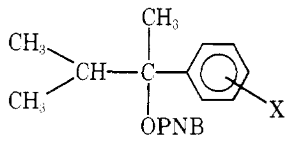

9

$\rho^{+} = -4.76$

presented in Table II. Thus the electron releasing power of an isopropyl group is similar to that of a methyl group. With increasing electron demand at the cationic center, the rate enhancement observed for **3** is much greater than that observed for **2**. This is in agreement with the greater stabilizing effect of the cyclopropyl group compared with the phenyl group.

These results have important implications. Many different approaches are now available for establishing the relative order of stabilization of a cationic center by methyl, phenyl, and cyclopropyl groups. The earlier solvolytic and equilibrium studies revealed that the trend of delocalization of charge increases in the order methyl < phenyl < cyclopropyl.[4] From a study of the ^{13}C shifts of alkyl carbonium ions Olah concluded that a phenyl group is more effective in stabilizing a cationic center than a cyclopropyl group.[3] However, the application of the tool of increasing electron demand supports the conclusions reached earlier based on solvolysis and equilibria studies. Therefore, caution is in order at this time in utilizing ^{13}C shifts to draw conclusions as to the charge densities in carbonium ions.

Experimental Section

All melting points are uncorrected. IR spectra were taken on a Perkin-Elmer Model 137 spectrometer and NMR spectra were recorded on a Varian T-60 spectrometer.

Preparation of Tertiary Alcohols. The *tert*-cumyl alcohols were prepared by the addition of the appropriate Grignard reagents to acetone in ether. 1-Aryl-1-phenyl-1-ethylcarbinols were also similarly prepared starting from acetophenone. The following procedure for the Grignard reaction is representative. A solution of the ketone (30 mmol) in ether (25 ml) was slowly added to a solution of the Grignard reagent (32.5 mmol, prepared by reacting the aryl halide with magnesium in ether) at 0 °C. After the addition, the reaction mixture was stirred at room temperature for 1 h and then refluxed for 2 h. The reaction mixture was then decomposed with ice-cooled ammonium chloride and extracted with ether. The ether extracts were dried over anhydrous magnesium sulfate and solvent evaporated. The tertiary alcohols were used for *p*-nitrobenzoate preparation without further purification.

Preparation of *p*-Nitrobenzoates. The *p*-nitrobenzoates were obtained by treating the tertiary alcohols with *n*-butyllithium and *p*-nitrobenzoyl chloride.[18] The properties and analysis of the *p*-nitrobenzoates prepared in this study are summarized in Table III.

Kinetic Procedure. The procedure employed for determining the rate constants was described earlier.[18]

References and Notes

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Revised Structure of the Dimer of 3,3,6,6-Tetramethylcyclohexyne

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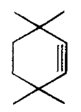
The dimerization of 3,3,6,6-tetramethylcyclohexyne has been reinvestigated and the structure of the dimer reassigned as a moncyclic conjugated enyne (3).

The dimer of 3,3,6,6-tetramethylcyclohexyne (**1**) was described by us in 1972[1] and was assigned structure **2** on the basis of spectroscopic evidence and partial degradation. The formation of **2** was interpreted through dimerization of **1** to a cyclobutadiene and subsequent rearrangement.



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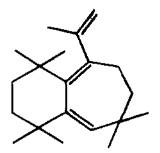
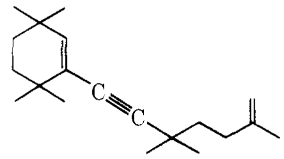


2

Another structure considered[1] for the dimer was **3**, which was consistent with most of the data, but the dimer lacked acetylenic infrared absorption at 2250–2270 cm^{-1}, expected for vinylacetylenes,[2] and **3** would not have been expected to give the observed acetic acid in oxidation with permanganate–periodate.



3

An intensive but unsuccessful effort to find independent evidence for the supposed cyclobutadiene intermediate has forced reconsideration of the structural assignment of the dimer. For the reasons which follow, we now conclude that the dimer is **3**.

