

## Diastereofacial Selectivity in the Cycloaddition of Chiral Glyoxylate Imines to Cyclopentadiene and Indene: Synthesis of Optically Active Tetrahydroquinolines

Elisabetta Borrione, Maurizio Prato,\* Gianfranco Scorrano, and Mariano Stivanello  
 Centro C.N.R. di Studio sui Meccanismi di Reazioni Organiche, Dipartimento di Chimica Organica, Via  
 Marzolo 1, I-35131 Padova, Italy

Vittorio Lucchini

Dipartimento di Scienze Ambientali, Università di Venezia, Dorsoduro 2137, I-30123 Venezia, Italy

Giovanni Valle

Centro C.N.R. di Studio sui Biopolimeri, Dipartimento di Chimica Organica, Via Marzolo 1, I-35131, Padova, Italy

Imines (**1**) cycloadd to cyclopentadiene and indene to afford substituted tetrahydroquinolines with high diastereoisomeric (corresponding to enantiomeric) selectivity when (–)-8-phenylmenthol is used as a chiral auxiliary. Solvent polarity and temperature greatly affect the diastereoisomeric ratios.

The preparation of heterocycles through hetero Diels–Alder additions is receiving increasing attention.<sup>1</sup> This methodology, combined with the recent achievements in asymmetric synthesis,<sup>2</sup> has become a powerful practice in the chemistry of natural products as well as in the study of reaction mechanisms. However, while the reactivity of heterodienophiles bearing a chiral auxiliary group has been relatively well explored,<sup>1</sup> very few reports describe the reverse approach, *i.e.* asymmetric synthesis with chiral heterodienes.<sup>1,3</sup>

We have recently reported<sup>4,5</sup> that *N*-aryl imines, activated by ketone or ester substitution at the carbon end, can easily add as dienes, under Lewis acid catalysis, to a series of electron-rich dienophiles, such as vinyl ethers, indene, cyclopentadiene, cyclohexa-1,3-diene, and buta-1,3-diene, to afford substituted tetrahydroquinolines in high yields and with a high degree of regio- and stereo-selectivity. These findings, together with the potential of these additions for generating three chiral centres at a time and the possibility of application of this methodology to the field of natural product synthesis,<sup>6</sup> prompted us to investigate the behaviour of aromatic imines bearing a chiral prosthetic group.

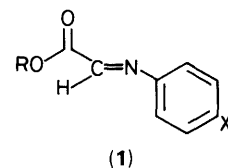
In this paper we describe the reaction of (–)-bornyl [*endo*-1,7,7-trimethyl-bicyclo[2.2.1]hept-2-yl] (**1a**), (–)-menthyl [(1*R*,2*S*,5*S*)-5-methyl-2-(1-methylethyl)cyclohexyl] (**1b**), and (–)-8-phenylmenthyl [(1*R*,2*S*,5*R*)-5-methyl-2-(1-methyl-1-phenylethyl)cyclohexyl] (**1c**), *N*-arylimino esters with the model dienophiles cyclopentadiene and indene.

### Results

**Preparation and Characterization of the Reagents.**—The imines (**1a–c**) were prepared by the reaction of 4-chloroaniline with the corresponding glyoxylate esters.<sup>4,5</sup> As any attempt of purification or isolation led to extensive decomposition, the crude mixtures (showing a purity > 90%, by <sup>1</sup>H n.m.r.) were directly subjected to the cycloadditions.

The imines (**1a–d**) were expected to possess the *E* configuration, which is common for substituted Schiff bases.<sup>7</sup> This configuration could in fact be ascertained by means of <sup>1</sup>H n.m.r. n.O.e. analysis in the differential mode<sup>8</sup> [because the chemical shifts of the diagnostic protons in imine (**1c**) are nearly identical, n.O.e. analysis was performed on the *p*-methoxy analogue (**1d**); see Experimental section]. The configuration is presumably not altered when the imine is complexed with the Lewis acid.<sup>4</sup>

On the other hand, the far greater diastereoselective efficiency of the phenylmenthyl with respect to the menthyl auxiliary is



- a; R = (–)-bornyl, X = Cl  
 b; R = (–)-menthyl, X = Cl  
 c; R = (–)-8-phenylmenthyl, X = Cl  
 d; R = (–)-8-phenylmenthyl, X = OMe

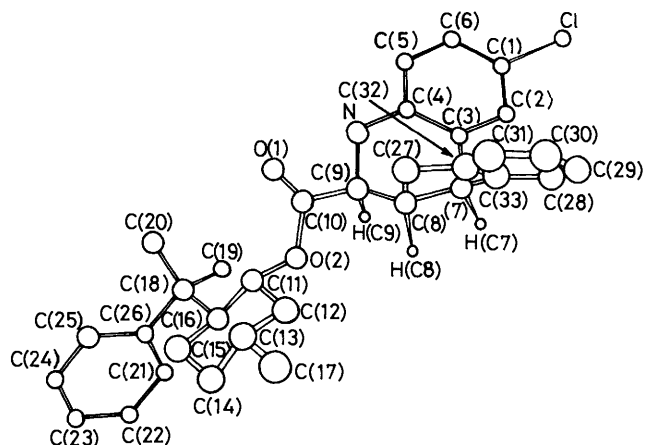
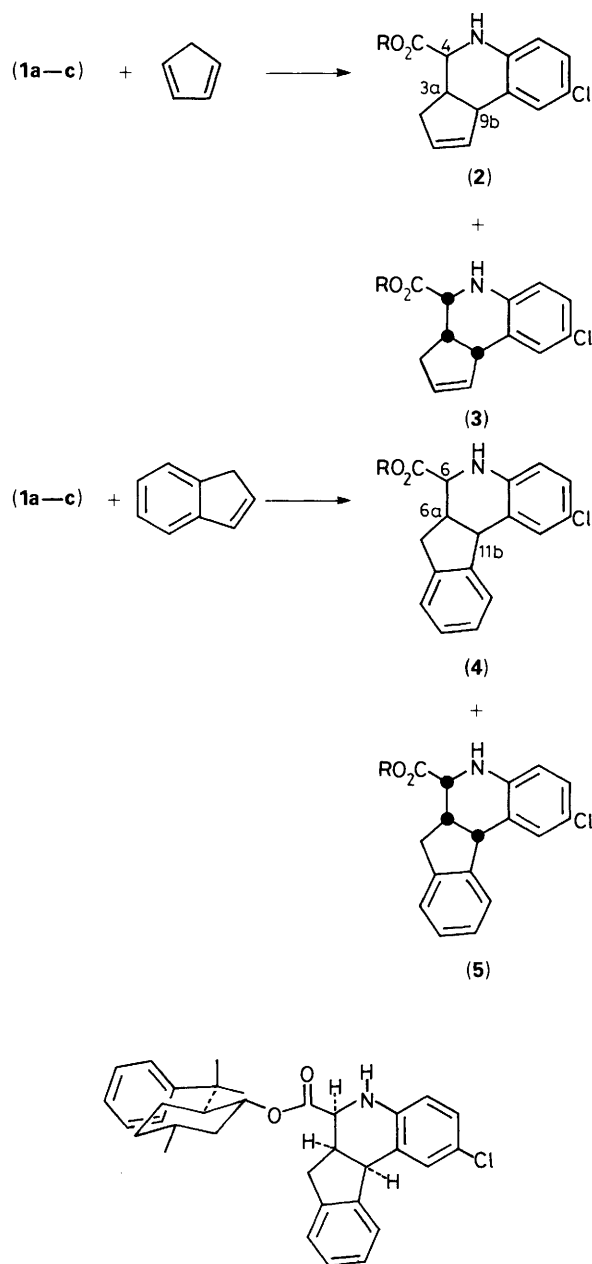
generally attributed to the hindrance offered by the phenyl group, which, in the present case and by analogy with other systems,<sup>9</sup> may be supposed to lie directly behind the conjugated unsaturated system of the iminoester moiety. Unfortunately, the azomethine proton and the phenylmenthyl aromatic protons are nearly isochronous, thus preventing any n.O.e. measurement. However, this orientation of the phenyl group may be deduced from the relative upfield shift of the azomethine proton in (**1c**) ( $\delta$  6.80 in CDCl<sub>3</sub>), compared with  $\delta$  7.89 for the corresponding proton in (**1b**) induced by the anisotropy of the aromatic ring current. This argument is commonly invoked as evidence of  $\pi$ -stacking effects between the aryl ring and unsaturated systems in 8-phenylmenthyl derivatives.<sup>9</sup>

