Cycloadditions in Syntheses. Part 47.[1] 2-Monosubstituted 1,3-Dioxin-4-ones: Diastereofacial Selectivity in Pericyclic Reactions and its Explanation[2]

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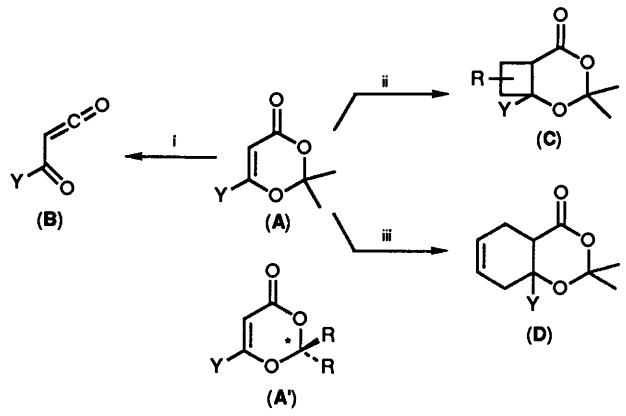
Photo[2 + 2]cycloaddition and Diels–Alder reactions of 2-monosubstituted 1,3-dioxin-4-ones have been examined for the first time. The observed stereoselectivities [the *a*-side (bottom side of sofa-type conformation of the dioxinone ring) preference for these pericyclic reactions and the *b*-side (top side of the sofa conformation) preferences for conjugated addition by lithium dimethylcuprate and catalytic hydrogenation] are the same with those reported previously for the dioxinones having a spirocyclic chiral auxiliary at the 2-position. A mechanism accounting for all the types of asymmetric reaction of these two types of chiral dioxinone is proposed.

The successful use of 1,3-dioxin-4-ones as versatile synthons has been well documented.[3–5] Two important characteristics of these compounds are shown in Scheme 1 taking (**A**) as a typical



Scheme 1. *Reagents and conditions:* i, heat or *hν* (254 nm); ii, *hν* (≥300 nm), $RCH{=}CH_2$; iii, heat, buta-1,3-diene.

example: (i) ready ring-opening of compounds (**A**) to afford acyl ketenes (**B**) under either thermal or photochemical conditions, and (ii) the C=C double bond in the dioxinone moiety acts as the enol form of a masked acylacetic acid [*e.g.*, (**A**) ⟶ (**C**) or (**D**)]. Both of these characteristic properties provide an efficient method for the preparation of important building blocks in organic synthesis. In addition, the latter characteristic provides for the possibility that a compound (**A'**) may serve as an enol form of a chiral acylacetic acid which could be used for the synthesis of a variety of enantiomerically pure compounds (EPCs), if suitable functionalities are introduced into the dioxinones [*cf.* (**A'**)] in order not only to make them chiral but also to provide diastereofacial selectivity at the dioxinone double bond.

Two important developments (outlined below) concerned with characteristic (ii) have been made recently which use chiral dioxinones as synthons of EPCs. (1) Seebach *et al.*[6] have synthesized 2,6-disubstituted dioxinones [*e.g.*, chiral 2-t-butyl derivative (**E**)] and have examined their chemical behaviour. They found remarkable *b*-side preference for some thermal reactions (catalytic hydrogenation, Michael addition, and conjugate addition) and reasoned that the selectivity observed was due to pyramidalization of all sp^2 carbon atoms as depicted in formula (**E**) (Figure 1). (2) Demuth *et al.*,[7] on the other hand, have found that chiral spirocyclic dioxinones [*e.g.*, (**F**)] exhibit

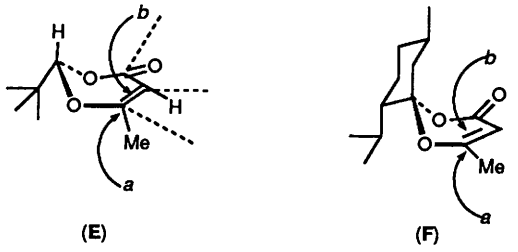


Figure 1.

remarkable *a*-side preference in their photoaddition to alkenes, and they explained the selectivity by assuming that the alkenes approach from the more exposed *a*-side of the sofa conformation as depicted in formula (**F**). Though both assumptions [pyramidalization of all sp^2 carbon atoms to the side of the acetal carbon of compound (**E**) and gross sofa conformations of both models (**E**) and (**F**)] were verified by X-ray crystallographic analysis, Seebach has suggested that *a*-side preference in the photocycloaddition is due to the reverse pyramidalization (the pyramidalization to the opposite side of the acetal carbon) in the triplet excited species of these dioxinones.

