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STEREOCHEMISTRY OF DIELS-ALDER REACTION AT HIGH PRESSURE: ASYMMETRIC INDUCTION IN THE REACTION OF 1-METHOXYBUTA-1,3-DIENE WITH SUGAR ALDEHYDES[1]

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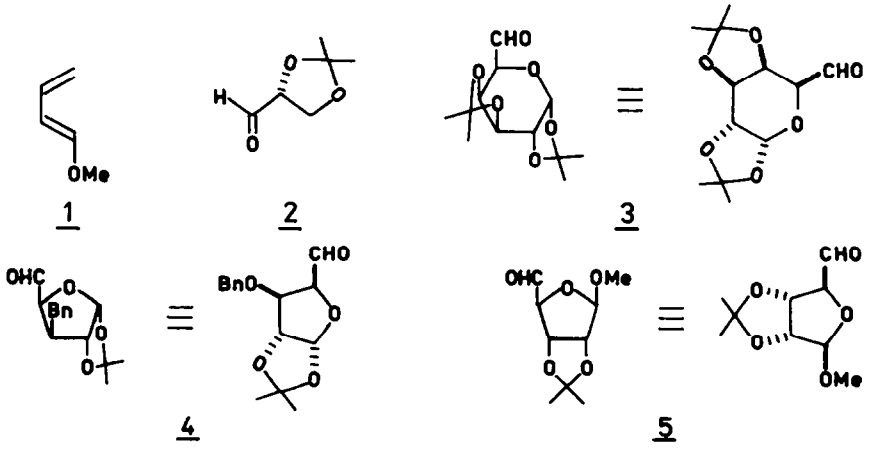
Abstract - High-pressure (4+2)cycloaddition of 1-methoxybuta-1,3-diene (1) to three representative sugar aldehydes 3, 4, and 5 in the presence and without $Eu(fod)_3$ was studied. The effects of pressure and catalyst on asymmetric induction were examined. Stereochemical models were used for interpretation of the results.

Since several years, at this laboratory extensive studies have been made of the effect of pressure on asymmetric induction in the Diels-Alder reaction whose highly ordered transition state promises good optical yield. Special attention has been given to (4+2)cycloaddition with the use of chiral heterodienophiles which in reactions with buta-1,3-diene derivatives afford optically active 6-substituted-5,6-dihydro-2H-pyrans. These compounds, in particular the products of the reaction of 1-methoxybuta-1,3-diene (1) with carbonyl dienophiles, are versatile synthons for the syntheses of sugars,[2,3] antibiotics,[4] and pheromones.[5]

The so far performed studies of (4+2)cycloadditions with the use of optically active glyoxylates[6-9] have led us to the conclusion that in non-catalyzed reactions - even under high-pressure conditions - localization of the inducing centre in position γ relative to the reacting formyl group fails to enable high asymmetric induction. The results of these studies as well as our earlier development of the conditions for effective carrying out of high-pressure Diels-Alder reactions with the use of non-activated heterodienophiles[10,11] have led us to apply aldehydes with the centre of chirality in position α relative to the formyl group. We have selected 2,3-O-isopropylidene-D-glyceraldehyde (2)[12] easily obtainable from natural D-mannitol.



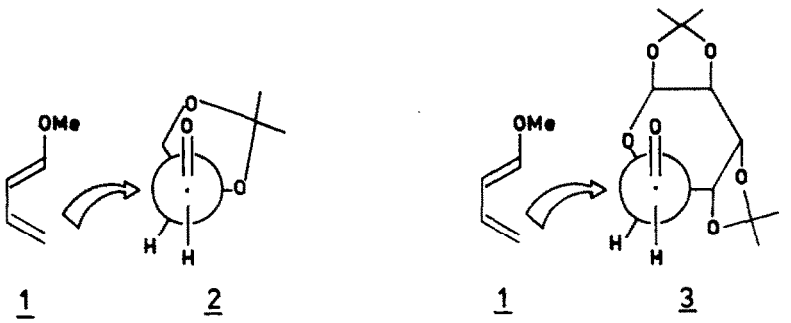
1 2 3

4 5

Chart 1

The reaction of aldehyde 2 with diene 1 under high-pressure conditions has afforded a mixture of diastereoisomeric adducts with high asymmetric induction (up to 74% d.e.).[12,13] So high a stereoselectivity results from substantial differentiation of the diastereotopic faces of the formyl group by the dioxolane ring present in aldehyde 2.[13,14] This explanation has been fully confirmed by our studies on the effect of the size of the protecting groups in D-glyceraldehyde molecule on asymmetric induction in its reaction with diene 1.[15]

An analysis of the results obtained for asymmetric induction in high-pressure reactions of diene 1 with differently protected D-glyceraldehyde derivatives has shown that in these cases it is hardly probable to attain a stereoselectivity approaching 100%. Therefore we resolved to select some other, more selective dienophiles of this type. Examination of the models of aldehydes with a chirality centre in position α relative to the formyl group showed that introduction of a bulky group, e.g. a sugar ring, into the molecule ought to cause stronger shielding of one of the diastereotopic faces of the carbonyl group, and thus should substantially increase asymmetric induction. This assumption is illustrated in Scheme 1 presenting a comparison of the approach of diene 1 to the less hindered sides of aldehydes 2 and 3.



