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_4) δ 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 ($CHCl_3$) 3660, 3610, 3580, 3450 (m), 2980, 2860 (s), 1460 (m), 1380 (m), 1350 (m), 1240 (s), 1210 (s) 1040 cm^{-1}; MSpec (80 eV), *m*/*z* (relative intensity) 171 (63, P – *t*-Bu), 153 (7, P – *t*-Bu and H_2O), 135 (11, P – *t*-Bu and $2H_2O$), 113 (25), 107 (25), 97 (25), 83 (25), 69 (36), 57 (100, M$^+$), 55 (38), 43 (73), 41 (30).

Anal. Calcd for $C_{14}H_{28}O_2$: 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.[21,22] 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_4) δ 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_4) 3045 (m), 2980 (s), 2860 (s), 1695 (w), 1480, 1460, 1395, 1370, 1260, 1250 cm^{-1}; MS (80 eV), *m*/*z* (relative intensity) 192 (3, P), 119 (19), 105 (5), 91 (5), 57 (100, M$^+$), 41 (20), 29 (10); UV (cyclohexane) 260 nm (ϵ 6070).

Anal. Calcd for $C_{14}H_{24}$: 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.[23] 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_2SO_4, and aqueous $NaHCO_3$ and dried over Na_2SO_4. 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_4) δ 0.84 (s, 9), 0.93 (s, 9), 1.1–1.8 (m, 8), 2.0 (s, 3, $COCH_3$), 4.8–5.1 (br m, 1); IR ($CHCl_3$), 3620, 3500 (br), 2970 (s), 2880, 1730 (s), 1470, 1370, 1240, 1078, 1030 cm^{-1}.

Anal. Calcd for $C_{16}H_{30}O_3$: 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_2 (calcined in air at 530 °C in N_2 or at 400 °C in H_2 and cooled in N_2)[24] 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 (nonpolar) or colume B (polar): NMR (CCl_4) δ 0.88 (s, 9), 0.98 (s, 9), 1.1–1.24 (m, 8); IR (CCl_4) 2980 (s), 2870, 1720 (s), 1490, 1370 (s), 1250 (s), 1193, 1158 (s), 1102, 1087, 1035, 992, 897 cm^{-1}.

Anal. Calcd for $C_{14}H_{26}O$: C, 79.93; H, 12.45. Found: C, 79.74; H, 12.60.

2,5-Di-*tert*-butylcyclohexanone, mp 45 °C: NMR ($CHCl_3$) δ 0.87 (s, 9), 0.97 (s, 9), 1.2–2.4 (m, 8); IR ($CHCl_3$) 2980 (s), 2920, 2880, 1700 (s), 1470, 1460, 1395, 1360, 1250 (s), 1220, 865 (s) cm^{-1}.

Anal. Calcd for $C_{14}H_{26}O$: 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.

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Dienes as Possible Intermediates in the Catalytic Hydrogenation of Aromatic Hydrocarbons. 2. Dienes Derived from 1,3-Di-*tert*-butylbenzene and a Rhodium Catalyst[1]

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The evolution of the products from the catalytic hydrogenation (Rh/Al_2O_3) 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_2 are 3.8:2.7:2.6 × 10^{-2}:1.00. Under these conditions the turnover number of cyclohexene is 0.40 mol s^{-1} (mol of surface Rh)$^{-1}$.

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

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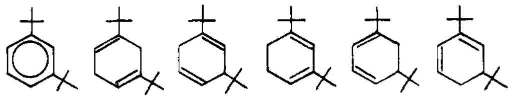
stereochemistry of the reaction.[2,3] In the preceding paper we examined the possibility that the structure of the adsorbed diene, which is presumed to be formed in the rate-limiting surface reaction of 1,4-di-*tert*-butylbenzene (1), might be deduced from a comparison of the evolution of observable products from the arene with those formed from the several dienic derivatives of 1.[3] Of the three dienes examined, 2,5-di-*tert*-butyl-1,3-cyclohexadiene (8) best exhibited the results to be expected if it forms on adsorption the structure that is formed when the second hydrogen atom adds to 1.

In this paper, the preparation of the dihydro derivatives of 1,3-di-*tert*-butylbenzene (9) and the hydrogenation of


9 10 11 12 13 14

these dienes over a supported rhodium catalyst is described.[4] The results indicate that although appreciable amounts of dienes are unlikely to desorb from the catalyst during the hydrogenation of this arene, the orientation of the addition of hydrogen is directed by the substituents and thereby determines the fraction of the arene that forms *tert*-butyl-substituted cyclohexenes that do desorb and are the precursors of the *trans*-1,3-di-*tert*-butylcyclohexene that is produced.[2,3,5]

Results

Preparation and Relative Stability of the Dienes. The Birch reduction of 1,3-di-*tert*-butylbenzene and 3,5-di-*tert*-butyl-1-methoxybenzene furnished the most useful routes to the dienes.[6-8] Except for the preparation of 1,5-di-*tert*-butyl-1,3-cyclohexadiene (13), all of the methods used gave mixtures that were separated by GC. The conjugated dienes 13 and 14 had to be diluted with pentane before injection of samples into the GC to avoid isomerization in the heated injection port. The isomerization proceeded from 13 → 14 → 12, apparently by successive 1,5 intramolecular hydrogen migrations.[9] Diene 10 was converted to 12 in a refluxing solution of lithium ethylamide in ethylamine, the conjugated diene 12 being the more stable.

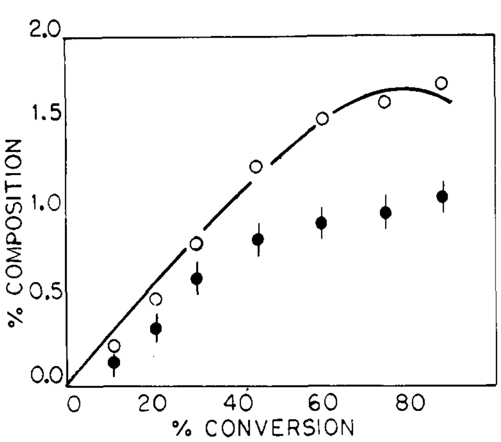


Figure 1. Formation of alkenes (mole percent) during the hydrogenation of 1,3-di-*tert*-butylbenzene (9) at 0.84 atm (0.50% Rh/Al_2O_3). The conditions are identical with those described for the rate measurements): (●) 1,5-di-*tert*-butylcyclohexene (16), (○) sum of 16 and 1,3-di-*tert*-butylcyclohexene (15). See text for the significance of the curve.

Scheme I. Simplified Kinetic Scheme for the Formation of Cyclohexene Intermediates (B) from the Hydrogenation of an Arene (A)

$$\begin{tikzcd}
A \arrow[r, "(1-a)k_1"] \arrow[rr, bend right, "ak_1"'] & B \arrow[r, "k_2"] & C
\end{tikzcd}$$

Recently, the relative stability of the dienes has been found to be 14 < 11 < 10 < 13 ≪ 12.[10] Apparently the *tert*-butyl groups affect the relationship between structure and stability in dienes like less bulky alkyl groups.[11] The dienes differ little in stability; the greatest difference falls between 12 and 13, which differ at 55 °C by about 0.5 kcal/mol ($\Delta G°$).

