

$N(CH_2)_4CH_2$ , 14446-67-4;  $CH_2=CHCH_2N(CH_3)C_6H_5$ , 6628-07-5; *n*-BuLi, 109-72-8; 1-octene, 111-66-0; cyclohexene, 110-83-8; cyclooctene, 931-88-4; 2-methyl-2-butene, 513-35-9; mesityl oxide, 141-79-7; phenylacetylene, 536-74-3; diphenylacetylene, 501-65-5; 1-octyne, 629-05-0; dodecanal, 112-54-9; *p*-methoxybenzaldehyde, 123-11-5; *p*-chlorobenzaldehyde, 104-88-1; 2-hexanal, 505-57-7; anthrone, 90-44-8; phenyllithium, 591-51-5; chlorotrimethylsilane, 75-77-4.

**Supplementary Material Available:** Electron micrographs showing the PS-Pd, PS-*b*-Pd, and PS-anthracene-Pd catalysts (Figure 1), a tabular comparison of the yields and reaction times for decarbonylation of aldehydes by PS-*b*-Pd, and 1% Pd/C (Table III), and a tabular summary of the effect of functional groups on polystyrene on hydrogenation of 1-octene by palladium/polystyrene catalysts (Table V) (3 pages). Ordering information is given on any current masthead page.

## Dienes as Possible Intermediates in the Catalytic Hydrogenation of Aromatic Hydrocarbons. 1. Dienes Derived from 1,4-Di-*tert*-butylbenzene and a Rhodium Catalyst<sup>1</sup>

James F. Outlaw, Jr., James Ray Cozort, Nissim Garti, and Samuel Siegel\*

Department of Chemistry, University of Arkansas, Fayetteville, Arkansas 72701

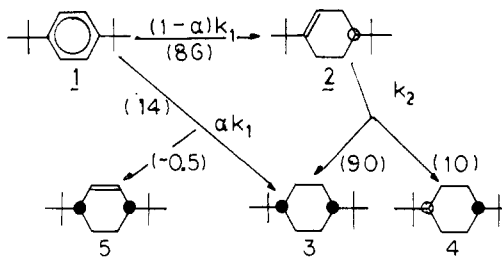
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The evolution of the products upon hydrogenating three diene derivatives of 1,4-di-*tert*-butylbenzene (1) is compared with the formation of 1,4-di-*tert*-butylcyclohexene (2) and *cis*- and *trans*-1,4-di-*tert*-butylcyclohexane (3 and 4) from 1 on an alumina-supported rhodium catalyst to determine which diene (or dienes), upon adsorption on the catalyst, best represents the structure of the intermediate formed in the rate-determining surface reaction of 1. Of the dienes 1,4-di-*tert*-butyl-1,4-cyclohexadiene (6), 1,4-di-*tert*-butyl-1,3-cyclohexadiene (7), and 2,5-di-*tert*-butyl-1,3-cyclohexadiene (8), the last exhibits best the properties expected if it forms the same adsorbed intermediate as does 1 at the same hydrogen pressure. Unlike the arene, however, the dienes do not yield the *cis*-saturated isomer 3 as an initial product at low hydrogen pressures. Instead, *cis*-3,6-di-*tert*-butylcyclohexene (5) is formed along with ene 2 and arene 1; the dienes tend to exclude the cycloalkenes from the catalyst, their effectiveness increasing in the order  $6 < 7 < 8$ . The result indicates that at low pressures little of arene 1 (less than 5%) is transformed directly to *cis*-1,4-di-*tert*-butylcyclohexane (3); instead enes 2 and 5 are produced initially, and because the concentration of the intermediate adsorbed dienes remains low during the hydrogenation of the arene, *cis* ene 5 is rapidly converted to 3 in the presence of the arene. At high hydrogen pressures, the *cis* arene 3 is an initial hydrogenation product of the dienes as it is of 1.

### Introduction

Stereochemistry has furnished useful probes into the mechanism of catalytic hydrogenation.<sup>2,3</sup> Comparison between the stereochemistry of the hydrogenation (over reduced platinum oxide) of the xylenes and the derived dimethylcyclohexenes indicated that the *trans*-dimethylcyclohexanes, which are formed from the xylenes, result from the addition of hydrogen to desorbed cyclohexene intermediates.<sup>4</sup> Such intermediates are detected easily if ruthenium or rhodium catalysts are used.<sup>5-7</sup> Particularly large amounts of substituted cyclohexenes are produced from arenes with bulky substituents, for example, 1,2- and 1,4-di-*tert*-butylbenzene or 2-*tert*-butylbenzoic acid; the *trans* products appear only after the intermediates begin to be reduced.<sup>8</sup>

Scheme I. Simplified Kinetic Scheme for the Formation of Alkene Intermediates in the Hydrogenation of 1,4-Di-*tert*-butylbenzene (1)<sup>12</sup>



The kinetics of hydrogenation of aromatic hydrocarbons indicates that dienic structures are formed in the rate-controlling surface reaction.<sup>9</sup> Although, in principle, dienes may desorb from the catalyst, the reported isolation of a cyclohexadiene from the catalytic hydrogenation of an aromatic hydrocarbon has not been confirmed.<sup>10,11</sup> The orientation of the addition of hydrogen to an adsorbed substituted arene, however, may be directed by the relative position and character of the substituents. And although dienes may not desorb from the catalyst, the dienic structure formed in the rate-controlling step may deter-

(1) (a) Presented in part at the 165th National Meeting of the American Chemical Society, Dallas, TX, April 1973. (b) Taken from the Ph.D. dissertations of James Outlaw, Jr., University of Arkansas (1971) and of James Ray Cozort, University of Arkansas (1975). (c) This research was supported by grants from the Petroleum Research Fund, administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of the said fund.

