SYNTHESIS OF POLYCYCLIC SYSTEMS *VIA* DIELS-ALDER REACTIONS OF SUGAR DERIVED DIENES

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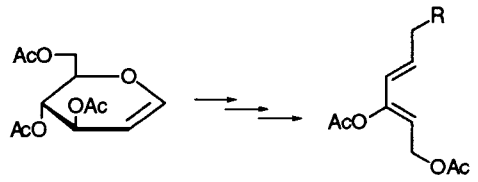
Abstract- Several Diels-Alder reactions of sugar derived dienes (2*Z*, 4*E*)-1,3,6-triacetoxyhexa-2,4-diene (**2**) and (2*Z*, 4*E*)-1,3-diacetoxy-6-cyclohexylamino-hexa-2,4-diene (**3**) with a number of electron-deficient dienophiles were carried out in a completely stereoselective manner to give the corresponding cycloadducts or cascade reaction products. Subsequent chemical transformations yielded highly functionalized polycyclic systems having a controlled stereochemistry. The new compounds described in here keep the *all-cis* configuration at their chiral centers.

INTRODUCTION

Despite its longevity, the Diels-Alder reaction still constitutes one of the most powerful methodologies in organic synthesis. Since its discovery in 1928, this versatile ring-forming reaction has expanded continuously, mainly as consequence of the numerous variations that in both reactants, diene and dienophile, can be incorporated.[1,2] In this sense, carbohydrates also represent valuable substrates, and their potential have been considered in the preparation of a great variety of natural and unnatural products.[3]

As part of our continuing studies involving unsaturated sugar derivatives and their application to Diels-Alder processes, we have described[4,5] the syntheses of dienes (**2**) and (**3**), which were easily available from commercial 3,4,6-tri-*O*-acetyl-D-glucal (Scheme 1). Besides their functionalities on C-1 and C-4,



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2 R = OAc
3 R = NH-C_6H_{11}

Scheme 1

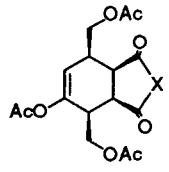
those both dienes have an acyloxy group on C-2, thus permitting the access to suitable Diels-Alder adducts for the construction of cyclohexanone systems, as well as for their participation in tandem reactions leading to polycyclic compounds. Similar cyclohexene rings to those we have obtained by using *N*-phenylmaleimide or maleic anhydride as dienophiles, were used as starting materials for the synthesis of several natural products, such as mevinic acids[6] or cytochalasins.[7-9] In addition, the cyclohexanones

described in this work show structural similitudes with paeonilactones, a class of compounds that have been isolated from the root extracts from plants of the paeony family, and have been used in an analgesic salve for soothing muscle pain.[10]

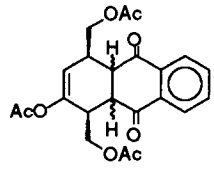
This paper details on Diels-Alder reactivity of dienes (**2**) and (**3**) with several electron-deficient dienophiles, and describes in full the adducts we obtained. Furthermore, through chemical transformations of these (including tandem cascade reactions[11]), highly functionalized bicyclic or triciclyc heteroatomic systems have been prepared.

RESULTS AND DISCUSSION

Cycloaddition reactions between diene (**2**) and maleic anhydride or *N*-phenylmaleimide occurred in a completely *endo*-stereoselective way, yielding compounds (**4**) or (**5**), respectively. The relative *all-cis* stereochemistry for substituents in these adducts was the result of the reaction mechanism, being supported by analytical and spectroscopic evidences; thus the ^{1}H NMR coupling constants $J_{2,3}$ and $J_{1,6}$ showed values of *ca.* 6 Hz, in agreement with a *cis* relationship between the hydrogens concerned, with torsion angles H-2/H-3 and H-1/H-6 of *ca.* 45° in a boat-like conformation of the cyclohexene ring.[12,13] This conformation was also consistent with the high values observed for couplings $J_{1,2}$ (≈ 9 Hz), indicating that the fusion between rings in both adducts requires a practically eclipsed arrangement between H-1 and H-2. As expected, the singlet corresponding to the methyl vinylic acetate is somewhat deshielded (δ ≈ 2.17 ppm) when it is compared with those of acetate groups at C-7 and C-8 (δ ≈ 2.07 and 2.09 ppm). Vinylic hydrogen (H-5) appeared as a double doublet due to a vicinal coupling with H-6 ($J_{5,6}$ = 3.3 Hz) and to an allylic coupling with H-3 ($J_{3,5}$ = 2.9 Hz). The ^{13}C NMR spectrum of **4** showed a signal at 147.1 ppm that disappeared in DEPT experiments, and was assigned to C-4; the resonance of the carbonyl group of vinylic acetate was located at 168.9 ppm, whereas the imide carbonyl groups showed their usual shifts at 175.0 and 175.5 ppm. Similar spectral data were found for the adduct (**5**), with the exception of the chemical shifts for H-1 and H-2, which were shielded by about 0.2 ppm by comparing with these same protons in **4**.



4 X = O
5 X = N-Ph



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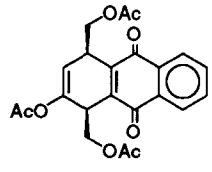

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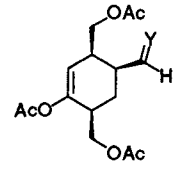
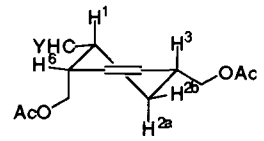


8 Y = O
9 Y = DNPH



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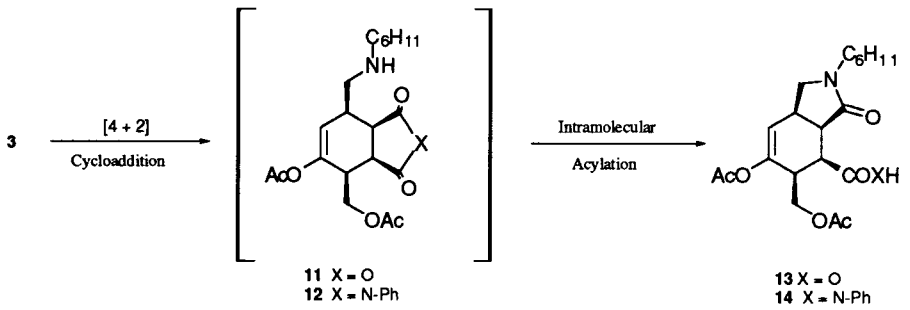
Treatment of diene (**2**) with 1,4-naphthoquinone in toluene at reflux for 11 days afforded *cis*-2-acetoxy-1,4-diacetoxymethyl-1,4-dihydroanthraquinone (**7**); this compound must be the result of a dehydrogenation of the initially formed mixture (**6**) of *endo* and *exo* adducts. Thus, when reaction time was reduced to 9 days, we could isolate, in addition to **7**, a small quantity of an oil that consisted in *endo*-**6** and *exo*-**6** in a 3.5:1 ratio (determined from the ^{1}H NMR spectrum of the mixture (**6**), by integration of the signals corresponding to vinyl protons of each steroisomer); furthermore, by refluxing of this oil in toluene, it was completely converted into **7**. The ^{1}H NMR spectrum of **6** showed signals for H-4a and H-9a at 3.63 and 3.75 ppm, respectively, which were assigned as corresponding to the major *endo* adduct on the basis of their coupling constants $J_{4,4a}$ and $J_{1,9a}$ (6.0 Hz), similar to those observed for analogous