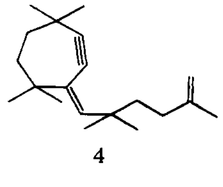
The original objections to **3** are swept away by two observations. First is that while there is indeed no easily detectable C≡C stretching band in the infrared, there is an intense band at 2211 cm^{-1} in the Raman spectrum, which was not available to us in the earlier work, and a thick film infrared spectrum does show a weak band at 2220 cm^{-1}. Second is that the permanganate–periodate oxidation method of von Rudolf[3,4] has been found unreliable in our hands for the detection of acetic acid product, since blank reactions with the solvent, *tert*-butyl alcohol or pyridine, give GLC peaks with the retention time of acetic acid.

More positive evidence for **3** has also been gathered. The ^{13}C NMR spectrum shows four olefinic carbons at 109.5, 128.5, 142.1, and 146.5 ppm from Me_4Si, with splitting in the off-resonance decoupled spectrum showing one proton on the carbon at 142.1 ppm and two protons on the carbon at 109.5 ppm. The spectrum shows two signals in the acetylenic region[5–7] at 80.3 and 95.5 ppm, neither being split by off-resonance decoupling.

Irradiation of the dimer in ether solution with ultraviolet light converted it to an isomer, as shown by mass spectrometry and analysis. The structure of the isomer will not be assigned here, but its spectroscopic properties bear significantly upon the structure of its progenitor.[8] Loss of the conjugated unsaturation is shown by the disappearance of the UV band at 227 nm, there being only weak end absorption in the photoproduct. The ^{13}C NMR spectrum of the photoisomer shows loss of the two olefinic carbons at 128.5 and 142.1 ppm. The acetylenic carbons appear still as bands at 81.7 and 87.2 ppm. The Raman spectrum confirms the existence of the acetylenic group at 2222 cm^{-1} and shows disappearance of a C=C stretching band at 1620 cm^{-1}, present before irradiation. The infrared spectrum shows acetylenic absorption at 2241 cm^{-1}, and with a band at 1660 cm^{-1} suggests that the terminal methylene group (which appeared at 1650 cm^{-1} in the cyclohexyne dimer[1]) was unaffected by irradiation. The ^{1}H NMR spectrum shows a terminal methylene group still present at δ 4.69 (at δ 4.65 before irradiation[1]) but the single olefinic peak at δ 5.54 in the dimer is missing in its photoisomer.

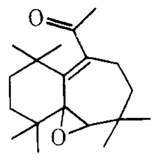
The ^{13}C NMR spectra of the dimer and the photoisomer strongly suggest that the isopropenyl group[1] is remote from the site of structural change, since the chemical shifts assigned to the three carbons of that group are essentially unchanged (22.7, 109.5, and 146.5 ppm in the dimer; 22.7, 109.3, and 146.9 ppm in the photoisomer). This leaves a conjugated enyne as the only plausible chromophore for the UV absorption in the dimer at 227 nm. Conjugated enynes generally possess UV absorptions in the 225–230-nm region.[9]

To summarize the structural requirements for the cyclohexyne dimer as reported here and previously,[1] it contains a conjugated enyne with the double bond trisubstituted, an isopropenyl group not conjugated with the other unsaturation present, three pairs of methyl groups with three different chemical shifts (^{1}NMR), none of the three showing spin–spin splitting, one group $-CH_2CH_2-$ which appears as a complex pair of multiplets at δ 1.8–2.4 and 1.2–1.7, and one group $-CH_2CH_2-$ which appears as a singlet at δ 1.46. Also, these groups must be so arranged as to give $\alpha,\alpha,\alpha',\alpha'$-tetramethyladipic acid upon oxidation with permanganate–periodate. Only structure **3** seems plausibly to meet all of these requirements. Structure **4** is a formal possibility, but would not be expected to have the observed stability.



