A New Synthesis of 1,5-Di-*tert*-butyl-1,3-cyclopentadiene by Dehydration of an Epoxide and Characterization of its Diels−Alder Dimer

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Introduction

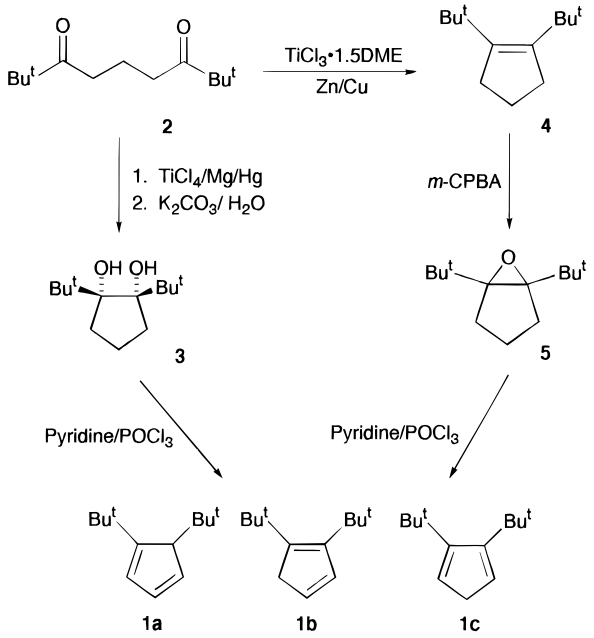
Our interest in the preparation of cyclopentadienes and their anions arose from a desire to study the conformational effects of sterically demanding groups in organometallic complexes containing vicinally disubstituted cyclopentadienyl ligands.[1,2] As a result, we developed the route to 1,5-di-*tert*-butyl-1,3-cyclopentadiene (**1a**) from diketone **2** via diol **3**, as shown in Scheme 1.[1] Isomer **1a** was identified as the principal valence tautomer in solution, although traces of **1b** and **1c** were observable by NMR spectroscopy. Deprotonation to give the corresponding 1,2-di-*tert*-butylcyclopentadienyl anion was facile and provided a route into the organometallic chemistry of this new ligand.[1] There are a number of problems with the ring-forming step in this synthetic scheme: this reaction is exothermic and difficult to control on a large scale; it affords **3** from **2** in only 41% yield, and it requires use of a magnesium amalgam with consequent generation of mercury-containing wastes. Increasingly prohibitive waste disposal costs, the practical necessity of a larger scale, higher yield synthesis, and the desire to achieve a more environmentally benign approach led us to investigate alternative routes.

Olefins can be prepared by the dehydration of alcohols using $POCl_3$ in pyridine,[3,4] a variation of which we have previously used to prepare **1** from the 1,2-diol **3**.[1] While the *deoxygenation* of an epoxide to an olefin is a well known reaction,[5] to the best of our knowledge the net *dehydration* of an epoxide to a diene has apparently not been reported previously. Here we report the first example of this transformation.

Results and Discussion

Improved Synthesis of Di-*tert*-butyl-1,3-cyclopentadiene (1). The synthesis of 1,2-di-*tert*-butylcyclopentene, **4**, was carried out in 88% yield by the reaction of 2,2,8,8-tetramethylnonane-3,7-dione (**2**) under McMurry coupling conditions, using $TiCl_3$/Zn/Cu (Scheme 1).[6] Positive identification of **4** was achieved *via* ^{1}H, ^{13}C, and DEPT NMR spectra. A triplet (δ_H 2.49) is observed for the four symmetry related ring protons at C_3 and C_5 while a quintet (δ_H 1.50) is observed for the two protons on C_4. The *tert*-butyl proton resonances are observed at δ_H 1.19.

