oxygenation under the same conditions.[13] This procedure extends greatly the usefulness of TPPO as a reagent for the thermal generation of singlet oxygen. A typical procedure is as follows.

Triphenyl phosphite ozonide was prepared in the usual way by passing a stream of dry ozone through cold methylene chloride (-78 °C) while slowly adding 0.0232 g (0.074 mmol) of triphenyl phosphite at such a rate as to maintain the deep blue color of the ozone solution. After addition of the phosphite was complete (30-45 min) the solution was purged of ozone by passing a stream of dry nitrogen through it for 30 min. A separate solution of 10 mg (0.037 mmol) of biadamantylidene (Ad=Ad) was prepared in 1.5 mL of methylene chloride at -78 °C. This solution was added to that of the phosphite ozonide, followed by 1.0 mL of a 50:50 mixture of methanol-pyridine, also at -78 °C.

Under these conditions, in the absence of a singlet oxygen acceptor, oxygen bubbles off rapidly. In the presence of Ad=Ad but without the methanol-pyridine, no direct reaction occurs between Ad=Ad and TPPO.[7d] Under the present conditions, when the highly colored rubrene is used instead of Ad=Ad, the rubrene color is discharged within minutes after addition of the methanol-pyridine.

In the present experiment, TLC indicated no remaining Ad=Ad after about 5 min of reaction. The solution was then allowed to warm to room temperature, the solvent was removed, and the remaining syrup was subjected to preparative TLC, yielding 0.0102 g (91.1%) of the dioxetane of biadamantylidene.[12] The purified dioxetane decomposes at about 150 °C. The adamantanone produced remelts at 250-255 °C. A mixture of the dioxetane and 9,10-dibromoanthracene (DBA) on heating to 150 °C shows the blue luminescence characteristic of Ad=Ad dioxetane.

Acknowledgment. We thank the National Science Foundation, the National Institutes of Health, and the Robert A. Welch Foundation for support of this work.

Registry No. Triphenyl phosphite ozonide, 29833-83-8; biadamantylidene, 30541-56-1; dioxetane of biadamantylidene, 35544-39-9; adamantanone, 700-58-3; oxygen, 7782-44-7; sodium azide, 26628-22-8; *N,N*-dimethylbenzamine, 121-69-7; *N*-methylbenzamine, 100-61-8; *N,N*-diethylethanamine, 121-44-8; hydrazine, 302-01-2; *N*-ethylethanamine, 109-89-7; ammonia, 7664-41-7; benzenamine, 62-53-3; *N*-phenylbenzenamine, 122-39-4; 2,2,6,6-tetramethyl-4-piperidine-1-oxyl, 2896-70-0; *N,N*-bis(phenylmethyl)benzenemethanamine, 620-40-6; *N,N*-diphenylbenzenamine, 603-34-9; pyridine, 110-86-1; *N,N,N',N'*-tetramethyl-1,4-benzenediamine, 100-22-1.

(13) As these observations imply, the role of the pyridine is to enhance reactivity of the hydroxylic solvent, which replaces successive phenoxy groups from the TPPO, each replacement increasing the thermal lability of the ozonide (Lonzetta, C. M. Ph.D. Thesis, Harvard University, 1976; Bartlett, P. D.; Lonzetta, C. M., forthcoming paper).

The Steric Effect of a Bulky Group: The Stereochemistry of 1,4-Di-*tert*-butyl-1,4-dihydronaphthalene and 1-*tert*-Butyl-1,4-dihydronaphthalene

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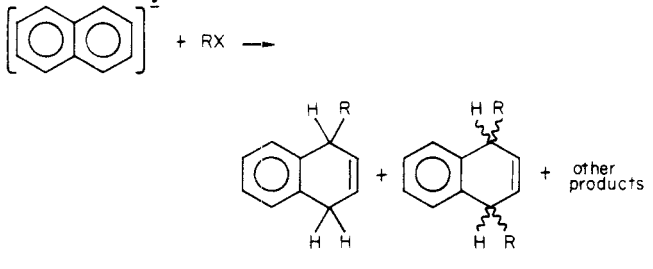
The stereochemistry of the mono- and di-*tert*-butyldihydronaphthalene derivatives was investigated with the aid of ^{1}H NMR, ^{13}C NMR, and the LAOCOON III program of the parent hydrocarbons and of an epoxide derivative. The di-*tert*-butyl derivative is distinguished by a nearly planar cyclohexadiene ring in which the *tert*-butyl groups are trans. In the mono-*tert*-butyl derivative, the cyclohexadiene ring is unusual because the ring appears to be twisted, presumably to permit relief of steric strain.

