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2,3-Bis[(trimethylsilyl)methyl]-1,3-butadiene as a versatile bis-nucleophilic reagent for the preparation of polyfunctional 1,3-diene derivatives

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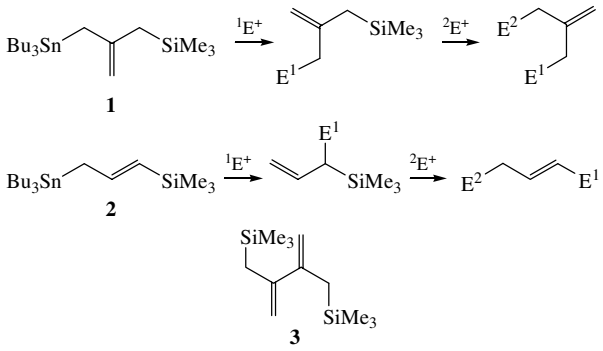
A new tandem C–C bond forming process has been developed, which utilises silyl-capped dienic bis-nucleophile **3** and various electrophiles under Lewis acid conditions; a short route for synthesis of functionalised 1,6-enynes has been proposed.

Carbon nucleophiles bearing allyl bis(trialkylsilyl) or trialkyltin moieties such as **1** or **2** are attractive synthetic tools as allyldimetal equivalents capable of participating in two alkylation steps with different electrophiles ($^1E^+$ and $^2E^+$) (Scheme 1).[1] These reactions were used for the preparation of various functionalised alkene derivatives, which are valuable synthetic intermediates.[2]



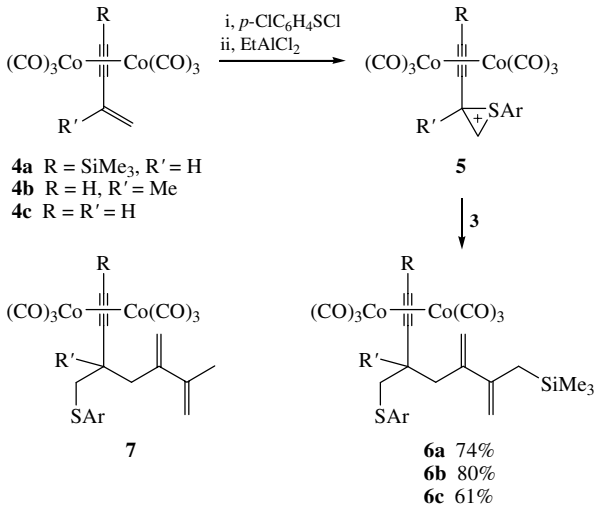
Scheme 1

We speculated that readily available[3] 2,3-bis[(trimethylsilyl)-methyl]-1,3-butadiene **3** could be employed as a bidentate carbon nucleophile in the above sequence. While the utilization of this diene as a conjunctive reagent for the tandem Diels–Alder reaction is well-documented,[4] to the best of our knowledge, no attempts were made to elucidate the course of Ad_E reactions with **3**.

Here, we report that the functionalization of **3** can be carried out as a controlled sequence of two kinetically independent reactions with different electrophiles and this sequence can be employed for the preparation of functionalised 1,3-butadienes.

Recently, we suggested a protocol for the modified Nicolas reaction, which involves a stepwise Ad_E reaction of arylsulfenyl chlorides with dicobalt hexacarbonyl (DCHC) complexes of conjugated enynes followed by the conversion of the formed adduct into an episulfonium ion intermediate and the interaction of the latter with π-donors like allylsilanes.[5]

We found that the reaction of episulfonium ion intermediate **5** formed from DCHC complexes **4a–c** proceeds as a selective monoalkylation of bis-silylated C-nucleophile **3** to give dienyne



Scheme 2

derivatives **6a–c** bearing a synthetically useful allylsilane moiety, as shown in Scheme 2.§

According to the previous data,[5] various Lewis acids can be employed for the generation of intermediate **5**. In this case, $EtAlCl_2$ is the best promoter of the reaction. In order to avoid the formation of bis-alkylated products in the reaction of intermediates **5** with **3**, it is necessary to use two equivalents of the latter. The procedure for the final quenching of the reaction mixture turned out to be very important. Thus, conventional quenching with aqueous $NaHCO_3$ leads to the partial desilylation of **6** to give adduct **7**. However, if the reaction mixture is treated with Et_3N–MeOH at –78 °C, the desired products are isolated as individual compounds in satisfactory or good yields.

To examine the possibility of electrophilic addition to allyl silanes **6**, the reactions of **6a**,**c** with methyl orthoformate and 2,2-dimethoxypropane in the presence of Lewis acids were studied (Scheme 3).