protons in the above cited *endo* adducts (**4**) and (**5**); however, the $J_{4a,9a}$ value is now somewhat smaller, probably because in **6** the atoms H-4a and H-9a are on carbons belonging to two six-membered rings[14] (and not to rings of five and six members). Concerning ^{13}C NMR data for *endo*-**6**, C-4a and C-9a appeared at 47.5 and 49.4 ppm, whereas ketonic carbons were located at 196.0 and 196.1 ppm, clearly more downfield shifted than these same atoms in dehydrogenated **7** (183.0 and 183.1 ppm), in which they are presenting an additional conjugation. Since only a few NMR signals for minor *exo*-**6** could be observed, structural assignment of this compound was made tentatively and based also in the chromatographic homogeneity of mixture (**6**), together with the above mentioned conversion into **7**.

Cycloaddition of **2** with acrolein in toluene under thermic conditions (26 days heating) yielded unseparable mixtures of the four possible adducts, together with some non-reacted starting material. In order to improve these results, and after trials with catalysts such as $SnCl_4$, F_3B-Et_2O and Al_2O_3, the best results were obtained with $ZnCl_2$ under nitrogen in toluene at room temperature, with a reaction time of 5 h. In these conditions, process was complete and we obtained compound (**8**) (57% isolated yield) as resulting of an *endo* interaction between diene and dienophile. The oily adduct (**8**) afforded a solid 2,4-dinitrophenylhydrazone derivative (**9**), being its regio- and stereochemistry determined by NMR spectral data. Thus, the H-5 signal appeared as a double doublet with couplings $J_{5,6}$ (5.8 Hz) and $J_{3,5}$ (1.9 Hz), whereas H-6 showed a coupling with H-1 ($J_{1,6}$ 4.7 Hz); hence, the formyl group must be located at C-1, in agreement with the FMO theory predictions. The high values for couplings $J_{1,2a}$ and $J_{2a,3}$ (> 10 Hz) in **8** and its hydrazone derivative (**9**) were consistent with an *endo* stereochemistry for cycloaddition, and also with the cyclohexene conformation depicted in **10**, in which the three protons H-1, H-2a and H-3 are in axial positions.

As shown in Scheme 2, Diels-Alder reactions between readily available[4] alkylaminodiene (**3**) and maleic anhydride or *N*-phenylmaleimide led to bicyclic lactams (**13**) and (**14**), respectively. Formation of these compounds can be explained through a cascade reaction, so that an initial *endo* cycloaddition to give the



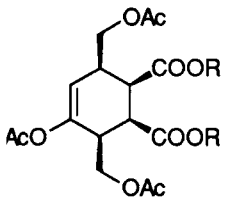
Scheme 2

nonisolated adducts (**11**) and (**12**) must be followed by an intramolecular acylation. Although the combination of a Diels-Alder reaction with an intramolecular acylation has no been reported very often,[15] it constitutes an interesting method for the rapid and selective building of highly functionalized polycyclic systems. Structures of **13** and **14** are supported on elemental analyses and spectroscopic data. The NMR spectra were closely similar, the main differences arising from the presence of the phenyl ring in **14**; this group promoted a shielding effect on the chemical shifts of adjacent atoms; thus, the signal due to methyl acetate on C-8 was at 1.68 ppm, whereas in **13** this same signal appeared at 2.07 ppm. This effect was also observed for the absortion of the lactam carbonyl group, that was at 169.7 ppm in **14** and at 173.5 ppm in **13**. Furthermore, the influence of the aromatic ring is according with an *all-cis* stereochemistry

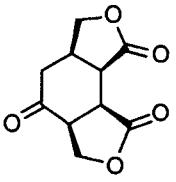
and, since it was not observed for compound (**5**), we rejected the possible bicyclic structure (**12**). In the case of **13**, the structure (**11**) could be discarded because of the absence of an IR absortion for the carbonyl group at about 1795 cm^{-1}.

One of the most useful structural features in cycloadducts described in this paper is the presence of a vinylic acetate group, thus making of them convenient cyclohexanone precursors. Focussing our attention on this objective, we have studied the selective hydrolysis of **4** and **5** under different reaction conditions. In this way, by treatment of **4** in refluxing water, there was an opening of the anhydride ring and dicarboxylic acid (**15**) was formed in quantitative yield; NMR spectra of this compound were closely similar to those of its precursor, the main differences arising from the presence of the two carboxylic protons, which appeared as a broad singlet at 8.99 ppm. Also, the coupling constant $J_{1,2}$ showed a value that is clearly smaller (3.6 Hz) than that observed in **4** (9.6 Hz), thus supporting a *cis* axial-equatorial relationship between H-1 and H-2. By reaction of **4** with 1,3-dicyclohexylcarbodiimide and 4-dimethylaminopyridine in methanol, we obtained the dimethyl ester (**16**); as expected, with the exceptions due to signals of methyl groups, its NMR spectra were totally similar to those of **15**, thus corroborating the proposed structure and conformation of the cyclohexene ring.

When hydrolysis of **4** was carried out under acid conditions (refluxing 4N HCl), a new cascade process happened, and the tricyclic *bis*carbolactone (**17**) was obtained. Formation of this compound supported the *endo*-stereochemistry in Diels-Alder reaction leading to *all-cis* adduct (**4**); sequentially, the involved steps could be the anhydride ring opening, the hydrolysis of the three acetate groups (including a keto-enol tautomerism, which gives rise to cyclohexanone ring), and the double lactonization that yielded the final product. IR spectrum of **17** showed strong bands at 1710 cm^{-1} (ketonic carbonyl group), together with others at 1755 and 1770 cm^{-1}, which were assigned to lactonic carbonyl groups on a five-membered ring; in ^{13}C NMR, these signals were evident at 208.5, 176.1 and 176.0, respectively.



