LIGHT-MEDIATED TRANSFORMATIONS OF OLEFINS INTO ALCOHOLS: REACTIONS OF HYDROXYL RADICALS WITH CYCLOALKENES^a,^b

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Abstract: Reactions of hydroxyl radicals, generated by photodecomposition of hydrogen peroxide in acetonitrile, with a wide variety of cycloalkenes have been examined. The results show that the major reaction is the addition of hydroxyl radicals to the less substituted end of the double bond, furnishing the secondary alcohols. The reactivity pattern and the observed regio- and stereoselectivity clearly reveal that the steric parameters associated with the substrates play a dominant role in directing the addition reactions. More importantly, this study led to the development of a new methodology for the facile conversions of olefins essentially into secondary alcohols, and includes a few examples which demonstrate the potential of the method.

The conversion of olefins into saturated alcohols is one of the most useful reactions in organic synthesis. This reaction can, in principle, be considered as addition of the elements of water to a carbon-carbon double bond wherein, depending upon the mode of addition, two distinct regioisomeric alcohols can be expected from an unsymmetrical olefin. Available methods for this purpose both direct and indirect, essentially furnish tertiary alcohols under electrophilic conditions¹ in the case of trisubstituted olefins. In the case of olefins with other acid sensitive sites, of the indirect methods, oxymercuration and demercuration has been the method of choice². With trisubstituted olefins, while no direct method appears to exist to furnish secondary alcohols, hydroboration followed by oxidation with H_2O_2 has been the most versatile indirect preparative method³. Among other analogous methods, hydrometallation/ oxidation reactions such as hydroallumination⁴, hydrozirconation⁵, and hydrosilylation⁶ may be mentioned although these reactions are not of much practical utility.

In this context, it appears that in order to develop a methodology for direct conversion of trisubstituted olefins into secondary alcohols, a free radical approach has certain merits, since free radicals are known to attack the less substituted end of a double bond^{7a}. From this point of view, the addition reactions of hydroxyl radicals to olefins appeared attractive^{7b} Although this reaction has been studied since a long time, its study from preparative point of view seems to have remained practically unexplored. For instance, Milas et al⁸ were the first to report the reactions of hydroxyl radicals generated by the photodecomposition of H_2O_2 with some unsaturated alcohols and acids; they reported the transformation of allyl alcohol, crotonic acid and maleic acid into glycerol, dihydroxybutyric acid and mesotartaric acid, respectively. Later, in a reinvestigation of this reaction under comparable conditions, Volman and Chen⁹

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percentage of the products; instead, polyhydroxy compounds were suspected to be the major products. During the subsequent period, the study of the reactions of hydroxyl radicals appears to have been restricted to aromatic compounds and the work in this area has been reviewed¹⁰.

As a part of our ongoing programme on the reactions of hydroxyl radicals with organic compounds^{11a,b}, we have investigated these reactions with a variety of cycloalkenes. The substrates chosen for this study include the monocyclic 1 - 5, the bicyclic 6 and 7, and the tricyclic olefin 8. In order to check the reaction site selectivity of hydroxyl radicals, benzonorbornadiene 9 was included as it possesses various types of reactive sites. As hydrogen peroxide is readily available and its facile photodecomposition into OH radicals (uv of H_2O_2 195-400 nm) is well documented^{12a}, it is used as a convenient source of OH radicals in the present study. Of the various solvents checked for this reaction, acetonitrile was found to be superior in many respects; particularly from the point of view of homogeneity of the reaction medium and its absence of chemical participation leading to undesired side products¹³. Reactions were generally carried out employing a solution of H_2O_2 (#80%) and the olefin in 1:10 molar ratio in CH₃CN. The products in each case were separated by standard techniques and characterized on the basis of their spectral data. The structural assignments were confirmed either by direct comparison of spectral data with those reported in literature or by preparation of authentic samples by known procedures.

