

Anal. Calcd for $C_{14}H_{15}O_5N$: C, 60.65; H, 5.45. Found: C, 60.9; H, 5.6.

Diethyl 5-Hydroxy-3-methylphthalate (4b)
Viscous colorless oil; yield: 93%. On standing it solidified after several days (low melting solid).

IR (neat): 3450, 3120, 1718, 1603, 1465 cm^{-1}.

^1H NMR: δ = 1.31 (t, *J* = 7.4 Hz, 3 H), 1.34 (t, *J* = 7.4 Hz, 3 H), 2.40 (s, 3 H), 4.31 (q, *J* = 7.4 Hz, 2 H), 4.42 (q, *J* = 7.4 Hz, 2 H), 6.81 (br s, 1 H), 6.94 (br s, 1 H), 7.58 (very br s, 1 H, OH).

^{13}C NMR: δ = 13.88, 13.99, 21.16, 61.43, 61.82, 114.37, 121.50, 131.19, 136.48, 146.79, 161.32, 166.53, 169.61.

MS: *m*/*z* (%) = 252 (M^+, 23), 206 (35), 178 (44), 162 (33), 134 (100), 106 (21).

Diethyl 5-Hydroxy-3,4-dimethylphthalate (4c)
Colorless solid; yield: 95%; mp 40–42 °C (EtOH–hexane).

IR (Nujol): 3100–3410, 1715, 1585, 1464 cm& ndash;1.

^1H NMR: δ = 1.41 (br t, *J* = 7.3 Hz, 6 H), 2.23 (s, 3 H), 2.45 (s, 3 H), 4.26 (q, *J* = 7.3

Hz, 2 H), 4.40 (q, *J* = 7.3 Hz, 2 H), 6.81 (br s, 1 H), 6.87 (s, 1 H). The OH signal is missing.

^{13}C NMR: δ = 12.02, 13.90, 14.12, 20.27, 61.34, 61.86, 120.05, 127.82, 128.73, 132.51, 144.33, 159.24, 169.71, 169.84.

MS: *m*/*z* (%) = 266 (M^+, 25), 220 (52), 192 (100), 174 (31), 148 (80), 120 (21).

Anal. Calcd for $C_{14}H_{18}O_5$: C, 63.15; H, 6.81. Found: C, 63.3; H, 6.9.

Reaction of 2 with Electrophiles; General Procedure
To a stirred solution of the silyl dienol ether **2a**,**c** (5 mmol) in THF (20 mL), cooled at –78 °C, was added BuLi (5.5 mmol in hexane) added dropwise. After stirring for 30 min at that temperature, Br_2 or MeIor EtBr (6 mmol) was added and the resulting mixture was left to warm up from –78 °C to r.t. Then, aq HCl (pH 4, 30 mL) was added and the mixture was extracted with Et_2O (3 × 30 mL). The extracts were dried and the solvent was removed under reduced pressure. The products **5a**,**c**, **6a**,**c** and **7a** were purified by column chromatography using CH_2Cl_2 as eluent.

1-Bromo-3-cyanopenta-2,4-dione (5a)
Yellow oil; yield: 77%; bp 100–103 °C/0.7 mbar.

IR (neat): 3410 (enol form), 2210, 1735 (weak), 1620, 1600 cm^{-1}.

^1H NMR: δ = 2.57 (s, 3 H), 4.23 (s, 2 H), 5.5 (br s, 1 H, OH enol form).

^{13}C NMR: δ = 198.18, 184.07, 117.32, 95.85, 41.29, 29.11.

MS: *m*/*z* (%) = 203 (M^+, 3), 205 (3), 124 (28), 95 (7), 93 (7), 43 (100).

3-Cyanohexa-2,4-dione (6a)
White solid; yield: 75%; mp 53–55 °C (EtOH–hexane).

IR (CCl_4): 3450 (enol form), 2213, 1742 (weak), 1650, 1600 cm^{-1}.

^1H NMR: δ = 1.26 (t, *J* = 8.3 Hz, 3 H), 2.37 (s, 3 H), 2.69 (q, *J* = 8.3 Hz, 2 H), 4.7 (br s, 1 H, OH enol form).

^{13}C NMR: δ = 201.34, 187.22, 115.12, 97.09, 32.19, 28.57, 11.48.

MS: *m*/*z* (%) = 139 (M^+, 20), 124 (11), 110 (13), 82 (27), 43 (100).

Anal. Calcd for $C_7H_9O_2N$: C, 60.42; H, 6.52. Found: C, 60.7; H, 6.7.

3-Cyanohepta-2,4-dione (7a)
Yellowish solid; yield: 81%; mp 98–100 °C (EtOH–hexane).

IR (Nujol): 3400–3100 (enol form), 2206, 1605 cm^{-1}.

^1H NMR: δ = 0.88 (t, *J* = 8.1 Hz, 3 H), 1.26 (m, 2 H), 2.16 (s, 3 H), 2.38 (t, *J* = 8.3 Hz, 2 H), 5.1 (br s, 1 H, OH enol form).

^{13}C NMR: δ = 200.53, 185.31, 115.66, 99.48, 39.85, 29.14, 21.02, 8.53.

MS: *m*/*z* (%) = 153 (M^+, 15), 138 (8), 110 (23), 71 (37), 43 (100).

Anal. Calcd for $C_8H_{11}O_2N$: C, 62.73; H, 7.24. Found: C, 62.8; H, 7.2.

1-Bromo-3-methylpenta-2,4-dione (5c)
Unstable oil; yield: 70%.

IR (neat): 3250–3600 (enol form), 1650, 1590 cm^{-1}.

^1H NMR: δ = 2.01 (s, 3 H), 2.47 (s, 3 H), 4.39 (s, 2 H), 5.8 (br s, 1 H, OH enol form).

^{13}C NMR: δ = 197.18, 163.26, 121.43, 42.57, 27.41, 31.20.

MS: *m*/*z* (%) = 192 (M^+, 1), 194 (1), 150 (10), 152 (10), 121 (5), 123 (5), 93 (7), 95 (7), 43 (100).

3-Methylhexa-2,4-dione (6c)[13]
Colorless oil; yield: 76%; bp 85–88 °C /11 mbar.

IR (neat): 3210–3420 (enol form), 1731 (keto form), 1685, 1600 cm^{-1}.

^1H NMR: δ = 1.11 (t, *J* = 7.1 Hz, 3 H), 1.34 (d, *J* = 7.8 Hz, 3 H, keto form), 2.04 (s, 3 H), 2.26 (s, 3 H), 2.42 (q, *J* = 7.1 Hz, 2 H), 3.53 (q, *J* = 7.8 Hz, 1 H, keto form), 8.6 (br s, 1 H, OH enol form).

MS: *m*/*z* (%) = 128 (M^+, 5), 114 (18), 99 (24), 86 (33), 71 (43), 57 (30), 43 (100).

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