(2) Siegel, S. *Adv. Catal.* 1966, 16, 123-177.

(3) Burwell, R. L., Jr. *Intra-Sci. Chem. Rep.* 1972, 6, 135-149.

(4) Siegel, S.; Smith, G. V.; Dmuhovskiy, B.; Dubbel, D.; Halpern, W. *J. Am. Chem. Soc.* 1962, 84, 3136-3139.

(5) Hartog, F.; Zwietering, P. *J. Catal.* 1963, 2, 79-81.

(6) Siegel, S.; Ku, V. *Proc. Int. Congr. Catal.*, 3rd, 1964 1965, pp 1199-1209.

(7) Weitkamp, A. W. *Adv. Catal.* 1968, 18, 1-110.

(8) (a) Van Bekkum, H. *Proc. Int. Congr. Catal.*, 3rd, 1964 1965, p 1208. (b) Van de Graaf, B.; Van Bekkum, H.; Wepster, B. M. *Recl. Trav. Chim. Pays-Bas*, 1968, 87, 777-785. (c) Van Bekkum, H.; Buurmans, H. M. A.; Van Minnen-Pathuis, G.; Wepster, B. M. *Ibid.* 1969, 88, 779-794.

(9) Madden, W. F.; Kemball, C. *J. Chem. Soc.* 1961, 302-308.

(10) Cram, D. S.; Allinger, M. L. *J. Am. Chem. Soc.* 1955, 77, 6289-6294.

(11) The diene isolated by Cram and Allinger (ref 10) from the hydrogenation of [2.2]paracyclophane is one of three isomers that are formed. None appear to have the 1,4-cyclohexadienic structure proposed by Cram and Allinger. Unpublished research in this laboratory by R. L. Yates, D. L. Wharry, N. Garti, S.-T. Lin, and S. Siegel.

Table I. Initial Product Distributions (Mole Percent) in the Hydrogenation of Dienes Derived from 1,4-Di-*tert*-butylbenzene as a Function of Pressure

compd	<i>P</i> , atm	1,4-ene	3,6-ene	cis-ane	arene
arene	0.84	86	0.5	14	
6	0.42	35	5	0	60
	0.84	56	10	0	34
	1.04	56	10	0	34
	1.38	61	11	0	28
	68	60	6	32	2
7	0.84	55	30	0	15
	68	53	18	16	11
8	0.42	69	12	0	20
	0.84	70	12	0	19

mine the amount and structure of the subsequently produced cyclohexenes that do escape from the catalytic sites. Such a hypothesis might explain why, using a rhodium catalyst at about 1 atm of hydrogen, 1,3- and 1,4-di-*tert*-butylbenzene yield strikingly different maximum amounts of the intermediate cyclohexenes; the 1,3-arene yields no more than 1% or 2%, the 1,4-arene over 30 mol %.<sup>12</sup>

The goal of the present study was the determination of the initial product distributions obtained upon hydrogenating the various dienes that are dihydro derivatives of 1,3- and 1,4-di-*tert*-butylbenzene, respectively. If a particular diene yields an initial distribution of products that can be correlated with the initial distribution given by the parent arene, then one may presume that the diene yields on adsorption a species that is the same as that formed from the arene in its rate-controlling step.

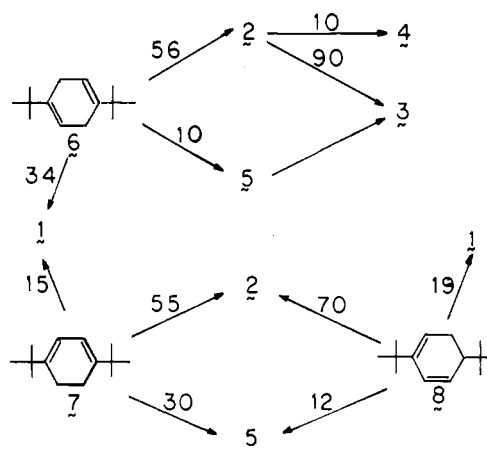
In this paper we describe the preparation of the dienes derived from 1,4-di-*tert*-butylbenzene (1) and the evolution of products from the dienes when a rhodium catalyst is used. Subsequent papers will describe experiments with dienes related to 1,3-di-*tert*-butylbenzene and compare the variation in the distribution of products from 1,4-di-*tert*-butyl-1,3-cyclohexadiene and 1,4-di-*tert*-butyl-1,4-cyclohexadiene as a function of different catalysts and the pressure of hydrogen.

