actions, these stock solutions were serially diluted, and concentrations were calculated on the basis of the volume ratios.

Acknowledgment. We thank J. A. Cella for fruitful discussion and encouragement and C. G. Overberger for the significant suggestion that initiated this work.

Registry No. 1a, 50-29-3; 1b, 2971-22-4; 1c, 4413-31-4; 1d, 72-43-5; 1e, 2971-36-0; 2a, 72-55-9; 2b, 2779-69-3; 2c, 5432-01-9; 2d, 2132-70-9; 2e, 14868-03-2; 2-(o-hydroxyphenyl)-2-(p-hydroxyphenyl)-1,1,1-trichloroethane, 6621-68-7; methylamine, 74-89-5; ammonia, 7664-41-7; 2,2-bis(4-hydroxyphenyl)-1-chloroethylene, 68118-92-3; trichloroacetaldehyde, 75-87-6; chlorobenzene, 108-90-7; benzene, 71-43-2; methylbenzene, 108-88-3; methoxybenzene, 100-66-3; phenol, 108-95-2; 2-(o-hydroxyphenyl)-2-(p-hydroxyphenyl)-1,1-dichloroethene, 71032-16-1.

Stereochemistry of Diels–Alder Reactions at High Pressure. 4. Asymmetric Induction in High-Pressure Cycloadditions of (*R*)-(−)-Menthyl Glyoxylate and Symmetric 1,3-Dienes[1]

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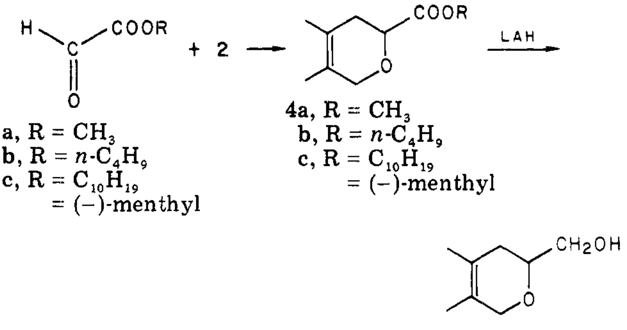
Received December 18, 1978

High-pressure cycloaddition of (*R*)-(−)-menthyl glyoxylate and 2,3-dimethylbuta-1,3-diene and cyclohexa-1,3-diene was studied. Optical yields of the cycloadditions were 2.4–20.9%, and the induced absolute configuration was *R* in all cases. Results were interpreted by using the concept of parallel formation of four endo boundary active complexes corresponding to the transoid and cisoid conformation of (*R*)-(−)-menthyl glyoxylate in the transition state.

We have recently observed the considerable effect, heretofore unreported, of high pressure on the direction and magnitude of asymmetric induction in the Diels–Alder reaction between unsymmetric 1-methoxybuta-1,3-diene and the heterodienophile (*R*)-(−)-menthyl glyoxylate (**1c**).[1,2]



1a, R = CH_3
b, R = n-C_4H_9
c, R = $C_{10}H_{19}$ = (−)-menthyl

4a, R = CH_3
b, R = n-C_4H_9
c, R = $C_{10}H_{19}$ = (−)-menthyl

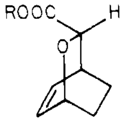
5

It would be worthwhile to extend stereochemical studies to high-pressure [2 + 4] heterocycloaddition of symmetric 1,3-dienes in order to describe more precisely the cycloaddition transition states.

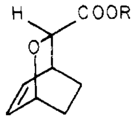
In this study we have selected two representative symmetric dienes: 2,3-dimethylbuta-1,3-diene (**2**) and cyclohexa-1,3-diene (**3**). Compound **2** is known[3] to react with alkyl glyoxylates (**1a**,**b**) at high temperatures (140 °C), affording low yields of the racemic esters of 4,5-dimethyl-2,3-dihydro-2*H*-pyran-2-carboxylic acid (**4a**,**b**), which have only one chiral center at atom C-2. Reduction of adducts **4** with lithium aluminum hydride leads to the racemic alcohol **5**.

Drastic conditions (140 °C) and low product yields of the thermal reaction between **1a** and **2** exclude its application to stereochemical studies. Under the reaction conditions the products of cycloaddition are very likely to be partly decomposed. On the other hand, application of high pressure allows the reaction to occur under mild conditions. Thus, use of (*R*)-(−)-menthyl glyoxylate (**1c**) under such mild conditions could be expected to bring about asymmetric induction.

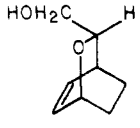
The second symmetric 1,3-diene which we selected, cyclohexa-1,3-diene (**3**), reacts with **1b** at 120 °C in satisfactory yield affording a mixture of endo (**6a**) and exo (**7a**) adducts in a ratio of 9:1.[4] Lithium aluminum hydride reduction of endo adduct **6a**, separable by column chromatography from exo adduct **7a**, affords alcohol **8**. Clearly it is necessary to establish only the absolute configuration of atom C-3, since the configuration of the other two chiral centers results from the diastereomeric geometries of the molecules.



6a, R = n-C_4H_9
b, R = $C_{10}H_{19}$ = (−)-menthyl
c, R = H



7a, R = n-C_4H
b, R = $C_{10}H_{19}$ = (−)-menthyl
c, R = H



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Thermal endo addition at 120 °C of **1c** and **3** gives both diastereomers of adduct **6b** in equal amounts, which after reduction afford racemic alcohol **8**. The same considerations apply to exo addition. Thus, asymmetric induction could be expected from application of high pressure.