Scheme 1



Attempts to generate the *cis*−diol, **3** by dihydroxylation of **4** with a catalytic amount of OsO_4, using conditions described in the literature,[7−11] were unsuccessful, and only starting olefin was recovered. However, olefin **4** is easily epoxidized by *m*-chloroperoxybenzoic acid at −78 °C to give 1,2-di-*tert*-butylcyclopentene oxide, **5**, in 88% yield. ^{1}H, ^{13}C, and DEPT NMR spectra were used to make unambiguous peaks assignments for **5**. The spectra closely resemble those of **4** except for the characteristic upfield shift of the resonance of the epoxide carbon atoms in the ^{13}C NMR, to 77.8 ppm from the characteristic olefinic resonance of 141.4 ppm in **4**. Opening of the epoxide under acidic conditions leads to the *trans*-diol which appears to be resistant to dehydration, as opposed to the *cis*-diol **3** formed by the $TiCl_4$/Hg/Mg system.[1]

Finally, direct dehydration of epoxide **5** was attempted. Using conditions identical to those reported for the $POCl_3$ dehydration of **3**,[1] and other tertiary alcohols,[3,12,13] corresponding dehydration of epoxide **5** affords an identical tautomeric mixture of cyclopentadienes **1** in 64% yield. The overall yield of **1** in three steps from **2** is 48%; the corresponding overall yield of **1** from **2** in two steps[1] from diol **3** is 33%. This procedure represents an improvement in overall yield without requiring mercury.

Diels−Alder Dimerization of 1,5-Di-*tert*-butyl-1,3-cyclopentadiene (1a). The Diels−Alder dimerization of 1,3-cyclopentadienes is a well understood reaction.[14−17] While the Diels−Alder dimerization of the parent 1,3-

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Table 1. NMR Spectral Data for 6 in $CDCl_3$[a]

position[b]	^{13}C (δ in ppm)	^{1}H (δ in ppm)	J (Hz)	COSY[c]
1	59.8	1.80 (dd)	2	H_4
			2	H_5
				H_3
2	156.6			
3	133.4	5.45 (br s)		H_1
				H_4
4	55.9	3.17 (ddd)	1	H_3
			2	H_1
			8	H_5
5	46.4	2.36 (ddd)	2	H_1
			4	H_6
			8	H_4
6	51.0	2.71 (dd)	3	H_7
			4	H_5
7	128.3	5.68 (dd)	3	H_6
			6	H_8
8	133.5	5.56 (d)	6	H_7
9	69.1			
10	75.5	1.58 (s)		

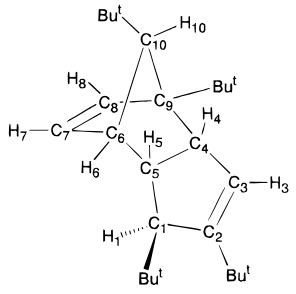
[a] Data for the *tert*-butyl groups are not included. [b] Position numbers as shown in line drawing for **6**. [c] This column lists those protons for which COSY reveals couplings to the proton listed in the position column.

cyclopentadiene proceeds at room temperature to give *endo*−dicyclopentadiene, there are analogues which do not dimerize at all, or do so only under nonstandard conditions. For example, monomeric pentamethylcyclopentadiene[18] and 1,3,5-tri-*tert*-butylcyclopentadiene[19] are reported to exist indefinitely as colorless to light yellow oils under ambient conditions. Sitzmann and co-workers have demonstrated the acid-catalyzed dimerization of a mixture of 1,4- and 1,3-di-*tert*-butyl-1,3-cyclopentadiene to give (*E*,*E*)-3,3′,5,5′-tetra-*tert*-butyl-4,5,4′,5′-tetrahydro-1,1′-bis(cyclopentadienylidene), but this dimer is not the Diels−Alder dimerization product.[20] Venier and Casserly have suggested that only the 2,5-isomer of di-*tert*-butyl-1,3-cyclopentadiene undergoes Diels−Alder dimerization, but only upon standing at room temperature over several days.[21]

In contrast to these reports, the neat yellow oil **1** solidifies in about 1 h at room temperature with quantitative conversion to a white solid. NMR spectroscopy indicates that this product is a single compound. It can be recrystallized from hot hexanes, albeit in low yield. While single crystals suitable for X-ray diffraction could not be obtained, the structure of this material was identified as that of the Diels−Alder dimer **6** of 1,5-di-*tert*-butyl-1,3-cyclopentadiene (**1a**) using NMR spectroscopy. ^{1}H, ^{13}C, and COSY NMR results are shown in Table 1.

