Experimental Section

Materials.—*n*-Propyl, isopropyl, *n*-butyl, isobutyl, *n*-pentyl, and neopentyl sulfite were prepared by the reaction of the corresponding alcohol with thionyl chloride.[13] Dimethyl and diethyl sulfite were commercially available. Alkyl chlorosulfinates were prepared by the reaction of alcohols with excess thionyl chloride.[14]

Di-*n*-propyl and di-*n*-butyl sulfate were prepared by the reaction of the corresponding sulfite with sulfuryl chloride. Dimethyl and diethyl sulfate were commercially available materials.

(13) A. H. Blatt, "Organic Syntheses," Coll. Vol. II, Wiley, New York, N. Y., 1943, p 112; p 111.

(14) P. D. Bartlett and H. F. Herbrandson, *J. Amer. Chem. Soc.*, **74**, 5971 (1952).

Nmr Spectra.—Varian Associates Model A-56/60A spectrometer, equipped with a variable temperature probe, was used for all spectra. Chemical shifts are reported in ppm (δ) from external (capillary) tetramethylsilane, as in previous publications in this series.

Preparation of Solutions.—The procedure used for the preparation of solutions of the protonated sulfites and sulfates was identical with that described previously.[15]

Acknowledgment.—Support of our work by a grant from the National Institutes of Health is gratefully acknowledged.

(15) G. A. Olah, D. H. O'Brien, and A. M. White, *ibid.*, **89**, 5694 (1967)

The Synthesis of 1,8-Di-*tert*-butylnaphthalenes

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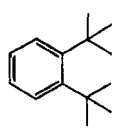
A direct synthetic route to *peri*-di-*tert*-butylnaphthalenes, **23**, **24**, and **25**, is described. A key step involves Diels–Alder reaction of a benzene with *tert*-butylfurans. Reaction of the naphthalenes with acid serve to demonstrate behavior that is different from the di-*tert*-butylbenzene case. Thus, crowding in **23** results in diminished reactivity at the peri position due to hindrance rather than increased reactivity resulting from relief of strain. Similarly, **25** is 1–2 orders of magnitude less reactive than **21** under identical acid conditions. Extreme structural perturbation is also detected *via* nmr and uv spectroscopy.

One approach to the study of van der Waals repulsion effects has been to synthesize aromatic hydrocarbons where the geometric requirements for π orbital overlap force crowding of bulky substituents located on the aromatic ring. The resulting balance between relief of strain and distortion of the planar aromatic framework has been examined by both physical and chemical probes. Examples of structures that have been studied are *o*-di-*tert*-butylbenzene (**1**)[2] and 1,12-dimethylbenzo[*c*]phenanthrene (**2**),[3] as well as related



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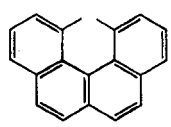

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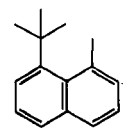
systems such as *o*-di-*tert*-butylquinoxaline[4] and β,β'-dihydroxy-2,3-di-*tert*-butylnaphthalene.[5] The present work on *peri*-*tert*-butylnaphthalenes developed from the principle stated by Newman to estimate qualitatively the steric effects of ortho substituents in aromatic compounds:[6] (1) a fused aromatic ring is equivalent to a methyl group, and (2) either (a) a fused aromatic ring containing a methyl group in the adjacent peri position, or (b) two continuously angularly fused aromatic rings is equivalent to a *tert*-butyl group. Thus it was our estimate that a 1-*tert*-butyl-8-methylnaphthalene (**3**) is comparable in its crowding to *o*-di-*tert*-butylbenzene (**1**) and that a 1,8-di-*tert*-butylnaphthalene (**4**) is more crowded than **1** or **3**. A strain energy of 22 kcal/mol has been determined for **1**,[2a] and using a value of 6–7 kcal/mol for the strain in *o*-*tert*-butyltoluene, one can assign a 15–16 kcal/mol increment for the replacement of methyl by *tert*-butyl.[7] Thus we can estimate that the substitution of the methyl in **3** by *tert*-butyl in **4** would result in a strain energy of 37–38 kcal/mol.



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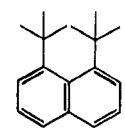

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Syntheses of 1-*tert*-butylnaphthalene have been reviewed recently.[8] Our experience with the use of a *tert*-butylbenzyne–furan reaction followed by aromatization to afford 1,4-di-*tert*-butylnaphthalene led us to extend the method to the peri-crowded series.[9] The sequence shown below was developed for the preparation of a *tert*-butylbenzyne **8**, with the critical step being the aprotic diazotization and decarboxylative elimination of the anthranilic acid (**7**).[10]

Two results of some interest, although not germane to the naphthalene problem have been obtained with **7** and **8**. When acid **7** was treated with dicyclohexylcarbodiimide, the benzoxazine **9** (20% yield) was

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(1) (a) Portions of this work have been previously reported: R. W. Franck and E. G. Leser, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, ORGN 167; R. W. Franck and E. G. Leser, *J. Amer. Chem. Soc*, **91**, 1577 (1969). (b) This paper is based on the Ph.D. Thesis of E. G. L., Fordham University, 1970. (c) This research was supported in part by Fordham University funds, NSF Grant GP 7754, and an NSF Traineeship for E. G. L.

(2) (a) E. M. Arnett, J. C. Sanda, J. M. Bollinger, and M. Barber, *J. Amer. Chem. Soc.*, **89**, 5389 (1967); (b) A. W. Burgstahler, P. Chien, and M. O. Abdel-Rahman, *ibid.*, **86**, 5281 (1964).

(3) M. A. Frisch, C. Barker, J. L. Margrave, and M. S. Newman, *ibid.*, **85**, 2356 (1963).

(4) G. J. Visser, A. Vos, A. deGroot, and H. Wynberg, *ibid.*, **90**, 3253 (1968).

(5) L. R. C. Barclay, G. R. Nixon, H. M. Foote, and S. L. Barclay, *Can. J. Chem.*, **47**, 4313 (1969).

(6) M. S. Newman and W. H. Powell, *J. Org. Chem.*, **26**, 812 (1961).

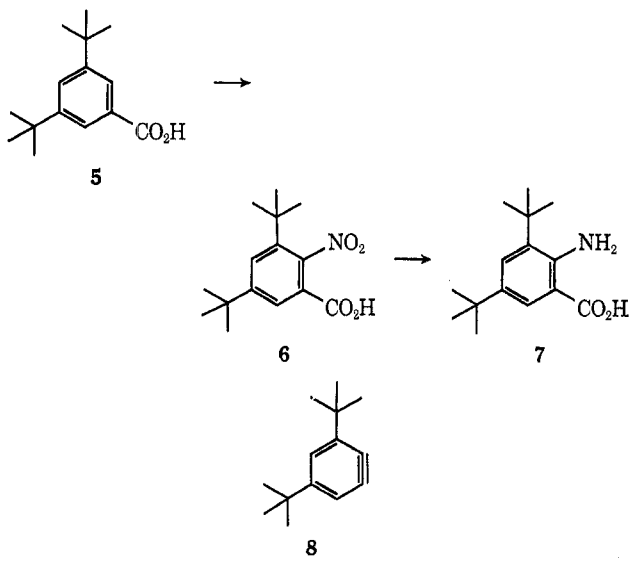
(7) H. C. Brown, *J. Chem. Soc.*, 1248 (1956); (b) J. Packer, J. Vaughan, and E. Wong, *J. Amer. Chem. Soc.*, **80**, 905 (1958); (c) H. C. Brown and A. Cahn, *ibid.*, **77**, 1715 (1955).

(8) H. Van Bekkum, T. J. Nieuwstad, J. Van Barneveld, P. Klapwijk, and B. M. Wepster, *Recl. Trav. Chim. Pays-Bas.*, **88**, 1028 (1969).