4

An interesting ozonolysis product of the dimer was previously assigned structure **5**, in agreement with its spectroscopic properties, and reasonably formed from structure **2**.



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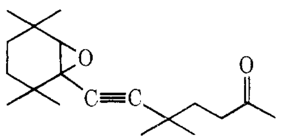
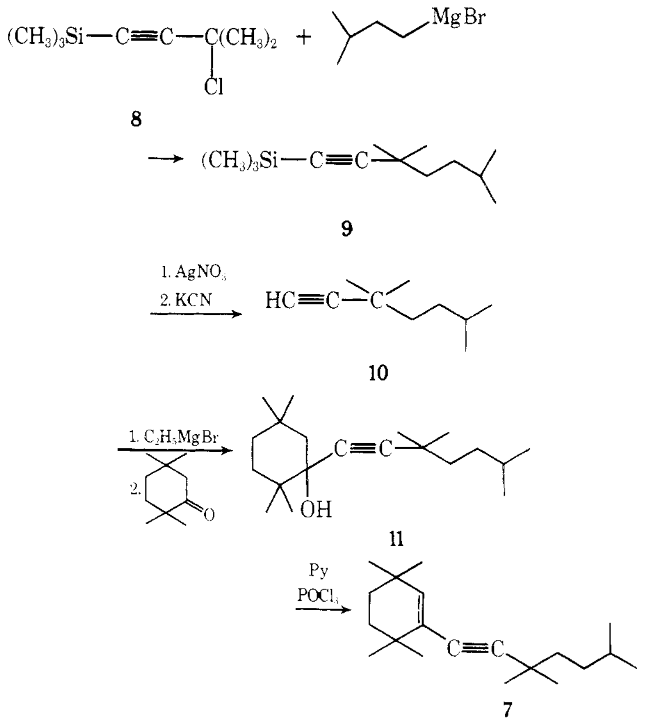


6

The ozonolysis product may now be assigned structure **6**, which seems equally satisfactory in relation to the spectroscopic data. The infrared spectrum of this product does contain a weak band at about 2235 cm^{-1} attributable to the triple bond but previously discounted. While it may be surprising that the triple bond survived ozonolysis, it has been observed by others that in compounds with both double and triple bonds, ozone attacks the double bonds preferentially.[10]

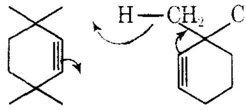
Synthetic approaches to **3** were investigated to further confirm the structure. All attempts were unsuccessful, but a related compound, **7**, was prepared by the route outlined in Scheme I.

Scheme I



Compound **7** had Raman bands at 2200 and 1611 cm^{-1}, corresponding to those at 2211 and 1620 cm^{-1} in **3**. The most convincing case for the structures of both **3** and **7**, however, is found in the comparison of their ^{1}H NMR spectra. The protons remote from the isopropenyl (or isopropyl) group in the two molecules display nearly identical signals, with singlets at δ 5.63 (1 H), 1.41 (4 H), 1.20 (6 H), 1.08 (6 H), and 0.97 (6 H) in **7** corresponding respectively to those at δ 5.54, 1.46, 1.23, 1.05, and 0.97 in **3**. The isopropyl group in **7** appears as a doublet (6 H, J = 6 Hz) at δ 0.87, while the peaks at δ 1.75 and 4.64 in **3**, attributed to the isopropenyl group, are missing in **7**.

The reassignment of the tetramethylcyclohexyne dimer as **3** rather than **2** reopens the question of mechanism of dimerization. While a cyclobutadiene intermediate is still a formal



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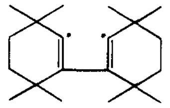


13

possibility, there is no evidence to support it. Rather, a concerted [$_\pi 2 + _\sigma 4$] mechanism (**12**) or a two-step process through biradical **13** seems a simpler explanation. The reaction appears to be unprecedented for acetylenes, strained or otherwise. It may be viewed as further indication of the reluctance to form cyclobutadienes when other pathways, with or without precedent, are available.