A good deal of interest has been shown in the reactions of the naphthalene radical anion with alkyl halides.[1] Whereas the mechanism of the reaction has attracted a great deal of attention, the stereochemistry of the products has received little attention. The stereochemistry of



previously defined dihydronaphthalenes may be described in terms of a cyclohexadiene ring which is either a "flattened boat" or "highly puckered", or some intermediate structure.[2] Because there is interest both in radical anion reactions and the stereochemistries of cyclohexadienes containing bulky groups, we undertook a study of the mono- and di-*tert*-butyl derivatives of dihydronaphthalene. While this study was underway, a report appeared[3] which described the alkylation of 1-alkyl-1,4-dihydronaphthalenes with akyl halides; this report claimed that the methylation of 1-methyl-1,4-dihydronaphthalene gave exclusively cis 1,4-dialkylated product, while the isopropylation of 1-isopropyl-1,4-dihydronaphthalene gave only trans 1,4-dialkylated product. These assignments were made on the basis of trends in the mixed dialkyl products, which in turn were stereochemically assigned by

(1) For leading references, see J. F. Garst, *Acc. Chem. Res.*, 4, 400 (1971).

(2) For a recent review, see P. W. Rabideau, *Acc. Chem. Res.*, 11, 141 (1978).

(3) P. W. Rabideau and E. G. Burkholder, *J. Org. Chem.*, 44, 2354 (1979).

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Table I. NMR Data for Various Dihydronaphthalenes, Anthracenes, and Benzene

	chemical shifts,[a] ppm					coupling constants, Hz									
compd[b]	H_1 (H_9)	H_2	H_3	H_4 (H_{10})	$H_{4'}$ ($H_{10'}$)	$J_{1,2}$	$J_{1,3}$	$J_{1,4}$ ($J_{9,10}$), J_{cis}	$J_{1,4'}$ ($J_{9,10'}$) J_{trans}	$J_{2,3}$	$J_{2,4}$	$J_{2,4'}$	$J_{3,4}$	$J_{3,4'}$	$J_{4,4'}$
1	3.13	6.13	6.13	3.13		3.7	1.8				1.8		3.7		
2	2.86	6.48	5.99	2.63	2.78	2.3	0.0	<1	<1	10.3	0.0	0.0	3.2	0.0	20.0
3	3.25			3.25		1.95				6.10					
4a[c]	3.83			3.83											
4b[c]	3.97			3.97											
5[d]	3.57			3.65	4.11			0.4	1.3						18.8
6[e]						5.2	≤1	1.8	3.0	9.6	≤1	2.0	5.0	2.0	20.5
7[e,f]						1.6	2.8	8.5		9.6	3.1		1.4		
8[g]	4.55	6.07	6.25	3.47	3.63	4.6	1.2	3.8	4.4	9.6	1.2	3.0	4.6	2.4	21.9
9[h]						3.1	1.5	7.4	8.6	10.3	1.5	1.5	3.0	3.0	21.7