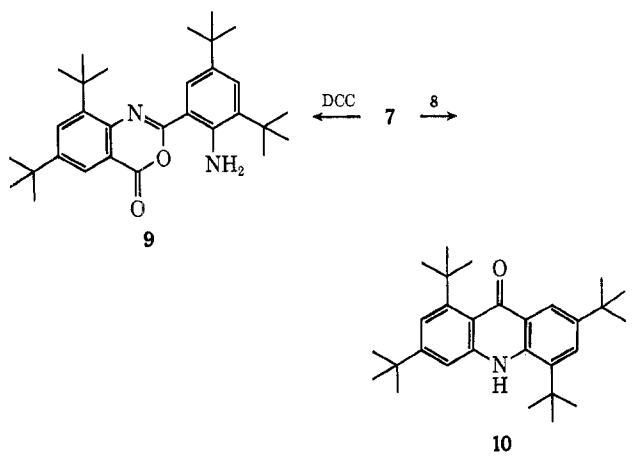
(9) R. W. Franck and K. Yanagi, *J. Org. Chem.*, **33**, 811 (1968).

(10) L. Friedman and F. M. Logullo, *ibid.*, **34**, 3089 (1969).

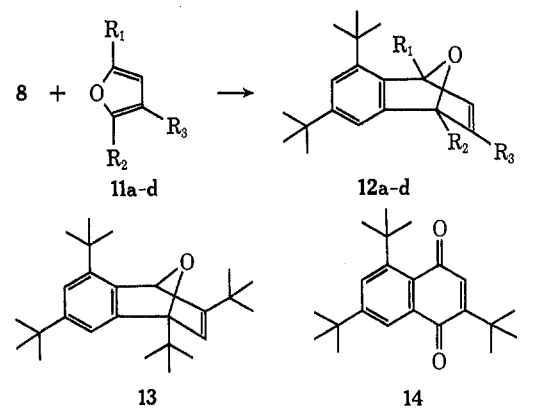
formed.[11] When no diene was present in the diazotization–elimination step to form **8**, leaving **7** as the only



benzyne trap, there was formed the acridone **10**.[12] The proof that **10** was the C_s isomer rather than the C_{2v} possibility required an nmr solvent shift study (see Experimental Section).

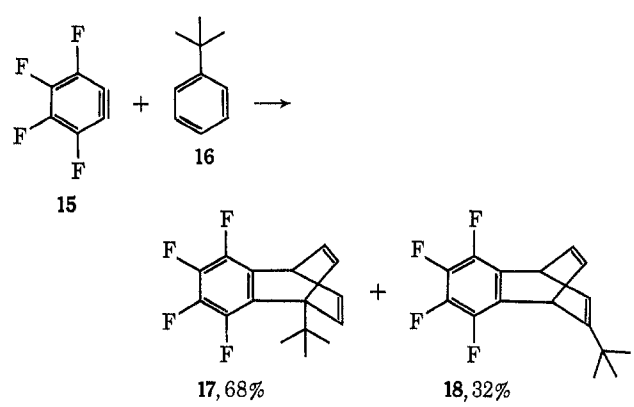


Generation of the benzyne **8** in the presence of furans **11a–c** afforded Diels–Alder adducts **12a–c** in yields of 94, 89, and 9%, respectively. The reaction with di-*tert*-butylfuran **11c** was sensitive to time and concentration. The acridone **10** was formed in moderate yield (23%) in some cases. We postulated that the *tert*-butyl *vs.* *tert*-butyl repulsion in the transition state for **12c** formation prevented the attainment of optimal overlap and that side reactions became competitive. Thus when furan **11d** was reacted with benzyne **8**, the expected product was the uncrowded adduct **13**. The adduct isolated (34–37%), however, proved to be **12d** (as shown conclusively by later conversions). The crude reaction mixture was shown (glpc) to consist of **12d** (six parts), and unknown substance [not conclusively **13** (three parts)], and quinone **14** (one part). A simple explanation for the formation of **12d** in good yield is that the transition state for this Diels–Alder



a, $R_1 = R_2 = R_3 = H$
b, $R_1 = R_2 = CH_3$; $R_3 = H$
c, $R_1 = R_2 =$ *tert*-Bu; $R_3 = H$
d, $R_1 = R_3 =$ *tert*-Bu; $R_2 = H$

reaction does not have both new bonds formed to the same extent. Even though 4 + 2 cycloadditions of benzyne have been predicted to be concerted[13] and demonstrated to be stereospecific,[14] the present case may be an example of nonsimultaneity in bond formation. The unhindered benzyne and furan termini with no steric repulsions could develop more bonding earlier in the reaction coordinate than the more hindered termini. A similar argument may be adduced for the observed ratios of adducts obtained in the reaction of tetrafluorobenzyne (**15**) with *tert*-butylbenzene (**16**).[15] The change in reactivity of arylisobenzofurans toward



vinylene carbonate has been rationalized in a similar manner.[16] The appearance of quinone **14** in the reaction mixture was rationalized as coming from **12d** *via* a reaction sequence involving acid-catalyzed ring opening, de-*tert*-butylation, and air oxidation. When a sample of **12d** was treated with ethanolic HCl for several minutes in the absence of air, a phenolic substance could be detected by ir spectroscopy. Exposure of the presumed phenol to air resulted in the appearance of carbonyl bands, and a sample of quinone **14** could be isolated.

(11) G. Schroeter, *Justus Liebigs Ann. Chem.*, **367**, 129, 153 (1909).
(12) (a) S. F. Dyke, A. R. Marshall, and J. P. Watson, *Tetrahedron*, **22**, 2515 (1966); (b) R. Howe, *J. Chem. Soc. C*, 478 (1966).
(13) R. Hoffman, A. Inamura, and W. J. Hehre, *J. Amer. Chem. Soc.*, **90**, 1499 (1968).
(14) (a) M. Jones, Jr., and R. H. Levin, *ibid.*, **91**, 6411 (1969); (b) R. W. Atkin and C. W. Rees, *Chem. Commun.*, 152 (1969).
(15) J. P. N. Brewer, I. F. Eckhard, H. Heaney, and B. A. Marples, *J. Chem. Soc. C*, 664 (1968).
(16) M. Newman, *J. Org. Chem.*, **26**, 2630 (1961).

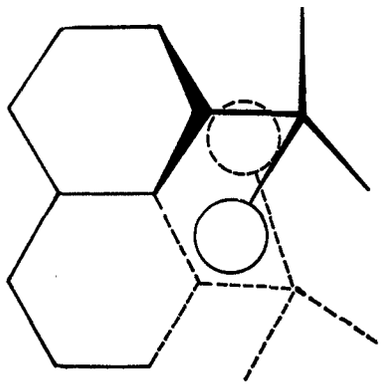
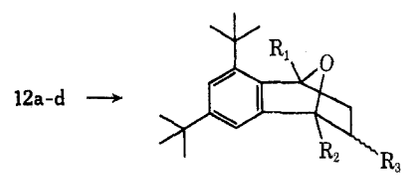


Figure 1.—The steric shielding of a peri carbon by a neighboring *tert*-butyl group.

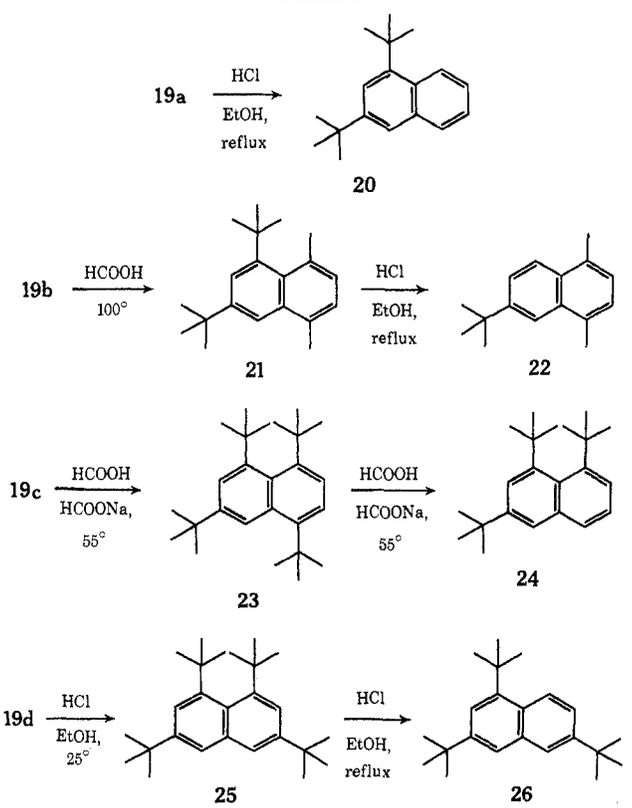
Catalytic hydrogenation of the adducts **12a–d** proceeded in high yield to form the saturated endoxides **19a–d**. This series of compounds was then subjected