Results and Discussion

Determination of the absolute configuration of ester **4c**, formed by asymmetric synthesis, was based on analysis of the optical and spectral properties of alcohol **5** as compared

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(1) Part 3: J. Jurczak, *Pol. J. Chem.*, in press.

(2) J. Jurczak and B. Baranowski, *Pol. J. Chem.*, **52**, 1857 (1978).

(3) O. Achmatowicz Jr., M. Chmielewski, J. Jurczak, L. Kozerski, and A. Zamojski, *Org. Magn. Reson.*, **4**, 537 (1972).

(4) O. Achmatowicz Jr., J. Jurczak, and J. St. Pyrek, *Rocz. Chem.*, **49**, 1831 (1975).

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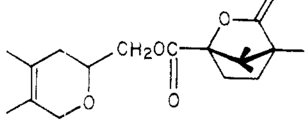
Table I. Cycloaddition of 2,3-Dimethylbuta-1,3-diene (2) with (*R*)-(−)-Menthyl Glyoxylate (1c) in Different Solvents under High Pressure at 20 °C

		adduct 4c			alcohol 5			
solvent	ΔP, kbar	yield, %	$[\alpha]^{20}_{578}$ in C_6H_6, deg	*c*	$[\alpha]^{20}_{578}$ in CH_2Cl_2, deg	*c*	abs conf at C-2	optical yield, %
$C_6H_5CH_3$	6.2	22	−56.2	0.98	+30.6	2.25	*R*	16.2
$C_6H_5CH_3$	7.5	28	−55.7	1.05	+34.7	1.80	*R*	18.4
$C_6H_5CH_3$	8.9	32	−55.3	1.04	+39.4	3.40	*R*	20.9
n-C_6H_{14}	7.1	19	−56.5	1.07	+29.5	2.60	*R*	15.7
n-C_6H_{14}	8.4	26	−56.0	1.00	+33.5	1.40	*R*	17.8
n-C_6H_{14}	9.5	29	−55.9	1.05	+36.5	2.07	*R*	19.4
n-C_6H_{14}	10.2	30	−55.6	1.01	+38.7	1.95	*R*	20.5
CH_2Cl_2	6.4	34	−66.5	1.03	+4.5	4.00	*R*	2.4
CH_2Cl_2	7.0	40	−65.6	1.02	+7.5	4.00	*R*	4.0
CH_2Cl_2	7.9	42	−65.0	1.08	+12.3	4.30	*R*	6.5
CH_2Cl_2	8.3	46	−64.5	1.01	+14.1	2.55	*R*	7.5

with those of compounds of known configuration. Lithium aluminum hydride reduction of adduct **4c**, formed by high-pressure cycloaddition of **1c** and **2**, afforded dextrorotatory alcohol **5**. Cycloaddition of **1c** and buta-1,3-diene, carried out under the same conditions, yielded adduct **9**, from which dextrorotatory alcohol **10** was obtained after reduction. Hydrogenation of alcohol **10** in the presence of platinum catalyst afforded levorotatory saturated alcohol **11** of absolute configuration *R*, as earlier established by Lemieux and Martin via chemical methods (Scheme I).[5]

A similar configurational correlation applies to alcohol *trans*-(+)-**13**, whose absolute configuration 6*R* was established earlier by two independent chemical pathways.[6,7] Hydrogenation of alcohol (+)-**13** led to levorotatory saturated alcohol **14**, which, of course, retains its 6*R* configuration.[7] On the basis of these correlations, the chiral center of adduct **4c**, induced as a result of high-pressure asymmetric synthesis, was assigned absolute configuration *R*.

Absolute rotation of alcohol (*R*)-(+)-**5** was determined by separation of the racemate by crystallization of the camphanic acid ester **15** according to our previously described procedure.[8] Absolute rotations of pure enantiomer (*R*)-(+)-**5**, measured in methylene chloride (*c* 2.43), were $[\alpha]^{20}_{589}$ +178.6°, $[\alpha]^{20}_{578}$ +188.4°, $[\alpha]^{20}_{546}$ +215.0°, and $[\alpha]^{20}_{436}$ +382.5°.



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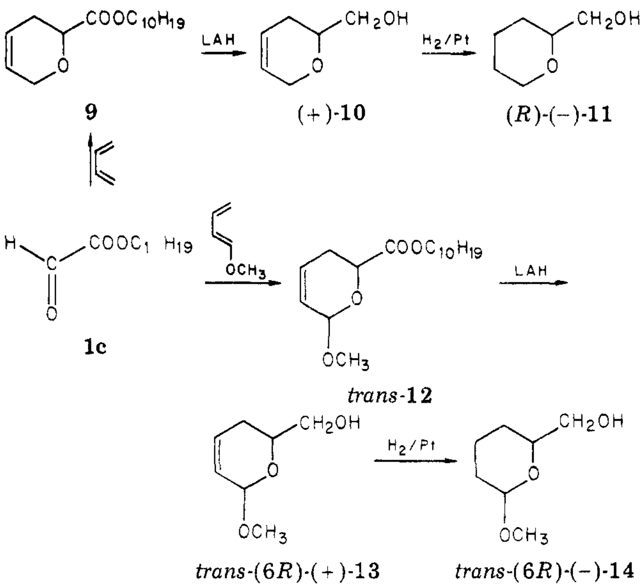
High-pressure cycloadditions of **1c** and **2** were carried out in three solvents: toluene, *n*-hexane, and methylene chloride. Results are given in Table I, which presents the yields and specific rotations of adduct **4c**, as well as the optical yields and configuration of the center induced on atom C-2 of alcohol **5**.

