

of *tert*-butoxy by a factor of 60–100. The values of the rate constants used for these calculations thus lead to calculated concentrations that are in agreement with the observed facts, *i.e.*, predominant termination by hydrocarbon radical coupling. At equimolar concentrations of hydrocarbon and hypochlorite, the concentration of hydrocarbon radicals is calculated to exceed that of *tert*-butoxy by about 2.5:1; at this level terminations by eq 5 and 6 may begin to make a contribution.

Experimental Section

Materials. The chemicals were reagent grade, were checked for purity by gas chromatography, and were used as received except as noted. Cyclohexane and toluene were percolated through freshly activated alumina immediately before use; in addition, the toluene was sulfuric acid washed. The AIBN (K & K Laboratories) assayed between 98 and 102% by the amount of N₂ evolved on complete decomposition. *tert*-Butyl hypochlorite was prepared from the alcohol and a twofold excess of hypochlorous acid, obtained by neutralization of Clorox (Procter and Gamble, 0.6–0.8 M sodium hypochlorite).

Procedures. The solutions for the kinetic runs were prepared immediately before use and were immersed in an ice–water–salt slurry in a glove bag. Dry nitrogen was bubbled through the solution for 2.5 hr in the dark; the solution was then passed through

activated alumina and was added to a 1.000-cm path length uv cell which was capped by a ground glass stopper held down by springs, the whole procedure being performed in the glove bag. Evaporative losses were not serious with slow N₂ throughputs during the deaeration; such losses were monitored, usually amounted to less than 5% by volume, and were assumed to consist of solvent. The extinction coefficient of the hypochlorite was determined to be 14.5 at 305 nm and Beer's law was obeyed up to 1.2 absorbance units with a Perkin-Elmer 450 spectrophotometer. The uv cell was jacketed and water was circulated through from a constant temperature bath maintained at 40° and regulated to 0.05°; the return water from the jacket was found to be 40° probably because the cell compartment attains close to that temperature after 5 min of instrument warm up.

A 150-W spot lamp was used for the light-initiated runs. Since it was found that the induction period usually lasted until 25–30% of the hypochlorite was consumed, the spot lamp was also used to quickly consume about 30% of the hypochlorite before the zero reading for the AIBN-initiated runs was taken, thus shortening the time of the experiment. Also passing the solution through alumina removed some hypochlorite; therefore, an appropriate excess of hypochlorite was used and its "initial" concentration was determined spectrophotometrically at "zero" time. The instrument beam was "on" only when readings were being taken, even though it did not provide a sufficient light intensity to cause any significant rate; each reading included a base-line scan to guard against instrument drifts. $A - A_{\infty}$ at 305 nm was used to calculate concentrations. The duration of the kinetic runs was such that less than 1% of the AIBN decomposed.

Peri Interactions in Some 1,8-Di-*tert*-butylnaphthalene Compounds. Rotation and Flipping of the *tert*-Butyl Groups

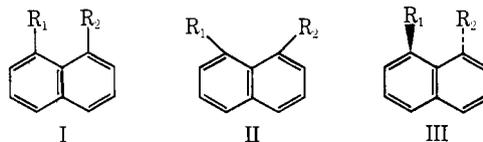
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Abstract: Because of steric interactions there is considerable twisting in 1,8-di-*tert*-butylnaphthalenes, the *tert*-butyl groups being found on opposite sides of the mean plane of the naphthalene ring. The barrier to flipping of these groups to give a mirror-image conformation is greater than 24 kcal/mol. The same steric interactions give rise, in contrast, to a particularly low barrier to rotation about the *tert*-butylnaphthalene bonds of about 6.5 kcal/mol.

The essence of conformational analysis is the study of how molecules accommodate strain. Acyclic and simple cyclic molecules can do this rather well; thus in the case of steric strain, an acyclic molecule will prefer to adopt a conformation with bulky groups *trans* while a substituted cyclohexane will choose that conformation which has most bulky groups equatorial. In more rigid molecules, there is a greater scope for intramolecular strain yet there may be much less scope for the accommodation of it, so that striking effects may occur.

Substituted naphthalenes with substituents in the 1 and 8 positions (*peri* substituents, I) are a case in point and much work has been done on the subject. This



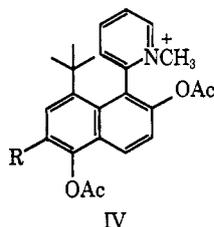
has recently been reviewed by Balasubramanian.² It is interesting that here steric strain and the relief of it have to be balanced against distortion of the aromatic nucleus and, as a consequence, reduction of aromatic stability. Groups R₁ and R₂ may be accommodated by distortion of the *peri* bonds both in (II) and out of the plane (III) of the naphthalene nucleus.

Our interests in these molecules came together over the 1,8-di-*tert*-butylnaphthalenes prepared earlier,^{3,4} with the hope that evidence of the interaction of the

(1) (a) University College; (b) Fordham University; (c) a part of this research has been presented by J. E. Anderson, R. W. Franck, and W. L. Mandella, 3rd Northeast Regional Meeting of the American Chemical Society Abstracts, 182; (d) acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society for Grant 5150-D4 in support of R. W. Franck while on sabbatical in the United Kingdom.

