mmol) was dissolved in THF (10 mL) and $LiEt_3BH$ (5.7 mL of 0.97 M solution, 5.5 mmol) was added to it. The mixture was stirred for 1 h and water (1-2 mL) was added dropwise to hydrolyze the mixture. Oxidation of the mixture with alkaline hydrogen peroxide and extraction with ether gave the alcohols: *cis*-β-methylstyrene oxide gave 615 mg (92%) of 1-phenyl-1-propanol, ^1H NMR ($CDCl_3$, 60 MHz) δ 7.25 (s, 5 H), 4.47 (t, 1 H), 2.67 (s, 1 H), 1.66 (q, 2 H), 0.87 (t, 3 H); *trans*-β-methylstyrene oxide gave 620 mg (93%) of 1-phenyl-2-propanol, ^1H NMR ($CDCl_3$, 60 MHz) δ 7.25 (s, 5 H), 3.95 (q, 1 H), 2.73 (d, 2 H), 2.1 (s, 1 H), 1.2 (d, 3 H). Both products were confirmed by coinjection with authentic samples in GC and also by mass spectra.

Kinetic Isotope Effect. The procedure for the kinetic experiments with lithium triethylborodeuteride was exactly as described earlier for the corresponding hydrogen reagent.

Competitive Experiments and Mass Spectral Analysis. *cis*-β-Methylene oxide (660 mg, 5 mmol) was reduced with a mixture of 5 mmol each of $LiEt_3BH$ and $LiEt_3BD$. The product was worked up as described above. The mixture of normal and deuterated alcohols was found to contain 44.6% of deuterated compound by mass spectral analysis. A similar experiment with trans epoxide showed a 43.5% incorporation of deuterium (the peaks at *m/e* values of 119 and 120 were compared, EI 70 eV). Application of the Ingold-Shaw equation,[9]

$$\frac{k_H}{k_D} = \frac{\log [H_0] - \log [H]}{\log [D_0] - \log [D]}$$

where k_H and k_D are the rate constants for hydride and deuteride, respectively, and $[H_0]$ and $[D_0]$ are the initial concentrations and [H] and [D] are the final concentrations of $LiEt_3BH$ and $LiEt_3BD$, respectively, gives the k_H/k_D value of 1.36 and 1.45 for the *cis*- and *trans*-epoxides, respectively.

Acknowledgment. We thank the U.S. Army Research Office for support of this research (Grant ARO DAAG-29-79-C-0027).

Registry No. **1**, 106-88-7; **2**, 1758-33-4; **3**, 5076-19-7; **4**, 5076-20-0; **5**, 2245-30-9; **6**, 285-67-6; **7**, 286-45-3; **8**, 286-20-4; **9**, 3146-39-2; **10**, 1713-33-3; **11**, 96-09-3; **12**, 21490-63-1; **13**, 4541-87-1; **14**, 23355-97-7; $LiEt_3BH$, 22560-16-3; $LiBH_4$, 16949-15-8; Et_3B, 97-94-9; D_2, 7782-39-0.

Diels-Alder Syntheses with 1,4-Di-*tert*-butoxy-1,3-butadiene[1]

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The title compound (DTBU) enters into [4 + 2] cycloadditions with fumaronitrile, tetracyanoethene, maleic anhydride, diethyl azodicarboxylate, 1,2-dibenzoylethene, dimethyl acetylenedicarboxylate, *p*-benzoquinone, 2-carbomethoxybenzoquinone, 2-methylbenzoquinone, 1,4-naphthoquinone, 2-methyl-1,4-naphthoquinone, and 5-hydroxy-1,4-naphthoquinone. When prepared the DTBU isomers are present in the ratio *E,Z*:*Z,Z*:*E,E* = 45:45:10. Of these, *Z,Z*-DTBU appears to be unreactive. In several cases where multiple Diels-Alder products were possible, two related to *E,Z*- or *E,E*-DTBU were obtained. A connection between ^1H NMR data (δ and *J*) and stereochemical configuration and conformation was elaborated for adducts of DTBU with *p*-benzoquinones or maleic anhydride.

