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A Short Enantiospecific Route to Isodaucane Sesquiterpenes from Limonene. On the Absolute Configuration of (+)-Aphanamol I and II

Thomas Hansson and Börje Wickberg*

Organic Chemistry 2, Lund Institute of Technology, P.O.B. 124, S-221 00 Lund, Sweden

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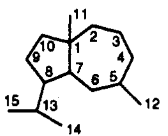
The isodaucane sesquiterpenes (+)-aphanamol I (**3**) and (−)-2-oxoisodauc-5-en-12-al [(−)-**6**] have been prepared in a short reaction sequence from 5(*S*)-isopropyl-2-methyl-1-cyclopentene-1-carbaldehyde (*S*)-**23** (readily obtainable from (+)-limonene). Key steps were a de Mayo type photocyclization of an 3-acyloxy-2-cyclopenten-1-one with 3(S)-isopropyl-1-methylcyclopentene [(*S*)-**24**] to a $[5.3.0.0^{2,6}]$tricyclodecanone (e.g., (−)-**28**) with the desired configuration at all stereocenters and the formation of **3** by a base-catalyzed fragmentation of the γ,δ-epoxyalcohol intermediate **33** (R = H), which produced all the desired functional groups in one step. The stereochemical assignments were supported by CD data as well as by the synthesis of (−)-norbourbonone (**29**) from (*S*)-**24**, which is a novel chiral intermediate. These results are in confliction with some earlier assignments of the absolute configuration in the isodaucane group of sesquiterpenes.

Introduction

Seven hydroazulene sesquiterpenes of the isodaucane (**1**) group[1] have been found in nature. (−)-Mintsulfide (**2**), a constitutent of peppermint oil, was the first to be isolated, and is the only one with its absolute configuration rigorously established by X-ray crystal analysis.[2] The minor toxic principles (+)-aphanamol I (**3**) and II (**5**) have been isolated from the fruits of the timber tree *Aphanamixis grandifolia*,[3] 2-oxoisodauc-5-en-12-al (**6**) occurs together with **5** in the Paraguayan medicinal plant *Chromolaena laevigata*[1a] and has also been found in a *Neomiranda* sp.,[4] while **5** is present together with its 7,8-epimer **7** in *Critonia quadrangularis*[5] and **3**, **5**, and **6** have been reported as constituents of *Senecio crassiflorus*.[6] Quite recently, the isonitrile **8** and the isothiocyanate **9** were isolated from the marine sponge *Acanthella acuta*.[7] The 2,6-epoxide analogue of mintsulfide and isodauc-5(12)-en-2-one have been isolated from clary sage oil (a steam distillate of *Salvia sclarea*).[8] Periplanone A, a pheromone component of the American cockroach *Periplaneta mericana*, was initially assigned an isodaucane carbon skeleton but was later shown to be a germacrane derivative.[9] The relative configurations of all the natural isodaucanes have been established, all except **7** showing a cis relationship between the methyl group, isopropyl group and the H-7 angular proton.

It has been suggested that the α-cadinol derived aldehyde **10** could be a biosynthetic precursor to the isodaucane **6** as well as to other sesquiterpenes from *C. laevigata*.[1a] Biomimetic transformations of (−)-germacrene D and (±)-epoxygermacrene D led to products with an isodaucane carbon framework; in this way (−)-mintsulfide (**2**) and (±)-aphanamol II (**5**) have been prepared.[2,10] Recently, as a part of a general synthetic study of terpenes containing the 1-isopropyl-3-methylcyclopentane unit, Mehta et al. developed an enantioselective synthesis of the aphanamol I enantiomer **11** (via 2-oxoisodauc-5-en-12-al **6**) in 14 steps from the cyclopentene aldehyde (*S*)-**23**,[11] which is readily obtainable in four steps from (+)-(*R*)-limonene (**22**).[12] On the basis of this study, naturally occurring (+)-aphanamol I and II were assigned the absolute configuration indicated in formulae **11** and **12**.



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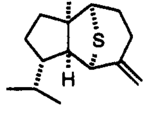

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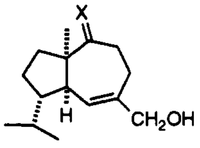
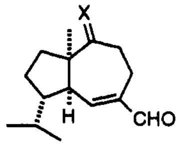
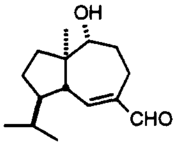


3 X = O
4 X = α-H, β-OH



5 X = α-OH, β-H
(-)-**6** X = O



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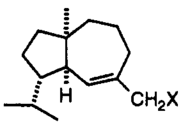
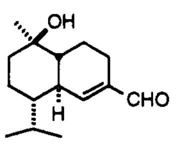


8 X = NC
9 X = NCS



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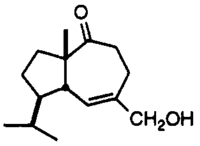
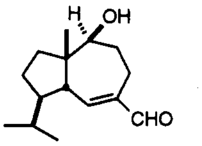


11



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Results and Discussion

A retrosynthetic scheme for the synthesis of isodaucane-type sesquiterpenes is shown in Scheme I. The strategy depends upon a deMayo-type sequence[13] which

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(1) (a) Misra, L. N.; Jakupovic, J.; Bohlmann, F.; Schmeda-Hirschmann, G. *Tetrahedron* **1985**, *41*, 5353. (b) Somewhat earlier, the synonymous name "salvialane" was suggested for isodaucane.[7] For numbering, see also ref 10.

(2) Yoshida, T.; Muraki, S.; Takahashi, T.; Kato, K.; Kabuto, C.; Suzuki, T.; Uyehara, T.; Ohnuma, T. *J. Chem. Soc. Chem. Commun.* **1979**, 512.

(3) Nishizawa, M.; Inoue, A.; Hayashi, Y.; Sastrapradja, S.; Kosela, S.; Iwashita, T. *J. Org. Chem.* **1984**, *49*, 3660.

(4) Jakupovic, J., private communication.

(5) Jakupovic, J.; Castro, V.; Bohlmann, F. *Phytochemistry* **1987**, *26*, 451.

(6) Jares, E. A.; Pomilio, A. B. *J. High Resolut. Chromatogr.* **1989**, *12*, 565.

(7) Mayol, L.; Piccialli, V.; Sica, D. *Tetrahedron* **1987**, *43*, 5381.

(8) Maurer, B.; Hauser, A. *Helv. Chim. Acta* **1983**, *66*, 2223.

(9) (a) Kuwahara, S.; Mori, K. *Tetrahedron* **1990**, *46*, 8083. (b) Hauptmann, H.; Mühlbauer, G.; Sass, H. *Tetrehedron Lett.* **1986**, *27*, 6189.

(10) Shizuri, Y.; Yamaguchi, S.; Terada, Y.; Yamamura, S. *Tetrahedron Lett.* **1986**, *27*, 57.

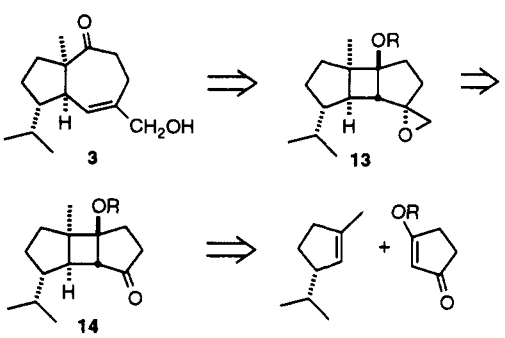
(11) (a) Mehta, G.; Krishnamurthy, N.; Karra, S. R. *J. Chem. Soc., Chem. Commun.* **1989**, 1299. (b) Mehta, G.; Krishnamurthy, N.; Karra, S. R. *J. Am. Chem. Soc.* **1991**, *113*, 5765.

(12) (a) van Tamelen, E. E.; Milne, G. M.; Suffness, M. I.; Rudler Chauvin, M. C.; Anderson, R. J.; Achini, R. S. *J. Am. Chem. Soc.* **1970**, *92*, 7202. (b) Lange, G. L.; Neidert, E. E.; Orrom, W. J.; Wallace, D. J. *Can. J. Chem.* **1978**, *56*, 1628.

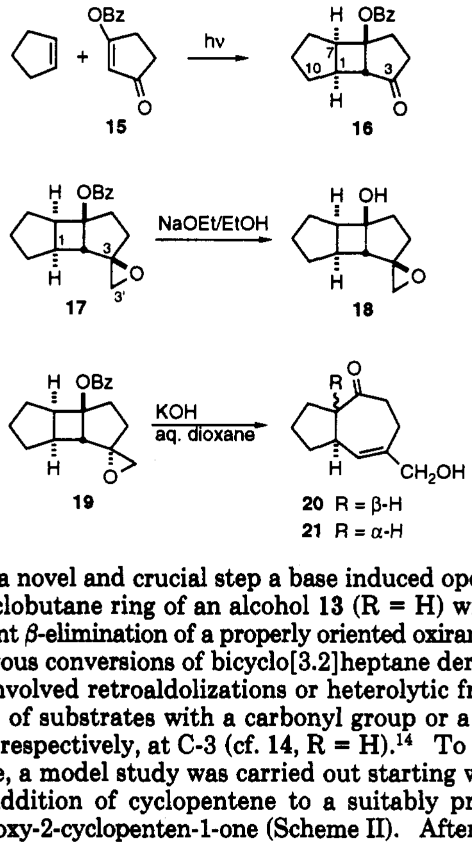
(13) Ho, T.-L. *Carbocycle Construction in Terpene Synthesis*; VCH Publishers: New York, 1988; pp 655–660.