Lewis acids, which are usually used to promote the formylation of allyl silanes[6] ($TiCl_4$, Me_3SiI and Me_3SiOTf), are inefficient, while $EtAlCl_2$, which was not used before in similar reactions, is the best promoter of this process. In the reaction of **6a** with 2,2-dimethoxypropane, Me_3SiOTf promoted the process most efficiently.

The similarity of the reaction conditions employed in the first and second electrophilic alkylations (Schemes 2 and 3) prompted the opportunity to carry out both transformations as a

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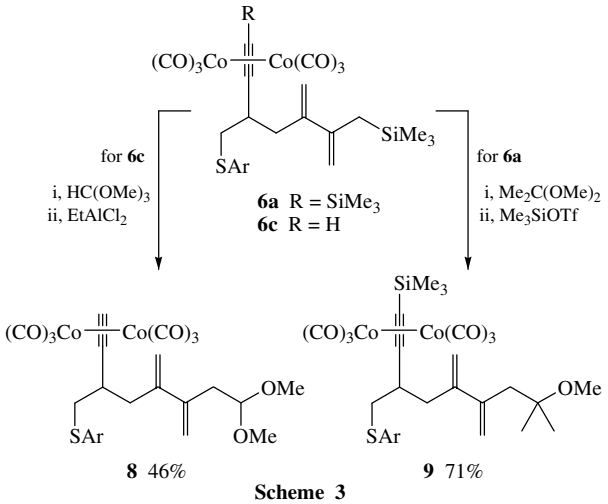
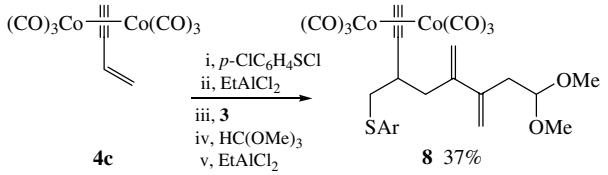


Scheme 3

one-pot reaction. The viability of this option was checked for the preparation of adduct **8** *via* a successive addition of the required reactants to starting DCHC complexes **4c** (Scheme 4). The overall yield of **8** was 37%. We believe that, with an additional optimization of the procedure, this sequence might become a promising protocol for a short-route assembly of various functionalised 1,3-dienes derivatives.

We found that the yields of all products were better if purification on silica gel was carried out at a low temperature.¶ The products thus obtained are stable for several days when stored in a fridge.

The functionality pattern of prepared adducts **6**, **8** and **9** secures an opportunity of their further utilization as substrates for intra- and intermolecular transformations such as the Pauson–Khand cyclization and/or Diels–Alder reaction, and these options are under study.



Scheme 4

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§ *A typical procedure for the preparation of adducts* **6a–c**. To a cooled (–78°) solution of DCHC complex **4a** (410 mg, 1 mmol) in absolute CH_2Cl_2 (4 ml), a 1 M *p*-ClC_6H_4SCl solution (1 ml, 1 mmol) in CH_2Cl_2 was gradually added under argon. After 5 min a 1 M $EtAlCl_2$ solution in hexane (1.1 ml, 1.1 mmol) and diene **3** (470 mg, 2 mmol) were added successively at –70 °C. The reaction mixture was kept at –30 °C for 9 h, then cooled to –78 °C (at higher temperatures, the cobalt carbonyl fragment is unstable in the presence of Et_3N) and quenched with Et_3N–MeOH (1:1) (4.4 equiv.). The mixture was poured into saturated aqueous $NaHCO_3$ (5 ml) and extracted with light petroleum (10 ml). After additional extraction the combined organic layers were immediately filtered through silica gel and eluted with cooled (–30 °C) light petroleum. The solvents were removed under a reduced pressure. The residue was purified by column chromatography on silica gel [eluent: cooled (–30 °C) light petroleum] to give **6a** (520 mg, 74%).

6a: R_f 0.34 (light petroleum). ^{1}H NMR ($CDCl_3$) δ: 0.02 (s, 9H), 0.37 (s, 9H), 1.73 (s, 2H), 2.44 (dd, 1H, J_1 14.6 Hz, J_2 11.0 Hz), 2.80–2.86 (m, 1H), 2.93 (dd, 1H, J_1 14.6 Hz, J_2 2.5 Hz), 3.24–3.37 (m, 2H), 4.78 (s, 1H), 4.95 (s, 1H), 5.05 (s, 1H), 5.18 (s, 1H), 7.21 (d, 4H, *J* 2.3 Hz).