19a–d

to acid-catalyzed dehydration conditions to form the naphthalenes as depicted in the scheme below (Scheme I). Whereas naphthalene **20** was stable toward re-

SCHEME I



fluxing ethanol saturated with HCl, the *o*-di-*tert*-butylbenzene analog **21** readily lost (half-life 0.05 hr) the crowded 1-*tert*-butyl group to yield **22**. This facile dealkylation to relieve steric repulsion is similar to that in the benzene series, except that in the latter case, a stronger Lewis acid was required to protonate the unactivated ring.[2] The exclusive formation of naphthalene **23** without further acid-catalyzed de-*tert*-butylation to produce **24** was not achieved. The Experimental Section summarizes a wide variety of experiments conducted in search of proper conditions of acidity. That the less hindered *tert*-butyl group in **23** was lost was demonstrated by nmr data (*vide infra*) which are quite unique for each possible *tert*-butyl environment. The unexpected dealkylation under mild conditions deserves further comment. One possible distortion to relieve crowding by the *peri*-di-*tert*-butyl groups could be a twisting of the naphthalene framework so that the stability of the aromatic nucleus would be reduced and would be susceptible to protonation by weak acids. The greatest relief of crowding would occur if one of the peri-disubstituted positions were protonated. Model studies show that there is extra steric shielding of one peri carbon by the adjacent *tert*-butyl (if the naphthalene ring is indeed twisted), thus preventing the approach of the protonating solvent from the lateral direction that would allow σ complex formation[17] (Figure 1). Thus, the less hindered carbon is protonated and the *tert*-butyl is lost because of the relief of the 6–7 kcal/mol of *o*-*tert*-butyltoluene strain. The observed stability of 1-*tert*-butylnaphthalene to H_3PO_4–BF_3 acid conditions[18] can be explained by noting that these conditions are known to be nonrearranging and perhaps insufficient to protonate 1-*tert*-butylnaphthalene. Alternately, one could argue that the 5-*tert*-butyl in **23** is more strained than a simple 1-*tert*-butyl group because of the buttressing effect of the 3-*tert*-butyl on the peri H at C_4. The HCl-catalyzed dealkylation of **25** to form **26** has a half-life of 1.8 hr, an order of magnitude greater than the corresponding dealkylation of **21**. Although the greater relief of strain to be achieved in the de-*tert*-butylation of **25** would account for *a priori* a faster rate of protonation and dealkylation than for **21**, one can rationalize the observed slower rate by reinvoking the argument of steric hindrance to lateral approach of acid that was developed for **23**.

Nmr Spectra.—Molecular interactions in peri-substituted naphthalenes have been investigated by nmr methods, including the effect of peri substituents which cause significant deshielding of the neighboring peri proton.[8,9] This magnetic deshielding of protons due to intramolecular steric interactions has been the subject of a recent analysis by Cheney.[19] It was pointed out that the degree of deshielding observed for a compressed proton H is dependent upon the conformational geometry existing between the C–H bond and the interacting proton H′. The magnitude of the steric shift was shown to depend upon the component of the nonbonded proton–proton repulsive force along the C–H bond axis. Using our earlier work on 1,4-di-*tert*-butylnaphthalenes as a precedent, assignments of resonances were made as listed in Table I. It will be observed that β-*tert*-butyl resonances serve as an excellent internal standard and that the downfield shifts for peri H's compressed by *tert*-butyls are consistent with previous work. It can be seen in the cases of naphthalenes

(17) E. Berliner, *Progr. Phys. Org. Chem.*, **2**, 253 (1964).
(18) H. M. Friedman and A. L. Nelson, *ibid.*, **34**, 3211 (1969).
(19) B. V. Cheney, *J. Amer. Chem. Soc.*, **90**, 5386 (1968).

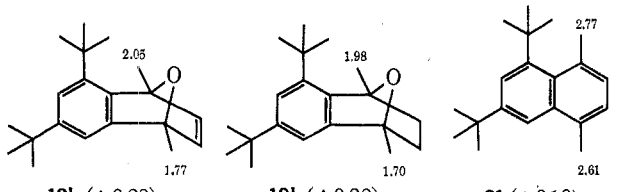
TABLE I

NMR DATA FOR *tert*-BUTYLNAPHTHALENES

Compd	β	α	peri	Other resonances[a]
20	1.40	1.64		7.17-7.82 (m, 3), 7.50 (s, 2), 8.30 (m, 1, H_8)
21	1.42	1.59		2.61 (s, 3, C-5 CH_3), 2.77 (s, 3, C-8 CH_3), 6.99 (s, 2, H_6 and H_7), 7.66 (d, 1, J_{24} = 2 Hz, H_2), 7.72 (d, 1, J_{42} = 2 Hz, H_4).
22	1.40			2.58 (s, 3), 2.62 (s, 3), 7.03 (s, 2, H_2 and H_3), 7.46 (dd, 1, J_{78} = 9 Hz and J_{75} = 2 Hz, H_7), 7.83 (d, 1, J_{87} = 9 Hz, H_8), 7.83 (d, 1, J_{57} = 2 Hz, H_5).
23	1.42	1.57	1.22 1.24	7.10 (d, J = 8 Hz), 7.28 (d, 1, J = 8 Hz), 7.43 (d, 1, J = 1.8 Hz, H_2), 7.90 (d, 1, J = 1.8 Hz, H_4).
23	1.40		1.27 1.28	7.1-7.6 (m, 5).
25	1.40		1.30	7.22 (d, 2, J = 1.7 Hz, H_2 and H_7), 7.48 (d, 2, J = 1.7 Hz, H_4 and H_5).
26	1.43	1.65		7.48 (dd, 1, J_{78} = 9.2 Hz and J_{75} = 2 Hz, H_7), 7.57 (d—overlapping with part of H_7 absorption, 2, J_{42} = J_{57} = 2 Hz, H_2 and H_5), 7.78 (d, 1, J_{24} = 2 Hz, H_4), 8.34 (d, 1, J_{87} = 9.2 Hz, H_8).

[a] Chemical shifts are in parts per million (ppm) relative to TMS as an internal standard, CCl_4 solvent.

24 and **25**, which were not the expected products, that the nmr data obtained would not be consistent with that predicted for the isomeric compounds originally expected. The J_{78} in naphthalene **26** is supportive evidence for the recently proposed theory of J_{HH} coupling in conjugated carbocyclic molecules.[20] The introduction of a *peri-tert*-butyl increases J *ortho* from 8.30 to 8.88 Hz. In benzene, a *tert*-butyl increases J by 0.32 Hz. Thus, the expected J *ortho* in **26** is (8.30 + 0.58 + 0.32) = 9.2 Hz, in good agreement with experiment. It is informative to compare the chemical shifts of the crowded and uncrowded methyl groups in the series **12b**, **19b**, **21**. A simple assumption of a direct relationship between the degree of crowding and the magnitude of the compression shift *is not* correct. The peri methyl in **21**, compared to the internal standard of the other methyl, is more compressed than in the precursors **12b** and **19b**, yet it is deshielded to a lesser extent; and in fact, the shift is approximately the same as that observed in 1,3,5,8-tetramethylnaphthalene (0.18 ppm).[21] In *o*-di-*tert*-butylbenzenes, the resonances of the *tert*-butyls have been deshielded by about 0.2 ppm from that of uncrowded *tert*-butyls. In our peri-crowded *tert*-butyls in **23**, **24**, and **25**, an upfield shift is observed. This information can be rationalized using the same twisting argument (*vide supra*) that explained the observed chemical inertness of the peri positions. If the framework is twisted so that the *tert*-butyls lie above and below the mean plane of the ring, the protons will be out of the zone of maximum deshielding of the aromatic system. Hence, their resonance would occur upfield from "normal" expectation. Also, models of this twisted naphthalene indicate that the *tert*-butyls would be free to rotate, thus explaining the nonobservance of line broadening or signal multiplicity.[15] The assumption of a twisted naphthalene framework has a corollary requirement that the naphthalenes be chiral. An nmr method of detecting chirality without resolution is to use a chiral solvent so as to form diastereoisomeric solvates and induce a doubling of nmr peaks.[22] When the spectrum of naphthalene **25** was examined in l-carvone, the 1,8-*tert*-butyl resonance, at 60 MHz, was broadened relative to the 3,6-*tert*-butyl band. However, at 220 MHz, the line widths and peak heights of the two bands were identical.[23] Since increasing the field strength in the nmr determination did not enhance the apparent broadening which might have been the beginnings of peak doubling, the results are best explained by relaxation arguments. Relaxation of spin is directly proportional to solvent viscosity (and carvone is viscous), while it is inversely proportional to the square of the field strength (that contribution to relaxation from anisotropic shielding).[24] Thus the viscosity effect observed at 60 MHz is countered by a field strength effect at 220 MHz.