Our report on 1,4-dimethoxy-1,3-butadiene (DMBU)[2] prompted the suggestion that replacement of methyl by *tert*-butyl might lead to useful changes in reaction selectivity.[3] After preparing the title diene (DTBU) and exploring its [4 + 2] cycloadditions, we can report that no unusual selectivity was found. What was possible, however, was the identification of several isomeric pairs of bicyclic products and the association of ^1H NMR data with structure. Indeed the adducts of DTBU with 1,4-quinones or maleic anhydride provide useful models of the stereochemical possibilities inherent in (partly) reduced bicyclic systems.[4a] However, the regioselectivity of further reactions of these adducts, e.g., naphthoquinones on their way to anthracyclinones,[4b] is often influenced or even controlled by the substituents. It is also in these and more complex structures that stereochemical or leaving group preferences deriving from DTBU as the precursor should be in evidence.

Table I. Analysis of the DTBU Isomers[a]

	Z,Z	*E,Z*	*E,E*
NMR (alkene protons)[b,c]	41	48	11
NMR (*t*-Bu protons)[b,d]	46	46	8
GC[d]	45	45	10

[a] Given as percent of total. [b] At 300 MHz. [c] Less reliable. [d] More reliable (± 2).

Interest in the construction of new dienes[4] and adaptation of old ones for particular purposes, e.g., mechanistic, synthetic, etc., remain high.[5,6] In large measure this must be ascribed to the search for dienes whose reactivities are often inadequately foreseen on the basis of past experience, intuition, or theory. It will be useful, therefore, to outline some of the properties of DTBU so that its virtues and deficiences will be apparent.

(1) Presented in part at the 16th ACS Great Lakes Regional Meeting, Normal, IL, June, 1982. **Added in Proof.** Even as our report on DMBU was made,[2] similar routes to DMBU and DTBU were already in press: van Rijn, P. E.; Everhardus, R. H.; van der Ven, J.; Brandsma, L. *Recl. Trav. Chim. Pays-Bas* **1981**, *100*, 372. We thank Dr. van Rijn for informing us of their work.

(2) Hiranuma, H.; Miller, S. I. *J. Org. Chem.* **1982**, *47*, 5083, presented at the 33rd Southeast Regional Meeting of the American Chemical Society, Lexington, KY, Nov, 1981.

(3) We wish to thank Professor R. T. Taylor, Miami University, Oxford, OH, for this suggestion.

(4) (a) Carter, M. J.; Fleming, I.; Percival, A. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2415. (b) Kelly, T. R., Parekh, N. D., Trachtenberg, E. N. *J. Org. Chem.* **1982**, *47*, 5009. (c) Dowd, P.; Weber, W. *Tetrahedron Lett.* **1982**, 2155; *J. Org. Chem.* **1982**, *47*, 4774. (d) Koreeda, M.; Ciufolini, M. A. *J. Am. Chem. Soc.* **1982**, *104*, 2308. (e) Schmidt, R. R.; Wagner, A. *Synthesis* **1981**, 273.

(5) (a) Ballistreri, F. P.; Maccarone, E.; Perrini, G.; Tomaselli, G. A.; Torre, M. *J. Chem. Soc. Perkin Trans. 2* **1982**, 273. (b) Fukuzumi, S.; Kochi, J. K. *Tetrahedron* **1982**, *38*, 1035.

(6) (a) Petrzilka, M.; Grayson, J. I. *Synthesis* **1981**, 753. (b) Roberge, G.; Brassard, P. *J. Org. Chem.* **1981**, *46*, 4161.

