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Intramolecular [2 + 2] Photocycloaddition of Alkenes Incorporated in a Carbohydrate Template. Synthesis of Enantiopure Bicyclo[3.2.0]heptanes and -[6.3.0]undecanes

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Received December 31, 2002

Intramolecular [2 + 2] photocycloaddition of alkenes with a furano sugar placed between them have been investigated under both copper(I)-catalyzed and sensitized conditions. The copper(I)-catalyzed photocycloaddition of the dienes **4a**, **4b**, and **4c** led to unexpected formation of the thermodynamically less stable cis−syn−cis 4−5−5 tricyclic adducts **5a, 5b**, and **5c**, respectively. The sensitized photocycloaddition of the diene **14** also gave the cis−syn−cis adduct **15** showing that the copper(I) catalyst does not have any influence on the stereochemical course through coordination with the anomeric ring oxygen of the furano sugar. The identical stereochemical course observed under both catalyzed and sensitized photoaddition reactions have been attributed to be of steric origin. Bis(dienes) **25a** and **25b**, which gave an intractable mixture on copper(I)-catalyzed irradiation, underwent smooth photocycloaddition in the presence of benzophenone, and the resulting 1,2-divinyl cyclobutanes underwent spontaneous [3.3]-rearrangement at room temperature to produce bicyclo[6.3.0]undecanes **30a** and **30b**, respectively. This investigation provides an approach for the construction of enantiopure bicyclo[3.2.0]heptanes and -[6.3.0]undecanes.

Introduction

The [2 + 2] photocycloaddition of alkenes offers an excellent stereoselective[1] pathway for rapid access to systems of significant complexity incorporating cyclobutanes. In general, the [2 + 2] photocycloaddition of an alkene to a conjugated system such as an enone or a diene can be achieved either on direct irradiation or irradiation in the presence of a photosensitizer. On the other hand, photoaddition of an alkene to a nonconjugated alkene is possible only in the presence of metal catalyst,[2] except in few examples[3] where the reacting alkenes are either strained or closely held in conformationally rigid molecules. The bis(copper(I)trifluoromethane sulfonate)−benzene complex $[(CuSO_3CF_3)_2{\cdot}C_6H_6](CuOTf)$ introduced by Salomon and Kochi[4] has been found to be the most efficient catalyst for accomplishing both inter- and intramolecular additions.

Despite great synthetic utility of the [2 + 2] photocycloaddition reaction,[1] asymmetric induction during this reaction using either chiral auxiliary or metal complexes with chiral ligands as catalysts has not been very successful.[5] Carbohydrates, being highly functionalized and commercially available, have served over the years as a source of chirality. A variety of C−C bond-forming reactions and ring annulation have been accomplished using carbohydrates either as chiral auxiliary[6] or as chiral building blocks.[7] Cycloaddition reactions such as Diels−Alder[7b] or 1,3-dipolar[8] reactions have also been investigated. The [2 + 2] photocycloaddition reaction in pyranosugar templates has been occasionally studied.[9] However, the [2 + 2] photocycloaddition reaction of alkenes attached to furanosugar have not been explored.

In connection to our interest in the synthesis of cyclopentanoids,[10] we had the occasion to investigate the reactivity and stereoselectivity in intramolecular [2 + 2] photocycloaddition of 1,6-dienes using CuOTf as catalyst. The seminal work by Salomon et al.[11] and subsequently our own work[9c,10b,c] have established that the stereochemical outcome in these reactions is strongly influenced by steric and electronic effects of the alkyl and hydroxyl substituents at the allylic position. Carbohydrates en-

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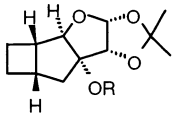
10.1021/jo026920c CCC: $25.00
Published on Web 04/16/2003

dowed with multiple oxygen functionality are thus expected to exert profound influence on the stereochemical course during photoaddition reaction of the alkenes attached to them. We initiated an investigation involving intramolecular [2 + 2] photocycloaddition of alkenes attached to a furanosugar with the following objectives: to determine the influence of the intervening sugar unit on the stereochemical outcome, under both catalyzed and sensitized conditions; to prepare enantiopure bicyclo-[3.2.0]heptanes; and to employ appropriately functionalized bicyclo[3.2.0]heptanes for the construction of bicyclo-[6.3.0]undecanes. The results of this investigation are presented here.[12]

Results and Discussion

The diene **4a** with alkenes linked by a furanosugar was initially chosen for [2 + 2] photocycloaddition. It was expected that this would provide rapid access to the enantiopure cis−anti−cis 4−5−5 oxatricyclic system **7** (R = Me). The carbocyclic structure analogous to **7** is



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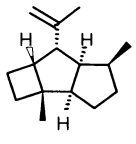

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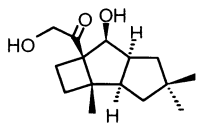

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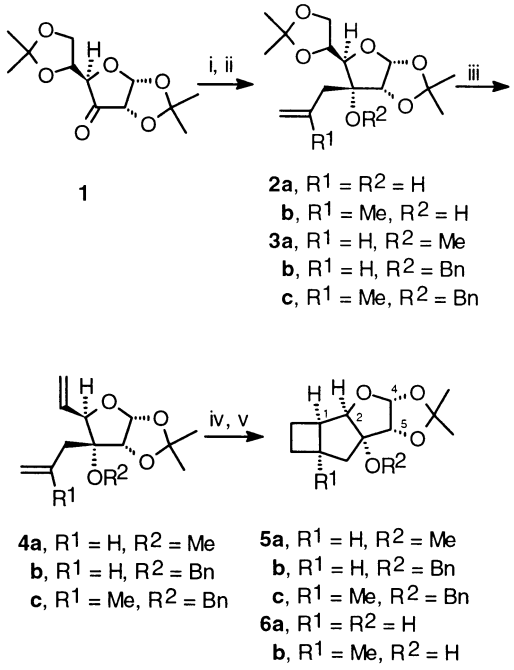
present in a number of structurally novel sesquiterpenes such as kelsoene (**8**)[13] and sulcatine G (**9**),[14] which in recent years have elicited considerable interest among the synthetic organic chemists. The diene **4** was prepared from the known ketone **1** derived from D-glucose as delineated in Scheme 1. Reaction of the ketone **1** with allylmagnesium bromide provided the homoallyl alcohol **2a** in 79% yield. The hydroxyl group in the alcohol **2a**[15]

SCHEME 1[a]



[a] Reagents and conditions: (i) CH_2=$CHCH_2MgBr$, THF, rt, 80% (for **2a**); CH_2=$C(Me)CH_2MgCl$, THF, rt, 70% (for **2b**); (ii) NaH, CH_3I, THF, reflux, 2 h, 90% (for **3a**); NaH, BnBr, THF, reflux, 2 h, 70−80% (for **3a** and **3b**); (iii) (a) 75% aq AcOH, rt, 12 h, (b) I_2, PPh_3, imidazole, PhMe, reflux, 2 h, 53−60%; (iv) *hν*, CuOTf, Et_2O, 3.5h, 72−77%; (v) 10% Pd−C, H_2, MeOH, AcOH, $HClO_4$, 80−85%.

was then protected to provide the methyl ether **3a** in 90% yield. The ether **3a** was then converted to the diene **4a** in 60% yield through a two-step sequence involving selective deprotection of the 5,6-acetonide moiety followed by conversion of the resulting diol to alkene. Cycloaddition of the diene **4a** could be achieved only on irradiation in the presence of CuOTf as catalyst, producing a single photoadduct **5a** in 60% yield as a colorless liquid. The gross structure of the photoadduct was clearly evident from ^1H and ^{13}C NMR spectral data. The C_2–H appeared as a doublet at δ 4.38 with J = 5.1 Hz. It was difficult to ascertain the stereochemistry at the 4/5 ring fusion based on it.

The failure to assign stereochemistry led us to search for a crystalline analogue. Irradation of the diene **4b** having a benzyloxy group instead of OMe in the presence of CuOTf as catalyst indeed afforded a crystalline photoadduct **5b** in 72% yield, mp 52 °C. However, crystals of this compound were not suitable for X-ray structure determination. The C_2–H in the ^1H NMR spectrum of its debenzylated analogue **6a**, obtained through hydrogenolysis of **5b**, appeared at δ 4.15 as a doublet with a coupling constant of 5.5 Hz. This indicates that cycloaddition of both the dienes **4a** and **4b** proceeded with same stereochemical outcome. An attempt to distinguish the cis−anti−cis structure **7** from the cis−syn−cis structure **5** by comparison of the observed coupling constants for the C_2–H's in the photoadducts **5a** and **5b** with those reported[11a] for the proton α to the OH group in a series of *exo*- and *endo*-2-hydroxybicyclo[3.2.0]heptanes (4.5 Hz and 6−8 Hz respectively) was not conclusive.

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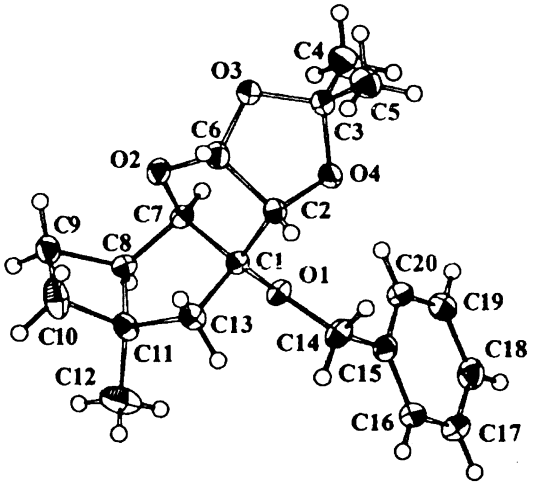
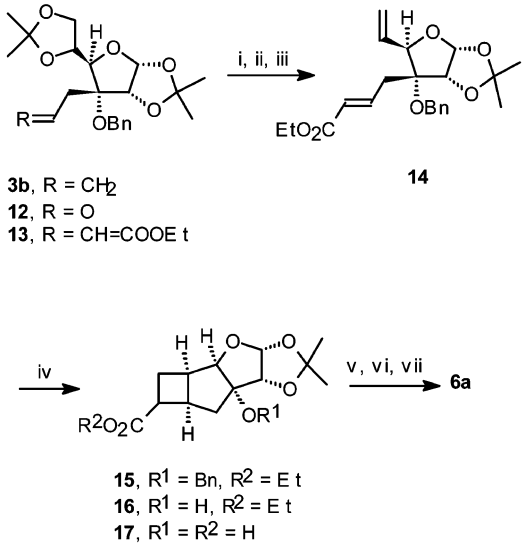


FIGURE 1. ORTEP diagram of the photoadduct **5c**.

