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Photoinduced Vinylcyclopropane-Cyclopentene Rearrangement: A Methodology for Chiral Bicyclo[3.2.0]heptenes. Formal Syntheses of (±)-Grandisol and Naturally Occurring (-)-$\Delta^{9(12)}$-Capnellene and its Antipode#

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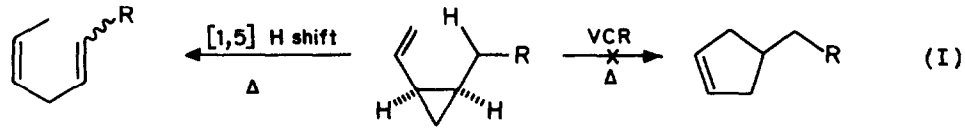
Abstract: The problem of achieving reaction selectivity in cis-alkyl vinylcyclopropanes in favour of their rearrangement to cyclopentenes, obviating the competing low energy process of the [1,5] (homo)sigmatropic hydrogen shift, is addressed. It has been demonstrated that the readily available bicyclo[4.1.0]heptenes derived from (+)-Δ^3-carene (1), upon photosensitized irradiation, are conveniently transformed into chiral cis-bicyclo[3.2.0]heptenes. The synthetic potential of this strategy has been demonstrated in realization of efficient formal syntheses of the important insect sex pheromone (±)-grandisol (2) and both the enantiomers of $\Delta^{9(12)}$-capnellene (3) from readily available 1, a major component of Indian turpentine oil.

INTRODUCTION

Among the three fundamental types of bond reorganizations in vinyl cyclopropanes,[1] viz. (i) cis-trans isomerization, (ii) ring opening to pentadienes and (iii) ring enlargement leading to cyclopentenes, the latter has received much attention owing to its versatility. An extensive investigation[2] of this rearrangement reaction has resulted in the development of numerous methodologies for realizing functionalized cyclopentenes. Moreover, the ready accessibility of vinylcyclopropanes and their presence as structural units of several natural products, have triggered considerable efforts in utilizing this reaction in organic synthesis.[2]

Despite the widespread demonstrations of the synthetic potential of vinylcyclopropane-cyclopentene rearrangements (VCR), its application, especially in the case of cis-alkyl vinylcyclopropanes is severely constrained by the competing [1,5] (homo)sigmatropic hydrogen shift (eqn. I), a considerably lower energy process[3] (~35 Kcal/mole; VCR, ~ 50Kcal/mole).[4] In this paper, we describe a photochemical method[5] to solve this problem. This strategy not only obviated the occurrence of the sigmatropic shift but led to a convenient and efficient methodology for the synthesis of chiral bicyclo[3.2.0]heptenes from Δ^2-carene derivatives which are readily



(I)

accessible from (+)-Δ^3-carene (1). The utility of this photochemical VCR methodology is demonstrated by the formal syntheses of the insect sex pheromone (±)-grandisol[6] (2) and both the enantiomers of the marine natural product $\Delta^{9(12)}$-capnellene (3).[7]

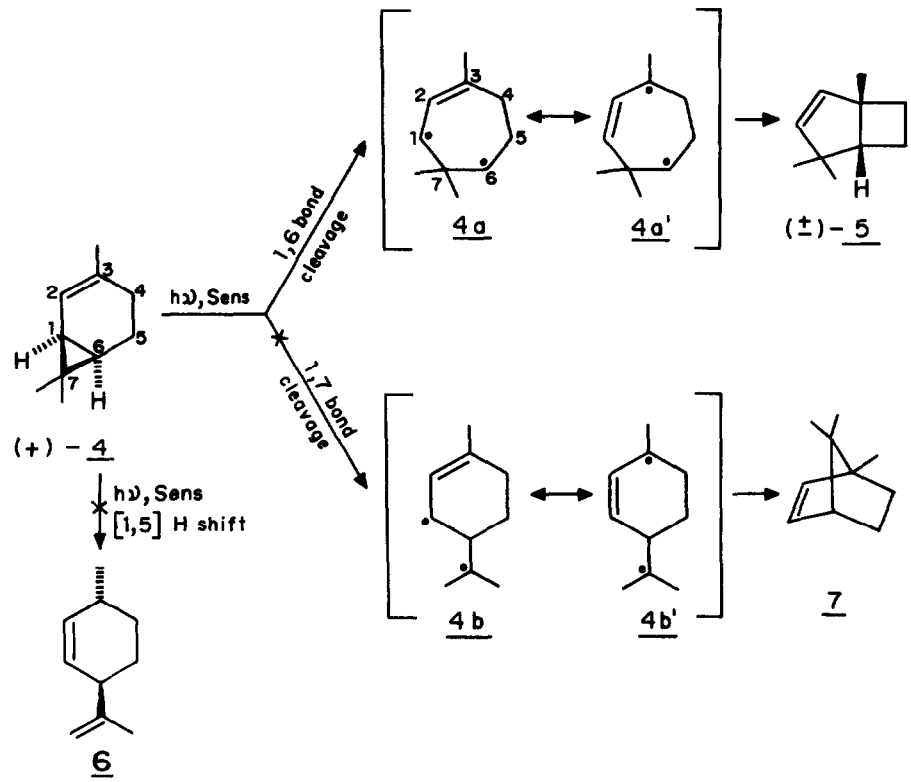
cis-Bicyclo[3.2.0]heptenes: These bicyclic carbon frameworks derive their synthetic importance from their potential to generate a wide array of functionalized four, five and seven-membered ring compounds by fragmentation of different C-C bonds.[8] Some modifications requisite for fragmentation can be effected with a high degree of stereoselectivity due to the envelope-like shape of the cis-fused system thereby dictating the approach of the reagent from the exo face. Thus, by virtue of these structural features, cis-fused bicyclo[3.2.0]heptenes have emerged as versatile synthons in organic synthesis, exemplified by the synthesis of prostaglandin intermediates.[8]

RESULTS AND DISCUSSION

During our study aimed at the transformation of(+)-Δ^2-carene (4) into useful products, we envisaged to subject it to the VCR reaction. The problem of [1,5] sigmatropic hydrogen shift in 4 was imminent and had to be solved. Although this problem in general was addressed earlier elsewhere, a satisfactory solution was not yet realized. For example, Hudlicky and Koszyk[9] showed that from the methyl vinylcyclopropane, viz. 6β-ethenyl-1- p-methylbicyclo[3.1.0]hexan-2-one, under flash pyrolytic conditions at higher temperatures (600°C), especially under $PbCO_3$ conditioned Vycor column, essentially VCR products could be obtained; in the absence of such stringent experimental conditions, however, products from both the types of reactions were realized in varying proportions. Thus, the goal of achieving the reaction selectivity especially in favour of VCR still remained to be accomplished.