We also have been interested in using chiral spirocyclic dioxinones as synthons of EPCs and have so far reported successful results on the EPC syntheses of both Corey's lactone analogue[8] and iridoids[9] by photocycloaddition, carbocyclic *C*-nucleosides[10] by Diels–Alder reaction, and 3-hydroxyalkanoic acids[11] either by catalytic hydrogenation or by conjugate addition. The selectivities observed in the above reactions are the same as those reported by other workers[6,7] except for the Diels–Alder reaction, which has never been examined before. Remarkably, although the Diels–Alder reaction proceeds with almost complete *a*-side preference, it is obviously a *thermal* reaction. Thus, at least, the mechanism based on the reverse pyramidalization in the triplet excited species for *a*-side preference in the photoaddition reaction cannot be extended to explain the Diels–Alder reaction.

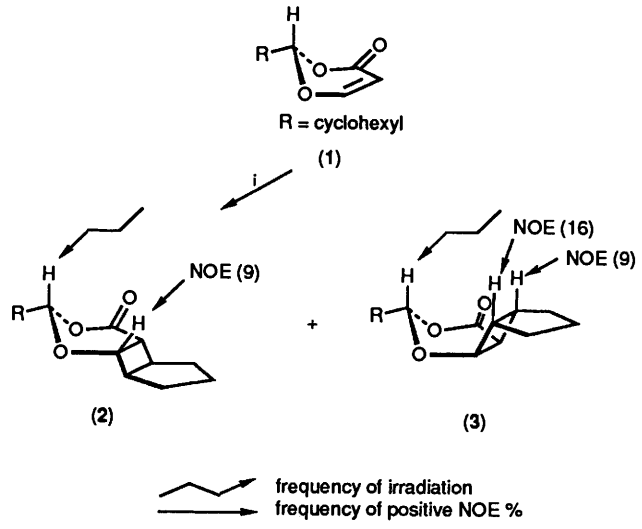
In this paper, we will describe our results concerning both the use of chiral 2-monosubstituted dioxinones as synthons for EPCs and the comparison of the diastereofacial selectivities between two kinds of dioxinones; we also propose a general mechanistic scheme for the selectivities covering all asymmetric reactions of these dioxinones [(**E**) and (**F**)].

Results and Discussion

A Model Study for the Use of 2-Monosubstituted Dioxinones

as Synthons for EPCs.—Three racemic dioxinones (**1**), (**5a**), and (**5b**) were used as typical substrates for photochemical and thermal pericyclic reactions. Though these dioxinones are available as EPCs* it was unnecessary to use EPCs in the present study.

First, since the diastereofacial selectivity in the photoaddition of the 2-monosubstutited dioxinones to alkenes had not been studied, irradiation (300 nm) of compound (**1**) in ethyl acetate containing cyclopentene was examined. On room temperature irradiation, a mixture of two diastereoisomers (**2**) and (**3**) was obtained (Scheme 2). Two isomers were readily separated by

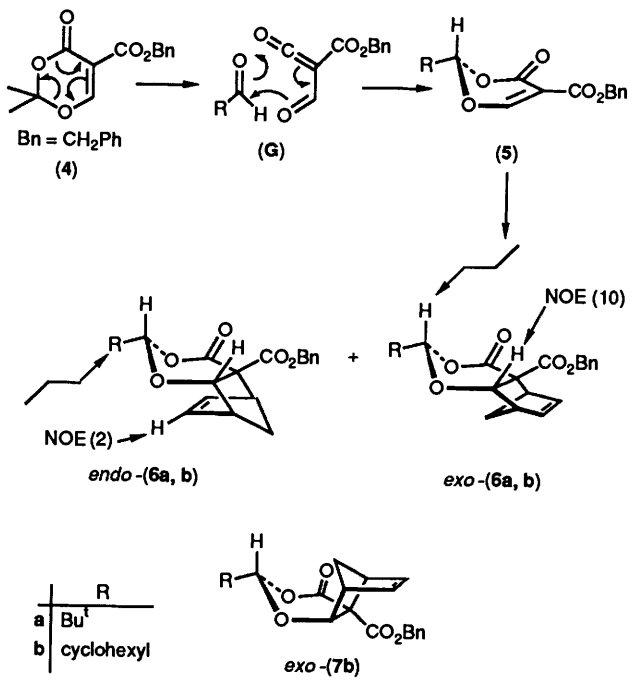


Scheme 2. *Reagents and conditions:* i, *hv*, cyclopentene.