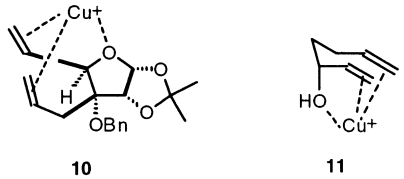
We next focused on the photocycloaddition of the diene **4c**, as this would incorporate the angular Me group required for the natural products. The diene **4c** was prepared by a sequence similar to that used for preparing the diene **4b** after addition of methylallylmagnesium chloride to the ketone **1**. Irradiation of the diene **4c** in the presence of CuOTf as catalyst afforded the crystalline photoadduct **5c**, mp 58 °C in 77% yield. The C_2–H in the debenzylated analogue **6b** appeared as a doublet at δ 4.15 with $J = 6.3$ Hz. Thus, all the three dienes, irrespective of the substituent on the alkene or the nature of the alkoxy groups, behaved similarly in the CuOTf-catalyzed photocycloaddition reaction. A single-crystal X-ray structure determination[16] of this photoadduct showed that it possesses a cis−syn−cis structure (Figure 1). This establishes the cis−syn−cis structure for the phtoadducts **5a** and **5b**.

Exclusive formation of a thermodynamically less stable cis−syn−cis linearly arranged tricyclic system in a cycloaddition reaction is noteworthy. The formation of cis−syn−cis adducts in a [2 + 2] photocycloaddition has been observed[17] only when the reacting alkenes are tethered through a long chain. AM1 calculations[18] (using MOPAC, version 1.10) indicates that the cis−syn−cis adduct **5b** ($E = -4865.8857$ kcal mol^{-1}) is less stable than the corresponding cis−anti−cis adduct **7** (R = Bn) ($E = -4869.0894$ kcal mol^{-1}) by 3.2 kcal mol^{-1} in the gas phase. Thus, one would expect the formation of the cis−anti−cis adduct **7** (R = Bn) from photocycloaddition of the diene **4b**. A plausible explantion for the formation of the cis−syn−cis adducts is the involvement of the tricoordinated Cu(I) complex **10** formed prior to cycloaddition. This complex preorganizes the diene for cycloaddition to take place syn to the furanose ring, leading to the formation of the cis−syn−cis adducts. The involvement of analogous tricoordinated Cu(I) complexes **11** during photocycloaddition of 3-hydroxy-1,6-heptadienes has been invoked[11a] to explain the predominant formation of *endo*-2-hydroxy bicyclo[3.2.0]heptanes.

SCHEME 2[a]



[a] Reagents and conditions: (i) OsO_4, $NaIO_4$, H_2O, Et_2O, 79%; (ii) NaH, $(EtO)_2P(O)CH_2CO_2Et$, THF, rt, 18 h, 67%; (iii) (a) 75% aq AcOH, rt, 12h, (b) I_2, PPh_3, imidazole, PhMe, reflux, 2 h, 54%; (iv) *hν*, Ph_2CO, CH_3CN, 6 h, 50%;(v) 10% Pd−C, H_2, EtOH, AcOH, $HClO_4$, 65%;(vi) KOH, H_2O, EtOH, reflux, 2 h, 83%; (vii) *hν*, quinoline, t-BuSH, C_6H_6,7 h, 40%.



10 **11**

To determine the stereochemical outcome in a [2 + 2] photocycloaddition in the absence of Cu(I) catalyst, the diene **14** with a conjugated ester moiety was chosen. The diene **14** was prepared as outlined in Scheme 2. Oxidative cleavage of the alkene unit in the benzyl derivative **3b** followed by Wittig−Horner reaction of the resulting aldehyde **12** afforded exclusively the *E*-isomer **13**. The ester **13** was then converted to the diene **14** by following a sequence similar to the transformation of the diacetonide **3b** to the diene **4b**.

The diene **14** could be made to undergo cycloaddition on irradiation in acetonitrile with benzophenone as a sensitizer. A single photoadduct **15** was obtained as a liquid in 50% yield. The stereochemical assignment to the adduct **15** was based on its transformation to the cyclobutane derivative **6a** through debenzylation, hydrolysis, and photodecarboxylation[19] of the resulting hydroxy acid **17**. Thus, sensitized photocycloaddition of the dienic ester **14** provided also a cis−syn−cis adduct **15**.

The observed stereochemical outcome in the photocycloaddition of the diene **14** may be explained by the

(16) Crystallographic data for compound **5c** has been deposited with the Cambridge Crystallographic Data Centre as deposition number CCDC 158331. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44(0) (122 3) - 336033. E-mail: deposit@ccdc.cam.ac.uk].

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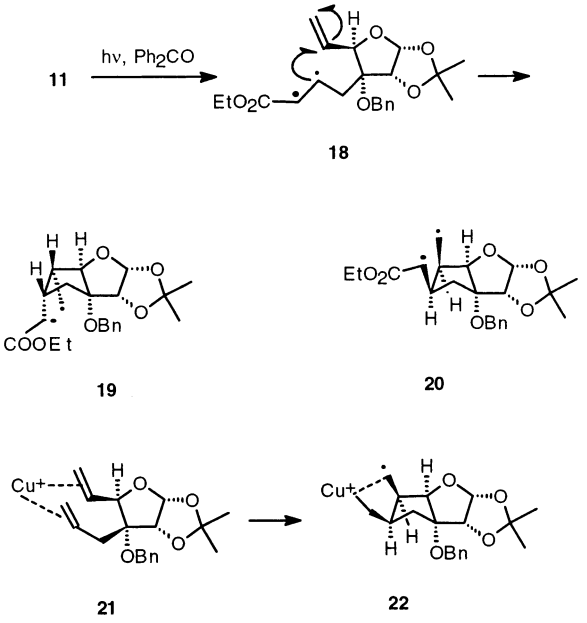
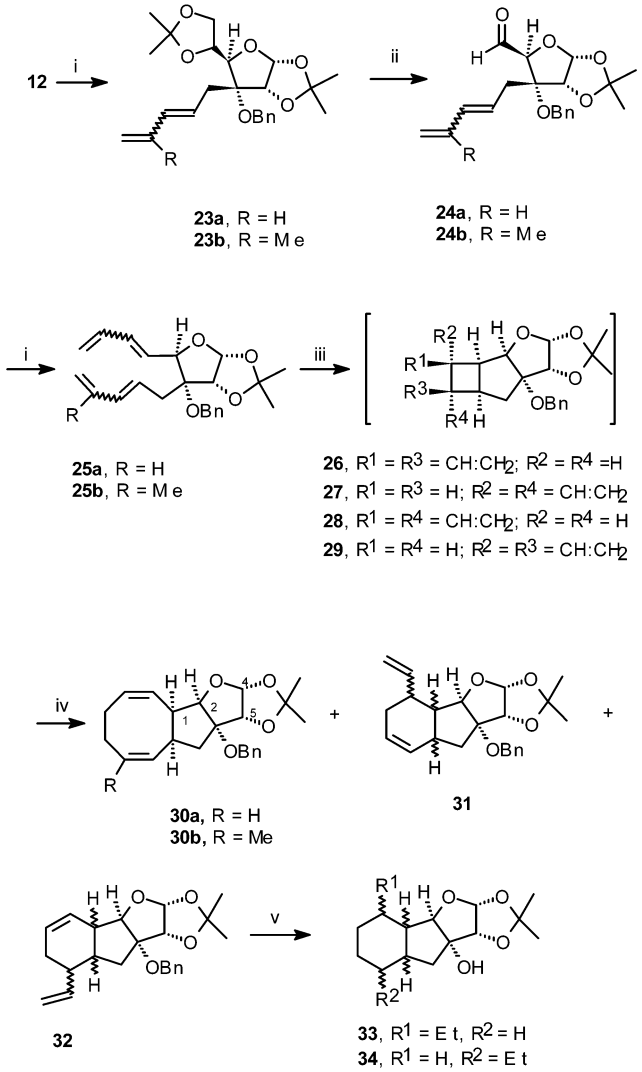
SCHEME 3



well-accepted pathway,[20] as delineated in Scheme 3. Triplet sensitization of the conjugated ester **14** leads to the biradical intermediate **18**. 5-Exo-trig addition of the high-energy β-radical to the double bond may give rise to two new biradical intermediates, **19** and **20**. Preferential formation of the biradical **20** is expected over the biradical **19**, as the later experiences severe 1,3-diaxial interactions involving the alkoxy group and the radical-bearing alkyl chains. The crystal structure of the photoadduct **5c** (Figure 1) points out that such interaction in the structure **19** is possible. Further, such 1,3-diaxial interactions between alkoxy and alkyl groups have been found[21] to determine the stereochemistry of the product in 5-exo-trig radical cyclizations. Ring closure of the 1,4-biradical **20** then leads to the product **15**. In the light of this observation, it is apparent that photocycloaddition of the diene **4** in the presence of Cu(I) catalyst may not necessarily need formation of the sterically crowded complex **10**. Instead, it probably proceeds through photoexcitation of the complex **21**.[2] Sequential bond formation, similar to the sensitized process, preferentially leads to the radical intermediate **22**, which finally collapses to the product. Thus, the unusual stereochemical outcome in both the Cu(I)-catalyzed and sensitized photocycloadditions arises from the steric effect of the substituents in the sugar template.

To extend the scope of this reaction, we next focused on the [2 + 2] photocycloaddition of the bis(dienes) **25** interconnected through the same furanosugar, anticipating that the resulting 1,2-divinyl cyclobutanes would rearrange[22,23] to afford a fused 5−8 ring system. The bis(diene) **25a** was prepared as follows. Wittig olefination of the aldehyde **12** with the ylide generated from allyl triphenyl phosphonium chloride afforded the diene **23a** in 64% yield as an inseparable mixture of *E* and *Z* isomers. The diene **23a** was converted to the aldehyde **24a** in 65% yield using a two-step sequence involving selective deprotection of the 5,6-acetonide moiety followed by cleavage of the resulting vicinal diol. A nonstereoselective Wittig olefination of the aldehyde **24a** finally afforded the bis(diene) **25a** in 63% yield as a mixture of geometrical isomers. Irradiation of an ether solution of the bis(diene) **25a** for 3 h in the presence of CuOTf as catalyst led to an intractable mixture of products. However, irradiation of its hexane solution in the presence of benzophenone as sensitizer led to complete consumption of the bis(diene) **25a** (R_f 0.53) in 6 h, producing a new component (R_f 0.42), as revealed by TLC (1:19 ethyl acetate/petroleum ether). The product was rapidly freed from benzophenone through silica gel column chromatography. ^{1}H and ^{13}C NMR spectra showed it to be a

SCHEME 4[a]



[a] Reagents and conditions: (i) allyltriphenyl phosphonium chloride, n-BuLi, Et_2O, 0 °C, 64% (for **23a**); methallyltriphenyl phosphonium chloride, n-BuLi, Et_2O, 0 °C, 63% (for **23b**);(ii) (a) 75% aq AcOH, rt, 12 h, (b) $NaIO_4$, CH_3CN, H_2O, rt, 65%; (iii) *hν*, Ph_2CO, *n*-hexane, 6 h; (iv) rt, 20 days, 35−40% (for **26** and **27**); 200 °C, sealed tube, PhMe, 22 h, 10−12% (for **28** and **29**); (v) 10% Pd−C, H_2, MeOH, 81%.