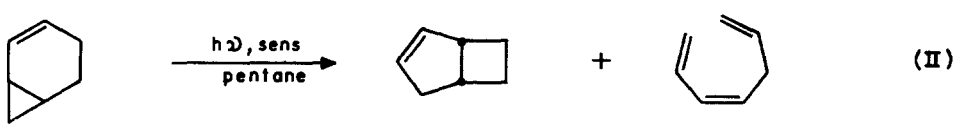
As the photo-VCR[10] appeared attractive, the photoreaction of 4 was checked. To our satisfaction, we found[6] that toluene sensitized irradiation of (+)-4 afforded (±)-5 in a 60% yield; the product 6 arising by the [1,5] sigmatropic hydrogen shift was conspicuously absent (Scheme I). The cleavage of the cyclopropane 1,7-bond in the rearrangement was ruled out as it would lead to norbornylene 7 which was not detected. The relative cis-geometry of the ring junctions was assumed[11],as the trans-fused bicyclo[3.2.0] heptene system would be highly strained, although such a geometry is known in the corresponding saturated system. It is noteworthy that the bicyclic product 5 arising from optically active pure 4 was racemic.

SCHEME-I



Despite extensive investigations, there is still no definite agreement on the question of concerted [1,3] sigmatropic migration versus biradical nature of the reaction. In this context, the mechanistic study by Leigh and Srinivasan[12], of the sensitized photolysis of 2-norcarene (8) which led to a mixture of two products, 9 and 10 needs to be mentioned (eqn. II).

Although a radical mechanism was suggested for the formation of both the products it was not conclusively proved. The present study in which the optically pure (+)-4 afforded the racemic product 5 clearly demonstrates the intermediacy of the biradical 4a' (Scheme I);this was further corroborated by the reduced rotation of the recovered starting material.



8 9 10 (II)

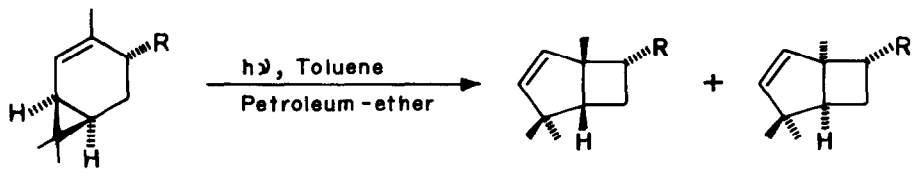
This result suggested the need of introducing an optical handle in the parent molecule so that this methodology might lead to the asymmetric synthesis of these bicycloheptene systems.

We therefore, prepared a number of 4α-substituted Δ^2-carene derivatives (**11a-g**) and subjected them to toluene sensitized photolysis[5a]. These were smoothly transformed into 7-substituted bicyclo[3.2.0]heptenes (**12a-g** and **13a-g**) in excellent yields and with significant diastereoselectivity (Table I). It was also found that the diastereomeric distribution of the products was largely governed by the nature of the 4α-substituent in **11**. Moreover, the fact that the substituents at C-7 in the products can be readily interconverted by simple chemical operations, offers a convenient route to the desired diastereomer.Thus, the photoreaction not only offered a solution to the problem of the competing [1,5] sigmatropic hydrogen shift, but resulted in a convenient methodology for the synthesis of optically active cis-fused bicycloheptenes.

(±)-Grandisol (2). Constituting the most important component of male Boll Weevil sex pheromone[13],**2** has been the subject of many synthetic investigations.[14] A careful examination of the bicyclic product **5** obtained from the photolysis of **4** reveals that it possesses the essential structural features of **2**; being a structural isomer of the monoterpene **4**, all ten carbon atoms required for **2** are present. The cyclobutane ring with the methyl and hydrogen in a 1,2-relationship with the correct cis stereochemistry; the availability of the geminally dimethyl substituted carbon atom adjacent to the ring junction with its potential for transformation into an isopropylidene group; the presence of the olefinic group for the required functional group manipulations; these features make the selection of the further sequence of reactions obvious (Scheme II). Treatment of **5** with B_2H_6 followed by alkaline H_2O_2, however, led to an alcoholic mixture comprising the 2-ol **16** as a major component as confirmed by its oxidation to the known 2-one[15] **18**. This result could be ascribed to the steric hindrance by the gem-dimethyl group in **5** for the boron addition at the C-3 carbon. However, this problem was circumvented when the epoxidation of **5** furnished a product mixture of predominantly the exo epoxide **14b** along with the minor endo-isomer **14a** (70:30). The mixture of secondary alcohols **15** and **16**, obtained by the LAH reduction of the epoxides, when subjected to oxidation with PCC in CH_2Cl_2 furnished the corresponding ketones **17** and **18** in a 7:3 ratio. Preparative GLC of the ketone mixture comprising predominantly of the 3-one **17** enabled its isolation in the pure form. As the ketone **17** has already been converted[16] to **2**, the present synthesis of **17** constitutes a formal synthesis of **2**. The significant feature of this synthesis is the construction of the cyclobutane ring by utilizing the VCR of the endocyclic vinylcyclopropane present in **4** in lieu of the generally employed [2+2] photocycloaddition of ethylene to enones.[14] This also constitutes an example of a transformation of an inexpensive and readily available natural product into a high value product. The methodology also has the distinct potential to deliver the synthesis of optically active **2**, starting from **12f** or **13f**, with suitable chemical transformations.

TABLE-I

PRODUCTS FROM PHOTOLYSIS OF VINYLCYCLOPROPANES 11a-g



11a-g 12a-g 13a-g

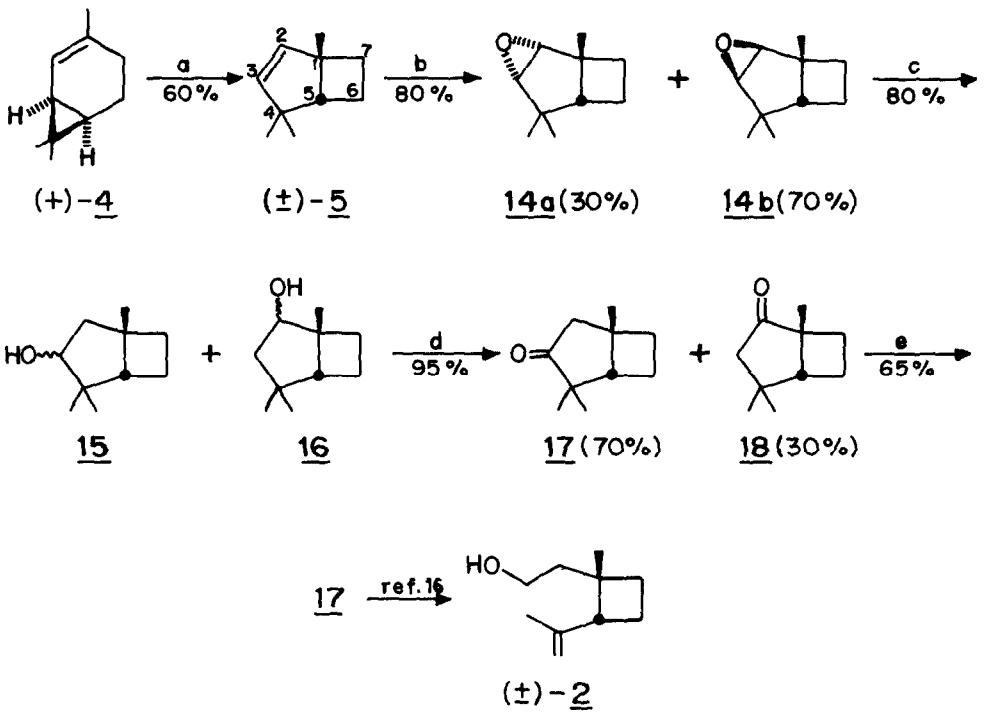
Substrate		Time, h	Conversion[i] %	Yield[ii] %	Product Distribution[i] %	
No.	R				12a-g	13a-g
11a	$COCH_3$[iii]	25	60	90	45	55
11b	CH(OH)CH_3 threo	25	77	80	60	40
11c	CH(OH)CH_3 erythro	18	86	80	20	80
11d	CH_2OCOCH_3	18	93	75	20	80
11e	$COOCH_3$	25	77	60	16	84
11f	OH	23	94	60	30	70
11g	$OCOCH_3$	15	97	91	65	35