**Addition to Cyclopentadiene and Indene.**—The dienophilic additions of cyclopentadiene to *N*-aryl imines which do not possess a chiral auxiliary occur with total regio- and stereo-selectivity, affording only tetrahydro-3*H*-cyclopenta[*c*]quinoline adducts with substituents on the same side of the tetrahydropyridine ring.<sup>4</sup>

These selectivities are also encountered in the addition of (**1c**) to indene,<sup>†</sup> from which the two isomeric adducts (**4c**) and (**5c**) could be separated by chromatography [when (**4c**) is obtained in large excess, it can be purified by crystallization].

The measurement of the n.O.e. interactions between 6-H, 6a-H, and 11b-H (*c.f.* Experimental section) shows that in both isomers the protons lie on the same side of the tetrahydropyridine ring, thus proving that both adducts originate from *endo* addition of the imine (**1c**) in the *E* configuration.<sup>4</sup> The two

<sup>†</sup> For the closely related cycloaddition of ethyl glyoxylate imines see ref. 5.



**Figure.** Perspective drawing of (4c). View showing the stereochemistry of the three newly generated chiral centres C(6), C(8), and C(9). Numbering is referred to Table 2

isomers (4a) and (5a) arising from the addition to indene. The resonance patterns for both isomer pairs are fully consistent with the proposed regio- and stereo-chemistry; however, the patterns are very similar, thus hampering a correct assignment to either isomer.

The adducts derived from (1b) could be separated by crystallization (from the reaction with cyclopentadiene) or by chromatography (from the reaction with indene). In this case also the resonance patterns of the (2b), (3b) pair [and those of the (4b), (5b) pair] are consistent with the proposed structures, but, again, absolute assignments were not possible.

The diastereoisomeric ratios (2c):(3c) and (4c):(5c) for the additions of (1c) are reported in Table 1, as function of temperature, solvent, and catalyst. As the absolute configurations in the adducts formed in the reactions of (1a) and (1b) are not known, we can only report the corresponding diastereoisomeric excesses (d.e.s) (obtained either from integration of selected peaks in the n.m.r. spectra of the crude reaction mixtures, or from h.p.l.c.), not referenced to a particular diastereoisomer. It can be appreciated that the 8-phenylmethyl chiral auxiliary is uniquely effective (up to 93% d.e. at low temperatures in relatively polar solvents), while bornyl and menthyl are much less efficient (0–10% d.e.).

## Discussion

The diastereoselective efficiency of the 8-phenylmethyl group is customarily attributed to the shielding effect of the phenyl ring, which directs the dienophile attack to the diene face opposite to the phenyl group.<sup>9</sup> A high degree of diastereoselectivity also requires that the Lewis acid complex exhibit a strong preference for only one of the conformations arising from rotation of the C–O, O–(CO), and (CO)–C bonds.

Following the generally proposed orientation for  $\alpha,\beta$ -unsaturated esters of secondary alcohols,<sup>2d</sup> we assume an average value of 0° for the dihedral angle H–C–O–(CO). We are therefore left with the two possibilities indicated by the *anti*- and *syn*-periplanar conformations (6) and (7).

As we have already pointed out, the Lewis acid complexation (either at the imine nitrogen or at the carbonyl oxygen) is not expected to alter the *E* configuration of the C=N double bond.<sup>4</sup> However, in imines nitrogen is a stronger basic centre than the carbonyl oxygen in esters.\* It can therefore be assumed that

isomers therefore possess the absolute configurations shown in formulae (4c) and (5c). Isomer (4c), obtained as the major component when the reaction conditions induce the greatest diastereoisomeric selectivity, was subjected to *X*-ray crystallographic analysis, from which the configurations *S*, *R*, and *R* could be assigned to C(6), C(6a), and C(11b), respectively (see Figure).

The adducts (2c) and (3c) obtained from the addition of (1c) to cyclopentadiene could also be separated by chromatography. As protons 4-H and 9b-H are nearly isochronous, it was not possible to obtain any decisive information from n.O.e. measurement. The resonance patterns of the tetrahydropyridine protons of (2c) and (3c) are very similar to those of the corresponding protons in (4c) and (5c), respectively: it is therefore reasonable to attribute to (2c) and (3c) the same absolute configurations as (4c) and (5c), respectively.