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mixture of several components. Purification and characterization of the photoadducts became difficult as the mixture kept on changing to produce an additional component (R_f 0.36, 1:19 ethyl acetate/petroleum ether). The new component was isolated as a liquid by preparative TLC and was characterized as the cyclooctadiene derivative **30a** arising from [3.3] sigmatropic rearrangement of the intermediate 1,2-divinyl cyclobutanes. The photoadducts were stored at room temperature. Isolation of the cyclooctadiene **30a** from the mixture through preparative TLC on every alternate day was continued until (20 days) no cyclooctadiene **30a** was found to form. In this way cyclooctadiene derivative **30a** was isolated in 35% yield. The material that remained unchanged after separation of the cyclooctadiene derivative was heated in toluene in a sealed tube at 200 °C for 24 h to afford also the same cyclooctadiene **30a** in 10% yield. A small amount (5%) of material still remained unchanged. Thus the cyclooctadiene derivative **30a** was obtained in a combined yield of 45%. From this behavior of the photoadducts it is likely that the products that gave the cyclootadiene derivative at room temperature are the *cis*-1,2-divinyl cyclobutanes **26** and/or **27**, as *cis*-1,2-divinylcyclobutanes are known to undergo Cope rearrangement at temperatures much lower than that required for rearrangement of *trans*-1,2-divinylcyclobutanes.[22] Thus the fraction of the photoadducts that required heating at 200 °C for rearrangement are likely the *trans*-1,2-divinylcyclobutanes **28** and/or **29**. Comparison of the yields of the cyclootadiene derivative **30a** obtained at room temperature (35%) and on heating (10%) indicated that the photoaddition of the bis(diene) **25a** produced the *cis*-1,2-divinylcyclobutanes predominantly.

The material that remained unchanged even on heating the photoadducts was found to be a mixture of two components in ca. 1:1 ratio by ^{1}H NMR. For characterization, this mixture was hydrogenated over Pd/C to remove the double bonds and the benzyl protecting groups to lead to again a mixture (ca. 1:1) of two components. On the basis of spectral and microanalytical data, the gross structure of the hydrogenation product appeared to be either **33** and/or **34**. Hence, vinyl cyclohexenes **31** and/or **32** were formed through [1,3] rearrangement of the *trans*-1,2-divinylcyclobutanes, possibly during thermolysis,[24] along with the cyclooctadiene derivative.

The bis(diene) **25b** followed a similar reaction course on irradiation and subsequent thermolysis. Thus, the cyclootadiene derivative **30b** was obtained in 40% yield after storing the photoadduct at room temperature for 20 days. Another 12% yield of the cyclooctadiene derivative was obtained on heating the residual mass, thus indicating that *cis*-1,2-divinylcyclobutanes were obtained as the major photoadduct. The stereochemical assignment at the 4/5 ring fusion of the photoadducts **26**−**29** and hence that at 5/8 ring fusion in the tricycles **30a** and **30b** is based on analogy to the formation of the photoadducts **5** from [2 + 2] photocycloaddition of the dienes **4**.

In conclusion, we have demonstrated the influence of furanosugar on the reactivity and stereochemical course during intramolecular [2 + 2] photocycloaddition of alkenes leading to unusual formation of cis−syn−cis 4−5−5 tricyclic system in enantiomerically pure form. The stark concavity of these compounds suggests the possibility of their use as potential building blocks for chiral molecular clefts.[25] A sequence of [2 + 2] photocycloaddition of bis(diene) attached through the same furanosugar and facile [3.3] sigmatropic rearrangement provides an enantioselective approach for direct construction of bicyclo[6.3.0]undecanes.[26]

Experimental Section

All reactions were carried out under a blanket of N_2. Melting points were taken in open capillaries in a sulfuric acid bath and are uncorrected. Petroleum ether refers to the fraction having bp 60−80 °C. A usual workup of the reaction mixture consists of extraction with ether, washing with brine, drying over Na_2SO_4, and removal of solvent in vacuo. Column chromatography was carried out with silica gel (60−120 mesh). Peak positions in ^{1}H and ^{13}C NMR spectra are indicated in ppm downfield from internal TMS in δ units. NMR spectra were taken in $CDCl_3$ solution at 300 MHz for ^{1}H and 75 MHz for ^{13}C. ^{13}C peaks assignment is based on DEPT experiment. IR spectra were recorded as neat for liquids and in KBr for solids.

1:2,5:6-Di-*O*-isopropylidine-3-C-(2′-propenyl)-α-D-allofuranose 2a. To a stirred solution of allylmagnesium bromide [prepared from allyl bromide (1.5 mL, 17.44 mmol) and Mg (0.5 g, 23.24 mmol) in THF (30 mL)] at 0 °C was added dropwise a solution of the ketone **1** (3.0 g, 11.62 mmol) in THF (20 mL). After complete addition, the reaction mixture was stirred at room temperature for 6 h. The reaction mixture was cooled to 0 °C and quenched by adding saturated aqueous NH_4Cl solution. Usual workup of the reaction mixture followed by column chromatography using ether−petroleum ether (1:4) as eluent afforded the allofuranose **2a** (2.79 g, 80%): mp 124 °C; $[\alpha]^{30}_D$ + 42.8 (*c* 3.0, $CHCl_3$); ^{1}H NMR δ 1.34 (3H, s, CH_3), 1.36 (3H, s, CH_3), 1.45 (3H, s, CH_3), 1.58 (3H, s, CH_3), 2.17 (1H, dd, J = 8.8, 14.5 Hz, C*H*$_2$), 2.65 (1H, dd, J = 6.4, 15.5 Hz, CH_2), 2.69 (1H, s, OH), 3.81 (1H, d, J = 5.4 Hz, C_4–H), 3.91 (1H, m, CH), 4.13 (2H, m, CH_2), 4.35 (1H, d, J = 3.7 Hz, C_2–H), 5.15 (1H, d, J = 16.9 Hz, =CH_2), 5.19 (1H, d, J = 10.1 Hz, =CH_2), 5.67 (1H, d, J = 3.7 Hz, C_1–H), 5.99 (1H, m, =CH); ^{13}C NMR δ 25.7 (CH_3), 26.8 (CH_3), 27.1 (CH_3), 37.1 (CH_2), 68.4 (OCH_2), 73.6 (CH), 79.1 (C), 81.6 (CH), 82.5 (CH), 103.9 (CH), 110.1 (C), 112.9 (C), 119.3 (=CH_2), 132.9 (=CH−). Anal. Calcd for $C_{15}H_{24}O_6$: C, 59.98; H, 8.05. Found: C, 60.34; H, 8.29.

1:2,5:6-Di-*O*-isopropylidine-3-C-(2′-methyl-2′-propenyl)-α-D-allofuranose 2b. Following the above procedure, a solution of the ketone **1** (1.0 g, 3.18 mmol) in THF (10 mL) was allowed to react with methallylmagnesium chloride [prepared from methallyl chloride (0.4 mL, 3.82 mmol) and Mg (120 mg, 4.77 mmol)] and THF (10 mL) to afford the allofuranose **2b** (850 mg, 70%): mp 118 °C; $[\alpha]^{25}_D$ +48.2 (*c* 0.89, $CHCl_3$); ^{1}H NMR δ 1.35 (3H, s, CH_3), 1.37 (3H, s, CH_3), 1.50 (3H, s, CH_3), 1.59 (3H, s, CH_3), 1.91 (3H, s, CH_3), 2.12 (1H, d, J = 15 Hz,

(24) Thermolysis of 1,2-divinylcyclobutanes has been the subject of several investigations. It has been established that *cis*-1,2-divinylcyclobutanes produce cyclooctadienes as the major product while *trans*-1,2-divinyl cyclobutanes produce vinylcyclohexenes as the major product. See: (a) Hammond, G. S.; DeBoer, C. D. *J. Am. Chem. Soc.* **1964**, *86*, 899. (b) Trecker, D. J.; Henry, J. P. *J. Am. Chem. Soc.* **1964**, *86*, 902. (c) Berson, J. A.; Dervan, P. B.; Malherbe, R.; Jenkins, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 5937. Also see refs 22 and 23.

(25) Pascal, R. A., Jr.; Mathai, M. S.; Shen, X.; Ho, D. M. *Angew. Chem., Int. Ed.* **2001**, *40*, 4746.

(26) (a) For an account on the synthesis of 5−8 ring systems, see: Mehta, G.; Singh, V. *Chem. Rev.* **1999**, *99*, 881. (b) For selected recent work on the direct construction of 5−8 systems, see: (i) Stragies, R.; Blechert, S. *Synlett* **1998**, 169. (ii) Lo, P. C. K.; Snapper, M. L. *Org. Lett.* **2001**, *3*, 2819. (iii) Boyer, F. D.; Hanna, I.; Ricard, L. *Org. Lett.* **2001**, *3*, 3095.

CH_2), 2.54 (1H, d, J = 12 Hz, CH_2), 2.62 (1H, s, OH), 3.78 (1H, d, J = 9 Hz, CH), 3.91 (1H, m, CH), 4.11 (2H, m, CH_2), 4.45 (1H, d, J = 6 Hz, CH), 4.76 (1H, s, $=CH_2$), 4.94 (1H, s, $=CH_2$), 5.66 (1H, d, J = 6 Hz, CH); ^{13}C NMR δ 24.2 (CH_3), 25.2 (CH_3), 26.3 (CH_3), 26.5 (CH_3), 26.6 (CH_3), 39.6 (CH_2), 67.8 (CH_2), 72.9 (CH), 78.9 (C), 80.6 (CH), 82.4 (CH), 103.4 (CH), 109.5 (C), 112.4 (C), 115.0 (CH_2), 141.8 (C). Anal. Calcd for $C_{16}H_{26}O_6$: C, 61.13; H, 8.34. Found: C, 61.28; H, 8.51.