## Results

**Hydrogenations.** Previously, we had shown that during the hydrogenation of 1,4-di-*tert*-butylbenzene (1) on a rhodium catalyst (5% on alumina), the formation and disappearance of the intermediate cyclohexene 2 could be represented well by Scheme I in which  $\alpha$  is the fraction of the arene that is transformed directly to *cis*-1,4-di-*tert*-butylcyclohexane (3) and  $(1 - \alpha)$  is the remainder that forms cyclohexene 2.<sup>12</sup> The parameters  $\alpha$  and  $k_2/k_1$ , the relative rates of conversion of 2 and 1, respectively, are functions of the pressure of hydrogen, and at 0.84 atm, the values that provided the best fit to the data obtained over the complete course of the reaction are 0.20 and 1.30 for  $\alpha$  and  $k_2/k_1$ .<sup>12</sup> In Scheme I, the parenthesized numbers next to the arrows indicate in percent the division of products among the competing paths as determined from the initial distribution of products formed from the indicated precursor (1, 2, 5, etc.).<sup>12</sup>

For comparison, the initial distribution of the products from the several dienes obtained at the same temperature and pressure but with a 0.5% rhodium catalyst are given in Scheme II and for other conditions in Table I. The dienes are much more reactive than the arene; the rate of conversion of diene 6 is over 20 times as great as that of arene 1 on the 0.5% rhodium catalyst at 30 °C.

Scheme II. Initial Distribution of Products Obtained from Dienic Derivatives of 1,4-Di-*tert*-butylbenzene<sup>a</sup>



<sup>a</sup> The numbers above the arrows that emanate from a particular diene represent the mole percent of that product at 0.84 atm, 30 °C, 0.5% Rh/Al<sub>2</sub>O<sub>3</sub>.

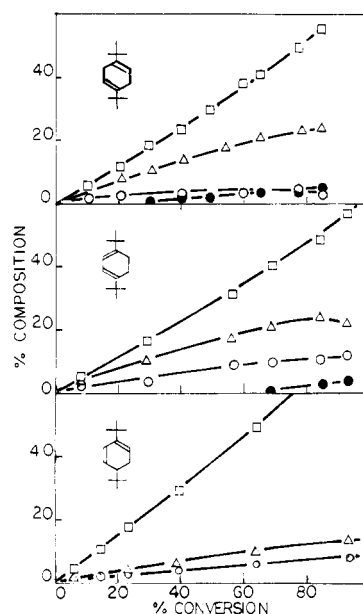


Figure 1. Product distributions (mole percent) in the hydrogenation of the dienic derivatives of 1,4-di-*tert*-butylbenzene catalyzed by 0.5% Rh/Al<sub>2</sub>O<sub>3</sub>, 30 °C, 0.84 atm: (□) 1,4-di-*tert*-butylcyclohexene (2), (○) *cis*-3,6-di-*tert*-butylcyclohexene (5), (Δ) 1,4-di-*tert*-butylbenzene (1), (●) *cis*-1,4-di-*tert*-butylcyclohexane (3).

When exposed to hydrogen (ca. 1 atm) and a rhodium catalyst, a portion of each diene reverts to 1,4-di-*tert*-butylbenzene (1), but the majority is transformed to a mixture of 1,4-di-*tert*-butylcyclohexene (2) and *cis*-3,6-di-*tert*-butylcyclohexene (5). Neither *cis*- nor *trans*-1,4-di-*tert*-butylcyclohexane (3 and 4) is formed initially. The *cis* isomer begins to appear from 1,4-di-*tert*-butyl-1,4-cyclohexadiene (6) at about 12% conversion, from 1,4-di-*tert*-butyl-1,3-cyclohexadiene (7) at about 70% conversion, and from 2,5-di-*tert*-butyl-1,3-cyclohexadiene (8) only after all of this diene has disappeared. The results are in keeping with the relative reactivity of the dienes in competition with one another, it being 1:3:30 for dienes 6, 7, and 8, respectively. Separately, the 1,3-diene 7 reacts at about twice the rate (2.2) as the 1,4-diene 6. Apparently, of the three dienes, the 1,3-diene 8 is the most strongly adsorbed because the *cis* ene 5 (produced from 8) does not react until virtually all of 8 has been transformed (Figure 1).<sup>13</sup> Clearly, *cis* ene 5 is the precursor of the saturated

(12) Siegel, S.; Outlaw, J. F., Jr.; Garti, N. *J. Catal.* 1979, 58, 370-382.

cis isomer 3 in these reductions.

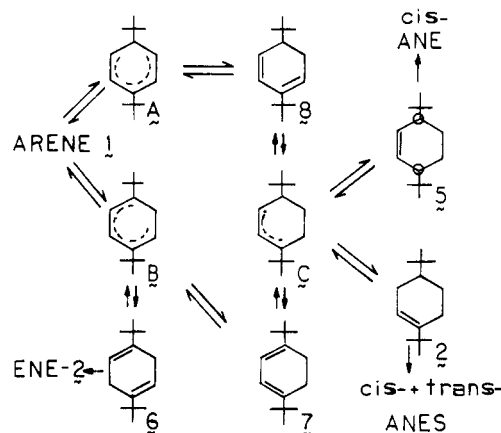
Lowering the hydrogen pressure (to 0.42 atm) increases the proportion of the diene that goes to the arene, but, except for diene 6, it does not affect the proportion of the isomeric alkenes that are formed (Table I). Increasing the pressure has a greater effect upon the distribution of products. When 1,4-di-*tert*-butyl-1,4-cyclohexadiene (6) is hydrogenated at 68 atm, the cis ane appears as an initial product (~30%); the 1,4-ene 2 and the cis 3,6-ene 5 also are initial products; however, the fraction of cyclohexenes that is the cis 3,6-ene is lowered to 6% (compared to 10% at 0.84 atm). Likewise at high pressure (68 atm), 1,4-di-*tert*-butyl-1,3-cyclohexadiene (7) yields initially the cis ane (ca. 16%) and *cis*-3,6-di-*tert*-butylcyclohexene (5) constitutes approximately 26% of the enes formed. As noted previously, 1,4-di-*tert*-butylbenzene yields a much larger fraction of *cis*-1,4-di-*tert*-butylcyclohexane as an initial product at high pressure (77% at 68 atm) than it does at about 1 atm (14%).<sup>12</sup>