(i) Determined by GLC

(ii) Overall isolated yields of distilled products

(iii) Acetone is used as solvent/sensitizer

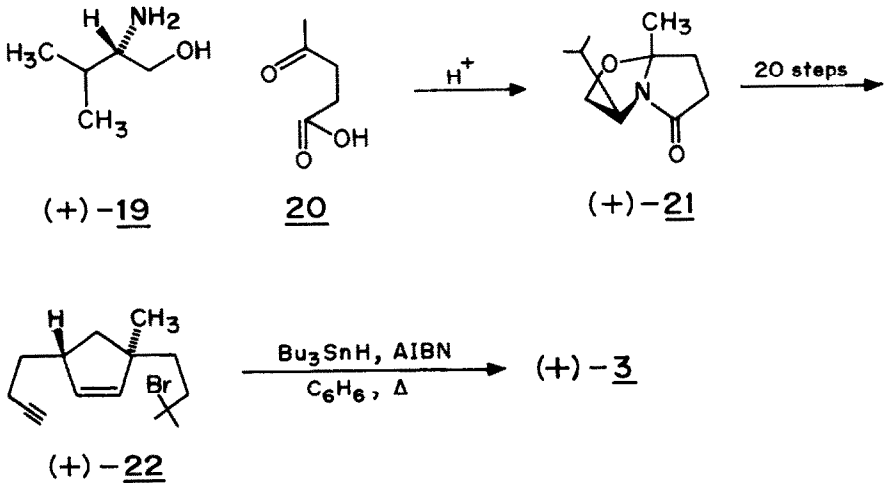
SCHEME-II



(a) hν, Toluene, Petroleum-ether ; (b) mCPBA, CH_2Cl_2 ; (c) $LiAlH_4$, ether ; (d) PCC, CH_2Cl_2 ; (e) SiO_2, Chromatography

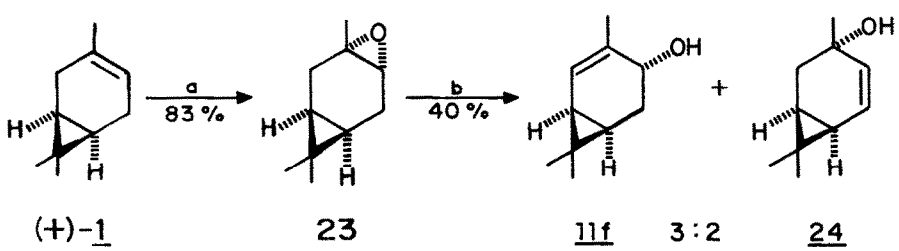
(-)-$\Delta^{9(12)}$-Capnellene (3) and its antipode. The marine natural product (-)-3 isolated[17] from the soft coral capnella imbricata is believed to be a biosynthetic precursor[18] to the capnellene family of sesquiterpenes, which seemingly possess biological properties against algae and microbial growth[19] and to prevent larval settlement[20]. This biological activity[21] and the synthetic challenge afforded by the cis-transoid-cis-tricyclco[6.3.0.$0^{2,6}$]undecane skeletal framework of capnellenes have triggered considerable synthetic efforts and capnellene has repeatedly served as a target molecule to check the efficacies of the cyclopentane annulation methodologies[22]. Although there are numerous syntheses of racemic[23] 3, the only asymmetric total synthesis of the unnatural isomer of (-)-3 has been reported recently by Meyers and Bienz[24] (Scheme III). This synthesis rests essentially on the utilization of the optically pure bicyclic lactam (+)-21 prepared from (S)-(+)-valinol (19) and levulinic acid (20) and Curran's tandem radical cyclization methodology[25]. Our success in utilization of the photo VCR in cyclopentane annulation and synthesis of (±)-2 encouraged us to employ this reaction for the synthesis of (-)- and (+)-3.

SCHEME-III



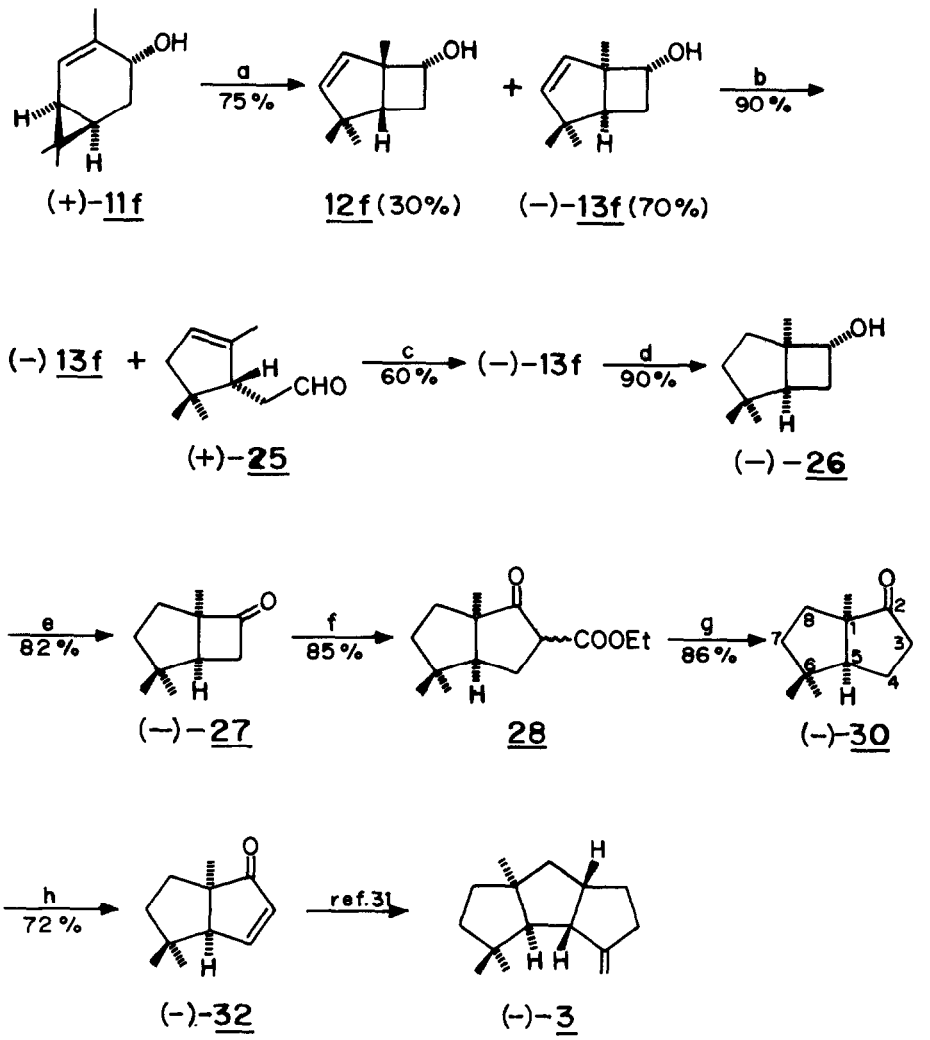
The epoxidation[26] of **1** (Scheme IV) with mCPBA readily furnished the α-epoxide (+)-**23** which on treatment with KO^{t}Bu in pyridine yielded the allylic alcohols (+)-**11f** and (-)-**24** in a 3:2 ratio.[27] The required secondary alcohol (+)-**11f** could be separated by a spinning band fractionation. Toluene-sensitized photolysis of (+)-**11f** gave a mixture of diastereoisomeric bicyclic olefinic alcohols **12f** and **13f** (3:7). An interesting phenomenon observed during the GLC analysis, i.e., the appearance of a new peak at the expense of the peak corresponding to the minor compound, prompted us to suspect a thermal rearrangement. An examination of the structural and stereochemical features (eqn.III) of the endo-isomer **12f** revealed that it was set for a [1,5] hydrogen sigmatropic shift[28].

