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STEREOCHEMISTRY OF DIELS-ALDER REACTION AT HIGH-PRESSURE: INFLUENCE OF PRESSURE ON ASYMMETRIC INDUCTION IN (4+2)CYCLOADDITION OF 1-METHOXYBUTA-1,3-DIENE TO 2,3-O-ISOPROPYLIDENE-D-GLYCERALDEHYDE

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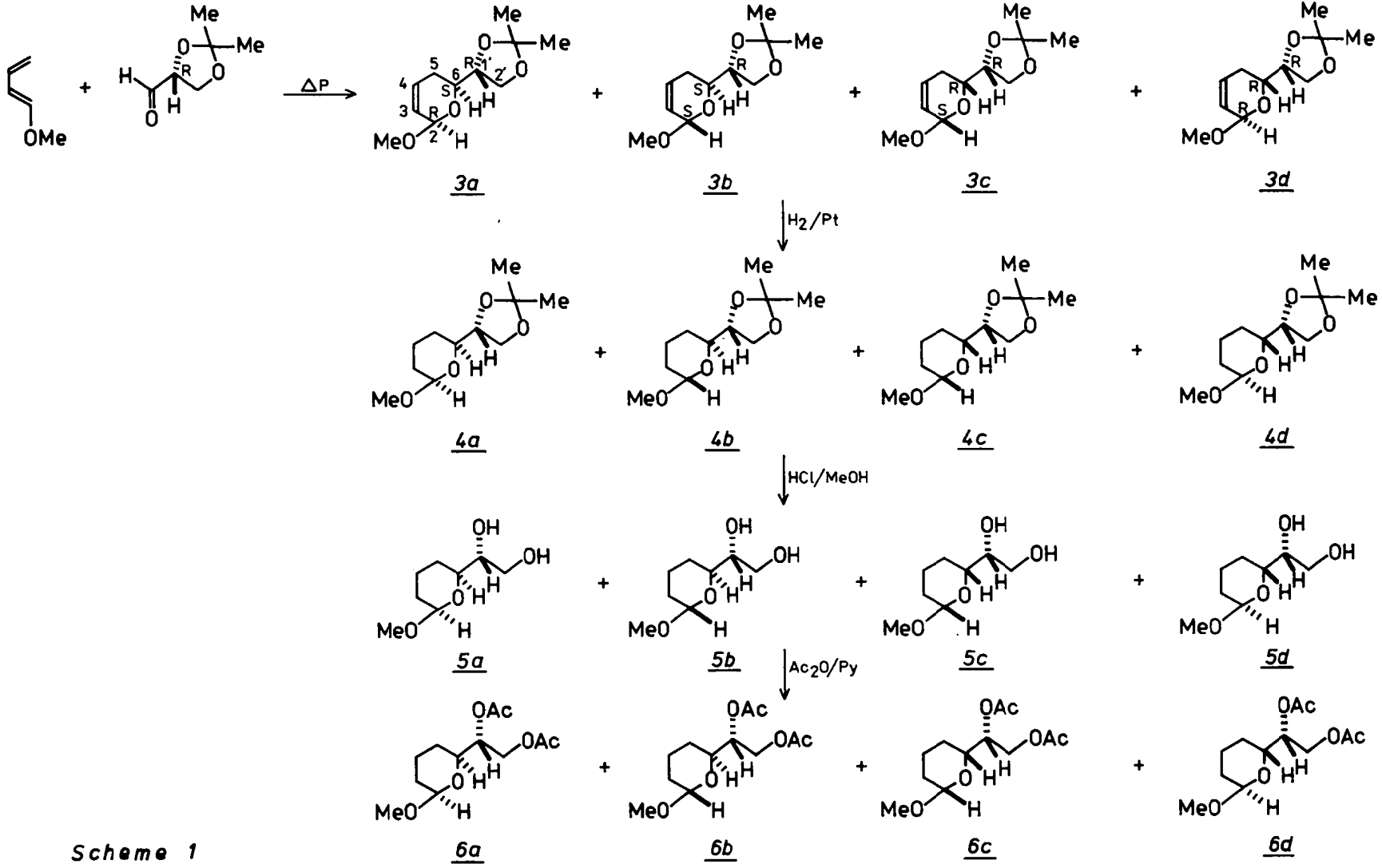
Abstract - High-pressure (4+2)cycloaddition of 1-methoxybuta-1,3-diene (1) to 2,3-O-isopropylidene-D-glyceraldehyde (2) afforded four diastereoisomeric 6-substituted 2-methoxy-5,6-dihydro-2H-pyrans (3), for which the diastereoisomeric excess and absolute configuration were determined. The effects of pressure, temperature and solvent on asymmetric induction were examined. Stereochemical models were used for interpretation of the results.

