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## Communications

### Nickel-Catalyzed Geminal Dimethylation of Allylic Dithioacetals<sup>1</sup>

**Summary:** A geminal dimethyl group is introduced regioselectively in excellent yield from the reactions of allylic dithioacetals and methylmagnesium iodide in the presence of 3 mol % of NiCl<sub>2</sub>(dppe) in refluxing ether–benzene.

**Sir:** We recently uncovered several versatile transformations of the dithioacetal functionality.<sup>2,3</sup> To illustrate this, nickel-catalyzed coupling reactions of Grignard reagents<sup>4</sup> with benzylic and allylic dithioacetals are particularly useful in the syntheses of styrenes,<sup>2a</sup> vinylsilanes,<sup>2b</sup> allylsilanes,<sup>2c</sup> and silylated dienes.<sup>2d</sup> These reactions involve a coupling process and an elimination step.<sup>2</sup> The sulfur moiety, particularly in allylic dithioacetals, may play a prime role in the regioselectivity of the coupling reaction.<sup>2d</sup> Theoretically, the two carbon–sulfur bonds in dithioacetals could both be replaced under the reaction conditions, hence geminal dialkyl groups being introduced. Although geminal dimethylation of a carbonyl equivalent can be achieved by several methods,<sup>5–9</sup> none of these procedures are applicable to  $\alpha,\beta$ -unsaturated carbonyl compounds because of poor regioselectivity. Recently, Kurosawa and

his co-workers reported that 18-electron ( $\eta^3$ -allyl- $\eta^1$ -aryl)nickel(II) complexes undergo rapid reductive elimination to give the coupling products.<sup>10</sup> Their observation prompted us to report our independent findings that reductive elimination is an extremely facile step in the catalytic reaction when an 18-electron ( $\eta^3$ -allyl)organonickel intermediate is involved. The reaction is particularly useful in introducing geminal dimethyl groups in the allylic system.

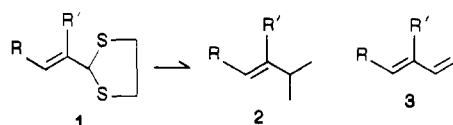
In the beginning of this study, we treated 1 with 3.5–4 equiv of CH<sub>3</sub>MgI in the presence of 3 mol % of NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> in ether–benzene for 12 h under refluxing conditions. After the usual workup and chromatographic purification, a mixture of the geminal dimethylated products 2 and butadienes 3<sup>11</sup> were obtained. The results are tabulated in Table I. It is noteworthy that no reaction oc-