Initial Products of Hydrogenation of 1,3-Di-*tert*-butylbenzene (9). The initial products of the hydrogenation of 1,3-di-*tert*-butylbenzene (9) at near atmospheric pressure consists mainly of *cis*-1,3-di-*tert*-butylcyclohexane (19); the remainder appears as a mixture of 1,3- and 1,5-di-*tert*-butylcyclohexene (15 and 16) whose reduction yields *trans*- as well as *cis*-1,3-di-*tert*-butylcyclohexane (20 and 19). In Figure 1, the results of this study are compared with a curve computed by using an equation derived from a simplified kinetic scheme that gives the relative concentration of the intermediate cyclohexenes (15 + 16) as a function of the conversion of arene (Scheme I).[2] The equation has two parameters: α, the initial fraction of arene that is converted directly to the cis ane 19, and k_1/k_2, the relative specific reactivities of the arene and the intermediate cycloalkene(s). In this way use is made of the information gained over the course of the reduction to obtain an estimate of the initial fraction of the arene that yields the cycloalkene intermediates. The curve in Figure 1 has been calculated with $\alpha = 0.97$ and $k_1/k_2 = 3.0$. This value of α is too large to account for the 3.8% *trans*-1,3-*tert*-butylcyclohexane found in the completely hydrogenated sample of 9 in part because the hydrogenation of 15 and 16 yield cis as well as trans saturated products and in part because the initial rate of appearance of the trans isomer is not zero. If one accepts the analysis of the completely saturated arene as correct, then a value of $\alpha = 0.92$ is obtained by assuming that each cycloalkene (15 and 16) yields the particularly ratio of cis to trans products that each one does when hydrogenated separately and that the ratio of 15 to 16 formed is 1:2. Accordingly, the fraction of arene 9 that is transformed to a mixture of the intermediate cycloalkenes when the hydrogenation

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[1] (a) Presented in part at the 165th National Meeting of the American Chemical Society, Dallas, TX, April 1973. (b) Taken in part from the Ph.D. dissertations of James F. Outlaw, Jr., University of Arkansas (1971) and of James R. Cozort, University of Arkansas (1975). (c) This research was supported in part 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. Support of the research was also received from the National Science Foundation, which we are pleased to acknowledge.

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Table I. Initial Product Distributions in the Hydrogenation of the Dihydro Derivatives of 1,3-Di-*tert*-butylbenzene (9; Mole Percent; 0.5% Rh/Al_2O_3)

reactant	*P*, atm	*cis*-17/19	*trans*-18+20	1,3-ene 15	2,4-ene 16	arene 9	dienes[a]
10	0.84	9/26	0.0	4	20	40	
12	0.84	11/18	0.0	35	18	18	
11	0.84	15/2	0.0	32	6	27	4 (12) 6 (14) 7 (13)
13	0.42	32/8	10	0	34	16	
	0.84	32/11	8	0	36	13	
	4.0	18/14	5	0	59	4	
14	0.42	21/4	3	19	29	17	6 (11)
	0.84	22/12	2	17	18	22	6 (11)
	4.0	18/24	3	28	21	3	3 (11)

[a] Only the detected dienes are indicated.

Table II. Reaction Rate and Generation of Products from 2,6-Di-*tert*-butyl-1,4-cyclohexadiene (11)[a]

	dienes				arene	enes			
time, min	11	13	14	12	9	15	16	17	ane 19
0.50	92.7	0.17	0.1	0.1	1.6	2.4	1.3	1.5	0.2
1.06	84.8	0.35	0.2	0.9	3.0	4.8	3.0	3.4	0.4
1.51	73.0	0.60	0.38	1.6	3.4	10.1	5.1	5.0	0.8
2.05	63.2	0.95	0.55	2.1	6.7	14.4	5.7	5.1	1.6
3.00	48.6	1.1	0.7	2.3	8.9	20.0	7.7	8.0	2.7
3.95	40.1	0.9	0.6	2.6	10.0	23.9	8.9	9.3	3.7
5.10	31.1	0.65	0.35	2.6	11.6	27.2	10.7	7.9	7.8
7.85	10.1	0.3	0.15	1.9	14.5	33.8	13.2	9.7	16.2
13.65	t	0.1	0.0	0.4	14.6	38.9	4.4	12.4	27.1

[a] At 30 °C, 0.89 atm of hydrogen, 0.50% Rh/Al_2O_3 (22.6 mg), 0.10 mL of 11, and cyclohexane (2.0 mL).

Table III. Reaction Rate and Generation of Products from 1,5-Di-*tert*-butyl-1,3-cyclohexadiene (13)[a]

	dienes		arene	enes				ane	
time, min	13	11	9	15	16	17	18	19	20
0	100								
1.0	82.1	0.2	4.5		3.2	3.0	1.4	0.8	
2.0	75.1	0.4	5.0		9	7.1	1.6	1.7	t
4.0	66.0	0.2	6.3	t	18	12.7	2.5	2.1	0.1
7.5	50.1	0.1	6.7	0.3	26	14.0	2.8	3.2	0.3
12.0	36.5	t	7.6	0.7	30	18.0	3.2	4.5	1.0
20.0	22.1	0.0	9.0	0.6	38	20.4	3.5	6.6	1.1
30.0	9.6	0.0	8.5	0.7	45	23.0	3.7	8.8	1.9
50.0	t	0.0	8.1	1.2	52	16.1	2.6	15.0	13.8
8 h	0.0	0.0	3.7	2.8	6	0.0	0.0	55.1	30.0

[a] At 30 °C, 0.86 atm of hydrogen, 0.50% Rh/Al_2O_3 (20.6 mg), 0.10 mL of **13**, and cyclohexane (2.0 mL).

is performed at near atmospheric pressure lies between 3% and 8%.

Products of Hydrogenation of the Dienes. Under conditions used to hydrogenate 1,3-di-*tert*-butylbenzene (**9**), each of the dienic derivatives of **9** yields a different distribution of initial products that arise from the loss of hydrogen, the addition of hydrogen, or the isomerization to other dienes. An increase in pressure results in a decrease in the fraction that reverts to the arene and an increase in the fraction that appears as completely saturated products. The initial proportions of 1,3- and 1,5-di-*tert*-butylcyclohexene (**15** and **16**) are also sensitive to changes in pressure; the changes that are seen correspond to an increase in the proportion of that cyclohexene which results from the reduction of the more exposed double bond (see Table I, dienes **13** and **14**).

Each of the dienes yields both *cis*-3,5-di-*tert*-butylcyclohexene (**17**) and the cis saturated product **19** as initial products. Initially dienes **13** and **14** also yield a product that has the trans configuration, *trans*-3,5-di-*tert*-butylcyclohexene (**18**), but not the saturated isomer **20**.

In some experiments the initial rate of formation of the arene (5–10% of the diene converted) appeared greater than during the midcourse of the reaction. The use of small amounts of catalyst tended to minimize the effect. Except for this, the relative rates of formation of the products was reproducible within the uncertainty of the GC analyses. The results in Table I and Figures 2 and 3 were obtained by combining the data from independent analyses using two different GC columns because neither column gave adequate resolution of all components in the instruments employed.[12] The results reported in Tables II and III were obtained later with use of a single analytical column in a different instrument, and the data agrees well with the prior results.

Kinetics. Noting the rapidity of the reactions of the dienes when exposed to the catalyst and hydrogen, we did not seek at first to obtain accurate reaction rates. Guided by recent work of Boudart and Burwell, however, we have obtained reliable rate data.[13,14] Key factors are the use of catalysts of small particle size (<325 mesh) and a well-stirred reactor so that the transfer of hydrogen to the

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[12] Complete details are reported in the PhD. Dissertation of J. R. Cozort; see ref 1b.