We have recently described high-pressure (4+2)cycloaddition of 1-methoxybuta-1,3-diene (1) to simple carbonyl compounds.[1] This process affords an easy access to 6-substituted 2-methoxy-5,6-dihydro-2H--pyrans, which are important synthons for the synthesis of sugars[2] and other natural products.[3,4] We have also observed a significant effect of pressure on the direction and magnitude of asymmetric induction in the Diels-Alder reaction of 1,3-dienes with (R)-(-)-menthyl glyoxylate, an activated heterodienophile.[5-7] The satisfactory results of these investigations have prompted us to apply 2,3-O--isopropylidene-D-glyceraldehyde (2), bearing a chiral centre located in the α-position with respect to the formyl group, as a dienophile in the high-pressure Diels-Alder reaction with diene 1. When the reaction has been carried out under high-pressure conditions (22 kbar, 50°C, diethyl ether as solvent), four diastereoisomeric adducts were formed: two *cis* diastereoisomers (3a and 3c) by *endo* addition, and two *trans* diastereoisomers (3b and 3d) by *exo* addition, in a ratio 3a:3b:3c:3d=66:16:13:5 (Scheme 1).[8] It has appeared worthwhile to extend stereochemical studies to an estimation of the influence of pressure, temperature and solvent on asymmetric induction in this (4+2)cycloaddition.

In the present study we used three solvents: diethyl ether, a mixture of toluene and benzene 7:3 (v/v), and methylene chloride. The reactions were carried out at three different pressures (14.5, 20 and 22 kbar) and at 25 or 50°C. Owing to application of high pressure, the reaction proceeded under mild conditions. Thus, the use of 2,3-O-isopropylidene-D-glyceraldehyde (2) under such mild conditions could be expected to bring about very high asymmetric induction.

RESULTS AND DISCUSSION

To establish the proportions of diastereoisomers 3 formed in high-pressure (4+2)cycloaddition of 1 to 2, the reaction mixture was separated by column chromatography, yielding two fractions which contained diastereoisomers 3a+3b and 3c+3d, respectively. Physical properties and elemental analyses of all compounds obtained are shown in Table 1. The ^{1}H NMR spectra of both fractions differed in the chemical shifts of the proton H-2 signals derived from *cis* (*i.e.* 3a or 3c) and *trans* (*i.e.* 3b or 3d) diastereoisomers. Assignments of proton signals in the ^{1}H NMR spectra of all compounds obtained are presented in Table 2. The above differentiation (0.1-0.2 ppm) was sufficient for precise integration, permitting determination of the composition of both fractions. The diastereoisomeric composition was independently confirmed by hydrogenation of 3a+3b over platinum black, affording a mixture of tetrahydropyran derivatives (4a+4b) in an almost quantitative yield. This mixture of diastereoisomers was