**Preparation of Dienes.** The 1,4- and 1,3-cyclohexadienes 6 and 7 were obtained via the Birch reduction of 1,4-di-*tert*-butylbenzene followed by the ethylamide-catalyzed isomerization of 1,4-diene 6 to 1,3-diene 7.<sup>18</sup> After several fruitless attempts, the preparation of 2,5-di-*tert*-butyl-1,3-cyclohexadiene (8) was accomplished by dehydration of 1,4-di-*tert*-butyl-1,2-cyclohexanediol over pyridine treated alumina at ca. 300 °C.<sup>21,22</sup> The isomeric 2,5-di-*tert*-butylcyclohexanones were the principal products; however, the pure diene 8 was isolated in 3.5% yield. Attempts to convert the diol to a diacetate were not successful; apparently, the tertiary hydroxyl group is too hindered to be acetylated under conditions that have been reported to be effective for other tertiary alcohols.<sup>23</sup>

### Discussion

Of the three dienes studied, 2,5-di-*tert*-butyl-1,3-cyclohexadiene (8) is the most likely candidate to represent the structure of the complex formed upon the addition of the second hydrogen to 1,4-di-*tert*-butylbenzene, the apparent rate-controlling surface reaction in the hydrogenation of this arene. Of the three, it is the most reactive and the most strongly attracted to the catalyst, as judged by its ability to prevent the hydrogenation of *cis*-3,6-di-*tert*-butylcyclohexene (5) and its ability to limit the rate of reduction of 1,4-di-*tert*-butyl-1,3-cyclohexadiene (7) when in competition with the latter. The initial ratio (5.8) of the product cyclohexenes, 1,4-di-*tert*-butylcyclohexene (2) and *cis*-3,6-di-*tert*-butylcyclohexene (5), is close to the observed ratio of the 1,4-ene to the cis 1,4-ane (6.1) obtained upon hydrogenating arene 1 at the same pressure. As shown previously, the hydrogenation of the cis 3,6-ene proceeds readily in the presence of arene 1.<sup>12</sup> Accordingly, if formed as an intermediate during the hydrogenation of

Scheme III. Location of Principal Cyclohexadienyl (A and B) and Cyclohexenyl (C) Intermediates within the Reaction Network<sup>a</sup>



<sup>a</sup> Presumably, adsorbed species intervene between A, B, and C and the indicated desorbed hydrocarbons.

the arene, its concentration would be expected to remain low.

Clearly, 1,4-di-*tert*-butyl-1,3-cyclohexadiene (7) yields much too large a fraction of the cis 3,6-ene to form, on adsorption, the key intermediate in the hydrogenation of arene 1. Although the proportion of cyclohexenes 2 and 5 formed from 1,4-diene 6 might indicate that on adsorption it forms the intermediate of interest, the reversal of the elementary processes by which the diene is formed is required to produce the cis 3,6-ene and accordingly diene 6 cannot lie on the most direct path to both observed product olefins (Scheme III).

If the addition of hydrogen to 1,4-di-*tert*-butylbenzene on this rhodium catalyst proceeds via single hydrogen atom transfers to carbon, then the first two hydrogen atoms go to the C<sub>1</sub> and C<sub>2</sub> positions. The transfer of the first hydrogen atom to the position bearing a *tert*-butyl group would be aided by the relief of strain between the adsorbed arene and the reactive site. The structure of this intermediate would resemble that of the substituted cyclohexadienyl group in (*cis*-6-*tert*-butyl-1,3,5-trimethylcyclohexadienyl)iron(II) in which the *tert*-butyl group is attached to the saturated carbon atom of the ring.<sup>14</sup>

The above conclusion is related to those of Nieuwstad et al. to account for the relative reactivity and stereospecificity of hydrogenating (Pd/C) a series of 1-alkyl-naphthalenes.<sup>15</sup> They proposed that the first hydrogen atom was transferred to the alkyl-substituted position. In this instance bulky substituents promoted the saturation of the substituted ring and the relief of peri strain was presumed to furnish the main driving force for the observed regiospecificity.

Although the data indicates that adsorbed 2,5-di-*tert*-butyl-1,3-cyclohexadiene (8) is a probable intermediate in the hydrogenation of arene 1, there is no indication that the diene is released from the active site. The fact that none of the saturated product is formed directly from the diene at near atmospheric pressure supports the possibility that the desorbed cyclohexenes 2 and 5 are the immediate precursors of virtually all the saturated products from upon hydrogenating 1,4-di-*tert*-butylbenzene under the same conditions even though *cis*-1,4-di-*tert*-butylcyclohexane appears to be an initial product. At high hydrogen pressures, the situation is altered and a major fraction of the arene is converted to *cis*-1,4-di-*tert*-butylcyclohexane without passing through any desorbed intermediates. The dienes behave in a like manner.

(13) Although the relative reactivity of the dienes in competition is likely to correspond to their relative rates of adsorption, this order should reflect the relative strengths of interaction between the diene and the catalyst site because of the expected relationship between the rate and the equilibrium constants of such closely related reactions.