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As was the case with DMBU,[2] the preparation of DTBU was simple (eq 1). We found that acid-catalyzed ether

$$HOCH_2C{\equiv}CCH_2OH \xrightarrow[H^+]{Me_2C=CH_2} t\text{-}BuOCH_2C{\equiv}CCH_2OBu\text{-}t \xrightarrow[Me_2SO]{KOBu\text{-}t} \underset{DTBU}{t\text{-}BuOCH{=}CH\text{-}CH{=}CHOBu\text{-}t} \quad (1)$$

formation between 1,4-dihydroxy-2-butyne and 2-methylpropene was cleaner and gave higher yields than reactions involving *tert*-butyl chloride or alcohol. Subsequent isomerization of alkyne to diene was catalyzed by potassium *tert*-butoxide.[7] Unlike the stereospecific syntheses of (*E*),(*E*)-1,3- and (*E*),(*E*)-1,4-dimethoxy-1,3-butadienes,[4c,8] our route to DTBU yields what appears to be close to an equilibrium mixture of three isomers, *Z*,-*Z*:*E*,*Z*:*E*,*E* = 45:45:10. These figures (±2) were obtained both by NMR and GC methods and are given in Table I. Because the isomers were cleanly resolved by TLC and GC, it appears that scaled-up separation of the three forms should be possible.

"All polyalkoxypolyenes obtained are sensitive to moisture and oxygen" and polymerize easily.[9] We found that DTBU discolors readily on storage and can absorb ca. 1 equiv of oxygen (at least) when exposed to air. As was the case with DMBU[2] and several di- and trimethoxy-1,3-butadienes, such oxidations may make purification of alkoxy dienes exceedingly difficult.[4c,8a,9] In this work all of the DTBU cycloadditions were carried out under nitrogen.

The yields of certain Diels–Alder reactions may be improved by the addition of catalysts and/or substances that inhibit competing reactions.[10] Our previous experience with DMBU indicated limitations on the type of additive that might be used. Acids such as aluminum trichloride, cinnamic, and possibly phenols consumed DMBU.[2] While it was necessary to carry out some cycloadditions under oxidizing conditions, the oxidant had to be appropriate. Thus, although oxidative acyloxylation of dienes is of synthetic interest,[11] it proved to be a diversion, since both DMBU[2] and DTBU were acyloxylated with lead tetraacetate (eq 2). Fortunately these dienes were reasonably stable toward silver(I) oxide.

$$DTBU + Pb(OAc)_4 \rightarrow t\text{-}BuO(AcO)CHCH{=}CHCH(OAc)OBu\text{-}t \quad (2)$$

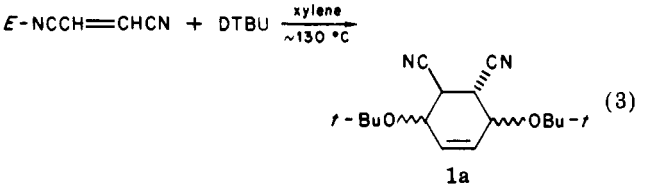
Cycloadditions. Theoretical calculations on [4+2] cycloadditions indicate that tetracyanoethene (TCNE) should react more rapidly with *E*,*E*-DMBU than with many other fairly common dienes.[8a,12] This, in fact, was observed, but there are other observations that should be appreciated. We found that the rates of cycloaddition of *E*,*E*- and *E*,*Z*-DMBU to TCNE were comparable and much higher than that of *Z*,*Z*-DMBU.[2] The same DMBU isomers also reacted with highly activated dienophiles, e.g., ethyl propiolate, 1,4-benzoquinone, etc. Although certain dienophiles, e.g., acrolein, ethyl cinnamate, ethyl phenylpropiolate, etc., might be expected to react with DMBU, we did not find suitable conditions for successful cycloaddition.[2] All of this experience with DMBU appears to carry over to DTBU. It is useful to remind oneself that few dienophiles possess the remarkable reactivity of TCNE!

Table II. Possible Stereoisomers from [4 + 2] Cycloadditions of DTBU

DTBU	dienophile	cycloadduct
E,*E* or *Z*,*Z*	RC≡CR or $R_2C{=}CR_2$	*Z*
E,*Z*		*E*
E,*E* or *Z*,*Z*	(*Z*)-RCH=CHR	*Z*,*Z*,*Z* or *E*,*Z*,*E*
E,*Z*		*E*,*Z*,*Z*
E,*E* or *Z*,*Z*	(*E*)-RCH=CHR	*Z*,*E*,*E*
E,*Z*		*Z*,*E*,*Z* or *E*,*E*,*E*

