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## Catalysed 1,2- vs. 1,4-Addition of 3,4-Dichlorocyclobut-3-ene-1,2-dione with Unsaturated Organosilanes

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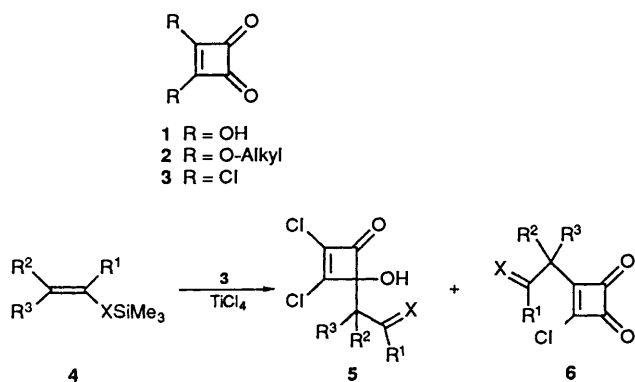
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3,4-Dichlorocyclobut-3-ene-1,2-dione (squaric acid chloride) reacts with allylsilanes and silyl enol ethers in the presence of  $\text{TiCl}_4$  at C-1 and/or C-4, depending on the substitution pattern of the organosilane.

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Squaric acid **1** has long been known as a small ring system having unique characteristics the derivatives of which have wide application.<sup>1,2</sup> Recently they have attracted attention in synthesis as a C-4 building block.<sup>3,4</sup> Derivatization of **1** has been achieved under both nucleophilic and electrophilic conditions; thus, the ester **2** was shown to react with  $\text{RMgX}$  via 1,4-

addition and with  $\text{RLi}$  via 1,2-addition,<sup>5</sup> and the acid chloride **3** with an enamine via 1,4-addition.<sup>6</sup> Friedel-Crafts conditions were employed for the reaction **3** with aromatic compounds.<sup>7</sup> We now report the novel Lewis acid-catalysed addition of **3** with allylsilanes and silyl enol ethers **4**,<sup>8</sup> in which a remarkable substituent effect was observed.



Typically, the acid chloride **3** reacted with allyltrimethylsilane **4a** in the presence of  $\text{TiCl}_4$  at  $-78^\circ\text{C}$  in dichloromethane within 5 min. Work-up and separation by silica gel column chromatography afforded the product. Primarily the mass spectral and elemental analyses supported a simple 1:1 adduct which retained two chlorine atoms. The IR spectrum showed hydroxy and carbonyl absorption at 3319 and 1784  $\text{cm}^{-1}$  respectively and the  $^1\text{H}$  NMR spectrum indicated the presence of an allyl group as an ABC pattern at  $\delta$  5.27–5.98; the  $^{13}\text{C}$  NMR spectrum indicated a ring structure containing one  $\text{sp}^3$  ( $\delta$  93.2) and three  $\text{sp}^2$  carbons ( $\delta$  187.7, 170.7 and 133.7). These results allowed the assignment of structure **5a**, 2-allyl-3,3-dichloro-2-hydroxycyclobut-3-enone, to the compound. Similarly, methallyl- and crotyl-silanes **4b,c** gave the corresponding 1,2-addition products **5b,c**. In contrast, prenylsilane **4d** underwent 1,4-addition followed by dechlorosilylation, to give 3-allyl-4-chlorocyclobut-3-ene-1,2-dione **6d** as the predominant product. The structure of the latter was characterized by the following spectral data: a mass measurement showed the presence of only one chlorine atom whilst IR and  $^{13}\text{C}$  NMR spectroscopy showed the absence of hydroxy absorption but the presence of two different carbonyl groups (1779 and 1807  $\text{cm}^{-1}$ ) and four  $\text{sp}^2$  carbons ( $\delta$  195.6, 193.1, 179.3 and 168.9) on the ring. The observed trend in reactivity seemed to be a result of double  $\gamma$ -substitution in the allylsilane and this was confirmed by reactions with a series of silyl enol ethers **4e–g**. These reactions were complete within 1 min, and gave phenacyl-substituted products **5e–g** and **6g**. With an increase in the number of methyl substituents on the enol ether (*i.e.*, 0 to 2), the addition manner changed from 1,2 to 1,4. In the bulky silyl enol ethers **4h–i** both 1,2- and 1,4-addition products were obtained. These facts suggest that bulkiness around the carbon  $\gamma$  to a silyl group altered the attacking site on the ring. The results obtained are summarized in Table 1. The reaction temperature was also found to have an effect on those reactions; thus, when the reaction of **3** with **4e** was carried out at  $-95^\circ\text{C}$  for 5 min the 1,4-adduct **6e** was obtained in 32% yield.