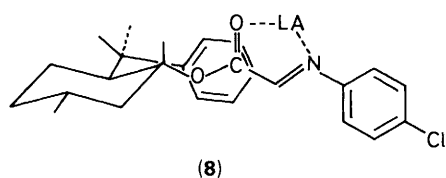
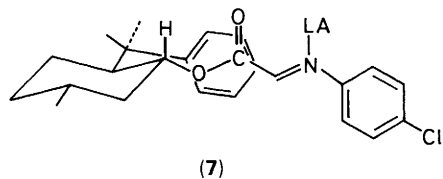
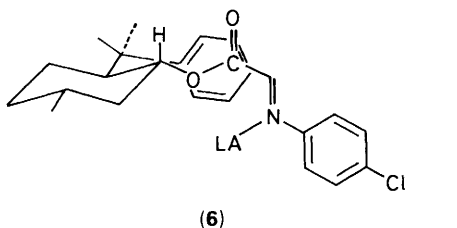
The isomers (2a) and (3a) derived from the addition of the iminoester (1a) to cyclopentadiene were inseparable, as were the

\*  $pK_{BH^+}$  of imine of benzophenone, 7.2;<sup>10a</sup>  $pK_{BH^+}$  of ethyl cinnamate, –5.06.<sup>10b</sup>

**Table 1.** Asymmetric induction in the reactions of (1a-c) with cyclopentadiene (cy) and indene (ind)

Entry	Diene	Dienophile	Solvent	Lewis acid	(mol eq.)	Temp.	Time	D.e. <sup>b</sup>
1	(1a)	cy	PhMe	BF <sub>3</sub> <sup>a</sup>	(0.1)	-78	4h	4 <sup>c</sup>
2	(1a)	ind	PhMe	BF <sub>3</sub> <sup>a</sup>	(0.1)	-78	4h	6 <sup>c</sup>
3	(1b)	cy	CH <sub>2</sub> Cl <sub>2</sub>	BF <sub>3</sub> <sup>a</sup>	(0.1)	20	4h	2(2)
4	(1b)	cy	CH <sub>2</sub> Cl <sub>2</sub>	BF <sub>3</sub> <sup>a</sup>	(0.1)	-78	4h	2(4)
5	(1b)	ind	CH <sub>2</sub> Cl <sub>2</sub>	BF <sub>3</sub> <sup>a</sup>	(0.1)	20	4h	0(4)
6	(1b)	ind	CH <sub>2</sub> Cl <sub>2</sub>	BF <sub>3</sub> <sup>a</sup>	(0.1)	-78	4h	10(8)
7	(1b)	ind	PhMe	TiCl <sub>4</sub>	(0.1)	-78	4h	8(10)
8	(1c)	cy	SO <sub>2</sub>	—	—	-78	6h	96:4 (97:3)
9	(1c)	cy	CH <sub>2</sub> Cl <sub>2</sub>	BF <sub>3</sub> <sup>a</sup>	(0.5)	-78	4h	92:8 (92:8)
10	(1c)	cy	CH <sub>2</sub> Cl <sub>2</sub>	BF <sub>3</sub> <sup>a</sup>	(0.5)	-95	4h	96:4 (95:5)
11	(1c)	cy	CH <sub>2</sub> Cl <sub>2</sub>	TiCl <sub>4</sub>	(0.5)	-78	8h	95:5 (95:5)
12	(1c)	ind	CH <sub>2</sub> Cl <sub>2</sub>	BF <sub>3</sub> <sup>a</sup>	(0.5)	-78	4h	93:7 (92:8)
13	(1c)	ind	CH <sub>2</sub> Cl <sub>2</sub>	TiCl <sub>4</sub>	(0.5)	-78	8h	96:4 (96:4)
14	(1c)	ind	CH <sub>2</sub> Cl <sub>2</sub>	TiCl <sub>4</sub>	(1.0)	-78	8h	93:7 (92:8)
15	(1c)	ind	CH <sub>2</sub> Cl <sub>2</sub>	TiCl <sub>4</sub>	(0.1)	-78	8h	95:5 (96:4)
16	(1c)	ind	CH <sub>2</sub> Cl <sub>2</sub>	TiCl <sub>4</sub>	(2.0)	-78	8h	<i>d</i>
17	(1c)	ind	CH <sub>2</sub> Cl <sub>2</sub>	TiCl <sub>4</sub>	(1.0)	20	1h	90:10 (91:9)
18	(1c)	ind	PhH	TiCl <sub>4</sub>	(0.1)	20	4h	80:20 (78:22)
19	(1c)	ind	PhMe	TiCl <sub>4</sub>	(0.5)	-78	8h	80:20 (81:19)
20	(1c)	ind	PhMe	TiCl <sub>4</sub>	(0.5)	20	4h	70:30 (70:30)
21	(1c)	ind	CH <sub>2</sub> Cl <sub>2</sub>	SnCl <sub>4</sub>	(1.0)	-78	4h	93:7 (92:8)
22	(1c)	ind	CH <sub>2</sub> Cl <sub>2</sub>	EtAlCl <sub>2</sub>	(1.0)	-78	4h	92:8 (93:7)
23	(1c)	cy	MeOH	TsOH <sup>e</sup>	(0.5)	20	30 min	85:15 (86:14)
24	(1c)	cy	MeNO <sub>2</sub>	BF <sub>3</sub> <sup>a</sup>	(0.5)	20	30 min	85:15 (85:15)
25	(1c)	cy	CH <sub>2</sub> Cl <sub>2</sub>	BF <sub>3</sub> <sup>a</sup>	(0.5)	20	30 min	80:20 (80:20)
26	(1c)	cy	PhMe	BF <sub>3</sub> <sup>a</sup>	(0.5)	20	30 min	42:58 (40:60)
27	(1c)	cy	PhH	BF <sub>3</sub> <sup>a</sup>	(0.5)	20	60 min	41:59 (42:58)
28	(1c)	cy	MeCN	BF <sub>3</sub> <sup>a</sup>	(0.5)	20	30 min	78:22 (78:22)
29	(1c)	cy	PhMe	BF <sub>3</sub> <sup>a</sup>	(0.5)	60	20 min	39:61 (40:60)

<sup>a</sup> BF<sub>3</sub> means boron trifluoride-diethyl ether. <sup>b</sup> Diastereoisomeric excesses [reactions of (1a) and (1b), see text] or diastereoisomeric ratios of (2c):(3c) (from cy) or (4c):(5c) (from ind) as measured by <sup>1</sup>H n.m.r. (or h.p.l.c., in parenthesis). <sup>c</sup> Not separable by h.p.l.c. <sup>d</sup> Only polymers could be detected by <sup>1</sup>H n.m.r. <sup>e</sup> Toluene-*p*-sulphonic acid.



LA = Lewis acid

complexation with a Lewis acid occurs preferentially at the imine nitrogen and *cis* with respect to the carbonyl group.

It should be noted that the diastereoisomers (2c) and (4c), which are formed as the major components when the reaction conditions favour the highest d.e., arise from the addition of the dienophile to the *Si* face of the C=N double bond in (1c). This is the free face in the complex with conformation (7), but the face protected by the prosthetic group in conformation (6).