Control experiments revealed that there was no reaction between an alkene and H_2O_2 in the absence of light; similarly, no reaction was detected when a solution of alkene in moist CH_3CN was irradiated without the use of H_2O_2 , indicating that water from H_2O_2 does not contribute to product formation.

RESULTS

Cyclohexene 1, cycloheptene 2 and cyclooctene 3

Reaction of <u>1</u> with H_2O_2 under the conditions described above resulted in a product comprising mainly cyclohexanol <u>10</u> and an allylic dimeric product arising obviously by the combination of cyclohexenyl radicals; the latter product was characterized as bicyclohex-2-enyl from its PMR and mass spectral data. Likewise, <u>2</u> and <u>3</u> reacted with equal ease and afforded essentially cycloheptanol <u>11</u> and cyclooctanol <u>12</u> respectively, along with some minor products, in good yields. These results along with those obtained from other alkenes are summarized in the table.

After having established that unsubstituted cycloalkenes readily undergo hydroxyl radical additions to furnish essentially saturated alcohols, the reactions of substituted cycloalkenes were studied to assess the regio- and stereoselectivities of this reaction. The alkenes $\underline{4}$ and $\underline{5}$ displayed similar reactivity pattern affording the secondary alcohols $\underline{14}$, $\underline{15}$ and $\underline{17}$ in higher proportions than the corresponding tertiary alcohols $\underline{13}$ and $\underline{16}$ along with other minor products (Experimental).

Car-3-ene $6, \ll$ -pinene 7 and isolongifolene 8

With <u>6</u> as the substrate, photoreaction of H_2O_2 gave <u>cis</u>-carane-trans-4-ol <u>19</u> as the major product along with its stereoisomer <u>20</u>, the tert. alcohol <u>18</u>, <u>cis</u>-carane-4-one and some allylic products. α



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The products from <u>7</u> were significantly derived from the cleavage of the cyclobutane ring. The occurrence of this type of ring cleavage appears to be typical of \ll -pinene in most of its radical addition reactions¹⁴. <u>Trans</u>-carvotanacetol <u>21</u> was obtained as the major product along with <u>trans</u>-carveol <u>22</u>, carvotanacetone <u>23</u>, <u>trans</u>-verbenol <u>24</u>, and some amount of allylic products. Chromatographic separations over SiO₂ furnished the pure products which were characterized as usual. The absence of any tertiary alcohol in the products from <u>7</u> is noteworthy.

Surprisingly, reaction of $\underline{8}$ with H_2O_2 under similar conditions was unusually sluggish. After a prolonged irradiation, it afforded a single product in 5% yield, which was identified as $6 - \alpha H$ isolongifolan- $5 - \alpha - 01 \ \underline{25}$, on the basis of its PMR spectrum and a direct comparison with an authentic sample prepared by the hydroboration/ H_2O_2 oxidation of $\underline{8}$. The possibility of $\underline{9}$ -geometry of the hydroxyl group at C-5 was ruled out by direct comparison with an authentic sample of $6 - \alpha - i$ solongifolan- $5 - \frac{1}{7} - 01$, prepared by a reported method¹⁵.

Benzonorbornadiene 9

The reaction of $\underline{9}$ with H_2O_2 furnished a relatively clean product comprising a major component and a minor one which were separated by standard techniques. The IR and PMR spectra of the products indicated that the major component is a secondary alcohol and the other, a hydrocarbon. The PMR spectrum of the hydrocarbon was conspicuous by the absence of olefinic protons and the appearance of a complex splitting pattern in 0.60 to 3.055 region, along with the signals due to aromatic protons; this indicated the occurrence of a photo-induced rearrangement of $\underline{9}$ in the formation of the hydrocarbon. As the substrate $\underline{9}$ is a typical 1,4-diene, its di- π -methane rearrangement (DPM) was suspected to have occurred and in fact, the product on hand was found to be $\underline{27}$, the DPM rearrangement $\frac{16}{7}$ product of $\underline{9}$ from its spectral data and also by the preparation of an authentic sample of 27 by a known method.