Experimental Section[11]

1-(3′,3′,6′,6′-Tetramethyl-1′-cyclohexenyl)-3,3,6-trimethylhept-1-yn-6-ene (3). An improved procedure for generation of 3,3,6,6-tetramethylcyclohexyne dimer uses active magnesium[12] in place of sodium.[1] The advantage of magnesium is that none of the previously described dihydro dimer[1] is formed. The magnesium was prepared by reaction of 12.7 g (0.134 mol) of anhydrous magnesium chloride with 9.8 g (0.251 g-atom) of potassium in 100 ml of refluxing tetrahydrofuran under argon. Magnesium was subsequently transferred from the cooled reaction mixture with a syringe.

To a mixture of approximately 10 mg-atoms of magnesium in 40 ml of tetrahydrofuran, a solution estimated by GLC analysis to contain 0.479 g (1.62 mmol) of 1,2-dibromo-3,3,6,6-tetramethylcyclohexene and 0.043 g (0.17 mmol) of 1-bromo-2-chloro-3,3,6,6-tetramethylcyclohexene in 10 ml of tetrahydrofuran was added; and the resulting mixture was stirred for 11 h at room temperature. The reaction mixture was then filtered to remove the unreacted magnesium, and the filtrate was poured into 100 ml of water and extracted twice with diethyl ether. The combined ether extracts were dried over $MgSO_4$ for 12 h. The $MgSO_4$ was removed by filtration. Concentration on a rotary evaporator followed by concentration in vacuo for 2 h at 1.0 mm gave 0.167 g of a yellow oil whose NMR spectrum and infrared spectrum were indistinguishable from those reported for **3**[1] and which was shown by GLC analysis on a column of 10% Ucon 550X on Chromosorb A at 200 °C, flow rate of 100 ml/min, to contain only hydrocarbon **3** (yield 0.61 mmol, 68%). Rinsing the unreacted magnesium several times with diethyl ether gave higher yields (up to 90%) of **3**.

The Raman spectrum possessed intense bands at 2920, 2211, and 1620 cm^{-1}, with numerous weak bands including one at 1650 cm^{-1}. The ^{13}C NMR spectrum in $CDCl_3$ solution included three methyl signals (quartets with off-resonance decoupling) at 22.7, 28.55, and 29.46 ppm downfield from tetramethylsilane. There were four aliphatic CH_2 signals (triplets with off-resonance decoupling) at 33.60, 33.92, 34.72, and 41.91 ppm; one olefinic $=CH_2$ at 109.45 ppm; one olefinic carbon split to a doublet with off-resonance decoupling at 142.05 ppm; and seven signals for carbons not bonded to hydrogens at 29.12, 31.63, and 32.60 ppm (quaternary), 80.25 and 95.52 ppm (acetylenic), and 128.46 and 146.51 ppm (olefinic).

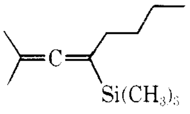
1-Trimethylsilyl-3-methyl-3-chloro-1-butyne (8). A mixture of 3.5 g (22.4 mmol) of 1-trimethylsilyl-3-methylbut-1-yn-3-ol and 14 g of concentrated hydrochloric acid was stirred for 30 min, diluted with 25 ml of water, and extracted with pentane. The pentane extract was dried over $MgSO_4$, and then concentrated to yield 3.1 g of a light yellow oil. Chromatography of this oil on 50 g of silica gel (pentane eluent) yielded 2.4 g of **8** (13.8 mmol, 62%), 98% pure by GLC. The NMR spectrum of this oil contained only two singlets at δ 0.18 (9 H) and 1.82 (6 H). The IR spectrum possessed absorptions at 2180 cm^{-1} (medium, sharp) and 860 cm^{-1} (strong, broad) among others. Distillation of the product from a similar preparation gave a colorless liquid, bp 54.5–55 °C (17 mm) [lit.[13] bp 49 °C (14 mm)] with $n^{24}D$ 1.4424 (lit.[13] $n^{20}D$ 1.4415).