SCHEME-IV

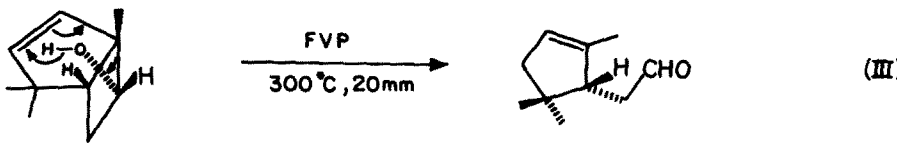


(a) mCPBA, $CHCl_3$ (b) KO ^{t}Bu, Pyridine, Δ

SCHEME-V



(a) hν, Toluene, Petroleum-ether ; (b) F.V.P., 300° C, 20 mm.;
(c) Column (SiO_2) Chromatography ; (d) H_2, 10% Pd/C, EtOH ;
(e) $(COCl)_2$, DMSO ; (f) $N_2CHCOOEt$, $SbCl_5$; (g) aq. DMSO, NaCl, Δ ;
(h) $PdCl_2$, $Pd(OAc)_2$, 40% aq. dioxane, O_2, Δ



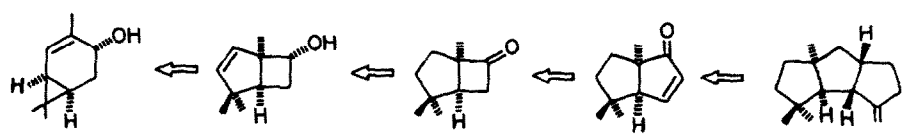
(III)

12f 25

Thus, flash vacuum pyrolysis of the mixture of diastereoisomers **12f** and **13f** resulted in the formation of the aldehyde (+)-**25**, while the major exo isomer was recovered unchanged (eqn.III). Chromatographic separation of the aldehyde and the alcohol mixture yielded the desired exo alcohol (-)-**13f**. Based on the IR, ^{1}H NMR and mass spectral characteristics of the aldehyde and the concerted nature of the rearrangement reaction, the aldehyde component was assigned the structure **25**.

The saturated alcohol (-)-**26** obtained on hydrogenation of (-)-**13f** was oxidized to the corresponding ketone (-)-**27** which was subjected to the ring expansion reaction[29a] using ethyl diazoacetate, BF_3-Et_2O. As this reaction offered a 7:3 mixture of the regioisomeric β-keto-esters **28** and **29**, the Greene's modification[29b] using $SbCl_5$ was resorted to, to obtain exclusively the desired β-keto-ester **28**. Decarboxylation[30] of **28** with NaCl/DMSO/H_2O gave ketone (-)-**30**; oxidation[29b] of the latter with Pd(II) readily yielded the enone (-)**32** whose spectral data was identical with that reported earlier by Piers et al. Keeping in mind the fact of the α-orientation of the C-4 hydroxyl in (+)-**11f**, the noninvolvement of the C-4 carbon in the rearrangement and utilization of the exo-diasteromer (-)-**13f** for the further transformation into naturally occurring (-)-**3**, the absolute configuration of the ring junction is consequently fixed as required (Scheme VI). The synthesis of (-)-**32** constitutes a formal synthesis of the target molecule (-)-**3** as (±)-**32** has been already transformed[31] into (±)-**3**.

SCHEME-VI



(+)-11f (-)-13f (-)-27 (-)-32 (-)-3

(+)-$\Delta^{9(12)}$-Capnellene (Antipode of the Natural Isomer). Sensitized-irradiation of the acetate (**11g**) (Table I), however, resulted in a reversed diastereoselectivity furnishing the endo compound **12g** as a major component (70:30). Repeated HPLC operations of the endo-rich mixture of alcohols **12f** and **13f** obtained by the hydrolysis of the acetates **12g** and

13g afforded the pure endo bicyclic alcohol **12f**. Repetition of the chemical transformations described for (-)-**13f** when carried out on this compound naturally yielded the required antipode of (-)-**32** in good overall yields. This optically pure intermediate should lead to the unnatural isomer of (+)-**3**.

SUMMARY

In summary, the photolysis of **4** and its derivatives resulted in an exclusive reaction selectivity leading to synthesis of useful building blocks, viz., chiral bicyclo[3.2.0]heptenes in good yields. The formal syntheses of (±)**2** and both the enantiomers of **3** illustrate the utility of this methodology.

EXPERIMENTAL

All melting points and boiling points are uncorrected. Usual work up refers to extraction of the reaction mixture with a suitable organic solvent (3 x 50 mL) (solvent used is specified in the individual experiments), washing the organic layer with water followed by brine and drying over anhydrous Na_2SO_4. It also includes concentration of the organic layer under reduced pressure, subjecting the residue to flash column chromatography on silica gel (ethyl acetate-petroleum ether), and bulb to bulb distillation of the product under reduced pressure. The boiling point in each case refers to the oil bath temperature. IR spectra were recorded as smears or nujol mulls (in case of solid samples) on a Perkin-Elmer Infracord model 137-E. Only significant V_{max} are reported and are expressed in reciprocal centimeters (cm^{-1}). Proton Magnetic Resonance spectra (^1H NMR) were recorded on a Varian FT-80A, Bruker FT-90 or Bruker MSL-300 instrument. Carbon Magnetic Resonance spectra (^{13}C NMR) were recorded on a Bruker MSL-300 instrument. All spectra were taken in $CDCl_3$ and chemical shifts are reported in parts per million (ppm) downfield from TMS. Mass spectra were recorded on a CEC mass spectrometer model 21-110B, using an ionization potential of 70 eV. The most abundant ions with their relative intensities have been mentioned. GLC: Analytical GLC of the starting materials and reaction products were carried out on a Hewlett Packard Gas Chromatograph, model 5793, with the following columns: Column A: FFAP (5%, 6' x 1/8", Aluminum column. Column B: OV-101, (5%, 6' x 1/8", Aluminum column). Nitrogen was used as carrier gas with FID detector. Preparative separations have been carried out on A-350-B Aerograph model employing column C: Carbowax (30%, 11.8'x 0.4" aluminum column packed on Chromosorb W 30-60 mesh). Hydrogen was used as carrier gas with TCD detector. Optical rotations were recorded on a JASCO digital polarimeter (model DIP 181).