In all three solvents, the high-pressure reactions gave moderate yields, 19–46%, of adduct **4c**, with absolute configuration 2*R*, regardless of the pressure applied; optical yields clearly depended on pressure. Concerning the effect of solvents, we noted that in toluene an increase in pressure from 6.2 to 8.9 kbar increased the optical yield from 16.2 to 20.9%, and a similar relationship was observed in *n*-hexane. In methylene chloride optical yields were much lower, although the nature of their dependence on pressure resembled that observed for the other solvents. Dependence of optical yields on pressure is presented graphically in Figure 1.

Scheme I



Thermal cycloaddition of **1c** and **3** yielded a mixture of four diastereomeric adducts: *endo*-**6bI** and -**6bII** and *exo*-**7bI** and -**7bII**. Fractions comprising a mixture of two exo diastereomers (**7bI**, **7bII**) and, separately, two pure endo diastereomers (**6bI**, **6bII**) were isolated by column chromatography on silica gel. Determination of the diastereomeric purity and assignment of the endo–exo configuration was based on the difference in the chemical shift of proton H-3.[4]

The hydrolysis of the isolated (*R*)-(−)-menthyl esters led in the case of a mixture of exo adducts (**7bI**, **7bII**) to racemic acid **7c**, whereas endo adducts **6bI** and **6bII** yielded the two respective enantiomers of acid **6c**, with specific rotations $[\alpha]^{20}_{589}$ −39.5° ($CHCl_3$) and $[\alpha]^{20}_{589}$ +40.0° ($CHCl_3$). Adduct **6bII**, which afforded dextrorotatory acid **6c**, was catalytically hydrogenated, and the resulting mixture of the two compounds **16** and **17** was separated on a silica gel column. The hydrolysis of product **17** yielded levorotatory hexahydromandelic acid **18**, known to have absolute configuration *R* (Scheme II).[9] Thus,

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[5] R. U. Lemieux and J. C. Martin, *Carbohydr. Res.*, **13**, 139 (1970).
[6] J. Jurczak and A. Zamojski, *Tetrahedron*, **28**, 1505 (1972).
[7] A. Konowal, J. Jurczak, and A. Zamojski, *Tetrahedron*, **32**, 2957 (1976).
[8] J. Jurczak and A. Konowal, *Pol. J. Chem.*, **52**, 1967 (1978).
[9] H. Lettré, H. Barbeck, and H. Staunau, *Ber. Dtsch. Chem. Ges.*, **69**, 1597 (1936).

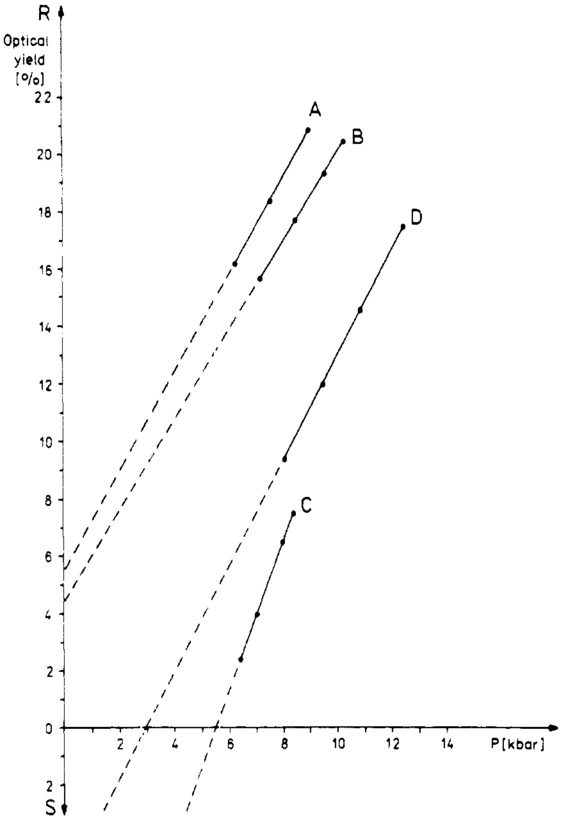
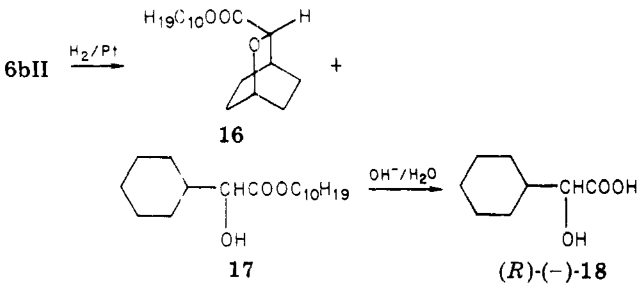


Figure 1. Dependence of optical yield on pressure in the reactions of **1c** with **2** carried out in toluene (A), *n*-hexane (B), and methylene chloride (C) and in the reaction of **1c** with **3** carried out in a mixture of toluene and benzene (D).

Scheme II



endo-(+)-2-oxabicyclo[2.2.2]oct-5-ene-3-carboxylic acid (**6c**) may reasonably be assigned the absolute configuration 1*S*,3*R*,4*R* and, likewise, the acid (−)-**6c** may be assigned configuration 1*R*,3*S*,4*S*.