1:2,5:6-Di-*O*-isopropylidine-3-C-(2′-propenyl)-3-O-methyl α-D-allofuranose 3a. To a magnetically stirred suspension of NaH (130 mg, 2.7 mmol, 50% in oil), freed from adhering oil by repeated washing with petroleum, in THF (5 mL) was added dropwise a solution of the alcohol **2a** (550 mg, 1.83 mmol) in THF (5 mL). The mixture was gently refluxed for 2 h and then cooled to room temperature. To it was added HMPA (0.5 mL) followed by CH_3I (0.3 mL, 3.6 mmol). After refluxing for 2 h, the reaction mixture was cooled to room temperature and quenched by adding saturated NH_4Cl solution (2 mL). Usual workup of the reaction mixture followed by column chromatography using ether−petroleum ether (1:9) as eluent afforded the methyl ether **3a** (520 mg, 90%) as a colorless viscous liquid: $[\alpha]^{25}_D$ +20.0 (*c* 1.56, $CHCl_3$); ^{1}H NMR δ 1.29 (3H, s, CH_3), 1.32 (3H, s, CH_3), 1.39 (3H, s, CH_3), 1.54 (3H, s, CH_3), 2.25 (1H, dd, J = 7.5, 15.2 Hz), 2.63 (1H, dd, J = 6.3, 15.2 Hz), 3.45 (3H, s, OMe), 3.84 (1H, d, J = 2.7 Hz), 4.03−4.09 (3H, m), 4.36 (1H, d, J = 3.5 Hz, C_{2-}H), 5.10−5.16 (2H, m), 5.52 (1H, d, J = 3.5 Hz, C_{1-}H), 5.85−5.99 (1H, m); ^{13}C NMR δ 25.8 (CH_3), 26.8 (CH_3), 26.9 (CH_3), 27.4 (CH_3), 34.5 (CH_2), 53.3 (OCH_3), 68.8 (CH_2), 73.1 (CH), 82.3 (CH), 83.5 (CH), 83.9 (C), 103.4 (CH), 110.0 (C), 113.0 (C), 119.0 (CH_2), 137.7 (CH). Anal. Calcd for $C_{16}H_{26}O_6$: C, 61.13; H, 8.34. Found: C, 61.51; H,8.32

1:2,5:6-Di-*O*-isopropylidine-3-C-(2′-propenyl)-3-O-benzyl-α-D-allofuranose 3b. Following the above procedure, the alcohol **2a** (800 mg, 2.66 mmol) was alkylated with BnBr (0.4 mL, 3.19 mmol) to afford the benzyl ether **3** (730 mg, 70%): mp 98 °C; $[\alpha]^{25}_D$ +20.5 (*c* 3.7, $CHCl_3$); ^{1}H NMR δ 1.33 (3H, s, CH_3), 1.34 (3H, s, CH_3), 1.37 (3H, s, CH_3), 1.59 (3H, s, CH_3), 2.41 (1H, dd, J = 7.2, 14.8 Hz, CH_2), 2.68 (1H, dd, J = 6.7, 14.8 Hz, CH_2), 3.95 (1H, m), 4.10 (1H, m), 4.22 (2H, m), 4.8 (1H, d, J = 3.6 Hz, C_2H), 4.72 (1H, d, J = 11.1 Hz, PhCH), 4.84 (1H, d, J = 11.1 Hz, PhCH), 5.15 (2H, m, CH_2), 5.62 (1H, d, J = 3.6 Hz, C_1H), 6.01 (1H, m, −CH=), 7.21−7.40 (5H, m, ArH); ^{13}C NMR δ 25.8 (CH_3), 26.9 (CH_3), 27.0 (CH_3), 27.4 (CH_3), 36.2 (CH_2), 67.3 (CH_2), 68.4 (CH_2), 73.4 (CH), 81.7 (CH), 83.4 (CH), 84.0(C), 103.9 (CH), 109.9(C), 113.1(C), 119.0 (CH_2), 127.5 (CH), 128.4 (CH), 133.0 (CH), 139.6(C). Anal. Calcd for $C_{22}H_{30}O_6$: C, 67.67; H, 7.74. Found: C, 68.02; H, 7.24.

1:2,5:6-Di-*O*-isopropylidine-3-C-(2′-methyl-2′-proprenyl)-3-O-benzyl-α-D-allofuranose 3c. Following the above procedure, the alcohol **2b** (850 mg, 2.70 mmol) was alkylated with BnBr (0.4 mL, 3.24 mmol) to afford the benzyl ether **3c** (870 mg, 80%) as a colorless viscous liquid: $[\alpha]^{25}_D$ +14.5 (*c* 0.57, $CHCl_3$); ^{1}H NMR δ 1.34 (9H, s, CH_3), 1.61 (3H, s, CH_3), 1.88 (3H, s, CH_3), 2.17 (1H, d, J = 15 Hz, CH_2), 2.67 (1H, d, J = 15 Hz, CH_2), 3.94 (1H, m), 4.16 (2H, m), 4.36 (1H, d, J = 6 Hz, CH), 4.62 (1H, d, J = 3.0 Hz, C_{2-}H), 4.77 (1H, d, J = 12 Hz, PhCH), 4.90 (2H, d, J = 18 Hz, $=CH_2$), 5.05 (1H, d, J = 12 Hz, PhCH), 5.61 (1H, d, J = 6 Hz, C_{1-}H), 7.23−7.39 (5H, m, ArH); ^{13}C NMR δ 24.3 (CH_3), 25.2 (CH_3), 26.2 (CH_3), 26.4 (CH_3), 27.0 (CH_3), 38.5 (CH_2), 67.1 (CH_2), 68.4 (CH_2), 72.5 (CH), 80.3 (CH), 83.1 (CH), 83.4 (C), 102.0 (CH), 109.5 (C), 112.6 (C), 115.1 (CH_2), 127.0 (CH), 127.3 (CH), 128.1 (CH), 139.3 (C), 141.4 (C). Anal. Calcd for $C_{23}H_{32}O_6$: C, 68.29; H, 9.79. Found: C, 68.02; H, 8.01.

1,2-Di-*O*-isopropylidine-3-C-(2′-propenyl)-3-O-methyl-4*β*-ethynyl-α-D-allofuranose 4a. A solution of the diacetonide **3a** (500 mg, 1.59 mmol) in aqueous acetic acid (5 mL, 75%) was stirred at room temperature for 12 h. The reaction mixture was diluted with ethyl acetate (30 mL) and washed repeatedly with saturated aqueous $NaHCO_3$ solution (5 × 3 mL) to make it free from acid. The organic layer was dried and concentrated to afford a colorless viscous liquid (400 mg). This diol was converted to the alkene following the procedure developed by Gregg and Samuelsson.[27] To a solution of this liquid in toluene (20 mL) was added imidazole (400 mg, 5.83 mmol) and PPh_3 (1.52 g, 5.83 mmol). This mixture was refluxed gently and iodine (1.11 g, 4.38 mmol) was added in small portions. Refluxing was continued for 2 h. The reaction mixture was cooled to room temperature and aqueous NaOH solution (5 mL, 20%) was added to it. Usual workup of this mixture followed by column chromatography using ether−petroleum ether (1:19) as eluent afforded the diene **4a** (230 mg, 60%) as a colorless viscous liquid: $[\alpha]^{25}_D$ +51.7 (*c* 5.4, $CHCl_3$); ^{1}H NMR δ 1.27 (3H, s, CH_3), 1.52 (3H, s, CH_3), 2.15 (1H, dd, J = 7.3, 15.0 Hz), 2.47 (1H, dd, J = 6.9, 15.0 Hz), 3.34 (3H, s, OMe), 4.33 (1H, d, J = 3.6 Hz, C_{2-}H), 4.50 (1H, d, J = 6.3 Hz, C_{4-}H), 5.03−5.09 (2H, m), 5.21−5.42 (2H, m), 5.57 (1H, d, J = 3.6 Hz, C_{1-}H), 5.75−5.86 (2H, m); ^{13}C NMR δ 26.8 (CH_3), 27.3 (CH_3), 34.5 (CH_2), 52.9 (OCH_3), 82.4 (2CH), 84.4 (C), 103.8 (CH), 112.9 (C), 118.8 (CH_2), 119.4 (CH_2), 132.8 (CH), 132.9 (CH).

1,2-Di-*O*-isopropylidine-3-C-(2′-propenyl)-3-O-benzyl-4*β*-ethynyl-α-D-allofuranose 4b. Following the above procedure the diacetonide **3b** (1.5 g, 3.84 mmol) was converted to the diene **4b** (470 mg, 53%) as a colorless viscous liquid: $[\alpha]^{25}_D$ +13.6 (*c* 0.6, $CHCl_3$); ^{1}H NMR δ 1.35 (3H, s, CH_3), 1.60 (3H, s, CH_3), 2.33 (1H, dd, J = 7.2, 14.7 Hz, CH_2), 2.56 (1H, dd, J = 7.2, 14.7 Hz, CH_2), 4.49 (1H, d, J = 3.9 Hz, C_2H), 4.67 (2H, s, PhCH), 5.15 (2H, m, $=CH_2$), 5.27 (1H, d, J = 10.8 Hz, $=CH_2$), 5.43 (1H, d, J = 16.2 Hz, $=CH_2$), 5.69 (1H, d, J = 3.9 Hz, CH C_{1-}H), 5.85−5.96 (1H, m, =CH), 7.23−7.45 (5H, m, ArH); ^{13}C NMR δ 27.0 (CH_3), 27.3 (CH_3), 36.3 (CH_2), 67.2 (CH_2), 82.2 (CH), 82.4 (CH), 84.7(C), 104.2 (CH), 112.9(C), 118.7 (CH_2), 118.8 (CH_2), 127.8 (CH), 128.8 (CH), 132.6 (CH), 132.8 (CH), 133.1 (CH), 139.2 (C). Anal. Calcd for $C_{19}H_{24}O_4$: C, 72.12; H, 7.64. Found: C, 72.37; H, 7.21.

1,2-Di-*O*-isopropylidine-3-C-(2′-methyl-2′-propnyl)-3-O-benzyl-4*β*-ethenyl -α-D-allofuranose 4c. Following the above procedure the diacetonide **3c** (1.8 g, 4.45 mmol) was converted to the diene **4c** (840 mg, 57%) as a colorless viscous liquid: $[\alpha]^{21}_D$ +13.2 (*c* 0.93, $CHCl_3$); ^{1}H NMR δ 1.34 (3H, s, CH_3), 1.61 (3H, s, CH_3), 1.84 (3H, s, CH_3), 2.15 (1H, d, J = 15 Hz,), 2.50 (1H, d, J = 15 Hz,), 4.60 (1H, d, J = 3.6 Hz, C_{2-}H), 4.70 (1H, d, J = 11.5 Hz, PhCH), 4.82 (4H, m), 5.26 (1H, d, J = 10.65 Hz, $=CH_2$), 5.37 (1H, dt, J = 1.5, 17.2 Hz), 5.67 (1H, d, J = 3.6 Hz, C_{1-}H), 5.82−5.93 (1H, m, =CH−), 7.20−7.37 (5H, m, ArH); ^{13}C NMR δ 24.4 (CH_3), 26.50 (CH_3), 26.9 (CH_3), 37.6 (CH_2), 66.5 (CH_2), 80.7 (CH), 82.2 (CH), 84.2 (C), 103.1 (CH), 112.5 (C), 115.2 (CH_2), 119.2 (CH_2), 127.1 (CH), 127.2 (CH), 128.2 (CH), 132.5 (CH), 138.9 (C), 141.4 (C). Anal. Calcd for $C_{20}H_{26}O_4$: C, 72.70; H, 7.93. Found: C, 72.32; H, 8.16.