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(11) Typical procedure: To a mixture of 1a (2.0 mmol) and NiCl<sub>2</sub>(dppe) (3 mol %) in benzene (8.0 mL) was added MeMgI (4.0 mL, 2.0 M ether solution, 8.0 mmol). The mixture was heated under reflux overnight and cooled with an ice bath. Water was cautiously introduced to quench the reaction. Ether (30 mL) was added, and organic layer was separated, washed with aqueous NaOH (10%) and water, and then dried with anhydrous sodium sulfate. After filtration, the organic solution was evaporated in vacuo, and the residue was chromatographed on silica gel and eluted with hexane to give 2a (1.86 mmol, 93%). All new compounds gave satisfactory spectroscopic properties and accurate mass. The <sup>1</sup>H NMR [ $\delta$  (CDCl<sub>3</sub>)] are as follows. 2a: 7.12–7.40 (m, 5 H), 6.35 (d,  $J$  = 16 Hz, 1 H), 6.20 (dd,  $J$  = 16, 6.6 Hz, 1 H), 2.48 (m, 1 H), 1.10 (d,  $J$  = 7 Hz, 6 H). 2b: 7.23 (d,  $J$  = 8.2 Hz, 2 H), 7.08 (d,  $J$  = 8.2 Hz, 2 H), 6.30 (d,  $J$  = 16 Hz, 1 H), 6.12 (dd,  $J$  = 16, 6.6 Hz, 1 H), 2.44 (m, 1 H), 2.31 (s, 3 H), 1.08 (d,  $J$  = 6.7 Hz, 6 H). 2c: 7.20 (t,  $J$  = 8 Hz, 1 H), 6.94 (d,  $J$  = 8 Hz, 1 H), 6.88 (s, 1 H), 6.75 (d,  $J$  = 8 Hz, 1 H), 6.31 (d,  $J$  = 16 Hz, 1 H), 6.18 (dd,  $J$  = 16, 6.4 Hz, 1 H), 3.79 (s, 3 H), 2.45 (m, 1 H), 1.08 (d,  $J$  = 6.8 Hz, 6 H). 2d: 8.14 (d,  $J$  = 8 Hz, 1 H), 7.81 (d,  $J$  = 8 Hz, 1 H), 7.72 (d,  $J$  = 8 Hz, 1 H), 7.36–7.60 (m, 4 H), 7.07 (d,  $J$  = 16 Hz, 1 H), 6.21 (dd,  $J$  = 16, 6.5 Hz, 1 H), 2.60 (m, 1 H), 1.18 (d,  $J$  = 6.8 Hz, 6 H). 2e: 7.41 (d,  $J$  = 8.2 Hz, 1 H), 7.17 (t,  $J$  = 8.2 Hz, 1 H), 6.90 (t,  $J$  = 8.2 Hz), 6.81 (d,  $J$  = 8.2 Hz, 1 H), 6.68 (d,  $J$  = 16 Hz, 1 H), 6.18 (dd,  $J$  = 16, 6.8 Hz, 1 H), 3.80 (s, 3 H), 2.50 (m, 1 H), 1.05 (d,  $J$  = 7.0 Hz, 6 H). 2f: 7.20 (m, 5 H), 6.06 (s, 1 H), 2.41 (heptet,  $J$  = 6.7 Hz, 1 H), 1.81 (s, 3 H), 1.08 (d,  $J$  = 6.7 Hz, 6 H). 2g: 7.12–7.38 (m, 5 H), 6.25 (s, 1 H), 2.43 (heptet,  $J$  = 6.8 Hz, 1 H), 2.27 (q,  $J$  = 6.7 Hz, 2 H), 1.13 (d,  $J$  = 6.8 Hz, 6 H), 1.05 (t,  $J$  = 6.7 Hz, 3 H). 3f: 7.18–7.40 (m, 5 H), 6.58 (dd,  $J$  = 18, 10 Hz, 1 H), 6.53 (s, 1 H), 5.26 (d,  $J$  = 18 Hz, 1 H), 5.15 (d,  $J$  = 10 Hz, 1 H), 2.18 (s, 3 H). 3g: 7.20–7.40 (m, 5 H), 6.49 (dd,  $J$  = 18, 10 Hz, 1 H), 6.42 (s, 1 H), 5.35 (d,  $J$  = 18 Hz, 1 H), 5.18 (d,  $J$  = 10 Hz, 1 H), 2.49 (q,  $J$  = 7.5 Hz, 2 H), 1.90 (t,  $J$  = 7.5 Hz, 3 H).

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Table I. Nickel-Catalyzed Geminal Dimethylation of Allylic Dithioacetals

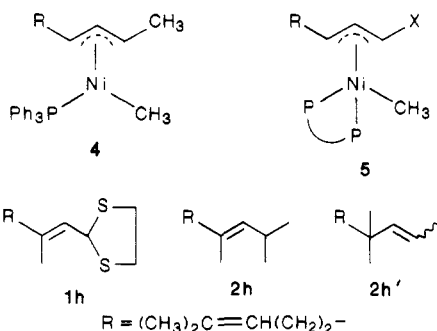


entry	compd	R	R'	catalyst <sup>a</sup>	% yield	ratio (2:3)
1	a	Ph	H	A	85	70:30
2				B	93	100:0
3				C	91	100:0
4				D	90	100:0
5	b	4-MeC <sub>6</sub> H <sub>4</sub>	H	B	98	100:0
6				B	95	100:0
7	d	2-Naphthyl	H	B	95	100:0
8	e	2-MeOC <sub>6</sub> H <sub>4</sub>	H	B	92	96:4
9	f	Ph	Me	A	88	57:43
10				B	92	77:23
11				A	71	31:69
12	g	Ph	Et	B	96	68:32

<sup>a</sup>A: NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>. B: NiCl<sub>2</sub>(dppe). C: NiCl<sub>2</sub>(dppp). D: NiCl<sub>2</sub>(dppb).

curred in the absence of the nickel catalyst.