In cataloging the cycloadducts of DTBU, we shall describe those for which we found one product and proceed to those for which evidence of more than one was obtained. The reader should, however, keep in mind the three isomers of DTBU and the possibilities in Table II. In view of the low reactivity of *Z*,*Z*-DTBU, the maximum possible yields will often be ≤55%. Moreover, since the ratio of *E*,*Z* to *E*,*E* is 4.5:1, the relative amounts of product isomers will often be indicative of their stereochemistry.[13]

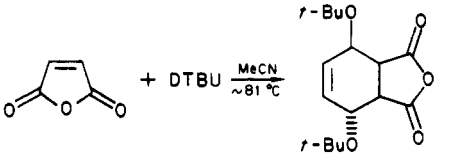
In accordance with expectation,[12] the reaction of DTBU with fumaronitrile was slower than with TCNE. Some unreacted *Z*,*Z*-DTBU was recovered so that the [4 + 2] adduct (eq 3) presumably derives chiefly from *E*,*Z*-DTBU.



(3)

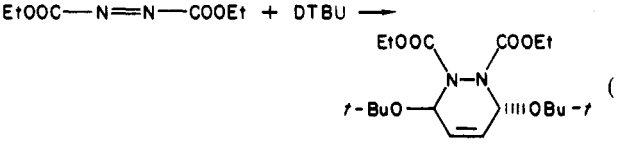
1a

The same *E*,*Z* isomer presumably leads to the products of maleic anhydride (eq 4) and diethyl azodicarboxylate (eq 5). In one example we found that the weak Lewis acid,



(4)

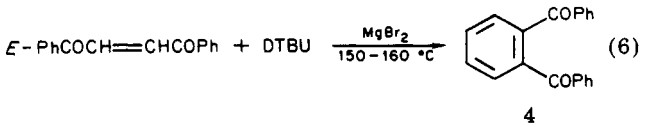
2



(5)

3a

magnesium bromide, facilitated the formation of adduct 4 from DTBU and 1,2-dibenzoylethene (eq 6).



(6)

4

(7) Brandsma, L. "Preparative Acetylenic Chemistry", Elsevier: Amsterdam, 1971, pp 173, 144.

(8) (a) Rücher, C.; Lang, D.; Sauer, J.; Friege, H; Sustmann, R. *Chem. Ber.* **1980**, *113*, 1663. (b) Meister, H. *Ibid.* **1963**, *96*, 1688.

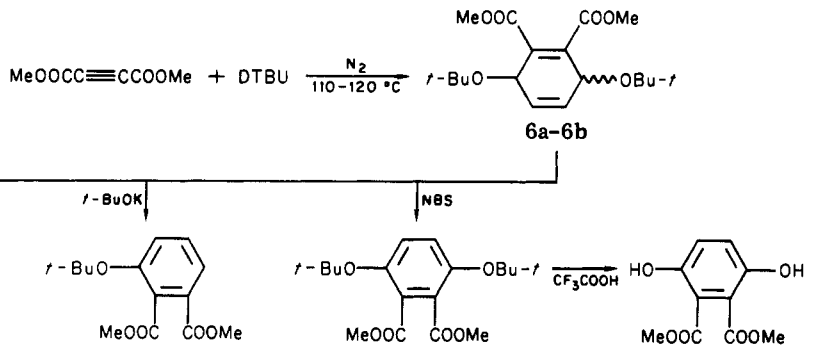
(9) Scheeren, J. W.; Marcelis, A. T. M.; Aben, R. W.; Nivard, R. J. F. *Recl. Trav. Chim. Pays-Bas* **1975**, *94*, 1960.

(10) (a) Schlessinger, R. H.; Lopes, A. *J. Org. Chem.* **1981**, *46*, 5252. (b) Corey, E. J.; Estreicher, H. *Tetrahedron Lett.* **1981**, 603. (c) Trost, B. M.; Bridges, A. J. *J. Am. Chem. Soc.* **1976**, *98*, 5017.