column chromatography over silica gel to give nearly equal amounts of isomers (**2**) and (**3**), both of which had the *cis-anti-cis* structure as evidenced by ^{1}H NMR spectroscopy (see Experimental section). The selective formation of the *cis-anti-cis* adduct has been previously noted when 2,2-dimethyldioxinone (an achiral compound) was photoadded to cyclopentene.[12] The structure of each adduct was determined from the nuclear Overhauser effect (NOE) as depicted in the formulae [(**2**) is the *a*-side addition product and (**3**) the *b*-side addition product].

Though the ratio of isomers was nearly 1:1 in the above reaction, preferential formation of isomer (**2**) over isomer (**3**) was observed when the irradiation was performed at −78 °C. The exact ratio of products (**2**):(**3**) was determined to be 8:5 (DE 23%) by high-pressure liquid chromatography (HPLC).

Next, Diels–Alder reaction of the ester (**5a**) with cyclopentadiene was examined. Ester (**5a**) and related dienophile (**5b**) were synthesized readily by [4 + 2]cycloaddition of aldehydes to the formylketene (**G**) thermally generated from the 2,2-dimethyldioxinone (**4**).[13] When compound (**5a**) was treated in toluene with the diene at room temperature, an adduct was formed in 20% yield. The structure of the adduct was deduced as the *exo* product by the coupling constant (*J* 0 Hz) between the proton on the dioxanone ring and the vicinal proton, and was determined as *exo*-(**6a**) by the NOE (10%) as depicted in Scheme 3. The use of diethylaluminium chloride as catalyst accelerated the reaction. The same adduct *exo*-(**6a**) (31%) was obtained even at 0 °C. The use of high pressure for the above



Scheme 3.

Diels–Alder reactions increased the yield of the adduct appreciably. Thus, at 11 kbar, the dioxinone (**5a**) afforded adduct *exo*-(**6a**) in 64% yield. It seems noteworthy that, in this case, an *endo*-adduct, which showed a coupling constant (*J* 4 Hz) between the proton on the dioxanone ring and the vicinal proton, was obtained in 5% yield and its structure was determined as *endo*-(**6a**) again by the NOE (2%) as depicted in the formula (Scheme 3).

When the dioxinone (**5b**) was treated in toluene with the diene at room temperature, in addition to the expected major adduct [*exo*-(**6b**) (30%)] an *endo*-adduct [*endo*-(**6b**)] was obtained in minor amounts (5%). The *endo*- or *exo*-configuration of each adduct was deduced by the coupling constants (*J* 4 Hz for *endo* and *J* 0 Hz for *exo*) between the corresponding vicinal protons. The use of diethylaluminium chloride as catalyst accelerated the reaction. The major adduct [*exo*-(**6b**) 33%] was obtained even at 0 °C. In this reaction, however, none of *endo*-(**6b**) adduct was obtained. Instead, a third adduct was obtained in 11% yield. The structure of this adduct is apparently *exo*-(**7b**) as judged from the coupling constant of the proton on the dioxanone ring (*J* 0 Hz).