(14) Mathew, M.; Palenik, G. *J. Inorg. Chem.* **1972**, *11*, 2809-2812.

(15) Nieuwstad, Th. J.; Klapwijk, P.; Van Bekkum, H. *J. Catal.* **1973**, *29*, 404-411.

(16) Wolovsky, R. *J. Am. Chem. Soc.* **1965**, *87*, 3638-3644.

(17) Levy, R. L.; Murray, D. A.; Gesser, H. D.; Hougen, F. W. *Anal. Chem.* **1968**, *40*, 459-461.

(18) Burgstahler, A. W.; Chien, P.-L.; Abdel-Rahman, M. O. *J. Am. Chem. Soc.* **1964**, *86*, 5281-5290.

(19) Stolow, R. D.; Ward, J. A. *J. Org. Chem.* **1966**, *31*, 965-966.

(20) Wiberg, K. B.; Saageborth, K. A. *J. Am. Chem. Soc.*, **1957**, *79*, 2822-2824.

(21) Pines, H.; Haag, W. O. *J. Am. Chem. Soc.* **1960**, *82*, 2471-2483.

(22) Von Rudloff, E. *Can. J. Chem.* **1961**, *39*, 1860-1864.

(23) Steglich, W.; Hoefle, G. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 981.

The proportion of trans disubstituted cyclohexane that results from hydrogenating a disubstituted benzene is determined by the fraction that is converted to desorbed cyclohexenes and the stereochemistry of hydrogenation of the latter. The evidence indicates that the distribution and amounts of the olefinic intermediates formed is determined by the structure of the diene(s) formed in the rate-controlling step and the way the latter interacts with the catalyst and hydrogen.

### Experimental Section

**General Procedures.** A Varian A-60 spectrophotometer was used to obtain NMR spectra. Infrared spectra was recorded on a Perkin-Elmer Model 337 grating spectrophotometer and UV spectra on a Cary Model 14 spectrometer. Mass spectra were obtained at 80 eV on a Hitachi RMU-6E double-focusing mass spectrometer. Elemental analysis were performed by Micro-Tech Laboratories, Inc., Skokie, IL. All melting and boiling points are uncorrected.

**Chromatographic Techniques.** LC separations were done on a 90 cm × 20 mm column of 25% silver nitrate on basic alumina (Woelm's activity grade 1), using 95% petroleum ether (30–60 °C) and 5% benzene as eluent.<sup>16</sup> Preparative-scale GC separations were accomplished with a Varian Model 90-P chromatograph with a thermal conductivity detector. The columns used were (A) 13 ft × 1/4 in. 5% Apiezon L and (B) 10 ft × 3/8 in. 10% FFAP on 60/80 mesh Chromosorb W.

A Varian Model 204-B gas chromatograph equipped with a hydrogen flame detector was used for quantitative analysis. The measurement of the peak areas was accomplished by a Disc integrator attached to a Sargent Model SRG recorder and/or by a Varian Model 485 digital integrator. *tert*-Butylbenzene was added to the analytical samples as an internal standard. The column generally used was a 300 ft × 0.02 in. i.d. stainless steel capillary coated by the method of Levy et al.<sup>8b,17</sup> with purified Apiezon-L grease. At 104–107 °C and a carrier gas (N<sub>2</sub>) flow rate of 6.0 mL/min, the retention times relative to cyclohexane (9.0 min) were as follows: diene 8 (13.5), diene 7 (14.8), arene 1 (15.9), *cis* ene 5 (17.0), ene 2 (17.8), *cis* ane 3 (18.3), *trans* ane 4 (18.9), and diene 6 (20.0).

**Hydrogenations.** At hydrogen pressures of 1 or less, a semimicro apparatus that automatically maintained a predetermined constant pressure was used.<sup>12</sup> At pressures of 1–5 atm, the hydrogenations were performed in a Fischer-Porter aerosol reaction vessel (12-oz. size) that was fitted with a septum for sampling, attached to a rocker arm for agitation, and immersed in a constant-temperature bath. Reactions at higher pressure were conducted in a high-pressure stirred autoclave. The general procedures have been described previously.<sup>12</sup> The 0.5% rhodium on alumina (Engelhard Industries, Inc., Lot 10-368) was activated by heating for 24 h at 140 ± 5 °C in a stream of hydrogen. The heating chamber was cooled to room temperature under hydrogen and flushed with nitrogen before the catalyst was exposed to air. The 0.5% rhodium on alumina was obtained in the form of pellets and was converted to a fine powder by using a mortar and pestle.

Experiments performed at near 1 atm in the semimicro apparatus used 0.05–0.10 g of the diene, 4.0 mL of cyclohexane, and 0.025–0.075 g of the catalyst. Experiments conducted in the higher pressure apparatus used proportionately more reactant; solvent, and catalyst because of the greater volume of these reactors.<sup>12</sup>

**1,4-Di-*tert*-butyl-1,4-cyclohexadiene (6).** The procedure was based upon the reported reduction of *o*-di-*tert*-butylbenzene.<sup>18</sup> To 600 mL of ammonia, condensed directly from a cylinder, was added dropwise 4.0 g of 1 (0.021 mol) in 300 mL of tetrahydrofuran plus 300 mL of isopropyl alcohol. Lithium shot (3.8 g, 0.54 mol) was added with stirring, in several small portions.