0022-3263/92/1957-5370$03.00/0

Scheme I. Retrosynthetic Plan for Aphanamol I Synthesis



Scheme II. Model Study



has as a novel and crucial step a base induced opening of the cyclobutane ring of an alcohol **13** (R = H) with concomitant β-elimination of a properly oriented oxirane bond. Analogous conversions of bicyclo[3.2]heptane derivatives have involved retroaldolizations or heterolytic fragmentations of substrates with a carbonyl group or a leaving group, respectively, at C-3 (cf. **14**, R = H).[14] To test the scheme, a model study was carried out starting with the photoaddition of cyclopentene to a suitably protected 3-hydroxy-2-cyclopenten-1-one (Scheme II). After several protective groups had been tried, the benzoate **15** was chosen since it is easily prepared from 1,3-cyclopentanedione, it gives a good yield in the photoaddition with cyclopentene, and it should be stable enough to allow freedom of choice of reagents for further transformations of the tricyclic photoadduct **16**. Thus, irradiation of **15** in an excess of cyclopentene using a medium-pressure mercury lamp through a Pyrex filter gave the cis, anti, cis photoadduct **16** in 69% yield. For mechanistic reasons we assumed that in order to achieve a smooth formation of a cycloheptene ring, the epoxide oxygen had to be oriented trans to the benzoyloxy group as in **19** and that the diastereomeric exo- and endo epoxides **17** and **19** would therefore undergo fission of the cyclobutane ring with different rates.

Reaction of **16** with dimethyloxosulfonium methylide[15] in THF led to the epoxides **17** and **19** in 14% and 47% yields, respectively. When instead dimethylsulfonium methylide was used for epoxide synthesis, the endo epoxide **19** was obtained in 42% yield, and now no formation of exo epoxide **17** was seen. Such stereochemical differences between the sulfonium and the oxosulfonium methylides in the addition to ketones have been observed earlier.[16] The exo epoxide **17** was prepared by first reacting the ketone **16** with methylenetriphenylphosphorane. The tricyclic exomethylene derivative thus obtained was treated with *m*-chloroperbenzoic acid (*m*-CPBA) to give **17** in a modest overall yield from **16**. The stereochemical assignments of the epoxides were made on the reasonable assumption that the steric hindrance for addition to the carbonyl group of the cis, anti, cis photoadduct **16** should preferentially give an endo epoxide in reactions with sulfur ylides, but lead to exo product when the Wittig–*m*-CPBA methodology was used.

When the exo epoxide **17** was debenzoylated in ethanolic ethoxide solution, the epoxide alcohol **18** was not unexpectedly the main product with no signs of cleavage of the cyclobutane ring. Saponification of **19** with KOH in water–dioxane, on the other hand, was accompanied by cleavage of the cyclobutane and oxirane rings to give a 3:1 mixture of the diastereomeric hydroazulenes **20** and **21** in moderate yield. The assignment of trans structure **20** to the major isomer could not be made from NMR data alone and rests primarily on the known preference for trans fusion in this type of hydroazulenes.[14b] It is well-known that the basic conditions normally required for the hydrolysis of protective ester groups in deMayo reactions will promote epimerizations if hydrogen is present in an α-position to the newly formed carbonyl group.[14] This particular problem may be overcome by the use of silyl protected enols in the photocyclization reaction and subsequent deprotection with fluoride ion.[14b,17] But apart from the hydrolytic instability of silyl ethers of acidic enols, they also have the drawback of giving significantly increased amounts of undesired cis, syn, cis photoadducts. Exploratory experiments with silyl protective groups substantiated these premonitions.

However, aphanamol I (**3**) cannot epimerize to a trans fused isomer and therefore seemed amenable to the synthetic scheme delineated above. The oxygen functionalization would be correct, and substituting 3-isopropyl-1-methylcyclopentene for cyclopentene, the correct configuration at the stereocenters would be created in the photoaddition owing to steric preference for the enone to approach the cyclopentene ring from the face opposite to the isopropyl substituent. (Such high stereoselectivity was obtained in an analogous (±)-bourbonene (**29**, O = CH_2) synthesis from (*SR*)-**24**.[18]) The use of enantiomerically pure 3-isopropyl-1-methylcyclopentene should also allow control of the absolute configuration. On the other hand, photoadditions of enones to unsymmetrical alkenes lacking polar substituents generally show low regioselectivity and often give a 1:1 ratio between "head to head" and "head to tail" products.[19]

The (*S*)- and (*R*)-enantiomers of cyclopentene **24** were prepared from (+)-(*R*)- and (−)-(*S*)-limonene (**22**),[20] respectively, via the readily available aldehyde **23**[12] and

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[14] (a) Challand, B. D.; Hikino, H.; Kornis, G.; Lange, G.; de Mayo, P. *J. Org. Chem.* **1969**, *34*, 794. (b) Tietze, L.-F.; Reichert, U. *Angew. Chem.* **1980**, *92*, 832.

[15] Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1353.

[16] Trost, B. M.; Melvin, L. S., Jr., *Sulfur Ylides*; Academic Press: New York, 1975; pp 40–42, 56–57.

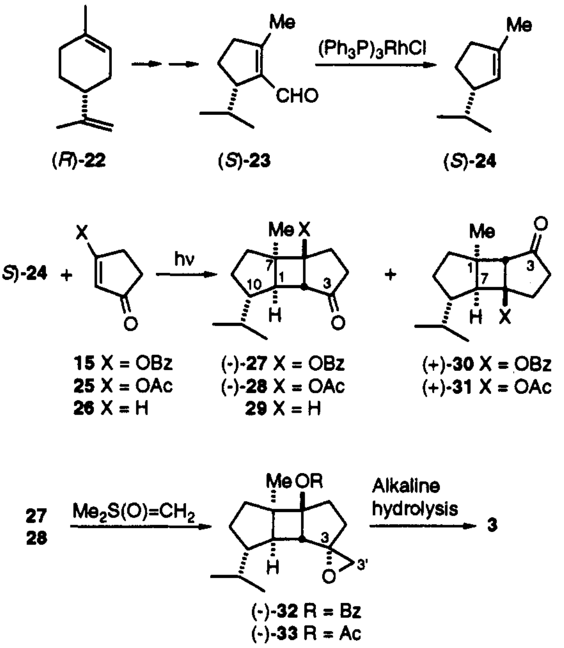
[17] Pak, C. S.; Kim, S. K.; Lee, H. K. *Tetrahedron Lett.* **1991**, *42*, 6011.

[18] White, J. D.; Gupta, D. N. *J. Am. Chem. Soc.* **1968**, *90*, 6171.

[19] For a recent discussion of the cause of the regioselectivity in photoadditions see: Weedon, A. C.; Hastings, D. J. *J. Am. Chem. Soc.* **1991**, *113*, 8525.

[20] (+)-Limonene had $[\alpha]^{20}_{D}$ +120.5° and (−)-limonene $[\alpha]^{20}_{D}$ −95.0° [lit. (+)-limonene $[\alpha]^{20}_{D}$ +126.6° (Pliva, J. Herout, V. *Collect. Trav. Chim. Tchec.* **1950**, *15*, 160)]. Commercially available (−)-limonene is usually of lower enantiomeric purity than the (+)-enantiomer.

Scheme III



decarbonylation of the latter using a stoichiometric quantity of Wilkinson's catalyst in benzonitrile[21] (Scheme III). Attempts to run the decarbonylation of **23** catalytically using chlorobis[1,3-bis(diphenylphosphine)-propane]rhodium were unsuccessful.[22] Small-scale fractional distillation afforded **24** in high chemical yields but with ca. 10–75% of benzonitrile as the only impurity. This was, however, of no consequence in the subsequent photoaddition, where the distillate could be used without further purification and with the benzonitrile serving as an internal GC standard.

Some 81 years ago, Wallach showed that "apofenchene", a degradation product of fenchone, was actually a mixture of **24** with 4-isopropyl-1-methylcyclopentene,[23] which resisted preparative-scale separation even after the advent of GLC.[24] This seems to have been overlooked in two well-known handbooks, in which the optical rotation of the "apofenchene" mixture has erroneously been cited for each individual isomer.[25] This is therefore the first time that the optical rotation of (*S*)-**24** has been established unambiguously.[26] As to be expected, the (*R*)-enantiomer of **24** prepared from (−)-limonene showed a lower optical activity (75–80% ee).

In parallel experiments, (*S*)-**24** was irradiated together with a slight excess of either 3-(benzoyloxy)-2-cyclopenten-1-one (**15**) or 3-acetoxy-2-cyclopenten-1-one (**25**)[14a] in acetonitrile, using a medium-pressure mercury lamp with a Pyrex filter. Both experiments gave rather complex mixtures of isomeric photoadducts, which could only be separated with difficulty by preparative HPLC. Irradiation of (*S*)-**24** together with benzoate **15** afforded the regioisomers (−)-**27** and (+)-**30**, both in 20% yield, while the photoreaction with **25** gave the analogous regioisomers (−)-**28** and (+)-**31** in 23% and 20% yield, respectively. (All fractions were contaminated by ca. 5% of the respective regioisomer.) The structural assignments relied mainly on NMR methods. Most indicative were NOESY experiments, revealing that all four isomers had a cis configuration with respect to the isopropyl group, methyl group, and the H-1 or H-7 angular proton. ^{1}H NMR of **27** and **28** showed a coupling between the angular protons while in **30** and **31** both were singlets. (In both photocyclization experiments a third isomer was isolated in ca. 7% yield, the structure of which could not be readily established.)

Reaction of (−)-**27** and (−)-**28** with dimethyloxosulfonium methylide in THF gave the endo-epoxides (−)-**32** and (−)-**33** in 68% and 50% yields, respectively. In contrast to the analogous experiments with **16**, no diastereomeric exo epoxides were obtained, presumably due to the additional steric hindrance by the methyl and the isopropyl groups. The benzoate was hydrolyzed by refluxing (−)-**32** in methanolic potassium methoxide giving (+)-aphanamol I (**3**) ($[\alpha]_D$ +23°) in 32% yield. NMR spectra were in accordance with published data.[3] The rather harsh conditions required for hydrolysis of the benzoate group also led to a substantial alcoholysis of the oxirane ring. This side reaction was less prominent in the hydrolysis of epoxide (−)-**33** by refluxing with LiOMe in methanol, giving **3** ($[\alpha]_D$ +25.8°) in 70% yield. The analogous synthetic sequence starting with the photoaddition of benzoate **15** to the enantiomerically less pure (*R*)-3-isopropyl-1-methylcyclopentene afforded (−)-aphanamol I (**11**) with $[\alpha]_D$ −22°.