Comparison of the Diastereofacial Selectivities Between the Reactions of Two Kinds of Dioxinone (**E**) *and* (**F**)*, and Analysis of their Mechanistic Differences.*—From the researches of our and other groups concerning diastereofacial selectivity of two kinds of dioxinones (**E**) and (**F**), the following preferences have already been observed. (i) Catalytic hydrogenation and conjugate addition proceed with almost compete *b*-side preference for both (**E**)[6] and (**F**).[11] (ii) For the photoaddition of cyclopentene to (**F**), a high *a*-side preference was observed by Demuth[7] and by us[8,9,11] even when irradiation was carried out at room temperature. (iii) The same *a*-side preference was also found in the Diels–Alder reaction of the spirocyclic dioxinones [*e.g.*, (**F**)] carrying an electron-withdrawing substituent on their C=C double bond.[10]

As described in the foregoing section we have now found for the first time that either photoadditions to alkenes or Diels–Alder reactions with alkadienes of 2-monosubstituted dioxinones [*e.g.*, (**E**)] proceed with *a*-side preference, though the

* Seebach *et al.* synthesized 2-t-butyl-6-methyl-4*H*-1,3-dioxin-4-one as an EPC starting from (*S*)-3-hydroxybutanoic acid.[6] Later, they established the preparative method for a variety of 2-monosubstituted dioxinones as EPCs by chromatographic separation of the corresponding racemic dioxinones on a chiral column: D. Seebach, S. G. Muller, U. Gysel, and J. Zimmermann, *Helv. Chim. Acta*, 1988, **71**, 1303.

diastereofacial excesses (DEs) of the photoaddition reactions are much lower than those of the corresponding reactions of spirocyclic dioxinones (**F**).

It is obvious from the above experimental data that the preference (*a*- or *b*-side) depends only upon the type of reaction and not upon the kind of dioxinone used [(**E**) and (**F**)].

Previously, we explained the *a*-side preference in the photoreactions of dioxinones (**F**) by assuming that the spirocyclic dioxinones exist in an equilibrium between two sofa conformers (**H**) and (**I**) and that the major conformer (**H**) (its conformation was verified by X-ray crystallographic analysis) takes the major role when the attacking reagents are relatively small, so as to accept them from the more exposed *a*-side, while when the reagents are much more bulky they only attack the least hindered *b'*-side of the minor conformer (**I**) (Figure 2).[11] However, our explanation for *b'*-side (*b*-side) attack is not correct, because as mentioned above it has already been demonstrated that catalytic hydrogenation and conjugate addition reactions of substrate (**E**) [t-butyl group is too bulky to allow the molecule to assume a significant proportion of conformer (**I**)] proceed with complete *b*-side preference, and DEs of the reaction products of 2,6-disubstituted dioxinones are uniformly high irrespective of the nature of the 2-substituent [*e.g.*, methyl instead of t-butyl in (**F**)].[6]

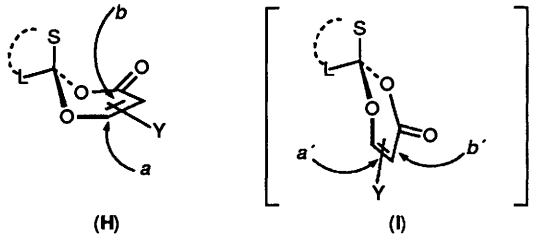


Figure 2. S and L represent small and large substituents or a chiral cyclic system.

For the *b*-side preference in catalytic hydrogenation and conjugate addition reactions of substrates (**E**), Seebach *et al.* have proposed the following novel idea: the steric course of attack on a trigonal centre can be predicted from the direction of its pyramidalization, and reaction occurs preferentially from the direction into which the centre is pyramidalized.[6] If the assumption that the single conformer (**H**) is the only species present in the reaction medium is valid (*vide supra*), this idea could surely be extended to the same reactions (*i.e.*, conjugate addition and catalytic hydrogenation) of the spirocyclic dioxinones (**F**). Though they did not examine the photoaddition reactions of substrates (**E**), they explained the *a*-side preference in the photoreactions of substrates (**F**) reported by both Demuth[7] and us[11] by the reverse pyramidalization (the pyramidalization of the opposite side of the acetal carbon) in the triplet excited species of dioxinones (**F**). Since the preponderance of *a*-side attack in the Diels–Alder reactions of both dioxinones (**E**) and (**F**) has been demonstrated clearly, it is obvious that there exists another mechanism for the *a*-side preference in the pericyclic reactions irrespective of the electronic state of these dioxinones (**E**) and (**F**).

It is tempting to propose that the *a*-side attack is due solely to the preferential attack of appropriate alkenes (the photoaddition reactions) and dienes (the Diels–Alder reactions) to the conformer (H) [of either (**E**) or (**F**)] from the less hindered side, irrespective of the electronic states of the substrates. Thus, we may conclude that essentially all the reactions (under either kinetic or thermodynamic control) should proceed by *a*-side preference, so long as these dioxinones assume the sofa conformation. Some thermal reactions which proceeded by *b*-side preference under kinetic control are rather exceptional, for which the above mentioned pyramidalization could well be the reason.