U.V. Lamps: Irradiations were performed using either 200 Watt (lamp A), 450 watt (lamp B) Hanovia medium pressure mercury lamps or Rayonet RPR 208 photoreactor fitted with 254nm lamps.

Purification of solvents : Petroleum ether (boiling range 60-80°C), which was generally used as a solvent in photolysis was purified by wash-

ing with concentrated H_2SO_4 repeatedly. It was then successively washed with water, 5% aq. Na_2CO_3, brine and dried over $CaCl_2$. The fraction boiling in the range of 60-80° was collected and kept over sodium wire. Petroleum ether (40-60°) used in the photolysis of **4** was similarly purified. Toluene and benzene were treated with concentrated sulfuric acid to remove traces of methyl thiophene and thiophene impurities and processed as above. CH_2Cl_2 was distilled over P_2O_5 and stored over molecular sieves (4A°). THF was freshly distilled over sodium-benzophenone ketyl. DMSO was distilled over CaH_2 and stored over molecular sieves (4A°).

Materials: $PdCl_2$ and BF_3:Et_2O were procured from Aldrich Chemical Co. $Pd(OAc)_2$ was prepared using a known procedure. $SbCl_5$ was purchased from Fluka Chemie AG. $(COCl)_2$ (Fluka make) was freshly distilled before use. Similarly, (+)-**4** was freshly distilled over sodium, b.p. 166-170°, $[\alpha]_D^{25}$ + 96° (neat), [lit.[32] $[\alpha]_D$ +97.7 (neat)]. UV: λmax (CH_3OH) 210nm (ϵ 5450). For ^1H NMR see ref.33

General procedure for irradiation: The photolyses were carried out by employing a Hanovia high pressure mercury lamp placed in a ACE double-walled, water cooled, quartz immersion well. This was fitted in a pyrex reaction vessel equipped with a magnetic bar, condenser and a nitrogen inlet. Generally, a 1-2% solution of the compound in petroleum ether containing about 3% of toluene was used for irradiations. A minute steady flow of oxygen-free N_2 was bubbled through the reaction mixture during irradiation. The progress of the reaction was monitored by GLC analysis of aliquots drawn periodically. After about 62-90% conversions, the solvent was stripped off from the reaction mixture and the residue distilled under reduced pressure.

Methodology for <u>cis</u>-bicyclo[3.2.0]heptenes (Table - I).

(+)-4α-Acetyl-carene (11a). The preparation and photolysis of this compound to give **12a** and **13a** has been reported earlier.[5b]

Photolysis of (+)-4α-[1'(R)-hydroxyethyl]-2-carene[34] (**11b**) carried out according to the general procedure gave two products **12b** and **13b** which, however, could not be separated.

7-<u>endo</u>-(1'(R)-Hydroxyethyl)-1,4,4-Trimethyl-<u>cis</u>-bicyclo[3.3.0]hept-2-ene (12b) and its exo isomer (13b). IR: 3365, 1630. ^1H NMR: 0.98(s,3H), 1.00(s,3H), 1.09(s,3H), 1.16(s,3H), 1.18(s,3H), 1.40(s,3H), 3.99(m,2H), 5.40(m,4H). GC-MS: **12b**, m/z 190(M^+,3), 135(5), 121(4), 119(5), 108(91), 94(12), 93(100), 91(10). **13b**, m/z 190(M^+,2), 147(3), 135(2), 121(4), 119(3), 108(100), 93(43), 91(10).

PCC oxidation of the mixture of **12b** and **13b**. To a suspension of PCC (559 mg, 2.6 mmol) and NaOAc (33 mg, 0.4 mmol) in CH_2Cl_2 (10 mL), was added a mixture of alcohols **12b** and **13b** (234 mg, 1.3 mmol), in CH_2Cl_2 (2 mL), while stirring at room temperature. The reaction mixture was stirred for 1 h and usual workup afforded a mixture of ketones (213 mg, 92%) **12a** and **13a** which were separated by column chromatography. Identification of the products was confirmed by comparison with reported spectral data[5b].

Photolysis of (+)-4α-[1'(S)-hydroxyethyl]-2-carene (11c). This compound was prepared[34] and photolysed to give **12c** and **13c** which were sepa-

rated by preparative chromatography using column C.

(-)-7-endo-(1'(S)-Hydroxyethyl)-1,4,4-Trimethyl-cis-bicyclo[3.2.0] hept-2-ene (12c). bp 105-107°C/2mm. $[\alpha]_D^{25}$ -81° (c 0.74 in $CHCl_3$). IR: 3571, 1610. ^1H NMR: 0.94(s,3H), 0.96(s,3H), 1.22 (s,3H), 1.08(d,J=6Hz,3H), 3.75-4.18(m,1H), 5.38(q,J=4Hz,2H).m/z 180(M^+,2), 136(4), 119(5), 109(15), 108(100), 107(16), 93(58), 91(14). Anal. Calcd. for $C_{12}H_{20}O$: C,79.94; H,11.18. Found: C,79.89; H,11.15.

(+)-7-exo-(1'(S)-Hydroxyethyl)-1,4,4-Trimethyl-cis-bicyclo[3.2.0] hept-2-ene (13c) bp 100-103°C/2mm. $[\alpha]_D^{25}$ +75° (c 1.5 in $CHCl_3$. IR: 3367, 1630. ^1H NMR:0.94(s,6H), 1.00(d,J=6Hz,3H), 1.26(s,3H), 3.46-3.79(m,1H), 5.46(s,2H). m/z 180(M^+,1), 136(4), 122(6), 119(5), 108(100), 107(13), 93(56), 78(8). Anal. Calcd. for $C_{12}H_{20}O$: C,79.94; H,11.18. Found: C,79.81; H,11.01.

Oxidation of the alcohols **12c** and **13c** with PCC gave the known ketones **12a** and **13a**.

Photolysis of (+)-4α-acetoxymethyl-2-carene[35] (**11d**) gave a mixture of two products which were separated by preparative GLC.

(+)-7-endo-Acetoxymethyl-1,4,4-Trimethyl-cis-bicyclo[3.2.0]hept-2-ene (12d). $[\alpha]_D^{25}$ + 89° (c 1.68 in $CHCl_3$). IR: 1745, 1640. ^1H NMR: 0.96(s,6H), 1.20(s,3H), 2.0(s,3H), 3.94(d,J=5Hz,2H), 5.40(q,J=4Hz,?H). m/z 208 (M^+,2), 148(6), 133(9), 108(100), 107(17), 105(32), 93(94), 91(32), 77(21). Anal. Calcd. for $C_{13}H_{20}O_2$: C,74.96; H,9.68. Found: C,75.10; H,9.69.