The ensuing blue solution discharged its color after ca. 50 min. After we cautiously added 100 mL of methanol and allowed the ammonia to evaporate at room temperature, the resulting solution was taken up in 600 mL of water and extracted with low-boiling petroleum ether. The combined ether extracts were washed with water and dried (MgSO<sub>4</sub>). Evaporation of the ether gave white crystals composed of 6 (95%) along with a mixture of 1, 2, and 5. Recrystallization of the crude mixture from methanol reduced the total impurities to 2.8% (by GLC). The recrystallized mixture

was chromatographed over the 25% silver nitrate on basic alumina column. Arene 1 eluted first, followed by 2, 6, and 5. Diene 6 was colorless and pure (99%): mp 61–62 °C; NMR (CCl<sub>4</sub>) δ 1.1 (s, 18, *t*-Bu), 2.7 (m, 4, allylic), 5.4–5.5 (m, 2, vinyl); UV (C<sub>2</sub>H<sub>5</sub>OH) adsorption below 230 nm.

Anal. Calcd for C<sub>14</sub>H<sub>24</sub>: C, 87.42; H, 12.58. Found: C, 87.37; H, 12.81.

**1,4-Di-*tert*-butyl-1,3-cyclohexadiene (7).** The procedure was based upon the reported isomerization of 2,3-di-*tert*-butyl-1,4-cyclohexadiene to 1,6-di-*tert*-butyl-1,3-cyclohexadiene.<sup>18</sup> Diene 6 (0.66 g, 0.0034 mol) was added to a stirred solution of lithium ethylamide in ethylamine prepared by stirring lithium shot (0.273 g, 0.039 mol) in 120 mL of ethylamine until the blue color discharged. The solution was refluxed for 2 h after which the ethylamine was allowed to evaporate at room temperature. The resulting solid residue was taken up in water and extracted with low-boiling petroleum ether and the ether extract was dried over NaSO<sub>4</sub>. Evaporation of the ether afforded a white crystalline mixture (0.63 g) composed of 6 (80%) and 7 (20%). To increase the yield of 7, the 0.63-g mixture was subjected to the above procedure but with greater care to exclude moisture from the system. This resulted in a 89:11 crystalline mixture of 7 and 6, respectively. Preparative GLC using column A gave a white crystalline sample of 7 (99% by GLC): mp 39–40 °C; NMR (CCl<sub>4</sub>) δ 1.03 (s, 18, *t*-Bu), 2.03 (s, 4, allylic), 5.50 (s, 2, vinyl); UV max (C<sub>2</sub>H<sub>5</sub>OH) 260 nm (ε 4500).

Anal. Calcd for C<sub>14</sub>H<sub>24</sub>: C, 87.42; H, 12.58. Found: C, 87.35; H, 12.76.

***cis*-3,6-Di-*tert*-butylcyclohexene (5).** A mixture containing 5 (17.9%), 1 (6.1%), 2 (32.5%), 6 (20.2%), and 7 (23.3%) was obtained by partially reducing a 74:26 mixture of 7 and 6, respectively, in cyclohexane over 5% rhodium on alumina (30 °C, 0.84 atm of hydrogen). After removal of the catalyst by filtration, the mixture was concentrated and chromatographed over the 25% silver nitrate on alumina column. Fractions containing 7 and 5, which eluted together, were pooled and concentrated in vacuo. Preparative GLC of the concentrate on column A gave a sample of 5 (99% by GLC): NMR (CCl<sub>4</sub>) δ 0.88 (s, 18, 2 *t*-Bu), 1.4–1.8 (m, 6, ring), 5.7 (s, 2, vinyl); UV (C<sub>2</sub>H<sub>5</sub>OH) adsorption below 230 nm.

**1,4-Di-*tert*-butylcyclohexene (2)** was prepared by a variation of the procedure due to Stolow and Ward.<sup>19</sup> To a solution of *p*-di-*tert*-butylbenzene (19 g, 0.1 mol) in 450 mL of ethylenediamine (dried by distillation from sodium immediately before use) heated to 90–95 °C and stirred in a nitrogen atmosphere was added lithium shot (10 g, 1.4 mol), activated by an ethanol rinse to remove the fatty acid and oxide coatings, at a rate so as to maintain the temperature of the solution between 100 and 105 °C. Generation of a deep-blue color and vigorous evolution of heat accompanied the addition. After all the lithium had been added, the solution was heated under reflux for 1 h before additional lithium shot (2.5 g) was added. The mixture was heated for 3 h more before it was cooled. The mixture was then extracted eight times with 100-mL portions of 30–60 °C petroleum ether. The combined extracts were washed with 5% NH<sub>4</sub>Cl and dried (Na<sub>2</sub>SO<sub>4</sub>). Evaporation of the solvent gave 18.0 g (95%) of the crude olefin. Analysis by GLC showed the product to be 1.6% 5, 2.3% 1, and 96% 2. Chromatography over a 25% silver nitrate on basic alumina column furnished 2 as white crystals: 56.0 °C (lit.<sup>19</sup> mp 54–54.5 °C); >99% by GLC. The NMR spectrum agreed with literature reports:<sup>8b,19</sup> NMR (CCl<sub>4</sub>) δ 0.86 (s, 9, *t*-Bu), 1.00 (s, 9, *t*-Bu), 1.5–2.3 (m, 6, ring), 5.42 (m, 1, vinyl).