12b (Δ 0.28) **19b** (Δ 0.28) **21** (Δ 0.16)

Uv Spectra.—Dale has studied the variation in uv spectra as a function of group size in benzenes.[25] The *o*-di-*tert*-butyl interaction causes a slight loss of intensity and fine structure compared to the less crowded homologs. A large bathochromic shift is observed when three *tert*-butyl groups are on adjacent benzene ring positions.[26] For a comparison of the uv spectra of the naphthalenes prepared in this research with the analogous methylnaphthalene spectra in the literature, solvent differences and substituent differences must be accounted for. In fact, solvent variation effects in naphthalene uv spectra are nonexistent. Good examples for this rest in comparison of the spectra of 1,2,5- and 1,2,7-trimethylnaphthalenes taken in petroleum ether[27] and ethanol[28] which are identical, respectively. The nearly identical spectra of 1,3,6-trimethylnaphthalene (in petroleum ether) and 1,3,6-tri-*tert*-butylnaphthalene (**26**) (in ethanol) are compared in Figure 2. There is neither a solvent effect or a substituent effect in replacing methyl with *tert*-butyl. The comparison (Figure 3) of the uv of 1,3,8-trimethylnaphthalene (petroleum ether) and that of the

(20) M. A. Cooper and S. L. Manatt, *J. Amer. Chem. Soc.*, **91**, 6325 (1969); **92**, 4646 (1970). We thank the authors for this determination and a comment on its relevance.

(21) F. F. Yew, R. J. Kurland, and B. J. Mair, *Anal. Chem.*, **36**, 843 (1964).

(22) W. H. Pirkle and S. D. Beare, *J. Amer. Chem. Soc.*, **91**, 5150 (1969).

(23) We thank Professor W. Gibbons of Rockefeller University for this spectrum.

(24) E. D. Becker, "High Resolution NMR," Academic Press, New York, N. Y., 1969, pp 205-206.

(25) J. Dale, *Chem. Ber.*, **94**, 2821 (1961).

(26) E. M. Arnett and J. M. Bollinger, *Tetrahedron Lett.*, 3803 (1964).

(27) M. J. Kamlet, Ed., "Organic Electronic Spectral Data," Vol. I, Interscience, New York, N. Y., 1960, p 522.

(28) H. E. Ungnade, Ed., *ibid.*, Vol. II, p 363.

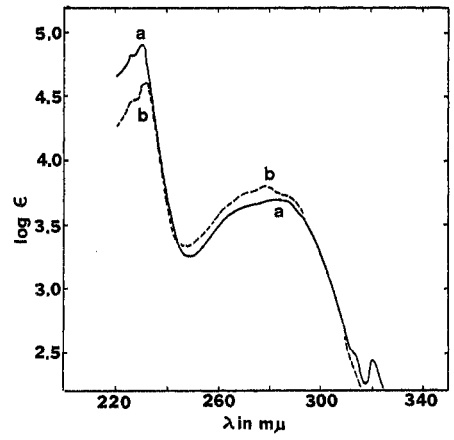


Figure 2.—Uv spectra of 1,3,6-trialkylnaphthalenes: a, 1,3,6-trimethylnaphthalene [E. Heilbronner, U. Fröhlicher, and Pl. A. Plattner, *Helv. Chim. Acta*, **32**, 2479 (1949)]; b, 1,3,6-tri-*tert*-butylnaphthalene (**26**).

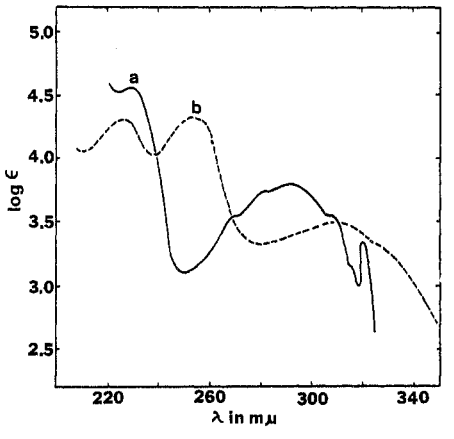


Figure 3.—Uv spectra of 1,3,8-trialkylnaphthalenes: a, 1,3,8-trimethylnaphthalene [E. Heilbronner, U. Fröhlicher, and Pl. A. Plattner, *Helv. Chim. Acta*, **32**, 2479 (1949)]; b, 1,3,8-tri-*tert*-butylnaphthalene (**24**).

peri-crowded 1,3,8-tri-*tert*-butylnaphthalene **24** (ethanol) shows the four effects of distortion due to the 1,8-*tert*-butyl interaction. Bathochromism of maxima (≈20 mμ), the appearance of a new band which is probably the result of a shift of a maximum in the 200 mμ range, reduction in intensity, and loss of fine structure are observed. Similar perturbations are seen in the comparison of spectra of 1,3,6,8-tetramethylnaphthalene (ethanol) and the homologous tetra-*tert*-butyl compound **25** (ethanol) in Figure 4. The spectra in ethanol of three 1,3,5,8-tetraalkylnaphthalenes are compared in Figure 5. The spectrum of **21**, the *o*-di-*tert*-butylbenzene homorph, shows the expected slight spectral differences from the model 1,3,5,8-tetramethylnaphthalene. Larger structural perturbation due to 1,8-*tert*-butyl interaction in **23** is evidenced again by the four effects listed above. The observed bathochromic shifts in our series correspond well with that observed for 1,2,3,5-tri-*tert*-butylbenzene.[26] In the development of synthetic methods for the *peri*-di-*tert*-butylnaphthalene system, we have already discovered chemistry that is not a logical extension of *o*-di-*tert*-butylbenzene studies. With a reasonable synthetic route in hand, further physical and chemical probing of this new system can be undertaken.

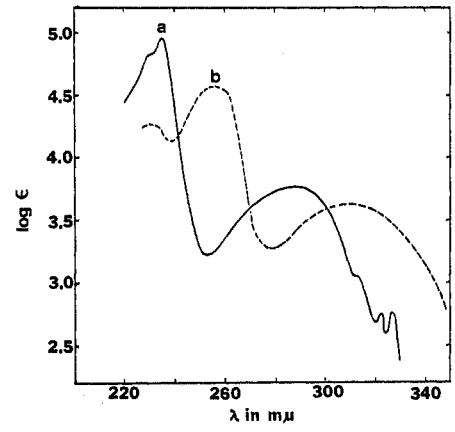


Figure 4.—Uv spectra of 1,3,6,8-tetraalkylnaphthalenes: a, 1,3,6,8-tetramethylnaphthalene [P. Canonne and A. Regnault, *Can. J. Chem.*, **45**, 1267 (1967); we thank Professor Cannone for a gift of this naphthalene]; b, 1,3,6,8-tetra-*tert*-butylnaphthalene (**25**).

Experimental Section[29]

3,5-Di-*tert*-butylbenzoic Acid (5).—Following the procedure of Wepster,[30] 88.0 g (0.432 mol) of 3,5-di-*tert*-butyltoluene[31] was converted to 80.1 g (79%) of acid **5**: mp 177–178° (lit.[27] mp 172–173°); ir (CCl_4) 3.1–3.4 (acid OH), 3.44 (*tert*-butyl), 3.7–4.0 (several weak bands), 5.79 (monomeric C=O), 5.95 (dimeric C=O), and 8.00 μ.