[a] Relative to internal standard tetramethylsilane. [b] For numbering of hydrogens, refer to structures. [c] Taken from P. O. Fu, R. G. Harvey, J. W. Paschal, and P. W. Rabideau, *J. Am. Chem. Soc.*, 97, 1145 (1975). [d] From A. W. Brinkman, M. Gordon, R. G. Harvey, P. W. Rabideau, J. B. Stothers and A. L. Ternay, Jr., *J. Am. Chem. Soc.*, 92, 5912 (1970). [e] P. W. Rabideau, E. G. Burkholder, M. J. Yates, and J. W. Paschal, *J. Am. Chem. Soc.*, 99, 3596 (1977). [f] The values are similar in the study by M. C. Grossel and R. C. Hayward, *J. Chem. Soc., Perkin Trans. 2*, 851 (1976). [g] J. L. Marshall, A. M. Ihrig, and P. N. Jenkins, *J. Org. Chem.*, 37, 1863 (1972); J. L. Marshall and T. K. Folsom, *J. Org. Chem.*, 36, 2011 (1971). [h] P. W. Rabideau, J. W. Paschal, and L. E. Patterson, *J. Am. Chem. Soc.*, 97, 5700 (1975).

means of proton NMR arguments. We were concerned about such arguments because of the danger of deceptively simple spectra[4] and further we noted that stereochemical assignments on symmetrical systems (e.g., 1,4-diisopropyl-1,4-dihydronaphthalene) on the basis of proton NMR would be virtually impossible. In this paper a means is described whereby the stereochemistry of 1,4-di-*tert*-butyl-1,4-dihydronaphthalene was unequivocally established.

Results and Discussion

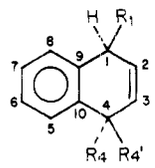
Preparation of 1,4-Di-*tert*-butyl-1,4-dihydronaphthalene and 1-*tert*-Butyl-1,4-diydronaphthalene. The title compounds were prepared by addition of *tert*-butyl chloride to a tetrahydrofuran solution of sodium naphthalene. The reaction was terminated by addition of water after disappearance of the green color of the radical anion. The reaction led to a great variety of products and use of a very long chromatography column was required to purify the mono-*tert*-butyldihydronaphthalene. Attempts to isolate pure materials from the reaction of sodium naphthalene with isopropyl, ethyl, and methyl halides were frustrated by the complexity and similar chromatographic properties of the products.

Stereochemistry of 1,4-Di-*tert*-butyl-1,4-dihydronaphthalene (1). The 60-MHz ^1H NMR spectrum of 1 revealed four regions of signals centered at δ 7.08, 6.16, 3.15, and 0.90 that integrated in the respective ratio of 4:2:2:18. The ^1H NMR parameters were analyzed by using the LAOCOON III program[5] and the results are listed in Table I.

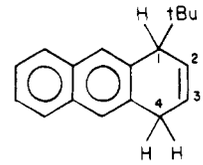
Because of chemical equivalence of H_1 and H_4, the homoallylic coupling constant (a potential measure of the conformation of the dihydro ring in 1[2,6,7]) cannot be determined. Instead, only the vicinal and allylic coupling constants could be used. Comparison of these values ($J_{1,2}$ = 3.7 Hz and $J_{1,3}$ = 1.8 Hz) with those in other systems suggest a flat, or nearly so, dihydro ring in 1. For a number of dihydro systems[2,6-8] an equatorial hydrogen in a puckered ring has a vicinal coupling constant ($J_{1,2}$) of 4.6–5.8 Hz and an allylic coupling constant of ≤1.0–1.2 Hz (e.g., see compound 6 in Table I); an axial hydrogen[2,9,10] in a puckered ring has a vicinal coupling constant ($J_{1,2}$) of 1.6–2.5 Hz and an allylic coupling constant ($J_{1,3}$) of 2.4–3.0 Hz (e.g., see compound 7 in Table I). By contrast, in flat systems[7,9] the vicinal coupling constant ($J_{1,2}$) is 3.0–3.4 Hz and the allylic coupling constant ($J_{1,3}$) is 1.5–1.7 Hz (e.g., see compound 9 in Table I), in closer agreement with the $J_{1,2}$ and $J_{1,3}$ values in 1. In dihydrobenzene derivatives with cis substituents at the 1 and 4 positions (*cis*-1-phenyl-4-trityl-1,4-dihydrobenzene) a puckered conformation was proposed with the substituents equatorial,[13] and a later work[11] maintained this contention. The substituents in these dialkylanthracene compounds[12] are axial because of interactions of the substituents with the peri protons and presumably are equatorial in *cis*-1-phenyl-4-trityl-1,4-dihydrobenzene because of steric interaction between the two substituents. Compound 1, with only one peri interaction for each *tert*-butyl group, might be intermediate between the dialkyldihydroanthracenes and *cis*-1-phenyl-4-trityldihydrobenzene and might very well be cis and flat. However, compound 1 could also be trans and flat (*trans*-1-phenyl-4-trityldihydrobenzene is flat[11,12]). Thus, it is impossible at this point to determine whether compound 1 is cis or trans, but it does seem clear that 1 is flat (or nearly so).