Naturally occurring **3** is reported to have $[\alpha]_D$ +13°.[3] It is, however, not uncommon that natural terpenoids occur as mixtures of enantiomers, and this could explain the higher specific rotation of our preparation of **3**. In line with this, synthetic diol **4** prepared by reduction of **3** with sodium borohydride exhibited $[\alpha]_D$ +40° as compared with $[\alpha]_D$ +21.2° reported for the same compound prepared from naturally occurring **3**.[3] These values would be consistent with an enantiomeric excess of ca. 50% for the latter. On the other hand, we see no obvious explanation why our findings regarding the absolute configuration of **3** are in conflict with the results of Mehta et al., who report $[\alpha]_D$ +10° for their preparation of **11**, the configuration of which should be beyond doubt.[11]

We feel confident about our own structural and stereochemical assignments for the following reasons. Samples of **3**, repeatedly prepared from both benzoate **15** and acetate **25**, have consistently shown the same optical activity within experimental errors and are pure according to NMR analyses. (The estimated lower limit for detection of impurities in the ^{13}C NMR spectra was ca. 3%.) The optical rotation of naturally occurring 2-oxoisodauc-5-en-12-al (**6**) was not reported originally,[1a] but after submitting this paper for publication, we learned that keto aldehyde **6** from a *Neomiranda* sp. had $[\alpha]_D$ −7°.[4] This value compares well with $[\alpha]_D$ −6° observed by us for (−)-**6**, which was obtained in a good yield by perruthenate-catalyzed oxidation[27] of **3**.[28] On the other hand, an enantiomer of **6** with reported $[\alpha]_D$ +33° was the last intermediate in the

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[21] (a) Tsuji, J.; Ohno, K. *Synthesis* **1969**, *157*. (b) The expensive Rh reagent may easily be regenerated from recovered bis(triphenylphosphine)carbonylrhodium chloride: Fries, R. W.; Stille, J. K. *Synth. Inorg. Met.-Org. Chem.* 1971, *1*, 295.

[22] Doughty, D. H.; Pignolet, L. H. *J. Am. Chem. Soc.* **1978**, *100*, 7083.

[23] Wallach, O. *Liebigs Ann. Chem.* **1911**, *379*, 182.

[24] Varech, D.; Ouannes, C.; Jacques, J. *Bull. Soc. Chim. Fr.* **1965**, 1662.

[25] (a) Buckingham, J., Ed. *Dictionary of Organic Compounds*, 5th ed.; Chapman & Hall: New York, 1982; Vol. 3, p 3447. (b) Klyne, W.; Buckingham, J. *Atlas of Stereochemistry*; Chapman & Hall: London, 1974; Vol. 1, p 86.

[26] The specific optical rotation of **24** was calculated with correction for the benzonitrile content as determined by NMR spectra.

[27] (a) Griffith, W. P.; Ley, S. V.; Whitcombe, G. P.; White, A. D. *J. Chem. Soc., Chem. Commun.* **1987**, 1625. (b) Griffith, W. P.; Ley, S. V. *Aldrichim. Acta* **1990**, *23*, 13.

[28] We thank Dr. J. Jakupovic, Technical of Berlin, for kindly providing us with reference spectra of **6** isolated from *C. laevigata* and also for checking them with our spectra of synthetic **6**. The spectra were identical.

synthesis of aphanamol I enantiomer **11** by Mehta et al.[11] The numerical differences between these optical rotations cannot be explained only in terms of enantiomeric differences. Reduction of (−)-**6** with $NaBH_4$–Ce^{3+} resulted in a low yield of **3** ($[\alpha]_D$ +18°) together with the diol **4** ($[\alpha]_D$ +44°).

Our assignments of absolute configurations were corroborated by CD recordings on carefully purified photoadduct (+)-**27**, which exhibited a positive θ value (+740 at 301 nm). This rigid tricyclic ketone is ideally suited for application of the octant rule. CD recordings were also made on (−)-aphanamol I (**11**), $[\theta]_{293}$ −470, but the interpretation is less straightforward here, since the molecule occupies regions giving both positive and negative ellipticity contributions. As a final check, the cyclopentene (*S*)-**24** was converted, essentially following a known procedure for racemic product,[18] into (−)-norbourbonone (**29**) ($[\alpha]_D$ −182°), which is a natural product with established absolute configuration and reported $[\alpha]_D$ values varying from −181° to −213°.[29]

We have thus found a short enantiospecific route to the isodaucanes, in particular **3** in 7% total yield in four steps from **23** and **25**. The internal consistency of our results suggests that the absolute configuration of (+)-aphanamol I and II should be revised as **3** and **5** and that the enantiomer **11** of Mehta et al. consequently represents (−)-aphanamol I.

Experimental Section

NMR spectra were recorded at 300 MHz. Chemical shifts are relative Me_4Si. The CD recordings were made in acetonitrile with a JASCO Model J-500 A spectropolarimeter. The θ values are not corrected for ee $\neq$ 1. Melting points are uncorrected. TLC was performed on Merck Kieselgel $60F_{254}$. Unless stated otherwise, Merck Kieselgel 60 (0.040–0.063 mm) or Grace Amicon Kieselgel 60 (0.035–0.070 mm) were used for preparative liquid chromatography. GC was performed on a 9.7-m RSL-300 polyphenylmethylsiloxane capillary column with N_2 as carrier gas, oven temperature 100 °C. Photochemical reactions were carried out with an internal medium-pressure mercury lamp using a Pyrex filter. Organic solutions were dried over Na_2SO_4. 1,3-Cyclopentanedione was prepared by a published method.[30] 3-Acetoxy-2-cyclopenten-1-one (**25**)[14a] was prepared as described for 3-acetoxy-2-methylcyclopenten-1-one.[31] (+)-(*R*)- and (−)-(*S*)-limonene were purchased from Fluka and distilled to 97.5% purity (GC).[20] The enantiomers of **23** were prepared from limonene in 35% yield.[12]

3-(Benzoyloxy)-2-cyclopenten-1-one (15). Benzoyl chloride (21.2 g, 0.15 mol) was added at 0 °C to a solution of 1,3-cyclopentadione (5.0 g, 51 mmol) and pyridine (19.6 g, 0.25 mol) in CH_2Cl_2 (250 mL). Cooling was interrupted, and more CH_2Cl_2 (200 mL) was added after stirring for 3 h. The reaction mixture was then washed sequentially with 10% aqueous AcOH (200 mL), saturated aqueous $NaHCO_3$ (200 mL), and water (200 mL) and was then then dried and concentrated. Column chromatography (SiO_2, 1:1 EtOAc–heptane) afforded crystalline **15** (9.36 g, 88%); mp 115–116 °C; IR (CCl_4) 1760, 1720, 1600, 1250, 1240, 1230, 1150, 1040, 1020 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.13 (dd, 2 H, *J* = 8.5, 1.3 Hz, *o*-ArH), 7.67 (tt, 1 H, *J* = 7.4, 1.3 Hz, *p*-ArH), 7.55 (dd, 2 H, *J* = 8.1, 7.9 Hz, *m*-ArH), 6.39 (t, 1 H, *J* = 1.6 Hz, H-2), 2.92 (m, 2 H, H_2-4), 2.53 (m, 2 H, H_2-5); ^{13}C NMR ($CDCl_3$) δ 206.7 (s, C-1), 179.9 (s, C-3), 162.2 (s, $PhCO_2$), 134.5 (d, *p*-Ar), 130.6 (s, Ar), 130.4 (d, *o*-Ar), 128.9 (d, *m*-Ar), 116.9 (d, C-2), 33.5 (t, C-5), 28.9 (t, C-4); LRMS *m/z* (relative intensity) (EI) 202 (M^+, 0.4), 122 (2), 105 (100), 84 (7), 77 (48), 69 (6), 51 (17); HRMS *m/z* exact mass calcd for $C_{12}H_{10}O_3$ 202.0630, found 202.0626.

(1*SR*,2*RS*,6*RS*,7*RS*)-6-(Benzoyloxy)tricyclo[5.3.0.0^{2,6}]-3-decanone (16). A solution of cyclopentene (19 g, 0.28 mol) in cyclohexane (100 mL) and diethyl ether (50 mL) was purged with N_2 for 30 min and then irradiated with UV light, while a solution of **15** (1.5 g, 7.4 mmol) dissolved in a mixture of toluene (30 mL), diethyl ether (20 mL), and cyclopentene (9.5 g, 0.14 mol) was added during 30 min. Irradiation was continued for 4 h; the solution was then concentrated on a rotavapor. On standing overnight at 2 °C the residue deposited white crystals. These were washed with cold MeOH giving **16** (0.99 g). Column chromatography (SiO_2, 1:6 EtOAc–heptane) of the concentrated mother liquors gave a further quantity of **16** (0.40 g), providing a total of 1.39 g (69%) of crystalline **16** with mp 116–117 °C: IR (CCl_4) 2960, 2880, 1740, 1720, 1450, 1315, 1290, 1270, 1110, 1100, 1070, 1025 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.00 (dd, 2 H, *J* = 8.4, 1.4 Hz, *o*-ArH), 7.58 (tt, 1 H, *J* = 7.4, 1.4 Hz, *p*-ArH), 7.45 (dd, 2 H, *J* = 7.7, 7.7 Hz, *m*-ArH), 3.05 (dd, 1 H, *J* = 6.6, 6.6 Hz, H-7), 2.71–2.45 (m, 6 H, H-1, H-2, H_2-4, H_2-5), 2.04–1.95 (m, 1 H, H_a-8), 1.89–1.79 (m, 2 H, H_a-9, H_a-10), 1.76–1.53 (m, 3 H, H_b-8, H_b-9, H_b-10); ^{13}C NMR δ 217.6 (s, C-3), 165.5 (s, $PhCO_2$), 133.2 (d, *p*-Ar), 130.1 (s, Ar), 129.5 (d, *o*-Ar), 128.5 (d, *m*-Ar), 80.5 (s, C-6), 55.5 (d, C-1), 49.3 (d, C-7), 38.1 (d, C-2), 37.7 (t, C-4), 35.7 (t, C-5), 33.3 (t, C-10), 28.0 (t, C-8), 25.2 (t, C-9); LRMS *m/z* (relative intensity) (EI) 270 (M^+, 1.4), 203 (11), 105 (100), 91 (3), 77 (28), 67 (4), 51 (5), 41 (3); HRMS *m/z* exact mass calcd for $C_{17}H_{18}O_3$ 270.1256, found 270.1254.