Photocycloaddition of the Dienes. *cis*−*syn*−*cis*-4α,5α-Di-*O*-isopropylidine-6α-methoxy-3-oxatricyclo[3.2.0.0^{2,6}]-decane 5a. A magnetically stirred solution of the diene **4a** (110 mg, 0.46 mmol) in dry ether (150 mL) containing CuOTf (10 mg, 0.03 mmol) under an argon atmosphere was irradiated with a 450 W medium-pressure mercury vapor lamp (Hanovia) through a double-walled water-cooled quartz immersion well for 3.5 h. The reaction mixture was then washed successively with ice-cold NH_4OH (35%, 3 × 10 mL) and water (2 × 10 mL) and dried. After evaporation of the solvent the residual mass was chromatographed using ether−petroleum ether (1:19) as eluent to afford the cyclobutane derivative **5a** (80 mg, 73%) as a colorless viscous liquid: $[\alpha]^{25}_D$ +35.4 (*c* 1.05, $CHCl_3$); ^{1}H NMR δ 1.37 (3H, s, CH_3), 1.59 (3H, s, CH_3), 1.93−2.38 (6H, m), 2.87 (2H, m), 3.32 (3H, s, OCH_3), 4.38 (1H, d, J = 5.1 Hz, C_{2-}H), 4.52 (1H, d, J = 3.9 Hz, C_{5-}H), 5.94 (1H, d, J = 3.6 Hz, C_{4-}H); ^{13}C NMR δ 16.6 (CH_2), 26.6 (CH_3), 26.9 (CH_2), 27.1 (CH_3), 37.5 (CH_2), 38.5 (CH), 41.0 (CH), 52.3 (OCH_3), 80.4 (CH), 86.4 (CH), 98.1 (C), 106.0 (CH), 112.5 (C). Anal. Calcd for $C_{13}H_{20}O_4$: C, 64.96; H, 8.39. Found: C, 64.88; H, 8.51.

(27) Gregg, P. J.; Samuelsson, B. *Synthesis* **1979**, 469.

***cis*−*syn*−*cis*-4α,5α-Di-*O*-isopropylidine-6α-benzyloxy-3-oxatricyclo[3.2.0.0^{2,6}]decane 5b.** Irradiation of a solution of the diene **4b** (470 mg, 1.48 mmol) in dry ether (250 mL) containing CuOTf (0.05 g, 0.1 mmol) under argon using the above-mentioned procedure afforded the cyclobutane derivative **5b** (340 mg, 72%): mp 52 °C; $[\alpha]^{25}_D$ +6.93 (*c* 1.32, $CHCl_3$); ^{1}H NMR δ 1.38 (3H, s, CH_3), 1.60 (3H, s, CH_3), 1.95−2.41 (6H, m), 2.90 (2H, m), 4.46−4.50 (2H, m, PhCH and C_{2-}H), 4.59 (1H, d, J = 3.6 Hz, C_{5-}H), 4.60 (1H, d, J = 14.4 Hz, PhCH), 5.99 (1H, d, J = 3.9 Hz, C_{4-}H), 7.14−7.37 (5H, m, ArH); ^{13}C NMR δ 17.2 (CH_2), 27.0 (CH_2), 27.4 (CH_3), 27.5 (CH_3), 39.1 (CH_2), 39.09 (CH), 41.3 (CH), 67.4 (CH_2), 80.9 (CH), 87.0 (CH), 98.7(C), 106.9 (CH), 112.9(C), 127.9 (CH), 128.6 (CH), 139.1(C). Anal. Calcd for $C_{19}H_{24}O_4$: C, 72.12; H, 7.64. Found: C, 71.57; H, 7.27.

***cis*−*syn*−*cis*-4α,5α-Di-*O*-isopropylidine-6α-benzyloxy-8α-methyl-3-oxatricyclo[3.2.0.0^{2,6}]decane 5c.** Irradiation of a solution of the diene **4c** (800 mg, 2.42 mmol) in dry diethyl ether (250 mL) containing CuOTf (0.06 g, 0.11 mmol) under an argon atmosphere afforded the corresponding cyclobutane derivative **5c** (620 mg, 77%): mp 58 °C; $[\alpha]^{21}_D$ +15.1 (*c* 0.89, $CHCl_3$); ^{1}H NMR δ 1.26 (3H, s, CH_3), 1.36 (3H, s, CH_3), 1.59 (3H, s, CH_3), 1.76−2.15 (6H, m), 2.46 (1H, m), 4.47−4.57 (4H, m, PhCH, C_{5-}H and C_{2-}H), 5.99 (1H, d, J = 3.9 Hz, C_{4-}H), 7.24−7.4 (5H, m, ArH); ^{13}C NMR δ 13.1 (CH_2), 26.9 (CH_3), 27.0 (CH_3), 27.8 (CH_3), 34.3 (CH_2), 38.1 (C), 44.6 (CH_2), 46.6 (CH), 67.0 (CH_2), 80.6 (CH), 87.4 (CH), 97.4 (C), 106.5 (CH), 112.5 (C), 127.4 (CH), 127.9 (CH), 128.2 (CH), 128.4 (CH), 128.8 (CH), 138.3 (C). Anal. Calcd for $C_{20}H_{26}O_4$: C, 72.70; H, 7.93. Found: C, 72.35; H, 8.25.

***cis*−*syn*−*cis*-4α,5α-Di-*O*-isopropylidine-6α-hydroxy-3-oxatricyclo[3.2.0.0^{2,6}]decane 6a.** A solution of the photoadduct **5b** (120 mg, 0.37 mmol) in dry methanol (4 mL) containing acetic acid (0.2 mL), perchloric acid (0.05 mL), and Pd−C (5%) (20 mg) was stirred under hydrogen atmosphere at room temperature for 2 h. The mixture was filtered and treated with saturated aqueous $NaHCO_3$ solution (2 mL) to make it alkaline. MeOH was removed and the residue was worked up in the usual way. The crude mass obtained was chromatographed using ether−petroleum ether (1:4) to afford the hydroxy compound **6a** (70 mg, 80%) as a colorless viscous liquid: $[\alpha]^{25}_D$ +28.5 (*c* 0.23, $CHCl_3$); ^{1}H NMR δ 1.37 (3H, s, CH_3), 1.57 (3H, s, CH_3), 1.99−2.24 (6H, m), 2.98 (2H, m), 4.15 (1H, d, J = 5.5 Hz, C_{2-}H), 4.39 (1H, d, J = 3.7 Hz, C_{5-}H), 5.98 (1H, J = 3.7 Hz, C_{4-}H); ^{13}C NMR δ 17.2 (CH_2), 27.0 (CH_3), 27.1 (CH_2), 27.2 (CH_3), 39.7 (CH), 40.9 (CH), 42.6 (CH_2), 81.4 (CH), 87.7 (CH), 93.0(C), 106.2 (CH), 112.5(C). Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.84; H, 7.70.

***cis*−*syn*−*cis*-4α,5α-Di-*O*-isopropylidine-6α-hydroxy-8α-methyl-3-oxatricyclo[3.2.0.0^{2,6}]decane 6b.** Hydrogenolysis of the photoadduct **5c** (120 mg, 0.36 mmol) in dry methanol (4 mL) following the above procedure afforded the hydroxy compound **6b** (75 mg, 85%) as a colorless viscous liquid: $[\alpha]^{25}_D$ +33.6 (*c* 0.60, $CHCl_3$); ^{1}H NMR δ 1.28 (3H, s, CH_3), 1.36 (3H, s, CH_3), 1.54 (3H, s, CH_3), 1.79−2.1 (6H, m), 2.48 (1H, m), 4.15 (1H, d, J = 6.3 Hz, C_{2-}H), 4.27 (1H, d, J = 3.6 Hz, C_{5-}H), 5.89 (1H, d, J = 3.6 Hz, C_{4-}H); ^{13}C NMR δ 13.3 (CH_2), 26.7 (CH_3), 26.9 (CH_3), 28.0 (CH_3), 29.7 (C), 34.2 (CH_2), 46.7 (CH), 48.8 (CH_2), 81.3 (CH), 88.2 (CH), 92.0 (C), 105.8 (CH), 112.4 (C). Anal. Calcd for $C_{13}H_{20}O_4$: C, 64.97; H, 8.38. Found: C, 64.36; H, 8.11.

1:2,5:6-Di-*O*-isopropylidine-3-C-(2′-oxopropyl)-3-O-benzyl-α-D-allofuranose 12. To a stirred suspension of $NaIO_4$ (1.64 g, 7.68 mmol) in water (10 mL) was added the alkene **3b** (500 mg, 1.28 mmol) in diethyl ether (20 mL). After stirring the mixture for 15 min, a catalytic amount of OsO_4 was added and the mixture stirred at room temperature till complete disappearance of the starting alkene. The organic layer was separated and washed with saturated aqueous $NaHCO_3$ solution (2 × 3 mL). The organic layer was dried and concentrated. The residual mass was chromatographed using ether−petroleum ether (1:4) as eluent to afford the aldehyde **12** (400 mg, 79%) as a colorless viscous liquid: $[\alpha]^{30}_D$ +21.8 (*c* 6.4, $CHCl_3$); IR 1720.4 cm^{-1}; ^{1}H NMR δ 1.33 (3H, s, CH_3), 1.35 (3H, s, CH_3), 1.40 (3H, s, CH_3), 1.60 (3H, s, CH_3), 2.65 (1H, dd, J = 2.5, 15.3 Hz), 2.79 (1H, dd, J = 2.5, 15.3 Hz), 3.96 (1H, m), 4.10 (2H, m), 4.25 (1H, d, J = 5.4 Hz), 4.56 (1H, d, J = 3.9 Hz, C_{2-}H), 4.79 (1H, d, J = 10.8 Hz, PhCH), 4.83 (1H, d, J = 10.8 Hz, PhCH), 5.65 (1H, d, J = 3.9 Hz, C_{1-}H), 7.23−7.38 (5H, m, ArH), 9.95 (1H, t, J = 2.6 Hz, CHO); ^{13}C NMR δ 25.5 (CH_3), 26.93 (CH_3), 26.95 (CH_3), 27.2 (CH_3), 45.0 (CH_2), 67.9 (CH_2), 68.7 (CH_2), 73.6 (CH), 80.2 (CH), 83.8 (CH), 84.3 (C), 103.7 (CH), 110.4 (C), 113.5 (C), 127.6 (CH), 127.8 (CH), 128.6 (CH), 138.7 (C), 201.3 (CHO). Anal. Calcd for $C_{21}H_{28}O_7$: C, 64.27; H, 7.19. Found: C, 64.54; H, 7.51.