**1,4-Di-*tert*-butyl-1,2-cyclohexanediol** was prepared following the general method of Wiberg and Saegborth.<sup>20</sup>

1,4-Di-*tert*-butylcyclohexene (18 g, 0.095 mol) was added to a solution of 800 mL of *tert*-butyl alcohol and 160 mL of water, which was then cooled, with constant stirring, to 0 °C. Potassium permanganate (25 g, 0.16 mol) and NaOH (4.5 g, 0.11 mol) were added to 650 mL of water, which was then also cooled to 0 °C. Crushed ice (400 g) was added to the cold *tert*-butyl alcohol solution, followed by the cold alkaline permanganate solution. The reaction mixture was stirred at 0 °C for 3–4 h after which the remaining permanganate was reduced by bubbling SO<sub>2</sub> through the solution until it was colorless. The solution was filtered, using vacuum suction, and the residue dissolved as completely as possible in hot ether. The hot solution was filtered,

the inorganic residue discarded, and the ether evaporated. The remaining solid was recrystallized from heptane, giving 6.3 g (35%) of a white solid melting at 158–151 °C. Analysis by GLC (column B; 160 °C, 70 mL/min) showed the material to be 98% one compound with a 21-min retention time. Recrystallization of this material gave a white powder melting sharply at 159.5 °C.

Distillation of the *tert*-butyl alcohol from the filtrate of the first filtration above gave a semisolid organic material insoluble in the remaining aqueous solution. Recrystallization from pentane gave 3.6 g (20%) of a white solid melting at 140–158 °C; GLC on column B indicated a composition of 95% diol. The total yield of crude (95+%) diol was 9.9 g (55%). The purified diol, mp 159.5 °C, had the following properties: NMR (CCl<sub>4</sub>)  $\delta$  0.84 (s, 9, *t*-Bu), 1.01 (s, 9, *t*-Bu), 1.02–2.0 (m, 8, ring), 2.7 (m, 1, OH), 3.7 (m, 1, OH); IR (CHCl<sub>3</sub>) 3660, 3610, 3580, 3450 (m), 2980, 2860 (s), 1460 (m), 1380 (m), 1350 (m), 1240 (s), 1210 (s), 1040 cm<sup>-1</sup>; MSpec (80 eV), *m/z* (relative intensity) 171 (63, *P* - *t*-Bu), 153 (7, *P* - *t*-Bu and H<sub>2</sub>O), 135 (11, *P* - *t*-Bu and 2H<sub>2</sub>O), 113 (25), 107 (25), 97 (25), 83 (25), 69 (36), 57 (100, M<sup>+</sup>), 55 (38), 43 (73), 41 (30).

Anal. Calcd for C<sub>14</sub>H<sub>28</sub>O<sub>2</sub>: C, 73.63; H, 12.36. Found: C, 73.65; H, 12.72.

**2,5-Di-*tert*-butyl-1,3-cyclohexadiene** was prepared by dehydration of the diol over alumina (Woelm's basic, activity grade 1), which had been further treated with pyridine before use.<sup>21,22</sup> A 40 cm × 12 mm o.d. Pyrex tube was packed to a depth of 3.5 cm with treated alumina and topped with glass helices. The tube was heated to 295–305 °C under nitrogen and the diol slowly added (without exposing the system to air).

Liquid eluted from the bottom of the pyrolysis column within 30 s of the first addition. The yield was 15–20% of a mixture of arene 1, diene 7, and diene 8 and 50–60% of ketones from a thermodynamically more favorable competing dehydrogenation as well as lower molecular weight hydrocarbons. The hydrocarbon material was separated from the ketones by preparative GLC, using column B at 160 °C. The hydrocarbons were then separated on the silver nitrate–alumina liquid chromatography column. Finally, the diene was further purified by rechromatographing on column B. An initial 5.25 g of diol gave 0.177 g of pure 2,5-di-*tert*-butyl-1,3-cyclohexadiene (8): mp 24 °C (3.5% from the diol); NMR (CCl<sub>4</sub>)  $\delta$  0.88 (s, 9, *t*-Bu), 1.02 (s, 9, *t*-Bu), 1.98 (unsym d, 3, allyl), 5.48 (m, 1, vinyl), 5.68 (m, 1, vinyl), 5.74 (m, 1, vinyl); IR (CCl<sub>4</sub>) 3045 (m), 2980 (s), 2860 (s), 1695 (w), 1480, 1460, 1395, 1370, 1260, 1250 cm<sup>-1</sup>; MS (80 eV), *m/z* (relative intensity) 192 (3, P), 119 (19), 105 (5), 91 (5), 57 (100, M<sup>+</sup>), 41 (20), 29 (10); UV (cyclohexane) 260 nm ( $\epsilon$  6070).

Anal. Calcd for C<sub>14</sub>H<sub>24</sub>: C, 87.43; H, 12.57. Found: C, 87.20; H, 12.66.

**2-Acetoxy-1,4-di-*tert*-butylcyclohexanol** was prepared from the above described diol (2.28 g, 0.010 mol), acetic anhydride (4.0 mL), triethylamine (4.0 mL), and *N,N*-dimethyl-4-pyridinamine (0.1 g) in 5 mL of ether.<sup>23</sup> The mixture was stirred at ambient temperature for 17 h and refluxed for 6 h before water and additional ether was added. The ether layer was separated, washed with water, 10% H<sub>2</sub>SO<sub>4</sub>, and aqueous NaHCO<sub>3</sub> and dried over Na<sub>2</sub>SO<sub>4</sub>. Removal of the ether gave 2.7 g (100%) of 2-acetoxy-1,4-di-*tert*-butylcyclohexanol: mp 125–127 °C, 127–128 °C after vacuum sublimation; NMR (CCl<sub>4</sub>)  $\delta$  0.84 (s, 9), 0.93 (s, 9), 1.1–1.8 (m, 8), 2.0 (s, 3, COCH<sub>3</sub>), 4.8–5.1 (br m, 1); IR (CHCl<sub>3</sub>) 3620, 3500 (br), 2970 (s), 2880, 1730 (s), 1470, 1370, 1240, 1078, 1030 cm<sup>-1</sup>.