ΔP
H2/Pt
HCl/MeOH
Ac2O/Py
3a
3b
3c
3d
4a
4b
4c
4d
5a
5b
5c
5d
6a
6b
6c
6d

Scheme 1

Table 1. Physical, analytical and IR data of compounds 3, 4, 5, and 6

Compound	B.p.[a] (°C/mm Hg)	$(\alpha)_D^{20}$ in C_6H_6	Formula	Analysis (%) Calcd. C	Calcd. H	Found C	Found H	IR (cm^{-1}) C=C	C–O–C	OH	C=O
3a+3b	70/0.05	-13.2°(c 4.0)	$C_{11}H_{18}O_4$	61.7	8.5	61.4	8.6	1660	1050	-	-
3c+3d	70/0.05	+61.1°(c 3.2)	(214.3)			62.2	8.6	1670	1065	-	-
4a	70/0.05	-28.3°(c 2.7)	$C_{11}H_{20}O_4$	61.1	9.3	60.9	9.3	-	1080,1040	-	-
4b	70/0.05	+98.2°(c 2.5)	(216.3)			61.0	9.2	-	1065,1040	-	-
4c	70/0.05	+58.7°(c 2.7)				61.1	9.4	-	1080,1040	-	-
4d	70/0.05	-72.9°(c 2.5)				61.0	9.4	-	1065,1040	-	-
5a	115/0.4	-47.6°(c 2.2)	$C_8H_{16}O_4$	54.5	9.2	b		-	1070,1035	3400	-
5b	115/0.4	+130.6°(c 2.1)	(176.2)			b		-	1060,1035	3400	-
5c	115/0.4	-17.2°(c2.05)				b		-	1070,1030	3400	-
5d	115/0.4	-112.1°(c 2.0)				b		-	1060,1025	3400	-
6a	95/0.2	-20.5°(c 2.0)	$C_{12}H_{20}O_6$	55.4	7.8	55.2	7.8	-	1070,1030	-	1740
6b	95/0.2	+107.1°(c 2.3)	(260.3)			55.3	7.8	-	1055,1030	-	1740
6c	95/0.2	+30.3°(c2.95)				55.5	7.8	-	1070,1025	-	1740
6d	95/0.2	-43.1°(c 2.1)				55.7	8.0	-	1055,1030	-	1740

[a] Air-bath temperature. [b] Samples of compounds 5a, b, c, and d, obtained from different experiments and which were identical (chromatographic and spectral data) gave inconsistent elemental analyses.

Table 2. ^1H NMR chemical shifts of compounds 3, 4, 5, and 6 (δ scale)

Compound	H-2	H-3	H-4	$H-5_a$	$H-5_b$	H-6	H-1′	$H-2'_a$	$H-2'_b$	OCH_3	$C(CH_3)_2$	OH	$COCH_3$
3a	4.96 s,1H	5.66 m,1H	5.98 m,1H	2.4 - 2.0 m,2H		3.68 m,1H	4.18 m,1H	4.09 m,1H	3.99 m,1H	3.43 s,3H	1.41,1.34 2×s,6H	-	-
3b	4.84 s,1H	5.72 m,1H	6.03 m,1H	2.4 - 2.0 m,2H		3.82 m,1H	4.14 m,1H	4.06 m,1H	3.90 m,1H	3.41 s,3H	1.42,1.35 2×s,6H	-	-
3c	5.11 s,1H	5.66 m,1H	6.00 m,1H	2.13 m,1H	1.96 m,1H	3.88 m,1H	4.29 m,1H	4.02 m,1H	3.82 m,1H	3.47 s,3H	1.44,1.38 2×s,6H	-	-
3d	4.91 s,1H	5.76 m,1H	6.01 m,1H	2.15 m,1H	1.88 m,1H	3.86 m,1H	4.18 m,1H	4.04 m,1H	3.84 m,1H	3.44 s,3H	1.43,1.35 2×s,6H	-	-
4a	4.38 d,1H		2.00 - 1.10 m,6H			3.45 m,1H	4.25 - 3.95 m,3H			3.51 s,3H	1.44,1.43 2×s,6H	-	-
4b	4.77 s,1H		2.00 - 1.20 m,6H			3.65 m,1H	4.25 - 3.85 m,3H			3.35 s,3H	1.43,1.37 2×s,6H	-	-
4c	4.16 d,1H		2.10 - 1.10 m,6H			3.56 m,1H	4.45 - 3.75 m,3H			3.53 s,3H	1.44,1.38 2×s,6H	-	-
4d	4.83 s,1H		1.85 - 1.15 m,6H			4.25 - 3.55 m,4H				3.47 s,3H	1.48,1.42 2× s,6H	-	-
5a	4.41 d,1H		2.20 - 1.20 m,6H			3.95 - 3.15 m,4H				3.57 s,3H	-	2.81	-
5b	4.80 s,1H		2.00 - 1.15 m,6H			4.00 - 3.10 m,4H				3.42 s,3H	-	3.00	-
5c	4.44 d,1H		2.15 - 1.15 m,6H			4.00 - 3.45 m,4H				3.54 s,3H	-	3.00	-
5d	4.84 s,1H		2.10 - 1.30 m,6H			4.00 - 3.40 m,4H				3.42 s,3H	-	2.66	-
6a	4.45 d,1H		2.10 - 1.10 m,6H			3.60 m,1H	5.13 m,1H	4.65-4.20 m,2H		3.53 s,3H	-	-	2.10 s,6H
6b	4.82 s,1H		2.20 - 1.20 m,6H			3.98 m,1H	5.06 m,1H	4.65-4.10 m,2H		3.46 s,3H	-	-	2.13,2.11 2×s,6H
6c	4.43 d,1H		2.05 - 1.10 m,6H			3.71 m,1H	5.25 m,1H	4.65-4.10 m,2H		3.54 s,3H	-	-	2.16,2.08 2×s,6H
6d	4.83 s,1H		2.25 - 1.25 m,6H			4.02 m,1H	5.17 m,1H	4.55-4.10 m,2H		3.40 s,3H	-	-	2.13,2.04 2×s,6H