In conclusion, the results described in this paper suggest that the use of chiral dioxinones (**E**) and (**F**) makes it possible to design new rational synthetic methods for a variety of EPCs only if suitable care is taken when predicting diastereofacial selectivities.

Experimental

M.p.s were determined on a Yanaco micromelting point apparatus (MP-S2), and are uncorrected. IR spectra were recorded on a JASCO A-102 spectrophotometer. ^{1}H NMR spectra were recorded with tetramethylsilane as internal standard on a JEOL JNM PMX-6 OSI or a JNM-FX500 spectrometer at 60 MHz and 500 MHz, respectively. High-resolution mass spectra were recorded on a JEOL JNM-01SG-2 system. Wakogel (C-200) was employed for silica gel column chromatography. Merck Kieselgel 60F 254 was employed for TLC. High-pressure liquid chromatography (HPLC) was performed with a Waters μ-PORASIL column (25 cm). Medium-pressure liquid chromatography (MPLC) was performed with a Merck Lobar column (LiChroprep Si 60). The irradiation source used for photoreactions was a Rayonet photochemical reactor lamp (Cat. No. RPR-3000 Å) and the reactions were carried out in a quartz vessel.

*Benzyl 2-t-Butyl-4-oxo-*4H*-1,3-dioxine-5-carboxylate* (**5a**).—A solution of benzyl 2,2-dimethyl-4-oxo-4*H*-1,3-dioxine-5-carboxylate[14] (**4**) (3.14 g, 12 mmol) and pivalaldehyde (3.10 g, 36 mmol) in dry benzene (50 ml) was heated under reflux for 20 min. Evaporation of the solvent and an excess of the aldehyde under reduced pressure gave almost pure title compound (**5a**) (2.97 g, 85%). Recrystallization from diethyl ether–pentane afforded *compound* (**5a**) as needles, m.p. 46–48 °C (Found: M^+, 290.1158. $C_{16}H_{18}O_5$ requires *M*, 290.1154); ν_{max}($CHCl_3$) 1 779, 1 715, and 1 601 cm^{-1}; δ_H($CDCl_3$) 1.05 (9 H, s, Bu^t), 5.20 (1 H, s, 2-H), 5.33 (2 H, s, PhCH_2), 7.40 (5 H, br s, Ph), and 8.38 (1 H, s, 6-H).

*Benzyl 2-Cyclohexyl-4-oxo-*4H*-1,3-dioxine-5-carboxylate* (**5b**).—A solution of compound (**4**) (2.62 g, 10 mmol) and cyclohexanecarbaldehyde (2.24 g, 20 mmol) in dry benzene (50 ml) was heated under reflux for 1 h. The residue obtained after evaporation of the solvent and an excess of the aldehyde under reduced pressure was cooled in ice–water. Pentane was added to the crystalline residue, and insoluble crystals were filtered off and washed with pentane to give compound (**5b**) (3.61 g, 95%) as almost pure crystals. Recrystallization from diethyl ether–pentane gave the *title ester* (**5b**) as prisms, m.p. 69–70 °C (Found: M^+, 316.1310. $C_{18}H_{20}O_5$ requires *M*, 316.1310); ν_{max}($CHCl_3$) 1 779, 1 715, and 1 601 cm^{-1}; δ_H($CDCl_3$) 0.92–2.30 (11 H, m, cyclohexyl), 5.30 (2 H, s, PhCH_2), 5.33 (1 H, s, 2-H), 7.40 (5 H, br s, Ph), and 8.30 (1 H, s, 6-H).