2-Nitro-3,5-di-*tert*-butylbenzoic Acid (6).—Employing a salt–ice bath, 81 ml of fuming nitric acid (sp gr 1.59–1.60) was cooled to below 10°. This temperature was maintained throughout the *slow* addition of 27.5 g (0.118 mol) of 3,5-di-*tert*-butylbenzoic acid to the rapidly stirred nitric acid. After addition was completed, the solution was stirred at this temperature (5°) for 15 min and then at room temperature for 30 min. The product comes out of solution during the addition of the benzoic acid.

The reaction mixture was poured into ice–water, and the precipitate was filtered, washed acid free, and air-dried. Recrystallization of the crude material from ethanol gave 26.8 g (82%) of pure **6**: mp 206–208°; ir ($CHCl_3$) 3.1–3.4 (acid OH), 3.7–4.0 (several weak bands), 5.76 (monomeric C=O) 5.90 (dimeric C=O), 6.55 (NO_2), and 7.32 μ (NO_2); nmr ($CDCl_3$) δ 1.38 (s, 9), 1.45 (s, 9), 7.98 (d, 1, J = 2 Hz), 8.13 (d, 1, J = 2 Hz), and 10.22 ppm (s, 1).

Anal. Calcd for $C_{15}H_{21}NO_4$: C, 64.50; H, 7.58; N, 5.01. Found: C, 64.39; H, 7.59; N, 5.07.

3,5-Di-*tert*-butylanthranilic Acid (7).—To 10 ml of absolute ethanol was added 1.85 g (6.62 mmol) of 2-nitro-3,5-di-*tert*-butyl benzoic acid with stirring. After the nitro compound was dissolved, 5.4 ml of 85% hydrazine hydrate and 0.040 g of 10% palladium-on-carbon catalyst were added. The mixture was refluxed for 2 hr, after which it was cooled and the catalyst was *carefully* filtered and washed with ethanol. The ethanol solution was evaporated and the residue refluxed with 50 ml of 10% sodium hydroxide solution for 3.5 hr. This alkaline solution was

(29) Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Analyses were determined by Spang Microanalytical Laboratory, Ann Arbor, Mich. Infrared spectra were recorded on Perkin-Elmer Model 137 and 337 spectrophotometers. Ultraviolet spectra were recorded on a Cary 15 spectrophotometer. Nuclear magnetic resonance spectra were measured with a Varian A-60A instrument, probe temperature 38°, with signals reported relative to internal tetramethylsilane. Eastman practical grade isopentyl nitrite was purified by washing with saturated sodium bicarbonate solution and saturated sodium chloride solution, drying with anhydrous sodium sulfate, and distillation. Thin layer chromatography was done using Merck silica gel G on precleaned microslides. Florisil (Fisher, 60–100 mesh) was used as the adsorbant for separations by column chromatography. Gas–liquid partition chromatography (glpc) was performed on a F & M Model 810 instrument equipped with thermal conductivity detectors. One or both of the following columns were used throughout this work: column A (6 ft × 0.25 in., 10% silicon gum rubber SE-30 (methyl) on 80–100 mesh Chromosorb W, carrier gas flow 90 ml/min); column B (6 ft × 0.25 in., 10% polyphenyl ether (6 ring) on 60–80 mesh Chromosorb W, carrier gas flow 80 ml/min).

(30) W. Van Hartingsveldt, P. E. Verkade, and B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, **75**, 349 (1956).

(31) J. Geuse, C. Ruinard, J. Soeterbroek, P. E. Verkade, and B. M. Wepster, *ibid.*, **75**, 301 (1956).

TABLE II

PHYSICAL PROPERTY OF DIELS–ALDER ADDUCTS

Compd	% yield	Mp, °C	Formula	% calcd C	% calcd H	% found C	% found H	Infrared, μ (CCl_4)	Nmr spectrum, ppm (TMS, CCl_4)
12a	94	95–96	$C_{18}H_{24}O$	84.32	9.44	84.42	9.41	3.43, 6.81, 6.90, 7.22, 7.39, 11.35, 11.54	1.30 (9 H, s), 1.36 (9 H, s), 5.45 (1 H, s-broad), 5.95 (1 H, s-broad), 6.88 (3 H, s-broad), 7.07 (1 H, d, J = 2 Hz)
12b	89	76–78	$C_{20}H_{28}O$	84.45	9.92	84.52	9.86	3.43, 6.81, 6.91, 7.21, 7.30, 7.39, 8.63, 11.46, 11.53	1.30 (9 H, s), 1.38 (9 H, s), 1.77 (3 H, s), 2.05 (3 H, s), 6.63 (2 H, AB quartet, J_{AB} = 5 Hz), 6.91 (2 H, AB quartet, J_{AB} = 2 Hz).
12c	9.2	149–150	$C_{26}H_{40}O$	84.72	10.94	84.60	10.87	3.40, 6.79, 7.33, 8.03, 9.13, 11.58	1.25 (9 H, s), 1.28 (9 H, s), 1.35 (9 H, s), 1.38 (9 H, s), 6.81 (2 H, s), 6.93 (1 H, d, J_{AB} = 2 cps), 7.18 (1 H, d, J_{AB} = 2 Hz)
12d	34	135–137	$C_{26}H_{40}O$	84.72	10.94	84.89	11.09	3.42, 6.82, 6.90. 7.23, 7.39, 11.35	1.00 (9 H, s), 1.29 (9 H, s), 1.34 (9 H, s), 1.40 (9 H, s), 5.25 (1 H, s), 6.18 (1 H, s), 6.98 (2 H, s)

cooled, acidified with concentrated hydrochloric acid, and extracted with ether. Ether evaporation gave a pale yellow solid which upon recrystallization from ethanol–water afforded 1.28 g (77.8%) of the desired product: mp 256–258°; ir ($CHCl_3$) 2.90 (NH_2), 3.05 (NH_2), 3.1–3.4 (acid OH), 3.7–3.9 (several weak bands), 5.96 (monomeric C=O), and 6.07 μ (dimeric C=O); nmr [$(CD_3)_2CO$] δ 1.32 (s, 9), 1.48 (s, 9), 7.69 (d, 1, J = 2 Hz), and 8.07 ppm (d, 1, J = 2 Hz).

Anal. Calcd for $C_{15}H_{23}NO_2$: C, 72.25; H, 9.30; N, 5.62. Found: C, 72.09; H, 9.21; N, 5.55.

2-(2′-Amino-3′,5′-di-*tert*-butylphenyl)-6,8-di-*tert*-butyl-4-one-4*H*-3,1-benzoxazine (9).—To a stirred solution of 0.498 g (2.42 mmol) of dicyclohexylcarbodiimide dissolved in 15 ml of acetone at room temperature was added (2 mmol) of anthranilic acid **7**. After five min, precipitation of dicyclohexylurea began. Stirring was continued for 20 min, after which the formed dicyclohexylurea was filtered, mp 223–225° (lit.[32] 229–230°), and the acetone solution evaporated. The crude material was shown to consist of unreacted anthranilic acid and a single product by tlc analysis.

The product was isolated by chromatography of the crude material on 10 g of Florisil, eluting with 1% ether–hexane. Recrystallization from ethanol gave 0.090 g (20%) of yellow crystals of pure **9**: mp 174–176°; uv max (95% C_2H_5OH) 239 mμ (log ϵ 4.48), 292 (4.04), 305 (4.04), and 396 (3.87); ir (CCl_4) 2.84 (NH_2), 3.06 (NH_2), 3.41 (*tert*-butyl), and 5.07 μ (an α-pyrone C=O); nmr (CCl_4) δ 1.37 (s, 9), 1.42 (s, 9), 1.52 (s, 9), 1.64 (s, 9), 6.73 (br s, $W_{1/2}$ = 5 Hz, 2, NH_2, exchangeable with deuterium), 7.42 (d, 1, J = 2 Hz), 7.81 (d, 1, J = 2 Hz), and 8.08 ppm (t, 2, J = 2 Hz, two overlapping doublets); mass spectrum (70 eV) m/e (rel intensity) 462 (71.2), 447 (100), 231 (3.9), 216 (37.2).