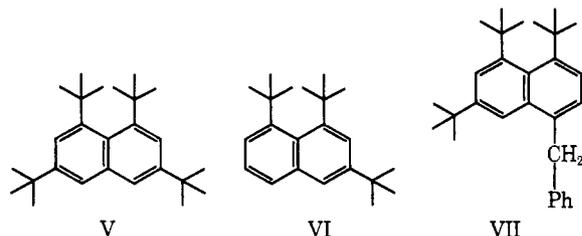
(2) V. Balasubramanian, *Chem. Rev.*, **66**, 567 (1966).
 (3) R. W. Franck and E. G. Leser, *J. Amer. Chem. Soc.*, **91**, 1577 (1969).
 (4) R. W. Franck and E. G. Leser, *J. Org. Chem.*, **35**, 3932 (1970).

tert-butyl groups in the form of hindered rotation could be obtained and quantified by way of a temperature-dependent nmr spectrum.⁵ This would not be unprecedented since House and his coworkers have shown^{6,7} that, when R₁ and R₂ are suitably substituted phenyl groups, temperature-dependent nmr spectra are obtained reflecting barriers to rotation about the phenyl-naphthalene bond of 15–16 kcal/mol. More recently Fields and Regan⁸ have shown that the molecule IV



(R = Br or OAc) has the *tert*-butyl group and the 2-pyridyl group on opposite sides of the mean plane of the ring. The barrier to flipping of the two groups is not less than 12.0 kcal/mol.⁹ There are other nmr works of some relevance,^{10–13} and preparation of optically active binaphthyls¹⁴ indicates that barriers to rotation about *peri* bonds may be as high as 28 kcal/mol. In so far as a *tert*-butyl group is generally considered to be larger than a phenyl group, it is surprising that in work up to now on *peri-tert*-butylnaphthalenes the *tert*-butyl signals have appeared as a single sharp line in the nmr spectrum.^{3,4} By way of explanation it was suggested that if distortion out of the plane of the naphthalene III be sufficiently great, interaction of the substituents and, therefore, steric inhibition of rotation may be reduced, so that changes in the nmr spectrum associated with hindered rotation may not be observed.³

We now report that in the molecules V, VI, and VII



the barrier to *tert*-butyl rotation is about 6.5 kcal/mol. More importantly the methylene hydrogens of VII are diastereotopic up to 195° indicating that the *peri-tert*-

(5) J. E. Anderson and A. C. Oehlschlager, *Chem. Commun.*, 284 (1968).

(6) H. O. House and R. W. Bashe, *J. Org. Chem.*, **32**, 784 (1967).

(7) H. O. House, W. J. Campbell, and M. Gall, *ibid.*, **35**, 1815 (1970).

(8) D. L. Fields and T. H. Regan, *ibid.*, **36**, 2986 (1971).

(9) Fields and Regan⁸ report this barrier as 12.0 kcal/mol. The spectral changes on which they base this conclusion are indicative of slow flipping of these groups and slow rotation about the pyridinium-naphthalene bond. It is not sufficient that only one of these processes be slow. Thus the barrier to either rotation or flipping is 12.0 kcal/mol, the barrier to the other process is 12.0 kcal/mol or greater, and there is nothing in Fields and Regan's results to allow a distinction between the two processes.

(10) G. W. Everett and R. H. Holm, *J. Amer. Chem. Soc.*, **87**, 2117 (1965).

(11) K. D. Bartle, P. M. G. Bavin, D. W. Jones, and R. L. 'Amie, *Tetrahedron*, **26**, 911 (1970).

(12) J. Almog, A. Y. Meyer, and E. D. Bergman, *Chem. Commun.*, 1011 (1970).

(13) A. Mannschreck and L. Ernst, *Chem. Ber.*, **104**, 228 (1971).

(14) M. M. Harris, R. Z. Mazengo, and A. S. Cooke, *J. Chem. Soc.*, 2575 (1967), and earlier references therein.

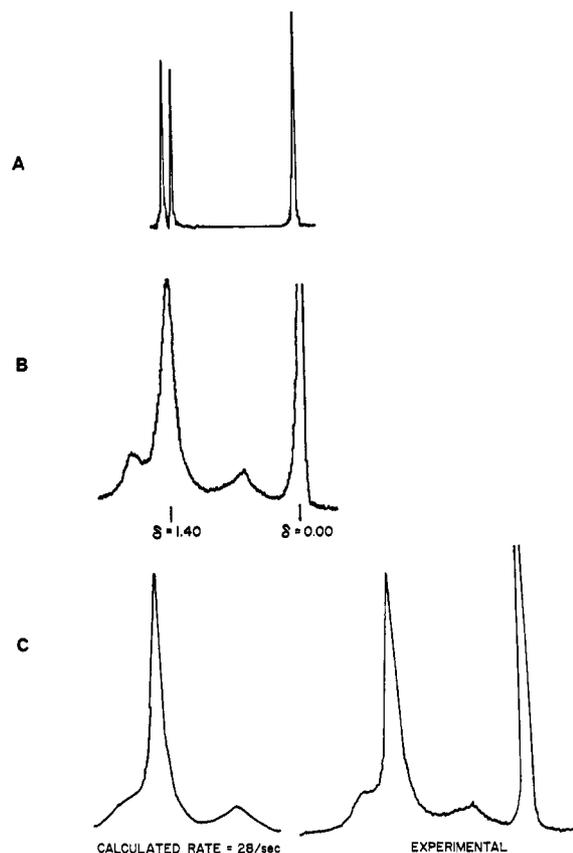
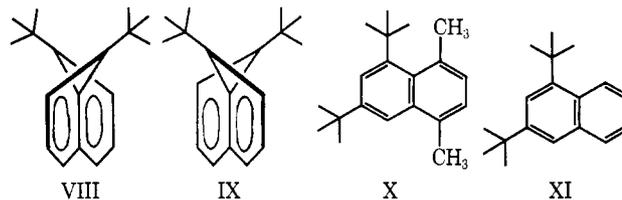


Figure 1. Nmr spectrum of the *tert*-butyl region of V at (A) -35° , (B) -146° , (C) -142° , calculated and experimental. The peak at the right in experimental spectra is TMS.

butyl groups are twisted out of the plane of the naphthalene as in VIII and that interconversion between VIII and its mirror-image form IX is slow on the nmr



time scale even at 195°. In X and XI rotation of the *peri-tert*-butyl is fast on the nmr time scale even at -150° .