(1R*,2S*,6R*,7S*,9S*)- *and* (1R*,2S*,6R*,7S*,9R*)-9-*Cyclohexyl-*8,10-*dioxatricyclo*[5.4.0.0^{2,6}]*undecan-*11-*one* (**2**) *and* (**3**).—(a) *Irradiation at room temperature.* A solution of compound (**1**)[14] (182 mg, 1 mmol) and cyclopentene (1.36 g, 20 mmol) in ethyl acetate (20 ml) was treated with bubbling argon for 5 min and then irradiated for 18 h. By this time, all of the reactant (**1**) had been consumed (TLC). HPLC [hexane–tetrahydrofuran (THF) (50:1)] of the reaction product revealed that only two adducts were formed, in almost equal amounts. The residue obtained after evaporation of the solvent was chromatographed over silica gel (10 g) with hexane–ethyl acetate (10:1) as eluant to give a mixture of the two adducts (179 mg, 72%).

Separation of this mixture by MPLC [hexane–ethyl acetate (10:1)] gave compound (**3**) (less polar; 84 mg, 34%) and compound (**2**) (more polar; 65 mg, 26%).

For *compound* (**3**), m.p. 78–80 °C (prisms from pentane) (Found: C, 71.7; H, 8.75. $C_{15}H_{22}O_3$ requires C, 71.95; H, 8.85%); $\nu_{max}CHCl_3$) 1 725 cm^{-1}; $\delta_H(CDCl_3$; 500 MHz)† 1.13–1.31 (6 H, m, 3′-, 4′-, and 5′-H_2), 1.55–1.95 (11 H, m, 2′-, 6′-, 3-, 4-, and 5-H_2 and 1′-H), 2.77 (1 H, ddd, *J* 7.5, 5.0, and 1.4 Hz, 1-H), 2.84–2.89 (1 H, m, 6-H), 2.92 (1 H, dt, *J* 7.5 and 6.0 Hz, 2-H), 4.11 (1 H, dd, *J* 7.5 and 2.3 Hz, 7-H), and 5.53 (1 H, d, *J* 5 Hz, 9-H).

For *compound* (**2**), m.p. 72–73 °C (prisms from pentane) (Found: C, 72.35; H, 8.85%); $\nu_{max}(CHCl_3)$ 1 730 cm^{-1}; $\delta_H(CDCl_3$; 500 MHz)† 1.09–1.25 (6 H, m, 3′-, 4′-, and 5′-H_2), 1.46–1.94 (11 H, m, 2′-, 6′-, 3-, 4-, and 5-H_2 and 1′-H), 2.59 (1 H, ddd, *J* 7.5, 5.0, and 1.5 Hz, 1-H), 2.75 (1 H, dt, *J* 7.0 and 1.4 Hz, 6-H), 3.12 (1 H, dt, *J* 7.0 and 5.0 Hz, 2-H), 4.07 (1 H, dd, *J* 7.0 and 2.0 Hz, 7-H), and 4.88 (1 H, d, *J* 5.0 Hz, 9-H).

(b) *Irradiation at* −78 °C. Irradiation was performed under the same conditions as in (a) above except that the solution was kept at −78 °C throughout by solid CO_2–acetone. After irradiation, the ratio of products (**2**):(**3**) was determined as 1.6:1 by HPLC.

Diels–Alder Reaction of Compound (**5a**) *with Cyclopentadiene* {*Benzyl* (1R*,2R*.4R*,7S*,8S*)-4-*t-Butyl*-6-*oxo*-3,5-*dioxatricyclo*[6.2.1.$0^{2,7}$]*undec*-9-*ene*-7-*carboxylate* [exo-(**6a**)] *and Benzyl* (1R*,2S*,4S*,7R*,8S*)-4-*t-Butyl*-6-*oxo*-3,5-*dioxatricyclo*[6.2.1.$0^{2,7}$]*undec*-9-*ene*-7-*carboxylate* [endo-(**6a**)]}.—(a) *Reaction in toluene without catalyst.* To a solution of compound (**5a**) (290 mg, 1.0 mmol) in dry toluene (10 ml) was added cyclopentadiene (3.3 g, 50 mmol). The mixture was kept for 10 days at room temperature while cyclopentadiene (3.3 g, 50 mmol) was added every day. The residue obtained after evaporation of the solvent was chromatographed over silica gel (50 g). Elution with hexane–ethyl acetate (75:1) gave the dimer of cyclopentadiene. Elution with hexane–ethyl acetate (30:1) gave *adduct* exo-(**6a**) (72 mg, 20%) as needles, m.p. 91–92 °C (from pentane) (Found: M^+, 356.1629. $C_{21}H_{24}O_5$ requires *M*, 356.1622); $\nu_{max}(CHCl_3)$ 1 758 and 1 723 cm^{-1}; $\delta_H(CDCl_3$; 500 MHz) 0.97 (9 H, s, Bu^t), 1.66 (1 H, dd, *J* 10.0 and 2.0 Hz, 11-H), 1.75 (1 H, d, *J* 10.0 Hz, 11-H), 3.02–3.05 (1 H, m, 1-H), 3.70–3.73 (1 H, m, 8-H), 4.37 (1 H, d, *J* 2.0 Hz, 2-H), 5.10 (1 H, d, *J* 12.5 Hz, PhC*H*), 5.12 (1 H, s, 4-H), 5.21 (1 H, d, *J* 12.5 Hz, PhC*H*), 6.09 (1 H, dd, *J* 5.1 and 4.0 Hz, 10-H), 6.17 (1 H, dd, *J* 5.1 and 4.0 Hz, 9-H), and 7.30–7.40 (5 H, m, Ph).