(-)-7-exo-Acetoxymethyl-1,4,4-Trimethyl-cis-bicyclo[3.2.0]hept-2-ene (13d). $[\alpha]_D^{25}$ - 78° (c 1.11 in $CHCl_3$). IR: 1740, 1645. ^1H NMR: 0.91(s,3H), 0.93(s,3H), 1.03(s,3H), 1.98(s,3H), 3.96-4.28(m,2H), 5.32(s,2H). m/z 208(M^+,4), 193(4), 178(5), 148(50), 133(42), 119(24), 108(100), 105(60), 93(80). Anal. Calcd. for $C_{13}H_{20}O_2$: C,74.96; H,9.68. Found: C,75.16; H,9.54.

Alkaline hydrolysis of **12d** and **13d**. To a 10% ethanolic solution of KOH (10 mL) was added the mixture of **12d** and **13d** (208 mg, 1 mmol) and the reaction mixture was stirred overnight. Usual workup afforded a product (158 mg, 94%), bp 120-125°C, which displayed spectral data identical with that of the known[11] endo alcohol **12**, (R = CH_2OH). A similar hydrolysis of the exo-acetate **13d** afforded the known[11] alcohol **13**, (R = CH_2OH).

Photolysis of (+)-4α-carbomethoxy-2-carene[36] (**11e**) gave a mixture of two products **12e** and **13e** which, however, could not be separated by preparative GLC.

7-endo-Carbomethoxy-1,4,4-Trimethyl-cis-bicyclo[3.2.0]hept-2-ene (12e) and its exo isomer (13e). IR: 1740, 1620. ^1H NMR: 0.94(s,3H), 0.97 (s,3H), 1.00(s,3H), 1.07(s,3H), 1.31(s,3H), 2.70-2.85 (m,2H), 3.59-3.64 (2s,3H each), 5.24-5.46(m,4H). m/z 194(M^+,12), 179(8), 163(4), 137(22), 119(41), 108(20), 93(100), 87(23), 79(31).

LAH reduction of the mixture of esters **12e** and **13e**. Treatment of the mixture of alcohols (194 mg, 1 mmol) with LAH (190 mg, 5 mmol) in ether under dry conditions followed by a standard workup afforded a mixture of the two known[11] alcohols (**12** and **13**, R = CH_2OH).

Synthesis of (±)-Grandisol (2) (Scheme - II).

1,4,4-Trimethyl-cis-bicyclo[3.2.0]hept-2-ene (5): Photolysis of **4**: A solution of **4**, $[\alpha]_D^{25}$ + 10.2° (c 0.60 in $CHCl_3$), (4.08 g, 30 mmol) in

petroleum ether (40-60°C range, 500 mL) containing toluene (3.1 mL) was irradiated with lamp B using a Vycor filter. The reaction was monitored by GLC and was continued until 93% conversion (50 h) had occurred. The solvent was slowly distilled out using a Vigreux fractionating column and the residue was distilled, bp 130-140°C (3.04 g). The product **5** was purified by preparative GLC. IR: 1600 cm^{-1}. ^1H NMR: 0.94(s,3H), 0.97 (s,3H), 1.16(s,3H), 1.56-1.87(m,4H), 1.8-2.1 (m,1H), 5.38(s,2H). m/z 136(M^+,16), 121(45), 108(64), 107(19), 105(12), 93(100), 91(32), 77(16). Anal. Calcd. for $C_{10}H_{16}$: C,88.16; H,11.84. Found: C,87.96; H,11.83.

Unreacted **4** was separated by preparative GLC its specific rotation was found to have decreased. $[\alpha]_D^{25}$ + 6.3° (c 0 6 in $CHCl_3$).

Hydroboration of the bicyclic olefin 5: To a solution of **5** (406 mg, 3 mmol) in anhydrous THF (10 mL) was added a 1 M solution of B_2H_6 in THF (3.0 mL) in a dropwise manner, at 0°C, maintaining an atmosphere of N_2. The reaction mixture was stirred for 21 h at room temperature and after cooling the reaction mixture to about 0°C, 3N aq. NaOH (5 mL) was added followed by 30% H_2O_2 (5 mL). The resulting solution was neutralized with 15% HCl, saturated with NaCl and thoroughly extracted with ether (3 x 20 mL). A standard workup gave a colorless product (370 mg, 80%). GLC showed it to consist of two components **15**(30%) and **16**(70%). IR: 3378. ^1H NMR: 0.84(s, 6H, signal of high intensity), 1.19(s,3H signal of high intensity), 0.78, 0.98 and 1.15 (3s, 3H each, signals of low intensity), 3.55-4.29 (m, 2H). m/z 154(M^+,57), 139(96), 136(81), 126(100), 121(87), 111(77), 96(54), 84(41).

PCC oxidation of the mixture of 15 and 16: To a suspension of PCC (860 mg, 4 mmol) and NaOAc (54 mg, 0.6 mmol) in dry CH_2Cl_2 (10 mL) was added, while stirring at room temperature, the mixture of alcohols **15** and **16** (309 mg, 2.0 mmol) in CH_2Cl_2 (3 mL). The reaction mixture was stirred for 1 h and worked up as usual to obtain a product, bp 132-140°C/25 mm (288 mg, 95%). GLC showed it to comprise two components **17** (32%) and **18** (68%). IR: 1740. ^1H NMR: 0.91, 1.04 and 1.23 (3s, 3H each, signals with high intensity). 0.96, 0.99 and 1.33 (3s, 3H each, signals with low intensity. m/z 152 (M^+).

Epoxidation of the bicyclic olefin 5: A solution of mCPBA (1.03 g, 6 mmol) in $CHCl_3$ (10 mL) was slowly added at room temperature to a stirred solution of **5** (546 mg, 4 mmol) taken in $CHCl_3$ (5mL). Stirring was continued till the disappearance of **5**, (TLC) (3 h); the reaction mixture, after a standard workup, afforded a product (511 mg, 80%) whose GLC showed it to comprise of two components, **14a** (30%) and **14b** (70%). IR: 3003, 2976, 2874, 1470, 1455, 1400, 1360,1265, 1100, 1020, 890, 840, 760 cm^{-1}. ^1H NMR: 0.80, 0.96 and 1.07 (3 s,3 H each, signals of high intensity); 1.00 and 1.18 (2 s,9H, signals of low intensity) and 2.80-3.16 (m,4H).

Treatment of epoxide mixture with LAH: The mixture of **14a** and **14b** (455 mg, 3 mmol) taken in dry THF (3 mL) was added to a well-stirred slurry of LAH (570 mg, 15 mmol) in THF (10 mL) maintaining an atmosphere of N_2. The reaction mixture was heated under reflux and the reaction monitored by GLC. When the starting material had been consumed (16 h) the reaction mixture was worked up in a standard manner to get the product (392 mg, 80%). GLC showed it to comprise of two components **15**(70%) and **16**

(31%). H NMR: 0.78, 0.98 and 1.15 (3s,3H each, signals of high intensity); 0.74, 0.90 and 1.20 (3s,3H each, signals of low intensity) and 3.64-4.27 (m,2H,). m/z 154(M^+).