Stereochemistry of 1-*tert*-Butyl-1,4-dihydronaphthalene (2). Vicinal ($J_{1,2}$), allylic ($J_{1,3}$), and homoallylic ($J_{1,4}$) coupling constants follow consistent trends for a wide variety of dihydrobenzenes, dihydronaphthalenes, and dihydroanthracenes and are clear indicators[2,6] of the conformations of these dihydro compounds as being flat or puckered to varying extents. In contrast, the J values for compound 2 are somewhat puzzling because they depart from previously observed patterns. The vicinal ($J_{1,2}$)

(4) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy", Vol. 1, Pergamon Press, New York, 1965, p 363.
(5) A. A. Bothner-by and S. M. Castellano, "Computer Programs for Chemistry", D. F. DeTar, Ed., Benjamin, New York, 1968, p 10.
(6) J. L. Marshall, L. G. Faehl, C. R. McDaniel, Jr., and N. D. Ledford, *J. Am. Chem. Soc.*, 99, 321 (1977).
(7) M. Barfield and S. Sternhell, *J. Am. Chem. Soc.*, 94, 1905 (1972).
(8) J. L. Marshall and T. K. Folsom, *J. Org. Chem.*, 36, 2011 (1971).
(9) P. W. Rabideau, J. W. Paschal, and J. L. Marshall, *J. Chem. Soc., Perkin Trans. 2*, 842 (1977).
(10) P. W. Rabideau, E. G. Burkholder, M. J. Yates, and J. W Paschal, *J. Am. Chem. Soc.*, 99, 3596 (1977).
(11) J. W. Paschal and P. W. Rabideau, *J. Am. Chem. Soc.*, 96, 272 (1974).
(12) P. O. Fu, R. G. Harvey, J. W. Paschal, and P. W. Rabideau, *J. Am. Chem. Soc.*, 97, 1145 (1975).
(13) L. J. Durham, J. Studebaker, and M. J. Perkins, *Chem. Commun.*, 456 (1965).



1, $R_1 = R_4 = t$-Bu; $R_4' = H$
2, $R_1 = t$-Bu; $R_4 = R_4' = H$
6, $R_1 = (CH_3)_2COH$, $R_4 = R_4' = H$
8, $R_1 = CO_2H$; $R_4 = R_4' = H$
10, $R_1 = R_4 = R_4' = H$



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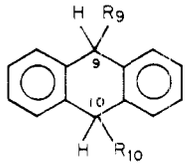
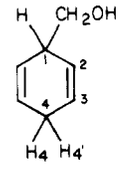


4a (trans), $R_9 = R_{10} = t$-Bu
4b (cis), $R_9 = R_{10} = t$-Bu
5, $R_9 = CO_2H$, $R_{10} = H$



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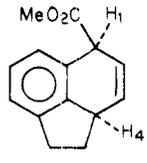

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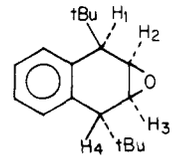


11

values suggests an equatorial substituent, the allylic ($J_{1,3}$) an axial substituent, and the homoallylic values an axial substituent. Furthermore, the small homoallylic values for **2** (<1 Hz) are not found in other dihydronaphthalenes systems (e.g., see **6**–**8** in Table I). In view of these surprising results, a study was conducted to see if the problem lay in the LAOCOON analysis.[14] Accordingly, the vicinal and homoallylic values in **2** were varied over a large range in a LAOCOON simulation and plotting study, whose results confirmed the values for **2** in Table I.