(1*SR*,2*RS*,3*SR*,6*RS*,7*RS*)-Tricyclo[5.3.0.0^{2,6}]decane-3-spiro-2′-oxiran-6-yl Benzoate (17). A suspension of methyltriphenylphosphonium bromide (422 mg, 1.20 mmol) in diethyl ether (5.0 mL) was added to 1.5 M butyllithium in hexane (0.80 mL, 1.20 mmol). After the mixture was stirred for 3 h at rt, **16** (200 mg, 0.74 mmol) was added. The mixture was stirred for 16 h at rt, water (10 mL) was then added, and the organic phase was separated. The aqueous phase was extracted with diethyl ether (2 × 10 mL), and the combined ethereal phases were dried and concentrated to give the 3-exomethylene derivative (63 mg) of good purity. This product was dissolved in CH_2Cl_2 (7.5 mL), and *m*-CPBA (90%, 69 mg, 0.39 mmol) in CH_2Cl_2 (5 mL) was added slowly. The solution was stirred for 2.5 h at rt and then quenched by adding aqueous 10% sodium sulfite solution (15 mL). The mixture was stirred at rt for 30 min, and the organic phase was then separated. The aqueous phase was extracted with CH_2Cl_2 (15 mL), and the combined organic phases were washed sequentially with saturated aqueous $NaHCO_3$ (15 mL) and NaCl solution (15 mL) and then dried and concentrated. Column chromatography (SiO_2, 1:4 EtOAc–heptane) gave **17** (43.5 mg, 21%) as a syrup: IR (CCl_4) 2950, 1720, 1450, 1315, 1300, 1280, 1200, 1110, 1100, 1070, 1025 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.04 (dd, 2 H, *J* = 8.5, 1.4 Hz, *o*-ArH), 7.56 (tt, 1 H, *J* = 7.4, 1.4 Hz, *p*-ArH), 7.43 (m, 2 H, *m*-ArH), 2.97 (dd, 1 H, *J* = 7.1, 7.1 Hz, H-7), 2.88 (1 H, d, *J* = 4.4 Hz, H_a-3′), 2.83 (d, 1 H, *J* = 4.3 Hz, H_b-3′), 2.69–2.41 (m, 2 H, H_2-5), 2.34–2.20 (m, 2 H, H-1, H_a-4), 1.93 (d, 1 H, *J* = 3.8 Hz, H-2), 1.78–1.46 (m, 7 H, H_b-4, H_2-8, H_2-9, H_2-10); ^{13}C NMR δ 165.6 (s, $PhCO_2$), 132.9 (d, *p*-Ar), 130.8 (s, Ar), 129.6 (d, *o*-Ar), 128.4 (d, *m*-Ar), 85.8 (s, C-6), 67.2 (s, C-3), 53.4 (d, C-2), 47.6 (t, C-3′), 46.6 (d, C-7), 37.7 (t, C-4), 36.5 (d, C-1), 33.3, 31.6, 28.8, 25.7 (t, C-5, C-8, C-9, C-10); LRMS *m/z* (relative intensity) (EI) 284 (M^+, 0.2), 283 (0.2), 255 (0.6), 216 (9), 162 (5), 134 (3), 119 (3), 105 (100), 91 (11), 77 (49), 67 (8), 51 (11), 41 (6); HRMS *m/z* exact mass calcd for $C_{18}H_{20}O_3$ 284.1412, found 284.1419.

(1*SR*,2*RS*,3*RS*,6*RS*,7*RS*)-Tricyclo[5.3.0.0^{2,6}]decane-3-spiro-2′-oxiran-6-yl Benzoate (19). A solution of **16** (300 mg, 0.90 mmol) in dry THF (4 mL) was added with stirring at rt to a solution of dimethyloxosulfonium methylide[14] (4.2 mL, 0.4 M in THF, 1.68 mmol). After 2.5 h, 0.3 M aqueous NaCl solution (20 mL) was added and the product was extracted with diethyl ether (3 × 25 mL). The combined organic phases were dried and concentrated, and the residue was purified by chromatography (SiO_2 1:6 EtOAc–heptane) affording **17** (43.1 mg, 14%, lower R_f) and **19** (146.6 mg, 47%, higher R_f) as syrups. For **19**: IR (CCl_4) 2960, 1720, 1600, 1450, 1315, 1300, 1280, 1260, 1200, 1185, 1110, 1095, 1070, 1025 cm^{-1}; ^1H NMR δ 8.02 (dd, 2 H, *J* = 7.1, 1.5 Hz, *o*-ArH), 7.57 (tt, 1 H, *J* = 7.5, 1.2 Hz, *p*-ArH), 7.45 (dd, 2 H, *J* = 7.5, 7.5 Hz, *m*-ArH), 2.98 (d, 1 H, *J* = 5.1 Hz, H_a-3′), 2.94 (d, 1 H, *J* = 4.9 Hz, H_b-3′), 2.97–2.90 (m, 1 H, H-7), 2.58 (dd, 1 H, *J* = 10.0 Hz, 6.1 Hz, H-1), 2.52–2.38 (m, 2 H, H_2-5) 2.31–2.20 (m, 1 H, H_a-4), 2.06 (d, 1 H, *J* = 3.7 Hz, H-2), 1.92–1.51 (m, 7 H, H_b-4, H_2-8, H_2-9, H_2-10); ^{13}C NMR δ 165.4 (s, $PhCO_2$), 133.0 (d, *p*-Ar),

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130.6 (s, Ar), 129.5 (d, *o*-Ar), 128.4 (d, *m*-Ar), 83.9 (s, C-6), 66.0 (s, C-3), 57.1 (t, C-3′), 50.6 (d, C-2), 47.2 (d, C-7), 36.3 (t, C-4), 34.7 (d, C-1), 33.4, 28.6, 25.7 (t, C-8, C-9, C-10), 30.3 (t, C-5); LRMS *m/z* (relative intensity) (EI) 284 (M^+, 2), 255 (5), 216 (100), 187 (17), 179 (8), 162 (57), 147 (8), 132 (27), 119 (20), 106 (82), 91 (36), 77 (52), 67 (23), 51 (20), 41 (13); HRMS *m/z* exact mass calcd for $C_{18}H_{20}O_3$ 284.1412, found 284.1416.

(1*SR*,2*RS*,3*SR*,6*RS*,7*RS*)-Tricyclo[5.3.0.0^{2,6}]decane-3-spiro-2′-oxiran-6-ol (18) by Hydrolysis of 17. A solution of 17 (15 mg, 0.05 mmol) in 0.06 M ethanolic sodium ethoxide (1 mL) was heated at 70 °C for 3 h. After the solution was cooled, water (5 mL) was added and the mixture was extracted with EtOAc (2 × 5 mL). The combined extracts were dried and concentrated, and the residue was subjected to chromatography (SiO_2, 1:1 EtOAc–heptane) to give 18 (5 mg, 50%) as an oil: IR (CCl_4) 3500, 2950, 1720, 1550, 1450, 1430, 1330, 1300, 1280, 1250, 1220, 1200 cm^{-1}; ^{1}H NMR δ 2.82 (d, 1 H, *J* = 4.3 Hz, H_a-3′), 2.76 (d, 1 H, *J* = 4.4 Hz, H_b-3′), 2.59 (dd, 1 H, *J* = 7.2, 7.2 Hz, H-7), 2.43 (ddd, 1 H, *J* = 13.9, 11.7, 8.8 Hz, H_a-5), 2.15 (m, 1 H, H-1) 2.06–1.96 (m, 2 H, H_a-4, H_b-5) 1.89–1.39 (m, 8 H, H_b-4, H_2-8, H_2-9, H_2-10, H-2); ^{13}C NMR δ 78.9 (s, C-6), 68.1 (s, C-3), 56.1 (d, C-2), 47.9 (t, C-3′), 46.6 (d, C-7), 40.5 (t, C-4), 35.3 (d, C-1), 33.0, 31.4, 26.8, 26.0 (t, C-5, C-8, C-9, C-10); LRMS *m/z* (relative intensity) (EI) 180 (M^+, 14), 162 (13), 149 (43), 131 (13), 120 (41), 112 (50), 107 (86), 91 (64), 84 (100), 83 (100), 79 (82), 67 (62), 55 (25), 47 (23), 41 (34); HRMS ($M + NH_4^+$) *m/z* exact mass calcd for $C_{11}H_{20}O_2N$ 198.1494, found 198.1503.

(1*SR*,7*RS*)-5-(Hydroxymethyl)bicyclo[5.3.0]-5-decen-2-one (20) and (1*RS*,7*RS*)-5-(Hydroxymethyl)bicyclo[5.3.0]-5-decen-2-one (21) by Hydrolysis of 19. Aqueous KOH (0.7 M, 1 mL) was added to a solution of 19 (42 mg, 0.15 mmol) in dioxane (2.0 mL). The stirred mixture was heated at 70 °C for 2 h. After the solution was cooled, water (10 mL) was added and the mixture extracted with EtOAc (3 × 10 mL). The combined extracts were dried and concentrated, and the residue was purified by chromatography (SiO_2, 1:1 EtOAc–heptane) affording a ~3:1 mixture (oil, 11 mg, 55%) of C-1 epimeric diastereomers **20** and **21** as estimated by ^{1}H NMR.

Major isomer **20** (lower R_f): IR (CCl_4) 3470, 2960, 2870, 1700, 1450, 1375, 1260, 1100, 1070, 1010, 910 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.89 (br s, 1 H, H-6), 4.08 (d, 2 H, *J* = 3.4 Hz, C*H*$_2$OH), 2.79 (ddd, 1 H, *J* = 11.5, 8.4, 8.4 Hz, H-1), 2.66 (ddd, 1 H, *J* = 14.7, 10.0, 2.2 Hz, H_a-3), 2.50–2.37 (m, 2 H, H-7, H_a-4), 2.27–2.05 (m, 3 H, H_b-3, H_b-4, H_a-10), 1.81–1.44 (m, 5 H, H_2-8, H_2-9, H_b-10); ^{13}C NMR δ 212.2 (s, C-2), 140.4 (s, C-5), 129.8 (d, C-6), 68.1 (t, *C*H$_2$OH), 57.3 (d, C-1), 43.2 (d, C-7), 42.1, 34.5 (t, C-3 and C-4), 25.3, 24.8, 22.9 (t, C-8, C-9, C-10); LRMS *m/z* (relative intensity) (EI) 180 (M^+, 37), 162 (30), 149 (100), 131 (21), 120 (81), 107 (100), 93 (72), 84 (69), 79 (78), 67 (71), 55 (14), 47 (9), 41 (15); HRMS *m/z* exact mass calcd for $C_{11}H_{16}O_2$: 180.1150, found 180.1151.