Lithium aluminum hydride reduction of endo adduct **6bII**, giving as a result of hydrolysis acid (+)-**6c**, led to levorotatory alcohol **8**, with an assigned absolute configuration 3*R*. The absolute rotations of pure enantiomers, obtained either by reduction of the corresponding diastereomerically pure adducts **6bI** and **6bII** or by separation of the racemate by crystallization of the camphanic ester of alcohol (+)-**8**, are presented in Table II.

High-pressure cycloadditions of **1c** and **3** were carried out in three solvent systems: methylene chloride, *n*-hexane, and a 7:3 molar ratio mixture of toluene and benzene. Recently, Baranowski[10] has observed an increase in the solidification pressure of binary mixtures of chloroform and benzene compared with that of either pure component. This fact led us to apply a mixed aromatic solvent. Solidification pressures at 20 °C of pure toluene and benzene are 8.8 and 0.5 kbar, respectively, whereas the freezing pressure of a mixture of these solvents in a 7:3 molar ratio is about 15 kbar. This permitted us to increase considerably the applied pressure.

Table II. Specific Rotations (deg) in Chloroform of Enantiomeric Alcohol 8 Obtained in Different Ways

	reduction of **6bI** *c* 2.25	reduction of **6bII** *c* 2.18	separation of camphanic ester **19** *c* 2.03
$[\alpha]^{20}_{578}$	+92.4	−93.8	−93.1
$[\alpha]^{20}_{546}$	+105.8	−107.3	−106.6
$[\alpha]^{20}_{436}$	+186.1	−189.0	−187.7

The results of high-pressure cycloadditions of **1c** and **3** are presented in Table III, giving yields of adduct **6b**, as well as the optical yields and absolute configuration of the induced center on atom C-3 of alcohol 8.

In all of the solvents we investigated, the high-pressure reactions proceeded in moderate yields (23–39%), leading essentially to pure endo adduct **6b**. The yield of exo adduct **7b** did not exceed 5%. The absolute configuration of the predominant diastereomer **6bII** was assigned as 1*S*,3*R*,4*R* (cf. Experimental Section). The dependence of optical yield on pressure was investigated only in aromatic solvents for **6b**. It was observed that an increase in pressure from 8.0 to 12.4 kbar induces a rise in optical yield from 9.4 to 17.5% (Figure 1).

The results so far obtained[6,11-15] of thermal asymmetric Diels–Alder reactions using open-chain dienophiles, i.e., esters of acrylic, fumaric, or glyoxylic acids and optically active alcohols, may be summarized briefly. Optical purities of the adducts obtained in thermal reactions are low (~1–13%). These low values are rather unexpected. Assuming a rigid transition state for the Diels–Alder reaction, higher induction would be anticipated. Reactions performed in the presence of Lewis acid catalyst ($AlCl_3$, BF_3, $SnCl_4$) afford adducts of high optical purity (46–88%). The direction of induction, i.e., the configuration of the chiral centers in the adducts, is dependent on such factors as catalysts, temperature, and solvents.

According to Walborsky,[12] the results of asymmetric induction in the thermal cycloaddition of buta-1,3-diene and (*R*)-(−)-dimenthyl fumarate may be explained by a "Prelog-like" conformation of the ester in the transition state, a transoid arrangement of the ethylenic bond relative to the carbonyl groups. On the other hand, when the same cycloaddition is carried out in the presence of $AlCl_3$, yielding an adduct of markedly increased optical purity and changed absolute configuration, a cisoid or twisted conformation of the ester should probably be assumed.

In an earlier study[6] we observed that the optical yields of adducts resulting from cycloaddition of 1-methoxybuta-1,3-diene and optically active glyoxylates are not directly related to the bulkiness of the substituents at chiral centers, as found on the other hand in Prelog's synthesis of atrolactic acid esters.[16] However, when all other reaction parameters are fixed, the configuration of the C-6 center in adduct **12** has been found to depend on the solvent used. For example, in methylene chloride, an

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(10) B. Baranowski, *Pol. J. Chem.*, **52**, 1789 (1978).

(11) A. J. Korolev and V. J. Mur, *Dokl. Akad. Nauk SSSR*, **59**, 251 (1948); A. J. Korolev, V. J. Mur, and V. G. Avaykyan, *Zh. Obshch. Khim.*, 34, 708 (1964).

(12) H. M. Walborsky, T. Barash, and T. C. Davis, *J. Org. Chem.*, **26**, 4778 (1961); *Tetrahedron*, **19**, 2333 (1963).

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(14) R. F. Farmer and J. Hamer, *J. Org. Chem.*, **31**, 2418 (1966).

(15) O. Cervinka and O. Kriz, *Collect. Czech. Chem. Commun.*, **33**, 2342 (1968).

(16) V. Prelog, *Helv. Chim. Acta*, **36**, 308 (1953); V. Prelog, O. Ceder, and M. Wilhelm, *ibid.*, **38**, 303 (1955).