(b) *Reaction in the presence of diethylaluminium chloride.* To an ice-cooled, stirred solution containing compound (**5a**) (290 mg, 1 mmol) and cyclopentadiene (660 mg, 10 mmol) in dry toluene (10 ml) was added a solution of diethylaluminium chloride in toluene (1 ml of a 0.1M solution, 0.1 mmol). After the mixture had been cooled in ice for 2 h, crushed ice (10 g) was added and the product was extracted with diethyl ether. After being washed with water, the extract was dried over magnesium sulphate. The residue obtained after evaporation was chromatographed on silica gel (30 g). Elution with hexane–ethyl acetate (75:1) gave the dimer of cyclopentadiene, and elution with hexane–ethyl acetate (30:1) gave adduct *exo*-(**6a**) (109 mg, 31%).

(c) *Reaction under high pressure.* Compound (**5a**) (145 mg, 0.5 mmol) and cyclopentadiene (330 mg, 5 mmol) were allowed to react in dichloromethane (1.2 ml) under 11 kbar pressure at room temperature for 2 days. Column chromatography on silica gel (15 g) with hexane–ethyl acetate as eluant afforded adduct *exo*-(**6a**) (114 mg, 64%) and then adduct *endo*-(**6a**) (19 mg, 6%).

Adduct endo-(**6a**) was obtained as needles, m.p. 99–101 °C (from pentane) (Found: M^+, 356.1627. $C_{21}H_{24}O_5$ requires *M*, 356.1622); $\nu_{max}(CHCl_3)$ 1 758 and 1 730 cm^{-1}; $\delta_H(CDCl_3$; 500 MHz) 0.87 (9 H, s, Bu^t), 1.58–1.60 (br d, 11-H, overlapped with signal of water), 1.74 (1 H, d, *J* 10 Hz, 11-H), 3.15–3.19 (1 H, m, 1-H), 3.61–3.65 (1 H, m, 8-H), 4.79 (1 H, d, *J* 4.5 Hz, 2-H), 4.95 (1 H, s, 4-H), 5.19 (1 H, d, *J* 12.5 Hz, PhC*H*), 5.28 (1 H, d, *J* 12.5 Hz, PhC*H*), 6.18 (1 H, dd, *J* 6.3 and 3.0 Hz, 10-H), 6.29 (1 H, dd, *J* 6.3 and 3.0 Hz, 9-H), and 7.31–7.40 (5 H, m, Ph).

Diels–Alder Reaction of Compound (**5b**) *with Cyclopentadiene* {*Benzyl* (1R*,2R*,4R*,7S*,8S*)-4-*Cyclohexyl*-6-*oxo*-3,5-*dioxatricyclo*[6.2.1.$0^{2,7}$]*undec*-9-*ene*-7-*carboxylate* [exo-(**6b**)], *Benzyl* (1R*,2S*,4S*,7R*,8S*)-4-*Cyclohexyl*-6-*oxo*-3,5-*dioxatricyclo*[6.2.1.$0^{2,7}$]*undec*-9-*ene*-7-*carboxylate* [endo-(**6b**)], *and Benzyl* (1R*,2R*,4S*,7S*,8S*)-4-*Cyclohexyl*-6-*oxo*-3,5-*dioxatricyclo*[6.2.1.$0^{2,7}$]*undec*-9-*ene*-7-*carboxylate* [exo-(**7b**)]}.—(a) *Without catalyst.* To a solution of compound (**5b**) (158 mg, 0.5 mmol) in dry toluene (3 ml) was added cyclopentadiene (1.65 g, 25 mmol). The mixture was kept for 5 days at room temperature while cyclopentadiene (1.65 g, 25 mmol) was added every day. The residue obtained after evaporation of the solvent was chromatographed on silica gel (15 g). Elution with hexane–ethyl acetate (75:1) gave the dimer of cyclopentadiene. Elution with hexane–ethyl acetate (30:1) gave at first the less polar adduct *exo*-(**6b**) (58 mg, 30%) and then the more polar adduct *endo*-(**6b**) (10 mg, 5%).