Anal. Calcd for $C_{30}H_{42}N_2O_2$: C, 77.88; H, 9.15; N, 6.05. Found: C, 77.97; H, 9.21; N, 6.00.

Diels–Alder Adducts 12a–d.—The details are given for the reactions forming **12c** and **d**. The physical data for the compounds in this series are tabulated in Table II.

1,4,5,7-Tetra-*tert*-butyl-1,4-dihydronaphthalene 1,4-Endoxide (12c).—To a refluxing solution of 1.124 g (9.6 mmol) of isopentyl nitrite and 0.865 g (4.8 mmol) of 2,5-di-*tert*-butylfuran[33] in 20 ml of methylene chloride was added over a period of 1.5 hr a solution of 0.600 g (2.4 mmol) of 3,5-di-*tert*-butylanthranilic acid in 20 ml of acetone. The resulting solution was refluxed an additional hour after the initial addition period. The reaction mixture was evaporated in a base-washed vessel, and the residue chromatographed on 20 g of Florisil using hexane as the eluent. Unreacted 2,5-di-*tert*-butylfuran was separated from the lead fractions under vacuum (0.05 mm, room temperature), and collected in the Dry Ice trap of the pump. The amount of starting furan recovered in this manner varied over several experiments. The solid residue from the chromatographic fractions was recrystallized from methanol and then dried under vacuum to give 0.055 g (6.2%) of pure **12c**, mp 149–150°.

In another experiment, employing the reagent quantities given above, the anthranilic acid solution was added over 1 hr to the refluxing solution of the other reactants. The resulting solution was refluxed an addition 15 min after the addition period was over. Evaporation of this solution, followed by extraction of the residue with pentane, afforded 0.230 g (22.8%) of pentane insoluble material which was shown to be 1,3,5,7-tetra-*tert*-butylacridone (**10**), mp 293–295°. The pentane filtrate was chromatographed as described above, the starting furan removed, and the crude adduct recrystallized to give 0.081 g (9.2%) of pure **12c**, mp 149–150°.

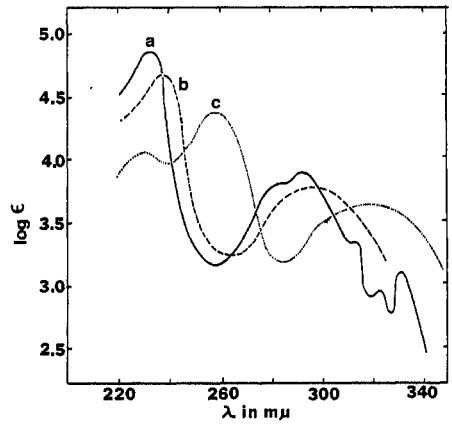


Figure 5.—Uv spectra of 1,3,5,8-tetraalkylnaphthalenes: a, 1,3,5,8-tetramethylnaphthalene [W. L. Mosby, *J. Amer. Chem. Soc.*, **75**, 3348 (1953)]; b, 1,3-di-*tert*-butyl-5,8-dimethylnaphthalene (**21**); c, 1,3,5,8-tetra-*tert*-butylnaphthalene (**23**).

1,3,6,8-Tetra-*tert*-butyl-1,4-dihydronaphthalene 1,4-Endoxide (12d).—A solution of 0.600 g (2.4 mmol) of anthranilic acid **7** in 20 ml of acetone was added over 1.5 hr to a refluxing solution of 0.865 g (4.8 mmol) of 2,4-di-*tert*-butylfuran[34] and 1.124 g (9.6 mmol) of isopentyl nitrite in 20 ml of methylene chloride. The solution was refluxed for an additional 15 min after the addition period was over. Evaporation of the reaction mixture, chromatography of the residue over 20 g of Florisil employing hexane as the eluent, followed by removal of starting furan from the lead fractions (0.05 mm, room temperature) gave the crude material. Two recrystallizations from pentane afforded 0.300 g (34%) of pure **12d**, mp 135–137°.

In another experiment, employing the same reagent and solvent ratios given above, the anthranilic acid solution was added over 4 hr to the refluxing solution of the other reactants. The resulting solution was refluxed for an additional 1.5 hr after the addition period was over and was then evaporated at room temperature under vacuum. The residue was dissolved in hexane, extracted several times with saturated sodium bicarbonate solution, washed with saturated sodium chloride solution, and dried over anhydrous sodium sulfate.

Analysis of this reaction mixture by glpc (column A, isothermal at 240°) showed that it consisted approximately of 60% **12d**, 30% of a substance which might be isomeric to **12d**, and a very small amount of a compound later identified as 2,5,7-tri-*tert*-butyl-1,4-

(32) A. Skita and H. Rolfes, *Chem. Ber.*, **53**, 1248 (1920).

(33) A. Ramasseul and A. Rassat, *Bull. Soc. Chim. Fr.*, 2214 (1963).

(34) E. E. Van Tamelen and T. H. Whitesides, *J. Amer. Chem. Soc.*, **90**, 3895 (1968).

naphthoquinone (14). In addition, a number of impurities were revealed, most of them low boiling components. Evaporation of the above hexane solution afforded the crude product, which after two recrystallizations from pentane gave 0.515 g (37%) of pure **12d**, mp 134–136°.

1,3,5,7-Tetra-*tert*-butylacridone (10).—To a stirred, refluxing solution of 0.422 g (3.6 mmol) of isopentyl nitrite in 20 ml of methylene chloride was added, over a period of 1 hr, a solution of 0.600 g (2.4 mmol) of 3,5-di-*tert*-butylanthranilic acid in 20 ml of acetone. The solution was refluxed an additional 1.5 hr after the addition period was over. Evaporation of the solvent and washing the crystalline residue with pentane gave 0.208 g (41.3%) of the pale yellow acridone **10**, mp 297–299°. Benzene recrystallization afforded an analytical sample: mp 300–302°; uv max (95% C_2H_5OH) mμ 220 (log ε 4.30), 265 (4.67), 298 (3.58), and 390 (3.83); ir ($CHCl_3$) 2.87 (NH), 3.35 (*tert*-butyl), 6.10, 6.18, and 6.24 μ; nmr (summarized in Table III).

TABLE III

NMR DATA FOR 1,3,5,7-TETRA-*tert*-BUTYLACRIDONE (10)

Solvent	Resonances (δ, relative to TMS)
CH_2Cl_2	1.42 (s, 18), 1.65 (s, 18), 7.10 (d, 1, J = 2 Hz), 7.49 (d, 1, J = 2 Hz), 7.76 (d, 1, J = 2 Hz), 8.21 (broad, 1, exchangeable), 8.35 (d, 1, J = 2 Hz)
$CDCl_3$	1.42 (s, 18), 1.63 (s, 9), 1.69 (s, 9), 7.02 (d, 1, J = 2 Hz), 7.48 (d, 1, J = 2 Hz), 7.72 (d, 1, J = 2 Hz), 8.18 (broad, 1, exchangeable), 8.43 (d, 1, J = 2 Hz).
Benzene	1.29 (s, 9), 1.33 (s, 9), 1.35 (s, 9), 1.97 (s, 9).

Anal. Calcd for $C_{29}H_{41}NO$: C, 83.00; H, 9.85; N, 3.34. Found: C, 82.71; H, 9.88; N, 3.29.

A sample of acridone **10** was dissolved in $CDCl_3$ in an nmr tube, a few drops of NaOD and D_2O were added, and the mixture was heated in the steam bath for 15 min and then let stand overnight. The NH absorption in the nmr was removed. The compound was reisolated: mp 296–298°; ir ($CHCl_3$) 3.92 μ (ND).