Results¹⁵

The nmr spectrum in the region δ 1–2 of a vinyl chloride solution of the compound V comprises two signals of equal intensity at δ 1.29 attributed to *peri-tert*-butyl groups and at δ 1.39 attributed to the other *tert*-butyl groups. As the temperature is lowered below about -80° the signal of the *peri-tert*-butyl groups begins to broaden, and it eventually splits. At about -153° , the spectrum in this region comprises three broad lines (half-bandwidth about 20 Hz) of relative intensities 1:4:1 at about δ 0.61, 1.40, and 1.78 (see Figure 1). The signal of the *peri* groups is then a 1:1:1 triplet at this temperature, the middle line of which coincides

(15) Where appropriate spectral details agree with those already published,^{3,4} small differences are explained by differences in solvent. Assignment of signals follows that given earlier.^{3,4}

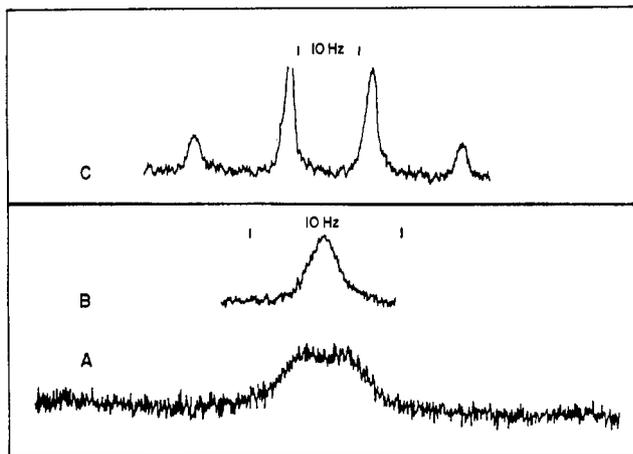


Figure 2. The CH_2 region of the spectrum of VII (A) at 100 MHz at ambient probe temperature for 1-bromonaphthalene solution, (B) same as A but at 195° , (C) at 220 MHz at ambient probe temperature in deuteriobenzene solution. The appearance of the *tert*-butyl region at low temperature is very similar to that shown in Figure 1.

with the substantially unaltered singlet of the other *tert*-butyl groups. A computer fit for the spectrum at -142° gives a rate constant of 28 sec^{-1} for the rate process producing the changes in the spectrum, whence the free energy of activation for the process is $6.6 \pm 0.3 \text{ kcal/mol}$ at this temperature.

In the case of the compound VI at room temperature only a singlet absorption at $\delta 1.27$ is seen for the two chemically different *peri* groups. This signal is of twice the intensity of the signal of the remaining *tert*-butyl group at $\delta 1.38$. As the temperature is lowered, the behavior of the first signal is very similar to that of V, and at low temperatures three equal broad signals are seen at $\delta 0.58, 1.37,$ and 1.63 . Treatment of the results as before suggests a rate for the conformational process of about 150 sec^{-1} at -137° , whence the free energy of activation is $6.4 \pm 0.3 \text{ kcal/mol}$.

There are three *tert*-butyl signals on the nmr spectrum of compound VII at $\delta 1.26, 1.27,$ and 1.29 . As the temperature is lowered the two upfield of these signals broaden. At about -146° these two signals appear as three broad singlets at $\delta 0.60, 1.40,$ and 1.72 in a manner very similar to compound V. The barrier to rotation of the *tert*-butyl groups is about 6.5 kcal/mol . Of greater interest is the spectrum of the benzylmethylene group of this compound which appears as an AB quartet at ambient temperature (Figure 2). The relative shift of the A and B parts is small compared with the coupling constant of 16 Hz (see Table I) so that the separation of the inner two lines of the quartet is small and the intensity of the outer lines is low. As the tem-

Table I. Relative Chemical Shift of A and B Parts of the Signal of the Methylene Group of VII and the Separation of the Inner Two Lines of the AB Quartet (100 MHz) at Ambient Probe Temperature

Solvent	$\delta\nu_{AB}$, ppm	Separation of inner lines, Hz
Benzene- d_6	0.113	3.5
Toluene- d_6	0.091	2.4
1-Bromonaphthalene	0.099	2.8

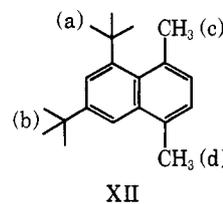
perature of a sample in 1-bromonaphthalene solution is raised, the relative shift of A and B is reduced so that the inner lines move even closer together, and soon appear as a single broad line and the outer lines become vanishingly small. The variation of the total width of the central part of the AB quartet is shown in Table II.