Oxidation of the mixture of 15 and 16: The mixture of alcohols was oxidized with PCC as described earlier to obtain a product (95%) comprising two components **17** (70)% and **18** (30%). Preparative GLC afforded the pure compounds, **1,4,4-Trimethyl-cis-bicyclo[3.2.0]heptan-3-one**[16] (**17**) and **1,4,4-Trimethyl-cis-bicyclo[3.2.0]heptan-2-one**[15] (**18**). The IR and ^{1}H NMR spectral data of **17** and **18** were in agreement with those reported[15].

Synthesis of (-)-$\Delta^{9(12)}$-Capnellene (3) (Schemes IV and V).

3α,4α-Epoxy-carane (23): Prepared according to the known procedure[26]. bp 80-81°C/13mm. [lit.[26] 92-93°C/23mm]. $[\alpha]_D^{25}$ +12.5° (c 1.25, $CHCl_3$). ^{1}H NMR.[26]

Base Catalyzed opening of the epoxide[23] **(23).** The epoxide was opened using KO^tBu in anhydrous pyridine to yield a mixture of secondary and tertiary alcohols **11f** and **24** respectively. Fractional distillation of the mixture using a spinning band column afforded the two products in pure form. bp 82-83°C/7mm and 92-95°C/6m.

24: $[\alpha]_D^{25}$ -288 (c 5.46, C_6H_6), [lit.[27] -289 (c 3.6 in C_6H_6). IR and ^{1}H NMR.[27]

11f: $[\alpha]_D$ +191(c 5.1, C_6H_6), [lit.[27] + 203.8(c 3.2 in C_6H_6)]. UV: λ_{max} (CH_3OH): 210nm (ε 5554). IR and ^{1}H NMR.[27].

Photolysis of (+)-4α-Hydroxy-2-carene (11f): A solution of **11f** (2.5 g, 16.5 mmol) in pet. ether (60-80°, 1000 mL) containing toluene (25 mL) was thoroughly degassed by oxygen free N_2 and distributed equally among quartz tubes (45 cms x 3 cm). The stoppered tubes were housed in a Rayonet photoreactor (RPR 208) fitted with 254 nm lamps. Irradiation was carried out till almost total consumption of **11f** (> 90%) as checked by GLC (40h). The reaction mixture from all the tubes was pooled, filtered and concentrated. The material obtained after the distillation of the solvent and toluene, was distilled under diminished pressure to yield a colorless oil b.p. 115-120°/6 mm; yield 2 g (80%); GLC showed it to comprise two components **12f** and **13f** in 3:7 ratio. Passage of the mixture through a SiO_2 column, eluting with 20:1 pet.ether:Et_2O, refined the material, furnishing the products (1.87g,75%). IR: 3357, 1610. GC-MS: (minor component of lower RT) m/z 152(M^+,1), 137(5),123(6), 119(8), 108(100), 95(9), 93(78), 77(12) and (major component of higher RT): m/z 152(M^+,1), 137(2), 123(2), 108(100), 94(25), 93(95), 79(8), 77(14).

Pyrolysis of the mixture of homoallylic alcohols 12f and 13f: The flash vacuum pyrolysis unit employed consisted of a quartz column (35 cm X 1 cm) packed with fine pieces of quartz and was electrically heated by a nichrome winding. A fine temperature control could be realized by the use of a dimmerstat and the temperature inside the reactor was measured using a chromium-aluminum thermocouple. The mixture of alcohols **12f** and **13f** (3.04 g, 20 mmol) was vaporized into the system maintained at about 300°C under a vacuum of 5-8 mm. The product of pyrolysis was collected in a flask housed in a liquid N_2/acetone bath. Yield (2.95g, quantitative). The GLC showed two components which were separated by column chromatography on SiO_2. Initial elutions with 5% ether-petether brought forth the aldehyde

25, followed by the unchanged exo alcohol **13f. 2-(2,5,5-trimethyl-2-cyclopentyl)-ethanal, (25)** (730 mg, 24%), b.p. 115-120°C/5 mm $[\alpha]_D^{25}$ + 39° (c 1.20 in $CHCl_3$). IR: 1730, 1660cm^{-1}. ^1H NMR: 0.84(s,3H), 1.02 (s, 3H), 1.58(s,3H), 2.00(m,2H), 2.20-2.35(m,3H),5.24(bs,1H) and 9.80(ill-resolved t,1H each). m/z 152(M^+,6), 137(6), 108(100), 95(70), 93(84), 91(73), 81(89), 79(59), 77(61). Anal. Calcd. for $C_{10}H_{16}O$; C,78.89; H,10.59%; Found; C, 78.78; H, 10.59.

(-)-1,4,4-Trimethyl-cis-bicyclo[3.2.0]hept-2-en-7-ol (13f) bp 115-120°C/6mm. Yield 1.823 g, 60%. $[\alpha]_D^{25}$ - 62° (c 0.90 in $CHCl_3$). IR: 3357, 1610 cm^-. ^1H NMR: 0.98(s,6H), 1.14(s,3H), 1.67-2.32(m,4H), 3.90 (m,1H), 5.39(s,2H). Anal. Calcd. for $C_{10}H_{16}O$: C,78.89; H,10.59%. Found: C,78.73; H, 10.61.

(-)-1,4,4-Trimethyl-cis-bicyclo[3.2.0]heptan-7-ol (26). A solution of **13f** (1 g, 6.58 mmol) in EtOH (50 mL), Pd/C (100 mg) and a few drops of glacial AcOH were placed in a pressure bottle. Hydrogenation at 50-60 psi at room temperature was conducted in a Parr Hydrogenation unit (12 h). The reaction mixture was filtered, concentrated and the usual workup followed by distillation under reduced pressure yielded the product **26** as a pale yellow oil (912 mg, 90%). bp 90°C/1.5mm. $[\alpha]_D^{25}$ -44.8° (c 0.48 in hexane). IR: 3350 cm^{-1}. ^1H NMR (300MHz): 0.88(s,3H), 0.92 (s,3H), 1.2(s,3H), 1.3-1.5(m,3H), 1.65-1.80(m,2H), 1.90-2.15(m,1H), 2.2-2.3(m,1H), 2.41 (br.s, 1H), 3.84(t,J=10Hz,1H). Anal. Calcd. for $C_{10}H_{18}O$: C,77.86; H,11.76. Found: C,77.52; H,11.61.

(-)-(1R)-1,4,4-Trimethyl-cis-bicyclo[3.2.0]heptan-7-one[37] (27). Freshly distilled $(COCl)_2$ (750 mg, 6.25 mmol) and CH_2Cl_2 (25 mL) were taken in a dry three-necked flask equipped with a N_2 inlet, $CaCl_2$ guard tube and a dropping funnel. The reaction mixture was stirred and cooled to -50°-60°C; then DMSO (975 mg, 12.5 mmol) in CH_2Cl_2 (10 mL) was introduced over a period of five min. After stirring the mixture for 10 min **26** (770 mg, 5 mmol) in CH_2Cl_2 (10 mL) was added in a dropwise manner (10 min) keeping the temperature at -50°C. After a lapse of 20 min, Et_3N (3 mL, 21 mmol) was introduced and the stirring continued for about 15-20 min. The reaction flask was allowed to warm to 20°C (70 min), water (50 mL) was added and the layers were separated. A normal workup afforded a crude product which on passage through a short column of silica gel and elution with 5% ether:pet-ether furnished a colourless homogeneous material, bp 75°C/1.5mm (623 mg, 82%). $[\alpha]_D^{25}$ -172.6° (c 1.02 in hexane). IR: 1780. ^1H NMR (300 MHz): 1.03(s,3H), 1.05(s,3H), 1.28(s,3H), 1.48-1.72(m,3H), 1.88-2.16(m,2H), 2.6(dd,J= 12 and 3.5Hz,1H), 2.94(dd, J= 12 and 6 Hz, 1H). m/z 152(M^+,5), 137(10), 124(67), 110(20), 95(100), 91(8), 81(13), 77(8), 69(16). Anal. Calcd. for $C_{10}H_{16}O$: C,78.89; H,10.59. Found: C,79.10; H,10.42.