Inspection of molecular models of the two complexes would suggest that the steric hindrance between the Lewis acid and the phenylmethyl skeleton in the antiperiplanar conformer (6) is not greater, or is even smaller, than that between the Lewis acid and the dimethylbenzyl group in the synperiplanar conformer (7). The greater stability of the conformer (7) is perhaps associated with the possibility that the Lewis acid binds synchronously to both basic centres as in structure (8). The binding to the carbonyl oxygen may be favoured by entropy contributions; complexation by the other ester oxygen, in principle possible in (6), is less probable as it is considered a weaker basic centre than carbonyl oxygen.<sup>11</sup>

The formation of a complex of structure (8) with TiCl<sub>4</sub> is in accordance with the chelating properties of the metal centre.<sup>12</sup> Also the chelating attitudes of SO<sub>2</sub> are known.<sup>13</sup> On the other hand, the formation of a similar complex with BF<sub>3</sub> requires an unusually high co-ordination number for boron. However, this co-ordination mode of BF<sub>3</sub> has already been invoked for a rationalization of the steric outcome of reactions catalyzed by this Lewis acid.<sup>14</sup>

The consideration of a complex of type (8) may also rationalize the effect of temperature and solvent on the d.e. The order of decreasing enthalpy may be assumed to be

(8) < (6) < (7) [the extra bond in the chelated complex (8) confers the greatest stability, while the antiperiplanar conformation of the O=C=C=N system stabilizes (6) and the synperiplanar conformation destabilizes (7)]. Therefore at low temperature the formation of (2) [or (4)] is facilitated over that of (3) [or (5)] (entries 8–15, 19, 21, and 22 in Table 1). On the other hand, chelation confers greater rigidity to (8), and smaller entropy; complexes (6) and (7) are favoured at higher temperature, and the formation of (3) [or (5)] from the more stable complex (6) is enhanced (entries 17, 18, 20, and 24–29 in Table 1). Finally, a greater dipole moment may be associated with complexes (7) and (8) (synperiplanar conformation of the O=C=C=N system) which are therefore stabilized in polar solvents (*cf.* entries 8–15, 17, 21–25, and 28 with entries 18, 19, 26, 27, and 29 in Table 1).

The present study of asymmetric hetero Diels–Alder reactions has demonstrated that a high (up to 92% d.e.) diastereoisomeric induction (corresponding to enantiomeric) can be achieved by using chiral 2-aza-1,3-dienes. As quinoline alkaloids are widespread in Nature, the proposed approach can be considered a new entry for the preparation of naturally occurring optically active compounds.

### Experimental

M.p.s are uncorrected. N.m.r. spectra were run on a Bruker WP 200 spectrometer at 200 MHz, in CDCl<sub>3</sub> with tetramethylsilane as an internal standard. Mass spectra were recorded on a 5970 HP mass spectrometer coupled with a 5890 HP gas-chromatograph. H.p.l.c. analyses were performed on a Waters Ass. instrument, model 6000A equipped with an u.v. detector (model 440, at 254 nm) and a HP 3390A integrator, using a Beckman Ultrasphere column, ODS 5 μm, 4.6 × 150 mm, RP-18.

The glyoxylate esters of (–)-bornyl, (–)-menthyl, (–)-8-phenylmenthyl were prepared according to published procedures.<sup>15,9b</sup>

**Nuclear Overhauser Effect Determination.**—The measurement tubes were freed from oxygen by sonication under nitrogen flow. The usual routine for differential n.o.e. experiments was adopted; as the only modification, a multiplet was saturated with the least decoupling power by an 8 s cyclic perturbation of all multiplet lines.<sup>16</sup> The percentage enhancements were obtained from the coefficients of the reference spectrum, which resulted in exact matching with the perturbed spectrum in the region of interest. Errors were estimated at *ca.* 0.3%.

**Preparation of Imines (1a–d).**—Equimolar amounts of substituted aniline and glyoxylate ester were allowed to react in toluene at room temperature, in the presence of sodium sulphate as dehydrating agent. After 1 h the sodium sulphate was filtered off and the solvent was removed under reduced pressure. The resulting oils were characterized by <sup>1</sup>H n.m.r. as follows: endo-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 2-(4-chlorophenylimino)acetate (**1a**), δ<sub>H</sub> 0.86 (3 H, d, *J* 6.4 Hz, Me), 0.90 (3 H, s, Me), 0.95 (3 H, s, Me), 1.11–2.10 (7 H, m, born), 2.47 (1 H, *J* 13.4 and 3.4 Hz, born), 5.14 (1 H, ddd, *J* 9.8, 3.4, and 2.1 Hz, born), 7.24 (2 H, m, *m*-ArH), 7.37 (2 H, m, *o*-ArH), and 7.92 (1 H, s, azomethine-H); (1*R*,2*S*,5*S*)-5-methyl-2-(1-methylethyl)cyclohexyl 2-(4-chlorophenylimino)acetate (**1b**) δ<sub>H</sub> 0.81 (3 H, d, *J* 6.7 Hz, Me), 0.92 (3 H, d, *J* 6.4 Hz, Me), 0.94 (3 H, d, *J* 6.4 Hz, Me), 1.00–2.18 (9 H, m, menth), 4.97 (1 H, td, *J* 10.7 and 4.6 Hz, menth), 7.24 (2 H, m, *m*-ArH), 7.39 (2 H, m, *o*-ArH), and 7.89 (s, azomethine-H); (1*R*,2*S*,5*R*)-5-methyl-2-(1-methyl-1-phenylethyl)cyclohexyl 2-(4-chlorophenylimino)acetate (**1c**), δ<sub>H</sub> 0.92 (3 H, d, *J* 6.4 Hz, Me), 1.08–2.20 (8 H, m, menth), 1.22 (3 H,

s, Me), 1.34 (3 H, s, Me), 5.08 (1 H, td, *J* 10.7 and 4.5 Hz, menth), 6.80 (1 H, s, azomethine-H), 7.15–7.30 (5 H, m, Ph), 7.10 (2 H, m, *m*-ArH), and 7.36 (2 H, m, *o*-ArH); (1*R*,2*S*,5*R*)-5-methyl-2-(1-methyl-1-phenylethyl)cyclohexyl 2-(4-methoxyphenylimino)acetate (**1d**), δ<sub>H</sub> 0.90 (3 H, d, *J* 6.4 Hz, Me), 1.07–2.18 (8 H, m, menth), 1.23 (3 H, s, Me), 1.34 (3 H, s, Me), 3.84 (3 H, s, OMe), 5.06 (1 H, td, *J* 10.7 and 4.5 Hz, menth), 6.86 (1 H, s, azomethine-H), 6.91 (2 H, m, *m*-ArH), 7.05–7.31 (5 H, m, Ph), 7.23 (2 H, m, *o*-ArH). Selected n.o.e. measurements for imine (**1d**); azomethine-H, 24.4 {H<sub>o</sub> of *p*-OMeC<sub>6</sub>H<sub>4</sub>}; H<sub>o</sub> of *p*-OMeC<sub>6</sub>H<sub>4</sub>, 14.6 {azomethine-H}.

**Addition of (1a–c) to Cyclopentadiene and Indene.**—**General Procedure.** The Lewis acid (in the amount noted in Table 1) was added to a solution of the imine (**1a–c**) (1 mmol) in solvent (5 ml) under nitrogen. The resulting yellow–red solution was brought to the stated temperature (see Table 1) and then the dienophile (1.2 mmol) was added. On disappearance of the substrate by t.l.c. analysis (see Table 1), the reaction was quenched by addition of aqueous sodium hydrogen carbonate. The organic solution was extracted, washed with water, dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated under reduced pressure. The residues were treated differently depending on substrate and dienophile.