Anal. Calcd for C<sub>16</sub>H<sub>30</sub>O<sub>3</sub>: C, 71.07; H, 11.18. Found: C, 70.60; H, 11.19.

**Isomeric 2,5-Di-*tert*-butylcyclohexanones.** Two ketones (mp 104–105 and 45 °C), which are the principal products of the dehydration of the diol, were isolated by chromatography on column B at 160 °C. The two ketones were formed in a ratio of about 3:1, the higher melting compound predominating in the glycol dehydration reported above as well as in other attempted dehydrations over alumina at other temperatures (210–300 °C) or ThO<sub>2</sub> (calcined in air at 530 °C in N<sub>2</sub> or at 400 °C in H<sub>2</sub> and cooled in N<sub>2</sub>)<sup>24</sup> at temperatures from 250 to 350 °C. The sought for diene was never more than a minor component of the complex mixtures produced.

**2,5-Di-*tert*-butylcyclohexanone, mp 104–105 °C.** This ketone eluted before the lower melting isomer on column A (non-polar) or column B (polar): NMR (CCl<sub>4</sub>)  $\delta$  0.88 (s, 9), 0.98 (s, 9), 1.1–1.24 (m, 8); IR (CCl<sub>4</sub>) 2980 (s), 2870, 1720 (s), 1490, 1370 (s), 1250 (s), 1193, 1158 (s), 1102, 1087, 1035, 992, 897 cm<sup>-1</sup>.

Anal. Calcd for C<sub>14</sub>H<sub>26</sub>O: C, 79.93; H, 12.45. Found: C, 79.74; H, 12.60.

**2,5-Di-*tert*-butylcyclohexanone, mp 45 °C:** NMR (CHCl<sub>3</sub>)  $\delta$  0.87 (s, 9), 0.97 (s, 9), 1.2–2.4 (m, 8); IR (CHCl<sub>3</sub>) 2980 (s), 2920, 2880, 1700 (s), 1470, 1460, 1395, 1360, 1250 (s), 1220, 865 (s) cm<sup>-1</sup>.

Anal. Calcd for C<sub>14</sub>H<sub>26</sub>O: C, 79.93; H, 12.45. Found: C, 79.77; H, 12.55.

**Registry No.** 1, 1012-72-2; 2, 5009-02-9; 5, 86943-87-5; 6, 39000-62-9; 7, 86943-88-6; 8, 86943-89-7; 1,4-di-*tert*-butyl-1,2-cyclohexanediol, 86943-90-0; 2-acetoxy-1,4-di-*tert*-butylcyclohexanol, 86943-91-1; *cis*-2,5-di-*tert*-butylcyclohexanone, 15067-57-9; *trans*-2,5-di-*tert*-butylcyclohexanone, 14736-72-2; rhodium, 7440-16-6.

(24) Davis, B. H.; Brey, W. S., Jr. *J. Catal.* 1972, 25, 81–92.

## Dienes as Possible Intermediates in the Catalytic Hydrogenation of Aromatic Hydrocarbons. 2. Dienes Derived from 1,3-Di-*tert*-butylbenzene and a Rhodium Catalyst<sup>1</sup>

James Ray Cozort, James F. Outlaw, Jr., Adrian Hawkins, and Samuel Siegel\*

Department of Chemistry, University of Arkansas, Fayetteville, Arkansas 72701

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The evolution of the products from the catalytic hydrogenation (Rh/Al<sub>2</sub>O<sub>3</sub>) of the five isomeric diene derivatives of 1,3-di-*tert*-butylbenzene (9) is compared with the formation of the observable cyclohexene intermediates and the saturated products from arene 9 to determine which diene (or dienes), upon adsorption on the catalyst, best represents the structure of the intermediate(s) formed in the rate-determining surface reaction of the arene. Although the comparison indicates that little or no diene is desorbed during the hydrogenation of the arene, the observed competitive reactivity of the dienes, their interconversions, and the products of hydrogen addition indicate that the preferred reaction path for the hydrogenation of the arene proceeds via the addition of the first hydrogen atom to a *tert*-butyl-substituted carbon atom. Relative to cyclohexene, the rates of conversion of 1,5-di-*tert*-butyl-1,3-cyclohexadiene (13), 1,3-di-*tert*-butyl-1,4-cyclohexadiene (11), arene 9, and cyclohexene at 30 °C and 0.88 atm of H<sub>2</sub> are 3.8:2.7:2.6 × 10<sup>-2</sup>:1.00. Under these conditions the turnover number of cyclohexene is 0.40 mol s<sup>-1</sup> (mol of surface Rh)<sup>-1</sup>.

In exploring the mechanism of the rhodium-catalyzed hydrogenation of aromatic hydrocarbons we have sought

evidence of the structure and reactivity of the intermediates that may effect the rate and, particularly, the