1 2 1 3

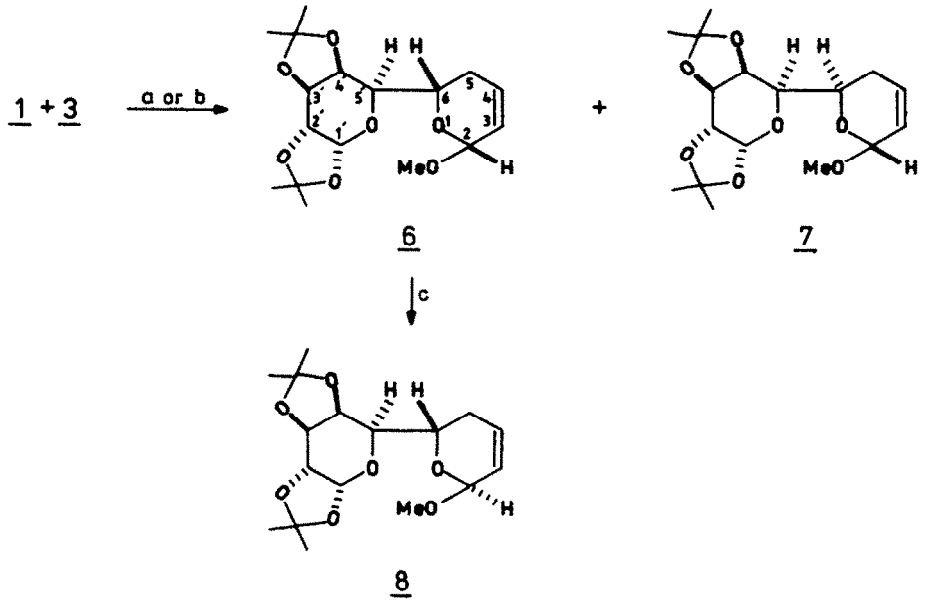
Scheme 1. Comparison of the approaches of diene 1 to the less hindered sides of dienophiles 2 and 3

For experimental verification of the above considerations, were selected three representative sugar aldehydes 3,[16] 4,[17] and 5,[16] and studied asymmetric induction in their high-pressure reactions with diene 1.

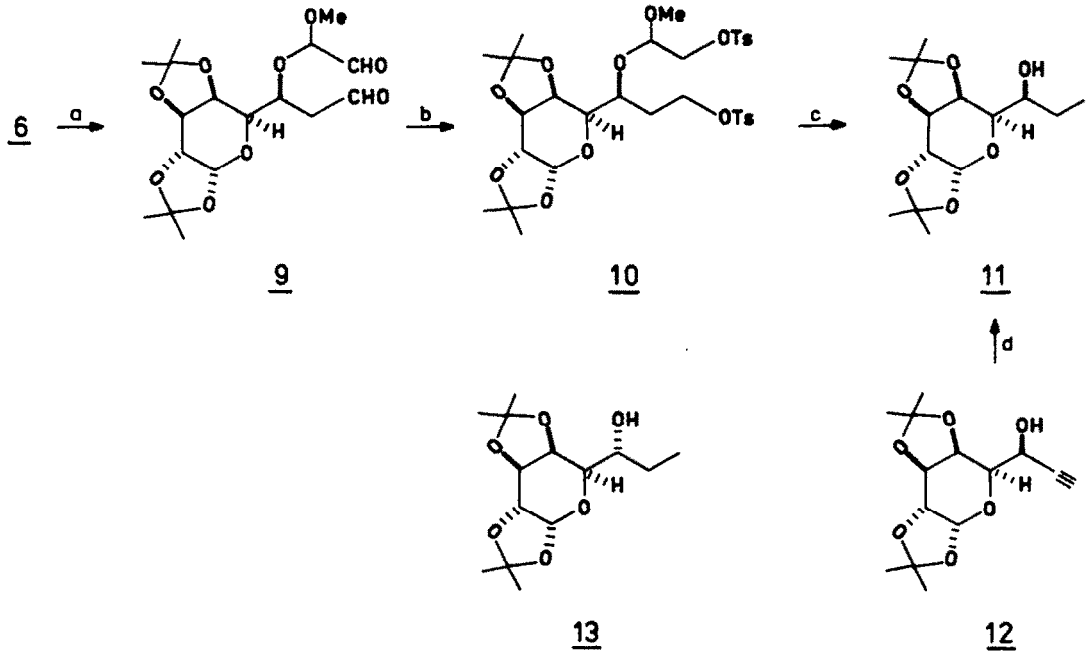
RESULTS AND DISCUSSION

The high-pressure (4+2)cycloaddition of 1 to 3, carried out in a piston-cylinder type apparatus[10] at 20 kbar and 53°C in ethyl ether as solvent, afforded cycloadduct 6 with complete stereoselectivity as shown in Scheme 2. The reaction of 1 with 3, carried out at 50°C under 11 kbar pressure and with $Eu(fod)_3$ as catalyst[11] yielded two diastereoisomeric adducts 6 and 7 in a 98:2 ratio (Table 1). Assignment of structure to the adducts and determination of their stereochemistry were based on isomerization, chemical correlation and analysis of ^1H NMR spectra (Table 2).

