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A Novel Reaction of Ethyl 2,3-Butadienoate with Aldehydes in the Presence of Base

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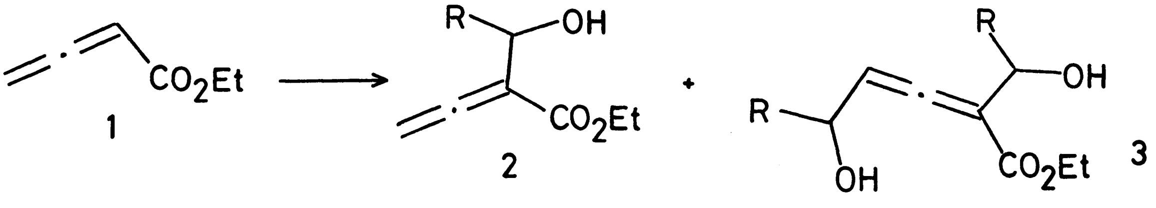
Reaction of ethyl 2,3-butadienoate with aldehydes in the presence of DABCO gave ethyl 2-(1-hydroxyalkyl)-2,3-butadienoate (**2**) in 41-54% yields. The reaction in the presence of butyl lithium gave **2** in 36-60% yields accompanied by ethyl 2,4-di(1-hydroxyalkyl)-2,3-butadienoate.

Recently, novel reactions of α,β-unsaturated carbonyl compounds with various electrophiles such as aldehydes[1,2] and benzylidenecarbamate[3] in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) have been reported, giving α-substituted compounds. In connection with our continuous interest in the chemistry of β-allenic esters,[4] we carried out the reaction of ethyl 2,3-butadienoate (**1**) with aldehydes in the presence of a base. The reaction of **1** with aliphatic aldehydes in the presence of DABCO for a long time at 0 °C—25 °C gave ethyl 2-(1-hydroxyalkyl)-2,3-butadienoate (**2**) in moderate yields. Furthermore, the reaction in the presence of butyl lithium at -75—-30 °C also gave **2** as a sole product and that at lower temperature afforded **2** along with ethyl 2,4-di(1-hydroxyalkyl)-2,3-butadienoate (**3**). These results are summarized in Table 1.



Typical experiments are described below. DABCO (44 mg, 0.39 mmol) was charged in a 5 ml two-necked flask and a solution of **1** (0.316 g, 2.82 mmol), and propionaldehyde (0.160 g, 2.76 mmol) in 1 ml of ether was added at -6 °C under an atmosphere of argon. The mixture was stirred for 16 h at 23 °C and poured into ice water. The organic material was extracted with ether, and the extract was washed with dilute HCl, water, and dried over $MgSO_4$. Evaporation of the solvent gave a pale brown oil, which was chromatographed on SiO_2 to give 0.194 g (42%) of ethyl 3-hydroxy-2-vinylidenepentanoate (**2a**): IR (neat) 3500,

Table1. Reaction of **1** with Aldehydes in the Presence of Base

No.	R	Base	Reaction conditions		Yield/% of product$^{a)}$	
			Temp/ °C	Time/h	**2**	**3**
a	CH_3CH_2	DABCO	-6—23	16	41	
b	$CH_3(CH_2)_5$	DABCO	0—25	34	54	
c	CH_3CH_2	n-BuLi	-75—-30	3	56	
d	CH_3CH_2	n-BuLi	-105—-99	5	58	6
e	$CH_3(CH_2)_5$	n-BuLi	-92	5	60	11

a) Isolated yield.

1965 (C=C=C), 1940 (C=C=C), 1710 (ester C=O); ^{1}H NMR (CCl_4) 0.93 (t, 3H, J = 7 Hz, CH_3), 1.29 (t, 3H, J = 7 Hz, CH_3), 1.60 (m, 2H, CH_2CH_3), 2.78 (s, 1H, OH), 4.16 (m, 3H, CO_2CH_3), 5.08 (s, 1H, C=CH_2), 5.11 (s, 1H, C=CH_2). Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29%. Found: C, 63.25: H, 8.16%.

Another example using butyl lithium is shown below. To a solution of **1** (0.138 g, 1.23 mmol) in THF (6 ml) was added 1.59 M butyl lithium in hexane (0.69 ml, 1.10 mmol) at -105 °C with stirring . After 1 h, a solution of propanal (70 mg, 1.20 mmol) was added dropwise. After the mixture was stirred for 5 h at -105— -99 °C, the reaction was quenched by the addition of wet THF. The mixture was worked up as usual and the crude product was chromatographed on SiO_2 to give 0.108 g (57.8%) of **2a**. Spectral data were identical with those of the previous sample.

The result of the latter case is different from that of the DABCO-catalyzed reaction of α,β-unsaturated carbonyl compounds with aldehydes.[1,2] Obviously, the formation of **2** and **3** in the n-BuLi-induced reaction suggests that the reaction underwent via the abstraction of α- and γ-olefinic protons of **1**. To our knowledge, this is the first example of butyl lithium-catalyzed substitution reaction of 2,3-alkadienoates.

References

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4) For example, see: S. Tsuboi, H. Wada, S. Mimura, and A. Takeda, Chem. Lett., 1987, 937 and references cited therein.

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