**Reaction of (1a) with cyclopentadiene (Table 1, entry 1).** The crude mixture was crystallized from ethanol. The white solid (yield 72%) was still a 1:1 mixture of the two diastereoisomers, endo-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl [3*aR*,4*S*,9*bS*]- and (3*aS*,4*R*,9*bR*)-8-chloro-3*a*,4,5,9*b*-tetrahydro-3*H*-cyclopenta[c]quinoline-4-carboxylates (**2a**) and (**3a**). Moreover, they had the same chromatographic properties and could not be separated [Found (for the mixture): C, 71.55; H, 7.35; N, 3.8; Cl, 9.15%. C<sub>23</sub>H<sub>28</sub>ClNO<sub>2</sub> requires C, 71.60; H, 7.26; N, 3.63; Cl, 9.21%].

**Reaction of (1a) with indene (Table 1, entry 2).** Same work-up as the reaction with cyclopentadiene gave, in 76% yield, a 1:1 mixture of endo-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl (6*S*,6*aR*,11*bR*)- and (6*R*,6*aS*,11*bS*)-2-chloro-5,6,6*a*,11*b*-tetrahydro-7*H*-indeno[2,1-*c*]quinoline-6-carboxylates (**4a**) and (**5a**) [Found (for the mixture): C, 74.5; H, 6.7; N, 3.2; Cl, 8.1%. C<sub>27</sub>H<sub>29</sub>ClNO<sub>2</sub> requires C, 74.57; H, 6.67; N, 3.22; Cl, 8.17%].

**Reaction of (1b) with cyclopentadiene (Table 1, entry 4).** The two isomers, (1*R*,2*S*,5*S*)-5-methyl-2-(1-methylethyl)cyclohexyl (3*aR*,4*S*,9*bS*)- and (3*aS*,4*R*,9*bR*)-8-chloro-3*a*,4,5,9*b*-tetrahydro-3*H*-cyclopenta[c]quinoline-4-carboxylates (**2b**) and (**3b**), had the same R<sub>F</sub> with several solvents and could not be separated by chromatography. Crystallization of the mixture from ethanol gave one pure product (41%), m.p. 82–84 °C (Found: C, 70.9; H, 7.85; Cl, 9.2; N, 3.6%; C<sub>23</sub>H<sub>30</sub>ClNO<sub>2</sub> requires C, 71.23; H, 7.74; Cl 9.16; N, 3.61%); [α]<sub>D</sub><sup>20</sup> = –157.2° (*c* 1.00 in CHCl<sub>3</sub>); δ<sub>H</sub> 0.79 (3 H, d, *J* 7.0 Hz, Me), 0.88 (3 H, d, *J* 7.0 Hz, Me), 0.90 (3 H, d, *J* 7.0 Hz, Me), 0.69–2.10 (9 H, m, menth), 2.26 (1 H, dd, *J*<sub>3,3'</sub> 16.5 Hz, *J*<sub>3',3*a*</sub> 9.5 Hz, 3'-H), 2.49 (1 H, dd, *J*<sub>3,3*a*</sub> 8.5 Hz, *J*<sub>2,3</sub> 2.8 Hz, 3-H), 3.32 (1 H, ddd, *J*<sub>3*a*,4</sub> 3.0 Hz, *J*<sub>3*a*,9*b*</sub> 8.9 Hz, 3*a*-H), 4.02 (1 H, d, 4-H), 4.08 (1 H, d, 9*b*-H), 4.20 (1 H, br s, 5-H), 4.78 (1 H, dd, *J* 10.7 and 4.3 Hz, menth), 5.69 (2 H, br s, 1-H and 2-H), 6.56 (1 H, d, *J*<sub>6,7</sub> 8.5 Hz, 6-H), 6.92 (1 H, dd, *J*<sub>7,9</sub> 2.4 Hz, 7-H), and 6.97 (1 H, d, 9-H).

**Reaction of (1b) with indene (Table 1, entry 6).** The crude product was chromatographed on silica gel (light petroleum–toluene, 6:4) affording the two diastereoisomers, (1*R*,2*S*,5*S*)-5-methyl-2-(1-methylethyl)cyclohexyl (6*S*,6*aR*,11*bR*)- and (6*R*,6*aS*,11*bS*)-2-chloro-5,6,6*a*,11*b*-tetrahydro-7*H*-indeno[2,1-*c*]quinoline-6-carboxylates (**4b**) and (**5b**), in 37 and 41% isolated yields. One isomer had m.p. 150–51 °C (Found C, 73.9; H, 7.4; Cl, 7.9; N, 3.0%. C<sub>27</sub>H<sub>32</sub>ClNO<sub>2</sub> requires C, 74.06; H, 7.31; N, 3.20; Cl, 8.11%); [α]<sub>D</sub><sup>20</sup> = –170.5° (*c* 0.97 in CHCl<sub>3</sub>); δ<sub>H</sub> 0.79 (3