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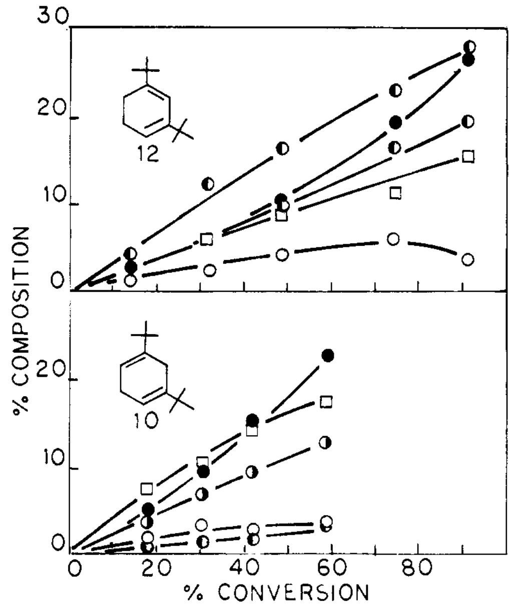


Figure 2. Product distributions (mole percent) in the hydrogenation of 1,3-di-*tert*-butyl-1,3-cyclohexadiene (**12**; upper) and 1,5-di-*tert*-butyl-1,4-cyclohexadiene (**10**, lower) catalyzed by 0.5% Rh/Al_2O_3, 30 °C, 0.84 atm: (◑) 1,3-di-*tert*-butylcyclohexene (**15**), (◐) 1,5-di-*tert*-butylcyclohexene (**16**), (○) *cis*-3,5-di-*tert*-butylcyclohexene (**17**), (●) *cis*-1,3-di-*tert*-butylcyclohexane (**19**), (□) 1,3-di-*tert*-butylbenzene (**9**).

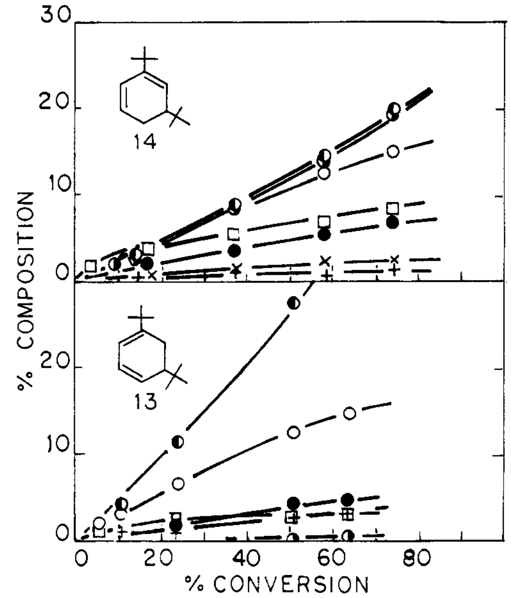


Figure 3. Product distributions (mole percent) in the hydrogenation of 2,6-di-*tert*-butyl-1,3-cyclohexadiene (**14**, upper) and 1,5-di-*tert*-butyl-1,3-cyclohexadiene (**13**, lower) catalyzed by 0.5% Rh/Al_2O_3, 30 °C, 0.85 atm: (◑) 1,3-di-*tert*-butylcyclohexene (**15**), (◐) 1,5-di-*tert*-butylcyclohexene (**16**), (○) *cis*-3,5-di-*tert*-butylcyclohexene (**17**), (●) *cis*-1,3-di-*tert*-butylcyclohexane (**19**), (□) 1,3-di-*tert*-butylbenzene (**9**), (+) sum of *trans*-3,5-di-*tert*-butylcyclohexene (**18**) and *trans*-1,3-di-*tert*-butylcyclohexane (**20**), (X) 1,3-di-*tert*-butyl-1,4-cyclohexadiene (**11**).

catalyst surface is not limited by diffusion (either inside or outside of the particle). For the purpose of this report, we note that the product distribution obtained in the later experiments with dienes are not significantly different from those obtained in the earlier performed work. Aromatization is enhanced at low pressures of hydrogen, and accordingly it would be increased if the catalyst particles are too large or stirring is inefficient. Aromatization, however, produces hydrogen at the catalytic site, which lowers the requirement for external hydrogen. The large amount of arene formed from diene **10** (Table I) may be due in part to diffusional limitations because the conversion of the diene was complete in less than 3 min.

The rates of reaction of dienes **13** and **11** and 1,3-di-*tert*-butylbenzene were determined on the laboratory-prepared 0.50% rhodium on alumina catalyst. Relative to cyclohexene, the rate of conversion at 30 °C and 0.88 atm are $3.79:2.70:2.6 \times 10^{-2}:1.00$ for diene **13**, diene **11**, arene **9**, and cyclohexene. Their relative rates of forming hydrogen addition products are $2.95:2.10:2.6 \times 10^{-2}:1.00$. Under these conditions the turnover numbers of cyclohexene is 0.40 mol s^{-1} (mol surface Rh)$^{-1}$.

Discussion

In the preceding paper, the initial distribution of the products from the hydrogenation (catalyzed by Rh/Al_2O_3) of three isomeric dienes, dihydro derivatives of 1,4-di-*tert*-butylbenzene (**1**), was compared with the initial distribution of products from the hydrogenation of the parent arene.[3] Of the dienes, 2,5-di-*tert*-butyl-1,3-cyclohexadiene (**8**) gave results that correspond best with those to be expected if upon adsorption it were to form the surface compound that is formed also in the rate-controlling surface reaction of the arene. The evidence, however, neither supported nor negated the possibility that a significant fraction of the adsorbed dienic intermediate might leave the catalyst during the hydrogenation of **1**.

1,3-Di-*tert*-butylbenzene (**9**) differs markedly from 1,4-di-*tert*-butylbenzene (**1**) with respect to the amount of unsaturated intermediates (disubstituted cyclohexenes) that can be detected during the hydrogenation of the respective arenes: 3–8% of the initial product from **9**, about 80% from **1**. Our expectation that these differences might be reflected in the properties of certain of the dihydro derivatives of these arenes are borne out by our results.

The present study indicates that of the five possible dienes related to 1,3-di-*tert*-butylbenzene (**9**), dienes **11**, **13**, and **14** are the most likely to form, on adsorption at a catalytic site, an intermediate that is(are) the principal product(s) of the rate-limiting surface reaction in the hydrogenation of arene **9**. Evidently, little or no diene is desorbed during the hydrogenation of **9** because the initial products from each diene studied contain too large a fraction of substituted cyclohexenes (**15** and **16**) that subsequently can yield *trans*-1,3-di-*tert*-butylcyclohexane (**20**).