A conclusion from the unusual J values for **2** is that distortion occurs; specifically, there is a lateral movement of the *tert*-butyl group caused by the steric interaction of the *tert*-butyl group with the methylene ($H_{4'}$) and peri (H_8) proton. Accordingly, the dihydro ring is twisted and coupling trends are not the same as those for other dihydro derivatives. Apparently no twisting occurs about the olefinic C_2–C_3 bond, because $J_{2,3}$ is normal. Inspection of models suggests that as the *tert*-butyl group moves away from $H_{4'}$ and from H_8 (the peri interaction) while not twisting the π bond, the vicinal dihedral angles increase (which would result in smaller vicinal J values), the H_1 hydrogen would move away from the olefin π cloud (which would result in smaller $J_{1,3}$, $J_{1,4}$, and $J_{1,4'}$ values) and the $H_{4'}$ hydrogen (axial) would move away from the olefin π-cloud (which would result in a smaller $J_{2,4'}$ value). Thus, the J values for compound **2** in Table I are consistent with a twisted dihydro ring where the *tert*-butyl moves laterally away from the methylene and peri hydrogens. However, it is realized that other possibilities occur, such as a rapid equilibrium between nonequivalent conformations.

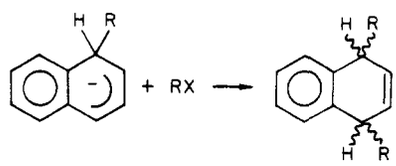
Geometry of Compound 1. Analysis of Epoxide Derivative 11. In order to remove the ambiguity of the stereochemistry of compound **1**, which could be either flat-cis or flat-trans, a derivative was sought which could resolve the problem. Accordingly, the epoxide derivative of **1** was prepared (**11**) and studied by ^1H and ^{13}C NMR. The ^1H NMR pattern was too compact to allow a ready analysis, and thus a lanthanide shift study was conducted.[15] As increasing amounts of $Eu(fod)_3$ were added to a $CDCl_3$ solution of **11**, the aliphatic protons journeyed in a manner that allowed unmistakable stereochemical assignment (see Table II). Specifically, each of the epoxide proton signals, the methine (benzylic) proton signals, and the *tert*-butyl proton signals all moved at different rates; these observations clearly indicated a lanthanide atom complexing with the Lewis base (epoxide) in an unsymmetrical manner (i.e., no mirror plane). Further, the nonequivalence between $J_{1,2}$ and $J_{3,4}$ in **11** indicates a geometry in which the dihedral angle of H_1 and H_2 is different from that of H_3 and H_4. The ^{13}C NMR spectrum of **11** also showed that there was no mirror plane in compound **11** (see Table III) and that **11** must therefore be trans.

Carbon-13 NMR Analysis. Carbon-13 NMR spectral data is given in Table III for compounds **1**, **2**, the unsubstituted parent dihydronaphthalene **10**, the "flattend boat" compound **8**, and the epoxide derivative **11**. Assignments were made generally on the basis of **8** and **10**. The assignments of C-1, C-4, C-α, and C-β in **2** were made unambiguously by off-resonance decoupling experiments. Comparison of **1** and **2** with the parent compound **10** shows little evidence of shielding of C-8, notwithstanding the peri interactions. This same observation is made for 1-substituted dihydroanthracene compounds[16] where peri interactions cause the substituent to be axial but no shielding effect is noticed on the peri carbon. Thus, this type of ^{13}C NMR data is not informative but is consistent with the idea of a substituent that swings away from C-8 as the substituent becomes large.

By contrast, a significant difference in the ^{13}C NMR chemical shift is noted for C-1: the value increases from δ 44.4 (for **2**) to 49.3 (for **1**) as the second *tert*-butyl group is substituted on the dihydro ring. This change of 4.9 ppm is reminiscent of the 5.6-ppm difference in the chemical shifts of the C-1 carbons of *trans*-1,4-di-*tert*-butylcyclohexane (which is in a chair conformation) and its cis isomer (which is in a twist-boat conformation)[17] and suggests a significant conformational difference between **1** and **2**. Furthermore, a significant difference is noted between the chemical shifts of the α-carbon (of the *tert*-butyl group) of **1** and **2** of 4.1 ppm, whereas for *trans*- and *cis*-1,4-di-*tert*-butylcyclohexane the corresponding difference is less than 1 ppm. This appears to reflect the difference of the position of the *tert*-butyl group with respect to the π system in **1** and **2**; in the di-*tert*-butylcyclohexanes, the *tert*-butyl groups are always equatorial or pseudoequatorial and show little change in chemical shift.