Isomerization of 6 to 8 (Scheme 2), carried out in acetone in the presence of pyridinium p-toluenesulphonate (PPTS)[18] as well as comparison of the ^1H NMR spectra of diastereoisomers 6, 7, and 8 proved the stereochemical purity of the original adduct 6. The ^1H NMR spectra of diastereoisomers *cis*-6 and *trans*-8 differed in chemical shifts for all proton signals derived from the dihydropyran moiety. These differences are in good agreement with those observed earlier for other pairs of *cis*- and *trans*-2,6-disubstituted-5,6-dihydro-2H-pyran derivatives.[19,20] The absolute configuration of the chirality centre created at C-6 was established by chemical correlation of 6 with sugar compound 11 whose absolute configuration is known, since it has been obtained from D-galactose.[21] This correlation is presented in Scheme 3. Ozonolysis of 6, followed by ozonide degradation with triphenylphosphine, afforded dialdehyde 9 which was reduced with lithiumaluminum hydride, whereupon the product was treated with p-toluenesulphonyl chloride affording ditosylate 10. Compound 10 was reduced with sodium borohydride in dimethylsulphoxide;[22] subsequent hydrolysis yielded deoxysugar 11. Optical rotation of 11 obtained in the present studies was $(\alpha)_D$ -53° (c 1, $CHCl_3$), whereas that of 11 synthesized according to Gonzales et al.[21] by hydrogenation of acetylenic compound 12 was found to be $(\alpha)_D$ -50° (c 1, $CHCl_3$). It is noteworthy that the optical rotation of diastereoisomer 13 with an opposite configuration at C-6 was $(\alpha)_D$ -81° (c 1, $CHCl_3$).[21]



Scheme 2. Reagents and reaction conditions: (a) 20 kbar, 53°C, Et_2O, 20 h; (b) 11 kbar, 50°C, 1% $Eu(fod)_3$, Et_2O, 20 h; (c) PPTS, acetone, RT, 24 h.



Scheme 3. Reagents and reaction conditions: (a) *i*. O_3, CH_2Cl_2, -78°C, 0.5 h; *ii*. Ph_3P, CH_2Cl_2, -78°C → RT; (b) *i*. $LiAlH_4$, Et_2O, RT, 1 h; *ii*. TsCl, pyridine, RT, 20 h; (c) *i*. $NaBH_4$, DMSO, 80°C, 6 h, *ii*. PTSA, acetone–H_2O (95:5 v/v), 55°C, 6 h; (d) H_2, Pt, AcOEt, RT, 1 atm, 1 h.

Table 1. Results of asymmetric induction of high-pressure (4+2)cycloaddition of diene 1 to sugar aldehydes 3, 4, and 5

Entry	Aldehyde	Catalyst[a]	P (kbar)	T (°C)	Yield[b] (%)	Diastereoisomeric composition (%)				*cis:trans* ratio	d.e.[c](%) *(endo)*	d.e.[c](%) *(exo)*
	3					6	7					
1		-	20	53	72	100.0	0			>100:1	100	-
2		$Eu(fod)_3$	11	50	56	98.0	2.0			98:2	100	100
	4					14	15	16	17			
3		-	20	53	55	65.3	26.7	5.5	2.5	71:29	84.5	82.9
4		$Eu(fod)_3$	11	50	33	54.1	26.2	12.7	7.0	67:33	62.0	57.8
	5					18	19	20	21			
5		-	20	53	50	88.0	0	12.0	0	>100:1	76.0	-
6		$Eu(fod)_3$	11	50	44	72.5	7.5	17.9	2.1	90:10	60.4	56.3

[a] 1 mol% of $Eu(fod)_3$ was used.

[b] Yield of isolated product.

[c] Diastereoisomeric excess (d.e.) for both addition types (*endo* and *exo*) was established using simple equations, for example: d.e.(*endo*) = ((14)-(16))/((14)+(16)); d.e.(*exo*) = ((15)-(17))/((15)+(17)).

