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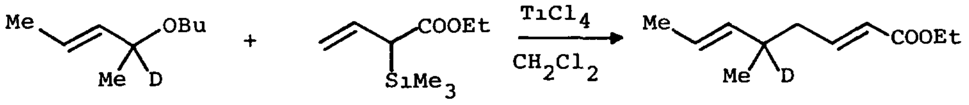
REGIOSELECTIVE COUPLING OF ALLYLIC ETHERS WITH ETHYL 2-TRIMETHYLSILYL-3-BUTENOATE

Yoshitomi Morizawa, Shigekazu Kanemoto, Koichiro Oshima,* and Hitosi Nozaki
Department of Industrial Chemistry, Faculty of Engineering
Kyoto University, Yoshida, Kyoto 606, Japan

Abstract In the presence of $TiCl_4$ the 4 position of the title silyl ester reacts with such electrophiles as allylic ethers or bromides carrying the leaving group on the secondary carbon without allylic rearrangement.

A recent publication concerned with the silicon-directed selective γ substitution of ethyl 3-methyl-2-trimethylsilyl-3-butenoate[1] prompts us to report our independent work on the regioselective allylation reaction

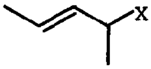
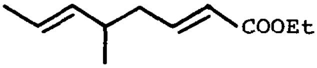
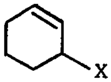
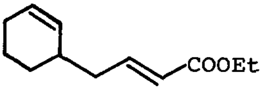
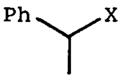
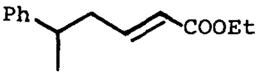
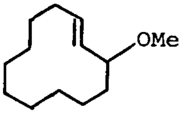
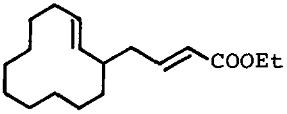
Table 1 summarizes the reaction of the title silyl ester[2] with some electrophiles Allylic ethers or halides having the leaving group on the secondary carbon gave the corresponding ethyl 2,6-dienoates in good yields, while primary halides such as $Me_2C{=}CHCH_2Br$, $CH_2{=}CHCH_2Br$, and $PhCH_2Br$ failed to give any coupling products. It is worth noting that the reaction proceeded exclusively on the α carbon of the allylic system Treatment of Ia with the silyl ester II in the presence of $TiCl_4$[3] gave III as a single isomer practically.[4] The allylic double bond remained untouched in the reaction of 1-deuterio-2-cyclohexenyl butyl ether or (2E)-1-deuterio-2-cyclododecenyl methyl ether with the silyl ester II



Ia II III

A flame-dried flask was charged with the silyl ester II (0 37 g, 2.0 mmol) and dichloromethane (6 0 ml) under argon atmosphere A solution of $TiCl_4$ in dichloromethane (1 0 M, 2 5 ml, 2.5 mmol) was added to the above solution at -78°C and the resulting mixture was stirred at the same temperature for 5 min Allylic bromide Id (0 60 g, 4 0 mmol) was added dropwise at -78°C and the whole was stirred for an additional 15 min The reaction mixture was diluted with dichloromethane (10 ml) and poured into 1N HCl (20 ml). The separated organic layer was washed with brine, dried, and concentrated. Purification by silica gel column chromatography gave ethyl (2E,6E)-5-methyl-2,6-octadienoate (0.30 g, 81% yield) as a colorless oil.[5,6]

Table 1 Reaction of Ethyl 2-Trimethylsilyl-3-butenoate with Allylic Ethers or Allylic Halides[a]

Electrophile (mmol)				$TiCl_4$ (mmol)	Reaction Time (min)	Product	Yield[b] (%)
	Ia	X=OBu	(1 2)	2.0	30		60
	Ib	X=OMe	(1 3)	1 3	2		64
	Ic	X=OSiMe$_3$	(2 0)	2 0	3		20
	Id	X=Br	(2 0)	1 2	10		81
	Ie	X=Cl	(1 3)	1.3	5		65
	IIa	X=OBu	(1.4)	2 0	15		62
	IIb	X=Br	(2 5)	1 4	6		88
	IIIa	X=OMe	(1 4)	3 0	15		92
	IIIb	X=OBu	(1 5)	3 0	30		68
	IIIc	X=Br	(1 1)	2 2	10		87
			(1 1)	2 0	5		73

[a] Reactions were performed in dichloromethane at -78°C. One mmol of the silyl ester II was employed [b] Isolated yields

References and Notes

1 P Albaugh-Robertson and J A Katzenellenbogen, *Tetrahedron Lett* , **23**, 723 (1982)

2 The silyl ester II was prepared in 65% yield from vinyl bromide and ethyl lithiotrimethylsilylacetate according to the method of Rathke (A A Millard and M W. Rathke, *J Am Chem Soc* , **99**, 4833 (1977) II bp 110-111°C (bath temp)/11 Torr, NMR (CCl$_4$, benzene as an internal standard) δ 0 08 (s, 9H), 1 21 (t, J = 7 2 Hz, 3H), 2 81 (d, J = 9 9 Hz, 1H), 4 03 (q, J = 7 2 Hz, 2H), 4 7-5 0 (m, 2H), 5 8-6 2 (m, 1H), IR (neat) 3090, 1724, 1637, 1258, 999, 900, 844 cm^{-1} Exact mass spectrum m/e 186 112 (Calcd for $C_9H_{18}O_2Si$ 186.108)

3. For recent reports on the reaction of allylsilane H Sakurai, K Sasaki, and A Hosomi, *Tetrahedron Lett* , **22**, 745 (1981), A Hosomi, M Endo, and H Sakurai, *Chem Lett* , **1978**, 499

4 The examination of the product by NMR showed that the product was contaminated by <5% of regioisomer, ethyl 7-deuterio-5-methyl-2,6-octadienoate

5 Bp 90-97°C (bath temp)/1 Torr, NMR (CCl$_4$) δ 1 00 (d, J = 6 6 Hz, 3H), 1 28 (t, J = 7 2 Hz, 3H), 1 65 (d, J = 5 4 Hz, 3H), 2 0-2 5 (m, 3H), 4 07 (q, J = 7 2 Hz, 2H), 5 2-5 4 (m, 2H), 5 65 (d, J = 15 6 Hz, 1H), 6 75 (dt, J = 15.6 and 7 2 Hz, 1H), IR (neat) 2980, 1732, 1660, 981, 965 cm^{-1} Found C, 72 31, H, 10 18 Calcd for $C_{11}H_{18}O_2$ C, 72 49, H, 9 95

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