**Table 2.** Positional parameters of (4c). Estimated standard deviations given in brackets

Atom	x	y	z	Atom	x	y	z
Cl	0.904 9(1)	0.642 3(2)	0.885 5(8)	(C17)	0.749 7(3)	-0.118 2(3)	0.602 0(10)
O(1)	0.865 6(2)	0.161 3(4)	0.215 4(11)			0.000 7(3)	0.002 1(10)
O(2)	0.872 1(2)	0.088 5(3)	0.535 9(10)	(C18)	0.939 1(3)	-0.043 5(3)	0.349 6(10)
N(1)	0.890 8(2)	0.307 9(3)	0.432 0(10)			0.000 5(3)	0.001 6(10)
		0.000 4(3)	0.001 4(10)	(C19)	0.932 0(4)	-0.024 6(3)	0.102 6(10)
(C1)	0.900 7(3)	0.542 9(3)	0.749 8(10)			0.000 6(3)	0.001 6(10)
		0.000 6(3)	0.002 3(10)	(C20)	0.964 9(3)	0.032 8(3)	0.454 7(10)
(C2)	0.875 1(3)	0.480 1(3)	0.849 0(10)			0.000 5(3)	0.002 1(10)
		0.000 6(3)	0.002 1(10)	(C21)	0.974 5(3)	-0.185 8(3)	0.219 1(10)
(C3)	0.870 0(3)	0.402 6(3)	0.741 8(10)			0.000 6(3)	0.001 9(10)
		0.000 5(3)	0.001 8(10)	(C22)	0.999 3(4)	-0.258 3(3)	0.261 6(10)
(C4)	0.893 6(3)	0.387 8(3)	0.541 1(10)			0.000 7(3)	0.002 3(10)
		0.000 6(3)	0.002 3(10)	(C23)	1.019 9(4)	-0.271 0(3)	0.458 8(10)
(C5)	0.918 5(4)	0.452 8(3)	0.441 3(10)			0.000 7(3)	0.002 4(10)
		0.000 7(3)	0.002 5(10)	(C24)	1.015 0(4)	-0.208 8(3)	0.616 7(10)
(C6)	0.923 2(4)	0.531 4(3)	0.548 7(10)			0.000 8(3)	0.002 5(10)
		0.000 7(3)	0.002 7(10)	(C25)	0.989 7(3)	-0.137 8(3)	0.587 3(10)
(C7)	0.841 2(4)	0.334 1(3)	0.848 9(10)			0.000 7(3)	0.002 0(10)
		0.000 6(3)	0.002 0(10)	(C26)	0.968 2(3)	-0.123 7(3)	0.381 9(10)
(C8)	0.835 4(3)	0.253 1(3)	0.699 8(10)			0.000 5(3)	0.001 8(10)
		0.000 6(3)	0.002 0(10)	(C27)	0.793 0(3)	0.270 6(3)	0.555 3(10)
(C9)	0.878 3(4)	0.236 9(3)	0.563 9(10)			0.000 6(3)	0.001 7(10)
		0.000 6(3)	0.002 1(10)	(C28)	0.773 2(3)	0.411 4(3)	0.040 4(10)
(C10)	0.871 7(3)	0.159 3(3)	0.411 0(10)			0.000 6(3)	0.002 0(10)
		0.000 5(3)	0.001 5(10)	(C29)	0.728 5(5)	0.426 8(3)	0.028 8(10)
(C11)	0.856 9(3)	0.007 1(3)	0.437 5(10)			0.000 7(3)	0.002 7(10)
		0.000 5(3)	0.001 7(10)	(C30)	0.702 2(4)	0.396 7(3)	0.859 5(10)
(C12)	0.813 7(3)	-0.012 2(3)	0.556 7(10)			0.000 7(3)	0.002 8(10)
		0.000 5(3)	0.001 9(10)	(C31)	0.719 1(3)	0.345 9(3)	0.689 4(10)
(C13)	0.794 9(3)	-0.099 2(3)	0.479 4(10)			0.000 7(3)	0.002 0(10)
		0.000 7(3)	0.001 8(10)	(C32)	0.765 6(3)	0.325 4(3)	0.705 5(10)
(C14)	0.829 9(3)	-0.165 3(3)	0.533 8(10)			0.000 6(3)	0.001 8(10)
		0.000 6(3)	0.001 9(10)	(C33)	0.792 7(3)	0.360 2(3)	0.875 6(10)
(C15)	0.873 3(3)	-0.148 2(3)	0.410 9(10)			0.000 6(3)	0.001 9(10)
		0.000 5(3)	0.001 9(10)				
(C16)	0.893 5(3)	-0.059 8(3)	0.474 8(10)				
		0.000 4(3)	0.001 5(10)				

H, d,  $J$  7.0 Hz, Me), 0.90 (3 H, d,  $J$  7.0 Hz, Me), 0.95 (3 H, d,  $J$  7.0 Hz, Me), 1.00—2.12 (9 H, m, menth), 2.75 (1 H, dd,  $J_{7,7'}$ , 15.6 Hz,  $J_{6a,7}$ , 7.9 Hz, 7'-H), 3.11 (1 H, dd,  $J_{6a,7}$ , 10.4 Hz, 7-H), 3.47 (1 H, m, 6a-H), 4.21 (1 H, d,  $J_{6,6a}$ , 3.4 Hz, 6-H), 4.38 (1 H, br s, 5-H), 4.46 (1 H, d,  $J_{6a,11b}$ , 8.5 Hz, 11b-H), 4.86 (1 H, dt,  $J$  11.0 and 4.3 Hz, menth), 6.53 (1 H, d,  $J_{3,4}$ , 8.85 Hz, 4-H), 6.90 (1 H, dd,  $J_{1,3}$ , 2.4 Hz, 3-H), 7.21 (1 H, dd,  $J_{1,11}$ , 0.9 Hz, 1-H), 7.14—7.24 (3 H, m), and 7.44—7.53 (1 H, m, 11-H). The other isomer had m.p. 74—5 °C (Found: C, 73.95; H, 7.4; Cl, 8.0; N, 3.0%);  $[\alpha]_D = +83.2^\circ$  ( $c$  1.32 in  $\text{CHCl}_3$ );  $\delta_{\text{H}}$  0.81 (3 H, d,  $J$  7.0 Hz, Me), 0.91 (3 H, d,  $J$  7.0 Hz, Me), 0.93 (3 H, d,  $J$  7.0 Hz, Me), 0.96—2.10 (9 H, m, menth), 2.70 (1 H, dd,  $J_{7,7'}$ , 15.3 Hz,  $J_{6a,7}$ , 7.9 Hz, 7'-H), 3.16 (1 H, dd,  $J_{6a,7}$ , 10.4 Hz, 7-H), 3.47 (1 H, m, 6a-H), 4.18 (1 H, d,  $J_{6,6a}$ , 3.0 Hz, 6-H), 4.34 (1 H, br s, 5-H), 4.47 (1 H, d,  $J_{6a,11b}$ , 8.2 Hz, 11b-H), 4.81 (1 H, dt,  $J$  10.7 and 4.3 Hz, menth), 6.53 (1 H, d,  $J_{3,4}$ , 8.5 Hz, 4-H), 6.90 (1 H, dd,  $J_{1,3}$ , 2.4 Hz, 3-H), 7.13—7.22 (3 H, m), 7.24 (1 H, dd,  $J_{1,11}$ , 0.9 Hz, 1-H), and 7.45—7.53 (1 H, m, 11-H).

**Reaction of (1c) with cyclopentadiene** (Table 1, entry 26). The crude mixture was chromatographed on silica gel (light petroleum-toluene, 7:3) affording two products, to which the structures (1R,2S,5R)-5-methyl-2-(1-methyl-1-phenylethyl)cyclohexyl (3aR,4S,9bR)-8-chloro-3a,4,5,9b-tetrahydro-3H-cyclopenta[c]-quinoline-4-carboxylate (2c) (1R,2S,5R)-5-methyl-2-(1-methyl-1-phenylethyl)cyclohexyl (3aS,4R,9bS)-8-chloro-3a,4,5,9b-tetrahydro-3H-cyclopenta[c]-quinoline-4-carboxylate (3c) were assigned by spectroscopic (n.m.r.) analogy to (4c) and (5c), respectively. Compound (2c): yield 35%; m.p. 82—84 °C (from EtOH) (Found: C, 74.6; H, 7.4; Cl, 8.05 N, 3.0%;  $\text{C}_{29}\text{H}_{34}\text{ClNO}_2$