Table 2. ^1H NMR chemical shifts of the diastereoisomeric adducts derived from aldehydes 3, 4, and 5

Compound	H-2	H-3	H-4	H-5,5	H-6	H-1′	H-2′	H-3′	H-4′	H-5′	OMe	CMe_2	CH_2Ph
6	5.04	5.66	6.00	2.22	4.04	5.50	4.29	4.61	4.49	3.84	3.49	1.51, 1.46, 1.38, 1.32	-
7	4.91	5.77	5.99	2.15	4.12	5.60	4.24	4.60	4.32	3.73	3.49	1.53, 1.44, 1.37, 1.33	-
8	4.85	5.73	6.05	2.22	4.16	5.52	4.30	4.60	4.48	3.69	3.44	1.55, 1.48, 1.41, 1.38	-
14	5.00	5.64	6.06	2.25	4.18	5.91	4.71	4.13	4.25	-	3.39	1.51, 1.49, 1.32	4.62, 7.34
15	4.85	5.74	6.06	2.25	4.18	5.91	4.71	4.13	4.25	-	3.31	1.51, 1.49, 1.32	4.62, 7.34
16	5.07	5.66	5.88	1.95	4.13	6.01	4.44	4.37	3.90	-	3.52	1.51, 1.50, 1.34	4.64, 7.34
17	4.89	5.75	5.88	1.95	4.22	6.01	4.44	4.37	3.90	-	3.44	1.51, 1.50, 1.34	4.64, 7.34
18	5.00	5.68	5.99	2.23	3.71	4.95	4.59	4.91	4.27	-	3.49 3.33	1.48, 1.34	-
19	5.00	5.74	5.99	2.23	3.71	4.95	4.59	4.91	4.27	-	3.49 3.33	1.48, 1.34	-
20	5.04	5.70	5.98	2.12	3.76	5.04	4.58	4.58	4.25	-	3.52 3.41	1.51, 1.33	-
21	5.04	5.76	5.98	2.12	3.76	5.04	4.58	4.58	4.25	-	3.52 3.41	1.51, 1.33	-

High-pressure reaction (20 kbar, 53°C) of diene 1 with aldehyde 4 yielded two chromatographically different products in a 92:8 ratio. The ^{1}H NMR spectra (Table 2) of two fractions separated by column chromatography indicated that each fraction is a mixture of diastereoisomeric adducts 14 + 15 (71:29) and 16 + 17 (69:31) (Scheme 4). The mixture of diastereoisomers 14 + 15 was treated with a PPTS solution in acetone; the ^{1}H NMR spectrum of the isomerization product exhibited the disappearance of the signal of the proton bound with carbon atom C-2 in the 5,6-dihydro-2H-pyran ring (δ 5.00), with a simultaneous increase in the intensity of the signal at δ 4.85. This confirmed the assumption that the mixture of 14 + 15 is a *cis - trans* mixture, i.e. that both diastereoisomers show the same configuration at carbon atom C-6. The mixture of 16 + 17, treated by the same procedure, afforded analogous results. The reaction of 1 with 4 carried out under high pressure (11 kbar, 50°C) - in the presence of $Eu(fod)_3$ as catalyst - also yielded a mixture of four diastereoisomers (Scheme 4), with a slight decrease in *cis - trans* selectivity, and - in the first place - with a marked reduction of asymmetric induction (Table 1).

High-pressure cycloaddition of 1 to 5 (20 kbar, 53°C) led to only two diastereoisomeric adducts 18 and 20 (88:12), being products of *endo* addition (Scheme 5). These compounds were separated by column chromatography; comparison of their ^{1}H NMR spectra showed that they differ in configuration on the chirality centre C-6. This conclusion was confirmed by isomerizations 18 → 19 and 20 → 21. Upon use of $Eu(fod)_3$ as catalyst, the high-pressure reaction between 1 and 5 (11 kbar, 50°C) yielded all four possible diastereoisomers 18, 19, 20, and 21 (Scheme 5), in proportions shown in Table 1.

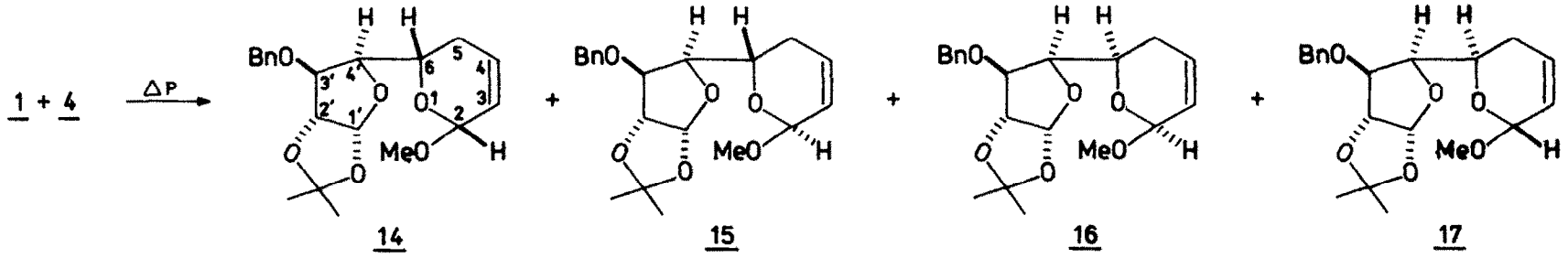
Absolute configuration at the newly formed chirality centres C-6 in the adducts obtained from the reaction of diene 1 with either aldehyde 4 or 5 was assigned on the grounds of their ^{1}H NMR spectra. Comparison was made of the chemical shifts of the diagnostic protons of these adducts with the data obtained for the products of the reaction of diene 1 with either aldehyde 2[13-15] or 3[1], whose absolute configuration has been definitively established by chemical correlations.