Table II. Width at Half-Height of the Central Peaks of the AB Quartet for the Methylene Hydrogens of VII in 1-Bromonaphthalene Solution

Temp, $^\circ\text{C}$	Width, Hz	Temp, $^\circ\text{C}$	Width, Hz
33	6.2	125	2.8
65	4.9	145	2.7
85	4.2	165	1.8
105	3.5	195	2.2

At room temperature this is the width of a partially merged doublet and at higher temperatures it is the width of a broad singlet. The fact that this passes through a minimum and then increases again to 195° suggests that while the A signal, at first downfield, moves upfield of the B signal, the two hydrogens of the methylene group remain diastereotopic. The fact that the AB quartet with relative chemical shift of about 5 Hz persists at 195° suggests that any process which would make the A and B hydrogens equivalent must have a barrier greater than about 24 kcal/mol .¹⁶

The spectrum of X shows no significant change down to -150° , but does show another interesting effect. Below about -80° , the signal of the *tert*-butyl group (b) which is not *peri* (see XII) and that of the methyl group



(d) which though *peri* is not adjacent to the *peri-tert*-butyl group begin to broaden relative to the other signals (see Figure 3 and Table III). At -149° , broadening of the *tert*-butyl group a signal has caught up with that of b but methyl d is still very much broader than c. We can see no explanation of these changes in terms of the usual kind of nmr rate process. The broadening associated with such processes takes place over a narrower temperature range and is much greater than is observed here for b and d though their broadening is genuine if signals a and c are used as references. One might qualify this last point insofar as it is not clear whether the correct observation is increased broadening of b and d or unusual narrowing of a and c.

It may be that the line widths of b and d or of a and c are determined by some relaxation process rather than by magnetic field homogeneity which is usually considered to be the controlling factor. It would be interesting if, as seems possible, this relaxation time could be linked to the correlation time for rotation of either

(16) The assertion that the A and B hydrogens remain diastereotopic at 195° is not completely unequivocal. We would emphasize however that the change in the line width can be explained in terms of changes in the chemical shift of A and B which are known to be taking place, and there are no anomalous changes in line width that could be attributed to the flipping process becoming rapid on the nmr time scale.

Table III. Relative Widths and Heights of Methyl and *tert*-Butyl Signals in XII

Temp, °C	CH ₃ signals			<i>tert</i> -Butyl signals		
	Rel height c/d	Width at half-height, Hz		Rel height a/b	Width at half-height, Hz	
		c	d		a	b
Ambient	0.96	2.0	2.1	1.06	1.28	1.28
-85	1.20	2.4	2.8	1.04	1.8	1.8
-95	1.28	2.4	3.0	1.05	2.1	2.1
-105	1.45	2.4	3.3	1.08	2.4	2.4
-115	1.49	2.8	4.3	1.18	3.4	3.8
-125	1.77	3.6	6.4	1.41	5.2	7.7
-130	1.92	<i>a</i>	<i>a</i>	1.49	<i>a</i>	<i>a</i>
-135	2.17	<i>a</i>	<i>a</i>	1.32	<i>a</i>	<i>a</i>
-140	2.29	<i>a</i>	<i>a</i>	1.05	<i>a</i>	<i>a</i>
-145	<i>b</i>	<i>a</i>	<i>a</i>	1.00	<i>a</i>	<i>a</i>
-149	<i>b</i>	<i>a</i>	<i>a</i>	0.90	<i>a</i>	<i>a</i>

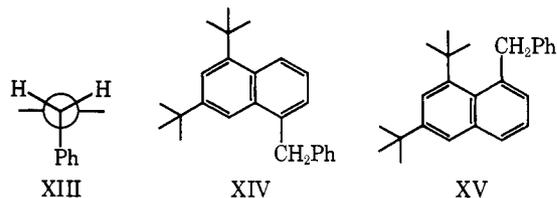
^a Signals overlap substantially. ^b Signals merged.

of the pairs of groups b and d, or a and c. We know of no precedent for this.

Discussion

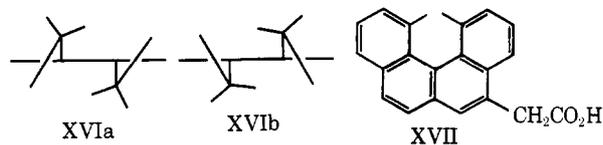
The fact that the methylene hydrogens of the benzyl group of VII are nonequivalent implies that at any instant there is an asymmetry about the mean plane of the naphthalene. There are two possible sources of this asymmetry which deserve discussion and associated with each there is a possible conformational process which would remove the asymmetry on the average.

It may be argued that rotation about the naphthalene-benzyl substituent bond is slow on the nmr time scale. If this is so, and if the preferred conformation about this bond is as in XIII,¹⁷ the observed nonequivalence of the benzyl hydrogens can be explained. We think it unlikely that the barrier to rotation of a benzyl group be greater than 24 kcal/mol. Further, examination of the model benzyl compounds XIV and XV down to



-110° in toluene-*d*₆ shows no such nonequivalence, a corollary behavior which we might reasonably expect if the AB quartet of VII were due to slow rotation of the benzyl group.

There is great steric interaction between the two *peri-tert*-butyl groups in VII and it is reasonable to postulate that to accommodate this strain these groups are twisted out of the mean plane of the naphthalene ring.¹⁸ If this is so, as with XVIa, then as far as a group attached to the naphthalene at any position is



(17) No single conformation with the benzylic hydrogens on opposite sides of the plane of a planar naphthalene molecule and the phenyl group in that plane can explain the observed spectrum.

(18) The distortion of these groups within the plane of the ring can be rejected as a cause of nonequivalence, since it will not render the hydrogens diastereotopic.