In summary, the ^{13}C NMR spectral analysis of **1** and **2** supports conclusions from proton NMR that the conformations of **1** and **2** are quite different.

Mechanism. The formation of the di-*tert*-butyl product in surprisingly high yield (15%) should be commented upon. The accepted mechanism for the second alkylation is considered to be an S_N2 reaction, based upon evidence in which RX was not a tertiary halide.[1] Formation of



(14) R. J. Abraham and S. M. Castellano, *J. Chem. Soc.*, 49 (1970).

(15) B. L. Shapiro, J. R. Hlubecek, G. R. Sullivan, and L. F. Johnson, *J. Am. Chem. Soc.*, **93**, 3281 (1971).

(16) J. L. Marshall, L. G. Faehl, A. M. Ihrig, and M. Barfield, *J. Am. Chem. Soc.*, **98**, 3406 (1976).

(17) J. D. Roberts, F. J. Weigert, J. I. Kroschwitz, and H. J. Reich, *J. Am. Chem. Soc.*, **92**, 1338 (1970).

Table II. ^{1}H NMR Lanthanide Study of the Epoxide 11[c]

proton no.	chemical shift[a] for Eu(fod)$_3$ concentrations[b] of 15.6	20.9	25.7	34.0	chemical shift / concentration Eu(fod)$_3$	R factor
1	2.36	3.09	3.32	3.69	0.0754	0.95
2	3.50	3.89	4.40	5.27	0.0981	>0.99
3	3.72	4.21	4.76	5.82	0.146	>0.99
4	2.38	3.13	3.38	3.79	0.0738	0.96
trans-tert-butyl	0.95	1.00	1.15	1.23	0.0162	0.97
cis-tert-butyl	1.33	1.41	1.60	1.88	0.0310	0.99

[a] Parts per million downfield from internal Me_4Si. [b] mg/mL of solution. [c] J values obtained from LAOCOON[5] analysis of the third (25.7 mg) run (RMS error = 0.03 Hz): $J_{1,2} = 1.89$, $J_{2,3} = 4.82$, $J_{3,4} = 0.51$ Hz. Assignments for the six listed protons made by J values (for protons 1-4) and by the comparison of the magnitude of the lanthanide shifts (for the *tert*-butyl protons). Chemical shifts for 11 without Eu(fod)$_3$ (approximate because of second-order spectrum): H_1, 2.30; H_2, 3.32; H_3, 3.51; H_4, 2.30; *trans-tert*-butyl, 0.94; *cis-tert*-butyl, 1.27 ppm.

Table III. ^{13}C NMR Data for Various Dihydronaphthalenes

compd	chemical shift[a] of carbon atoms 1	4	2	3	5	8	6	7	9	10	α-carbon (quaternary)	β-carbon (methyl)
1	49.3	49.3	123.8	123.8	128.7	128.7	128.4	128.4	137.5	137.5	37.1	28.9
2	44.4	29.4	126.3	125.6	130.9	128.0	127.6	126.9	135.8	133.9	33.0	27.4
10[b]	29.9	29.9	125.1	125.1	128.7	128.7	126.2	126.2	134.3	134.3		
8[b]	47.2	30.3	124.2	128.0	128.9	129.2	127.6	126.7	132.9	134.9		
11[c]	(47.1, 51.4)		(52.3, 54.0)		(128.4, 132.8)		(125.0, 125.9)		(135.1, 136.1)		(34.9, 35.9)	(28.9, 30.8)