Preliminary analysis of the ^{1}H NMR spectra (Table 2) indicated that the diagnostic signals permitting correlation of the stereochemistry of diastereoisomeric adducts comprise the signals derived from proton H-2 and from the methoxy group attached to the 5,6-dihydro-2H-pyran ring as well as the signal of anomeric proton (H-1′) from the sugar moiety.

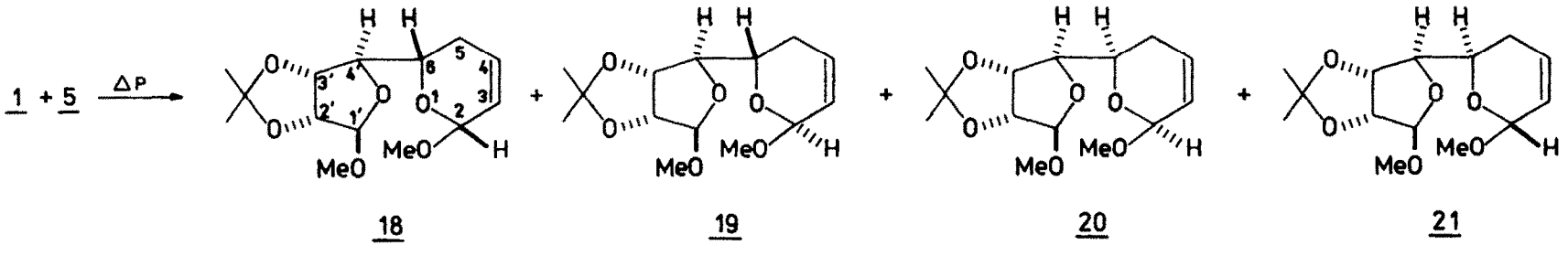
Protons H-2 were characterized by a down-field shift upon transition from the adduct of absolute configuration (6S) to its diastereoisomer (6R); the differences between chemical shifts remained within the range of 0.04 - 0.07 ppm. This regularity held through for diastereoisomeric pairs *cis* and *trans*. The same concerned the chemical shifts of anomeric protons from the sugar moiety; in this case, transition from adducts (6S) to their diastereoisomers (6R) caused a down-field shift of 0.09 - 0.10 ppm. As concerns the methoxy group attached to the 5,6-dihydro-2H-pyran ring, transition from (6S) to (6R) resulted also in a down-field shift of 0.03 - 0.13 ppm. These regularities are fully consistent with similar ones observed for the diastereoisomeric pair 7 and 8 (Table 2), as well as for the adducts obtained from the reaction of diene 1 with 2,3-O-isopropylidene-D-glyceraldehyde.[13-15]

The above results call for stereochemical rationalization. The relationships between the direction of addition of various reagents to the carbonyl group and the reagent structure, on the one hand, and the reaction conditions continue to be an object of extensive studies.[12] Attempts have been made to rationalize the results by proposing various models of diastereoisomeric transition states, describing the carbonyl substrate - reagent interactions.[23-28] For our interpretation of the stereochemical course of (4+2)cycloaddition, we selected Felkin's model[27] as modified by Nguyen Tronh Anh.[28]

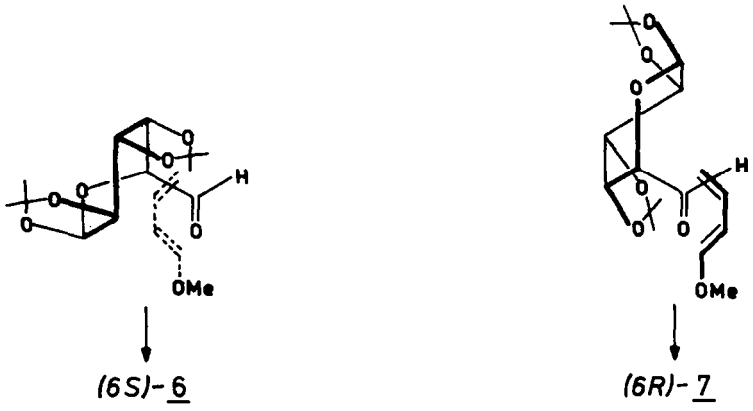
Scheme 6 shows the models proposed for cycloaddition of 1-methoxybuta-1,3-diene (1) to the formyl group of 3. Conformation of aldehyde 3 was assumed according to the results of the recent X-ray[29] and ^{1}H NMR[30] studies performed for several derivatives of 1,2:3,4-di-O-isopropylidene-α-D-galactopyranose. In a non-catalyzed high-pressure reaction of 1 with 3, only the *endo* approach of diene to dienophile from the less hindered side takes place (Scheme 6, left model), leading exclusively to the *cis*-diastereoisomer (6S)-6. In case of the $Eu(fod)_3$-mediated reaction, the products formed originate from *endo*-addition - the major *cis*-diastereoisomer (6S)-6, and from *exo*-addition - the minor *trans*-diastereoisomer (6R)-7 (Scheme 6, right model). The adducts originating from the two remaining transition states were detected neither in the non-catalyzed nor in the $Eu(fod)_3$-mediated reaction.