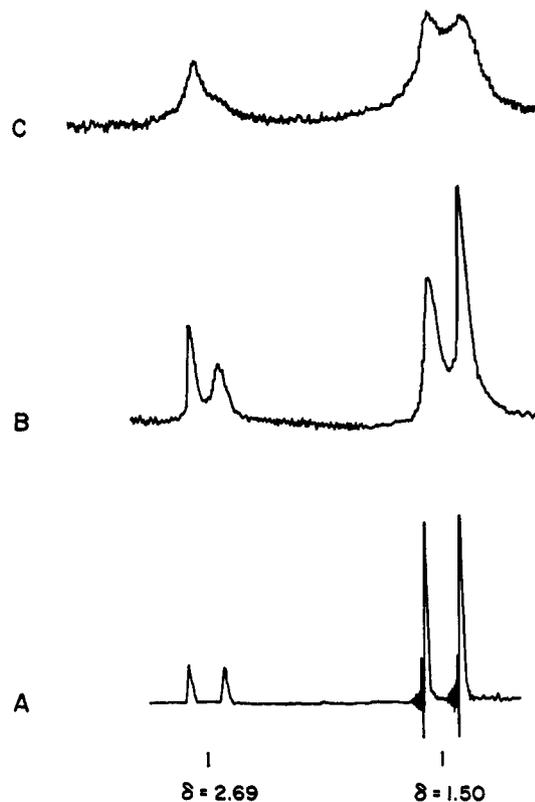


Figure 3. *tert*-Butyl and methyl signals of X (A) at ambient probe temperature, (B) at -130°, (C) at -149°.

concerned, the two faces of the molecule are different and this is sufficient to render the benzylic hydrogens diastereotopic. This nonequivalence is independent of the conformation around the benzyl-naphthalene bond that is adopted. The benzylic hydrogens become equivalent only when the *tert*-butyls flip through the mean plane of the naphthalene to the form XVIIb.

We suggest that it is this process which is slow on the nmr time scale for VII and that the barrier to this process is greater than 24 kcal/mol. This stability to inversion may be compared to that of the dimethylbenz-(*c*)phenanthrene XVII prepared by Newman, which racemizes rapidly, in a similar manner, at 300°.¹⁹

In the diagrams XVIa and XVIb we have presumed that the naphthalene rings are planar, whereas in the representations VIII and IX carbon atoms 1 and 8 are also out of the plane of the remaining carbon atoms. The nonequivalence of the benzylic hydrogens of VII indicates only that the *tert*-butyl groups are on opposite sides of the *mean* plane of the naphthalene. On the basis of the results for other sterically crowded naphthalenes² none of the carbon atoms need be in the mean plane so that each of VIII, IX, XVIa, and XVIb is a limiting representation of the structure.

It is reasonable to expect that the transition state for flipping of the *tert*-butyl groups is a form with the naphthalene ring planar and the *tert*-butyl groups in the plane of the ring, or some form of less energy.²⁰ The

(19) M. S. Newman and R. M. Wise, *J. Amer. Chem. Soc.*, **78**, 450 (1956).

(20) The former is less likely since interaction between the two *tert*-butyl groups and between each *tert*-butyl group and its adjacent ortho hydrogen is at its greatest. On the basis that this will be the maximum of energy, the actual transition state may be one with both *tert*-butyl groups on the same side of the mean plane. Experimental results give no information on this problem.

Table V. Saturated Adducts, Yields, Physical and Spectral Data

Compound	% yield	Mp °C	Formula	% calcd C	% calcd H	% found C	% found H	Ir, μ (CCl ₄)	Nmr, ppm (TMS, CCl ₄)
R ₁ = C(CH ₃) ₃ ; R ₂ = H XIXa	93.7	94.5-96.5	C ₂₂ H ₃₄ O	84.02	83.95			3.45, 6.81, 6.90, 7.22, 7.38, 9.61, 11.55	1.32 (18 H, s), 1.45 (9 H, s), 2.50 (4 H, m), 5.03 (1 H, m), 6.97 (1 H, d, <i>J</i> = 1.8 Hz), 7.24 (1 H, d, <i>J</i> = 1.8 Hz)
R ₁ = H; R ₂ = C(CH ₃) ₃ XIXb	100	84-86	C ₂₂ H ₃₄ O	84.02	83.82			3.43, 6.80, 6.89, 7.21, 7.37, 8.01, 10.30, 10.81, 11.60	1.22 (9 H, s), 1.32 (9 H, s), 1.39 (9 H, s), 1.87 (4 H, m), 5.55 (1 H, m), 7.08 (1 H, d, <i>J</i> = 1.5 Hz), 7.23 (1 H, d, <i>J</i> = 1.5 Hz)
R ₁ = H; R ₂ = CH ₂ Ph XIXd	100	95-108	C ₂₅ H ₃₂ O	86.15	85.91			3.43, 6.81, 6.90, 7.22, 7.39, 11.41	1.30 (9 H, s), 1.34 (9 H, s), 1.52 (9 H, s), 1.85 (8 H, m), AB quartet, 2 H, 3.46 H _A , 3.51 H _B , <i>J</i> _{AB} = 9 Hz, -CH ₂ Ph of XIXd, AB quartet, 2 H, 3.73 H _A , 3.98 H _B , <i>J</i> _{AB} = 14.5 Hz, -CH ₂ Ph of XIXc, 5.12 (1 H, m, methine of XIXc), 5.59 (1 H, m, methine of XIXd), 6.92-7.50 (14 H, m)
R ₁ = CH ₂ Ph; R ₂ = H XIXc									
R ₁ = C(CH ₃) ₃ ; R ₂ = CH ₂ Ph XIXe	100		C ₂₉ H ₄₀ O	86.08					1.30 (9 H, s), 1.35 (9 H, s), 1.48 (9 H, s), 2.09 (4 H, m), 3.45 (2 H, s), 6.92 (2 H, d, <i>J</i> = 2 Hz), 7.08-7.53 (5 H, m)
R ₁ = CH ₂ Ph; R ₂ = C(CH ₃) ₃ XIXf	100	112-116	C ₂₉ H ₄₀ O	86.08	85.98			3.40, 6.80, 6.89, 7.22, 7.37, 8.49 9.28, 11.17, 11.43 14.37	1.22 (9 H, s), 1.35 (9 H, s), 1.53 (9 H, s), 1.82 (4 H, m), AB quartet, 2 H, 3.66 H _A , 3.93 H _B , <i>J</i> _{AB} = 14 Hz, 7.05-7.53 (5 H, m)