Wittig−Horner Reaction of the Aldehyde 12. Synthesis of the Unsaturated Ester 13. To a magnetically stirred suspension of NaH (60 mg, 1.2 mmol, 50% in oil), freed from adhering oil by repeated washing with petroleum, was added a solution of triethyl phosphonoacetate (0.27 mL, 1.35 mmol) in dry THF (2 mL) dropwise at room temperature. After stirring of the resulting clear solution at room temperature for 40 min, the aldehyde **12** (380 mg, 0.97 mmol) in dry THF (5 mL) was added dropwise and allowed to stir for additional 12 h. The reaction mixture was cooled to 0 °C and quenched by adding saturated aqueous NH_4Cl (5 mL). Usual workup of the mixture followed by column chromatography [ether−petroleum ether (1:4)] afforded the unsaturated ester **13** (300 mg, 67%) as a colorless viscous liquid: $[\alpha]^{21}_D$ +17.6 (*c* 0.5 $CHCl_3$); IR 1718.5, 1652.9 cm^{-1}; ^{1}H NMR δ 1.16 (3H, t, J = 7.2 Hz, $COOCH_2CH_3$), 1.21 (6H, s, CH_3), 1.26 (3H, s, CH_3), 1.47 (3H, s, CH_3), 2.43 (1H, dd, J = 6.3, 7.8 Hz, CH_2), 2.64 (1H, dd, J = 1.5, 6.3 Hz, CH_2), 3.80 (1H, m), 4.05 (5H, m), 4.32 (1H, d, J = 3.6 Hz, C_{2-}H), 4.63 (1H, J = 11 Hz, PhCH), 4.70 (1H, J = 11 Hz, PhCH), 5.51 (1H, d, J = 3.6 Hz, C_{1-}H), 5.80 (1H, d, J = 14.7 Hz, =CH), 7.02−7.28 (6H, m); ^{13}C NMR δ 14.6 (CH_3), 25.6 (CH_3), 26.91 (CH_3), 26.97 (CH_3), 27.3 (CH_3), 34.6 (CH_2), 60.8 (CH_2), 67.6 (CH_2), 68.8 (CH_2), 73.3 (CH), 81.1 (CH), 83.6 (CH), 84.3 (C), 103.6 (CH), 110.2 (C), 113.4 (C), 125.0 (CH), 127.6 (CH), 128.0 (CH), 128.5 (CH), 139.2 (C), 143.4 (CH), 166 ($CO_2CH_2CH_3$). Anal. Calcd for $C_{25}H_{34}O_8$: C, 64.92; H, 7.41. Found: C, 64.45; H, 7.68.

Synthesis of the Diene 14. Following the procedure described above for the conversion of the diacetonide **3a** to the diene **4a**, the diacetonide **13** (1.1 g, 2.3 mmol) was transformed to the diene **14** (500 mg, 54%) as a colorless viscous liquid: $[\alpha]^{25}_D$ +9.31 (*c* 2.6, $CHCl_3$); IR 1716.5, 1651.0 cm^{-1}; ^{1}H NMR δ 1.27 (3H, t, J = 6 Hz, $COOCH_2CH_3$), 1.36 (3H, s, CH_3), 1.61 (3H, s, CH_3), 2.45 (1H, dd, J = 9.15 Hz, CH_2), 2.66 (1H, dd, J = 6, 15 Hz, CH_2), 4.19 (2H, q, J = 6 Hz, $COOCH_2CH_3$), 4.48 (1H, d, J = 3 Hz, C_{2-}H), 4.67 (3H, m), 5.32 (1H, d, J = 10.8 Hz, =CH_2), 5.46 (1H, d, J = 17.4 Hz, CH_2), 5.71 (1H, d, J = 3.9 Hz, C_{1-}H), 5.82−5.92 (2H, m), 7.05 (1H, dt, J = 8.4, 16 Hz, =CH), 7.24−7.39 (5H, m, ArH); ^{13}C NMR δ 14.6 (CH_3), 26.9 (CH_3), 27.2 (CH_3), 34.5 (CH_2), 60.8 (CH_2), 67.5 (CH_2), 81.5 (CH), 82.4 (CH), 84.8 (C), 103.9 (CH), 113.2 (C), 119.1 (CH_2), 124.9 (CH), 127.8 (CH), 128.0 (CH), 128.7 (CH), 132.2 (CH), 138.6 (C), 143.3 (CH), 166.3 ($CO_2CH_2CH_3$). Anal. Calcd for $C_{22}H_{28}O_6$: C, 68.02; H, 7.26. Found: C, 67.45; H, 7.17.

***cis*−*syn*−*cis*-4α,5α-Di-*O*-isopropylidine-6α-benzyloxy-9-carbethoxy-3-oxatricyclo[3.2.0.0^{2,6}]decane 15.** A solution of the unsaturated ester **14** (250 mg, 0.64 mmol) in acetonitrile (200 mL) was irradiated in the presence of benzophenone (20 mg, 0.1 mmol) through a water-cooled Pyrex immersion well with a medium-pressure mercury vapor Hanovia Lamp (450 W) for 3 h. The solvent was removed under vacuum. The residue was chromatograhed [ether−petroleum ether (1:5)] to afford the cyclobutane derivative **15** (125 mg, 50%) as a colorless viscous liquid: $[\alpha]^{21}_D$ +12.7 (*c* 2.4, $CHCl_3$); IR 1728.1 cm^{-1}; ^{1}H NMR δ 1.25 (3H, t, J = 7.2 Hz, $COOCH_2CH_3$), 1.39 (3H, s, CH_3), 1.61 (3H, s, CH_3), 2.21−2.50 (3H, m), 2.77−2.95 (3H, m), 3.09−3.20 (1H, m), 4.13 (2H, q, J = 7.2 Hz), 4.49 (1H, d, J = 11 Hz, PhCH), 4.50 (1H, d, J = 4.8 Hz, C_{7-}H), 4.61 (1H, d, J = 11 Hz, PhCH), 4.62 (1H, d, J = 3.9 Hz, C_{1-}H),

5.98 (1H, d, J = 3.9 Hz, C_{5-}H), 7.14−7.36 (5H, m, ArH); ^{13}C NMR δ 14.6 (CH_3), 21.0 (CH_2), 27.2 (CH_3), 38.6 (CH_2), 38.7 (CH), 42.3 (CH), 45.3 (CH), 60.8 (CH_2), 67.5 (CH_2), 81.1 (CH), 86.0 (CH), 98.7 (C), 106.4 (CH), 113.1 (C), 127.8 (CH), 127.9 (CH), 128.7 (CH), 138.8 (C), 175.9 ($CO_2CH_2CH_3$). Anal. Calcd for $C_{22}H_{28}O_6$: C, 68.02; H, 7.26. Found: C, 68.40; H, 7.33.

***cis*−*syn*−*cis*-4α,5α-Di-*O*-isopropylidine-6α-hydroxy-9-carbethoxy-3-oxatricyclo[3.2.0.0^{2,6}]decane 16.** A solution of the benzyl ether **15** (120 mg, 0.30 mmol) in dry EtOH (4 mL) containing acetic acid (0.2 mL), perchloric acid (0.05 mL), and Pd−C (20 mg, 5%) was stirred under hydrogen atmosphere for 2 h. Usual workup of the reaction mixture followed by column chromatography [ether−petroleum ether (1:4)] afforded the hydroxy ester **16** (60 mg, 65%) as a colorless viscous liquid: $[\alpha]^{21}_D$ +6.05 (*c* 0.79, $CHCl_3$); IR 1728.1, 3460 cm^{-1}; ^{1}H NMR δ 1.23 (3H, t, J = 6.9 Hz, $COOCH_2CH_3$), 1.38 (3H, s, CH_3), 1.57 (3H, s, CH_3), 2.14−2.38 (4H, m), 2.58 (1H, brs, OH), 2.76 (1H, m), 2.94 (1H, m), 3.21 (1H, m), 4.09−4.18 (3H, m), 4.43 (1H, d, J = 3.9 Hz, C_{5-}H), 5.97 (1H, d, J = 3.9 Hz, C_{4-}H); ^{13}C NMR δ 14.2 (CH_3), 20.6 (CH_2), 26.6 (CH_3), 26.8 (CH_3), 38.0 (CH), 41.8 (CH_2), 42.7 (CH), 44.9 (CH), 60.4 (CH_2), 81.5 (CH), 86.4 (CH), 92.8 (C), 105.4 (CH), 112.4 (C), 175.4 ($CO_2CH_2CH_3$). Anal. Calcd for $C_{15}H_{22}O_6$: C, 60.39; H, 7.43. Found: C, 61.01; H, 7.73.

Transformation of the Hydroxy Ester to the Cyclobutane Derivative 6a. A mixture of the hydroxy ester **16** (40 mg, 0.13 mmol), EtOH (1.5 mL), KOH (40 mg, 0.67 mmol), and water (0.2 mL) was refluxed for 2 h. The reaction mixture was cooled to 0 °C and acidified with aqueous HCl (10%). EtOH was removed under vacuum and the residue was extracted with $CHCl_3$ (2 × 5 mL). The organic extract was dried and concentrated to afford a yellowish white viscous mass, **17** (30 mg).

A solution of the hydroxy acid **17** in benzene (5 mL) (30 mg, 0.1 mmol) containing quinoline (20 mg) and tBuSH (0.2 mL) was irradiated externally with a medium-pressure 450-W Hanovia mercury-vapor lamp (Pyrex filter) for 7 h under argon. The mixture was then washed successively with cold 6 N HCl (3 × 1 mL), saturated aqueous $NaHCO_3$ solution, and brine. Evaporation of the solvent followed by chromatography [ether−petroleum ether (1:4)] afforded the cyclobutane derivative **6a** (10 mg, 40%).

1:2,5:6-Di-*O*-isopropylidine-3-C-(2′,4′-pentadienyl)-3-O-benzyl-α-D-allofuranose 23a. n-BuLi (1.22 mL, 1.90 mmol, 1.55 M) in hexane was added dropwise to a magnetically stirred and cooled (0 °C) suspension of allyltriphenyl phosphonium chloride (860 mg, 2.54 mmol) in ether (10 mL) under Ar. After stirring at 0 °C for 15 min, a solution of the aldehyde **12** (500 mg, 1.27 mmol) in ether (5 mL) was added over a period of 10 min. After stirring for 30 min at 0 °C, the reaction mixture was quenched by addition of cold water (5 mL). Usual workup of the reaction mixture followed by column chromatography using ether−petroleum ether (1:19) as eluent afforded the diene **23a** (340 mg, 64%) as a colorless viscous liquid: $[\alpha]^{32}_D$ +7.5 (*c* 7.6, $CHCl_3$); ^{1}H NMR δ (for both isomers) 1.33 (6H, s, CH_3), 1.38 (3H, s, CH_3), 1.58 (3H, s, CH_3), 2.40−2.77 (2H, m), 3.93 (1H, m), 3.96−4.23 (3H, m), 4.42 (1H, d, J = 3.7 Hz), 4.45 (1H, d, J = 3.7 Hz), 4.69−4.85 (2H, m), 5.01−5.28 (2H, m), 5.60 (1H, d, J = 3.6 Hz), 5.64 (1H, d, J = 3.6 Hz), 5.70−5.91 (1H, m), 6.11−6.66 (2H, m), 7.23−7.39 (5H, m, ArH); ^{13}C NMR δ 25.88 (CH_3), 25.39 (CH_3), 26.53 (CH_3), 25.54 (CH_3), 26.6 (CH_3), 26.6 (CH_3), 26.9 (CH_3), 29.11 (CH_2), 34.53 (CH_2), 66.90 (CH_2), 66.99 (CH_2), 68.08 (CH_2), 68.11 (CH_2), 73.02 (CH), 81.27 (CH), 81.29 (CH), 83.09 (CH), 83.24 (CH), 83.99, 84.09 (C), 103.46 (CH), 103.48 (CH), 109.52 (C), 109.55 (C), 112.68 (C), 112.70 (C), 116.33 (CH), 118.79 (CH), 125.32 (CH), 127.28 (CH), 128.18 (CH), 128.34 (CH), 128.53 (CH), 131.43 (CH), 131.71 (CH), 134.51 (CH), 136.62 (CH), 139.5 (C), 139.6 (C). Anal. Calcd for $C_{24}H_{32}O_6$: C, 69.20; H, 7.74. Found: C, 69.49; H, 8.04.