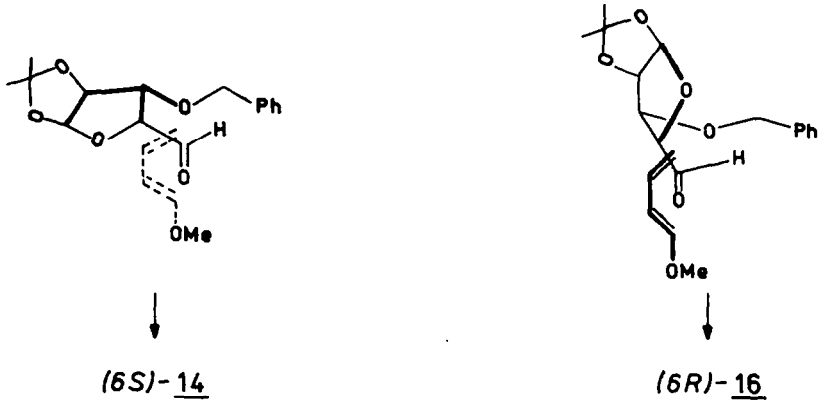
Scheme 4



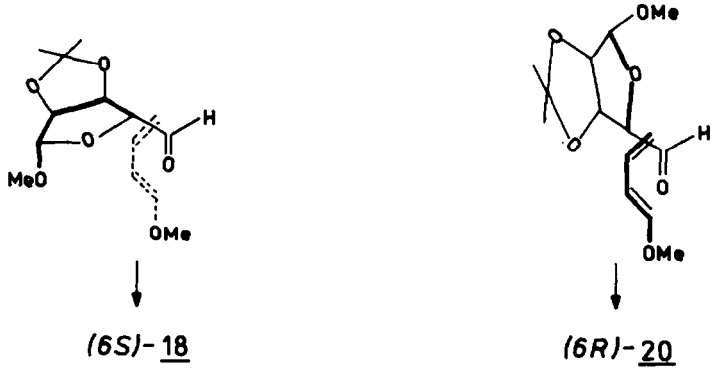
Scheme 5



Scheme 6. The stereochemical models proposed for *endo* (4+2)cycloaddition of 1 to 3



Scheme 7. The stereochemical models proposed for *endo* (4+2)cycloaddition of 1 to 4



Scheme 8. The stereochemical models proposed for *endo* (4+2)cycloaddition of 1 to 5

Schemes 7 and 8 show the models for *endo*-addition in the reactions of 1 with 4 and of 1 with 5, respectively, which lead to *cis*-diastereoisomers. The analogous models for *exo*-addition leading to *trans*-diastereoisomers were also considered.

The non-catalyzed reaction of 1 with 4 affords all four possible diastereoisomeric adducts resulting from the approach of diene to dienophile from both sides of the carbonyl group plane, in both types of *endo* and *exo* addition. The main product of this reaction consists of adduct (6S)-14 originating from *endo*-addition of diene 1 to the carbonyl group of 4 from the side of lower steric hindrance (Scheme 7, left model). The same reaction performed in the presence of $Eu(fod)_3$ also yields a mixture of all four possible adducts; as compared with the non-catalyzed reaction, the proportion of products is shifted towards the cycloadducts resulting from the approach of diene 1 to dienophile 4 from the side of higher steric hindrance - (6R)-16 in *endo*-addition (Scheme 7, right model) and (6R)-17 in *exo*-addition.

The reaction of 1 with 5 gives similar results. The non-catalyzed reaction yields exclusively the products formed by the approach of diene 1 to dienophile 5 from the side of lower steric hindrance in *endo*-addition (Scheme 8, left model) and *exo*-addition. The $Eu(fod)_3$-catalyzed reaction leads to all four possible adducts; this points to the occurrence of products formed by the approach of diene 1 to dienophile 5 from the side of higher steric hindrance in *endo*- (Scheme 8, right model) and *exo*-addition.