The ^{1}H NMR spectrum of **6** consists of eight resonances, each integrating for one proton, and four *tert*-butyl resonances, each integrating for 9 protons. The largest observed $^{1}H-^{1}H$ coupling is 8 Hz, indicating that there is no CH_2 group present in a bridging position. Only three resonances are observed in the olefinic region of the spectrum, revealing that one olefinic carbon atom bears a *tert*-butyl group. The $^{13}C\{^{1}H\}$ NMR spectrum of **6** shows ten resonances for the carbon atoms of the dimer skeleton, but only three resonances for the *tert*-butyl methyl carbon atoms and three resonances for the corresponding quaternary carbon atoms. The $^{1}H-^{13}C$ HETCOR spectrum demonstrates that the resonance at δ_C 29.72 actually corresponds to the superimposed peaks of two *tert*-butyl methyl groups, but the fourth quaternary carbon resonance could not be located. Four of the $^{13}C\{^{1}H\}$ peaks appear at low field (δ_C 128.3, 133.4, 133.5, and 156.5), consistent with the presence of two double bonds in the product; only three of these resonances correspond to CH groups. None of the ^{13}C resonances corresponds to a CH_2 group.

The absence of a CH_2 group clearly rules out any structure based on the Diels−Alder dimerization of cyclopentadiene tautomers **1b** or **1c**, either with themselves or with another tautomer. Consequently only the four isomers **6**−**9** resulting from *endo*-selective Diels−Alder dimerization of **1a** were considered. Initial assignment of the ^{1}H NMR resonances was made as follows: H_7 and H_8 are readily located at δ 5.68 and δ 5.56 since these are typical chemical shift values for norbornene-type olefinic protons (e.g. norbornene in $CDCl_3$; δ 5.98).[22] These resonances are coupled by 6 Hz, a value consistent with that observed for the olefinic hydrogens of norbornene[22] (J = 6 Hz) and *endo*-dicyclopentadiene.[23] Additional coupling (3 Hz) from the resonance at δ 2.71 to that at δ 5.68 is observed in the COSY spectrum. Consequently, these resonances are assigned as δ 5.56 (H_8), δ 5.68 (H_7), and δ 2.71 (H_6). The COSY spectrum reveals the coupling of H_6 to the resonance at δ 2.36 (H_5). Similarly H_5 is coupled (8 Hz) to the resonance at δ 3.17 (H_4); the analogous coupling constant in *endo*-dicyclopentadiene is 8.7 Hz.[23] The resonance at δ 1.80 is also coupled to H_5 by 2 Hz, and also to H_4 by 2 Hz, and is assigned to H_1. The resonance at δ 5.45 is a broad singlet, but the COSY spectrum shows coupling to H_4 and to H_1, identifying this as the resonance for H_3. By a process of elimination, the remaining singlet resonance at δ 1.58 was assigned to H_{10}.



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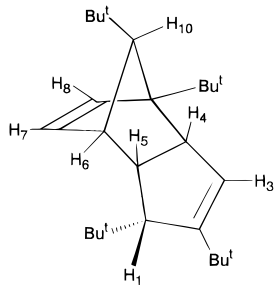

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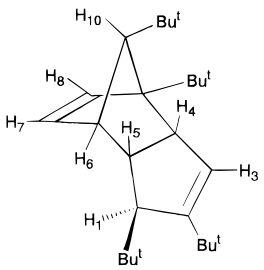

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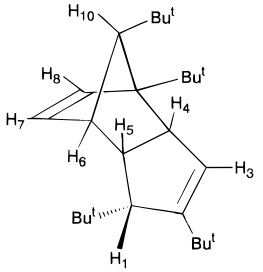

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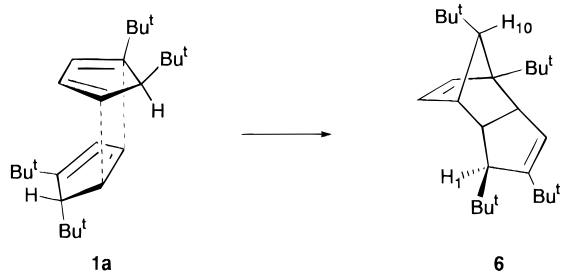
Scheme 2



While the major features of the structure can be deduced from the ^{1}H, ^{13}C, HETCOR, and COSY NMR data, the stereochemistries at C_{10} and C_1 were still unclear. Therefore, a rotating frame nuclear Overhauser enhancement (ROESY) experiment was used to determine the unidentified stereochemistry. Enhancement of H_{10} by H_4 and H_5 and the absence of enhancement of H_{10} by H_7 and H_8 clearly indicates that H_{10} resides on the same side of the bridge carbon as H_4 and H_5 and not on the side of H_7 and H_8. This observation also confirms the *endo* structure of the dimer and narrows the possibilities down to **6** and **7**.