The location of the *tert*-butyl groups in the dienes clearly influences the attractive interaction between diene and catalyst as shown in the competitive reactivity of the dienes. The position of the *tert*-butyl groups also affects the fraction of initial reduction products that are saturated completely. In the preceding paper, none of the diene derivatives of arene **1** were found to yield at near atmospheric pressure an initial product that was saturated; the fraction of *cis*-3,6-di-*tert*-butylcyclohexene formed from one of the dienes, however, was the same (within the experimental uncertainty) as the fraction of *cis*-1,4-di-*tert*-butylcyclohexane produced from **1** under comparable conditions. In contrast, each of the dienes derived from arene **9** yields *cis*-1,3-di-*tert*-butylcyclohexane (**19**) as an initial product and the fraction of cis products (including both saturated and unsaturated) formed initially is appreciably greater than that produced from the dienic derivatives of arene **1**. However, the fraction of enes **15** and **16** that are formed initially from the dienes is much larger than the estimated maximum amount (ca. 8%) of the initial hydrogenation products of arene **9**. These results show clearly that the amount of diene that desorbs during the hydrogenation of arene **9** must be small if any desorbs at all. Yet at least certain of the dienes should form, upon adsorption, structures that correspond to those that are produced in the apparent rate-controlling surface reaction of the related arene. If so, why do the product distributions from one of the dienes or a combination of dienes not correspond to the products of arene hydrogenation?

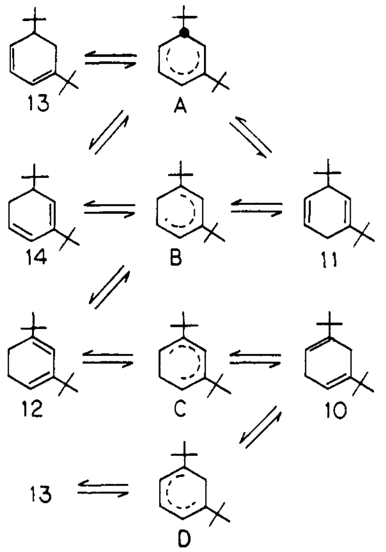
Consider first the consequences of diene adsorption. Because dienes **10** and **12** lack a tertiary hydrogen atom, the structure formed upon their adsorption on the catalyst does not depend upon which face of the double bond is presented to the catalytic site, and not surprisingly, no trans products are formed initially from them. Dienes **11**, **13**, and **14**, which have one *tert*-butyl group attached to a saturated carbon atom, on adsorption can yield diastereomeric complexes, one leading to cis products, the other to trans. Trans isomers are among the initial products of hydrogenation of conjugated dienes **13** and **14** but not of the 1,4-diene **11**. The fraction of trans isomers in the initial products of **13** and **14** is small (ca. 8% and 3%, respectively) and almost independent of pressure (0.4–4.0 atm), which appears to indicate that adsorption on the face that leads to cis products is greatly favored. This enantiotopic selectivity in the adsorption of these dienes, however, is not retained in the major fraction of the initial products, the cycloalkenes **15** and **16**. Furthermore, the form of the adsorbed diene in which the *tert*-butyl group is directed toward the catalyst would be expected to yield the larger fraction of enes **15** and **16** because their desorption would be aided by the relief of strain due to the nonbonded interactions between the *tert*-butyl group and the catalyst. Information regarding the stereoselectivity of the dienes on adsorption is also lost when the diastereomeric diene complexes that can form the cis isomers yield arene **9** and diene **10** or **12**; these reactions, however, can be minimized by an increase in hydrogen pressure.

Furthermore, a diene can be adsorbed in a configuration such that only one double bond (probably the least substituted) interacts with a catalytic site. Such an interaction would be weaker than if both double bonds were involved. The change from the less to the more stable adsorbed form would compete with reactions of each with hydrogen and one could thus explain why increasing the pressure of hydrogen increases markedly the initial fraction of the 2,4-ene **16** formed from diene **13** and the changes in the proportions of the 1,3-ene **15** and the 2,4-ene **16** formed from diene **14** to favor the formation of **15**. Diene **13**, which has the more exposed double bond, clearly is the more affected by the change in pressure.

The competitive reactivity of the dienes and the interconversions and dehydrogenation to the arene afford insight as to the most probable sequence of reactions that occur during the hydrogenation of arene **9**. Consider the following alternative reaction paths for the hydrogenation of **9** (Scheme II).

If the transfer of the second hydrogen to the arene is rate limiting, then the height of that barrier for the several parallel paths shown is likely to be related to the energy of the structure formed in that elementary step, e.g., the adsorbed diene. The evidence from the hydrogenation of the dienes indicate that in competition, the attraction between dienes and reactive site increases in the order **10** < **12** < **11** < **14** < **13**. However, adsorbed diene **13** cannot be the only important intermediate because **13** does not produce any appreciable amount of the 1,3-ene **15**, whereas the ratio of 1,3- to 2,4-di-*tert*-butylcyclohexene (**15** and **16**) formed initially from arene **9** is about 1:2. Therefore, an additional reaction path must be included. The formation of adsorbed diene **14** could furnish the second largest driving force for the presumed rate-controlling surface reaction and yield the balancing amount of the 1,3-ene, but diene **11** also is likely to be involved because of the apparent ease of interconversion with **13** (see Tables II and III).

Scheme II. Parallel Paths for the Transfer of Two Hydrogen Atoms to Adsorbed 1,3-Di-*tert*-butylbenzene (9) via Intermediates A–D[a]



[a] Presumably, adsorbed species intervene between the intermediates and the desorbed dienes.

Although each of these adsorbed dienes could be attained from the arene via more than one sequence of elementary steps, they could be formed also via a single path, namely, through the addition of the first hydrogen to a *tert*-butyl-substituted carbon atom. Interestingly, the same conclusion was reached in considering the most probable reaction path for the hydrogenation of 1,4-di-*tert*-butylbenzene (**1**).[3] It is also in harmony with the conclusions of Nieuwstad et al. to account for the regioselectivity and relative reactivity of a series of 1-alkylnaphthalenes in which they proposed that the first hydrogen atom was transferred to the alkyl-substituted position.[15]

That the reaction path through diene **13** is preferred in the hydrogenation of arene **9** is indicated by the observed distribution of dienes **13** and **14** formed from diene **11**. As indicated in Scheme II, **13** and **14** can be formed from diene **11** via a common intermediate. And if the rate-controlling step in the hydrogenation of arene **9** is the addition of hydrogen to this intermediate, then the path going through adsorbed diene **13** is favored over that via adsorbed diene **14** by more than 1.5, the ratio in which **13** and **14** are produced from diene **11**. This observed ratio of formation of *desorbed* dienes should be less than the ratio of formation of *adsorbed* dienes because diene **13**, the more effective competitor, would be expected to have the smaller rate constant for desorption. A relative ratio of these reaction paths of about 2.0 would also account for the distribution of enes **15** and **16** produced in the hydrogenation of the arene **9**.

An Alternative Path to the Formation of *trans*-1,3-Di-*tert*-butylcyclohexane from Arene 9. The difference between the two estimates of the fraction of arene that is converted to desorbed cycloalkenes indicates the existence of a route to the formation of the trans saturated

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[15] Nieuwstad, Th. J.; Klapwijk, P.; van Bekkum, J. *J. Catal.* **1973**, *29*, 404–411.

product that does not pass through the cycloalkenes released to the bulk phase. The *initial* rate of forming the trans isomer is not zero; indeed, it is about one-third of the rate of forming the sum of cycloalkenes **15** plus **16**. Because of the bulk of the *tert*-butyl group and the cyclic structure of the alkene, mechanisms of anti addition to adsorbed intermediates analogous to those postulated by Kung and Burwell appear to be unlikely.[16]

An apparent direct path could arise if the rate of readsorption of the alkene was fast compared to the rate of intraparticle diffusion. The rate of reaction observed using a powdered catalyst (<325 mesh) in an efficiently stirred reactor indicates that intraparticle diffusion should have a negligible effect upon the results. However the theory upon which these estimates are made neglect the consequence of molecular events that occur in the immediate vicinity of a site at which an alkene is formed. There is a finite probability that an alkene molecule that is generated at a reactive site will return and be readsorbed before it can escape into the bulk of the solution.[17,18] This phenomenon is to be compared with the "cage effect" in reactions between radical pairs generated in solution in a photochemically or thermally induced molecular decomposition. The readsorption should be unactivated, the site being coordinatively unsaturated, and the solvent, a saturated hydrocarbon, is an ineffective competitor for the site.[19] To account for the observed direct formation of *trans*-1,3-di-*tert*-butylcyclohexane, about one in three molecules of enes **15** or **16** that are formed at a site should be readsorbed; the remainder diffuse away and thereafter would compete with the arene for readsorption on a catalytic site.