Minor isomer **21** (higher R_f): IR (neat) 3400, 2940, 2850, 1735, 1700, 1450, 1370, 1240, 1100, 1070, 1040, 1010 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.55 (br s, 1 H, H-6), 4.02 (ddd, 2 H, *J* = 6.1, 1.4, 1.4 Hz, C*H*$_2$OH), 3.38 (ddd, 1 H, *J* = 10.1, 8.0, 5.9 Hz, H_a-3), 3.02 (m, 1 H, H-1), 2.66 (dd, 1 H, *J* = 5.1, 4.2 Hz, H-7), 2.54–2.45 (m, 1 H, H_a-4), 2.25–2.12 (m, 2 H, H_b-3, H_b-4), 1.81–1.30 (6 H, m, H_2-8, H_2-9, H_2-10); ^{13}C NMR δ 211.5 (s, C-2), 140.0 (s, C-5), 129.1 (d, C-6), 67.6 (t, *C*H$_2$OH), 52.3 (d, C-1), 44.4 (d, C-7), 42.1, 33.9 (t, C-3 and C-4), 25.9, 24.2, 24.1 (t, C-8, C-9, C-10); LRMS *m/z* (relative intensity) (EI) 180 (M^+, 27), 162 (19), 149 (59), 131 (41), 120 (51), 107 (100), 931 (53), 86 (100), 84 (100), 79 (67), 67 (52), 55 (17), 47 (71), 41 (18), 35 (26); HRMS *m/z* exact mass calcd for $C_{11}H_{16}O_2$ 180.1150, found 180.1146.

3(*S*)-Isopropyl-1-methylcyclopentene [(*S*)-24]. A mixture of (*S*)-**23**[12] (2.07 g, 13.6 mmol) and tris(triphenylphosphine)rhodium chloride (10.0 g, 10.8 mmol) in benzonitrile (40 mL) was heated at 130 °C for 1.5 h, during which time the dark red solution turned greenish yellow. After being cooled on ice, the solution was decanted from the solid deposit[32] and distilled through a Vigreux column at 75 mmHg. The first fraction, bp 80–90 °C, consisted of (*S*)-**24** (84%) and benzonitrile (16%), and the following fraction (bp 90–100 °C) contained (*S*)-**24** (33%) and benzonitrile (67%) according to NMR analysis. A total of 1.21 g of (*S*)-**24** (90%) contaminated with benzonitrile was obtained: $[\alpha]^{20}_D$ +108° (*c* 0.85, $CHCl_3$);[26] IR (CCl_4) 2950, 2870, 1650, 1470, 1450, 1380, 1360 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.30 (qd, 1 H, *J* = 1.6, 1.6 Hz, H-2), 2.46–2.35 (m, 1 H, H-3), 2.19 (t, 2 H, 7.3 Hz, H_2-5), 2.03–1.91 (m, 1 H, H_a-4), 1.72 (m, 3 H, Me), 1.56–1.40 (m, 2 H, C*H*Me$_2$, H_b-4), 0.88 (d, 3 H, *J* = 6.7 Hz, CH*Me*), 0.84 (d, 3 H, *J* = 6.7 Hz, CH*Me*); ^{13}C NMR δ 140.5 (s, C-1), 127.4 (d, C-2), 53.1 (d, C-3), 36.7 (t, C-5), 33.2 (d, *C*HMe$_2$), 28.3 (t, C-4), 20.6, 20.4 (q, CH*Me*$_2$), 16.7 (q, Me); LRMS *m/z* (relative intensity) (EI) 124 (M^+, 46), 91 (11), 81 (100), 79 (56), 75 (40); HRMS *m/z* exact mass calcd for C_9H_{10} 124.1252, found 124.1252.

3(*R*)-Isopropyl-1-methylcyclopentene [(*R*)-24]. Aldehyde (*R*)-**23** was treated essentially as above to give (*R*)-**24** (contaminated with benzonitrile); $[\alpha]^{20}_D$ −85° (*c* 0.85, $CHCl_3$).[26] NMR spectra were identical with those of the (*S*)-**24** enantiomer.

Photoadditon of (*S*)-24 to Enol Benzoate 15. A solution containing (*S*)-**24** (200 mg, 1.6 mmol), benzonitrile (200 mg), and **15** (640 mg, 3.2 mmol) in acetonitrile (12 mL) was purged with N_2 for 20 min and then irradiated with UV light for 9 h, when more **15** (320 mg, 1.6 mmol) in acetonitrile (3 mL) was added. The irradiation was interrupted after an additional 12 h, when GC analysis showed ca. 70% consumption of the alkene. The solution was concentrated and the residue subjected to chromatography (SiO_2, 1:4 EtOAc–heptane) to give a fraction containing isomeric photoadducts. This was further purified by preparative HPLC (LiChrosorb Si 60, 10 μm, 25-cm × 10.5-mm i.d.; mobile phase EtOAc–heptane (6:94), flow rate 6.0 mL/min; UV detection at 254 nm) affording ca. 95% pure (5% overlap) tricyclic regioisomers (−)-**27** (oil, 82.7 mg, 16%, 23% based on consumed (*S*)-**24**, higher R_f) and (+)-**30** (oil, 84 mg, 16%, 23% based on consumed (*S*)-**24**, lower R_f).

(1*R*,2*R*,6*S*,7*R*,10*S*)-6-(Benzoyloxy)-10-isopropyl-7-methyltricyclo[5.3.0.0^{2,6}]-3-decanone [(−)-27]: $[\alpha]^{20}_D$−99° (*c* 0.60, $CHCl_3$); IR (CCl_4) 2960, 2870, 1740, 1720, 1450, 1320, 1290, 1270, 1110, 1090 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.00 (d, 2 H, *J* = 7.4 Hz, *o*-ArH), 7.57 (t, 1 H, *J* = 7.4 Hz, *p*-ArH), 7.45 (dd, 2 H, *J* = 7.2, 7.2 Hz, *m*-ArH), 2.94 (ddd, 1 H, *J* = 14.1, 8.6, 5.7 Hz, H_a-4), 2.62 (d, 1 H, *J* = 3.6 Hz, H-2), 2.65–2.56 (m, 2 H, H_2-5), 2.19 (ddd, 1 H, *J* = 14.4, 10.1, 10.1 Hz, H_b-4), 2.01–1.80 (m, 2 H, H_a-8, H_a-9), 1.71 (d, 1 H, *J* = 3.6 Hz, H-1), 1.71–1.48 (m, 3 H, H_b-8, H_b-9, H-10), 1.38 (s, 3 H, Me), 1.37 (m, 1 H, *J* = 6.0 Hz, C*H*Me$_2$), 0.89 (3 H, d, *J* = 5.9 Hz, CH*Me*), 0.87 (3 H, d, *J* = 5.9 Hz, CH*Me*); ^{13}C NMR δ 216.6 (s, C-3), 165.6 (s, Ph*C*O$_2$), 133.2 (d, *p*-Ar), 130.1 (s, Ar), 129.5 (d, *o*-Ar), 128.5 (d, *m*-Ar), 83.9 (s, C-6), 56.7 (d, C-1), 56.4 (d, C-2), 51.9 (s, C-7), 48.4 (d, C-10), 37.6 (t, C-5), 35.3 (t, C-8), 31.7 (d, *C*HMe$_2$), 30.3 (t, C-9), 29.8 (t, C-4), 22.6 (q, Me), 21.6 (q, CH*Me*), 21.3 (q, CH*Me*); LRMS *m/z* (relative intensity) (EI) 326 (M^+, 0.7), 283 (0.5), 243 (1.1), 221 (0.6), 203 (23), 161 (1.9), 123 (6.7), 105 (100), 91 (6.7), 77 (32); HRMS *m/z* exact mass calcd for $C_{21}H_{26}O_3$ 326.1882, found 326.1873.

(1*R*,2*S*,6*S*,7*S*,8*S*)-6-(Benzoyloxy)-8-isopropyl-1-methyltricyclo[5.3.0.0^{2,6}]-3-decanone [(+)-30]: $[\alpha]^{20}_D$ +97° (c 2.0, $CHCl_3$); IR (CCl_4) 2960, 2870, 1740, 1720, 1450, 1320, 1290, 1250, 1180, 1110, 1070, 1030 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.00 (d, 2 H, *J* = 7.8 Hz, *o*-ArH), 7.57 (t, 1 H, *J* = 7.3 Hz, *p*-ArH), 7.45 (dd, 2 H, *J* = 7.3, 7.3 Hz, *m*-ArH), 2.90–2.38 (m, 4 H, H_2-4, H_2-5), 2.74 (s, 1 H, H-2), 2.41 (s, 1 H, H-7), 2.04–1.95 (m, 1 H, H-8), 1.90–1.66 (m, 3 H, H_2-9, H_a-10), 1.60 (m, 2 H, H_b-10, C*H*Me$_2$), 1.14 (s, 3 H, Me), 0.96 (3 H, d, *J* = 6.6 Hz, CH*Me*), 0.90 (3 H, d, *J* = 6.6 Hz, CH*Me*); ^{13}C NMR δ 218.3 (s, C-3), 165.6 (s, Ph*C*O$_2$), 133.2 (d, *p*-Ar), 130.3 (s, Ar), 129.5 (d, *o*-Ar), 128.5 (d, *m*-Ar), 79.7 (s, C-6), 60.2 (d, C-7), 59.5 (d, C-2), 48.1 (d, C-8), 44.4 (s, C-1), 41.8 (t, C-10), 39.6, 36.7 (t, C-4, C-5), 31.2 (d, *C*HMe$_2$), 29.0 (t, C-9), 22.1 (q, Me), 21.8 (q, CH*Me*), 20.9 (q, CH*Me*); LRMS *m/z* (relative intensity) (EI) 326 (M^+)(1), 221 (2), 203 (9), 161 (3), 123 (4), 105 (100), 91 (7), 81 (22), 77 (41); HRMS *m/z* exact mass calcd for $C_{21}H_{26}O_3$ 326.1882, found 326.1880.

