Carbohydrate Research, 160 (1987) c1–c2
Elsevier Science Publishers B V , Amsterdam – Printed in The Netherlands

Preliminary communication

Asymmetric induction in the Eu(fod)$_3$-mediated high-pressure (4 + 2)cycloaddition of 1-methoxybuta-1,3-diene to 2,3-di-*O*-benzyl-D-glyceraldehyde

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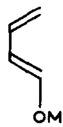
(Received July 23rd, 1986; accepted for publication, November 6th, 1986)

The Diels–Alder reaction of 2,3-*O*-isopropylidene-D-glyceraldehyde with 1-methoxybuta-1,3-diene (**1**) provides[1] an easy access to optically pure derivatives of 5,6-dihydro-2*H*-pyran which are important synthons for the synthesis of sugars[2]. We now report on the (4 + 2)cycloaddition of **1** to 2,3-di-*O*-benzyl-D-glyceraldehyde (**2**).

The reaction was carried out at 20 kbar and 50° in dichloromethane, using a piston-cylinder type apparatus[3], and afforded 36% of a mixture of four diastereoisomers: *cis* and *trans* 6*S* (**3a**) and 6*R* (**3b**). H.p.l.c. of the mixture yielded two fractions containing *cis,trans* diastereoisomers (6*S*)-**3a** and (6*R*)-**3b**, respectively, in the ratio of 74:26 (established on the basis of the four resonances for H-2 in the 360-MHz ^{1}H-n.m.r. spectrum).

Satisfactory analyses and spectral data were obtained for these compounds. A *cis,trans* mixture of 6*S* adducts (**3a**) was isolated by h.p.l.c. as an oil, $[\alpha]_D^{25}$ $-15°$ (*c* 1.6, chloroform); ν_{max}^{film} 1655, 1240, 1150, 1110, 1050, and 700 cm^{-1}. ^{1}H-N.m.r. data: δ 7.33 (m, 10 H, 2 Ph), 5.97 (m, 1 H, H-4), 5.64 (m, 1 H, H-3), 5.00 (s, 0.7 H, *cis* H-2), 4.85 (s, 0.3 H, *trans* H-2), 4.76 (ABq, 2 H, CH_2Ph), 4.55 (ABq, 2 H, CH_2Ph), 4.07 (m, 0.3 H, *trans* H-6), 3.91 (m, 0.7 H, *cis* H-6), 3.8–3.6 (m, 3 H, H-7,8,8′), 3.39 (s, 2.1 H, *cis* OMe), 3.37 (s, 0.9 H, *trans* OMe), 2.3–2.0 (m, 2 H, H-5,5′). A *cis,trans* mixture of 6*R* adducts (**3b**) was also isolated by h.p.l.c. as an oil, $[\alpha]_D^{25}$ +14° (*c* 0.5, chloroform); ν_{max}^{film} 1655, 1220, 1130, 1110, 1050, and 700 cm^{-1}. ^{1}H-N.m.r. data: δ 7.33 (m, 10 H, 2 Ph), 5.96 (m, 1 H, H-4), 5.67 (m, 1 H, H-3), 5.08 (s, 0.7 H, *cis* H-2), 4.90 (s, 0.3 H, *trans* H-2), 4.76 (ABq, 2 H, CH_2Ph), 4.55



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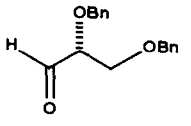

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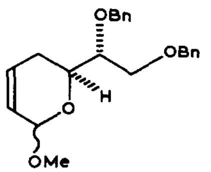
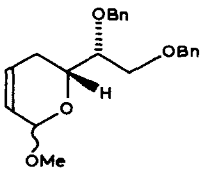


3a



3b

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TABLE I

(4 + 2)CYCLOADDITION OF **1** TO **2**

Reaction conditions		*Yield (%)*	*Absolute configuration*	*Diastereoisomeric excess (%)*
Pressure (kbar)	*Eu(fod)$_3$*			
20	—	36	6*S*	48
20	1 mol %	60	6*R*	38
15	1 mol %	48	6*R*	50
7	1 mol %	24	6*S*	2

(ABq, 2 H, CH_2Ph), 4.10 (m, 0.3 H, *trans* H-6), 3.99 (m, 0.7 H, *cis* H-6), 3.8–3.6 (m, 3 H, H-7,8,8′), 3.48 (s, 2.1 H, *cis* OMe), 3.39 (s, 0.9 H, *trans* OMe), 2.3–1.6 (m, 2 H, H-5,5′).

Since the yield was low, the cycloaddition was carried out[4,5] at 20 kbar and 50° in the presence of catalytic amounts of Eu(fod)$_3$. Although the yield was higher (60%), the direction of asymmetric induction was reversed and the ratio of **3a** and **3b** was 31:69. The effect of pressure on the direction and extent of asymmetric induction in Eu(fod)$_3$-mediated (4 + 2)cycloaddition of **1** to **2** at 50° is shown in Table I.

Thus, lowering of the pressure from 20 to 15 kbar leads to an increase in the proportion of (6*R*)-**3b** in the cycloaddition products. Reduction of the pressure to 7 kbar not only markedly lowers the degree of induction but also results in the preponderant formation of (6*S*)-**3a**.

The stereochemical results obtained for high-pressure (4 + 2)cycloaddition of **1** to **2**, in the absence of catalyst, are consistent with Felkin's model[6,7] but not when Eu(fod)$_3$ is present. Explanation of the stereochemical course of this reaction requires further studies.

ACKNOWLEDGMENTS

The authors thank Mr. Jan Kihlberg (The Lund Institute of Technology, Sweden) for recording the ^{1}H-n.m.r. spectra. This work was supported by the Polish Academy of Sciences MR-I-12 grant.

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