Experimental Section

General experimental procedures were the same as those described in the preceding paper with the following exceptions and additions.[3]

LC separations on a 90 cm × 20 mm column of 25% $AgNO_3$ on basic alumina (Woelm's activity grade 1) used 95% petroleum ether (30–60 °C) and 5% benzene as eluent, except that dienes **13** and **14** required a 10–15% concentration of benzene for proper elution.

Chromatographic columns used in preparative GC separations and the analysis of mixtures obtained in the course of the preparative work were as follows: (A) 10 ft × $^3/_8$ in. 10% FFAP on 60/80 Chromosorb W, (B) 5 ft × $^1/_4$ in. 10% FFAP on Chromosorb W, (C) 35 ft × $^3/_8$ in. 30% Carbowax 20M on 45/60 Chromosorb P, (D) 5 ft × $^1/_4$ in. 3% SE-30 on 100/120 Varaport N, (E) 10 ft × $^1/_4$ in. 5% Carbowax 20M on 60/80 Chromosorb W, (F) 20 ft × $^1/_8$ in. 10% Carbowax 20M on 80/100 Chromosorb W, acid washed, and (G) 13 ft × $^1/_4$ in. 5% Apiezon L on 60/80 Chromosorb W.

Analysis of the Hydrogenation Products. The results reported in Table I and in Figures 2 and 3 were obtained with use of the 300 ft × 0.02 in. i.d. stainless steel capillary coated with the purified Apiezon-L grease as described in the preceding paper or by a combination of columns for the analysis of dienes **13** and **14**, because, at the time, no one of the columns used gave adequate separations of all reactants and products. Later, a more efficient column and instrument system was used; however, whenever comparisons were made, the results agreed within the uncertainty of the earlier and less precise analyses. The later analyses were done with a 25 ft × $^1/_8$ in. copper column containing 60/80-mesh acid-washed Chromosorb W coated with 10% Carbowax 750 in a Varian 940 gas chromatograph with a flame ionization detector connected to a Laboratory Data Control Model 308 computing integrator. With a column temperature of 95 °C and a flow rate of 12–14 mL min^{-1}, the retention times relative to *tert*-butylbenzene (1.00) were as follows: cis ane **19** (1.16), ene **15** (1.18), diene **12** (1.34), diene **14** (1.44), ene **16** (1.45), trans ane **20** (1.48), cis ene **17** (1.55), diene **11** (1.64), trans ene **18** (1.72), diene **13** (1.98), diene **10** (2.24), and arene **9** (2.30). The flow rates was lowered to 5–6 mL min^{-1} to obtain satisfactory analysis of mixtures that contained **19** and **15**, **14** and **16**, or **9** and **10**. The results reported are the averages of duplicate or triplicate analyses with a maximum deviation for each component ±0.10 to ±0.17% of the total mixture of products.

Rate Measurements. The rates of reaction of 1,3-di-*tert*-butylbenzene (**9**) and the dienes were measured in a semimicro constant-pressure apparatus like that described previously except that the flask was shaken vigorously by a mixer like that used by Kung et al.[14] The hydrogenation of the dienes (Tables II and III) were sandwiched between reductions of cyclohexene.

Catalysts. For the rate measurements, the catalyst, 0.50% rhodium on alumina, was prepared by the impregnation of powdered (<325 mesh) precalcined alumina with an aqueous solution of rhodium chloride following standard procedures.[14,20] After being ground and sieved, the alumina (Catapal SB) of less than 325 mesh was calcined in air at 650 °C for 4 h and then rehydrated for 1 day in a closed chamber that contained an uncovered beaker of water. To this prepared alumina (5.00 g) was added a solution of $RhCl_3{\cdot}3H_2O$ (Alfa, 0.064 g) in 3 mL of doubly distilled water. The resulting slurry was stirred intermittently at room temperature for 4 h. The water was allowed to evaporate in a gentle flow of filtered air over a period of 6 days. The impregnated alumina was dried in air at 120 °C for 4 h and reduced in flowing hyrogen at 450 °C for 16 h. The resulting greyish-brown catalyst was then ground and sieved, and only particles smaller than 325 mesh were used in the reported rate measurements. The catalyst was rehydrated, dried over anhydrous sodium sulfate, and stored in clean, dry, glass sample bottles.[21] To obtain some measure of the catalyst's dispersion, the hydrogen–oxygen titration procedures of Wanke and Dougharty were followed.[20] After correction for the gas taken up by the support (less than 0.9% of the amount absorbed by the rhodium metal), the atoms of hydrogen or oxygen adsorbed per rhodium atom in the catalyst were found to be 1.47 ± 0.01 and 0.7, respectively, at 25 °C. By comparison with the detailed studies of Wanke and Dougharty, these results indicate a well-dispersed catalyst but do not yield a quantitative measure of the dispersion because the surface stoichiometry for the adsorption of these gases appears to be a function of metal particle size.

The 0.5% rhodium on alumina catalyst used for the product studies given in Table I and Figures 2 and 3 was obtained in the form of pellets (Englehard Industries, Lot. No. 10-368), which was ground into a fine powder with a mortar and pestle. Prior to use, the catalyst was heated to 140 ± 5 °C (12–15 h) in flowing hydrogen, cooled in hydrogen, and then flushed with nitrogen before exposure to air.

Preparation of 1,5-Di-*tert*-butyl-1,4-cyclohexadiene (10) and 1,3-Di-*tert*-butyl-1,4-cyclohexadiene (11). The method previously described for the lithium in ammonia reduction of 1,4-di-*tert*-butylbenzene was used.[3] To 1,3-di-*tert*-butylbenzene (**9**; 2 g, 0.01 mol) dissolved in a mixture of THF (50 mL), isopropyl alcohol (50 mL), and ammonia (100 mL) was added lithium shot (0.75 g, 0.108 mol) in small portions with stirring. The isolation procedure produced a liquid mixture containing arene **9** (25%), diene **10** (45%), diene **11** (9%), ene **15** (20%), and ene **16** (1%)

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(16) Kung, H. H.; Burwell, R. L., Jr. *J. Catal.* **1980**, *62*, 11–24.

(17) (a) Noyes, R. M. *J. Chem. Phys.* **1954**, *22*, 1349–1359. (b) Benson, S. W. "The Foundation of Chemical Kinetics"; McGraw-Hill: New York, 1960; pp 541–547.