1-Trimethylsilyl-3,3,6-trimethyl-1-heptyne (9). A solution of 3-methylbutylmagnesium bromide was prepared from 6.4 g (267 mg-atoms) of magnesium turnings and 40 g (265 mmol) of 3-methyl-1-bromobutane in 100 ml of diethyl ether. A solution of 3.4 g (19.5 mmol) of 1-trimethylsilyl-3-methyl-3-chloro-1-butyne (**8**) in 5 ml of diethyl ether was added over a period of 45 min to 76 ml of the solution of 3-methylbutylmagnesium bromide. The resulting mixture was stirred overnight under argon at room temperature and then heated under reflux for 4 h. The reaction mixture was then cooled with an ice bath, poured into 200 ml of 1 M HCl, and extracted three times with diethyl ether. The combined ether extracts were dried over $MgSO_4$ and concentrated on a rotary evaporator to yield 4 g of a yellow oil which was found by GLC analysis to contain at least seven components, in addition to a small amount of solvent. A small amount (0.28 g) of a white solid, mp 117–123 °C, was also isolated but not examined in detail.

Two of the components of the reaction mixture which comprised ca. 41% (estimated by GLC peak area analysis) of the crude product were isolated by GLC. The component in excess was found to have an IR spectrum with absorption at 2180 (medium, sharp) and 850 cm^{-1} (strong, broad) among others and an NMR spectrum with absorptions at δ 0.14 (s, 9 H), 0.89 (doublet, J = 5 Hz, 6 H), 1.16 (s, 6 H), and 2.15–1.20 (complex signal, 5 H), and was assigned the structure **9**.

Anal. Calcd for $C_{13}H_{26}Si$: C, 74.20; H, 12.45. Found: C, 74.30; H, 12.42.

The other component had an IR spectrum with absorptions at 1950 (medium, sharp) and 840 cm^{-1} (strong, broad) among others and an NMR spectrum with absorptions at δ 0.04 (s, 9 H), 0.88 (d, J = 5.5 Hz, 6 H), 1.61 (s, 6 H), 2.10–1.70 (m, 2 H), and 1.50–1.00 (m, 3 H), and was assigned structure **14**. The ratio of **9**:**14** was 1.27:1.00 as judged by the areas of the two GLC peaks.



14

3,3,6-Trimethyl-1-heptyne (10). A solution of 1.0 g (5.9 mmol) of silver nitrate in 3 ml of water and 3 ml of 95% ethanol was added dropwise to a solution of 0.17 g (0.81 mmol) of **9** in 6 ml of absolute ethanol. A white, cloudy mixture resulted which was stirred at room temperature for 40 min. A solution of 2 g (30.8 mmol) of potassium cyanide in 4 ml of water was then added slowly. The resulting solution was extracted with 50 ml of pentane, and the extract was dried over $MgSO_4$. The bulk of the pentane was distilled off (distillate bp up to 40 °C) and the residue (0.51 g) was examined for absorptions in its IR spectrum to confirm the presence of a terminal acetylene in the product mixture. A sharp absorption at 3300 cm^{-1} confirmed the presence of a terminal triple bond,[14] and no absorption which would indicate the presence of ethanol (i.e., a hydroxyl absorption at ca. 3400 cm^{-1}) could be detected in the same spectrum, so this material was used for the next reaction without purification. GLC analysis of this oil showed the presence of only one component in addition to pentane.

