A One-step Control of Four Stereogenic Centres during the Sakurai Reaction of 1,8-Bis(trimethylsilyl)octa-2,6-diene (BISTRO) to α,β-Enones

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The titanium tetrachloride mediated addition reaction of 1,8-bis(trimethylsilyl)octa-2,6-diene (BISTRO) with open-chain conjugated enones affords *syn-anti-syn*-4,7-divinyldecane-1,10-diones with a very high diastereoselectivity.

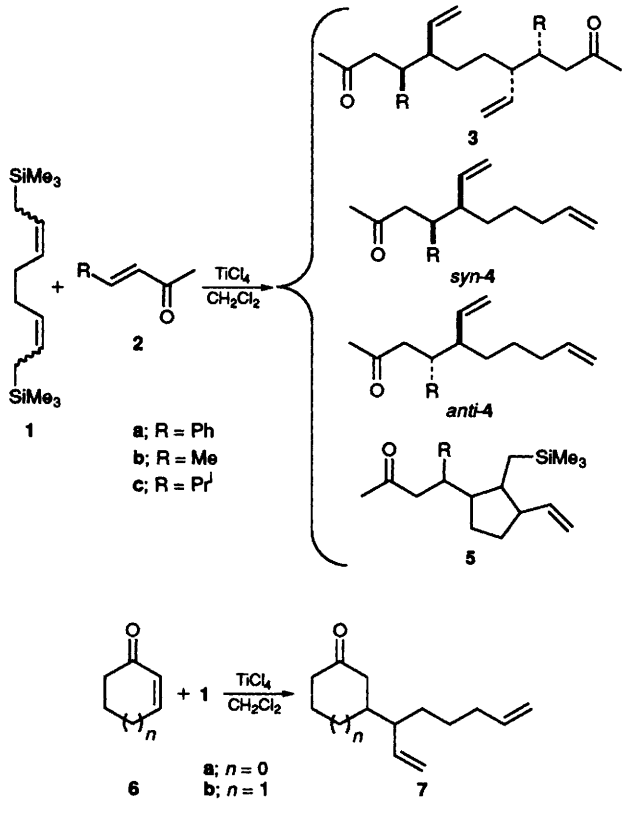
Recently, we have developed the chemistry of the 1,8-bis(trimethylsilyl)octa-2,6-diene (BISTRO) **1**, easily obtained in one step from buta-1,3-diene.[1]† The present paper is concerned with the Sakurai reaction of **1** with α,β-enones.[2]

Focusing on the Sakurai reaction of **1** with benzylideneacetone (*trans*-4-phenyl-3-buten-2-one) **2a**, we investigated the addition rection in order to improve its diastereoselectivity. **1** (2.2 equiv.) was allowed to react with **2a** in CH_2Cl_2 solution in the presence of $TiCl_4$ (1.3 equiv.) at −90 °C for 0.5 h then at −60 °C for 12 h. In addition to **2a** (19%), diketone **3a** (25%) and ketone **5a** (mixture of isomers) (41%) were isolated. A considerable improvement was achieved by the addition of nitromethane (4 equiv.) at the same time as **2a** and thus the diketone **3a** could be obtained as isolated product in 74% yield with ketones *syn*-**4a** and *anti*-**4a** (7:3) (26% yield).‡

The stereochemistry of **3a** determined by X-ray analysis showed that **3a** was the *meso*-isomer (4*S**, 5*R**, 8*S**, 9*R**)-4,9-diphenyl-5,8-divinyldodecane-2,11-dione (*syn-anti-syn*-isomer).§[5] Similar results were observed with ketone **2b** (**3b**, 61% yield; **4b**, 17%) and **2c** (**3c**, 74% yield; **4c**, 22%).¶

In contrast, the Sakurai addition of **1** to cyclopenten-2-one **6a** or cyclohexen-2-one **6b** was a non-stereoselective process.‖ Major products were ketones **7a** (18% yield, mixture of two isomers) or **7b** (56% yield, mixture of two isomers) resulting from a Sakurai addition followed by protodesilylation.

The preparation of **3** as only one diastereoisomer detectable (up to 95%, ^{1}H NMR analysis) constituted an unprecedented one-step control of four stereogenic centres on an acyclic product.