Stereochemistry at C_1 was confirmed by examination of the ROESY spectrum and also by comparison of the observed coupling constants with those predicted by PCMODEL using a modified Karplus equation and with those observed for dicyclopentadiene.[23,24] The ROESY spectrum shows an enhancement of H_1 by H_7, indicating close proximity of the two atoms on the *endo* side of the molecule, and favoring structure **6**. Further support is found in the calculated and experimental coupling constants. The values of $^3J_{H5-H1}$ in **6** and **7** are calculated to be 2 and 7 Hz, respectively. Experimentally, $^3J_{H5-H1}$ is found to be 2 Hz, providing strong support for structure **6**.

Structure **6** is also that obtained in the most sterically favorable Diels−Alder transition state for reaction of two molecules of **1a**, with the dienophile component reacting selectively at the less substituted double bond as the two molecules of the cyclopentadiene present each other with their sterically less hindered faces, and with their *tert*-butyl groups arranged to minimize steric hindrance, as illustrated in Scheme 2. This transition state also requires homochiral recognition by **1a**.

Dimer **6** represents a convenient form in which to store cyclopentadiene **1a** since the retro-Diels−Alder dimer cracking of **6** to **1a** can easily be achieved in refluxing hexane or toluene. Monitoring of the cracking process by ^{1}H NMR shows that the production of small amounts of **1a** from **6** occurs very rapidly at temperatures just above room temperature. While the equilibrium lies far to the dimer side, addition of n-BuLi to the mixture readily deprotonates **1a** to give the lithium salt of 1,2-di-*tert*-butylcyclopentadienide[1] and drives the cracking reaction to completion.

Experimental Section

Unless otherwise noted, all reactions were performed in oven-dried glassware, using standard Schlenk techniques, under an atmosphere of nitrogen which had been deoxygenated over BASF catalyst and dried using Aquasorb. Diethyl ether (Et_2O), dimethoxyethane (DME), and tetrahydrofuran (THF) were distilled under nitrogen from sodium, potassium, or NaK benzophenone ketyl; dichloromethane and hexanes from CaH_2. 2,2,8,8-Tetramethylnonane-3,7-dione **2**,[1,25] 1,2-di-*tert*-butylcyclopentane-1,2-diol **3**,[1] and the Zn/Cu couple[6] were prepared by literature methods. Other reagents were purchased from commercial sources. NMR spectra were run on a 300 MHz instrument; chemical shifts are reported as ppm downfield of internal TMS and are referenced to the solvent peak. IR spectra are reported in cm^{-1}.

1,2-Di-*tert*-butylcyclopentene (4). To a mixture of $TiCl_3$·1.5DME (21.59 g, 74.59 mmol) and Zn/Cu couple (17.0 g) was added DME (300 mL) and the mixture heated to reflux for 1.5 h. To the resulting mixture was added 2,2,8,8-tetramethylnonane-3,7-dione (10.00 g, 47.10 mmol) in DME (50 mL) via cannula. Again, the mixture was heated to reflux for 92 h. The solution was then cooled to room temperature, and hexane (200 mL) was added. The mixture was filtered through a frit in air and the solvent removed on a rotary evaporator. The murky oil was then applied to a silica gel column (2 × 20 cm) packed in hexanes and the product eluted with hexanes (200 mL). Removal of the solvent gave **4** (7.20 g, 85%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 2.49 (t, $^3J_{HH}$ = 7.69 Hz, 4H), 1.50 (quint, $^3J_{HH}$ = 7.69 Hz, 2H), 1.19 (s, 18H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ_C 141.4, 39.1, 33.8, 32.5, 21.1. Anal. Calcd for $C_{13}H_{24}$: C, 86.59; H, 13.41. Found: C, 85.75; H, 13.63.