Table III. Cycloaddition of Cyclohexa-1,3-diene (3) with (*R*)-(−)-Menthyl Glyoxylate (1c) in Different Solvents under High Pressure at 20 °C

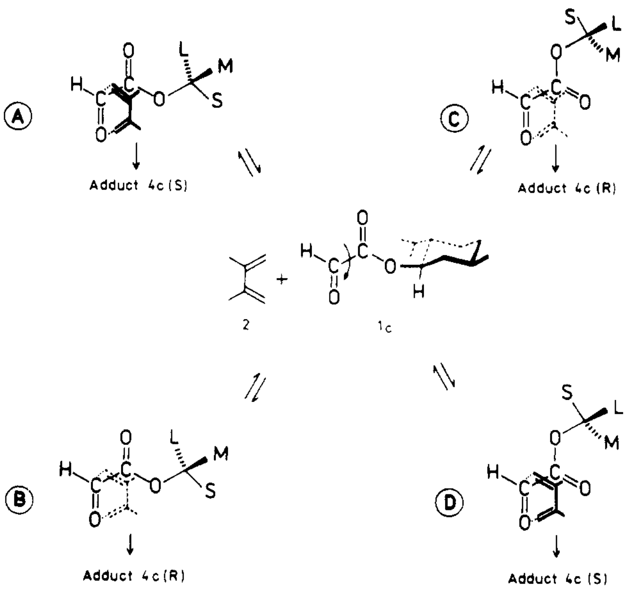
solvent	ΔP, kbar	adduct 6b yield, %	alcohol 8: $[\alpha]^{20}_{546}$ in CH_2Cl_2, deg	*c*	abs conf at C-3	optical yield, %
$7C_6H_5CH_3 + 3C_6H_6$	8.0	25	−10.1	2.08	*R*	9.4
$7C_6H_5CH_3 + 3C_6H_6$	9.4	27	−12.9	2.45	*R*	12.0
$7C_6H_5CH_3 + 3C_6H_6$	10.8	31	−15.7	2.70	*R*	14.6
$7C_6H_5CH_3 + 3C_6H_6$	12.4	37	−18.9	2.26	*R*	17.5
n-C_6H_{14}	8.4	23	−8.5	1.80	*R*	7.9
CH_2Cl_2	7.9	39	−5.4	2.58	*R*	5.0

absolute *S* configuration is induced, but in benzene an excess of the *R* compound is obtained.

Studies of the effect of pressure on asymmetric induction in the cycloaddition of 1-methoxybuta-1,3-diene and (*R*)-(−)-menthyl glyoxylate have fully confirmed the conclusions concerning the influence of the reaction parameters on the magnitude and direction of this induction.[1,2] In cycloadditions carried out in toluene solvent, *R* configurations are induced at carbon atom C-6 of adduct **12** in all cases. Optical yield markedly increases with a rise in pressure: from 3.6% at 1 atm to 8.8% at 8.7 kbar. For the reactions carried out in methylene chloride, an increase in pressure reduces the optical yield from 6.2% at 1 atm to 2.4% at 7.9 kbar. A tendency to induce the *S* configuration at C-6 in adduct **12** is consistently observed throughout the whole range of pressures applied. For *n*-hexane solvent and under atmospheric pressure, the *S* configuration with an optical yield of 4% is induced. The optical yield drops with a rise in pressure. It can be extrapolated to reach the zero point within the range of 6.8–9.3 kbar and then to increase with a further rise in pressure. Changes in optical yield are associated with a change in the direction of induction: *S* configuration is first induced between 3.1 and 6.8 kbar; subsequently, after transition through the zero point, *R* configuration is induced above 9.3 kbar.

The results of asymmetric induction in all Diels–Alder reactions studied so far, thermal, catalytic, and high-pressure, can be rationalized on the basis of the concept of parallel transition states.[6] In accord with current assumptions,[17] diene reactions involving asymmetric induction result from the different accessibility of the two sides of the chiral dienophile double bond, e.g., the formyl group in glyoxylate. Therefore, it is necessary to consider the conformation of the dienophile at the stage of active complex formation with the diene. However, little is known about the conformations of open-chain dienophiles in the transition state of the Diels–Alder reaction. By analogy to the α,β-unsaturated carbonyl system of cyclic dienophiles possessing either anti or syn C═C—C═O conformations, e.g., maleic anhydride, *p*-benzoquinone,[18] α-methylenecyclopentanone and cyclohexanone,[19] both cisoid and transoid conformations of acyclic dienophiles should be possible. On the basis of calculations by Salem[20] and his own subsequent kinetic studies, Cardenas[21] proposed a model for the transition state in which the dienophile prefers the cisoid conformation for the reactions of hexachlorocyclopentadiene with aliphatic diene dienophiles. However, an alternative proposal[6] suggests that parallel formation of active complexes with different conformations of acyclic dienophiles is possible. Furthermore, it has been assumed that the differences in free energy ($\Delta\Delta G^{\ddagger}$) between such complexes are small.

Scheme III



Consequently, for the high-pressure cycloaddition of 2,3-dimethylbuta-1,3-diene (**2**) and (*R*)-(−)-menthyl glyoxylate (**1c**), we postulate parallel formation of four complexes, differing in geometry, which correspond to the endo addition of **1c** in cisoid and transoid conformations (Scheme III).

According to Scheme III, **1c** in a transoid conformation induces predominantly the configuration 2*S* at the chiral center in adduct **4c** as a result of competition between transition states A and B, the former being favored. The same dienophile in a cisoid conformation induces predominantly the opposite configuration at C-2 as a result of competition between C and D, the former also being favored. The magnitude of asymmetric induction is a result of the "pseudo equilibria" A $\rightleftharpoons$ B $\rightleftharpoons$ C $\rightleftharpoons$ D, to which we shall refer to as "probabilities of formation of active complexes". The configuration of the induced chiral center in adduct **4c** should be related to the "pseudo equilibrium" A $\rightleftharpoons$ C. In turn, this "equilibrium" should depend on reaction parameters such as solvation, dipole moment of the solvent, temperature, and pressure.