requires C, 75.08; H, 7.34; Cl, 7.66 N, 3.02%);  $[\alpha]_D = +106.0^\circ$  ( $c$  1.10 in  $\text{CHCl}_3$ );  $\delta_{\text{H}}$  0.90 (3 H, d,  $J$  6.4 Hz, Me), 0.93—2.30 (10 H, m, 8H of menthyl and 3-H), 1.19 (3 H, s, Me), 1.29 (3 H, s, Me), 2.46 (1 H, dtd,  $J_{3a,9b}$ , 9.5 Hz,  $J_{3a,4}$ , 3.4 Hz,  $J_{3a,3}$ , 9.5 Hz,  $J_{3a,3'}$ , 8.4 Hz, 3a-H), 3.14 (1 H, dd,  $J_{3,4}$ , 0.9 Hz, 4-H), 3.75 (1 H, br d, 9b-H), 4.01 (1 H, br s, 5-H), 4.87 (1 H, td,  $J$  10.7 and 4.3 Hz, menth), 5.61 (2 H, m, 1-H and 2-H), 6.51 (1 H, m, 6-H), 6.88 (1 H, dd,  $J_{9,7}$ , 2.4 Hz,  $J_{9,6}$ , 0.6 Hz, 9-H), 6.92 (1 H, m, 7-H), and 7.09—7.32 (5 H, m, Ph). Selected n.O.e.: 3a-H, 7.2 {4-H}, 12.2 {9b-H};  $\text{H}_4$ , 13.8 {3a-H}, 5.6 {9b-H} (also from {NH}), nearly isochronous to 9b-H). 9b-H, 17.0 {3a-H}, not measurable from {4-H}, nearly isochronous to 9b-H.

**Compound (3c):** yield 48%; unstable white solid, decomposed on attempted crystallization and gave no reproducible m.p.;  $\delta_{\text{H}}$  0.90 (3 H, d,  $J$  6.4 Hz, Me), 0.92—2.29 (8 H, m, menth), 1.19 (3 H, s, Me), 1.33 (3 H, s, Me), 2.14—2.29 (2 H, m, 3-H), 2.46 (1 H, br s, 5-H), 3.12 (1 H, m, 3a-H), 3.44 (1 H, d,  $J_{3a,4}$ , 3.5 Hz, 4-H), 3.89 (1 H, br d,  $J_{3a,9b}$ , 9.5 Hz, 9b-H), 5.04 (1 H, td,  $J$  10.7 and 4.3 Hz, menth), 5.63 (2 H, m, 1-H and 2-H), 6.32 (1 H, d,  $J_{6,7}$ , 9.3 Hz, 6-H), 6.88 (1 H, m, 7-H and 9-H), and 7.07—7.39 (5 H, m, Ph). Selected n.O.e.: 3a-H, 13.0 {9b-H}, not measurable from {4-H}, nearly isochronous to 3a-H; 4-H not measurable from {3a-H} and {9b-H}, nearly isochronous to 4-H; 9b-H, 19.6 {3a-H}, not measurable from {4-H}, nearly isochronous to 9b-H.

**Reaction of (1c) with indene** (Table 1, entry 19). The crude mixture was chromatographed on silica gel (light petroleum-toluene, 8:2) affording two products, (1R,2S,5R)-5-methyl-2-(1-

*methyl-1-phenylethyl)cyclohexyl* (–)-(6*S*,6*aR*,11*bR*)-2-chloro-5,6,6*a*,11*b*-tetrahydro-7*H*-indeno[2,1-*c*]quinoline-6-carboxylate (**4c**), and (1*R*,2*S*,5*R*)-5-methyl-2-(1-methyl-1-phenylethyl)cyclohexyl (+)-(6*R*,6*aS*,11*bS*)-2-chloro-5,6,6*a*,11*b*-tetrahydro-7*H*-indeno[2,1-*c*]quinoline-6-carboxylate (**5c**). Alternatively (Table 1, entry 13), crystallization of the crude mixture from ethanol gave the major isomer (**4c**) (yield 74%, purity > 99% by <sup>1</sup>H n.m.r.).

Compound (**4c**): yield 64%; m.p. 181–182 °C (from EtOH) (Found: C, 76.9; H, 7.1; N, 2.6; Cl, 7.1%. C<sub>33</sub>H<sub>36</sub>ClNO<sub>2</sub> requires C, 77.12; H, 7.01; N, 2.73; Cl, 6.91%); [α]<sub>D</sub><sup>20</sup> = –81° (c 1.05 in CHCl<sub>3</sub>); δ<sub>H</sub> 0.93 (3 H, d, *J* 6.6 Hz, Me), 1.01–2.15 (8 H, m, menth), 1.19 (3 H, s, Me), 1.31 (3 H, s, Me), 2.50 and 2.89 (2 H, m, 7-H), 2.62 (1 H, m, 6*a*-H), 3.21 (1 H, d, *J*<sub>6,6*a*</sub> 2.9 Hz, 6-H), 4.15 (1 H, d, *J*<sub>6*a*,11*b*</sub> 7.5 Hz, 11*b*-H), 4.15 (1 H, br s, 5-H), 4.90 (1 H, td, *J* 10.8 and 4.5 Hz, menth), 6.47 (1 H, d, *J*<sub>3,4</sub> 8.5 Hz, 4-H), 6.88 (1 H, dd, *J*<sub>1,3</sub> 2.4 Hz, 3-H), 7.18 (1 H, d, 1-H), and 7.04–7.45 (9 H, m, 8-, 9-, 10-, 11-H, and Ph). Selected n.o.e.: 6-H, 11.4 {6*a*-H}, 11.4 {11*b*-H} (also from {NH}, nearly isochronous to 11*b*-H); 6*a*-H, 7.1 {6-H}, 11.0 {11*b*-H}; 11*b*-H, 2.6 {6-H}, 13.2 {6-H}.

Compound (**5c**): yield 16%; m.p. 90–92 °C (Found: C, 77.0; H, 6.95; Cl, 7.0 N, 2.7%); [α]<sub>D</sub><sup>20</sup> = +62° (c 0.89 in CHCl<sub>3</sub>); δ<sub>H</sub> 0.94 (3 H, d, *J* 6.4 Hz, Me), 1.01–2.25 (8 H, m, menth), 1.20 (3 H, s, Me), 1.34 (3 H, s, Me), 2.59 (1 H, br s, 5-H), 2.63 and 2.87 (2 H, m, 7-H), 3.26 (1 H, m, 6*a*-H), 3.56 (1 H, d, *J*<sub>6,6*a*</sub> 3.4 Hz, 6-H), 4.29 (1 H, d, *J*<sub>6*a*,11*b*</sub> 7.9 Hz, 11*b*-H), 5.06 (1 H, td, *J* 10.7 and 4.3 Hz, menth), 6.27 (1 H, d, *J*<sub>3,4</sub> 8.7 Hz, 4-H), 6.88 (1 H, dd, *J*<sub>1,3</sub> 2.4 Hz, 3-H), 7.16 (1 H, d, 1-H), and 7.07–7.44 (9 H, m, 8-, 9-, 10-, 11-H, and Ph). Selected n.o.e.: 6-H, 11.5 {6*a*-H}, 2.5 {11*b*-H}; 6*a*-H, 9.0 {6-H}, 6.4 {11*b*-H}; 11*b*-H, 3.3 {6-H}, 14.6 {6*a*-H}.