(18) This description of the molecular events associated with the desorption of an alkene may be compared to the "roll-over" mechanism proposed by Burwell to explain the distribution of deuterium in the initial products of exchange of D_2 with cycloalkanes catalyzed by group 7 metals. Burwell, R. L., Jr. *Acc. Chem. Res.* **1969**, *2*, 289–296.

(19) Crabtree, R. *Acc. Chem. Res.* **1979**, *12*, 331–338.

(20) Wanke, S. E.; Dougharty, N. A. *J. Catal.* **1972**, *24*, 367–384.

(21) A reviewer has suggested that the catalyst may retain chloride that might affect the properties of the catalyst, for example, its acidity. Comparing the conditions we used to reduce the impregnated catalyst with the studies of A. E. Newkirk and D. W. McKee (*J. Catal.* **1968**, *11*, 370–377) on the reduction of $RhCl_3{\cdot}3H_2O$ impregnated γ-alumina, we conclude that the amount of residual chloride must be small. Apparently, our catalyst is not acidic enough to cause the isomerization of the dienes we used; for example, diene **12** is not formed during the hydrogenation of diene **10** nor is the isomerization of any diene observed during the hydrogenations reported in the preceding paper.

(analysis on columns D and F).

The mixture was separated by LC on the $AgNO_3$/basic alumina column, the order of elution being arene **9**, **15**, **16**, diene **10**, and diene **11**. Appropriate fractions were combined, the solvent was evaporated, and the concentrate was subjected to a preparative GC purification.

A pure sample of 1,5-di-*tert*-butyl-1,4-cyclohexadiene (**10**) was obtained with use of column D: ^{1}H NMR (CCl_4) δ 1.06 (s, 18 *t*-Bu), 2.6 (br s, 4 allylic), 5.42 (br s, 2 vinyl); UV max (C_2H_5OH) below 230 nm.

Anal. Calcd for $C_{14}H_{24}$: C, 87.42; H, 12.58. Found: C, 87.65; H, 12.41.

The diene that eluted last from the $AgNO_3/Al_2O_3$ column was identified as 1,3-di-*tert*-butyl-1,4-cyclohexadiene (**11**): ^{1}H NMR (CCL_4) δ 0.86 (s, 9, 1-*t*-Bu), 1.06 (s, 9, 3-*t*-Bu), 2.52 (br s, 3), 5.52 (br s, 1 vinyl), 5.72 (br s, 2, vinyl); UV max (C_2H_5OH) below 230 nm.

Anal. Calcd for $C_{14}H_{24}$: C, 87.42; H, 12.58. Found: C, 86.65; H, 12.15.

Diimide Reduction of 1,5-Di-*tert*-butyl-1,4-cyclohexadiene (10). A mixture of diene **10** (0.058 g), diglyme (0.69 mL), benzenesulfonylhydrazine (0.069 g), and triethylamine (0.07 mL) was heated at 80 °C for 3 h in a sealed 8 mm × 150 mm Pyrex tube.[22] After the tube was cooled and opened, the product was taken up in petroleum ether and washed with 5% H_2SO_4, 5% KOH, and water. The dried extract was analyzed on the capillary column to show diene **10** (40%), ene **16** (58%), and the saturated product D (~2%).

Preparation of 1,3- and 2,4-Di-*tert*-butylcyclohexene (15 and 16). The method described for the reduction of 1,4-di-*tert*-butylbenzene by lithium in ethylenediamine was used.[3] Lithium shot (0.48 g, 0.069 mol) was added to a stirred solution (maintained at 100–105 °C) of 1,3-di-*tert*-butylbenzene (1 g, 0.0052 mol) in 30 mL of ethylenediamine. The product was isolated after the mixture had been refluxed for 2 h. The crude product was a liquid mixture composed of arene **9** (17%), ene **15** (45%), ene **16** (33%), and 5% of material that was not identified. The mixture was separated on the $AgNO_3$/basic alumina column, the order of elution being ene **15**, arene **9**, and, finally, ene **16**. Final purification of the cycloalkenes was by GC.

The alkene with the shorter retention time on either column E (GC) or $AgNO_3/Al_2O_3$ (LC) is 1,3-di-*tert*-butylcyclohexene (**15**): ^{1}H NMR (CCl_4) δ 0.9 (s, 9, 3-*t*-Bu), 1.1 (s, 9, 1-*t*-Bu), 1.4–2.1 (m, 7), 5.4 (br s, 1, vinyl); UV max (C_2H_5OH) below 230 nm.

The cycloalkene with the longer retention time is 2,4-di-*tert*-butylcyclohexene (**16**): ^{1}H NMR (CCl_4) δ 0.89 (s, 9, 4-*t*-Bu), 1.01 (s, 9, 2-*t*-Bu), 1.15–2.33 (m, 7), 5.40 (m, 1, vinyl); UV max (C_2H_5OH) below 230 nm. Ene **16** is also the only alkene formed from the diimide reduction of 1,5-di-*tert*-butyl-1,4-cyclohexadiene (**10**) (see above).

1,3-Di-*tert*-butyl-1,3-cyclohexadiene (12) was prepared by isomerizing 1,5-di-*tert*-butyl-1,4-cyclohexadiene (**10**) with lithium ethylamide.[3] A mixture of **10** (0.49 g, 0.0026 mol), lithium (0.20 g, 0.029 mol), and ethylamine (89 mL) was refluxed for 2 h. The product was a 95:5 mixture of **12** and **10** from which preparative chromatography on column G yielded pure **12** as a colorless liquid: ^{1}H NMR (CCl_4) δ 1.05 (s, 9), 1.08 (s, 9), 2.03 (m, 4 allylic), 5.42 (br s, 1 vinyl).

3,5-Di-*tert*-butyl-1-methoxybenzene (21) was prepared by the reaction of dimethyl sulfate with 3,5-di-*tert*-butylphenol (Aldrich Chemical Co.).[23] From the phenol (21 g, 0.1 mol), NaOH (10 g, 0.25 mol), and dimethyl sulfate (30 g, 0.24 mol) was obtained, after distillation of the crude product, 19 g (86%) of pure (single peak on column A) 3,5-di-*tert*-butyl-1-methoxybenzene (**21**): bp 100.5 °C (4 mm); ^{1}H NMR ($CDCl_3$) δ 1.29 (s, 18, *t*-Bu), 3.68 (s, 3, OCH_3), 6.61, 6.65 (unsym d or 2 s, 2, aromatic), 6.88 (m, 1, aromatic); IR (neat) 3060 (w, =CH), 2980 (s), 2860 (s, CH), 1810 (w), 1720 (w, 1,3,5-trisubstituted aromatic), 1395 (w), 1380 (w), 1250 (m), 1205 (m), 1065 (m) cm^{-1}; MS (80 eV), *m/e* (relative intensity) 221 (9, P + 1), 220 (52, P), 206 (16), 205 (100, M$^+$), 177 (4), 149 (11), 121 (5), 115 (3), 95 (4), 91 (6), 57 (36), 41 (9).

Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.95; H, 11.30.