Under high-pressure reaction conditions the active complex C was preferred in all solvents investigated. This transition state is responsible for formation of adduct **4c** with an absolute *R* configuration. On the other hand, the optical yield increased with a rise in pressure in all solvents used (cf. Figure 1). Extrapolation of the plots presented

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[17] J. J. Klabunowski, "Asymmetrische Synthese", Deutscher Verlag der Wissenschaften, Berlin, 1963; D. R. Boyd and M. A. McKervey, *Q. Rev., Chem. Soc.*, **22**, 95 (1968).

[18] M. Mousseron, R. Jacquier, and H. Christol, *Bull. Soc. Chim. Fr.*, 346 (1957); R. Jacquier and M. Mousseron, *ibid.*, 1653 (1956).

[19] N. V. Jelagina, V. M. Brusnikina, and B. A. Kazanskij, *Dokl. Akad. Nauk SSSR*, **106**, 1015 (1956); N. V. Jelagina, T. V. Stabnikova, and B. A. Kazanskij, *ibid.*, **124**, 1243 (1959); N. V. Jelagina, M. S. Martinkova, and B. A. Kazanskij, *Zh. Obshch. Khim.*, **29**, 4011 (1959).

[20] L. Salem, *J. Am. Chem. Soc.*, **90**, 553 (1968).

[21] C. G. Cardenas, *Chem. Commun.*, 134 (1970).

in Figure 1 to "zero conditions", atmospheric pressure, leads us to predict[22] the expected optical yield and the direction of asymmetric induction for this reaction when proceeding under atmospheric pressure and at room temperature.[23] One can expect in toluene an optical yield of about 5.5% and an absolute *R* configuration and in *n*-hexane an optical yield of about 4.5% and an *R* configuration. In methylene chloride an optical yield of about 14% and a change of absolute configuration to *S* can be expected.

The results of the above predictions and the preference for transition state C under high pressure suggest that for toluene solvent the influence of pressure is additive with solvation effect, while for methylene chloride the influences of pressure and solvation are antagonistic.

Results of asymmetric induction in high-pressure endo cycloaddition of cyclohexa-1,3-diene and (*R*)-(−)-menthyl glyoxylate (cf. Table III, Figure 1) are in good agreement with the present interpretation.

We offer general conclusions from the summary of our investigation and other recent observations.[1,2]

The concept of parallel transition states seems to be a useful tool for interpretation of asymmetric induction in Diels–Alder reactions.

Asymmetric Diels–Alder reactions using heterodienophiles of glyoxylate type should be carried out under maximally high pressure and in solvents with high freezing pressures, whose solvation effect on the direction of induction are additive with effect of pressure. Differences in the bulkiness of substituents on the inducing center of the dienophile should be as large as possible, and finally the structure of the diene should be maximally symmetric. Fulfilling these conditions should afford very high optical yields.

Since [2 + 4] cycloaddition products of heterodienophiles are versatile synthons in total syntheses of natural compounds, the utility of the above generalization when extended beyond the scope of our investigation is self-evident.

Experimental Section

Boiling points refer to air-bath temperatures. Melting points (uncorrected) were determined on a Kofler block. ^{1}H NMR spectra were recorded with a JEOL JNM-4H-100 spectrometer for CDCl$_3$ solutions (δ scale, δ(Me$_4$Sei) 0). IR spectra were taken with a Unicam SP-200 spectrophotometer on films for liquids and KBr disks for solids. Polarimetric measurements were performed with a Perkin-Elmer 141 automatic polarimeter. Silica gel G (Merck) was used for TLC, and silica gel, 100–200 mesh (Machery-Nagel), was used for column chromatography.

2,3-Dimethylbuta-1,3-diene and cyclohexa-1,3-diene were redistilled commercial (Fluka) reagents. (−)-ω-Camphanyl chloride was a commercial product (Chemipan, Warsaw). (*R*)-(−)-menthyl glyoxylate was prepared according to our earlier procedure.[25]

(*R*)-(−)-Menthyl Ester of 4,5-Dimethyl-2,3-dihydro-2*H*-pyran-2-carboxylic Acid (4c). Typical High-Pressure Procedure. The high-pressure apparatus[26] was filled with the reaction mixture [1.06 g (5 mmol) of **1c**, 0.82 g (10 mmol) of **2** and 10 mg of hydroquinone in 10 mL of methylene chloride] and the pressure was slowly elevated to 8.3 kbar at 20 ± 1 °C.[27] After stabilization of the pressure, the reaction mixture was kept under these conditions for 20 h. After decompression, the solvent was evaporated, the residue was dissolved in 50 mL of *n*-hexane, and the solution was filtered to remove a small amount of polymers. The filtrate was concentrated under reduced pressure and the residue was chromatographed on a silica gel column with a mixture of ligroin and ether 9:1 (v/v). The first fraction contained compound **4c**: 0.68 g (46%) (oil); bp 107–108 °C (0.05 mm); $[\alpha]^{20}_{578}$ −64.5° (*c* 1.01, C$_6$H$_6$). IR and ^{1}H NMR spectra were in good agreement with those of adducts **4a** and **4b** obtained previously by another route.[3,28] Anal. Calcd for C$_{18}$H$_{30}$O$_3$: C, 73.4; H, 10.3. Found: C, 73.1; H, 10.6. The second fraction [elution with a mixture of ligroin and ether (1:1)] contained pure (*R*)-(−)-menthyl glyoxylate (0.5 g).

