A Simple, One-Pot Synthesis of 2,3-Dihydro-4*H*-pyran-4-ones via the Acid-Catalysed [4+2]-Cycloaddition of 1-Alkoxy-3-trimethylsilyloxy-1,3-butadienes with Aldehydes

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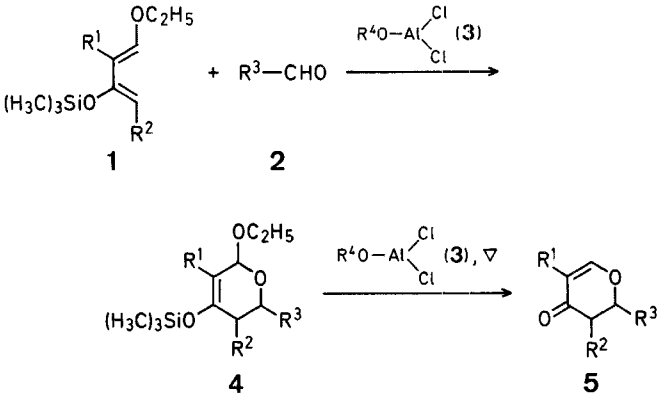
The Diels-Alder reaction of 1-alkoxy-3-trimethylsilyloxy-1,3-butadienes **1** with electron-deficient olefins has been shown to be a valuable route to cyclohexenones[1].

In a previous paper[2], we reported that the very electron-rich 1,1-dimethoxy-3-trimethylsilyloxy-1,3-butadienes also react with electron-poor *carbonyl* compounds, giving 6-methoxy-2,3-dihydro-4*H*-pyran-4-ones. It appeared that these reactions are catalysed by small amounts of zinc(II) chloride. In this way even simple aldehydes having no electron-withdrawing group at the carbonyl function can be used as dienophiles. Further investigations have revealed that catalysts of the alkoxyaluminium dichloride type **3** (Cl_2AlOR^4), which can easily be prepared[3] from the alcohol, aluminium chloride, and lithium alanate, are still more useful because of the reduced amount of decomposition of **1** under the reaction conditions. Although we did not study extensively which R group is the most suitable, it appeared that the yields for R^4 = bornyl were slightly better than for R^4 = propyl, isopropyl. Besides, we prefer this catalyst because we want to use it (and chiral analogs) for the induction of chirality in Diels-Alder reactions. In this way, several dienes of type **1**, all having a preferred *cisoid* conformation[3] and easily available by various methods[4,5] were converted into 2,3-dihydro-4*H*-pyran-4-ones **5** by reaction with a variety of aldehydes **2**.



The examples given show that the method has a wide scope and leads to dihydropyran-4-ones **5** which have not been prepared before or have only been obtained in a low yield[6,7].

The cycloadditions are strongly regio- and site-selective. α,β-Unsaturated aldehydes react at the carbonyl bond in the presence of the catalyst; without the catalyst the cycloaddition takes place at the carbon-carbon double bond of the aldehydes[1,5].

2,3-Dihydro-4*H*-pyran-4-ones 5; General Procedure:

To a mixture of **1** (100 mmol; 130 mmol for **1b** or **1d**) and an aldehyde **2** (100 mmol) a 0.55 molar solution of **3** (R^4 = bornyl) in diethyl ether[3] (3 ml) is added. The mixture is kept at the temperature given in the Table. When formaldehyde is used the aldehyde **2** (R^3 = H) is prepared by thermolysis of paraformaldehyde (0.3 mol) and blown over a solution of **1** (0.1 mol) in diethyl ether (50 ml) containing the 0.55 molar solution of **3** (R^4 = bornyl; 3 ml).

In the preparation of **5f** and **5h**, the reaction mixture is diluted after the time indicated in the Table with diethyl ether (75 ml), and successively washed with 10% hydrochloric acid and water. The organic phase is dried with sodium sulfate, concentrated in vacuo, and distilled. In the preparation of **5a–e, 5g,** and **5i** the reaction is completed by adding another portion of **3** (R^4 = bornyl) in diethyl ether (3 ml) and heating again for 5 min at 80 °C (45 min for **5a**). Work up is as described above. The products **5** obtained after distillation are more than 90% pure (from N.M.R.). Further purification can be achieved by preparative H.P.L.C. over silica gel, using diisopropyl ether/hexane 4/1 for **5a–e, 5g,** and **5i**; and hexane/ethyl acetate 5/1 for **5h** (Jobin Yvon chromatospac prep. 100). Yields, boiling points and spectro-

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Table. 2,3-Dihydro-4*H*-pyran-4-ones **5** from 1-Ethoxy-3-trimethylsilyloxy-1,3-butadienes **1a–d** and Aldehydes **2** in the presence of Bornyloxyaluminium Dichloride **3** (R^4 = bornyl)