(1*S*,2*S*,6*R*,7*S*,10*R*)-6-(Benzoyloxy)-10-isopropyl-7-methyltricyclo[5.3.0.0^{2,6}]-3-decanone [(+)-27] was obtained from the photoaddition of (*R*)-**24** to **15** essentially as described for (−)-**27**. For (+)-**27**: $[\alpha]^{20}_D$ +104° (*c* 0.96, $CHCl_3$); CD $[\theta]_{301}$ + 740. The NMR spectra were identical with those of the (−)-**27** enantiomer.

(1*S*,2*R*,6*R*,7*R*,8*R*)-6-(Benzoyloxy)-8-isopropyl-1-methyltricyclo[5.3.0.0^{2,6}]-3-decanone [(−)-30] was obtained together

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[32] After washing with ice-cold diethyl ether, this precipitate gave crystalline bis(triphenylphosphine)rhodiumcarbonyl chloride (5.84 g, 8.4 mmol).

with (+)-**27** from the photoaddition of (*R*)-**24** to **15**. For (−)-**30**: $[\alpha]^{20}_{D}$ − 80° (*c* 1.0, $CHCl_3$). The NMR spectra were identical with those of the (+)-**30** enantiomer.

Photoaddition of (S)-24 to Enol Acetate 25. A solution of (*S*)-**24** (340 mg, 2.7 mmol), benzonitrile (90 mg), and **25** (1.0 g, 7.1 mmol) in acetonitrile (12 mL) was purged with N_2 for 15 min and then irradiated for 5 h, when additional **25** (400 mg, 2.8 mmol) in acetonitrile (2 mL) was added. The irradiation was interrupted after a total of 13 h of irradiation, when GC showed ca. 80% consumption of the alkene. The solution was concentrated and the residue subjected to chromatography (SiO_2, 1:4 EtOAc–heptane) to give a fraction containing isomeric adducts (−)-**28** and (+)-**31**. This was further purified by preparative HPLC (LiChrosorb Si 60, 10 μm, 25-cm × 10.5-mm i.d.; mobile phase EtOAc–heptane (6:94), flow rate 6.0 mL/min; UV detection at 254 nm) affording tricyclic regioisomers (−)-**28** (oil, 129.7 mg. 18%, 23% based on consumed **24**, higher R_f) and (+)-**31** (oil, 93.8 mg, 15%, 20% based on consumed **24**, lower R_f).

(1*R*,2*R*,6*S*,7*R*,10*S*)-6-Acetoxy-10-isopropyl-7-methyltricyclo[5.3.0.0^{2,6}]-3-decanone [(−)-28]: $[\alpha]^{20}_{D}$ − 113° (*c* 0.75, $CHCl_3$); IR (CCl_4) 2960, 2870, 1740, 1470, 1450, 1370, 1250, 1180, 1050 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.82 (ddd, 1 H, *J* = 14.2, 8.6, 5.3 Hz, H_a-4), 2.57–2.49 (m, 2 H, H_2-5), 2.45 (d, 1 H, *J* = 4.4 Hz, H-2), 2.10–1.98 (m, 1 H, H_b-4), 2.04 (s, 3H, *Me*CO$_2$), 1.90–1.78 (m, 2 H, H_a-8, H_a-9), 1.62 (d, 1 H, *J* = 4.6 Hz, H-1), 1.70-1.42 (s, 3 H, H_b-8, H_b-9, H-10), 1.40-1.27 (m, 1 H, C*H*Me$_2$), 1.28 (s, 3 H, Me), 0.87 (6 H, d, *J* = 6.6 Hz, CH*Me*$_2$); ^{13}C NMR δ 219.8 (s, C-3), 170.1 (s, Me*C*O$_2$), 83.4 (s, C-6), 56.7 (d, C-1), 56.3 (d, C-2), 51.7 (s, C-7), 48.3 (d, C-10), 37.5 (t, C-5), 35.2 (t, C-8), 31.8 (d, *C*HMe$_2$), 30.3 (t, C-9), 29.7 (t, C-4), 22.4 (q, Me), 21.6 and 21.3 (q, CH*Me*$_2$), 21.1 (q, *Me*CO$_2$); LRMS *m/z* (relative intensity) (EI) 264 (M$^+$, 1.2) 222 (4), 161 (2), 141 (39), 123 (5), 105 (8), 99 (56), 91 (9), 81 (100), 67 (5), 55 (6), 43 (26); HRMS *m/z* exact mass calcd for $C_{16}H_{24}O_3$ 264.1725, found 264.1720.

(1*R*,2*S*,6*S*,7*S*,8*S*)-6-Acetoxy-8-isopropyl-1-methyltricyclo[5.3.0.0^{2,6}]-3-decanone [(+)-31]: $[\alpha]^{20}_{D}$ +127° (*c* 2.0, $CHCl_3$); IR (CCl_4) 2960, 2870, 1735, 1460, 1450, 1370, 1240, 1200, 1040 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.76–2.59 (m, 1 H, H_a-4), 2.56 (s, 1 H, H-2), 2.52–2.28 (m, 3 H, H_b-4, H_2-5), 2.26 (s, 1 H, H-7), 2.02 (s, 3 H, *Me*CO$_2$), 1.84–1.62 (m, 4 H, H-8, H_2-9, H_a-10), 1.39 (ddq, 1 H, *J* = 6.9, 6.9, 6.9 Hz, C*H*Me$_2$), 1.53–1.44 (m, 1 H, H_b-10), 1.06 (3 H, s, Me), 0.89 (3 H, d, *J* = 6.6 Hz, CH*Me*), 0.85 (3 H, d, *J* = 6.6 Hz, CH*Me*); ^{13}C NMR δ 221.6 (s, C-3), 170.1 (s, Me*C*O$_2$), 79.2 (s, C-6), 59.9 (d, C-7, 59.2 (d, C-2), 47.9 (d, C-8), 44.4 (s, C-1), 41.7 (t, C-10), 39.5 (t, C-4), 36.5 (t, C-5), 31.1 (d, *C*HMe$_2$), 28.8 (t, C-9), 22.0 (q, Me), 21.7 (q, CH*Me*), 21.3 (q, *Me*CO$_2$), 20.8 (q, CH*Me*); LRMS *m/z* (relative intensity) (EI) 264 (M$^+$, 1.6), 222 (7.7), 207 (5.8), 161 (9), 141 (16), 119 (8), 105 (10), 99 (50), 91 (15), 81 (57), 67 (9), 53 (14), 43 (64); HRMS *m/z* exact mass calcd for $C_{16}H_{24}O_3$ 264.1725, found 264.1727.

(1*R*,2*R*,3*R*,6*S*,7*R*,10*S*)-10-Isopropyl-7-methyltricyclo[5.3.0.0^{2,6}]decane-3-spiro-2′-oxiran-6-yl Benzoate [(−)-32]. A solution of (−)-**27** (130 mg, 0.40 mmol) in dry THF (1 mL) was added to THF containing 0.4 M dimethyloxosulfonium methylide[15] (1.75 mL, 0.70 mmol), and the resulting solution was allowed to stir at rt for 3.5 h. The reaction was quenched by addition of aqueous 0.3 M NaCl (20 mL), and the product was extracted with diethyl ether. The organic phase was dried and concentrated and the residue purified by chromatography (SiO_2 1:6 EtOAc–heptane) affording the epoxide (−)-**32** (92 mg, 68%) as an oil; $[\alpha]^{20}_{D}$ −34.0° (*c* 1.0, $CHCl_3$); IR (CCl_4) 2960, 2870, 1720, 1450, 1320, 1280, 1110, 1100, 1070, 1030 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.01 (dd, 2 H, *J* = 7.4, 1.4 Hz, *o*-ArH), 7.56 (tt, 1 H, *J* = 7.4, 1.4 Hz, *p*-ArH), 7.44 (dd, 2 H, *J* = 7.3, 6.0 Hz, *m*-ArH), 2.96 (d, 1 H, *J* = 5.3 Hz, H_a-3′), 2.93 (d, 1 H, *J* = 5.3 Hz, H_b-3′), 2.72 (ddd, 1 H, *J* = 13.5, 12.3, 1.8 Hz, H_a-5), 2.37–2.24 (m, 1 H, H_a-4), 2.13 (d, 1 H, *J* = 4.4 Hz, H-2), 2.01 (ddd, 1 H, *J* = 13.5, 12.3, 8.0 Hz, H_b-5) 1.89–1.75 (m, 4 H, H-1, H_b-4, H_a-8, H_a-9), 1.57–1.25 (m, 4 H, H_b-8, H_b-9, H-10, C*H*Me$_2$), 1.32 (s, 3 H, Me), 0.93 (d, 3 H, *J* = 6.2 Hz, CH*Me*), 0.87 (3 H, d, *J* = 6.3 Hz, CH*Me*); ^{13}C NMR δ 165.6 (s, Ph*C*O$_2$), 132.9 (d, *p*-Ar), 130.6 (s, Ar), 129.5 (d, *o*-Ar), 128.4 (d, *m*-Ar), 86.8 (s, C-6), 65.5 (s, C-3), 57.0 (d, C-10), 56.8 (t, C-3′), 51.5 (d, C-2), 50.4 (s, C-7), 45.3 (d, C-1), 35.4 (t, C-5), 32.0 (d, *C*HMe$_2$), 31.6 (t, C-4), 31.1, 30.4 (t, C-8, C-9), 21.6, 21.5 (q, CH*Me*$_2$) 21.4 (q, Me); LRMS *m/z* (relative intensity) (EI) 340 (M$^+$, 1), 216 (5), 189 (2), 175 (3), 149 (5), 133 (3), 123 (9), 105 (100), 91 (8), 77 (31), 67 (3), 55 (4), 41 (7); HRMS *m/z* exact mass calcd for $C_{22}H_{28}O_3$ 340.2038, found 340.2035.