2-(Hydroxymethyl)-4,5-dimethyl-2,3-dihydro-2*H*-pyran (5). Lithium aluminum hydride reduction of **4c** in ether solution at room temperature and workup yielded **5** (88%): bp 59–61 °C (0.5); IR (film) 3420 (OH), 1140, 1070 (COC) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.05 (s, 2 H, H-6, H-6′), 3.67 (m, 3 H, H-2 and CH$_2$O), 2.70 (bs, 1 H, OH), 1.80 (m, 2 H, H-3, H-3′), 1.70, 1.60 (2 s, 6 H, 2 CH$_3$). Anal. Calcd for C$_8$H$_{14}$O$_2$: C, 67.8; H, 9.7. Found: C, 67.6; H, 9.9.

Correlation of Adduct 9 with (*R*)-(−)-2-(Hydroxymethyl)tetrahydropyran (11). High-pressure cycloaddition of buta-1,3-diene and **1c** in toluene (8.0 kbar, 20 °C) and workup yielded adduct **9** (20%). Lithium aluminum hydride reduction of **9** gave unsaturated alcohol **10** (83%): bp 90–92 °C (15 mm); $[\alpha]^{20}_{578}$ +12.1° (*c* 2.09, CH$_2$Cl$_2$). A sample of alcohol **10** was hydrogenated in the presence of platinum black in an ethyl acetate solution. After conventional workup, the saturated alcohol **11** was obtained (91%): bp 85–88 °C (15 mm); $[\alpha]^{20}_{589}$ −3.3° (*c* 1.12, H$_2$O).

Synthesis and Resolution of the (−)-ω-Camphanic Ester of (±)-2-(Hydroxymethyl)-4,5-dimethyl-2,3-dihydro-2*H*-pyran (15). To the solution of (±)-**5** (7.1 g, 50 mmol) in 150 mL of anhydrous pyridine was added (−)-ω-camphanyl chloride (16.3 g, 75 mmol), and the mixture was left at room temperature. After 48 h the solution was poured into ice–water and extracted several times with CHCl$_3$. Combined chloroform extracts were washed with water, dried (MgSO$_4$), and evaporated to dryness. Crude ester **15** (89%) was crystallized four times from anhydrous ether, yielding 3.7 g of pure (+)-**15**: mp 104–105 °C; $[\alpha]^{20}_{578}$ +24.4° (*c* 1.20, C$_6$H$_6$). A Eu(fod)$_3$-shifted ^{1}H NMR spectrum showed only methyl group signals of a single diastereomer. Anal. Calcd for C$_{18}$H$_{26}$O$_5$: C, 67.1; H, 8.1. Found: C, 67.0; H, 8.3. Lithium aluminum hydride reduction of (+)-**15** yielded enantiomeric pure alcohol (+)-**5** (for specific rotation, see Results).

Synthesis and Resolution of the (−)-ω-Camphanic Ester of (±)-*endo*-3-(Hydroxymethyl)-2-oxabicyclo[2.2.2]oct-5-ene (19). In the above described manner the ester **19** was obtained and resolved. Six crystallizations from a mixture of anhydrous ether and *n*-hexane [1:1 (v/v)] gave the pure ester (−)-**19**: mp 104–105 °C; $[\alpha]^{20}_{578}$ −34.8° (*c* 1.70, C$_6$H$_6$). Anal. Calcd for C$_{18}$H$_{24}$O$_5$: C, 67.5; H, 7.6. Found: C, 67.6; H, 7.7. Lithium aluminum hydride reduction of (−)-**19** gave enantiomeric pure alcohol (−)-**8** (for specific rotation, see Table II).

Correlation of Adduct 6b and Alcohol 8 with (*R*)-(−)-Hexahydromandelic Acid (18). A sample of adduct **6bII** was hydrogenated in the presence of platinum black in an ethanol solution. The resulting two compounds were separated by column chromatography, and the less polar component (yield 30%) was hydrolyzed with 5% ethanolic potassium hydroxide. After neutralization of the reaction mixture, a product was isolated and sublimed under reduced pressure to yield (*R*)-(−)-hexahydromandelic acid (**18**):[4] $[\alpha]^{20}_{589}$−25.3° (*c* 1.05, acetic acid). The adduct

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[22] J. R. McCabe and C. A. Eckert, *Acc. Chem. Res.*, 7, 251 (1974), and references therein; high-pressure and atmospheric-pressure Diels–Alder reactions are characterized by the same type of concerted mechanism, which permits their comparison. For extrapolation of the plots to "zero conditions", linear dependence of optical yields on pressure below 6 kbar is assumed.

[23] Unfortunately, the investigated reaction does not take place under normal pressure and at room temperature. It is stressed, however, that optical yields and absolute configurations predicted by the same type of extrapolation for the reactions between 1-methoxybuta-1,3-diene and (*R*)-(−)-menthyl glyoxylate[1] or isoprene and (*R*)-(−)-dimenthyl fumarate,[24] carried out under normal pressure and at room temperature, have been found to be consistent with experimental results.

[24] J. Jurczak, *Bull. Chem. Soc. Jpn.*, in press.