The naphthalenes²³ were prepared using methods developed in previous work and outlined in the scheme. We were able to separate adducts XVIIa and b formed in a 35:65 ratio *via* chromatography on Florisil, and thus carry through isomerically homogenous a and b throughout the sequence. The good feature of having both isomers allowed the unambiguous assignment of structure to XXa, which had previously been deduced on spectroscopic arguments without a comparison isomer. Unfortunately the c and d isomers could not be separated at any stage of our work and they have been studied as a mixture. The assignment of structure to XXd and c is based on the nmr signals for the uncrowded and crowded benzylmethylenes at δ 4.38 and 4.71, respectively, and comparing this to the 1-benzyl-naphthalene resonance of δ 4.38.²⁴ This argument then serves as the basis for the assignments for XXe.

Although the XVIIIe and f adducts (58:42 ratio) were not separable, we were able to obtain a homogenous sample of XXe since XIXe aromatized at a faster rate than XIXf. Thus, on very short exposure of an XIXe and f mixture to acid, there resulted a mixture of XXe and XIXf which was easily separable *via* preparative tlc on silica gel.

Diels-Alder Adducts. Physical and spectral data appear in Table IV.

I. 4,5,7-Tri-*tert*-butyl-1,4-dihydronaphthalene 1,4-Endoxide (XVIIIa) and 1,5,7-Tri-*tert*-butyl-1,4-dihydronaphthalene 1,4-Endoxide (XVIIIb). To a vigorously stirring refluxing solution of 0.871 g (7.42 mmol) of isopentyl nitrite and 1.231 g (9.91 mmol) of 2-*tert*-butylfuran in 40 ml of methylene chloride was added over a period of 2 hr a solution of 1.239 g (4.96 mmol) of 3,5-di-*tert*-butylanthranilic acid in 40 ml of spectral grade acetone. The resulting solution was refluxed an additional 2 hr after the initial addition period. The reaction mixture was cooled and the solvents were evaporated under reduced pressure to yield an amber oil which was dissolved in pentane, washed four times with 10-ml portions of saturated sodium bicarbonate solution, washed once with saturated sodium chloride solution, and dried over sodium sulfate. The pentane was evaporated to yield an amber-white solid which was chromatographed over 180 g of Florisil using hexane and benzene as eluents. The hindered adduct XVIIIa was eluted first as a yellow-white solid with hexane. The unhindered adduct XVIIIb was then eluted off with benzene as a purple-white solid. Both adducts were then separately sublimed (0.05-0.10 mm, 80-90°) to yield light yellow-white solids which were recrystallized from pentane at Dry Ice temperatures to yield white solids; 0.392 g of XVIIIe; 0.495 g of XVIIIb. Vpc analysis of the reaction mixture (SE-30, 1/8 in., 240°) showed the adducts to be in a ratio of 35:65, hindered:unhindered.

(23) For internal consistency the naphthalenes in the experimental scheme have been renumbered as follows: VI = XXa, VII = XXe, XIV = XXd, and XV = XXc.

(24) L. A. Cort, R. G. Manders, and G. R. Parlett, *J. Chem. Soc.*, 2844 (1971).

4-Benzyl-5,7-di-*tert*-butyl-1,4-dihydronaphthalene 1,4-Endoxide (XVIIIc) and 1-Benzyl-5,7-di-*tert*-butyl-1,4-dihydronaphthalene 1,4-Endoxide (XVIIId). To a vigorously stirring refluxing solution of 0.560 g (4.78 mmol) of isopentyl nitrite and 1.003 g (6.31 mmol) of 2-benzylfuran in 30 ml of spectral grade methylene chloride was added over a period of 2.75 hr a solution of 0.788 g (3.16 mmol) of 3,5-di-*tert*-butylanthranilic acid in 30 ml of spectral grade acetone. The resulting solution was refluxed an additional 2 hr after the initial addition period. The reaction mixture was cooled and the solvents were removed under reduced pressure to yield an amber oil which was dissolved in pentane, washed three times with saturated sodium bicarbonate solution, washed once with saturated sodium chloride solution, and dried over sodium sulfate. The pentane was evaporated and the resulting amber oil was chromatographed over 30 g of Florisil with hexane as the eluent until the furan was completely separated (weight recovered, 0.525 g). The column was then eluted with methylene chloride, the solvent evaporated, and the resulting oil recrystallized from methanol to yield 0.619 g of the desired products as a white solid. Nmr showed the adducts to be in the ratio of 1.5:1, hindered:unhindered.