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Footnotes

† **1** synthesized by Li reduction of buta-1,3-diene in the presence of chlorotrimethylsilane is actually an inseparable mixture of (*Z,Z*)-isomer (*ca.* 50%), (*Z,E*)-isomer (*ca.* 40%) and (*E,E*)-isomer (4%) contaminated with two regioisomers.

‡ The influence of the nitro group during the reaction of **1** with various electrophilic compounds was previously discussed (*cf.* ref. 3).

§ Addition of *trans*-crotyltin to benzylideneacetone proceeded with assigned *anti*-selectivity (*anti*:*syn* 61:38) (*cf.* ref. 4).

¶ (4*S**, 5*R**, 8*S**, 9*R**)-4,9-diphenyl-5,8-divinyldodecane-2,11-dione **3a**. Mp 126–127 °C; IR ν/cm^{-1} (CCl_4) 3080, 3040, 1720, 920; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (4, t *J* 7.5 Hz), 7.15 (2, m), 7.04 (4, d *J* 7.5 Hz), 5.32 (1, ddd *J* 17.1, 9.9, 10.1), 5.28 (1, ddd *J* 17.1, 9.9, 10.1), 5.0 (1, d *J* 10.1 Hz), 4.97 (1, d *J* 10.1 Hz), 4.86 (2, d *J* 17.1 Hz), 3.17 (2, m, $W_{\frac{1}{2}}$ 12.4 Hz), 2.82–2.67 (4, m), 2.15–2.0 (2, m), 2.0 (6, s), 1.38–1.25 (2, m), 1.4–0.92 (2, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 207.6 (s)(2C), 141.2 (s), 141.1 (s), 139.3 (d), 139.1 (d), 128.7 (d)(2C), 128.6 (d)(2C), 127.7 (d)(4C), 126.2 (d)(2C), 116.6 (t), 116.5 (t), 48.6 (d), 47.9 (d), 47.3 (t), 47.1 (t), 44.3 (d), 44.1 (d), 30.5 (q)(2C), 29.7 (t)(2C); MS, *m/z* 402 (0.13), 384 (1.4), 344 (1.8), 274 (2.7), 238 (3.5), 197 (7), 184 (8), 147 (28), 43 (100); HRMS calc. for $C_{28}H_{34}O_2$ 402.2558, found 402.2568.

(4*S**, 5*R**, 8*S**, 9*R**)-4,9-dimethyl-5,8-divinyldodecane-2,11-dione **3b**. IR ν/cm^{-1} (neat) 3080, 1720, 920; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.51 (1, ddd *J* 17.1, 10.3, 9.5 Hz), 5.48 (1, ddd *J* 17.1, 10.3, 9.5 Hz), 5.03 (1, dd *J* 10.3, 2.7 Hz), 5.02 (1, dd *J* 10.3, 2.7 Hz), 4.91 (2, dm *J* 17.1 Hz), 2.41 (2, ½AB, d *J* 16.3, 5.9 Hz), 2.16 (2, ½AB, m *J* 16.3 Hz), 2.09 (6, s), 2.08 (2, m), 1.84 (2, m, $W_{\frac{1}{2}}$ 22 Hz), 1.4–1.1 (4, m), 0.79 (3, d *J* 6.83 Hz), 0.78 (3, d *J* 6.83 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 206.2 (s)(2C), 139.12 (d), 139.06 (d), 116.2 (t), 116.0 (t), 48.84 (t), 48.76 (t), 48.2 (d), 47.7 (d), 32.2 (d), 31.9 (d), 30.2 (q)(2C), 30.2 (t), 30.0 (t), 15.1 (q), 14.8 (q); MS, *m/z* 263 (0.8), 260 (0.7), 202 (2.3), 162 (12), 135 (11), 95 (13), 85 (22), 43 (100); HRMS calc. for $C_{17}H_{27}O_2$ (M^+ − Me) 263.20109, found 263.202, HRMS calc. for $C_{18}H_{28}O$ (M^+ − H_2O) 260.21400, found 260.214.

‖ The Sakurai reaction of *E*- and *Z*-crotylsilanes with cyclohexen-2-one or cyclopenten-2-one showed respectively high *syn* and low *anti*-selectivities (*cf.* ref. 6).

References

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