H_a and H_b refer to nonequivalent protons in the CH_2 group.

separated by column chromatography, and the resulting proportions of 4a and 4b were fully consistent with the spectrally (^{1}H NMR) determined diastereoisomeric composition of the fraction containing 3a and 3b. Hydrogenation of the mixture of diastereoisomers 3c+3d afforded analogous results.

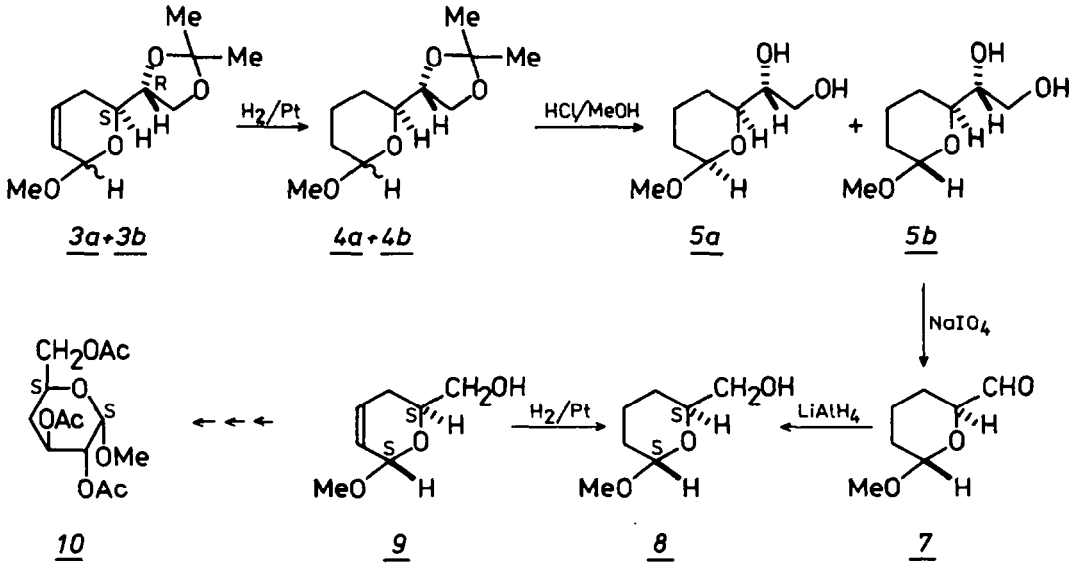
The above-presented determination of the diastereoisomeric composition was based mainly on the ^{1}H NMR spectra. Assignments of the proton signals of diastereoisomeric compounds 3 and of their saturated derivatives 4 were fully confirmed by analysis of the ^{1}H NMR spectra of four diastereoisomeric diols 5 and of their diacetyl derivatives 6 (Table 2). Diastereoisomerically pure diols 5a and 5b were prepared *via treatment of a mixture* 4a+4b *with* 1% HCl *in methanol*, followed by acetylation, chromatographic separation of the resulting mixture 6a+6b, and final reduction of pure compounds 6a and 6b. In case of the mixture 4c+4d, the deprotection reaction afforded also two products which were jointly acetylated to give, after chromatographic separation, the expected diacetyl derivatives 6c and 6d. Compounds 6c and 6d were reduced with lithium aluminum hydride to yield diastereoisomerically pure diols 5c and 5d, respectively.