Two pairs of stereoisomeric sturctures, viz. exo- and endo-2-benzonorbornenols, and syn- and anti-7-benzonorbornenols were considered for the major product. Its PMR spectrum displayed four dinstict groups of signals with relative intensities of 2:2:2:1 in the 1.0-3.5 gregion along with a 1H signal which exchanged with D_2O . A sharp 4-H singlet at 6.63, an \ll -carbinyl proton (3.5), a four line multiplet for 2H benzylic bridge head protons (2.87) indicated the presence of a plane of symmetry in the molecule, which enabled the placement of the hydroxyl group at C-7. Further support to this regio-assignment was obtained when the chromic acid oxidation of this alcohol furnished the known 7-oxobenzonorbornanone $\frac{17}{12}$. A direct comparison of the PMR data of the alcohol with those of the known¹⁸ syn- and anti-7-benzonorbornenols enabled its characterization as the anti-alcohol 26. This structural assignment was confirmed by the preparation of an authentic sample. Probable mode of formation of 26 is depicted in the scheme. The radical I arising from the preferred attack of the hydroxyl radical from the less hindered exo-phase of 9 undergoes a radical Wagner-Meerwein 1,2-aryl migration ^{19a} involving aromatic *m*-participation leading to the radical III. The latter, on hydrogen abstraction, furnishes the anti-alcohol 26. A similar type of radical rearrangement has also been observed by Cristol and Nachtigall 19a,b in the reaction of <u>9</u> with various halogenating agents.

DISCUSSION

The above results demonstrate that hydroxyl radicals preferentially undergo addition reaction although products from allylic hydrogen abstraction are also obtained in a few cases. This kind of direct approach for the conversion of olefins to alcohols does not appear to have been reported earlier. Although the

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present substrates excepting 2, 3 and 5 are basically cyclohexenes, it is significant to note that they have displayed wide differences in terms of reactivity and regio/stereoselectivity.



SCHEME : REACTION OF HYDROXYL RADICALS WITH BENZONORBORNADIENE 9

<u>Reactivity pattern</u>: It is apparent from the results (Table) that the monocylic olefins <u>1</u> to <u>5</u> react more readily with OH radicals in comparison with the bicyclic <u>6</u> and <u>7</u>, and the tricyclic <u>8</u> under the same conditions. This higher reactivity can be ascribed to the absence of steric hindrance in <u>1</u> to <u>5</u> for the approach of OH radicals. However, due to steric crowding by the gem-dimethyl groups in the bicylic olefins <u>6</u> and <u>7</u>, the approach of the reagent becomes more difficult, resulting in lower yields. An examination of the molecular model of the tricyclic olefin <u>8</u> reveals that both the exo-(2-methyl-3,4-H, 7-methyl and 11-H) and the endo-(2-methyl,4-H, 7-methyl and 8,9-H) faces are sterically crowded and it is significant to note that it has strikingly refused to react, demonstrating the importance of steric factors in these reactions.

<u>Regio- and stereoselectivity</u>: A high degree of regioselectivity has been observed with the addition of OH radicals to the less substituted end of the double bond in the trisubstituted 4-7. The electrophilic properties of the hydroxyl radical²⁰ and the presence of electron-releasing methyl groups in these olefins are expected to facilitate²¹ such an addition. The increasing order of regioselectivity as one goes from 4 to 8 is noteworthy; <u>tert</u>-alcohols are minor products in 4-6 while they are excluded in 7 and 8. These results, thus, not only demonstrate that primarily the steric factors govern the regio- and stereoselectivities in the reactions of OH radicals but are also found to be well in accord with the modern concepts of free radical additions developed by Tedder²¹ and Giese²².

The steric considerations can as well rationalize the observed stereoselectivity in product formation. For example, in the absence of any steric hindrance for the approach of OH radicals, 1-methylcylohexene afforded a 1:1 mixture of secondary alcohols while a high degree of stereoselectivity is noticed in the formation of the sec-alcohol <u>19</u> from car-3-ene wherein the p-face of the molecule is shielded by the gem-dimethyl groups. In the case of <u>7</u> and <u>8</u>, in addition to the shielding of the p-face, the double bond is flanked by only one methylene group as against two in <u>6</u>, thereby increasing stereoselectivity.