(-)-(1R)-1,6,6-Trimethyl-cis-bicyclo[3.3.0]octan-2-one (30). A similar experimental setup described above was used except that the dropping funnel was replaced by a septum. A solution of **27** (400 mg, 2.63 mmol) in CH_2Cl_2 (2 mL) taken in the flask was cooled to -78°C (dry ice/acetone cooling bath) and $SbCl_5$ (171 μL, 401 mg, 1.34 mmol) was introduced with a syringe. After 10 min of stirring, $N_2CHCOOEt$ (626 mg, 5.3 mmol) in CH_2Cl_2 (10 mL) was slowly added (15 min). After stirring the reaction mixture at

-78°C for 3 h it was allowed to warm to 0°C. A standard workup furnished the β-keto ester (**28**) as a pale yellow oil (533 mg, 85%).

A stirred mixture of the keto ester (357 mg, 1.5 mmol), DMSO (10 mL), water (0.1 mL) and NaCl (175 mg, 3 mmol) was heated in an oil bath (150-150°C) for 6h. On completion of the reaction (TLC), the reaction mixture was cooled to room temperature and poured into water. A usual workup furnished a homogeneous product, (214 mg, 86%). bp 88-90°C/1-1.5 mm. $[\alpha]_D^{25}$ - 112.5° (c 0.59 in hexane). ^{13}C NMR (300MHz): 20.70(t), 23.52(q), 25.19(q), 29.40q), 35.05(t), 37.69(t), 40.26(t), 42.44(s), 56.46(s), 58.63(d), 225.37(s). m/z 166(M^+,42), 151(82), 133(25), 123(48), 109(100), 95(43). Anal. Calcd. for $C_{11}H_{18}O$: C,79.46; H,10.92. Found: C,79.22; H,10.86. ^1H NMR, and IR.[31]

(1R)-1,6,6-Trimethyl-cis-bicyclo[3.3.0]octan-3-one (31). Ring expansion reaction of **27** with $N_2CHCOOEt$ and BF_3:Et_2O afforded a mixture of regio β-keto-esters **28** and **29** which further were transformed to the regioisomeric cyclopentanones **30** and **31**; column chromatography afforded pure **31**. IR: 1750. ^1H NMR: 0.83 (s,3H), 1.02(s,3H), 1.21(s,3H), 1.53-1.71 (m,2H), 1.77-1.93(m,1H), 2.11-2.40(m,4H). ^{13}C NMR (300MHz): 24.17 (q), 30.19(q), 30.33(q), 39.51(t), 39.77(t), 41.02(t), 41.61(s), 46.71(s), 52.78(t), 57.25(d), 220.31(s). m/z 166(M^+,88), 151(100), 137(11), 133 (23), 123(26), 109(7). Anal. Calcd. for $C_{11}H_{18}O$: C,79.46; H,10.92. Found: C,79.58; H,11.09.

(-)-(1R)-1,6,6-Trimethyl-cis-bicyclo[3.3.0]oct-3-en-2-one (32). A mixture of **30** (199 mg, 1.2 mmol), $PdCl_2$ 292 mg, 1.64 mmol), $Pd(OAc)_2$ (292 mg, 1.32 mmol) and 40% aq.dioxane (50 mL) was taken in a two-necked flask equipped with a gas inlet and a reflux condenser. A slow stream of O_2 was maintained through the reaction mixture which was refluxed at 100-105°C (15 h). Ice cold water was circulated in the condenser to prevent the loss of **30**. Ascertaining the completion of the reaction (GLC), the reaction mixture was cooled and diluted with water. A normal workup afforded the enone **32** as a colorless oil, bp 91-93°C/1-1.5 mm, (142 mg, 72%). $[\alpha]_D^{25}$ -191° (c 0.565 in hexane). ^{13}C NMR (300MHz): 23.50(q), 25.86(q), 28.71(q), 34.61(t), 38.42(t), 41.00(s), 54.55(s), 64.63(d), 132.98(d), 164.94(d), 214.23(s). m/z 164 (M^+,63), 149(54), 131(15), 121(23), 109(63), 96(100), 79(52), 69(82). Anal. Calcd. for $C_{11}H_{16}O$: C,78.89; H,10.59. Found: C,78.63; H,10.42. IR and ^1H NMR.[31]

Synthesis of (+)-$\Delta^{9(12)}$-Capnellene (3).

(+)-4α-Acetoxy-2-carene (11g). The acetate **11g** was prepared by treating **11f** with Ac_2O and pyridine at 0°C, warming to room temperature followed by a standard workup. bp 100-110/10 mm. $[\alpha]_D^{25}$ +151° (c 1.82). UV: λ_{max} (CH_3OH) 209 nm (ε 7760). IR: 1745, 1680 cm^{-1}. ^1H NMR: 0.85(s,3H), 0.90-1.02(m,2H), 1.08(s,3H), 1.68(s,3H), 1.80-1.99(m,2H), 2.02(s,3H), 4.93 (t,J=5Hz,1H), 5.76(br.s,1H). m/z 194(M^+,4), 150(7), 134(48), 120(31), 119(100), 99(24), 94(34), 93(50), 91(64).

Photolysis of (+)-4α-Acetoxy-2-carene (11g). Irradiation of **11g** under similar conditions described earlier for **11f** for 8-10 h furnished a 70:30 mixture of **12g** and **13g**. IR: 1740, 1610. ^1H NMR: 0.95 and (signals for $6CH_3$), 4.54-4.85(m,2H), 5.29-5.58(m,4H).

Hydrolysis of the Mixture of 12g and 13g. To a 10% ethanolic solution

of KOH (3 mL) was added, the mixture of **12g** and **13g** (58 mg, 0.3 mmol) and the reaction mixture stirred overnight (12h). The product was obtained after usual workup, (39 mg, 85%). bp 115-120°C/6 mm. The GLC of the product showed two components in a 30:70 ratio. The ^{1}H NMR spectrum of the above product was almost identical with that of the total photoproduct obtained from **11f**, except that the signals differed in their intensities suggesting a reversed composition. HPLC operations enabled the isolation of pure **12f** which was converted to the enone (+)-**32** by repetition of the same sequence of reactions described above for conversion of **13f** into (-)-**32**.((+)-**32**: $[\alpha]_D^{25}$ + 189 (c 0.565 in hexane); other spectral data identical to that of (-)-**32**).

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