1,3-Di-*tert*-butyl-5-methoxy-1,4-cyclohexadiene (22) was prepared by the lithium in ammonia reduction of ether **21**.[7] To 600 mL of ammonia, purified by distillation from sodium, was added, with stirring, a solution of ether **21** (9.9 g, 0.045 mol) in 150 mL of tetrahydrofuran (distilled from lithium aluminum hydride) and 150 mL of *tert*-butyl alcohol. Lithium shot (4.9 g, 0.7 mol) was added in several portions, and the mixture was stirred at reflux for 4 h or until the blue color was discharged. Methanol was added to destroy the unreacted lithium and the ammonia allowed to evaporate at room temperature overnight. The reaction flask was evacuated by water aspirator, 250 mL of water added with stirring, and the tetrahydrofuran distilled. An additional 250 mL of water was added and the flask was warmed slightly (about 35 °C) during the distillation. The product formed a layer atop the aqueous solution and was extracted with ether and dried (Na_2SO_4). Evaporation of the solvent gave 9.0 g of a product found to be 80% of **22**, 7% unreacted **21**, and 12% of unidentified material (analysis on column A). Pure **22** was obtained by preparative GC: ^{1}H NMR ($CDCl_3$) δ 0.84 (s, 9, 3-*t*-Bu), 1.02 (s, 9, 1-*t*-Bu), 1.9 (m, 1, allyl, C-3), 2.54 (m, 2, allyl, C-6), 3.45 (s, 3, OCH_3), 4.55 (m, 1, vinyl, C-4), 5.42 (m, 1, vinyl, C-2).

Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 81.27; H, 11.95.

3,5-Di-*tert*-butyl-3-cyclohexenone (23) was obtained through the oxalic acid catalyzed hydrolysis of **22**.[8] To the enol ether **22** (4.0 g, 0.018 mol) dissolved in 200 mL of methanol was added oxalic acid dihydrate (3.0 g, 0.024 mol) dissolved in 20 mL of water. The mixture was stirred at room temperature for 2 h and then was neutralized with Na_2CO_3. After most of the methanol was stripped off by aspirator vacuum, the ketone was extracted with ether, the extract was dried (Na_2SO_4), and the solvent was removed to yield 3.0 g of a mixture of 80% ketone **23** and conjugated isomer **24** for a 64% yield of the unconjugated ketone **23** from the ether (subsequent preparations were less successful, rarely giving more than 30% **23**). Analysis of the 80:20 mixture showed ketone **23** to have the following characteristics: ^{1}H NMR ($CDCl_3$) δ 0.88 (s, 9, *t*-Bu), 1.05 (s, 9, *t*-Bu), 2.31 (m, 3, allyl + C-5?), 2.80 (m, 2, allyl), 5.62 (m, 1, vinyl, appears as unsym t, *J* = 1.5 Hz); IR ($CDCl_3$) 3060 (m, =CH), 2980 (s, CH), 1705 (s), 1655 (m, unconjugated C=O and C=C), 1390 (w), 1370 (m), 1260 (m), 1225 (m) cm^{-1}.

3,5-Di-*tert*-butyl-2-cyclohexenone (24) was the product of the hydrochloric acid hydrolysis of vinyl ether **22**.[8] Ether **22** (4.0 g, 0.018 mol), 30 mL of methanol, and 30 mL of 2 N HCl were heated under reflux for 2.5 h. The solution was extracted with ether, which was then washed with aqueous $NaHCO_3$ and dried (Na_2SO_4). Evaporation of the ether gave 3.4 g (0.016 mol, 91%) of ketone **24**: ^{1}H NMR ($CDCl_3$) δ 0.94 (s, 9, 4-*t*-Bu), 1.12 (s, 9, 2-*t*-Bu), 1.7–2.7 (m, 5, ring), 5.83 (m, 1, vinyl, apparent unsym d, *J* = 2 Hz); IR 3060 (m, =CH), 2980 (s), 2960 (s, CH), 1655 (s), 1610 (m, O=CC=C), 1470 (m), 1460 (m), 1390 (w), 1360 (m), 1260 (m) cm^{-1}.

3,5-Di-*tert*-butyl-3-cyclohexenone benzenesulfonylhydrazone (25) was prepared by stirring 2.6 g (0.013 mol) of the mixture obtained in the preparation of **23** with 2.15 g (0.013 mol) of benzenesulfonylhydrazide in 10 mL of ethanol at 0 °C for 1 h. The yield was 2.0 g (44%) of an 80:20 mixture of hydrazones **27** and **28**, respectively, mp 174–177 °C. The composition of the mixture was established by NMR, with **25** having the following characteristics: ^{1}H NMR ($CDCl_3$) δ 0.78 (s, 9, *t*-Bu), 1.00 (s, 9, *t*-Bu), 1.8–2.5 (m, 3, ring), 2.70 (s, 3, allyl + NH?), 5.50 (m, 1, vinyl), 7.32–7.88 (m, 5, aromatic).

3,5-Di-*tert*-butyl-2-cyclohexenone benzenesulfonylhydrazone (26) was produced by refluxing 3.0 g (0.015 mol) of ketone **24** and 2.5 g (0.015 mol) of benzenesulfonylhydrazide in 20 mL of ethanol for 1 h. The hydrazone formed readily upon cooling. Recrystallization from ethanol (with a few drops of ethyl acetate added) gave 40 g (76%) of the hydrazone: mp 185 °C dec; ^{1}H NMR ($CDCl_3$) δ 0.85 (s, 9, *t*-Bu), 1.02 (s, 9, *t*-Bu), 1.45–2.7 (several peaks, 5, ring + NH), 5.88 (apparent d, *J* = 1.5 Hz, 1, vinyl), 7.32–7.88 (m, 5, aromatic ring); IR ($CDCl_3$) 3220 (m, NH), 3060 (w, =CH), 2970 (s), 2905 (s), 2870 (s, CH), 1630 (m, C=C and C=N), 1450 (m), 1390 (m), 1370 (m), 1340 (m, SO_2), 1170 (s, SO_2) cm^{-1}.

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1,5-Di-*tert*-butyl-1,3-cyclohexadiene (13) and 2,6-di-*tert*-butyl-1,3-cyclohexadiene (14) were prepared by reacting the respective hydrazones, **25** and **26**, with *n*-butyllithium.[24,25]

Hydrazone **26** (3.5 g, 0.0097 mol) was stirred with 0.025 mol of *n*-butyllithium (1.6 N in hexane; more than 2 mol of *n*-butyllithium/mol of hydrazone required) for 20 min at room temperature. The reaction was quenched with water, the organic layer taken up in ether, washed several times with water, and dried over sodium sulfate, and the ether evaporated under vacuum. The yield of crude (95+%) diene **13** was 1.43 g (0.0025 mol, 72%). The dienes, diluted with pentane, were purified by preparative GC (column A). If concentrated solutions or neat diene was used, extensive isomerization occurred in the injection port. After separation, the dienes were percolated through alumina (Woelm's basic, activity grade 1) and stored until used as approximately 10% solutions in cyclohexane.

Characterization of 1,5-di-*tert*-butyl-1,3-cyclohexadiene (13): ^{1}H NMR (CDCl$_3$) δ 0.90 (s, 9, *t*-Bu), 1.06 (s, 9, *t*-Bu), 1.75–2.3 (m, 3, ring), 5.40–6.00 (m, 3, vinyl); IR (CDCl$_3$) 3045 (m, =CH), 2960 (s), 2880 (s, CH), 1640 (m), 1580 (m, conjugated C=C), 1470 (m), 1460 (m), 1390 (m), 1360 (m, CH bend), 1255 (m, *t*-Bu), 1205 cm^{-1}; UV max (cyclohexane) 265 nm (ϵ 5920); MS (80 eV), *m/e* (relative intensity) 193 (3), 192 (8, P), 175 (4), 134 (3), 119 (23), 105 (7), 91 (11), 79 (6), 77 (8), 58 (16), 57 (110, M$^+$), 55 (6), 43 (12), 14 (45), 39 (14), 29 (21).