1-(3′,3′,6′,6′-Tetramethyl-1′-cyclohexenyl)-3,3,6-trimethyl-1-heptyne (7). A solution of ethylmagnesium bromide in diethyl ether was prepared from 21 g (0.202 mol) of ethyl bromide and 4.8 g (0.20 g-atom) of magnesium in 100 ml of diethyl ether. Titration of a hydrolyzed aliquot of this solution immediately prior to its use showed it to be 1.90 M. The crude product of the previous reaction was purified by chromatography on 20 g of silica gel; elution with 80 ml of pentane and concentration yielded 0.5 g of a presumed mixture of pentane and **10**. A solution of this material in 2 ml of diethyl ether was added under nitrogen dropwise to 2 ml (3.8 mmol) of the ethylmagnesium bromide solution. The resulting mixture was stirred for 5 h and then cooled with an ice bath. To the cooled reaction mixture, a solution of 0.55 g (3.57 mmol) of 2,2,5,5-tetramethylcyclohexanone[1] in 2 ml of diethyl ether was added over a period of 5 min. The ice bath was allowed to warm to room temperature, and the reaction mixture was stirred overnight (ca. 13 h). The reaction mixture was then treated with 20 ml of saturated ammonium chloride solution and extracted twice with diethyl ether. The combined ether extracts were dried over $MgSO_4$ and concentrated to yield 0.70 g of a light yellow oil. The IR spectrum of this oil possessed bands at 3450 and 1705 cm^{-1} indicating the presence of some alcohol and unreacted ketone in the crude product. No band was detected at 3300 cm^{-1}, indicating the absence of any unreacted **10**.

The above oil was mixed with 1 ml of pyridine and cooled with an ice bath. To this mixture was added a solution of 1 ml of phosphorus oxychloride in 2.5 ml of pyridine. The resulting mixture was stirred and cooled for 30 min and then heated to 90 °C for 60 min. The reaction mixture was then cooled, poured onto ice, and extracted twice with pentane. The combined pentane extracts were dried over $MgSO_4$ and concentrated to yield 0.65 g of a light yellow oil. The crude product was then chromatographed on 40 g of alumina (Woelm, activity I); elution with 250 ml of pentane yielded 39.1 mg of a colorless oil. Elution with 250 ml of 1:1 pentane/diethyl ether yielded 0.1 g (18%) of unreacted ketone as identified by its IR spectrum. Elution with 400 ml of diethyl ether yielded a small additional amount of unreacted ketone.

GLC analysis of the oil eluted with pentane indicated the presence of a component with a retention time close to that of **3**. This component was isolated by GLC (yield 9 mg). Its IR spectrum possessed absorptions of medium intensity at 2920, 1460, 1380, 1365, and 872 cm^{-1}, in addition to other weak absorptions. A 220-MHz NMR spectrum showed signals at δ 5.63 (s, 1 H), 1.41 (s, 4 H, superimposed on a multiplet from δ 1.68 to 1.27, 5 H), 1.20 (s, 6 H), 1.08 (s, 6 H), 0.97 (s, 6 H), and 0.87 (doublet, $J = 6$ Hz, 6 H). The Raman spectrum possessed intense bands at 2200 and 1611 cm^{-1} in addition to other weak bands.

Anal. Calcd for $C_{20}H_{34}$: C, 87.51; H, 12.49. Found: C, 87.93; H, 12.47.

The mass spectrum of the oil eluted with pentane possessed peaks at *m/e* 274 (12.98), 259 (10.20), 205 (22.36), and 203 (20.51) (calculated mass of parent ion of **7**, 274). In addition, a peak at *m/e* 166 (4.11%) was present indicating the presence of 3,3,6,6-tetramethyl-1-ethylcyclohexene ($C_{12}H_{22}$, mol wt 166) in this oil. In the 10-eV mass spectrum, the intensities of the *m/e* 274 and 166 peaks increased to 44.35 and 27.01, respectively.

Registry No.—**1**, 37494-11-4; **3**, 59129-90-7; **6**, 61075-98-7; **7**, 61075-99-8; **8**, 18387-63-8; **9**, 61076-00-4; **10**, 61076-01-5; **11**, 61076-02-6; **14**, 61104-52-7; 1-trimethylsilyl-3-methylbut-1-yn-3-ol, 5272-33-2; 3-methyl-1-bromobutane, 107-82-4; 2,2,5,5-tetramethylcyclohexanone, 15189-14-7; 3,3,6,6-tetramethyl-1-ethylcyclohexene, 61076-03-7.