[a] In parts per million relative to internal standard tetramethylsilane; measured in acetone-d_6. Assignments for **8**, **10**, and all carbons of 1 except C-5 and C-6 (which may be reversed) are secure; some assignments for the sp^2 carbons of 2 are tentative. [b] Taken from J. L. Marshall, L. G. Faehl, A. M. Ihrig, and M. Barfield, *J. Am. Chem. Soc.*, 98, 3406 (1976). [c] Assignment differentiation not possible between C-1 and C-4, C-2 and C-3, C-5 and C-8, C-6 and C-7, and C-9 and C-10.

dialkyldihydroanthracenes has been interpreted to be S_N2 for R = Me, Et, *i*-Pr, and *t*-Bu.[12] The point we wish to raise, however, is that there is very limited evidence in support of S_N2 reactions on tertiary halides[18] and when R = *t*-Bu it is more likely that the second alkylation is an electron-transfer process.

Experimental Section

Proton nuclear magnetic resonance spectra were taken on a Perkin-Elmer 24B spectrometer. Carbon nuclear magnetic spectra were recorded on JEOL PFT-100 NMR spectrometer operating at 25.16 MHz, utilizing 8000 data points and using tetramethylsilane as internal standard. Mass spectra were recorded on a Perkin-Elmer RMU 7 spectrometer, ionizing voltage 70 eV.

Reaction of Sodium Naphthalene with *tert*-Butyl Chloride. To 52.0 g (0.41 mol) of naphthalene in 500 mL of dry deoxygenated tetrahydrofuran was added 9.2 g (0.40 mol) of sodium. After the mixture was stirred under nitrogen for 14 h, 76.0 g (0.83 mol) of *tert*-butyl chloride was added dropwise while the solution was cooled in an ice–salt bath. After 0.5 h the green color of the radical anion had disappeared, 300 mL of water was slowly added, the mixture was neutralized, and the layers were separated. The aqueous layer was extracted twice with 100-mL portions of ethyl ether, and the organic portions were combined, washed once with 100 mL of water, dried over magnesium sulfate, and evaporated to leave 71.3 g of crude product. The naphthalene and dihydronaphthalene were largely removed by initially distilling the product at 10 mm, using a steam-heated condenser to prevent crystallization of the naphthalenes. The crude 1-*tert*-butyl-1,4-dihydronaphthalene (**2**)[19] was then distilled at 1 mm, bp 125–133 °C. This product was further purified by elution from a 2 × 900 cm alumina (MC & B), eluting with petroleum ether. By this procedure 4.2 g (6%) of the pure product was obtained, *m/e* 186 (base). The 1,4-di-*tert*-butyl-1,4-dihydronaphthalene (**1**) was purified by distillation at 0.5 mm: bp 160–65 °C; 14.5 g (15%); *m/e* 242 (base).

1,4-Di-*tert*-butyl-1,4-dihydronaphthalene Epoxide (11). A solution of 1.0 g of **1** and 1.56 g of *m*-chloroperbenzoic acid in 150 mL of methylene chloride was refluxed for 12 h, cooled, washed twice with sodium carbonate solution and then brine, treated with charcoal, dried (anhydrous magnesium sulfate), and concentrated to a thick syrup (0.9 g, 84%) which never crystallized: IR and ^{1}H and ^{13}C NMR (Tables II and III) consistent with **11**; mass spectrum, *m/e* 258 (M), 142 (M − 16).

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Registry No. **1**, 74877-15-9; **2**, 65482-09-9; **3**, 74877-16-0; **11**, 74877-17-1; naphthalene, 91-20-3; *tert*-butyl chloride, 507-20-0.

(18) T. M. Lowry and K. S. Richardson, "Mechanism and Theory in Organic Chemistry", Harper and Row, New York, 1976, p 179; D. Cook and A. J. Parker, *J. Chem. Soc. B*, 142 (1968).

(19) Previous syntheses of **2**: J. A. Dixon, D. H. Fishman, and R. S. Dudinyak, *Tetrahedron Lett.*, 613 (1964) (uncharacterized); J. Simonet M. Michel, and H. Lund, *Acta Chem. Scand., Ser. B*, **29**, 489 (1975) (unpurified).