For *adduct* exo-(**6b**): m.p. 58–59 °C (needles from pentane) (Found: M^+, 382.1780. $C_{23}H_{26}O_5$ requires *M*, 382.1779); $\nu_{max}(CHCl_3)$ 1 759 and 1 729 cm^{-1}; $\delta_H(CDCl_3$; 500 MHz)† 1.06–1.29 (6 H, m, 3′-, 4′-, and 5′-H_2), 1.64–1.88 (7 H, m, 2′-, 6′-, and 11-H_2 and 1′-H), 3.00–3.05 (1 H, m, 1-H), 3.70–3.73 (1 H, m, 8-H), 4.36–4.38 (1 H, m, 2-H), 5.10 (1 H, d, *J* 12.5 Hz, PhC*H*), 5.20 (1 H, d, *J* 12.5 Hz, PhC*H*), 5.26 (1 H, d, *J* 5.0 Hz, 4-H), 6.09 (1 H, dd, *J* 5.0 and 4.0 Hz, 10-H), 6.16 (1 H, dd, *J* 5.0 and 4.0 Hz, 9-H), and 7.27–7.45 (5 H, m, Ph).

For *adduct* endo-(**6b**): m.p. 71–72 °C (needles from pentane) (Found: M^+, 382.1757); $\nu_{max}(CHCl_3)$ 1 758 and 1 730 cm^{-1}; $\delta_H(CDCl_3)$ 0.70–2.10 (13 H, m, cyclohexyl and 11-H_2), 2.93–3.33 (1 H, m, 1-H), 3.50–3.80 (1 H, m, 8-H), 4.80 (1 H, d, *J* 4.0 Hz, 2-H), 5.10–5.40 (3 H, m, PhCH_2 and 4-H), 6.00–6.50 (2 H, m, 9- and 10-H), and 7.30 (5 H, br s, Ph).

(b) *In the presence of diethylaluminium chloride.* To a stirred ice-cooled solution of compound (**5a**) (316 mg, 1 mmol) and cyclopentadiene (660 mg, 10 mmol) in dry toluene (10 ml) was added a solution of diethylaluminium chloride in toluene (0.1M; 0.1 ml, 0.1 mmol). After the mixture had been stirred for 2 h at 0 °C, crushed ice (10 g) was added and the product was extracted with diethyl ether. The extract was dried ($MgSO_4$) and the solvent was evaporated off under reduced pressure. The residue was separated by column chromatography (silica gel, 38 g). Elution with hexane–ethyl acetate (75:1) afforded the dimer of cyclopentadiene. Elution with hexane–ethyl acetate (30:1) gave, first, adduct *exo*-(**6b**) (124 mg, 33%) and then adduct *exo*-(**7b**) (39 mg, 11%). *Adduct* exo-(**7b**) showed m.p. 86–87 °C (needles from pentane) (Found: M^+, 382.1785); $\nu_{max}(CHCl_3)$ 1 750 and 1 731 cm^{-1}; $\delta_H(CDCl_3)$ 0.73–2.20 (13 H, m, cyclohexyl and 11-H_2), 2.83–3.20 (1 H, m, 1-H), 3.50–3.80 (1 H, m, 8-H), 4.30–4.50 (1 H, m, 2-H), 4.97–5.30 (3 H, m, PhCH_2 and 4-H), 5.90–6.30 (2 H, m, 9- and 10-H), and 7.30 (5 H, br s, Ph).

† Primed locants refer to the cyclohexane moiety.

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