The determination of the diastereoisomeric composition enables estimation of the diastereoisomeric excess (d.e.) for both addition types ("*endo*" and "*exo*"), using simple equations:

$$\text{d.e.("}endo\text{")} = ([3a] - [3c]) / ([3a] + [3c])$$

$$\text{d.e.("}exo\text{")} = ([3b] - [3d]) / ([3b] + [3d])$$

After determination of the extent of asymmetric induction we resolved to study its direction by chemical correlation of a 3a+3b diastereoisomer mixture with compound 8 whose absolute configuration has been found by correlation with natural sugar 10 (Scheme 2). Hydrogenation of 3a+3b afforded a mixture of compounds 4a+4b, which was - without chromatographic separation - treated with 1% HCl in methanol; this removed the isopropylidene protection with simultaneous equilibration of the acetal centre to give a mixture 5a+5b in a diastereoisomeric ratio of 1:1. After chromatographic separation, the diastereoisomerically pure *trans*-diol 5b was cleaved with sodium periodate affording aldehyde 7 which upon reduction with lithium aluminum hydride gave alcohol 8. Specific rotation of alcohol 8 ($[\alpha]_D^{20}$ +129.7°) was almost identical with that found for 8 obtained by hydrogenation of unsaturated alcohol 9[2] whose 2S:6S absolute configuration was established by chemical correlation with known methyl 2,3,6-tri-O-acetyl-4-deoxy-α-D-*xylo*-hexopyranoside (10).[9]



Scheme 2

High-pressure (4+2)cycloadditions of 1 to 2 were carried out in three solvents: diethyl ether (A), a mixture of toluene and benzene 7:3 (v/v) (B), and methylene chloride (C). Three different pressures (14.5, 20, and 22 kbar) and two reaction temperatures (25 and 50°C) were applied. The re-

sults are given in Table 3 which presents the yields, proportions of *cis* and *trans* isomers, diastereoisomeric ratios as well as diastereoisomeric excesses (d.e.) for both - *endo* and *exo* additions.

Table 3. Influence of pressure on asymmetric induction in (4+2)cycloaddition 1+2

Entry	Solvent	P (kbar)	T (°C)	Yield (%)	Diastereoisomeric composition (%) 3a	3b	3c	3d	*cis:trans* ratio (3a+3c):(3b+3d)	d.e. (*endo*) (%)	d.e. (*exo*) (%)
1	A	14.5	50	42	63.0	15.5	15.0	6.5	78:22	61.5	40.9
2	A	18.0	50	74	65.0	15.0	14.0	6.0	79:21	64.6	42.9
3	A	20.0	25	15	69.0	15.0	12.0	4.0	81:19	70.4	57.9
4	A	20.0	50	75	65.5	14.5	14.5	5.5	80:20	63.8	45.0
5	A	22.0	25	18	71.5	14.5	10.5	3.5	82:18	74.4	61.1
6	A	22.0	50	80	66.0	16.0	13.0	5.0	79:21	67.1	52.4
7	B	14.5	50	40	61.5	16.0	15.5	7.0	77:23	59.1	39.1
8	B	20.0	25	11	74.0	13.0	10.0	3.0	84:16	76.2	62.5
9	B	20.0	50	71	66.0	14.5	14.0	5.5	80:20	65.0	45.0
10	B	22.0	50	73	67.5	14.0	13.5	5.0	81:19	66.7	47.4
11	C	14.5	50	58	55.0	18.0	18.0	9.0	73:27	50.7	33.3
12	C	20.0	25	20	64.0	16.0	14.0	6.0	78:22	64.1	45.5
13	C	20.0	50	79	59.5	16.5	16.5	7.5	76:24	56.6	37.5
14	C	22.0	25	21	68.5	13.5	13.5	4.5	82:18	67.1	50.0
15	C	22.0	50	86	64.0	15.0	15.0	6.0	79:21	62.0	42.9