In the case of $\underline{9}$, it may be observed that in spite of the presence of the other reaction sites, hydroxylation has occurred only at the double bond;

probably this may be attributed to the energetics of these reactions. The stereoselective formation of the anti-alcohol 26 has already been noted.

<u>Synthetic applications</u>: From the synthetic point of view, hydroxylation of cycloalkenes with H_2O_2 constitutes a simple and convenient method of obtaining secondary alcohols. For instance, the alcohols <u>19</u> and <u>20</u> are got in good yields. Oxidation of these alcohols forms an alternate method for the synthesis of 4-isocaranone²³. Another transformation of synthetic value is the first ever single step conversion of \ll -pinene into a natural product <u>trans</u>-carvotanacetol²⁴ <u>21</u> in good yields. The regio and stereoselective transformation of benzonor-bornadiene into the sec-alcohol <u>26</u> is worthy of mention. Thus, these examples indicate that further probe into this methodology is likely to generate some more single-step transformations of synthetic value.

CONCLUSIONS

In essence, the present study which concerns primarily with the reactions of hydroxyl radicals with cycloalkenes is significant in many ways: i) hydroxyl radicals generated by photodecomposition of H_2O_2 can be effectively utilized for the direct conversion of cycloalkenes into cycloalkanols, ii) it is observed that steric parameters not only govern the reactivity pattern of cycloalkenes but are also responsible for the regio and stereoselectivity in product formation and iii) the single-step transformations are highly suggestive of the potential of the present methodology.

EXPERIMENTAL

All m.ps and b.ps are uncorrected. All solvent extracts were finally washed with brine before drying over Na_2SO_4 .

IR spectra were recorded as smears or Nujol mulls (solids) on a Perkin-Elmer Infracord model-137E. PMR spectra were taken in 10-15% solution in CCl₄ on a Varian T-60 spectrometer, with TMS as internal standard. Mass spectra were recorded on a CEC mass spectrometer, model 21-110B, using an ionization potential of 70 ev. GLC analyses were carried out on "Aerograph" model A-350-B using Al columns. Col. A: 180 cm x 0.6 cm packed with 20% FFAP (carbowax-20M treated with terephthalic acid), Col. B: 150 cm x 0.6 cm packed with silicon QF₁ 5%. With Hewlett Packard-700, the following columns were used: Col. C: 180 cm x 0.6 cm packed with 5% SE-30, Col. D: 180 cm x 0.6 cm packed with 10% OV-101. Preparative GLCs were carried out on the Aerograph model with Col. E viz. 300 cm x 1.00 cm Al column packed with 30% FFAP.

Product compositions given in the table were determined employing the following conditions of GLC: For 1 - 3, Col. A, 100°, H₂ 60m1/min; 4 and 5, Col. B, 110°, H₂ 50 m1/min; 6 and 7, Col.A, 140°, H₂ 80 m1/min; 8, Col. D, 200°, H₂ 40 m1/min; 9, Col. C, 140°, H₂ 30 m1/min.

Materials:

Acetonitrile was refluxed over P_2O_5 and distilled; a redistillation over anhydrous K_2CO_3 gave pure and dry material. H_2O_2 (~80%) was prepared by slow removal of water from 30% H_2O_2 under reduced pressure (~30 mm) at 45-50°.

Cyclohexene and cycloheptene were prepared by the dehydration of cyclohexanol (BDH) and cycloheptanol (Koch-light) respectively over H₃PO₄ and were distilled over sodium. Dehydration of 1-methylcyclohexanol and 1-methyl-cycloheptanol (obtained by the Grigard reaction of the corresponding ketones) over iodine afforded 4 and 5 respectively. Cyclooctene was procured from Koch-Light; x-pinene 7, car-3-ene 6 and isolongifolene 8 were obtained from M/s. Camphor & Allied Products, Bareily, India. Benzonorbornadiene 9 was prepared by a reported²⁵ method. As the hydrocarbons 6 and 7 were not optically pure enough, rotations of the products arising from these are not recorded.

