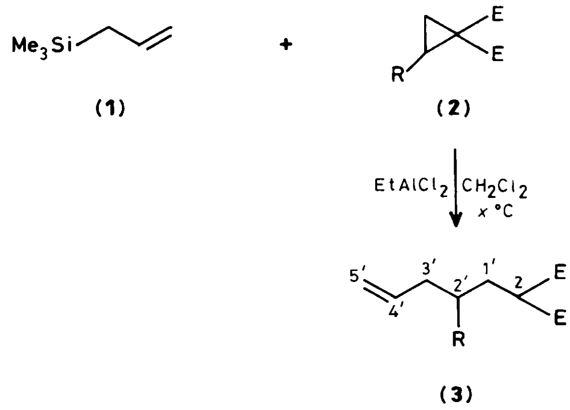
Conjugate Addition of Allyltrimethylsilane to Electrophilic Cyclopropanes

Ramesh Bambal and Raymond D. W. Kemmitt*

Inorganic Research Laboratories, The University, Leicester LE1 7RH, U.K.

Allyltrimethylsilane undergoes a Lewis-acid-assisted one-pot conjugate addition with cyclopropanes activated by geminal alkoxycarbonyl groups.

The nucleophilic ring opening of geminally activated cyclopropanes is a potentially useful reaction in the synthesis of natural products and prostaglandins.[1—3] The conjugate addition of alkyl, vinyl, and allyl groups to cyclopropanes activated by two electron-withdrawing groups by use of organocopper[2—5] or organoaluminium[6] reagents has been described. However, although the nucleophilic double bond properties of allylsilanes are well established,[7] and a homopentadienyl cation generated from a chrysanthemyl cation has been shown to be an efficient electrophile toward such organosilicon compounds,[8] the possibility that allylsilanes might undergo conjugate addition to electrophilic cyclopropanes seems hitherto to have been overlooked.



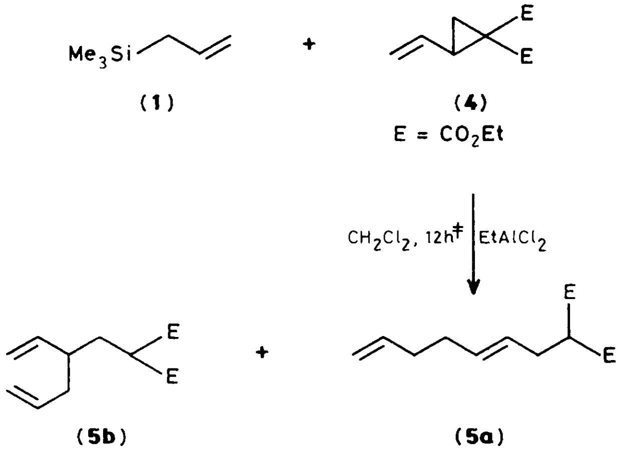
a; E = CO_2Et, R = H; x = 0; yield 78%
b; E = CO_2Me, R = H; x = 0; yield 76%
c; E = CO_2Et, R = Et; x = 0; yield 92%
d; EE = $Me_2C[OC(O)]_2$, R = H, x = −78, yield 49%

Scheme 1

Treatment of allyltrimethylsilane (**1**) with diethyl cyclopropane-1,1-dicarboxylate (**2a**) in the presence of ethylaluminium dichloride afforded the homoconjugate alkylation product (**3a**) in high yield.† The conjugate addition of allyltrimethylsilane to the ethylcyclopropane (**2c**) occurred regioselectively as judged by 300 MHz ^1H n.m.r. data. The general reaction is shown in Scheme 1. Preliminary studies on the reaction of allyltrimethylsilane with the vinylcyclopropane (**4**) indicate that this reaction is not regioselective. Column chromatography suggests the formation of a single product but careful g.l.c. analysis indicates the presence of two similar compounds (*ca.* 1 : 3) which has so far resisted satisfactory separation. The ^1H n.m.r. data are consistent with the presence of diethyl 2-(hepta-2,6-dienyl)malonate (**5a**) and 2-(2-vinylpent-4-enyl)malonate (**5b**), formed by 1,7- and

---

† Selected n.m.r. and mass spectroscopic data (J in Hz): (**3a**) ^1H (300 MHz; $CDCl_3$; room temp.) δ 5.77 (m, J 17.1, 10.1, and 6.5, 1H, H-4), 5.04 (m, J 1.98 and 1.54, 1H) and 4.98 (m, J 1.3, 1H) (H_2-5'), 4.2 (q, 4H, CO_2CH_2), 3.32 (t, J 7.46, 1H, H-2), 2.09 (dt, J 7.3, 2H, H-3'), 1.9 (dt, J 7.3 and 7.46, 2H, H_2-1'), 1.42 (m, 2H, H_2-2'), and 1.26 (t, 6H, 2 × CH_3). ^{13}C (75.4 MHz) δ 169.3 (s, C=O), 137.8 (d, J 55.9, C-4'), 115.8 (t, J 52.6, C-5'), 61.1 (t, $CO_2CH_2CH_3$), 51.8 (d, J 36.4 Hz, C-2) 33.2 (t, J 30.3, C-3'), 28.1 (t, J 27, C-1'), 26.4 (t, J 24.6, C-2'), and 14.0 (q, $CO_2CH_2CH_3$); m/z 227 ($M^+ - 1$).



Scheme 2

1,5-addition, respectively (Scheme 2). However, the n.m.r. signals are not sufficiently resolved to confirm which isomer is in excess.

A general procedure for the conjugate addition involves reaction of the cyclopropane derivative (1 mmol) in dry dichloromethane (2 cm^3) with ethylaluminium dichloride (3 mmol) under nitrogen at the temperature indicated (Schemes 1 and 2). After 3 min the allylsilane (1.2 mmol) is added and the mixture is allowed to reach room temperature and stirred overnight. After addition of saturated aqueous ammonium chloride, the solution is extracted with diethyl ether, and the extracts concentrated to an oil which is subjected to preparative t.l.c. to afford the desired product.

Interestingly, no conjugate addition of the allylsilane (**1**) to the cyclopropanes (**2**) was observed in the presence of a Lewis acid ($BF_3{\cdot}OEt_2$, $SnCl_4$, or $TiCl_4$).

We thank the S.E.R.C. for financial support.

Received, 11th November 1987; Com. 1644

References

1 S. Danishefsky, *Acc. Chem. Res.*, 1979, **12**, 66.
2 E. J. Corey and P. L. Fuchs, *J. Am. Chem. Soc.*, 1972, **94**, 4014.
3 R. D. Clark and C. H. Heathcock, *Tetrahedron Lett.*, 1975, 529.
4 G. Daviaud and P. Miginiac, *Tetrahedron Lett.*, 1972, 997.
5 A. Alexakis, G. Cahiez, and J. F. Normant, *Tetrahedron Lett.*, 1980, 1961.
6 K. Fugami, K. Oshima, K. Utimoto, and H. Nozaki, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 2509.
7 A. Hosomi and H. Sakurai, *J. Am. Chem. Soc.*, 1977, **99**, 1673.
8 M. Ohno, S. Matsuoka, and S. Eguchi, *J. Org. Chem.*, 1986, **51**, 4553.

---

‡ Reaction mixture allowed to warm from −78 to 25 °C.