Solvents: A - diethyl ether, B - toluene-benzene 7:3 (v/v), C - methylene chloride

The above-presented results may be summarized as follows:

1. The (4+2)cycloaddition yield increases with a rise of pressure and temperature.

2. The ratio of *cis:trans* diastereoisomers resulting from *endo* and *exo* addition, respectively, is consistent with Alder's rule;[10] the *cis* diastereoisomer content increases with a rise of pressure and diminishes with temperature elevation.

3. Within the investigated pressure and temperature ranges, the diastereoisomers of S configuration on C-6 carbon atom always predominate.

4. The value of asymmetric induction depends on pressure and temperature; a rise of pressure causes an increase in asymmetric induction, and temperature elevation - its decrease.

5. The value of asymmetric induction depends on the kind of solvent.

6. The value of asymmetric induction is higher in *endo* than in *exo* addition.

The relationships between the direction of addition of various reagents to the carbonyl group and the reagent structure, on the one hand, and reaction conditions continue to be an object of extensive studies.[11] Attempts have been made to rationalize the results by proposing various models of diastereoisomeric transition states, describing the carbonyl substrate - reagent interactions.[12-1] For our interpretation of the stereochemical course of (4+2)cycloaddition, we selected the Felkin's model[16] as modified by Nguyen Tronh Anh.[17] This model was selected on account of its suitability for an analysis of the reaction of 2,3-O-isopropylidene-D-glyceraldehyde (2) with 1,3-dienes.

Figure 1 presents the models proposed for (4+2)cycloaddition of 1-methoxybuta-1,3-diene (1) to the formyl group of 2. If it is assumed that the 2,3-O-isopropylidene grouping in 2 does not fully differentiate the diastereotopic sides of the carbonyl group, then two approaches of diene to dienophile are possible (Fig. 1), with predominance of the approach from the less hindered side, which leads to adducts 3a and 3b. In both cases additional differentiation resulting from *endo* and *exo* addition is involved. Therefore, *endo* addition affords adducts 3a and 3c of configurations 2R:6S and 2S:6R, respectively, and *exo* addition - adducts 3b and 3d of configurations 2S:6S and 2R:6R, respectively. The magnitude of asymmetric induction depends on the "pseudo-equilibria"[18] of four transition states presented in Fig. 1. These "equilibria" should be related to reaction parameters such as solvation, temperature, and pressure.