15 R = H
16 R = Me



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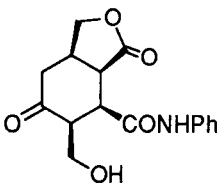

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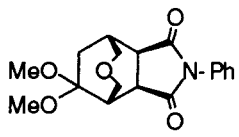

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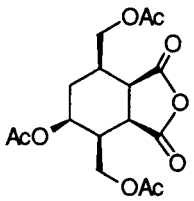

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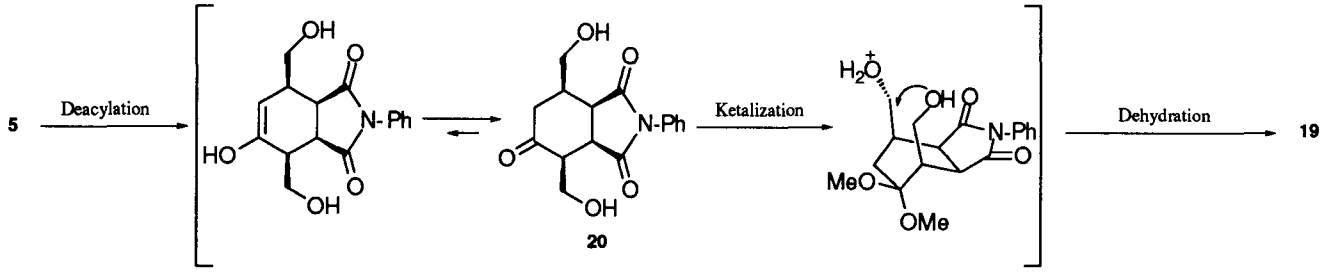
By using the above cited conditions, the acid hydrolysis of carboximide (**5**) yielded bicyclic cyclohexanone (**18**). Again, this product must be the result of a cascade reaction, although in this case the sequence of involved steps could be somewhat distinct from that we proposed previously. Since there was no reaction when **5** was refluxed in water, we think that under an acid aqueous medium, the most logical possibility is that the acetate groups could be hydrolyzed and then the resulting hydroxyl at C-7 can effect the opening of imide ring, with concomitant formation of the lactone. Compound (**18**) showed IR bands for the three types of carbonyl groups it presents: 1770 cm^{-1} (lactone), 1710 cm^{-1} (ketone) and 1680 cm^{-1} (amide). Formation of lactone ring through hydroxyl group at C-7, and not through the located at C-8, could be due to its greater nucleophicility, taking into account that the former is further from the ketonic carbonyl than the second. The close analogies in chemical shifts of the protons H-4, H-5, H-6ax, H-6eq, H-7' and H-7",

when they are compared with the analogues in the *bis*carbolactone (**17**), supported the joining of the lactone ring through C-4 and C-5 carbons of cyclohexene.

In order to find a procedure in which the imidic ring of **5** would not be oppened, we attempted deacetylation in less drastic conditions, as example in a basic medium with potassium carbonate in aqueous methanol; nevertheless, this method did not give satisfactory results, because inseparable complex mixtures of products were obtained. However, under acidic transesterification conditions with acetyl chloride in dry methanol[16,17] (methanolic hydrogen chloride) we isolated, in quantitative yield, a solid that showed to be the tricyclic cyclohexanone dimethyl acetal (**19**). This treatment has been used for deacetylation in those cases where the classic acid or basic conditions gave non-desired collateral reactions.[17,18] Formation of **19** may be explained again by a cascade process (Scheme 3) that should commence with a complete deacetylation of **5**, thus giving an enol that tautomerizes to its corresponding cyclohexanone (**20**); then, ketalization of the carbonyl group and dehydration will give the final product. The *cis*-relationship between



Scheme 3

hydroxymethyl substituents at C-3 and C-6 makes the dehydration possible; furthermore, as hydroxyl groups must be sufficiently close, the cyclohexanone dimethyl ketal ring must addopt a boat-like conformation. The structure of **19** was consistent with the absence of IR hydroxylic bands and the presence of an absortion at 1705 cm^{-1}, assigned to imide carbonyl group; in the ^{13}C NMR spectrum, the C-7 and C-8 carbons were evident at 71.9 and 68.4 ppm.

On the other hand, we have performed the catalytic hydrogenation of adduct (**4**) with 10% palladium on carbon in dry acetone. This process showed to be completely stereoselective, yielding the saturated anhydride (**21**) as the only product; in this way, the configuration at the new chiral center (C-4) would be determined by the steric crowding on the upper face in **4**, which causes the catalytic hydrogenation occurs

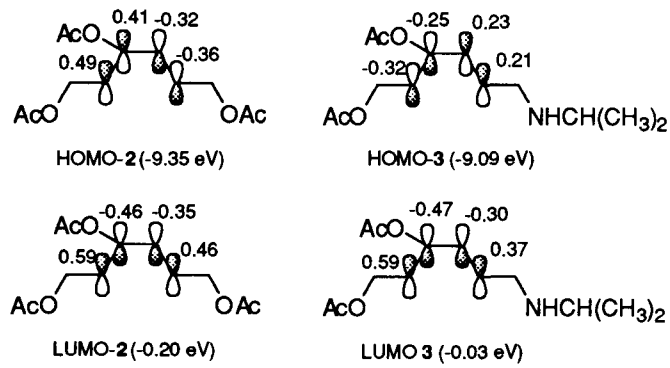


Figure 1 Atomic orbital coeficient values and energies for dienes (**2**) and (**3**).

entirely on the opposite face.[19] The coupling constants between H-1, H-2, H-3 and H-6 were in agreement with those observed for **4**, hence we deduce that these both compounds must present analogous conformations. Finally, the presence of the proton H-4 (br d, 5.20 ppm) and the absence of olefinic carbons in NMR spectra supported the proposed structure.

In Figure 1 are presented the values of frontier orbital energies and atomic coefficients for dienes (**2**) and (**3**) (to simplify, we have changed in the latter cyclohexyl by isopropyl). These values have been obtained by PM3 semiempirical calculations,[20] by using the GAUSSIAN 94W suite of programs.[21]

In agreement with the Frontier Molecular Orbital theory, the above data indicate that the Diels-Alder reactions we described in this work must be of normal electron-demand type (HOMO-diene LUMO-dienophile controlled), as it is dictated by the smallest separation between energy levels of HOMO-dienes and LUMO-dienophiles.