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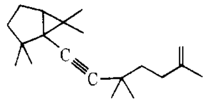
(8) One possible structure consistent with all of the observations is the following:



This and other possibilities are discussed in the Ph.D. Dissertation of C. N. Bush, University of Illinois, 1975.

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Notes

Optical Rotations and Absolute Configurations of 3-*tert*-Butylcyclohexene and of *trans*-3-*tert*-Butyl-6-methylcyclohexene

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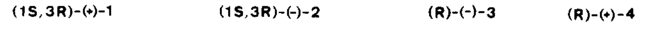
In connection with our interest in the asymmetric bromination of alkenes,[1] the chiroptical properties of some alkyl substituted cyclohexene derivatives were needed. In this paper we report the hitherto unknown relationship between optical rotations and absolute configurations of 3-*tert*-butylcyclohexene and of *trans*-3-*tert*-butyl-6-methylcyclohexene. The optical rotation of 4-*tert*-butylcyclohexene[1d] has also been revised.

(*R*)-(−)-3-*tert*-Butylcyclohexene (**3**) of high optical purity was obtained through an improvement of the route already followed[1d] for the preparation of the optically active 4-*tert*-butyl isomer (**4**), consisting in the dehydrotosylation of the tosylate (**2**) of (+)-*cis*-3-*tert*-butylcyclohexanol (**1**) (Scheme I). The (1*S*,3*R*) configuration had been firmly established[2] for (+)-**1** by the ORD curve of (+)-3-*tert*-butylcyclohexanone arising from its oxidation. A value of $[\alpha]^{30}\mathrm{D}$ +7.9° has been reported[2] for **1** obtained by resolution of the acid phthalate through the brucine salt and a very high optical purity was suggested by the obtainment of (+)-3-*tert*-butylcyclohexanone with the same optical rotation ($[\alpha]^{24.5}\mathrm{D}$ +25°) starting both from (+)-**1** and the diastereoisomeric (+)-*trans*-3-*tert*-butylcyclohexanol, which had been independently resolved through its 3β-acetoxy-Δ^5-etienate.[2] In our hands the resolution of the acid phthalate of (±)-**1** with brucine led to both enantiomeric alcohols, the dextrorotatory one having higher optical purity ($[\alpha]^{25}\mathrm{D}$ +8.9 and −8.1°). Treatment of both enantiomers with tosyl chloride afforded, after crystallization, the corresponding tosylates with very close absolute values of optical rotation ($[\alpha]^{25}\mathrm{D}$ −23.1 and +22.7°, respectively). Heating of (−)-**2** in quinoline gave a mixture of 3- and 4-*tert*-butylcyclohexene (**3** and **4**) in a 38:62 ratio. After chromatographic separation on a $AgNO_3/SiO_2$ column, the two olefins had the following rotations: (*R*)-**3**, $[\alpha]^{25}\mathrm{D}$ −6.2°; (*R*)-**4**, $[\alpha]^{25}\mathrm{D}$ +82.8°. The latter value is somewhat higher than the rough estimate of the maximum optical rotation previously made for **4**[1d] starting from a sample of (+)-**1** of lower optical purity and based on the maximum rotation ($[\alpha]^{30}\mathrm{D}$ +7.9°) reported at that time for **1**.

Scheme I



(3*R*,6*R*)-(+)-*trans*-3-*tert*-Butyl-6-methylcyclohexene (**9**), $[\alpha]^{25}\mathrm{D}$ +117.6 was obtained from optically pure natural (+)-pulegone (**5**) according to Scheme II.

The addition of methylmagnesium iodide to (+)-**5** in the presence of cuprous chloride, which acts as catalyst for 1,4 addition,[3] gave, as reported,[4] a 7:3 mixture of ketones **6** and **7**. The major diastereoisomer **6** was separated as the tos-