2,5,7-Tri-*tert*-butyl-1,4-naphthoquinone (14).—The Diels–Alder adduct **12d** (0.050 g, 0.136 mmol) was dissolved in 1 ml of absolute ethanol, the solution cooled, and hydrogen chloride gas bubbled into it for 15 min. The alcohol was removed under reduced pressure and the residue was exposed to the atmosphere for 4 days. Glpc analysis (column A, isothermal at 240°) of this material showed that approximately 66% of **14** and 34% of a presumed precursor were present. To complete the conversion to **14**, the material was dissolved in hexane and oxygen was bubbled through the solution for 1 hr. This material was then chromatographed twice over 1 g of silica gel (Fisher, 100–200 mesh) employing hexane–benzene (2:1) as the eluent. A yellow material separated first and upon solvent removal crystallized to give 0.020 g (45%) of **14**. Trituration with ethanol gave the analytical sample: mp 96–98°; uv max (95% C_2H_5OH) 255 mμ (log ε 4.80), and 352 (4.09); ir (CCl_4) 3.42 (*tert*-butyl), 6.04 (extended quinone C=O), 7.38, and 8.11 μ; nmr (CCl_4) δ 1.37 (s, 9), 1.42 (s, 9), 1.50 (s, 9), 6.75 (s, 1, H_3), 7.91 (d, 1, J = 2 Hz, H_6), and 8.17 ppm (d, 1, J = 2 Hz, H_8); mass spectrum (70 eV) m/e 326.

Anal. Calcd for $C_{22}H_{30}O_2 \cdot C_2H_5OH$: C, 77.38; H, 9.74. Found: C, 77.93; H, 9.22. Duplicate determination. C, 78.08; H, 9.17.

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 by small sample quantities could be accurately measured. The adduct to be hydrogenated was dissolved in absolute ethanol and added to the prereduced catalyst in ethanol contained in the reaction flask *via* a pressure equalizing addition funnel. All of the adducts were hydrogenated using the above apparatus and technique at atmospheric pressure and room temperature. The crude saturated endoxides were isolated by evaporation of the ethanol solvent after the hydrogenation catalyst had been first separated by filtration. The physical data for the compounds in this series (**19a–d**) are tabulated in Table IV.

Naphthalenes. 1,3-Di-*tert*-butylnaphthalene (20).—To a stirred 25-ml solution of absolute ethanol saturated with hydrogen chloride was added 0.515 g (1.99 mmol) of saturated endoxide **19a**. The resulting solution was refluxed 6 hr, after which the solvent was evaporated and the residue recrystallized from absolute ethanol to yield 0.436 g (91%) of pure **20**: mp 67–68°; uv max (95% C_2H_5OH) 228 mμ (log ε 4.99), 260 sh (3.58), 271 (3.72), 278 (3.77), and 287 (3.68); ir (CCl_4) 3.31 (aromatic CH shoulder), and 3.43 μ (*tert*-butyl CH).

Anal. Calcd for $C_{18}H_{24}$: C, 89.94; H, 10.06. Found: C, 90.04; H, 10.04.

1,3-Di-*tert*-butyl-5,8-dimethylnaphthalene (21).—A mixture of 0.690 g (2.40 mmol) of **19b** in 14 ml of 100% formic acid was immersed in a steam bath with rapid swirling for 20 min. The resulting solution was poured into ice–water and extracted with ether and the ether layer washed with saturated sodium bicarbonate solution until gas evolution ceased. The ether layer was then washed with saturated sodium chloride solution, dried with sodium sulfate, and evaporated to yield an essentially pure (by glpc analysis on column A, isothermal at 250°) yellow-white oil. Passage of this oil through 1.0 g of Florisil using hexane as the solvent gave 0.257 g (40%, the yield was not maximized) of pure **21**: bp 68° (0.03 mm); uv max (95% C_2H_5OH) 238 mμ (log ε 4.67), and 298 (3.78); ir (CCl_4) 3.40 and 3.48 μ.

Anal. Calcd for $C_{20}H_{28}$: C, 89.49; H, 10.51. Found: C, 89.25; H, 10.46.

6-*tert*-Butyl-1,4-dimethylnaphthalene (22). A. From Dihydroendoxide 19b.—To a stirred 25-ml solution of absolute ethanol saturated with hydrogen chloride was added 0.516 g (1.80 mmol) of **19b**. The resulting solution was refluxed overnight. Evaporation of the solvent gave a light brown oil which was extracted with pentane and separated from pentane insoluble material on the centrifuge. Concentration of this pentane extract and cooling gave 0.328 g (86%) of pure **22**: mp 30–31°; uv max (95% C_2H_5OH) 232 mμ (log ε 4.69), 278 (3.64), 288 (3.70), 293 sh (3.63), and 323 (2.69); ir (CCl_4) 3.30 and 3.42 μ.

Anal. Calcd for $C_{16}H_{20}$: C, 90.51; H, 9.49. Found: C, 90.43; H, 9.46.

B. From Naphthalene 21.—A mixture of 0.003 g of naphthalene **21** in 1 ml of the ethanol–hydrogen chloride reagent was refluxed for 0.5 hr. Evaporation of the solvent, followed by examination of the pentane extract of the residue by glpc (column A, isothermal at 250°) showed that the conversion to naphthalene **22** had been quantitative in this time period. Naphthalene **22** was identified by glpc peak enhancement with an authentic sample.

1,3,5,8-Tetra-*tert*-butylnaphthalene (23) and 1,3,8-Tri-*tert*-butylnaphthalene (24).—A mixture of 6.60 g of sodium formate, 132 ml of 97+% formic acid (Aldrich), and 0.330 g (0.89 mmol) of dihydroendoxide **19c** was stirred at a constant temperature of 60° for 169 hr. The dehydration was followed by glpc analyses (column A, isothermal at 250°) of reaction mixture aliquots taken at various times. Such analysis showed that after 48 hr, 80% of tetra-*tert*-butylnaphthalene **23** was present in the mixture. After 169 hr the reaction mixture was poured into water and extracted with hexane. The hexane extract was washed with water, saturated sodium bicarbonate solution, dried with sodium sulfate, and evaporated to give 0.256 g of a light yellow oil. Analysis of this oil showed the following approximate percentages of components: 26% tri-*tert*-butylnaphthalene **24** (retention time 2.5 min), 60% tetra-*tert*-butylnaphthalene **23** (3.0 min), and 14% dihydroendoxide **19c** (3.5 min). Separation of these three components proved to be ineffective on tlc and on a variety of columns (*e.g.*, alumina, silica gel, Florisil). The mixture was successfully separated by preparative gas chromatography. A Perkin-Elmer Model F21 instrument equipped with a 12 ft × 0.50 in. column of 18% QF 1 on 60–80 mesh Chromosorb W (AW-DMCS) was employed.

In this manner, 0.024 g (0.068 mmol) of 1,3,5,8-tetra-*tert*-butylnaphthalene (**23**) was isolated as a white, crystalline solid, mp 78–82°. One recrystallization from methanol gave the analytical sample: mp 83–86°; uv max (95% C_2H_5OH) 230 mμ (log ε 4.04), 258 (4.38), and 320 (3.63); ir (CCl_4) 3.31, 3.40, 6.80, 6.88, 7.20 and 7.36 μ.

Anal. Calcd for $C_{26}H_{40}$: C, 88.57; H, 11.43. Found: C, 88.56; H, 11.53.

In like manner, 0.015 g (0.050 mmol) of 1,3,8-tri-*tert*-butylnaphthalene (**24**) was isolated as a colorless liquid. Passage through 1.0 g of Florisil employing pentane as the solvent gave analytical sample: mp ~10°; uv max (95% C_2H_5OH) 223 mμ sh (log ε 4.28), 228 (4.31), 253 (4.32), and 310 (3.49); ir (CCl_4) 3.30, 3.40, 5.78, 6.84, 7.16, 7.25, and 7.32 μ.

Anal. Calcd for $C_{22}H_{32}$: C, 89.12; H, 10.88. Found: C, 88.86; H, 11.04.