EXPERIMENTAL

Silica gel 60 (Merck, 230-400 mesh ASTM for flash chromatography) was used for column chromatography, which was carried out using dry-column mode[22] (technique a) or flash mode[23] (technique b) and are specified in each case. Preparative TLC was performed using silica gel (Merck 60 GF_{254}). TLC was performed on precoated Merck Kieselgel 60 GF_{254} aluminum backed plates; bands were visualized by UV light. Reagents were used as supplied by Aldrich Chemical Co. NMR spectra were taken either on a Bruker AC-200 E instrument (200.13 MHz for ^1H and 50.33 MHz for ^{13}C) or on a Bruker AC/PC instrument (400.13 MHz for ^1H and 100.62 MHz for ^{13}C). Chemical shifts are reported in δ (ppm) with reference to Me_4Si (δ = 0.00 ppm) for ^1H spectra or $CDCl_3$ (δ = 77.00 ppm) for ^{13}C spectra as internal standards. Coupling constant values are recorded in Hz. When reported, characterization of NMR signals is based on spin decoupling, heteronuclear chemical shift correlation spectroscopy and DEPT experiments. HRMS (chemical ionization) were recorded on a VG Autospec spectrometer by the Servicio de Espectrometría de Masas de la Universidad de Córdoba; only significant fragment ions are reported, and only molecular ions are assigned. IR spectra were recorded on a Perkin-Elmer 399 and a FT-IR MIDAC Corporation spectrophotometers. Solid samples were run as KBr disks and liquids as thin films on NaCl plates. Details are reported as ν_{max}/cm^{-1}. Melting points were determined in open capillary tubes on a Electrothermal 8100 capillary melting points apparatus and are uncorrected.

(2*Z*,4*E*)-1,3,6-Triacetoxyhexa-2,4-diene (2)[5] and (2*E*,4*Z*)-1,3-diacetoxi-6-cyclohexylamino-hexa-2,4-diene (3)[4]. These compounds were obtained by the literature procedures as a 15:1 and 9:1 mixture of 2*Z*,4*E*- and 2*E*,4*E*-stereoisomers, respectively. Separation of the minor isomers was unnecessary for the Diels-Alder reactions because they proved to be unreactive and did not interfere with the isolation of the adducts.

***all cis*-4-Acetoxy-3,6-diacetoxymethylcyclohex-4-ene-1,2-maleic anhydride (4).** A mixture of diene (**2**) (1.69 g, 6.59 mmol), maleic anhydride (0.65 g, 6.59 mmol) and hydroquinone (catalytic amount) in dry toluene (34 mL) was refluxed for 48 h. The solvent was evaporated and the residue was dissolved in ethanol, to give the title compound (**4**), which was crystallized to give colourless needles (1.05 g, 55%), mp 128-130 °C (from ethanol). *Anal.* Calcd for $C_{16}H_{18}O_9$: C, 54.23; H, 5.12. Found: C,

53.97; H, 5.24; IR ν_{max}(KBr)/cm^{-1} 1795s (C=O anhydride), 1765s (C=O vinyl ester), 1735s (C=O ester) and 1250s (C-O-C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.60 (dd, $J_{3,5}$ 2.9, $J_{5,6}$ 3.3, H-5), 4.59 (dd, $J_{3,8'}$ 7.3, $J_{8',8''}$ 6.1, H-8'), 4.55 (dd, $J_{6,7'}$ 6.9, $J_{7',7''}$ 11.6, H-7'), 4.47 (dd, $J_{6,7''}$ 7.0, $J_{7',7''}$ 11.6, H-7''), 4.44 (dd, $J_{3,8''}$ 7.5, $J_{8',8''}$ 6.1, H-8''), 3.74 (dd, $J_{1,2}$ 9.6, $J_{2,3}$ 6.1, H-2), 3.61 (dd, $J_{1,6}$ 6.0, $J_{1,2}$ 9.6, H-1), 2.96 (m, H-3), 2.83 (m, H-6), 2.17 (s, 3H, vinyl OAc), 2.09 (s, 3H, OAc), 2.07 (s, 3H, OAc); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.5, 170.4 (*C*=O anhydride), 170.3, 170.1 and 168.9 (3 *C*O ester), 147.1 (C-4), 115.5 (C-5), 63.0 and 59.9 (C-7, C-8), 42.9 and 42.2 (C-1, C-2), 36.7 (C-3), 34.9 (C-6), 20.6 and 20.4 (3 OCO-*C*H_3).

***all cis*-4-Acetoxy-3,6-diacetoxymethylcyclohex-4-ene-1,2-*N*-phenyldicarboximide (5).** Prepared according to the procedure described above for **4**, using diene (**2**) and *N*-phenylmaleimide, with a heating time of 7.5 h. The product (**5**) was isolated as a solid (quant. yield), mp 139-141 °C (from ethanol) *Anal.* Calcd for $C_{22}H_{23}NO_8$: C, 61.53; H, 5.39; N, 3.26. Found: C, 61.44; H, 5.46; N, 3.10; IR ν_{max}(KBr)/cm^{-1} 1765s (C=O vinyl ester), 1735s (C=O ester), 1705s (C=O imide), 1600w and 1500m (arom); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.50-7.30 (m, 5H arom) 5.55 (d, $J_{5,6}$ 3.3, H-5), 4.71 (dd, $J_{6,7'}$ 6.7, $J_{7',7''}$ 11.2, H-7'), 4.60-4.50 (m, H-8, H-8'), 4.50 (dd, $J_{6,7''}$ 8.5, $J_{7',7''}$ 11.2, H-7''), 3.51 (dd, $J_{1,2}$ 8.9, $J_{2,3}$ 6.2, H-2), 3.44 (dd, $J_{1,2}$ 8.9, $J_{1,6}$ 5.9, H-1), 2.96 (m, $J_{3,5}$ 2.9, $J_{3,8}$ 6.2, $J_{3,8'}$ 6.2, H-3), 2.77 (m, $J_{6,7'}$ 6.7, H-6), 2.14 (s, 3H, vinyl OAc), 2.07 (s, 3H, OAc), 2.06 (s, 3H, OAc); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 175.5, 175.0 (*C*=O imide), 170.6, 170.3 and 168.8 (3*C*O ester), 131.5 (C-1arom), 128.9 (C-3arom, C-5arom), 128.6 (C-4arom), 126.6 (C-2arom, C-6arom), 147.1 (C-4), 115.6 (C-5), 63.8 and 60.5 (C-7, C-8), 42.2 and 41.7 (C-1, C-2), 37.6 (C-3), 35.8 (C-6), 20.7 and 20.3 (3 OCO-*C*H_3).