General procedure for photooxidation:

Photoirradiation was carried out using a Hanovia medium pressure mercury vapour lamp (200 w), suspended in a doubled-walled, water-cooled quartz well without any filter. The well was fitted into a cylindrical reaction containing a soln. of olefin (0.15 mole) and H_2O_2 (0.015 mole) in CH₃CN (350 ml). A minute steady flow of N₂ was maintained through the soln. throughout the course of the

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reaction. The reaction was monitored by the presence of H_2O_2 , as judged by a qualitative KI-AcOH test. When H_2O_2 had completely disappeared, the solvent was carefully distilled using a vigreux column and the residue fractionated to remove first the unreacted hydrocarbon and then to collect the product under diminished pressure. In all the cases except those of isolongifolene and bensonorbornadiene, the unreacted hydrocarbon partly distilled out alongwith the solvent.

Separation/identification of products:

(i) <u>Cyclohexene 1</u>: Cyclohexanol and bicyclohex-2-enyl (1:2 mixture of racemic and meso), the products from 1 were isolated by preparative GLC (Col. E, 175°, 60 ml H₂/min). The former was identified by direct comparison with an authentic sample and the latter from its PMR and mass spectral data. The above dimeric product separated into two components in GLC (<70°) with close retention times. PMR: 1.60 (methylene envelope, 7H), and 5.50 (t, 2H, vinylic protons), Mass: m/e 162 (H⁺) and a major peak at m/e 81. (Lit²⁶ PMR).

(ii) <u>Cycloheptene</u> 2: The products from 2 comprised essentially cycloheptanol which was separated from the minor components by preparative GLC and identified by comparison with an authentic sample. The minor, probably allylic dimeric products, were not investigated.

(iii) <u>Cyclooctene</u> 3: Cyclooctenol was the major product along with a minor amount of cyclooctenone (IR, PMR, authentic samples). In addition, the product from 3 comprised small amounts of three unidentified components probably arising from the photochemistry of cyclooctenone and by dimerization of allylic radicals.

(iv) <u>1-Methylcyclohexene</u> 4: 1-Methylcyclohexanol <u>13</u> (IR, PMR, authentic sample) and a mixture of <u>trans-2</u>-methyl cyclohexanol <u>14</u> and its <u>cis-isomer</u> 15 were the major products separated by preparative GLC (Col. C, 160⁻⁷, 80 ml H₂/min). PMR of the mixture of <u>14</u> and <u>15</u>: 1.00 (d, 3H), 1.75 (m, 9H), 2.83 (s, IH, exchanges with D₂O), 2.93 (m, 0.5 H, merging with the hydroxyl proton) and 3.50 (m, 0.5H), the spectrum was identical with that of 1:1 mixture of authentic samples of <u>14</u> and <u>15</u>. The minor products included 2-methylcyclohexanone (IR, PMR) and a ~4:1 mixture of dimeric products. Allylic dimers: IR: 2820, 1650, 1355, 1380, 1155, 975, 930, 900, 810 and 745 cm⁻¹. PMR: 1.64 (s, 6H, 2 vinylic methyls), 1.77 (m, 14 H, methylene and methine envelope) and 5.05 (m, 2H, olefinic); Mass: m/e 190 (M⁺), m/e 95 (base peak).