1-Benzyl-4,5,7-tri-*tert*-butyl-1,4-dihydronaphthalene 1,4-Endoxide (XVIIIe) and 4-Benzyl-1,5,7-tri-*tert*-butyl-1,4-dihydronaphthalene 1,4-Endoxide (XVIIIf). To a vigorously stirring refluxing solution of 1.647 g (14.02 mmol) of isopentyl nitrite and 1.502 g (7.01 mmol) of 1-benzyl-5-*tert*-butylfuran in 40 ml of methylene chloride was added over a period of 2.5 hr a solution of 0.876 g (3.51 mmol) of 3,5-di-*tert*-butylanthranilic acid in 40 ml of spectral grade acetone. The resulting solution was refluxed an additional 2 hr after the initial addition period. The solution was cooled and the solvents were removed under reduced pressure on a rotary evaporator to yield a dark brown liquid which was chromatographed over 40 g of Florisil using hexane as the eluent. The furan and products came off together. These fractions were then combined and subjected to short path distillation using a Kugelrohr oven. The furan came off first, bp 25-150° (0.35 mm). The endoxides came off together, bp 150-190° (0.35-0.55 mm), as an orange-yellow oil, 0.592 g, which solidified overnight. An attempt was made to separate the endoxides *via* column chromatography, 40 g of Florisil (60-100 mesh), using hexane as the eluent. This resulted only in obtaining fractions which were enriched in one isomer: 0.024 g of XVIIIe (>95% by nmr), mp 104.5-106°; 0.225 g of a 48:38 mixture of XVIIIe:XVIIIf, mp 81-125°; 0.103 g of XVIIIe (>95% by nmr), mp 135-138°. Total yield was 0.35 g, 25%; 11% XVIIIe, 14% XVIIIe. The 48:38 mixture was used for the hydrogenation.

Hydrogenation of Endoxides. A semimicro hydrogenation apparatus, consisting of a gas buret and a vacuum outlet system, was used so that the uptake of hydrogen in small quantities could be accurately measured. The adduct(s) to be hydrogenated was dissolved in absolute ethanol (except where otherwise noted) and added to the catalyst contained in the reaction flask. All the adducts were hydrogenated using the above apparatus and technique at atmo-

Table VI. Naphthalenes, Yield, Physical and Spectral Data

Compound	% yield	Mp, °C	Formula	% calcd		% found		Ir, μ (CCl ₄)	Nmr, ppm (TMS, CCl ₄)	Uv $\lambda_{\max}^{95\% \text{ EtOH}}$, nm (log ϵ)
				C	H	C	H			
R ₁ = (CH ₃) ₃ ; R ₂ = H XXa	91	54-57	C ₂₂ H ₃₂	89.12	10.88	88.98	10.93	3.30 (sh), 3.40, 6.78, 6.84, 7.16, 7.25, 7.32	1.27 (9 H, s, <i>peri-t</i> -butyl), 1.28 (9 H, s, <i>peri-t</i> - butyl), 1.40 (9 H, s, C ₃ - <i>t</i> -butyl), 7.1-7.6 (5 H, m)	223 (4.28), 228 (4.31), 253 (4.32), 310 (3.49)
R ₁ = H; R ₂ = C(CH ₃) ₃ XXb	75.4	91-93	C ₂₂ H ₃₂	89.12	10.88	89.02	10.82	3.35 (sh), 3.43, 6.79, 6.88, 7.20, 7.37, 11.32	1.45 (9 H, s, C ₃ - <i>t</i> -butyl), 1.65 (18 H, s, <i>peri-t</i> - butyl), 7.20-7.62 (3 H, m, H ₂ H ₆ H ₇), 8.25 (2 H, m, H ₄ , R ₁)	215 (4.39), 227 (4.82), 232 (5.02), 276 (3.84), 285 (3.93), 293 (3.86)
R ₁ = H; R ₂ = CH ₂ Ph XXd	61	Oil	C ₂₆ H ₃₀	90.85	9.15	91.02	9.14	3.30 (sh), 3.35 (sh), 3.45, 6.75, 6.80, 6.88, 6.72, 7.20, 7.38, 11.45	1.31 (9 H, s), 1.42 (9 H, s), 1.63 (18 H, s), 4.38 (2 H, s, -CH ₂ Ph of XXd), 4.71 (2 H, s, -CH ₂ Ph of XXc), 6.87-7.72 (16 H, m), 7.79 (2 H, m, <i>peri</i> H of XXc), 8.31 (2 H, d, d, <i>J</i> = 7.5 Hz, <i>J</i> = 2.5 Hz, <i>peri</i> H of XXd)	216 (4.62), 227 (4.81), 233 (4.90), 264 (3.69), 277 (3.89), 287 (3.99), 293 (3.93)
R ₁ = CH ₂ Ph; R ₂ = H XXc										
R ₁ = C(CH ₃) ₃ ; R ₂ = CH ₂ Ph XXe	74	61-62	C ₂₆ H ₃₈	90.09	9.91	90.14	9.86	3.35 (sh), 3.43, 3.50, 3.53, 6.78, 6.83, 6.92, 7.22, 7.40	1.28 (9 H, s), 1.29 (9 H, s), 1.31 (9 H, s), 4.28 (2 H, s), AB quartet, 2 H, 6.97 H _A , 7.39 H _B , <i>J</i> _{AB} = 7.5 Hz, 7.15 (5 H, s), AB quartet, 2 H, 7.44 H _A , 7.54 H _B , <i>J</i> _{AB} = 2 Hz	228 (4.26), 258 (4.56), 322 (3.76)

spheric pressure and room temperature. The crude saturated endoxides were isolated by evaporation of the solvent after the hydrogenation catalyst had been first separated by filtration. Yields and physical and spectral data appear in Table V.