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[27] The pressure inside the working volume was measured with a calibrated manganine coil with an accuracy of ±0.1 kbar. The accuracy of temperature measurements using a calibrated thermocouple was ±1 °C.

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6bII hydrolyzed with 5% ethanolic potassium hydroxide yielding acid (+)-**6c**: $[\alpha]^{20}_{589}$ +40.0° (*c* 0.80, $CHCl_3$). Lithium aluminum hydride reduction of **6bII** gave (-)-**8**.

Acknowledgment. This work was supported by grants from the Polish Academy of Sciences (MRI-12.1.1.1 and 03.10.7.01.01).

Registry No. (*R*)-(-)-**1c**, 26315-61-7; **2**, 513-81-5; **3**, 592-57-4; (-)-**4c**, 70766-03-9; (*R*)-(+)-**5**, 70766-04-0; (±)-**5**, 70811-71-1; (±)-**6b**, 70811-72-2; **6bI**, 58437-92-6; **6bII**, 58393-27-4; (+)-**6c**, 70811-73-3; (-)-**8**, 70811-74-4; (+)-**8**, 70811-75-5; **9**, 70775-20-1; (*R*)-(+)-**10**, 70766-05-1; (*R*)-(-)-**11**, 70766-06-2; (±)-**15**, 70766-07-3; (+)-**15**, 70811-76-6; **17**, 70766-08-4; (*R*)-(-)-**18**, 53585-93-6; (±)-**19**, 70766-09-5; (-)-**19**, 70811-77-7; buta-1,3-diene, 106-99-0; (-)-ω-camphanyl chloride, 67375-29-5.

Photochemical Reaction of Duroquinone with Allenes and Ketenimines. Photoinduced Cycloaddition and Molecular Rearrangement

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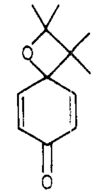
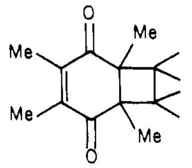
Received February 23, 1979

Photoinduced cycloadditions of duroquinone to allenes and some ketenimines and photoinduced molecular rearrangements of their adducts have been investigated. When irradiated in the presence of 1,1-dimethylallene, duroquinone afforded 7-methylenebicyclo[4.2.0]oct-3-ene-2,5-dione exclusively, whereas photocycloadditions of ketenimines occurred at the carbonyl function of duroquinone in spite of its π,π* triplet excited state. Diphenyl-*N*-phenylketenimine afforded spiro 2-imino- and 3-iminooxetanes. Dimethyl-*N*-substituted ketenimines reacted to give hexamethyl-2-imino-1-oxaspiro[3.5]nona-5,8-dien-7-one derivatives which were isomerized by further photolysis to two consecutive products: spiro bicyclo[3.1.0]hexenones and 2-imino-3,3a-dihydrobenzofuran-6-ones. The last compounds underwent facile hydrolysis to afford hexamethyl-3,3a-dihydrobenzofuran-2,6-dione in good yields. Structural and mechanistic investigations have been done.

In recent years, much attention has been paid to the photoinduced cycloadditions of saturated and conjugated carbonyl compounds to alkenes and alkynes.[1] In photochemical reactions, *p*-quinones afford cycloadducts: oxetanes and/or cyclobutanes.[2] The first involves cycloaddition of the carbonyl function to the unsaturated C–C bond to give the oxetanes or their rearranged products,[3] and the second involves cycloaddition of the ring double bond of *p*-quinones to a C–C double or triple bond.[4] From theoretical and experimental investigations,[5] *p*-benzoquinone is thought to react from a lowest triplet state of the n,π* excited state to yield exclusively oxetane adducts (**1**), while its tetramethyl derivative, duroquinone, whose lowest triplet should be π,π*,[6] affords only cyclobutanes (**2**).



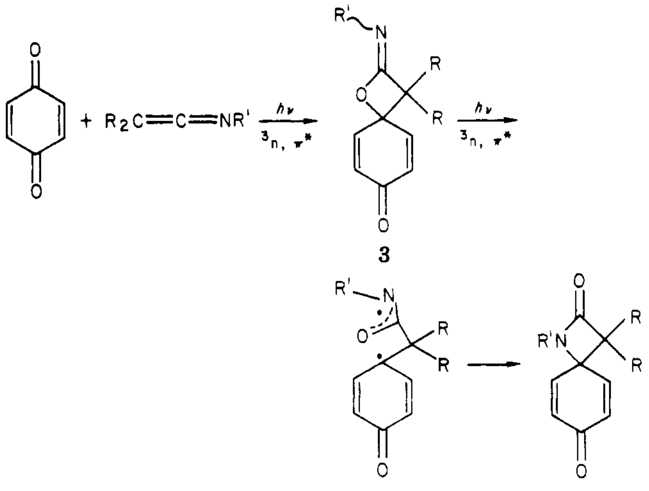
1



2

In addition, the photochemical transformations of cross-conjugated cyclohexadienones, i.e., santonin and related compounds, represent some of the most interesting and remarkable photochemical rearrangements.[7] The photoreactions of the simpler 4,4-diphenyl- and 4-methyl-4-(trichloromethyl)cyclohexa-2,5-dienones have been studied in great mechanistic detail.[8,9] In these studies, the presence of substituents on cyclohexadienones affects the types of rearrangements, solvent effects have been found to be very important, and reaction products are different, depending upon whether the solvent is neutral or acidic.[10]

Scheme I



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