6b: R_f 0.32 (light petroleum). ^{1}H NMR ($CDCl_3$) δ: 0.02 (s, 9H), 1.35 (s, 3H), 1.78 (d, 2H, *J* 1.5 Hz), 2.54 (d, 1H, *J* 13.2 Hz), 2.75 (d, 1H, *J* 14.4 Hz), 3.07 (d, 1H, *J* 11.8 Hz), 3.16 (d, 1H, *J* 11.7 Hz), 4.73 (s, 1H), 5.01 (d, 1H, *J* 1.5 Hz), 5.05 (d, 1H, *J* 1.4 Hz), 5.28 (d, 1H, *J* 2.2 Hz), 6.31 (s, 1H), 7.21 (d, 4H, *J* 1.5 Hz).

6c: R_f 0.31 (light petroleum). ^{1}H NMR ($CDCl_3$) δ: 0.00 (s, 9H), 1.67 (s, 2H), 2.51–2.72 (m, 2H), 2.89–2.99 (m, 1H), 3.05–3.17 (m, 2H), 4.73 (s, 1H), 4.95 (d, 2H, *J* 2.7 Hz), 5.17 (d, 1H, *J* 1.3 Hz), 6.22 (s, 1H), 7.25 (d, 4H, *J* 5.9 Hz).

¶ *Procedure for the preparation of DCHC complex of 5-[(4-chlorophenylthio)methyl]-2-(2,2-dimethoxyethyl)-3-methylenehept-1-en-6-yne* **8**. To the cooled (–40 °C) solution of **6c** (160 mg, 0.25 mmol) in absolute CH_2Cl_2 (1 ml), $HC(OMe)_3$ (79.5 mg, 0.75 mmol) and a 1 M $EtAlCl_2$ solution (0.3 ml, 0.3 mmol) were added successively under argon. After stirring at 0 °C for 6 h, the mixture was poured into saturated aqueous $NaHCO_3$ (10 ml), and extracted with light petroleum (3×5 ml). Combined organic layers were filtered through silica gel and eluted with cooled (–30 °C) EtOAc–light petroleum (1:10). The solvents were removed under a reduced pressure, and the residue was purified by column chromatography on silica gel [eluent: cooled (–30 °C) EtOAc–light petroleum (1:10)] to give **8** (89 mg, 46%). R_f 0.4 (EtOAc–light petroleum, 1:10). ^{1}H NMR ($CDCl_3$) δ: 2.54 (d, 2H, *J* 5.9 Hz), 2.59 (d, 1H, *J* 5.9 Hz), 2.69 (d, 1H, *J* 7.2 Hz), 2.93–2.98 (m, 1H), 3.08–3.17 (m, 2H), 3.31 (d, 6H, *J* 3.3 Hz), 4.50 (t, 1H, *J* 5.9 Hz), 5.02 (s, 1H), 5.07 (s, 1H), 5.16 (s, 1H), 5.25 (s, 1H), 6.21 (s, 1H), 7.25 (d, 4H, *J* 4.6 Hz).

Procedure for the preparation of DCHC complex of 5-[(4-chlorophenylthio)methyl]-2-(2-methoxy-2-methylpropyl)-3-methylenehept-1-en-6-yne **9**. To a cooled (–60 °C) solution of 2,2-dimethoxypropane (125 mg, 1.2 mmol) in absolute CH_2Cl_2 (1.5 ml), trimethylsilyl triflate (100 mg, 0.45 mmol) was added under CO and precipitate formation was observed immediately. Then, a solution of **6a** (210 mg, 0.3 mmol) in CH_2Cl_2 (1.5 ml) was added to the flask. The mixture was warmed to 0 °C, and a saturated aqueous $NaHCO_3$ solution (5 ml) was added. The mixture was extracted with light petroleum (3×5 ml). Combined organic layers were filtered through silica gel and eluted with cooled (–30 °C) EtOAc–light petroleum (1:10). The solvents were removed under a reduced pressure, and the residue was purified by column chromatography on silica gel [eluent: cooled (–30 °C) EtOAc–light petroleum, 1:10] to give **9** (150 mg, 71%). R_f 0.51 (EtOAc–light petroleum, 1:10). ^{1}H NMR ($CDCl_3$) δ: 0.37 (s, 9H), 1.15 (d, 6H, *J* 2.9 Hz), 2.33–2.49 (m, 3H), 2.85–2.90 (m, 1H), 2.91–2.98 (m, 1H), 3.17 (s, 3H), 3.22–3.27 (m, 2H), 5.01 (s, 2H), 5.17 (s, 1H), 5.23 (s, 1H), 7.22 (s, 4H).