In non-catalyzed high-pressure reactions, in all cases there is preference of transition states leading to *cis*-adducts with (6S) configuration (left models in Schemes 6, 7, and 8). This suggests that these transition states are more compact than the remaining ones, as evidenced by inspection of Dreiding's models. The participation of the remaining transition states in formation of diastereoisomeric adducts mainly depends on the effectiveness of shielding of both sides of the carbonyl group in sugar aldehydes 3, 4, and 5. In high-pressure reactions catalyzed by $Eu(fod)_3$, whereas there still applies the preference of *endo*-addition from the side of lower steric hindrance in the dienophile, the proportions of the products formed by *endo*- and *exo*-addition from the side of higher steric hindrance begin to increase. This is probably related to the location of the catalyst in the transition state. An atom of europium interacting with the oxygen-containing functional groups of the reagents probably causes a decrease in the differences in steric hindrance between both sides of the carbonyl group of the dienophile, this in turn resulting in smaller differentiation of the volumes of transition states. The activation volume being the driving force of high-pressure reactions represents the difference between the transition state volume and volume occupied by substrates; therefore, the effectiveness of parallel reactions leading *via* diastereoisomeric transition states to diastereoisomeric adducts ought to be related to the steric structure of the transition states. Our results obtained for non-catalyzed and $Eu(fod)_3$-mediated high-pressure Diels-Alder reactions seem to confirm the above considerations and are also consistent with the results of studies on the reaction of diene 1 with 2,3-O-isopropylidene-D-glyceraldehyde (2).[13-15]

The present results illustrate the usefulness of the high-pressure technique for solving stereochemical problems in organic synthesis. High-pressure conditions enable the title cycloaddition, which could not be performed under atmospheric pressure, to be carried out in a high yield and with very good stereoselectivity.

EXPERIMENTAL

The ^1H NMR spectra were recorded with Nicolet 360 MHz or Bruker AM-500 MHz spectrometers for $CDCl_3$ solutions (δ scale, TMS=0 ppm). The mass spectra were taken with a LKB 2091 spectrometer at 15 eV. Optical rotations were measured with a Perkin-Elmer 141 spectropolarimeter.

Column chromatography was performed on Merck Kieselgel 60 (230-400 mesh). All chromatographic separations were monitored by TLC carried out on Merck DC Alufolien Kieselgel 60F-254. The reported yields refer to chromatographically pure compounds.

All high-pressure reactions were carried out in a piston-cylinder type apparatus with working volume of about 90 mL. Construction details have been reported previously.[10] The pressure inside the working volume was measured with a calibrated coil exact to ± 0.1 kbar. The accuracy of temperature measurements using a calibrated thermocouple was $\pm 1^{\circ}C$.

trans-1-Methoxybuta-1,3-diene (1) was prepared according to the literature.[31] 1,2:3,4-Di-O-isopropylidene-α-D-*galacto*-hexapyranos-6-ulose (3) and methyl 2,3-O-isopropylidene-β-D-*ribo*-pentafuranos-5-ulose (5) were obtained from the corresponding monosaccharides by oxidation of the primary hydroxy group according to the procedure described by Horton et al.[16] 1,2-O-Isopropylidene-3-O-benzyl-α-D-*xylo*-pentafuranos-5-ulose (4) was prepared from 1,2-O-isopropylidene-3-O-benzyl-α-D-*gluco*-

hexafuranose according to the procedure of Wolfrom and Hanessian.[17]

(2R:6S)-2-Methoxy-6-(1′,2′:3′,4′-di-O-isopropylidene-α-D-*galacto*-hexapyranos)-5,6-dihydro-2H--pyran (6). A solution of 1 (0.2 mL, 2 mmol) and 3 (258 mg, 1 mmol) in methylene chloride (4 mL) was charged into a Teflon ampoule[32] which was placed in a high-pressure vessel filled with pentane as a transmission medium. The pressure was slowly elevated to 20 kbar at 53°C. After stabilization of pressure, the reaction mixture was kept under these conditions for 20 h. After cooling and decompression, the solvent was evaporated and the residue was chromatographed on a silica gel column with a mixture of hexane and ethyl acetate 9:1 (v/v), affording pure adduct 6 (246 mg, 72%). The analytical data of 6 are given in Table 3.

The reaction of 1 with 3, carried out in the same high-pressure apparatus under 11 kbar at 50°C in the presence of 1 mol% $Eu(fod)_3$, afforded diastereoisomers 6 and (2R:6R)-2-methoxy-6-(1′,2′:3′,4′--di-O-isopropylidene-α-D-*galacto*-hexapiranos)-5,6-dihydro-2H-pyran (7) in a 98:2 ratio (overall yield 56%).