***cis*-2-Acetoxy-1,4-diacetoxymethyl-1,4-dihydroanthraquinone (7).** Prepared according to the procedure described above for **4**, using diene (**2**) and naphthoquinone, with a heating time of 11 days. The solvent was evaporated giving a residue which was purified by flash chromatography (technique b, hexane-ethyl acetate 2:1) to yield **7** (46%), mp 148-150 °C (from ethanol). *Anal.* Calcd for $C_{22}H_{20}O_8$: C, 64.07; H, 4.89. Found: C, 64.04; H, 4.90; IR ν_{max}(KBr)/cm^{-1} 1760s (vinyl ester), 1735s (C=O ester), 1655s (C=O ketone), 1235s (C-O-C); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.10 (d, $J_{5,6}$ 5.9, H-5), 8.07 (d, $J_{7,8}$ 5.9, H-8), 7.75 (m, H-6, H-7), 5.81 (dd, $J_{1,3}$ 0.8, $J_{3,4}$ 4.3, H-3), 4.39 (d, $J_{12',12''}$ 7.3, H-12), 4.37 (dd, $J_{1,11'}$ 6.3, $J_{11',11''}$ 6.9, H-11'), 4.33 (dd, $J_{1,3}$ 0.8, $J_{1,11'}$ 6.3, $J_{1,11''}$ 7.3, H-1), 4.21 (t, $J_{1,11''}$ = $J_{11',11''}$ = 7.0, H-11''), 4.17 (dd, $J_{3,4}$ 4.3, $J_{4,12''}$ 3.3, H-4), 4.05 (dd, $J_{4,12''}$ 3.3, $J_{12',12''}$ 7.3, H-12''), 2.21 (s, 3H, vinyl OAc), 2.06 (s, 3H, OAc), 2.02 (s, 3H, OAc); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 183.1, 183.0 (C-9, C-10), 170.7, 170.6 (*C*=O ester), 168.8 (C=O vinyl ester),146.0 (C-2), 142.8 and 142.7 (C-4a and C-9a),134.0 (C-6, C-7),131.8 (C-5a, C-8a),126.5 (C-5, C-8), 114.8 (C-3), 20.9 and 20.8 (OCO-*C*H_3).

Shorter reaction times (9 days) permited to isolate from the column chromatography the *endo*/*exo* mixture of adducts (**6**) as an oil (ratio 3,5:1, 3% yield). Spectral data for the major *endo* component of **6**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.00 (m, H-5, H-8), 7.75 (m, H-6, H-7), 5.57 (dd, $J_{1,3}$ 2.0, $J_{3,4}$ 2.3, H-3), 4.25 (dd, $J_{12',12''}$ 4.6, $J_{4,12'}$ 6.9, H-12'), 4.13-4.20 (m, H-11', H-12''), 3.75 (t, $J_{4a,9a}$ 6.0, H-9a), 3.63 (t, $J_{4,4a}$ 6.0, H-4a), 3.20 (m, $J_{1,3}$ 2.0, $J_{1,9a}$ 6.0, $J_{1,11'}$ 6.0, $J_{1,11''}$ 2.7, H-1), 3.07 (m, $J_{4,4a}$ 6.0, $J_{4,12'}$ 6.9, $J_{4,12''}$ 6.3, H-4), 2.17 (s, 3H, vinyl OAc), 1.91 (s, 3H, OAc), 1.81 (s, 3H, OAc); ^{13}C NMR ($CDCl_3$, 50

MHz) δ 196.1, 196.0 (C-9, C-10), 170.4, 170.1 (*C*=O ester), 169.2 (*C*=O vinyl ester),145.8 (C-2), 134.4, 134.2 (C-6, C-7), 135.1, 134.7 (C-5a, C-8a), 126.5, 126.3 (C-5, C-8), 115.8 (C-3), 64.4 (C-12), 61.7 (C-11), 49.4, 47.5 (C-4a, C-9a), 37.8 (C-1), 36.4 (C-4), 20.8, 20.7 a nd 20.6 (OCO-*C*H_3).

***all cis*-4-Acetoxy-3,6-diacetoxymethylcyclohex-4-ene-1-carbaldehyde (8).** A solution of diene (**2**) (1.09 g, 4.25 mmol) and acrolein (0.54 mL, 8.51 mmol) in dry toluene (10 mL) was treated with zinc chloride (3.47 g, 25.50 mmol) and stirred under argon at rt for 5 h. The reaction mixture was diluted with ethyl acetate (50 mL), washed with 0.2N sodium bisulfite and water, and dried ($MgSO_4$). The solution was evaporated to an oil which consisted in a mixture of the four possible cycloadducts (^{1}H-NMR). Column chromatography of this crude product (technique b, eluent hexane-ethyl acetate 2:1) afforded the pure major product (**8**) as an oil (0.76 g, 57%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.87 (s,-C*H*O), 5.55 (dd, $J_{5,6}$ 5.8, $J_{3,5}$ 1.9, H-5), 4.13 (dd, $J_{3,8'}$ 5.4, $J_{8',8''}$ 11.2, H-8'), 4.08 (dd, $J_{7',7''}$ 11.5, $J_{6,7'}$ 4.8, H-7'), 4.05 (dd, $J_{8',8''}$ 11.2, $J_{3,8''}$ 3.8, H-8''), 3.97 (dd, $J_{6,7''}$ 8.9, $J_{7',7''}$ 11.5, H-7''), 3.26 (m, H-6), 2.88 (m, H-3), 2.82 (ddd, $J_{1,2a}$ 12.8, $J_{1,2b}$ 3.0, $J_{1,6}$ 4.7, H-1), 2.20 (ddd, $J_{1,2b}$ 3.0, $J_{2b,3}$ 6.5, $J_{2a,2b}$ 12.8, H-2b), 2.15 (s, 3H, vinyl OAc), 2.07 (s, 3H, OAc), 2.02 (s, 3H, OAc), 1.73 (td, $J_{2a,2b}$ 12.8, $J_{2a,3}$ 10.8, H-2a); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 200.1 (*C*=O aldehyde), 170.8, 170.3 and 169.0 (3 *C*=O ester), 150.1 (C-4), 115.4 (C-5), 63.3 and 64.0 (C-7, C-8), 48.5 (C-1), 36.3 and 34.3 (C-6, C-3), 21.4 (C-2), 20.8 and 20.7 (OCO-*C*H_3).