1,2-Di-*tert*-butylcyclopentene Oxide (5). *m*-Chloroperoxybenzoic acid (*m*-CPBA, 57−86%) (14.64 g) was suspended in CH_2Cl_2 (75 mL) and the mixture cooled to −78 °C. In a separate flask, **4** (10.20 g, 56.57 mmol) was dissolved in CH_2Cl_2 (25 mL) and the solution was cooled to −78 °C. The solution of **4** was then cannula transferred into the *m*-CPBA mixture, and the resulting mixture was stirred at −78 °C for 10 min before warming to room temperature. Stirring was continued for 2 h before removal of the solvent, under reduced pressure. The solid was extracted with hexanes (3 × 100 mL) with filtering through a frit, in air. The solvent was again removed under reduced pressure and the resulting cloudy oil applied to a silica gel column (2 × 20 cm) which was packed in hexanes. Elution with hexanes followed by solvent removal on a rotary evaporator yielded **5** (9.72 g, 88%) as a colorless oil. The oil obtained is sufficiently pure for subsequent reactions, but further purification may be achieved by distillation of the oil at 0.05 mmHg and 43−44 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.96 (m, 2H), 1.70 (m, 2H), 1.10 (s, 18H), 1.02 (m, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ_C 77.8, 33.0, 31.1, 29.9, 16.5. IR (neat, cm^{-1}): 1728 (C−O−C). Anal. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.33; H, 12.88.

Di-*tert*-butyl-1,3-cyclopentadiene (1). To a solution of **5** (9.72 g, 49.51 mmol) in pyridine (40 mL) was added $POCl_3$ (25.0 mL, 97.84 mmol). The resulting mixture was heated at 85 °C overnight. The dark brown solution was then cooled to ambient temperature, and hexanes (100 mL) were added. The resulting mixture was cooled in an ice bath, and distilled water (50 mL) was slowly added. With each small addition of water, a vigorous exothermic reaction ensued, and addition was continued only when the heat had subsided. After addition of the water was complete, stirring was continued until all the solid, formed during the water addition, had dissolved. The layers were separated, and the aqueous layer was extracted with hexanes (2 × 100 mL). The combined organic fractions were extracted with 20% HCl (3 × 150 mL) and saturated brine solution (3 × 50 mL) and then dried with $MgSO_4$ and filtered. Decolorizing charcoal was added to the orange solution and the mixture was heated to boiling and filtered hot. The solvent was removed under aspirator vacuum to give **1** (5.63 g, 64%) as a yellow oil. ^{1}H NMR for **1a** (300 MHz, C_6D_6): δ_H 6.32 (m, 3H), 2.89 (m, 1H), 1.22 (s, 9H), 1.04 (s, 9H); additional peaks for isomers **1b**,**c** included δ_H 2.95 (m), 2.54 (m), 1.36 (s), 1.33 (s), 1.23 (s). ^{13}C-{^{1}H} NMR for **1a** (75 MHz, C_6D_6): δ_C 159.9, 137.6, 130.6, 130.0, 64.6, 33.1, 32.6, 30.9; additional peaks for isomers **1b**,**c** included δ_C 34.5, 34.3, 33.3. Mass spectrum: 178 (M^+, 20), 163 (13), 121 ($C(CH_3)_3$, 16), 107 (73), 93 (9), 91 (98), 77 (49), 65 (28), 57 (100, base, $C(CH_3)_3$), 51 (17).

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Dimer (6) of 1,5-Di-*tert*-butyl-1,3-cyclopentadiene (1a). When neat **1** was allowed to stand at ambient temperature (<1 h), the yellow oil solidified to give **6** in quantitative yield, mp 67−68 °C. Assigned ^{1}H NMR and ^{13}C NMR data for the skeletal part of **6** are shown in Table 1. The *tert*-butyl groups appear as: ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.12, 1.06, 0.94, 0.93. ^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$): δ_C 35.0 ($C(CH_3)_3$), 33.5 ($C(CH_3)_3$), 32.9 ($C(CH_3)_3$), 32.5 ($C(CH_3)_3$), 32.3 ($C(CH_3)_3$), 29.7 (2 overlapping $C(CH_3)_3$). Note: One of the $C(CH_3)_3$ resonances is not observed. Mass spectrum: 356 (M^+, 0.2), 178 (17), 163 (15), 121 (8), 107 (27), 91 (8), 79 (3), 77 (3), 58 (7), 57 (100), 55 (6). An analytical sample was prepared by recrystallization from hexanes at −30 °C. Anal. Calcd for $C_{26}H_{44}$: C, 87.56; H, 12.44. Found: C, 87.52; H, 12.61.

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