As can be seen from Table I, the yield of **3** increases as the substituent at the C-2 position changes from hydrogen to methyl to ethyl groups (entries 1, 9, and 11).<sup>12</sup> The reaction may occur via a similar pathway as proposed earlier<sup>2</sup> to proceed presumably via a 16-electron intermediate **4**,<sup>10,13</sup> which may undergo competitively either  $\beta$ -elimination to yield **3** or reductive elimination to give **2**. The steric environment of the substrate **1** apparently affects the relative rate of these steps.



When NiCl<sub>2</sub>(dppe)<sup>14</sup> was employed as the catalyst, geminal dimethylated compounds were obtained as the sole products in excellent yields from cinnamaldehyde derivatives (entries 2 and 5–7).<sup>11</sup> The selectivity was improved substantially even for substrates having substituent at C-2 (entries 10 and 12). Other bidentate phosphine ligands<sup>14</sup> behaved similarly (entries 3 and 4).

It is known that nickel-catalyzed coupling reactions depend on the nature of the phosphine ligands.<sup>10,15</sup> Our results indicate that a bidentate phosphine ligand facilitates the reductive elimination process, leading to the geminal dimethyl product. The reaction might proceed via an 18-electron intermediate **5** when such ligands are employed. Accordingly,  $\beta$ -elimination in **5** would be unfavorable, and **2a-g** were formed in excellent yields.

It is particularly noteworthy that the formation of **2** was regioselective. Two factors may govern the selectivity. As suggested earlier,<sup>2d</sup> the sulfur moiety may somehow interact with the catalyst during the course of the reaction. Such interaction would result in the regioselective reductive elimination, which would introduce the first methyl group at the C-1 position, one of the two carbon-sulfur bonds in **1** remaining intact at this stage. The selective introduction of the second methyl group may arise from the conjugative preference.<sup>16</sup> Indeed, when geranial dithioacetal **1h** was treated with MeMgI in the usual manner, a mixture of dimethylated products **2h** and **2h'** were obtained.

In summary, we have demonstrated an unprecedented procedure for the introduction of geminal dimethyl functionality in the allylic system. The extension of this method in synthesis is in progress.

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**Registry No.** **1a**, 5616-58-0; **1b**, 119924-99-1; **1c**, 119925-00-7; **1d**, 119925-01-8; **1e**, 119925-02-9; **1f**, 119925-03-0; **1g**, 119925-04-1; **1h**, 119925-05-2; **2a**, 1608-28-2; **2b**, 32094-37-4; **2c**, 119925-06-3; **2d**, 30249-69-5; **2e**, 119925-07-4; **2f**, 36939-20-5; **2g**, 61777-12-6; **2h**, 119925-08-5; **2h'**, 72015-42-0; **3a**, 1515-78-2; **3e**, 119925-07-4; **3f**, 37580-42-0; **3g**, 119925-09-6; MeMgI, 917-64-6; NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, 14264-16-5; NiCl<sub>2</sub>(dppe), 14647-23-5; NiCl<sub>2</sub>(dppp), 15629-92-2; NiCl<sub>2</sub>(dppb), 18750-53-3.

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(12) The addition of excess Ph<sub>3</sub>P to the reaction mixture did not change the product distribution. Thus, a mixture of **2a** and **3a** (67:33) was obtained in 85% yield from the reaction of **1a** in the usual manner except in the presence of 16 mol % (relative to **1a**) of Ph<sub>3</sub>P.

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