TABLE IV

PHYSICAL PROPERTIES OF SATURATED ADDUCTS

Compd	% yield	Mp, °C	Formula	% calcd C	% calcd H	% found C	% found H	Infrared, μ (CCl_4)	Nmr spectrum, ppm (TMS, CCl_4)
19a	83	56–58	$C_{18}H_{26}O$	83.67	10.14	83.73	10.10	3.46, 6.82, 6.91, 7.23, 7.4, 10.61, 11.52	1.30 (9 H, s), 1.36 (9 H, s), 1.90 (4 H, m), 5.12 (1 H, m), 5.58 (1 H, m), 7.04 (2 H, AB quartet, J_{AB} = 2 Hz)
19b	100	86–88	$C_{20}H_{30}O$	83.86	10.56	83.68	10.54	3.45, 6.82, 6.91, 7.24, 7.32, 7.41 11.00, 11.57	1.30 (9 H, s), 1.42 (9 H, s), 1.67 (4 H, m), 1.70 (3 H, s), 1.98 (3 H, s), 6.88 (1 H, d, J_{AB} = 2 Hz), 7.14 (1 H, d, J_{AB} = 2 Hz)
19c	92	94–96	$C_{26}H_{42}O$	84.26	11.42	84.49	11.43	3.44, 6.82, 6.90, 7.23, 7.38, 8.49, 9.34, 11.30, 11.45	1.22 (9 H, s), 1.32 (18 H, s), 1.45 (9 H, s), 1.75 (4 H, m), 7.16 (2 H, s)
19d	88	129–131	$C_{26}H_{42}O$	84.26	11.42	84.31	11.47	3.40, 6.80, 7.22, 7.37, 11.63	0.49 (9 H, s), 1.27 (9 H, s), 1.29 (1 H, buried), 1.31 (9 H, s), 1.46 (9 H, s), 1.8–2.3 (2 H, m), 4.85 (1 H, d, J = 4 Hz), 7.00 (1 H, d, J = 2 Hz), 7.21 (1 H, d, J = 2 Hz)

TABLE V

DEHYDRATION OF 1,4,5,7-TETRA-*tert*-BUTYL-1,2,3,4-TETRAHYDRONAPHTHALENE 1,4-ENDOXIDE (**19c**)

Reaction conditions[a]	Yield,[b] % **19c**	**23**	**24**
100% HCOOH, 100°, 0.5[c]	27	64	9
100% HCOOH, 100°, 1	10	60	30
100% HCOOH, 100°, 3		50	50
Excess $(C_2H_5)_3O^+BF_4^-$, 25°, 26	60	9	31
Benzoic acid–nitrobenzene, 120°, 15	100		
CH_3COOH–$(CH_3CO)_2O$, 100°, 23	100		
CH_3COOH–HCOOH (1:1), 100°, 3		40	60
CH_3COOH–HCOOH (1:1), 100°, 12		20	70
HCOONa–HCOOH, 55°, 144	4	94	2
HCOONa–HCOOH, 60°,[d] 48	17	80	3
HCOONa–HCOOH, 60°,[d] 169	14	60	26

[a] The dehydrating reagent, the temperature, and the time (hr) are listed. [b] Reaction mixture composition was determined by glpc analysis on column A, isothermal at 250°. [c] The components of this reaction mixture were separated by glpc and were shown not to interconvert on the analysis column. [d] A constant temperature oil bath was used.

Table V lists the studies made to determine optimum acidity for this reaction.

1,3,6,8-Tetra-*tert*-butylnaphthalene (25). A.—To 10 ml of absolute ethanol saturated with anhydrous hydrogen chloride was added 0.095 g (0.256 mmol) of saturated endoxide **19d**. The mixture was refluxed for 10 min, the solvent boiled off, and the residue extracted with pentane. Evaporation of the pentane gave the crude product which upon recrystallization from methanol afforded 0.058 g (64.5%) of pure tetra-*tert*-butylnaphthalene **25**, mp 125–127°. Another recrystallization from methanol gave the analysis sample: mp 127–128°; uv max (95% C_2H_5OH) 231 mμ (log ε 4.26), 256 (4.57), and 310 (3.63); ir (CCl_4) 3.29, 3.37, 6.76, 6.85, 7.17, 7.34, and 11.28 μ.

Anal. Calcd for $C_{26}H_{40}$: C, 88.57; H, 11.43. Found: C, 88.61; H, 11.50.

B.—The conversion of dihydronaphthalene endoxide **19d** to naphthalene **25** at room temperature was found to proceed quickly and quantitatively with no further reaction of **25** occurring employing the following procedure.

To 0.002 g of **19d** dissolved in a few drops of absolute ethanol was added a cooled 0.5-ml solution of absolute ethanol saturated with hydrogen chloride. This mixture was swirled 2 min and then extracted with pentane. Analysis of the pentane extract by glpc on column A (isothermal at 260°) showed that no starting material **19d** remained; analysis on column B (isothermal at 260°) showed that only tetra-*tert*-butylnaphthalene **25** had formed and no tri-*tert*-butylnaphthalene **26** could be detected.

C.—The stability of tetra-*tert*-butylnaphthalene **25** toward ethanol–hydrogen chloride was demonstrated in the following experiments.

When the naphthalene **25** (0.002 g) was dissolved in ethanol–hydrogen chloride (0.5 ml) by warming on the steam bath for about 3 min, some conversion to **26** had taken place as evidenced by glpc analysis (column B, isothermal at 260°) of the pentane extract of the ethanol solution. Similarly, when **25** was dissolved in absolute ethanol and the resulting solution saturated with hydrogen chloride, glpc analysis again showed that **26** had started to form.

The naphthalene **25** was shown to be stable toward the ethanol–hydrogen chloride reagent at room temperature at least for short time periods. Naphthalene **25** (0.002 g) was dissolved in a few drops of absolute ethanol, the solution cooled, and to this was added a cooled solution (0.5 ml) of ethanol–hydrogen chloride. This mixture was swirled from 1 to 3 min, extracted with pentane, and analyzed by glpc (column B, isothermal at 260°). Only pure **25** was indicated.

1,3,6-Tri-*tert*-butylnaphthalene (26). A. From the Mother Liquors of 1,3,6,8-Tetra-*tert*-butylnaphthalene (25).—In the reaction of dihydroendoxide **19d** with refluxing hydrogen chloride–ethanol, a 64.5% yield of **25** was obtained. The remaining mother liquors upon glpc analysis with column A (isothermal at 260°) showed that no starting material **19d** remained and that only "one" product had formed. Examination of these same mother liquors on column B (isothermal at 260°) clearly showed that about 35% **25** and 65% **26** were present.

In one experiment, 0.160 g of the mother liquors of the above composition in 10 ml of the ethanol–hydrogen chloride reagent was refluxed 3 hr. Evaporation of the ethanol, followed by recrystallization of the product from methanol gave 0.109 g of pure **26**. Analysis (glpc column B, isothermal at 260°) of the remaining filtrate (0.050 g) showed that it consisted of about 35% **25** and 65% **26**. The physical properties of **26** are: mp 106–108°; uv max (95% C_2H_5OH) 227 sh mμ (log ε 4.47), 232 (4.61), 271 sh (3.75), 278 (3.80), and 286 sh (3.72); ir (CCl_4) 3.25 (sharp) and 3.30 (shoulder, both aromatic CH), 3.41 (*tert*-butyl), 6.82, 6.88, 7.22, 7.37, 11.07, and 11.26 μ.

Anal. Calcd for $C_{22}H_{32}$: C, 89.12; H, 10.88. Found: C, 89.15; H, 10.94.

B. From Pure Tetra-*tert*-butylnaphthalene 25.—In order to determine the approximate time for complete conversion of tetra-*tert*-butylnaphthalene **25** to tri-*tert*-butylnaphthalene **26**, the following glpc experiment was carried out. An analytically pure sample (0.005 g) of **25** was combined with 2.5 ml of the ethanol–hydrogen chloride reagent and refluxed for 12.5 hr. After removal of the solvent and extraction of the residue with pentane, glpc analysis on column B (isothermal at 260°) showed that the conversion of **25** to **26** was essentially complete (1% **25**, 99% **26**).

Registry No.—**6**, 26157-22-2; **7**, 26157-23-3; **9**, 26157-24-4; **10**, 26157-25-5; **12a**, 22495-81-4; **12b**, 22495-82-5; **12c**, 22495-83-6; **12d**, 22495-84-7; **14**, 26157-30-2; **19a**, 26157-31-3; **19b**, 26157-32-4; **19c**, 26157-33-5; **19d**, 26157-34-6; **20**, 22495-85-8; **21**, 22495-87-0; **22**, 22495-88-1; **23**, 22550-43-2; **24**, 22495-89-2; **25**, 22495-86-9; **26**, 26157-41-5.