(v) <u>1-Methylcycloheptene</u> 5: Preparative GLC of the total product (under the conditions of iv) afforded 1-methylcycloheptanol <u>16</u>, 2-methylcycloheptanone and a mixture of <u>cis</u> and <u>trans-2-methylcycloheptanols</u> <u>17</u> along with some minor products, probably arising from allylic radicals. PMR of <u>16</u>: 1.17 (s, 3H, t-CH₃), 1.53 (br.s, 12H, 6 x CH₂) and 1.80 (s, 1H, exchanges with D₂O); Mass: m/e <u>128</u> (H⁺) and m/e 71 (base peak). 2-Methylcycloheptanone was identified by a direct comparison with an authentic sample obtained by the oxidation of trans-2-methylcycloheptanol²⁷. IR of <u>17</u>: 3571, 3030, 1449, 1351, 995, and 962 cm⁻¹. PMR: 0.95 and 1.03 (2d, 3H together), 1.40 (s, 1H, exchanges with D₂O), 1.57 (brs, 11H), 3.31 and 3.85 (m, 1H together). The spectrum was comparable to that of trans-2-methylcycloheptanol²⁷ along with minor aignals for the <u>cis</u>-isomer.

(vi) Car-3-ene 6: Cis-carane-trans-3-ol 18, a 4:1 mixture of cis-carane-trans-4-ol 19 and its cis-isomer 20, cis-carane-4-one, and a 4:1 mixture of allylic dimers were the products from 6. A part of the total product was chromatographed on silica gel-II; initial elution with pet ether furnished the allylic dimeric products. The fractionseluted with 15-50% diethyl ether in pet ether on preparative GLC (Col. E, 110°, H₂ 90 ml/min) afforded pure 18 and a mixture of 19 and 20, and pure cis-carane-4-one. PMR of 18: 0.63 (m, 7H), 0.93 and 1.03 (2s, 3H each), 1.10 (s, 3H) and 1.72 (s, 1H, exchanges with D20). PMR of dimeric mixture: 0.77, 0.82, 1.00, 1.03 and 1.07 (5 signals), 1.58 and 1.63 (2 brs) and 5.53 (very br.s); the signals in the olefinic, vinylic methyl and quaternary methyl regions were in a 1:3:6 ratio. Mass: m/e 270 (M⁺, 100%), 135 (80%).

Analytical GC of the mixture of <u>19</u> and <u>20</u> indicated a 4:1 composition and the major component was enhanced when mixed with an authentic sample of <u>19</u>. PMR of the mixture: 0.96 and 1.02 (2s, 3H each), 1.01 (d, J-5Hz, 3H), 2.20 (br.s, IH, exchanges with D₂O), 2.98 (m, 1H) and 3.66 (m, 1H). In addition, the spectrum displayed weak signals overlapping with the major ones, for <u>20</u>. Oxidation of this mixture with chromic acid gave <u>cis</u>-carane-4-one. Confirmation of the assignments of <u>18</u> and <u>19</u> was done by a direct comparison with their authentic samples.

(vii) = -Pinene 7: Reaction of H₂O₂ with 7 afforded trans-carvotanacetol 21, trans-carveol 22, carvotanacetone 23, trans-verbenol 24, and products arising from allylic coupling. Dimeric products were isolated by loading the total

product on SiO₂-II and eluting with pet ether. Inverted Dry Column Chromatography²⁸ (EtOAC:benzene 1:9) of the material (free from dimeric products) furnished the other products pure.

 $\frac{\text{Trans-csrvotanscetol}}{(s, 3H), 2.67 (s, 1H, exchanges with D₂O), 3.82 (t, J=3Hz, 1H) and 5.37 (m, 1H).$

Trans-carveol 22: B.p. 90-2°/3 mm, PMR: 1.76 (s, 6H), 3.90 (m, 1H), 4.73 (s, 2H) and 5.53 (m, 1H).

<u>Carvotanacetone 23</u>: PMR: 0.95 (d, J=7Hz, 6H), 1.73 (e, 3H) and 6.58 (m, 1H). The assignments of 21 and 22 were confirmed by direct comparison with their authentic samples.

Trans-verbenol 24: PMB 0.87 and 1.33 (s, 3H each), 1.70 (m, 3H) 4.27 (m, 1H) and 5.34 (m, 1H) (Lit.²⁹ PMR).