Table 3. Analytical data of the adducts derived from aldehydes 3, 4, and 5

Compound	$(\alpha)_{589}^{20}$	Formula	Analysis (%) Calcd. C	H	Found C	H	Mass spectrometry m/z
6	-41.6° (c 3.08, C_6H_6)	$C_{17}H_{26}O_7$ (342.2)	59.63	7.65	59.48	8.00	-
14+15	-12.5° (c 1.60, $CHCl_3$)	$C_{20}H_{26}O_6$ (362.2)	66.28	7.23	66.20	7.56	362(M^+,0.6), 331(2.7), 249(25), 91(100)
16+17	-46.3° (c 3.02, $CHCl_3$)	$C_{20}H_{26}O_6$ (362.2)			-		362(M^+,0.5), 331(1.6), 249(19),, 91(100)
18+19	-15.5° (c 1.00, $CHCl_3$)	$C_{14}H_{22}O_6$ (286.2)	58.73	7.75	58.42	8.16	286(M^+,0.5), 285(5.1), 173(100), 113(65)
20+21	-21.1° (c 0.57, $CHCl_3$)	$C_{14}H_{22}O_6$ (286.2)			-		286(M^+,0.3), 285(3.8), 173(100), 113(65)

(2R:6S)-, (2S:6S)-, (2S:6R)-, and (2R:6R)-2-methoxy-6-(3′-O-benzyl-1′,2′-O-isopropylidene-α-D--*xylo*-pentafuranos)-5,6-dihydro-2H-pyran (14, 15, 16, and 17). The reaction between 1 and 4, carried out on a scale of 1 mmol similarly as for preparation of 6, afforded with 55% yield a mixture of four diastereoisomers 14, 15, 16, and 17 in a ratio given in Table 1. The post-reaction mixture was chromatographed on a silica gel column with a mixture of hexane and ethyl acetate 9:1 (v/v). The first fraction contained a diastereoisomeric mixture of 14+15, and the second one - of 16+17. The analytical data of both fractions are given in Table 3.

The high-pressure reaction of 1 with 4, catalyzed by $Eu(fod)_3$, was performed under the same conditions as for the reaction of 1 with 3.

(2R:6S)-, (2S:6S)-, (2S:6R)-, and (2R:6R)-2-methoxy-6-(methyl 2′,3′-O-isopropylidene-β-D-*ribo*--pentafuranosid)-5,6-dihydro-2H-pyran (18, 19, 20, and 21). The high-pressure $Eu(fod)_3$-mediated reaction between 1 and 5, carried out on a scale of 1 mmol in an analogous manner as in case of the reaction of 1 with 3, afforded with 33% yield a mixture of four diastereoisomers 18, 19, 20, and 21 in a ratio given in Table 1. The chromatographic separation of the post-reaction mixture, performed on a silica gel column with a mixture of hexane and ethyl acetate 9:1 (v/v), yielded two fractions containing diastereoisomers 18+19 and 20+21, respectively. The analytical data of both fractions are given in Table 3.

The high-pressure non-catalyzed reaction of 1 with 5 was carried out under the same conditions as for the reaction of 1 with 3; it afforded a mixture of two diastereoisomers 18 and 20 in a 88:12 ratio.

(2S:6S)-2-Methoxy-6-(1′,2′:3′,4′-di-O-isopropylidene-α-D-*galacto*-hexapyranos)-5,6-dihydro-2H--pyran (8). Adduct 6 (342 mg, 1 mmol) was dissolved in anhydrous acetone (10 mL), and pyridinium p-toluenesulphonate (25 mg, 0.1 mmol) was added. The reaction mixture was stirred at room temperature for 24 h and then solid $NaHCO_3$ (80 mg) was added. After additional 2-h stirring, the precipitate was removed by filtration and the solvent was evaporated. The residue was passed through a short silica gel column to give chromatographically pure 8 (308 mg, 90%).

Correlation of 6 with 7,8-dideoxy-1,2:3,4-di-O-isopropylidene-D-*glycero*-α-D-*galacto*-octopyranose (11). Adduct 6 (530 mg, 1.38 mmol) was treated with ozone in methylene chloride (25 mL) at -78°C. The ozonide was decomposed with triphenylphosphine and the solvent was evaporated. The crude residue was reduced with lithiumaluminum hydride. The crude diol thus obtained was esterified with p-toluenesulphonyl chloride in pyridine affording ditosylate 10. Compound 10 was reduced with sodium borohydride in dimethylsulphoxide at 80°C.[22] The post-reaction mixture was poured into water and extracted with ethyl ether, whereupon the extract was dried over magnesium sulphate. After evaporation of the solvent, the residue was hydrolyzed with p-toluenesulphonic acid in a mixture of acetone and water 95:5 (v/v). After neutralization, solvents were evaporated and the residue was chromatographed on a silica gel column using a mixture of hexane and ethyl acetate 8:2 (v/v) to yield 14 mg (3.5% overall yield) of deoxysugar 11, $(\alpha)_{589}^{20}$ -53.0° (c 1.00, CHCl). All properties of 11 were identical with those described by Gonzales and Llamas.[21]

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