(1*R*,2*R*,3*S*,6*S*,7*R*,10*S*)-10-Isopropyl-7-methyltricyclo[5.3.0.0^{2,6}]decane-3-spiro-2′-oxiran-6-yl Benzoate [(+)-32]. Compound (+)-**27** was treated essentially as above to give (+)-**32**: $[\alpha]^{20}_{D}$ +30° (*c* 0.48, $CHCl_3$). The NMR spectra were identical with those of the (−)-**32** enantiomer.

(1*R*,2*R*,3*R*,6*S*,7*R*,10*S*)-10-Isopropyl-7-methyltricyclo[5.3.0.0^{2,6}]decane-3-spiro-2′-oxiran-6-yl Acetate [(−)-33]. A solution of (−)-**28** (63 mg, 0.24 mmol) in dry THF (0.6 mL) was added to THF containing 0.4 M dimethyloxosulfonium methylide[15] (1.0 mL, 0.40 mmol) and left stirring at rt for 16 h. The reaction was quenched by the addition of aqueous 0.3 M NaCl (10 mL); workup as described for (−)-**32** yielded the epoxide (−)-**33** as an oil (32.8 mg, 50%); $[\alpha]^{20}_{D}$ − 34.0° (*c* 1.0, $CHCl_3$); IR (CCl_4) 2960, 2870, 1740, 1460, 1370, 1250, 1200, 1180, 1020 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.89 (d, 1 H, *J* = 5.2 Hz, H_a-3′), 2.84 (dd, 1 H, *J* = 5.2, 1.0 Hz, H_b-3′), 2.60 (ddd, 1 H, *J* = 13.3, 7.8, 3.0 Hz, H_a-5), 2.23 (ddd, 1 H, *J* = 12.3, 12.3, 7.9 Hz, H_a-4), 2.02 (s, 3 H, *Me*CO$_2$), 1.94 (d, 1 H, *J* = 4.6 Hz, H-2), 1.90-1.67 (m, 5 H, H-1, H_b-4, H_b-5, H_a-8, H_a-9,), 1.55–1.29 (m, 4 H, H_b-8, H_b-9, H-10, C*H*Me$_2$), 1.22 (s, 3 H, Me), 0.91 (d, 3 H, *J* = 6.2 Hz, CH*Me*), 0.86 (3 H, d, *J* = 6.3 Hz, CH*Me*); ^{13}C NMR δ 170.1 (s, Me*C*O$_2$), 86.2 (s, C-6), 65.4 (s, C-3), 57.0 (d, C-10), 56.6 (t, C-3′), 51.4 (d, C-2), 50.2 (s, C-7), 45.2 (d, C-1), 35.3 (t, C-5), 32.0 (d, *C*HMe$_2$), 31.5 (t, C-4), 31.0, 30.4 (t, C-8, C-9), 21.6, 21.5 (q, CH*Me*$_2$) 21.3 (q, –Me), 21.2 (q, *Me*CO$_2$); LRMS *m/z* (relative intensity) (EI) 278 (M$^+$, 0.9), 277 (1.5), 236 (0.7), 235 (0.7), 218 (5), 203 (3), 189 (6), 175 (11), 161 (4), 147 (8), 133 (8), 123 (34), 113 (48), 112 (51), 105 (17), 91 (29), 81 (100), 67 (13), 55 (17), 63 (59); HRMS *m/z* exact mass calcd for $C_{17}H_{26}O_3$ 278.1882, found 278.1881.

(+)-Aphanamol I (3) from (−)-32. A solution of (−)-**32** (92 mg, 0.27 mmol) and KOH (120 mg, 0.47 mmol) in MeOH (6 mL) was heated under reflux for 2 h. The cooled reaction mixture was diluted with water (30 mL) and extracted with EtOAc (4 × 20 mL). The combined organic phases were dried and concentrated, and the residue was purified by chromatography (SiO_2, 2:5 EtOAc–heptane) *to give* **3** *as a syrup (20.4 mg, 32%);* $[\alpha]^{20}_{D}$ +23.0° (*c* 2.0, $CHCl_3$)(lit.[3] $[\alpha]^{20}_{D}$ +13°) $[\alpha]^{20}_{578}$ + 23.8° (*c* 2.0, $CHCl_3$), $[\alpha]^{20}_{546}$ +28.5° (*c* 2.0, $CHCl_3$), $[\alpha]^{20}_{436}$ +62.0° (*c* 2.0, $CHCl_3$), $[\alpha]^{20}_{365}$ + 135.3° (*c* 2.0, $CHCl_3$); IR (CCl_4) 3450, 2960, 2870, 1700, 1460, 1420, 1385, 1370, 1250, 1075, 1000 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.51 (d, 1 H, *J* = 4.4 Hz, H-6), 4.02 (d, 2 H, *J* = 5.8 Hz, H_2-12), 2.82 (ddd, 1 H, *J* = 7.3, 3.7, 13.8 Hz, H_a-3), 2.54 (ddd, 1 H, *J* = 5.3, 12.3, 12.3 Hz H_a-4), 2.41 (ddd, 1 H, *J* = 5.2, 11.5, 13.8 Hz, H_b-3), 2.29 (m, 1 H, H_b-4), 2.26 (m, 1 H, H-7), 2.07 (m, 1 H, H_a-10), 1.80 (m, 1 H, H_a-9), 1.66 (m, 1 H, H-8), 1.58 (m, 1 H, H-13), 1.41–1.29 (m, 2 H, H_b-9, H_b-10), 1.26 (s, H_3-11), 0.92 (d, 3 H, *J* = 3.7 Hz, H_3-14/15), 0.89 (d, 3 H, *J* = 3.7 Hz, H_3-14/15); ^{13}C NMR δ 213.6 (s, C-2), 141.7 (s, C-5), 132.9 (d, C-6), 67.2 (t, C-12), 59.0 (s, C-1), 56.1 (d, C-8), 51.5 (d, C-7), 39.9 (t, C-3), 34.6 (t, C-10), 33.0 (d, C-13), 27.1 (t, C-9), 25.0 (t, C-4), 24.7 (q, C-11), 22.1 (q, C-14/15), 19.9 (q, C-14/15); LRMS *m/z* (relative intensity) (EI) 236 (M$^+$, 16), 218 (5), 193 (17), 175 (10), 147 (13), 133 (19), 123 (33), 105 (57), 91 (100), 79 (100), 67 (36), 55 (54), 41 (75); HRMS *m/z* exact mass calcd for $C_{15}H_{24}O_2$ 236.1776, found 236.1774.

(−)-Aphanamol I (11). Compound (+)-**32** was treated essentially as described above for (−)-**32** to give (−)-**11** with the following characteristics: $[\alpha]^{20}_{D}$ −22° (*c* 0.30, $CDCl_3$); CD $[\theta]_{312}$ −195, $[\theta]_{302}$ −410, $[\theta]_{293}$ −470; NMR spectra are identical with those of the enantiomer (+)-**2**.

(+)-Aphanamol I (3) from (−)-33. A solution of (−)-**33** (30 mg, 0.11 mmol) in 0.36 M methanolic LiOMe (3.1 mL, 0.11 mmol) was heated at reflux for 1 h. Water (10 mL) was added to the cooled reaction mixture which was then extracted with EtOAc (4 × 10 mL). The combined organic phases were dried and concentrated, and the residue was purified by chromatography (SiO_2, 2:5 EtOAc–heptane) to give **3** as a syrup (17.9 mg, 70%); $[\alpha]^{20}_{D}$ +25.8° (*c* 0.5, $CHCl_3$), $[\alpha]^{20}_{578}$ + 24.6° (*c* 0.5, $CHCl_3$), $[\alpha]^{20}_{546}$ +29.0° (*c* 0.5, $CHCl_3$), $[\alpha]^{20}_{436}$ +63.8° (*c* 0.5, $CHCl_3$), $[\alpha]^{20}_{365}$ + 140.0° (*c* 0.5, $CHCl_3$).

(1*R*,2*S*,7*R*,8*S*)-Isodauc-5-ene-2,12-diol (4). Sodium borohydride (6.5 mg, 170 μmol) was added at rt to a stirred solution of **3** (10 mg, 42 μmol) in ethanol–water (7:3, 1 mL). Water (5 mL) was added after 45 min, and the solution was extracted with CH_2Cl_2 (4 × 5 mL). The combined organic phases were dried and concentrated, and the residue was purified by chromatography (SiO_2, 1:2 EtOAc–heptane) affording **4** as a syrup (6.0 mg, 60%): $[\alpha]^{20}_{D}$ +40° (*c* 0.80, $CHCl_3$); IR (CCl_4) 3420, 2960, 2930, 2870, 1725, 1465, 1450, 1400, 1385, 1370, 1260, 1100, 1070, 1050, 1010 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.59 (d, 1 H, J = 4.3 Hz, H-6), 4.07 (br, 2 H s, H_2-12), 3.51 (br, 1 H s, H-2), 2.40 (m, 1 H, H_a-4), 2.22–1.86 (m, 5 H, H_2-3, H_b-4, H_a-10, H-7), 1.76–1.52 (m, 3 H, H-8, H_a-9, H-13), 1.40–1.17 (m, 2 H, H_b-9, H_b-10), 1.06 (s, 3 H, H_3-11), 0.92 (d, 3 H, J = 6.6 Hz, H_3-14/15), 0.88 (d, 3 H, J = 6.6 Hz, H_3-14/15); ^{13}C NMR δ 141.9 (s, C-5), 133.2 (d, C-6), 76.7 (d, C-2), 67.6 (t, C-12), 56.8 (d, C-8), 49.9 (d, C-7), 48.5 (s, C-1), 35.8 (t, C-10), 32.3 (d, C-13), 30.5 (t, C-3), 27.3 (q, C-11), 26.7 (t, C-9), 25.3 (t, C-4), 22.4 (q, C-14/15), 19.5 (q, C-14/15); LRMS *m/z* (relative intensity) (CI-NH_3) 254 ($M + NH_4^+$, 12), 238 (M^+, 100), 221 (62), 203 (18), 123 (6), 111 (6); HRMS *m/z* (EI) exact mass calcd for ($M-H_2O$) $C_{15}H_{24}O$ 220.1827, found 220.1824. HRMS *m/z* (CI-CH_4) exact mass calcd for ($M^+ - OH$) $C_{15}H_{25}O$ 221.1905, found 221.1905.