Diene	R^1	R^2	R^3	Product	Reaction Conditions time/temperature	Yield [%][a]	b.p. [°C]/torr	Molecular formula[b] or Lit. b.p.	I.R. (KBr) [cm^{-1}][c] $\nu_{C=C}$	$\nu_{C=O}$	^{1}H-N.M.R. (CCl_4/TMS)[d] δ [ppm]
1a	H	H	H	**5a**	—	50	64°/15	$C_5H_6O_2$ (98.1)	1600	1675	2.47 (t, J=7 Hz, 2H); 4.42 (t, J=7 Hz, 2H); 5.18 (d, J=6 Hz, 1H); 7.23 (d, J=6 Hz, 1H)
1a	H	H	i-C_3H_7	**5b**	15 min/75 °C	65	48°/0.5	$C_8H_{12}O_2$ (140.2)	1598	1675	1.01 (d, J=7 Hz, 6H); 1.69–2.13 (m, 1H); 2.29 (s, 1H); 2.40 (d, J=5 Hz, 1H); 3.98–4.28 (m, 1H); 5.20 (d, J=6 Hz, 1H); 7.27 (d, J=6 Hz, 1H)
1a	H	H	H_2C=CH—	**5c**	3 h/25 °C	60	85°/15	$C_7H_8O_2$[h] (124.1)	1600	1670	2.43 (d, J=9 Hz, 2H); 4.67–5.47 (m, 4H); 5.70–6.27 (m, 1H); 7.25 (d, J=6 Hz, 1H)
1a	H	H	H_3C—CH=CH—	**5d**	3 h/25 °C	60	54°/0.5	$C_8H_{10}O_2$ (138.2)	1600	1670	1.77 (d, J=7 Hz, 3H); 2.36 (s, 1H); 2.49 (d, J=1.5 Hz, 1H); 4.58–4.25 (m, 1H); 5.23 (d, J=6 Hz, 1H); 5.60–6.11 (m, 2H); 7.20 (d, J=6 Hz, 1H)
1a	H	H	C_6H_5	**5e**	20 min/50 °C	70	110°/0.5	$C_{11}H_{10}O_2$ (174.2)	1600	1675	2.52–2.73 (m, 2H); 5.14–5.44 (m, 2H); 7.28 (s, 5H); 7.33 (part of doublet 1H)
1b	H	C_2H_5	i-C_3H_7	*cis*-**5f**[e]	36 h/50 °C	35	54°/0.8	$C_{10}H_{16}O_2$ (168.2)	1603	1670	0.77–2.43 (m, 13H); 3.89–4.12 (J=5, J=8 Hz, 1H); 5.17 (d, J=6 Hz, 1H); 7.17 (d, J=6 Hz, 1H)
				trans-**5f**[e]							0.75–2.26 (m, 13H); 3.68–3.88 (d of d, J=3 Hz, J=11 Hz, 1H); 5.12 (d with fine splitting, J=6 Hz, 1H); 7.17 (d, J=6 Hz, 1H)
1c	C_2H_5	H	C_6H_5	**5g**	36 h/50 °C	60	170°/0.2[f]	$C_{13}H_{14}O_2$ (202.2)	1607	1670	1.03 (t, J=7 Hz, 3H); 1.92–2.30 (m, 2H); 2.52 (s, 1H); 2.66 (d, J=5 Hz, 1H); 5.07–5.35 (m, 1H); 7.17 (b.s., part of doublet 1H); 7.28 (b.s., 5H)
1d	H	C_2H_5O	i-C_3H_7	**5h**[g]	24 h/50 °C	45	58°/0.5	$C_{10}H_{16}O_3$ (184.2)	1600	1668	0.92–1.25 (m, 9H); 1.90–2.64 (m, 1H); 3.10–4.17 (m, 4H); 5.09–5.27 (m, 1H); 7.29 (d, J=6 Hz, 1H)
1e	C_2H_5O	H	C_6H_5	**5i**	24 h/50 °C	45	108°/0.2[f]	$C_{13}H_{14}O_3$ (218.2)	1612	1682	1.23 (t, J=7 Hz, 3H); 2.58 (d, J=1 Hz, 1H); 2.73 (d, J=9 Hz, 1H); 3.97 (q, J=7 Hz, 2H); 5.13–5.43 (d of d, J=5 and J=12 Hz, 1H); 7.33 (b.s., 6H)

[a] Yield of product after purification by H.P.L.C.
[b] Satisfactory microanalyses obtained: C ±0.35, H ±0.20.
[c] Perkin-Elmer 257 spectrophotometer.
[d] Varian T-60 spectrometer.
[e] Obtained from a 3:1 *cis*/*trans* mixture after separation with H.P.L.C. *cis*- and *trans*-configurations are tentatively ascribed on account of the coupling constants of the CH(5)—CH(6) protons ($J_{HH\,cis}$ = 8 Hz; $J_{HH\,trans}$ = 11 Hz). Decoupling Varian EM 390.
[f] Temperature of bulb-to-bulb distillation.
[g] *cis*/*trans* mixture which could not be separated by H.P.L.C.
[h] Obtained in a purity of ~95% (N.M.R.).

scopic data (^{1}H-N.M.R. and I.R.) are given in the Table. Mass spectra (Finigan 3100 GCMS) are in agreement with the given structures; all mass spectra show the characteristic M−(CHR^2—CHR^3) peaks.

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