In conclusion, carbon–carbon bond formation on the cyclobutendione ring was achieved by  $\text{TiCl}_4$ -catalysed reaction of **3** with unsaturated organosilanes **4**, in which the substitution pattern and reaction temperature influenced 1,2- vs. 1,4-addition reactivity.

## Experimental

*Typical Procedure for the Addition of the Acid Chloride 3 with Unsaturated Organosilanes: 2,3-Dichloro-4-hydroxy-4-prop-2-*

**Table 1** Addition of **3** with unsaturated organosilanes **4**

| Silane    | X               | R <sup>1</sup>  | R <sup>2</sup> | R <sup>3</sup> | Product (% yield) <sup>a</sup> |
|-----------|-----------------|-----------------|----------------|----------------|--------------------------------|
| <b>4a</b> | CH <sub>2</sub> | H               | H              | H              | <b>5a</b> (54)                 |
| <b>4b</b> | CH <sub>2</sub> | Me              | H              | H              | <b>5b</b> (50)                 |
| <b>4c</b> | CH <sub>2</sub> | H               | Me             | H              | <b>5c</b> (26)                 |
| <b>4d</b> | CH <sub>2</sub> | H               | Me             | Me             | <b>5d/6d</b> (8/68)            |
| <b>4e</b> | O               | Ph              | H              | H              | <b>5e</b> (52)                 |
| <b>4f</b> | O               | Ph              | Me             | H              | <b>5f</b> (38)                 |
| <b>4g</b> | O               | Ph              | Me             | Me             | <b>5g/6g</b> (7/82)            |
| <b>4h</b> | O               | Ad <sup>b</sup> | H              | H              | <b>5h/6h</b> (32/40)           |
| <b>4i</b> | O               |                 |                | H              | <b>5i/6i</b> (73/26)           |

<sup>a</sup> Products were fully characterized by IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, and mass spectrometry. Isolated yields were given. <sup>b</sup> 1-Adamantyl.

*enylcyclobut-2-enone 5a*.—To a solution of the acid chloride **3** (75 mg, 0.5 mmol) and allyltrimethylsilane (114 mg, 1 mmol) in dry dichloromethane (2 ml) was added  $\text{TiCl}_4$  (0.06 ml, 0.5 mmol) at  $-78^\circ\text{C}$ , and the reaction mixture was stirred for 5 min. The resulted brown solution was poured into cold water and extracted with dichloromethane. The colourless extract was washed with water, dried ( $\text{Na}_2\text{SO}_4$ ) and evaporated to dryness. Chromatography of the residue on silica gel with hexane–ethyl acetate (15:2) as the eluent afforded the 1,2-adduct **5a** (53 mg, 54%) as an oil (Found: C, 43.8; H, 3.3.  $\text{C}_7\text{H}_6\text{Cl}_2\text{O}_2$  requires C, 43.6; H, 3.1);  $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$  3319 (OH), 1784, 1579 (cyclobutenone) and 1642 (vinyl);  $\delta_{\text{H}}$ (200 MHz,  $\text{CDCl}_3$ ) 2.67 (2 H, d,  $J$  7.4,  $\text{CH}_2\text{CH}=\text{CH}_2$ ), 2.75 (1 H, br s, OH), 5.27 (2 H, m,  $\text{CH}_2\text{CH}=\text{CH}_2$ ) and 5.78 (1 H, m,  $\text{CH}_2\text{CH}=\text{CH}_2$ );  $\delta_{\text{C}}$ (200 MHz,  $\text{CDCl}_3$ ) 37.5, 93.2, 122.1, 130.2, 133.7, 170.7 and 187.7;  $m/z$  196, 194, 192 ( $\text{M}^+ + 4$ ,  $\text{M}^+ + 2$ ,  $\text{M}^+$ ; 1:6:9), 168, 166, 162 ( $\text{M}^+ + 4 - \text{CO}$ ,  $\text{M}^+ + 2 - \text{CO}$ ,  $\text{M}^+ - \text{CO}$ ; 1:6:9) and 131, 129 ( $\text{M}^+ + 2 - \text{CO-Cl}$ ,  $\text{M}^+ - \text{CO-Cl}$ ; 1:3; base).

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