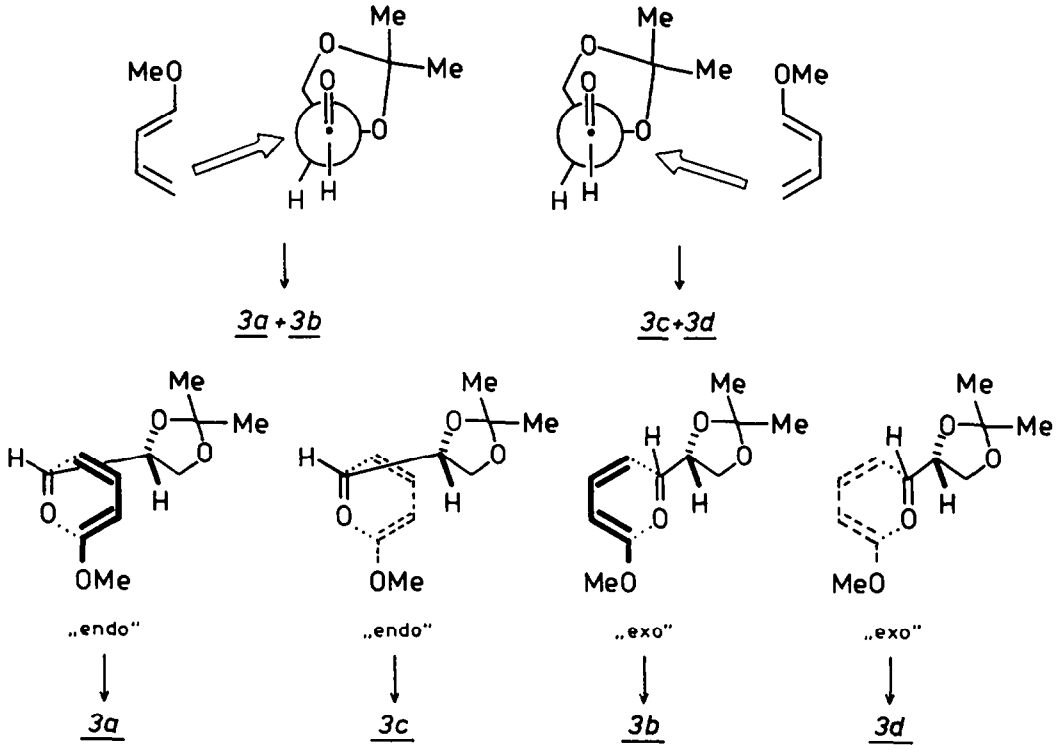


Figure 1. The stereochemical models proposed for (4+2)cycloaddition of 1 to 2

Under high-pressure conditions, the transition state leading to adduct 3a was preferred in all solvents investigated, this suggesting that it is more compact than three other ones. The probability of formation of this active complex augments with increasing pressure which is in practice the most important parameter determining the optical yield. In *exo* addition the transition state leading to adduct 3b, as compared with that leading to adduct 3d, is favoured by pressure; the difference in their compactness is smaller than that for *endo* addition.

We offer general conclusions from the present results and from other recent observations.[8,19-21] Asymmetric Diels-Alder reactions using heterodienophiles of glyceraldehyde type should be carried out under maximally high pressure and in solvents with high freezing pressures, whose solvation effects on the direction of asymmetric induction are additive with the effect of pressure. Differences in the bulkiness of substituents on the inducing centre of the dienophile should be as big as possible. Fulfilling of these conditions should afford very high optical yields.

Since (4+2)cycloaddition products of D-glyceraldehyde derivatives are versatile synthons in total syntheses of natural compounds,[11,22,23] the utility of the above generalization, when extended beyond the scope of our investigations, is selfevident.

EXPERIMENTAL

Boiling points refer to air-bath temperatures. The ^{1}H NMR spectra were recorded with a Jeol JNM-4H-100 or Nicolet 360 MHz spectrometer for $CDCl_3$ solutions (δ scale, TMS=0 ppm). The IR spectra were taken with a Beckman Acculab spectrophotometer on films. Optical rotations were measured with a Perkin-Elmer spectropolarimeter. Column chromatography was performed on Merck Kieselgel 60 (230--400 mesh). All chromatographic separations were monitored by TLC and/or ^{1}H NMR. TLC was performed 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 a working volume of about 90 mL. Construction details have been reported previously.[1] The pressure inside the working volume was measured with a calibrated manganine coil with an accuracy of $\pm$0.1 kbar. The accuracy of temperature measurements using a calibrated thermocouple was $\pm$1°C.

trans-1-Methoxybuta-1,3-diene (1) was prepared according to the literature.[24] 2,3-O-Isopropylidene-D-glyceraldehyde (2) was prepared from D-mannitol according to Kierstead's modification[25] of the known procedure.[26]

(4+2)Cycloaddition of 1-methoxybuta-1,3-diene (1) to 2,3-O-isopropylidene-D-glyceraldehyde (2). Typical high-pressure procedure. A solution of 1 (0.7 mL, 6 mmol) and freshly prepared 2 (404 mg; 3 mmol) in methylene chloride (4 mL) was charged into a Teflon ampoule[27] which was placed in a high-pressure vessel filled with pentane as a transmission medium. The pressure was slowly elevated to 22 kbar at 50°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). The first fraction contained the diastereoisomeric mixture 3a+3b (437 mg, 68%). The second fraction contained the diastereoisomeric mixture 3c+3d (116 mg, 18%).