Anal. Calcd for C$_{14}$H$_{24}$: C, 87.42; H, 12.58. Found: C, 87.25; H, 12.73.

Characterization of 2,6-di-*tert*-butyl-1,3-cyclohexadiene (14): ^{1}H NMR (CDCl$_3$) δ 0.86 (s, 9, *t*-Bu), 1.03 (s, 9, *t*-Bu), 1.98 (sharp m, 3, allyl), 5.37 (s, 1, vinyl C-1), 5.7–6.1 (br m, 2, vinyl C-2, C-3); IR (CDCl$_3$) 3040 (m, =CH), 2960 (s), 2870 (s, CH), 1640 (m), 1590 (w, conjugated C=C), 1470 (m), 1460 (m), 1390 (m), 1360 (m, CH bend), 1245 (m, *t*-Bu), 1205 (w), 1075 (m) cm^{-1}; UV max (cyclohexane) 254 nm (ϵ 11 000); MS (80 eV), *m/e* (relative intensity) 193 (2), 192 (7, P), 175 (4), 134 (5), 119 (32), 105 (5), 91 (9), 86 (13), 84 20), 77 (6), 58 (12), 57 (100, M$^+$), 55 (6), 43 (6), 41 (30), 39 (9), 29 (22).

Anal. Calcd for C$_{14}$H$_{24}$: C, 87.42; H, 12.58. Found: C, 87.44; H, 12.78.

3,5-Di-*tert*-butylcyclohexanol (27) was prepared by the hydrogenation of 3,5-di-*tert*-butylphenol (20.0 g, 0.1 mol) in 50 mL of glacial acetic acid over 3.0 g of 50% rhodium on carbon at 45 psi of hydrogen pressure at room temperature for 16 h.[26] Analysis of the reaction mixture by NMR showed complete reduction of the phenol. Analysis by GC (column B) showed peaks due to isomeric alcohols at 11 (30%) and 14.5 (65%) min and 5% of acetate at 6.5 and 9 min. Recovery of material was quantitative. The mixture of alcohols that was obtained, after removal of the acetates by GC, had the following properties: ^{1}H NMR (CDCl$_3$) δ 0.86 (s, 18, 2-*t*-Bu groups), 1.0–2.2 (m, 8–9, ring H + **OH**[27]), 3.5 and 4.16 (m, 1, carbinol proton), 3.5 represents isomer with axial H (equatorial OH), 4.16 isomer with equatorial H (axial OH[26]); IR (CHCl$_3$) 3730, 3440 (s, free and H-bonded OH), 2980 (s), 2870 (s, CH), 1470 (s), 1395 (s), 1365 (s), 1230 (s), 1050 (m) cm^{-1}.

3,5-Di-*tert*-butylcyclohexyl Acetate (28). Alcohol **27** (42 g, 0.2 mol) and dimethylaniline (32 mL, 0.25 mol) were added to 200 mL of dry (distilled from LiAlH$_4$) ethyl ether in a predried reaction flask. Acetyl chloride (18 g, 0.23 mol) in approximately 50 mL of dry ethyl ether was added cautiously, and upon completion of the addition of acetyl chloride, the reaction mixture was refluxed overnight.[28] The usual isolation procedure gave 44 g (84%) of crude product found to be 96.7% acetate isomers and 3.3% unreacted alcohol (one isomer) by GC (column B). A sample purified by GC on column A had the following characteristics: ^{1}H NMR (CHCl$_3$) δ 0.84 (s, 18, 2 *t*-Bu), 1.1–2.1 (m, ca. 8, ring), 1.98 (s, ca. 3, acetate methyl[a]), 5.12 (m, 1, ring H β to acetate group); IR (CHCl$_3$) 2980 (s), 2870 (s, CH), 1730 (s, ester C=O), 1480 (m), 1460 (m, CH bend), 1380, 1250 cm^{-1}.

***cis*- and *trans*-3,5-di-*tert*-butylcyclohexene (17 and 18)** were prepared by the pyrolysis of acetate **28**.[29] The acetate (44 g, 0.17 mol) was passed slowly (5 h) in a stream of nitrogen at 450 °C through a tube packed with fine glass beads and glass helicies. The system had been cleaned with alcoholic potassium hydroxide, rinsed thoroughly with water, and dried before use. Distillation of the pyrolyzed material gave 22.0 g (0.11 mol, 65%) of the olefin, bp 106 °C (13 mm). Analysis using the capillary column showed 96.7% of **17** and 2.3% of **18**; hydrogenation of the mixture over 5% Rh/Al$_2$O$_3$ gave the same ratio ($\pm$0.1%) of cis and trans alkane. The isomers, separated by GC (column C) at 175 °C had the following characteristics.

***cis*-3,5-Di-*tert*-butylcyclohexene (17)**: ^{1}H NMR (neat) δ 0.86 (s, 18, 2 *t*-Bu), 1.0–2.0 (m, 6, ring), 5.52 (br s, 2, vinyl); IR (neat) 3040 (m, vinyl CH), 2960 (s), 2870 (s, CH), 1645 (w, C=C), 1470 (m), 1395 (m, CH bend), 1240 (m), 1220 (m, CH, *t*-Bu) cm^{-1}; MS (80 eV), *m/e* (relative intensity) 194 (11, P), 138 (18), 137 (13), 136 (10), 95 (4), 82 (18), 81 (17), 80 (32), 79 (18), 78 (18), 67 (16), 58 (9), 57 (100, M$^+$), 55 (9), 43 (7), 41 (25), 29 (13).

***trans*-3,5-Di-*tert*-butylcyclohexene (18)**: ^{1}H NMR (CDCl$_3$) δ 0.84 (s, 9, *t*-Bu), 0.92 (s, 9, *t*-Bu), 1.0–2.0 (m, 6, ring), 5.62 (br s, 2, vinyl); IR (CDCl$_3$) 3020 (m, vinyl CH), 2960 (s), 2870 (s, CH), 1650 (m, C=C), 1470 (m), 1460 (m), 1390 (m), 1360 (m) cm^{-1}; MS (80 eV), *m/e* (relative intensity) 194 (6, P), 138 (9), 137 (6), 136 (6), 95 (6), 82 (12), 81 (13), 80 (22), 79 (17), 78 (14), 77 (5), 67 (14), 58 (9), 57 (100, M$^+$), 55 (9), 43 (10), 41 (32), 29 (23).

Anal. (of isomeric mixture) Calcd for C$_{14}$H$_{26}$: C, 86.52; H, 13.48. Found: C, 86.50; H, 13.76.

Registry No. **9**, 1014-60-4; **10**, 87012-26-8; **11**, 87012-28-0; **12**, 87012-27-9; **13**, 87012-29-1; **14**, 87012-30-4; **15**, 87012-31-5; **16**, 3419-75-8; **17**, 5132-52-5; **18**, 64672-58-8; **21**, 68039-43-0; **22**, 87012-32-6; **23**, 87012-33-7; **24**, 87012-34-8; **25**, 87012-35-9; **26**, 87012-36-0; **27**, 13049-48-4; **28**, 87012-37-1; Rh, 7440-16-6; 3,5-di-*tert*-butylphenol, 1138-52-9; benzenesulfonylhydrazide, 80-17-1.

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