(−)-2-Oxoisodauc-5-en-12-al (6). A solution of (+)-aphanamol I (**3**) (10.6 mg, 45 μmol) and 4-methylmorpholine *N*-oxide (10 mg, 75 μmol) in CH_2Cl_2 (0.5 mL) containing a suspension of powered 4-Å molecular sieves (~15 mg) was stirred for 10 min at rt. Then tetra-*n*-propylammonium perruthenate (1 mg, 7 mol%) was added, and the suspension was stirred at rt for 30 min.[27] The reaction mixture was then directly subjected to chromatography (SiO_2, 1:4 EtOAc–heptane) to give **6** (8.3 mg, 79%): $[\alpha]^{20}_{D}$ −5.9° (*c* 0.76, $CDCl_3$)(lit.[4] $[\alpha]^{20}_{D}$ −7°), $[\alpha]^{20}_{578}$ −18.4° (*c* 0.76, $CDCl_3$), $[\alpha]^{20}_{546}$ −16.4° (*c* 0.76, $CDCl_3$), $[\alpha]^{20}_{436}$ +19.7° (*c* 0.76, $CDCl_3$), $[\alpha]^{20}_{365}$ + 303° (*c* 0.76, $CDCl_3$); IR (CCl_4) 2960, 2930, 2870, 2810, 2710, 1700, 1690, 1640, 1460, 1390, 1370, 1250, 1190, 1170 cm^{-1}; ^1H NMR (C_6D_6) δ 9.14 (s, 1 H, H-12), 6.00 (d, 1 H, J = 5.4 Hz, H-6), 2.62 (ddd, 1 H, J = 14.4, 4.9, 4.9 Hz, H_a-4), 2.39–2.18 (m, 3 H, H_2-3, H_a-10), 2.15 (ddd, 1 H, J = 15.0, 8.6, 8.6 Hz, H_b-4), 2.03 (dd, 1 H, J = 5.4, 9.0 Hz, H-7), 1.60 (dddd, 1 H, J = 12.1, 7.2, 7.2, 2.7 Hz, H_a-9), 1.41 (dddd, 1 H, J = 9.3, 9.3, 7.1, 7.1 Hz, H-8), 1.28 (dq, 1 H, J = 7.1, 6.8 Hz, H-13), 1.24 (ddd, 1 H, J = 15, 7.1, 2.5 Hz, H_b-10), 1.10 (m, 1 H, H_b-9), 0.89 (s, 3 H, H_3-11), 0.74 (d, 3 H, J = 6.6 Hz, H_3-14/15), 0.71 (d, 3 H, J = 6.4 Hz, H_3-14/15); ^{13}C NMR (C_6D_6) δ 209.9 (s, C-2), 191.7 (d, C-12), 157.2 (d, C-6), 144.3 (s, C-5), 59.4 (s, C-1), 55.0 (d, C-8), 53.1 (d, C-7), 39.0 (t, C-3), 35.4 (t, C-4), 32.4 (d, C-13), 26.9 (t, C-10), 24.7 (q, C-11), 21.9 (q, C-14/15), 19.8 (t, C-9), 19.5 (q, C-14/15); LRMS *m/z* (relative intensity) (EI) 234 (M^+ 40), 219 (14), 206 (6), 191 (83), 173 (16), 163 (55), 151 (96), 144 (28), 131 (23), 123 (81), 105 (51), 91 (69), 77 (78), 69 (39), 55 (67), 41 (100); HRMS *m/z* (EI) exact mass calcd for $C_{15}H_{22}O_2$ 234.1620, found 234.1613.

(+)-Aphanamol (3) from 6. $NaBH_4$ (1.3 mg, 34 μmol) was added with stirring at rt to a solution of **6** (7.6 mg, 32 μmol) in methanolic $CeCl_3{\cdot}7H_2O$ (0.4 M, 90 μL, 36 μmol). After 5 min the reaction mixture was directly subjected to chromatography (SiO_2, 1:2 EtOAc–heptane) to give **3** (1.6 mg, 21%) with $[\alpha]^{20}_{D}$ +18° and **4** (2.9 mg, 38%); $[\alpha]^{20}_{D}$ +44°.

(−)-Norbourbonone (29). A solution of (*S*)-1-methyl-3-isopropylcyclopentene (**24**) (320 mg, 2.74 mmol), benzonitrile (80 mg), and 2-cyclopenten-1-one (**26**) (340 mg, 4.14 mmol) in acetonitrile (12 mL) was purged with N_2 for 20 min and then irradiated with UV light. Additional lots of **26** (340 mg, 4.14 mmol) in acetonitrile (1 mL) were added after 4 and 8 h, respectively. The irradiation was interrupted after a total of 12 h, when GC indicated ca. 80% consumption of the alkene. The solution was concentrated and the residue subjected to chromatography (SiO_2, 1:10 EtOAc–heptane) to give a crude product (0.30 g) containing **29** and two isomeric compounds.

A mixture of the crude product (100 mg), semicarbazide hydrochloride (100 mg, 0.90 mmol) and sodium acetate trihydrate (150 mg, 1.10 mmol) in 1:1 water–EtOH (1.6 mL) was stirred for 1 h. Water (5 mL) was added, and the mixture was extracted with diethyl ether (4 × 5 mL). The combined ethereal extracts were dried and concentrated, and the residue was subjected to chromatography (SiO_2, EtOAc) to give three fractions. The first fraction (22.9 mg) consisted of a mixture of unreacted photoadduct isomers practically free of **29**. The second fraction consisted of a semicarbazone (12.4 mg), probably formed from one of the isomers of **29**. The third fraction consisted of the semicarbazone (54.6 mg; mp 118–120 °C) of the sterically less hindered **29**. This semicarbazone (42.2 mg) was immediately hydrolyzed by heating under reflux with 20% sulfuric acid (2 mL) for 20 min. After being cooled, the mixture was extracted with pentane (3 × 4 mL), and the combined extracts were dried and subjected to chromatography (SiO_2, 1:10 EtOAc–heptane) affording **29** (12.2 mg) which crystallized as needles upon standing overnight at 4 °C: mp ca. 20 °C (lit.[29] mp 24.5–25.5 °C); $[\alpha]^{20}_{D}$ −182° (*c* 0.50, $CHCl_3$);[29] IR (CCl_4) 2950, 2870, 1730, 1460, 1450, 1410, 1385, 1375, 1365, 1160, cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.57 (ddd, 1 H, J = 18.5, 12.3, 9.7 Hz, H_a-4), 2.44 (dd, 1 H, J = 7.3, 7.3 Hz, H-6), 2.26 (dddd, 1 H, J = 18.3, 9.3, 1.9, 1.9 Hz, H_b-4), 2.19 (m, 1 H, H-2), 2.13–1.79 (m, 4 H, H-1, H_2-5, H_a-9), 1.75–1.65 (m, 1 H, H_b-9), 1.60–1.47 (m, 3 H, H_2-8, H-10), 1.34–1.21 (m, 1 H, C*H*Me$_2$), 1.13 (s, 3 H, Me), 0.87 (d, 3 H, J = 1.7 Hz,CH*Me*), 0.85 (d, 3 H, J = 1.7 Hz,CH*Me*); ^{13}C NMR δ 222.8 (s, C-3), 55.7 (d, C-10), 51.9 (d, C-1), 48.3 (d, C-2), 44.9 (s, C-7), 41.7 (d, C-6), 41.5 (t, C-8), 37.4 (t, C-4), 30.8 (d, *C*HMe$_2$), 29.1 (t, C-9), 22.8 (t, C-5), 22.3 (q, Me), 21.7 (q, CH*Me*), 21.2 (q,CH*Me*); LRMS *m/z* (relative intensity) (EI) 206 (M^+ 22), 191 (6), 164 (42), 163 (66), 145 (22), 124 (80), 123 (100), 107 (48), 93 (51), 91 (55), 81 (100), 80 (100), 79 (75); HRMS *m/z* (EI) exact mass calcd for $C_{14}H_{22}O$ 206.1670, found 206.1673.

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Note Added in Proof. By the courtesy of Professor G. Mehta, we have had the opportunity to compare the ^1H and ^{13}C NMR spectra of our respective preparations of synthetic aphanamol I and have found them to be identical. We thank Professor Mehta for his kind cooperation. After this paper was submitted, there has been a report on a related application of a base-catalyzed fragmentation of a γ,δ-epoxy alcohol with concomitant opening of a cyclobutane ring (Wender, P. A.; Mucciaro, T. P. *J. Am. Chem. Soc.* **1992**, *114*, 5878).

Registry No. **3**, 91410-61-6; **4**, 143003-94-5; **5**, 91410-62-7; **6**, 100324-71-8; **11**, 143003-95-6; **15**, 73039-22-2; (±)-**16**, 142895-94-1; (±)-**16** (3-methylene derivative), 142896-04-6; (±)-**17**, 142895-95-2; (±)-**18**, 142895-96-3; (±)-**19**, 143003-96-7; (±)-**20**, 142895-97-4; (±)-**21**, 142928-69-6; (*R*)-**22**, 5989-27-5; (*S*)-**22**, 5989-54-8; (*S*)-**23**, 62994-35-8; (*R*)-**23**, 30460-43-6; (*S*)-**24**, 143003-97-8; (*R*)-**24**, 2698-97-7; **25**, 18766-96-6; **26**, 930-30-3; (−)-**27**, 142895-98-5; (+)-**27**, 143003-98-9; (−)-**28**, 142895-99-6; (−)-**29**, 13844-03-6; **29** semicarbazone, 142896-07-9; **29** regioisomer, 142896-05-7; **29** regioisomer, semicarbazone, 142896-06-8; (+)-**30**, 142896-00-2; (−)-**30**, 143003-99-0; (+)-**31**, 142896-01-3; (−)-**32**, 142896-02-4; (+)-**32**, 143004-00-6; (−)-**33**, 142896-03-5; cyclopentene, 142-29-0; 1,3-cyclopentanedione, 3859-41-4.

Supplementary Material Available: ^1H NMR spectra of all compounds described in the Experimental Section (18 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.