Correlation of the diastereoisomeric mixture of (2R:6S:1'R)- and (2S:6S:1'R)-2-methoxy-6-(1',2'-dihydroxyethyl)-5,6-dihydro-2H-pyran 1',2'-isopropylidene acetal (3a+3b) with (2S:6S)-2-methoxy-6-hydroxymethyltetrahydropyran (8). The mixture 3a+3b (642 mg, 3 mmol) was dissolved in ethyl acetate (30 mL) and hydrogenated in the presence of platinum black, until absorption of hydrogen ceased. The crude mixture 4a+4b (615 mg) was refluxed in 50 mL of an 1% methanolic solution of hydrogen chloride for 1.5 h. The reaction mixture was neutralized with Amberlite IR-45 and methanol was evaporated. The residue was distilled in *vacuo* to yield 442 mg (88%) of the mixture 5a+5b, which was chromatographed on a silica gel column with a mixture of hexane and ethyl acetate 2:8 (v/v). The first fraction contained pure diol 5b (211 mg) which, after evaporation of the eluent, was dissolved in ethyl ether (20 mL); the solution was added to an aqueous solution of sodium periodate (580 mg/20 mL) and stirred at room temperature for 0.5 h. After separation, the aqueous layer was extracted three times with ethyl ether (3×10 mL). The combined organic layer and extracts were dried over anhydrous potassium carbonate and the solvent was evaporated. The crude product - aldehyde 7 was subjected to reduction with lithium aluminum hydride, carried out in anhydrous ethyl ether at room temperature for 2 h. After conventional workup, the saturated alcohol 8 was obtained as an oil, b.p. 55°C/0.4 mm Hg, $(\alpha)_{589}^{20}$ +129.7° (c 2.0, benzene); (43 mg, 30%).

Diastereoisomerically pure (2R:6S:1'R)-, (2S:6S:1'R)-, (2S:6R:1'R)-, and (2R:6R:1'R)-2-methoxy-6-(1',2'-dihydroxyethyl)tetrahydropyran 1',2'-isopropylidene acetal (4a, 4b, 4c, and 4d). Hydrogenation of the mixture 3a+3b in ethyl acetate in the presence of platinum black, followed by chromatographic separation on a silica gel column with a mixture of hexane and ethyl acetate 95:5 (v/v), afforded pure 4a and 4b in almost quantitative yield. Likewise, from the mixture 3c+3d pure compounds 4c and 4d were obtained.

Diastereoisomerically pure (2R:6S:1'R)- and (2S:6S:1'R)-2-methoxy-6-(1',2'-dihydroxyethyl)tetrahydropyran (5a and 5b) and their 1',2'-di-O-acetyl derivatives (6a and 6b). Hydrolysis of the mixture 4a+4b with an 1% methanolic solution of hydrogen chloride, followed by acetylation with acetyl anhydride in pyridine, afforded - after conventional workup - a crude mixture 6a+6b (overall yield 70%). The mixture was chromatographed on a silica gel column with a mixture of hexane and ethyl acetate 9:1 (v/v) to give pure di-O-acetyl derivatives 6a and 6b. Compounds 6a and 6b were separately reduced with lithium aluminum hydride in anhydrous ethyl ether to afford, in 90% yield, diastereoisomerically pure diols 5a and 5b, respectively.

Diastereoisomerically pure (2S:6R:1'R)- and (2R:6R:1'R)-2-methoxy-6-(1',2'-dihydroxyethyl)tetrahydropyran (5c and 5d) and their 1',2'-di-O-acetyl derivatives (6c and 6d). Identical treatment (hydrolysis, acetylation) of the mixture 4c+4d yielded a crude mixture 6c+6d (overall yield 77%). The mixture was chromatographed on a silica gel column with a mixture of hexane and ethyl acetate 9:1 (v/v), to give diastereoisomerically pure 6c and 6d. Compounds 6c and 6d were separately reduced with lithium aluminum hydride to afford diastereoisomerically pure diols 5c and 5d, respectively.

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