***all cis*-4-Acetoxy-3,6-diacetoxymethylcyclohex-4-ene-1-carbaldehyde 2,4-dinitrophenylhydrazone (9).** A solution of aldehyde (**8**) (0.76 g, 2.40 mmol) in methanol (30 mL) was treated with 2,4-dinitrophenylhydrazine (0.51 g, 2.50 mmol) and stirred at rt for 12 h. The solvent was evaporated and the residue was extracted with benzene (3 x 20 mL). The extracts were washed successively with 10% H_2SO_4, 5% $NaHCO_3$, and water, dried ($MgSO_4$) and concentrated. Column chromatography (technique b, hexane-ethyl acetate 2:1) of the residue yielded **9** as a solid (0.265 g, 22%), mp 133-135 °C (from benzene-ethyl ether) *Anal.* Calcd for $C_{21}H_{24}N_4O_{10}$: C, 51.22; H, 4.91; N, 11.37. Found: C, 51.30; H, 4.84; N, 11.21; IR ν_{max}(KBr)/cm^{-1} 1750m (C=O vinyl ester), 1725s (C=O ester), 1525m and 1340m (NO_2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.10 (s, N*H*), 9.16 (d, $J_{3ar,5ar}$ 2.7, H-3arom), 8.37 (dd, $J_{3ar,5ar}$ 2.7, $J_{5ar,6ar}$ 9.5, H-5arom), 7.94 (d, $J_{5ar,6ar}$ 9.5, H-6arom), 7.65 (d, $J_{H,4}$ 4.5, C*H*-N), 5.60 (dd, $J_{5,6}$ 5.7, $J_{3,5}$ 1.6, H-5), 3.12 (ddd, $J_{1,2a}$ 11.0, $J_{1,2b}$ 2.3, $J_{1,6}$ 4.7, H-1), 2.99 (m, H-6, H-3), 2.25 (ddd, $J_{1,2b}$ 2.3, $J_{2b,2a}$ 12.9, $J_{2b,3}$ 6.7, H-2b), 1.92 (dt, $J_{2b,2a}$ 12.9, $J_{2a,3}$ 11.0, H-2a), 4.22 (dd, $J_{6,8''}$ 5.1, $J_{8',8''}$ 11.2, H-8'), 4.13 (dd, $J_{8',8''}$ 11.2, $J_{6,8''}$ 7.1, H-8''), 4.08 (dd, $J_{6,7'}$ 4.2, $J_{7',7''}$ 11.3, H-7'), 4.06 (dd, $J_{7',7''}$ 11.3, $J_{6,7''}$ 5.5, H-7''), 2.19 (s, 3H, vinyl OAc), 2.12 (s, 3H, OAc), 2.05 (s, 3H, OAc); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.8, 170.3 and 169.0 (3 *C*O ester), 149.6 (C-4), 145.0 (C-1arom), 138.3 (C-4arom), 130.1 (C-5arom), 129.2 (C-2arom), 123.4 (C-3arom), 116.5 (C-6arom), 116.1 (C-5), 64.1 and 63.8 (C-7, C-8), 38.8 (C-6), 36.5 (C-3. C-1), 25.1 (C-2) and 20.9 (O-CO-*C*H_3).

***all cis*-1:6-(4-Acetoxy-3-acetoxymethyl-6-methylcyclohex-4-ene)-*N*-cyclohexylcarbolactam-2-carboxylic acid (13).** Prepared according to the procedure described above for **4**, using diene (**3**) and maleic anhydride, with a heating time of 15 h. The solvent was evaporated giving a residue which was purified by flash chromatography (technique b, eluent chloroform-acetone 9:2), to give **13** (1.12 g, 47%), mp 139-141 °C (from hexane-ethyl acetate 2:1) *Anal.* Calcd for $C_{20}H_{27}NO_7$: C, 61.06; H, 6.92; N, 3.56. Found: C, 61.13; H, 7.10; N, 3.46; IR ν_{max}(KBr)/cm^{-1} 3500-2500 (OH acid), 1760s (C=O vinyl ester), 1745s (C=O acid, ester), 1720s (C=O lactam), 1515m and 1560m; ^{1}H NMR ($CDCl_3$, 400 MHz) δ

5.79 (br s, H-5), 4.21 (dd, $J_{8',8''}$ 11.4, $J_{3,8'}$ 3.5, H-8'), 4.06 (dd, $J_{8',8''}$ 11.4, $J_{3,8''}$ 7.9, H-8''), 3.94 (m, N-C*H*), 3.51 (dd, $J_{6,7'}$ 6.7, $J_{7',7''}$ 8.5, H-7'), 3.41 (d, $J_{1,2}$ 4.0, H-2), 3.28 (m, H-3), 3.04 (dd, $J_{7',7''}$ 8.5, $J_{6,7''}$ 10.6, H-7''), 2.94 (m, H-6), 2.50 (dd, $J_{1,2}$ 4.0, $J_{1,6}$ 12.8, H-1), 2.16 (s, 3H, vinyl OAc), 2.07 (s, 3H, OAc); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.5 (*C*=O amide), 172.8 (*C*=O acid), 170.8 and 168.8 (2 *C*O ester), 146.8 (C-4), 116.3 (C-5), 64.0 (C-8), 50.8 (C-N), 45.3 (C-7), 44.6 (C-2), 39.8 and 39.4 (C-1, C-6), 34.0 (C-3), 30.4, 30.3, 25.3 and 25.2 (cyclohexyl), 21.1 and, 20.8 (O-CO-*C*H_3).

***N*-Phenyl-[*all cis*-1:6-(4-acetoxy-3-acetoxymethyl-6-methylcyclohex-4-ene)-*N*-cyclohexylcarbolactam]-2-carboxamide (14).** Prepared according to the procedure described above for **4**, using diene (**3**) and *N*-phenylmaleimide, with a heating time of 15 h. The solvent was evaporated giving a residue which was purified by flash chromatography (technique b, eluent hexane-ethyl acetate 10:25) gave **14** (32%), mp 180-182 °C (from ethanol). *Anal.* Calcd for $C_{26}H_{32}N_2O_6$: C, 66.65; H, 6.88; N, 5.94. Found: C, 66.59; H, 6.86; N, 6.01; IR ν_{max}(KBr)/cm^{-1} 3290m (N-H), 1760s (C=O vinyl ester), 1745s (C=O ester), 1690s (I amide band); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 12.05 (br s, N*H*), 7.68 (d, J = 7.9, 2Harom), 7.30 (m, 2Harom), 7.06 (t, J = 7.4, 1Harom), 5.37 (s, H-5), 4.31 (dd, $J_{3,8'}$ 4.4, $J_{8',8''}$ 11.5, H-8'), 4.14 (dd, $J_{8',8''}$ 11.5, $J_{3,8''}$ 8.6, H-8''), 3.98 (m, N-C*H*), 3.58 (dd, $J_{6,7'}$ 7.1, $J_{7',7''}$ 9.4, H-7'), 3.29-3.16 (m, H-1, H-2, H-3, H-6, H-7''), 2.16 (s, 3H, vinyl OAc), 1.68 (s, 3H, OAc); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.9 (*C*=O amide), 170.6, 168.8 (*C*=O ester), 169.7 (*C*=O lactam), 148.4 (C-4), 139.1 (C-1arom), 128.7 (C-3arom, C-5arom), 123.7 (C-4arom), 119.9 (C-2arom, C-6arom), 117.1, 62.9 (C-8), 51.3 (*C*-N), 47.5 (C-7), 47.0, 40.9, 39.0, 33.1 (C-3), 30.0, 29.8, 25.3 and 25.2 (cyclohexyl), 20.9 and 20.5 (OCO-*C*H_3).