Allylic dimers: The components eluted out from the column with pet. ether showed relatively high retention times in GLC; these have been characterized as mixture of dimeric products (1:1 ratio). IR: 2778, 1675, 1610, 1471, 1449, 1385, 1370, 897 cm⁻¹. PMR: 0.87 and 1.33 (br. signals, 6H each, geminal methyls), 1.70 (br. signal, 6H, vinylic methyls), 4.93 and 5.13 (br.m, 2H, olefinic protons), Mass: m/e 270 (M⁺, 100%), 227 (78%), 135 (89%), 123 (60%) and 93 (90%).

(viii) Products from isolongifolene 8: GLC of the total product (Col. D, 200°, H2 40 ml/min) indicated a single component along with unreacted 8. The latter was distilled out and the residue was passed through a column of SiO₂. Initial elution with pet. ether eliminated the traces of 8, and elution with a 1:1 pet. ether-benzene mixture furnished a solid product, m.p. 71° which was characterized as 6-CH-isolongifolan-5-c-ol 25. IR: 3380 cm⁻¹; PMR: 0.86, 0.91, 1.05 and 1.09 (4s, 3H each) and 3.47 (m, TH). Mass: m/e 222 (M⁺, 87Z) and 207 (1002) C.it.³⁰ PMR, synthesis). Oxidation of 25 with chromic acid furnished the corresponding known ketone³⁰.

(ix) <u>Reaction of benzonorbornadiene 9</u>: A part of the total product was chromatographed over SIO_2/II . Initial elution with pet. ether brought out a mixture of unreacted 9 and the triene 27. Further elution with 50% Et_2O in pet. ether furnished the alcohol 26 pure.

Tetracyclo $(5.4.0.0^{2.4}0^{36})$ undeca-1(7), 8,10-triene 27: Unreacted 9 was removed by the following method. The mixture of unreacted 9 and 27 (2.1 g) was treated with N-bromo succinimide (5.0 g) suspended in water (10 ml) under stirring at RT (1.5 hr). A standard work-up afforded a product which was passed through a short column of SiO₂. Initial elution with pet ether afforded 27 (0.7 g) in pure form. IR 3060, 2940, 1615, 1480, 1260, 1030, 980, 800, 790, 760 and 680 cm⁻¹. PMR: 0.65 (m, 1H, H-2), 1.80 (m, 1H, H-6), 2.30 (m, 1H, H-5), 2.65 (m, 1H, H-3 or H-4), 3.05 (m, 2H, H-1 and the other of H₃ and H₄) and 6.50-7.60 (m, 4H aromatic protons). A direct comparison with an authentic sample confirmed the structural assignment.

Anti-7-benzonorbornenol 26: The material eluted with 1:1 ether-pet. ether mixture solidified and was crystallized from pet. ether, m.p. 104°. IR 3240 cm⁻¹; PMR: 1.06 and 1.96 (m, 2H each), 2.20 (m, 1H, exchanges with D_2O), 2.87 (m, 2H), 3.50 (br.s. 1H) and 6.63 (s. 4H) (authentic sample, Lit.³¹ m.p. 105°. PMR).

Authentic samples: 1-Methylcyclohexanol³² and cis- and trans-2-methylcyclohexanols³³ were prepared following known procedures. <u>Cis-carane-trans-3-o1</u> 18 was synthesized by the treatment of 3%, 4%-epoxy-<u>cis-carane³⁴</u> with LAH³⁵. Hydroboration²³ of car-3-ene and subsequent alkaline H₂O₂ oxidation afforded <u>cis-carane-4</u>«-ol 19. <u>Trans-carveol 22</u> was prepared by a reported method²⁴ and its selective hydrogenation afforded <u>trans-carvotanacetol</u>, 21. <u>6</u> «H-Isolongifolan-5«-ol³⁰, anti-7-benzonorbornenol³¹ <u>26</u> and the triene¹⁰ <u>27</u> were too prepared by reported methods.

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