1:2,5:6-Di-*O*-isoprepylidine-3-C-(4′-methyl-2′,4′-pentadienyl)-3-O-benzyl-α-D-allofuranose 23b. Following the above procedure, the aldehyde **12** (1.8 g, 4.6 mmol) on reaction with the ylide generated from methallyltriphenyl phosphonium chloride (3.23 g, 9.2 mmol) with n-BuLi (5.7 mL, 6.8 mmol, 1.2M) afforded, after workup and column chromatography [ether−petroleum ether (1:19)], the diene **23b** (1.2 g, 63%) as a colorless viscous liquid: $[\alpha]^{32}_D$ +6.4 (*c* 6.7, $CHCl_3$); ^{1}H NMR δ 1.34 (6H, s, CH_3), 1.39 (3H, s, CH_3), 1.60 (3H, s, CH_3), 1.83 (3H, s, CH_3), 1.88 (3H, s, CH_3), 2.49−2.79 (2H, m), 3.95 (1H, m), 4.07−4.25 (3H, m), 4.44 (1H, d, J = 3.7 Hz), 4.46 (1H, d, J = 3.7 Hz), 4.67−5.05 (5H, m), 5.62 (1H, d, J = 3.6 Hz), 5.66 (1H, d, J = 3.7 Hz), 5.74−5.88 (1H, m), 5.99 (1H, d, J = 12.0 Hz), 6.24 (1H, d, J = 15.7 Hz), 7.24−7.41 (5H, m, ArH); ^{13}C NMR δ 19.0 (CH_2), 23.8 (CH_2), 25.8 (CH_3), 25.81 (CH_3), 26.9 (CH_3), 27.0 (CH_3), 27.0 (CH_3), 27.3 (CH_3), 27.4 (CH_3), 29.9 (CH_2), 34.8 (CH_2), 67.1 (CH_2), 67.3 (CH_2), 68.3 (CH_2), 68.6 (CH_2), 73.4 (CH), 81.8 (CH), 81.9 (CH), 83.6 (CH), 83.8 (CH), 84.2 (C), 84.5 (C), 103.8 (CH), 103.9 (CH), 109.8 (C), 109.9 (C), 113.18 (C), 113.19 (C), 116.0 (CH_2), 116.4 (CH_2), 124.4 (CH), 124.6 (CH), 127.4 (CH), 127.5 (CH), 127.6 (CH), 128.47 (CH), 128.48 (CH), 128.8 (CH), 133.7 (CH), 136.7 (CH), 139.4 (C), 139.6 (C), 141.6 (C), 142.1 (C). Anal. Calcd for $C_{25}H_{34}O_6$: C, 69.74; H, 7.96. Found: C, 69.49; H, 8.18.

1,2-Di-*O*-isopropylidine-3-C-(2′,4′-pentadienyl)-3-O-benzyl-4β-formyl-α-D-allofuranose 24a. A solution of the diacetonide **23a** (1.5 g, 3.6 mmol) in aqueous acetic acid (15 mL, 75%) was stirred at room temperature for 12 h. The reaction mixture was diluted with ethyl acetate (60 mL) and washed repeatedly with saturated aqueous $NaHCO_3$ solution (6 × 10 mL) till it was alkaline. The organic layer was dried and concentrated to afford a colorless viscous liquid (1.2 g). A solution of this liquid in acetonitrile (10 mL) was added to a magnetically stirred suspension of $NaIO_4$ (1.02 g, 4.78 mmol) in water (5 mL) and stirring was continued for 1 h. Usual workup of the reaction mixture followed by column chromatography [ether−petroleum ether (1:9)] afforded the aldehyde **24a** (800 mg, 65%) as a colorless liquid: $[\alpha]^{30}_D$ +12.1 (*c* 3.5, $CHCl_3$); IR 1735, 1602 cm^{-1}; ^{1}H NMR δ 1.39 (3H, s, CH_3), 1.62 (3H, s, CH_3), 2.48−2.59 (1H, m, CH_2), 2.71 (1H, dd, J = 8.6, 16.1 Hz, CH_2), 4.51 (1H, d, J = 3.6 Hz), 4.67 (1H, d, J = 5.9 Hz), 4.69−4.79 (2H, m), 5.35 (2H, m), 5.53 (1H, q, J = 7.4 Hz, =CH−), 5.66 91H, quintet, J = 7.4 Hz), 5.85 (1H, d, J = 3.6 Hz), 5.89 (1H, d, J = 3.6 Hz), 6.13 (1H, m), 6.25−6.60 (1H, m), 7.32−7.46 (5H, m, ArH), 9.70 (1H, d, J = 5.4 Hz, CHO), 9.73 (1H, d, J = 6.9 Hz, CHO); ^{13}C NMR δ 27.03 (CH_3), 27.06 (CH_3), 27.36 (CH_3), 27.40 (CH_3), 29.35 (CH_2), 34.76 (CH_2), 67.70 (CH_2), 67.76 (CH_2), 82.95 (CH), 83.01 (CH), 85.59 (CH), 85.71 (CH), 86.98(C), 87.12(C), 104.70 (CH), 104.74 (CH), 113.89(C), 118.00 (CH_2), 120.27 (CH_2), 123.66 (CH), 126.41 (CH), 128.12 (CH), 128.15 (CH), 128.19 (CH), 128.19 (CH), 128.22 (CH), 128.78 (CH), 131.57 (CH), 131.57 (CH), 133.50 (CH), 136.51 (CH), 136.74 (CH), 138.13(C), 138.18(C), 198.20 (CO), 198.63 (CO). Anal. Calcd for $C_{20}H_{24}O_5$: C, 69.75; H, 7.02. Found: C, 69.95; H, 7.54.

1,2-Di-*O*-isopropylidine-3-C-(4′-methyl-2′,4′-pentadienyl)-3-O-benzyl-4β-formyl-α-D-allofuranose 24b. Following the above procedure, the diacetonide **23** (1.5 g, 3.4 mmol) was transformed to the aldehyde **24b** (720 mg, 56%) as a colorless liquid: $[\alpha]^{30}_D$ +40.4 (*c* 1.6, $CHCl_3$); IR 1733.9, 1608.5 cm^{-1}; ^{1}H NMR δ 1.40 (3H, s, CH_3), 1.62 (3H, s, CH_3), 1.85 (3H, s, CH_3), 1.90 (3H, s, CH_3), 2.50−2.88 (2H, m, CH_2), 4.50 (1H, d, J = 3.6 Hz), 4.52 (1H, d, J = 3.6 Hz), 4.64−4.77 (3H, m), 4.96 (2H, dd, J = 5.52−5.65 (1H, m), 5.85 (1H, d, J = 3.5 Hz), 5.89 (1H, d, J = 3.5 Hz), 6.01 (1H, d, J = 11.7 Hz), 6.20 (1H, d, J = 15.6 Hz), 7.29−7.51 (5H, m, ArH); ^{13}C NMR δ 18.9 (CH_3), 23.6 (CH_3), 27.0 (CH_3), 27.31 (CH_3), 27.35 (CH_3), 27.4 (CH_3), 29.6 (CH_2), 34.8 (CH_2), 67.5 (CH_2), 67.7 (CH_2), 83.0 (CH), 83.2 (CH), 85.6 (CH), 85.7 (CH), 86.8 (C), 87.2 (C), 104.71 (CH), 104.74 (CH), 113.8 (C), 116.8 (CH_2), 117.1 (CH_2), 122.4 (CH), 122.7 (CH), 128.0 (CH), 128.1 (CH), 128.2 (CH), 128.76 (CH), 128.78 (CH), 135.3 (CH), 138.1 (C), 138.2 (C), 138.6 (CH), 141.4 (C), 141.6 (C), 198.1 (CHO), 198.6 (CHO). Anal. Calcd for $C_{21}H_{26}O_5$: C, 70.37; H, 7.31. Found: C, 69.95; H, 7.05.

1,2-Di-*O*-isopropylidine-3-C-(2′,4′-pentadienyl)-3-O-benzyl-4*β*-(1,3-butadienyl)-α-D-allofuranose 25a. Wittig reaction of the aldehyde **24a** (800 mg, 2.32 mmol) with the ylide generated from allyltriphenyl phosphonium chloride (1.57 g, 4.65 mmol) and n-BuLi (2.5 mL, 3.48 mmol, 1.4 M) afforded the tetraene **25a** (540 mg, 63%) as a colorless liquid: $[\alpha]^{30}_D$ +6.9 (*c* 4.3, $CHCl_3$); ^{1}H NMR δ 1.27 (3H, s, CH_3), 1.54 (3H, s, CH_3), 2.17−2.59 (2H, m, CH_2), 4.35−4.42 (1H, m), 4.50−4.65 (3H, m), 4.92−5.20 (4H, m), 5.34−5.44 (1H, m), 5.49−5.90 (2H, m), 6.00−6.29 (2H, m), 6.50−6.76 (1H, m), 7.13−7.31 (5H, m, ArH); ^{13}C NMR δ 27.0 (CH_3), 27.02 (CH_3), 27.04 (CH_3), 27.34 (CH_3), 27.35 (CH_3), 27.39 (CH_3), 29.1 (CH_2), 34.5 (CH_2), 35.8 (CH_2), 66.9 (CH_2), 67.1 (CH_2), 67.3 (CH_2), 78.3 (CH), 78.49 (CH), 78.51 (CH), 82.32 (CH), 82.35 (CH), 82.55 (CH), 85.5 (C), 85.9 (C), 104.1 (CH), 104.2 (CH), 104.3 (CH), 104.4 (CH), 112.92 (C), 112.97 (C), 113.01 (C), 116.7 (CH_2), 118.8 (CH_2), 119.1 (CH_2), 120.2 (CH_2), 120.3 (CH_2), 125.76 (CH), 125.77 (CH), 125.8 (CH), 125.0 (CH), 127.50 (CH), 127.54 (CH), 127.61 (CH), 127.6 (CH), 127.9 (CH), 128.53 (CH), 128.55 (C), 128.6 (C), 128.7 (C), 131.85 (CH), 131.91 (CH), 132.99 (CH), 133.06 (CH), 133.10 (CH), 133.14 (CH), 134.6 (CH), 134.7 (CH), 134.74 (CH), 136.7 (CH), 137.1 (CH), 139.13 (C), 139.19 (C), 139.25 (C). Anal. Calcd for $C_{23}H_{28}O_4$: C, 74.97; H, 7.65. Found: C, 75.55; H, 7.59.