***all cis*-4-Acetoxy-3,6-diacetoxymethylcyclohex-4-ene-1,2-dicarboxylic acid (15).** A suspension of anhydride (**4**) (0.1 g, 0.28 mmol) in water (5 mL) was refluxed for 15 min. Solvent was evaporated to yield **15** (quant. yield) as a colourless oil [HRMS (CI) Found: (M + H)$^{+\cdot}$, 373.1145. $C_{16}H_{20}O_{10}$ + H requires *M*, 373.1134]; IR ν_{max}(film)/cm^{-1} 3500-2500 (OH acid), 1740s (C=O acid), 1735s (C=O ester); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.99 (m, 2 -CO-O*H*), 5.48 (m, $J_{5,6}$ 2.6, H-5), 4.41 (dd, $J_{3,8'}$ 5.2, $J_{8',8''}$ 11.7, H-8'), 4.38 (m, $J_{7,7''}$ 2.9, H-7'), 3.41 (dd, $J_{1,2}$ 3.6, $J_{2,3}$ 6.3, H-2), 3.34 (dd, $J_{1,2}$ 3.6, $J_{1,6}$ 6.0, H-1), 3.34 (m, $J_{6,7'}$ 8.0, $J_{6,7''}$ 8.0, H-6), 3.26 (m, $J_{3,5}$ < 1.0, $J_{3,8'}$ 5.2, $J_{3,8''}$ 5.8, H-3), 2.17 (s, 3H, vinyl OAc), 2.06 (s, 3H, OAc), 2.02 (s, 3H, OAc); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 175.1, 175.2 (*C*=O carboxylic acid), 171.5, 171.3 (*C*=O ester), 169.7 (*C*=O vinyl ester), 147.3 (C-4), 114.9 (C-5), 64.9 and 63.6 (C-7, C-8), 43.1, 40.5, 37.7 and 35.9 (C-1, C-2, C-3, C-6) and 20.7 (OCO-*C*H_3); *m/z* (CI) 373 (MH$^{+\cdot}$, 10%), 313 (19), 253 (100), 210 (74).

Dimethyl *all cis*-4-acetoxy-3,6-diacetoxymethylcyclohex-4-ene-1,2-dicarboxylate (16). A solution of anhydride (**4**) (0.20 g, 0.57 mmol) in dichloromethane (3 mL) was treated with 1,3-dicyclohexylcarbodiimide (0.118 g, 0.57 mmol), methanol (0.025 mL) and 4-dimethylaminopyridine (0.007 g, 0.057 mmol). The reaction mixture was stirred at rt for 15 h, filtered, washed successively with water, 5% acetic acid, water and dried ($MgSO_4$). Evaporation of solvent gave an oil which was purified by preparative TLC (eluent hexane-ethyl acetate 4:3). Ester (**16**) was obtained as an oil (0.147 g, 63%) [HRMS (CI) Found: (M + H)$^{+\cdot}$, 401.1425. $C_{18}H_{24}O_{10}$ + H requires *M*, 401.1447]; ν_{max}(film)/cm^{-1} 1730s (C=O ester), 1250s (C-O-C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.43 (dd, $J_{3,5}$ 2.7, $J_{5,6}$ 6.5, H-5), 4.33 (d, $J_{3,8'}$ = $J_{3,8''}$ 7.8, H-8', H-8''), 4.27 (dd, $J_{6,7'}$ 6.5, $J_{7',7''}$ 10.0, H-8), 3.98 (dd, $J_{7',7''}$ 10.0,

$J_{6,7''}$ 6.5, H-7''), 3.73 (s, COOCH_3), 3.70 (s, COOCH_3), 3.31 (dd, $J_{1,2}$ 3.7, $J_{2,3}$ 7.0, H-2), 3.21 (dd, $J_{1,2}$ 3.7, $J_{1,6}$ 6.3, H-1), 3.01 (m, H-6), 2.17 (s, 3H, vinyl OAc), 2.05 (s, 3H, OAc), 2.01 (s, 3H, OAc); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.5, 170.3 (2 *C*OOMe), 171.6, 171.5 and 169.5 (3 *C*O-CH_3), 147.4 (C-4), 114.2 (C-5), 64.5, 63.3 (C-8, C-7), 52.1 and 51.1 (2 COO*C*H_3), 43.3, 40.2, 37.6 and 36.1 (C-1, C-2, C-3, C-6), 20.9 and 20.8 (3 OCO-*C*H_3). *m/z* (CI) 401 ($MH^{+\cdot}$, 33%), 341 (100), 238 (88), 178 (24).

***all cis*-3,2:4,5-2,5-Dimethylcyclohexanone *bis*carbolactone (17).** A suspension of anhydride (**4**) (0.297 g, 0.84 mmol) in 4N HCl (9 mL) was heated under reflux for 30 min. Evaporation of solvent gave **17** as a solid (0.69 g, 39%); mp 149-151 °C (from acetone). *Anal.* Calcd for $C_{10}H_9O_5$: C, 57.58; H, 4.80. Found: C, 57.58; H, 5.04; IR ν_{max}(KBr)/cm^{-1} 1770f, 1755f (C=O lactone), 1710s (C=O ketone); ^{1}H NMR (DMSO-d_6, 400 MHz) δ 4.46 (dd, $J_{5,7'}$ 5.4, $J_{7',7''}$ 9.6, H-7'), 4.44 (m, H-8'), 4.08 (dd, $J_{7',7''}$ 9.6, $J_{5,7''}$ 1.7, H-7''), 4.06 (m, H-8''), 3.70 (m, $J_{3,4}$ 5.6, H-3), 3.63 (m, H-2), 3.51 (dd, $J_{3,4}$ 5.6, $J_{4,5}$ 8.4, H-4), 3.34 (m, H-5), 2.90 (dd, $J_{5,6ax}$ 9.8, $J_{6ax,6eq}$ 14.3, H-6ax), 2.24 (dd, $J_{6ax,6eq}$ 14.3, $J_{5,6eq}$ 2.7, H-6eq); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 208.5 (*C*=O, ketone), 176.1 and 176.0 (*C*=O, lactone), 74.0 and 67.2 (C-8, C-7), 45.5 (C-2), 41.9 (C-6), 38.8 (C-4), 38.6 (C-3) and 35.5 (C-5).