*Crystal Structure Determination of (4c)*.—C<sub>33</sub>H<sub>36</sub>ClNO<sub>2</sub>, *M* = 514.107; orthorhombic, space group P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 29.727(2) Å, *b* = 15.682(2) Å, *c* = 5.967(1) Å, *V* = 2781.7(6) Å<sup>3</sup>, *Z* = 4, *D*<sub>x</sub> = 1.227 g cm<sup>–3</sup>, μ = 1.3 cm<sup>–1</sup>. Single crystals (colourless needles) were prepared by recrystallization (ethanol). *D*<sub>m</sub> was not determined. The 2 829 independent reflections were read on a Philips PW 1100 diffractometer in ω scan mode to a 2θ = 50° using Mo-*K*<sub>α</sub> radiation (λ = 0.7107 Å). An absorption correction was not applied. Of 2 829 independent reflections, 1 125 with *I*<sub>0</sub> ≥ 3*r*(*I*<sub>0</sub>) were considered as observed, with a final *R* = 0.0459. The structure was solved with direct methods, using Multan 80 program and was refined by blocked least squares (*w* = 1) with non-hydrogen atom anisotropic thermal parameter. Hydrogen atoms were calculated and isotropically refined during the last cycles. The final difference Fourier shows no significant features, the difference density values ranging between +0.17 and –0.17 eÅ<sup>–3</sup>. All calculations were carried out using the SHELX 76 program.<sup>17</sup> Final positional parameters are given in Table 2. Hydrogen atom co-ordinates, thermal parameters, bond distances, and bond angles have been deposited at the Cambridge Crystallographic Data Centre.\*

\* For details see 'Instructions for Authors (1989)' in *J. Chem. Soc., Perkin Trans. I*, 1989, Issue 1.

## References

- (a) D. L. Boger and S. M. Weinreb, 'Hetero Diels-Alder Methodology in Organic Synthesis,' Academic Press, Orlando, 1987; (b) G. Desimoni, G. Tacconi, A. Barco, and G. P. Pollini, 'Natural Product Synthesis Through Pericyclic Reactions,' ACS Monograph 180, American Chemical Society, Washington, DC, 1984.
- (a) L. A. Paquette in 'Asymmetric Synthesis,' ed. J. D. Morrison, Academic Press, New York 1984, Vol. 3B, 455; (b) H. Wurziger, *Kontakte*, 1984, 3; (c) W. Oppolzer, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 876; (d) G. Helmchen, R. Karge, and J. Weetman, in 'Modern Synthetic Methods 1986,' ed. R. Scheffold, Springer Verlag, Berlin, 1986, Vol. 4, 261.
- (a) L. F. Tietze and K.-H. Glüsekamp, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 887; (b) R. Kober, K. Papadopoulos, W. Miltz, D. Enders, and W. Steglich, *Tetrahedron*, 1985, **41**, 1693.
- V. Lucchini, M. Prato, G. Scorrano, and P. Tecilla, *J. Org. Chem.*, 1988, **53**, 2251.
- E. Borrione, V. Lucchini, M. Prato, G. Scorrano, and M. Stivanello, *J. Heterocycl. Chem.*, 1988, **25**, 1831.
- For a recent review on stereoselective syntheses of nitrogen-containing natural products via cycloaddition reactions, see: C. Kibayashi, in 'Studies in Natural Products Chemistry,' ed. Atta-ur-Rahman, Elsevier Science, Amsterdam, 1988 Vol. 1A.
- (a) C. G. McCarthy, 'The Chemistry of Carbon-Nitrogen Double Bond,' ed. S. Patai, Wiley-Interscience, New York, 1970; (b) G. Merényi, G. Wettermark, and B. Ross, *Chem. Phys.*, 1973, 1340.
- J. H. Noggle and R. E. Schirmer, 'The Nuclear Overhauser Effect,' Academic Press, New York, 1970.
- (a) E. J. Corey and H. E. Ensley, *J. Am. Chem. Soc.*, 1975, **97**, 6908; (b) W. Oppolzer, M. Kurth, D. Reichlin, C. Chapuis, M. Mohnhaupt, and F. Moffatt, *Helv. Chim. Acta*, 1981, **64**, 2802; (c) W. Oppolzer and H. J. Löher, *ibid.*, 1981, **64**, 2808; (d) J. K. Whitesell, A. Battacharya, and K. Henke, *J. Chem. Soc., Chem. Commun.*, 1982, 988; (e) K. Whitesell, A. Battacharya, D. A. Aguilar, and K. Henke, *ibid.*, 1982, 989; (f) K. Whitesell, D. Deyo, and A. Battacharya, *ibid.*, 1983, 802; (g) Y. Yamamoto, H. Yagatai, Y. Ishihara, N. Maeda, and K. Maruyama, *Tetrahedron*, 1984, **40**, 2239; (h) For a recent study on the conformational analysis and crystal structure of 8-phenylmenthyl derivatives see: J. Runsink, H. Koch, A. Nehrings, H.-D. Scharf, E. Nowack, and T. Hahn, *J. Chem. Soc., Perkin Trans. 2*, 1988, 49.
- (a) J. B. Culbertson, *J. Am. Chem. Soc.*, 1951, **73**, 4818; (b) J. T. Edwards and S. C. Wong, *ibid.*, 1977, **99**, 4229.
- J. March, 'Advanced Organic Chemistry,' 3rd ed., Wiley-Interscience, New York, 1985, p. 222.
- E. N. Guryanova, I. P. Goldstein, and I. P. Romm, 'Donor-Acceptor Bond,' Wiley, N.Y., 1975.
- (a) E. Block, 'Reactions of Organosulfur Compounds,' Academic Press, New York, 1978; (b) I. Fleming, 'Frontier Orbitals and Organic Chemical Reactions,' Wiley, Chichester, 1976, p. 95; (c) O. De Lucchi and V. Lucchini, *J. Chem. Soc., Chem. Commun.*, 1982, 1105.
- (a) K. Maruyama, Y. Ishihara, and Y. Yamamoto, *Tetrahedron Lett.*, 1981, **22**, 4235; (b) M. T. Reetz, K. Kessler, and A. Jung, *ibid.*, 1984, **25**, 729.
- (a) J. Jurczak and A. Zamojski, *Tetrahedron*, 1972, **42**, 255; (b) P. Grossen, P. Herold, P. Mohr, and C. Tamm, *Helv. Chim. Acta*, 1984, **67**, 1625.
- M. Kinns and J. K. M. Sanders, *J. Magn. Reson.*, 1984, **56**, 518.
- G. M. Sheldrick, SHELX-76, Program for Crystal Structure Determinations, University of Cambridge, 1976.

Received 5th December 1988; Paper 8/04802I