1,2-Di-*O*-isopropylidine-3-C-(4′-methyl-2′,4′-pentadienyl)-3-O-benzyl-4*β*-(1″,3″-butadienyl)-α-D-allofuranose 25b. The aldehyde **24b** (920 mg, 2.5 mmol) on reaction with the ylide generated from allyltriphenyl phosphonium chloride (1.70 g, 5.13 mmol) and n-BuLi (2.6 mL, 3.75 mmol, 1.4 M) afforded the tetraene **25b** (420 mg, 61%) as a colorless liquid: $[\alpha]^{30}_D$ +14.0 (*c* 0.9, $CHCl_3$); ^{1}H NMR δ 1.37 (3H, s, CH_3), 1.64 (3H, s, CH_3), 1.82 (3H, s, CH_3), 1.88 (3H, s, CH_3), 2.37−2.89 (2H, m), 4.46−4.50 (1H, m), 4.56−4.75 (3H, m), 4.87−5.29 (5H, m), 5.47 (1H, dd, J = 11.9, 20.1 Hz), 5.63−5.97 (2H, m), 6.19−6.40 (1H, m), 6.74−6.78 (1H, m), 7.23−7.41 (5H, m, ArH); ^{13}C NMR δ 19.05 (CH_3), 23.8 (CH_3), 26.9 (CH_3), 27.0 (CH_3), 27.29 (CH_3), 27.35 (CH_3), 27.41 (CH_3), 29.3 (CH_2), 34.5 (CH_2), 34.8 (CH_2), 66.7 (CH_2), 67.0 (CH_2), 67.3 (CH_2), 77.5 (C), 78.11 (CH), 78.66 (CH), 81.78 (CH), 82.43 (CH), 82.61 (CH), 82.91 (CH), 85.54 (C), 85.56 (C), 86.0 (C), 104.17 (CH), 104.19 (CH), 104.35 (CH), 112.9 (C), 113.03 (C), 113.06 (C), 115.9 (CH_2), 116.2 (CH_2), 116.3 (CH_2), 118.39 (CH_2), 120.2 (CH_2), 120.3 (CH_2), 124.5 (CH), 124.6 (CH), 125.6 (CH), 125.9 (CH), 126.0 (CH), 127.5 (CH), 127.55 (CH), 127.60 (CH), 127.63 (CH), 127.8 (CH), 127.9 (CH), 128.05 (CH), 128.14 (CH), 128.53 (CH), 128.6 (CH), 128.65 (CH), 132.9 (CH), 133.1 (CH), 133.4 (CH), 134.3 (CH), 134.4 (CH), 134.6 (CH), 136.5 (CH), 136.62 (CH), 136.65 (CH), 139.0 (C), 139.2 (C), 141.7 (C), 142.16 (C), 142.18 (C). Anal. Calcd for $C_{24}H_{30}O_4$: C, 75.36; H, 7.91. Found: C, 74.97; H, 7.82.

***cis*−*syn*−*cis*-4α,5α-Di-*O*-isopropylidine-6α-benzyloxy-3-oxatricyclo[6.6.0.0^{2,6}]tetradeca-9,13-diene 30a.** A solution of the tetraene **25a** (370 mg, 1.0 mmol) in dry hexane (90 mL) was irradiated internally in the presence of benzophenone (40 mg, 0.21 mmol) for 6 h. The solvent was removed under reduced pressure. Benzophenone was removed by rapid chromatography through a short column of silica gel using ether−petroleum (1:19) as eluent to afford a colorless viscous liquid (220 mg) (R_f 0.53). The mixture was allowed to stand at room temperature for 20 days when a new spot (R_f 0.36) appeared in the TLC. The resulting mixture was purified through preparative TLC to afford the cyclooctadiene derivative **30a** (130 mg) and the unchanged component with R_f 0.53 (80 mg). Heating a solution of this component in toluene (2 mL) in a sealed tube at 200 °C for 24 h, followed by purification through preparative TLC, afforded the same cyclooctadiene derivative (40 mg) (total yield 45%). Another fraction (20 mg, 5%) with the same R_f 0.53 was also isolated which was found to be a mixture of two components by ^{1}H and ^{13}C NMR. **30a**: R_f 0.36 [ethyl acetate−petroleum ether (1:19)]; $[\alpha]^{32}_D$ +47.9 (*c* 0.61, $CHCl_3$); ^{1}H NMR δ 1.30 (3H, s, CH_3), 1.53 (3H, s, CH_3), 1.91−2.02 (2H, m), 2.40 (2H, m), 2.52 (2H, dd, J = 8.9, 14.8 Hz), 3.28 (1H, m), 3.50 (1H, br s), 4.42 (1H, d, J = 3.5 Hz, C_{2-}H), 4.47 (1H, d, J = 10.9 Hz, PhCH), 4.53 (1H, d, J = 3.8 Hz, C_{5-}H), 4.61 (1H, d, J = 10.9 Hz, PhCH), 5.13 (1H, m), 5.36 (1H, m), 5.57 (1H, m), 5.75 (1H, m), 5.79 (1H, d, J = 3.8 Hz, C_{4-}H), 7.18−7.34 (5H, m, ArH); ^{13}C NMR δ 27.3 (CH_3), 27.4 (CH_3), 27.8 (CH_2), 28.3 (CH_2), 41.2 (CH_2), 42.1 (CH), 47.8 (CH), 67.4 (CH_2), 82.3 (CH), 88.6 (CH), 91.9 (C), 106.2 (CH), 113.3 (C), 127.9 (CH), 128.0 (CH), 128.2 (CH), 128.6 (CH), 128.7 (CH), 135.4 (CH), 138.9 (C). Anal. Calcd for $C_{23}H_{28}O_4$: C, 74.97; H, 7.65. Found: C, 75.00; H, 7.62.

Without further characterization this material was hydrogenated over Pd−C (5 mg, 10%) in MeOH (2 mL).The catalyst was filtered off and the solvent was removed. The residue was purified through preparative TLC to afford the hydroxy compounds **33** and **34** (12.5 mg, 81%): mp 79 °C; ^{1}H NMR δ (for both isomer) 0.74 (6H, t, J = 7.29 Hz), 1.06−1.76 (21H, m), 1.27 (3H, s, CH_3), 1.47 (3H, s, CH_3), 1.49 (3H, s, CH_3), 1.91−2.18 (4H, m), 2.22−2.49 (2H, m), 2.81−2.88 (1H, m), 3.96 (1H, d, J = 4.47 Hz, C_{2-}H), 4.10 (1H, d, J = 6.48 Hz, C_{2-}H), 4.21 (1H, d, J = 3.84 Hz, C_{5-}H), 4.29 (1H, d, J = 3.84 Hz, C_{5-}H), 5.69 (1H, d, J = 3.84 Hz, C_{4-}H), 5.90 (1H, d, J = 3.84 Hz, C_{4-}H); ^{13}C NMR δ 11.8 (CH_3), 22.7 (CH_2), 26.1 (CH_2), 26.3 (CH_2), 27.05 (CH_3), 27.09 (CH_3), 27.2 (CH_3), 27.3 (CH_3), 30.0 (CH_2), 30.5 (CH_2), 31.8 (CH_2), 31.9 (CH_2), 32.6 (CH_2), 32.8 (CH), 36.6 (CH), 41.5 (CH), 42.1 (CH_2), 44.1 (CH), 43.8 (CH_2), 46.9 (CH), 81.0 (CH), 82.4 (CH), 85.4 (C), 87.9 (CH), 91.9 (CH), 93.3 (C), 105.4 (CH), 105.5 (CH), 112.4 (C), 112.5 (C). Anal. Calcd for $C_{16}H_{26}O_4$: C, 68.06; H, 9.28. Found: C, 68.13; H, 9.20.

***cis*−*syn*−*cis*-4α,5α-Di-*O*-isopropylidine-6α-benzyloxy-10-methyl-3-oxatricyclo[6.6.0.0^{2,6}]tetradeca-9,13-diene 30b.** A solution of the tetraene **26b** (340 mg, 0.89 mmol) in dry hexane (90 mL) was irradiated in the presence of benzophenone (30 mg, 0.18 mmol) for 6 h. The solvent was removed under reduced pressure. Benzophenone was removed by rapid chromatography through a short column of silica using ether−petroleum ether (1:19) as eluent to afford a colorless viscous liquid (230 mg) (R_f 0.54). The mixture was allowed to stand at room temperature for 20 days when a new spot (R_f 0.38) appeared in the TLC. The resulting mixture was purified through preparative TLC to afford the cyclooctadiene derivative **30b** (135 mg) and the unchanged component with R_f (0.54) (80 mg). Heating a solution of this component (80 mg) in toluene (2 mL) in a sealed tube at 200 °C for 24 h followed by purification through preparative TLC afforded a further crop of the cyclooctadiene derivative (40 mg) (total yield 52%). The rest of the material (20 mg) was not characterized further. **30b**: R_f 0.38 [ethyl acetate−petroleum ether (1:9)]; $[\alpha]^{32}_D$ +24.5 (*c* 3.8, $CHCl_3$); ^{1}H NMR δ 1.29 (3H, s, CH_3), 1.52 (3H, s, CH_3), 1.59 (3H, s, CH_3), 1.66−1.80 (1H, m), 1.94 (1H, m), 2.36−2.52 (4H, m), 3.27 (1H, m), 3.41 (1H, m), 4.40 (1H, d, J = 4.0 Hz, C_{2-}H), 4.47 (1H, d, J = 10.8 Hz, PhCH), 4.51 (1H, d, J = 3.8 Hz, C_{5-}H), 4.59 (1H, d, J = 10.8 Hz, PhCH), 4.95 (1H, d, J = 6.1 Hz, C_{9-}H), 5.49−5.58 (1H, m), 5.69 (1H, dd, J = 3.9, 11.1 Hz, C_{14-}H), 5.78 (1H, d, J = 3.7 Hz, C_{9-}H), 7.17−7.33 (5H, m, ArH); ^{13}C NMR δ 25.85 (CH_3), 27.27 (CH_2), 27.38 (CH_3), 27.49 (CH_3), 32.85 (CH_2), 40.18 (CH_2), 41.8 (CH), 47.23 (CH), 67.50 (CH_2), 81.87 (CH), 88.09 (CH), 92.15 (C), 106.29 (CH), 113.24 (C), 127.35 (CH), 127.69 (CH), 127.97 (CH), 128.73 (CH), 129.0 (CH), 129.76 (CH), 136.28 (C), 138.94 (C). Anal. Calcd for $C_{24}H_{30}O_4$: C, 75.36; H, 7.91. Found: C, 75.17; H, 7.81.

Acknowledgment. Financial support from DST, New Delhi, is gratefully acknowledged. S.P.B. thanks CSIR, New Delhi, for a Senior Research Fellowship.

Supporting Information Available: Copies of ^{1}H, ^{13}C, and DEPT NMR spectra of compounds **3a, 4a, 4b, 4c, 5a, 5b, 5c, 6a, 6b, 14, 15, 23a, 23b, 25a, 25b, 30a, 30b, 33,** and **34**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO026920C