***N*-Phenyl-[*all cis*-4:5-(2-hydroxymethyl-5-methylcyclohexanonecarbolactone)]-3-carboxamide (18).** A suspension of imide (**5**) (265 mg, 0.61 mmol) in 4N HCl (5 mL) was heated under reflux for 1 h. The reaction mixture was extracted with ethyl acetate, and the extract was washed successively with saturated aq. $NaHCO_3$ and water, and dried ($MgSO_4$). Evaporation of solvent gave **18** as a solid (70 mg, 38%); mp 212-214 °C. *Anal.* Calcd for $C_{16}H_{17}NO_5$: C, 63.36; H, 5.65. Found: C, 63.37; H, 5.70; [HRMS (CI) Found: $(M - H_2O)^{+\cdot}$, 285.1002. $C_{16}H_{17}NO_5 - H_2O$ requires *M*, 285.1001]; IR ν_{max} (KBr)/cm^{-1} 1770s, 1710s (C=O ketone), 1680s (C=O amide); ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.64 (d,J 7.8, 2Harom), 7.38 (t, J 7.8 2Harom), 7.16 (t, J 7.4, 1H arom), 4.46 (dd, $J_{5,7'}$ 6.4, $J_{7',7''}$ 9.2, H-7'), 4.06 (dd, $J_{7',7''}$ 9.2, $J_{5,7''}$ 2.6, H-7''), 3.95 (t, $J_{2,8'} = J_{8',8''}$ 9.5, H-8'), 3.66 (dd, $J_{3,4}$ 5.5, $J_{2,3}$ 8.9, H-3), 3.68 (dd, $J_{8',8''}$ 9.5, $J_{2,8''}$ 6.9, H-8''), 3.49 (ddd, $J_{2,8''}$ 6.9, $J_{2,3}$ 8.9, $J_{2,8'}$ 9.5, H-2), 3.43 (dd, $J_{4,5}$ 8.9, $J_{3,4}$ 5.5, H-4), 3.32 (m, H-5), 2.91 (dd, $J_{5,6eq}$ 9.8, $J_{6ax,6eq}$ 14.1, H-6eq), 2.26 (dd, $J_{6ax,6eq}$ 14.1, $J_{5,6ax}$ 3.3, H-6ax); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 209.4 (C=O ketone), 176.0 (C=O, lactone), 171.7 (C=O imide), 139.0 (C-1arom), 128.6 (C-3arom, C-5arom), 124.3 (C-4arom), 120.1 (C-2arom, C-6arom), 73.6 (C-7), 47.9 (C-8), 41.9 (C-6), 42.8, 41.9, 38.4 and 35.5 (C-2, C-3, C-4, C-5). *m/z* (CI) 285 ($M-H_2O^{+\cdot}$, 100%), 257 (15), 200 (27).

***all cis*-4,4-Dimethoxy-3,6-(methanoxymethano)cyclohexane-1,2-*N*-phenyldicarboximide (19).** To a solution of **5** (0.29 g, 0.67 mmol) in chloroform (2 mL) was added a solution[13] of acetyl chloride (0.14 mL) in methanol (3 mL). The reaction mixture was kept at rt for 5.5 h and then it was neutralized with 5% sodium hydrogen carbonate (30 mL), diluted (10 mL) and extracted with chloroform (3 x 10 mL). Organic extracts were washed with water and dried ($MgSO_4$). Evaporation of solvent gave **19** (quant. yield); mp 192-194 °C (from methanol). *Anal.* Calcd for $C_{18}H_{21}NO_5$: C, 65.24; H, 6.38; N, 4.22. Found: C, 64.98; H, 6.24; N, 4.18; [HRMS (CI) Found: $(M + H)^{+\cdot}$, 332.1500. $C_{18}H_{21}NO_5 + H$ requires *M*, 332.1497]; IR ν_{max}(KBr)/cm^{-1} 1705s (C=O imide), 1600w and 1500m (arom); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.47 (m, 2Harom), 7.39 (m, 1Harom), 7.29 (m, 2Harom), 3.87 (dd, $J_{6,7'}$ 3.1,

$J_{7',7''}$ 9.1, H-7'), 3.72 (dd, $J_{7',7''}$ 9.1, $J_{6,7''}$ 1.1, H-7''), 3.57 (dd, $J_{3,8'}$ 5.4, $J_{8',8''}$ 9.6, H-8'), 3.48 (dd, $J_{8',8''}$ 9.6, $J_{3,8''}$ 4.5, H-8''), 3.37 (s, 3H, O-CH_3), 3.36 (s, 3H, O-CH_3), 3.30 (m, $J_{1,2}$ 8.6, H-1, H-2), 3.09 (t, $J_{3,5''}$ 1.7, $J_{3,8'}$ 5.4, $J_{3,8''}$ 4.5, H-3), 2.95 (m, $J_{1,6}$ 4.5, H-6), 2.13 (d, $J_{5',5''}$ 12.0, H-5'), 2.04 (ddd, $J_{5',5''}$ 12.0, $J_{3,5''}$ 1.7, $J_{5'',6}$ 4.3, H-5''); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 177.7 (*C*=O amide), 177.2 (*C*=O amide), 132.0 (C-1arom), 129.1 (C-3arom and C-5arom), 128.5 (C-4arom), 126.2 (C-2arom and C-6arom), 108.7 (C-4), 71.9, 68.4 (C-7, C-8), 58.8, 49.5, 44.1, 43.5, 41.0 and 39.4 (C-1, C-2, C-3, C-6, 2*C*H_3O-) and 32.3 (C-5). *m/z* (CI) 332 ($MH^{+\cdot}$, 100%), ($MH^{+\cdot}$, 100%), 300 (40), 282 (73), 258 (28).

***all cis*-4-Acetoxy-3,6-diacetoxymethylcyclohexane-1,2-maleic anhydride (21).** To a solution of anhydride (**4**) (0.97 g, 0.27 mmol) in dry acetone (25 mL) was hydrogenated at atmospheric pressure in the presence of 10% Pd/C (catalityc amount). Absorption of hydrogen was complete after 18 h and the solution was filtered through Celite and evaporated to give compound (**21**) as an oil (0.88 g, 91%); [HRMS (CI) Found: $(M + H)^{+\cdot}$, 357.1171. $C_{16}H_{20}O_9$ + H requires *M*, 357.1185]; ν_{max}(neat)/cm^{-1} 1780f (C=O anhydride), 1735s (C=O ester); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.20 (br d, $J_{4,5}$ 7.4 H-4), 4.10-4.50 (m, H-7', H-7'', H-8', H-8''), 3.64 (dd, $J_{1,2}$ 11.0, $J_{2,3}$ 7.8, H-2), 3.50 (dd, $J_{1,2}$ 11.0, $J_{1,6}$ 6.7, H-1), 2.25-2.45 (m, H-3, H-6), 2.38 (m, $J_{5',5''}$ 13.4, $J_{5',6}$ 6.5, H-5'), 1.42 (m, $J_{5'',6}$ 13.4, H-5''), 2.08 (s, 3H, OAc), 2.07 (s, 3H, OAc), 2.02 (s, 3H, OAc); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.5, 171.1, 170.5 and 169.2 (*C*=O anhydride and ester), 66.5 (C-4), 64.3 and 61.3 (C-7, C-8), 39.5, 38.5 and 36.3, (C-1, C-2, C-3), 29.7 (C-6), 29.4 (C-5), 20.6 and 20.4 (OCO-*C*H_3); *m/z* (CI) 357 ($MH^{+\cdot}$, 10%), 297 (54), 255 (100), 241 (52), 181 (59).

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