4,5,7-Tri-*tert*-butyl-1,2,3,4-tetrahydronaphthalene 1,4-Endoxide (XIXa). Hydrogenation of 0.392 g (1.26 mmol) of adduct XVIIIa in 13 ml of absolute ethanol and 9 ml of ethyl acetate containing 0.056 g of 10% palladium on charcoal catalyst was complete in 1.25 hr. Recrystallization from pentane at Dry Ice temperatures yielded the analysis sample.

1,5,7-Tri-*tert*-butyl-1,2,3,4-tetrahydronaphthalene 1,4-Endoxide (XIXb). Hydrogenation of 0.493 g (1.58 mmol) of adduct XVIIIb in 27 ml of absolute ethanol containing 0.057 g of 10% palladium on charcoal catalyst was complete in 1 hr. Recrystallization from absolute ethanol afforded the analysis sample.

4-Benzyl-5,7-di-*tert*-butyl-1,2,3,4-tetrahydronaphthalene 1,4-Endoxide (XIXc) and 1-Benzyl-5,7-di-*tert*-butyl-1,2,3,4-tetrahydronaphthalene 1,4-Endoxide (XIXd). Hydrogenation of 0.535 g (1.54 mmol) of a mixture of adducts XVIIIc and XVIIId in 40 ml of absolute ethanol containing 0.117 g of 10% palladium on charcoal catalyst was complete in 2 hr. Evaporation of the ethanol yielded the analysis sample. Nmr showed the adducts to be in the ratio of 1.1:1, hindered:unhindered.

1-Benzyl-4,5,7-tri-*tert*-butyl-1,2,3,4-tetrahydronaphthalene 1,4-Endoxide (XIXe) and 4-Benzyl-1,5,7-tri-*tert*-butyl-1,2,3,4-tetrahydronaphthalene 1,4-Endoxide (XIX). Hydrogenation of 0.232 g (0.574 mmol) of the adducts in 20 ml of absolute ethanol containing 10 drops of ethyl acetate added to ensure complete solution and 0.07 g of 10% palladium on charcoal catalyst was complete in 1 hr. Nmr showed the products to be in the ratio of 75:67, hindered:unhindered.

Naphthalenes. Yields and physical and spectral data appear in Table VI.

1,3,8-Tri-*tert*-butylnaphthalene (XXa). The unsaturated adduct XIXa (0.118 g, 0.37 mmol) was placed in a 6-in. test tube and dissolved in 2 ml of absolute ethanol. A cooled (room temperature) solution (3.5 ml) of absolute ethanol saturated with hydrogen chloride was then added and the test tube was vigorously agitated for 2 min. The reaction mixture was then extracted three times with pentane which was evaporated to afford 0.102 g of the desired product. Recrystallization from warm (42°) methanol afforded the analysis sample.

1,3,5-Tri-*tert*-butylnaphthalene (XXb). XIXb (0.121 g, 0.385 mmol) was dissolved in 2 ml of absolute ethanol. A cooled (room

temperature) solution of absolute ethanol (3.5 ml) saturated with hydrogen chloride was added and the resulting solution was stirred for 2.5 hr. After about 0.25 hr, a white solid precipitated out of solution. After 2.5 hr, the solution was extracted with pentane which was evaporated and the white residue recrystallized from methanol to yield 0.086 g of the desired product as white crystals.

8-Benzyl-1,3-di-*tert*-butylnaphthalene (XXc) and 5-Benzyl-1,3-di-*tert*-butylnaphthalene (XXd). A mixture (0.370 g, 0.774 mmol) of saturated endoxides XIXc and XIXd was dissolved in absolute ethanol with warming. At room temperature the adducts were not completely dissolved in the ethanol. To this suspension was added 5.6 ml of a cooled (room temperature) solution of absolute ethanol saturated with hydrogen chloride. The resulting suspension was stirred for 2 hr. After 20 min, the reaction mixture was a clear yellow solution. After 2 hr, the solution was extracted with pentane to yield 0.178 g of an amber oil containing the desired products. The oil was crystallized from methanol at Dry Ice temperatures to a white solid but the solid existed as an amber oil at room temperature. The amber oil was subjected to short path distillation using a Kugelrohr oven (112-120° (0.10-0.15 mm)) to yield 0.164 g of the analytically pure naphthalenes as a pale yellow oil. Nmr showed the ratio of adducts to be 1.8:1, unhindered:hindered.

5-Benzyl-1,3,8-tri-*tert*-butylnaphthalene (XXe). The saturated adducts (0.212 g) were dissolved in 2.5 ml of absolute ethanol with warming. To this cooled (room temperature) solution was added 6.25 ml of a cooled (room temperature) solution of absolute ethanol saturated with anhydrous hydrogen chloride. The resulting solution was stirred for 3 min and extracted with three 15-ml portions of hexane; the hexane was evaporated under reduced pressure to yield a yellow oil which was subjected to vpc analysis (SE-30, 6 ft, 260°). Vpc showed the partial disappearance of one of the adducts with the product having the same retention time of the other adduct. The above procedure was repeated until vpc analysis showed only a small amount of the reacting saturated adduct, XIXe. Nmr analysis (CCl₄, internal TMS) showed a new product, some of its precursor, and an unreacted saturated adduct, XIXf. The total reaction time was 2.5 hr. Hexane evaporation yielded 194 mg of a yellow oil which was subjected to preparative tlc on silica gel using hexane as the eluent. Each plate was developed three times for maximum separation. Two bands were collected with R_f's 0.6-0.8 (naphthalene, 79 mg) and 0.3-0.6 (starting materials, 79 mg). Crystallization of the naphthalene from methanol afforded the analysis sample as white crystals.