(11) (a) Bäckvall, J.-E.; Nordberg, R. E.; Nyström, J.-E. *Tetrahedron Lett.* **1982**, 1617. (b) Uemura, S.; Fukuzawa, S.; Okano, M. *Ibid.* **1981**, 5331.

(12) Sauer, J. Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779.

(13) Products derived from *E*,*Z*-DTBU, i.e., having the *tert*-butoxy groups trans, will be designated **a**; those derived from *E*,*E*- or *Z*,*Z*-DTBU, i.e., having the *tert*-butoxy groups cis, will be designated **b**.



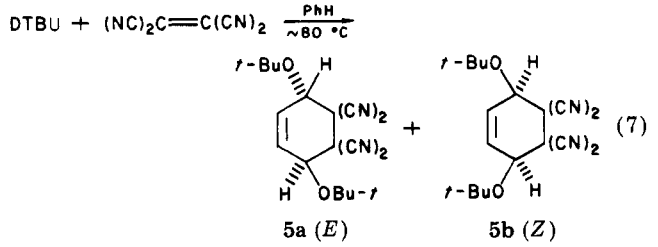
(8)

Table III. Stereoisomeric Products (3,6-Dialkoxy-1,1,2,2-tetracyanocyclohex-4-ene) of the TCNE Reaction with DMBU and DTBU

diene	product isomer	mp, °C	δ(R)	δ(CHOR)	δ(CH=)
E,E-DMBU[a]	*Z*	155-156[b]	3.80	4.43	6.10
E,Z-DMBU[a]	*E*	118-120	3.76	4.60	5.96
E,E-DTBU[c]	*Z* (**5b**)	168-169	1.33	4.53	5.80
E,Z-DTBU[c]	*E* (**5a**)	160-161	1.33	4.71	5.71

[a] Reference 2 except as indicated. [b] Reference 6a. [c] This work.

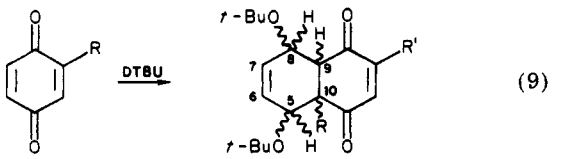
Taking into account the low reactivity of *Z,Z*-DTBU, which remains after *E,E*- and *E,Z*-DTBU are consumed, the reactions of the DTBU isomers with TCNE appear to produce the highest yields of adducts (eq 7). As in the case of DMBU and TCNE, the two possible isomeric products (**5**) were isolated.[2] Since Meister and Rücher et al. had prepared the *Z* product of DMBU,[8] this provided a point of reference for structural assignments to **5a** and **5b**. Now,



(7)

by comparing the NMR data (Table III) of the DMBU with the DTBU products, we could then assign the latter structures (**5**). Moreover, if we had only the yield figures available, the same assigment would have been plausible. The tacit assumption in the above reasoning, of course, is that the diene stereochemistry is carried over to the product[14] and that product isomerization is absent.

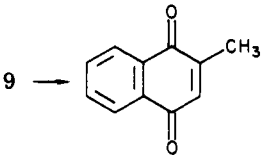
Dimethyl acetylenedicarboxylate and DTBU yielded two product isomers (**6**) whose structures could reasonably be assigned on the basis of yields (eq 8). Both could be aromatized either with base, in which alcohol was eliminated, or with *N*-bromosuccinimide (NBS), in which two hydrogen atoms were removed.[2] Subsequent treatment of the NBS product with trifluoroacetic acid selectively removed the *tert*-butyl groups but left the ester unscathed (eq 8). As noted earlier, the selective conversions of such DTBU adducts could be important in synthetic sequences.



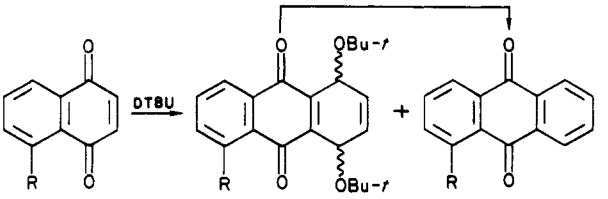
(9)

7a,b, R = R′ = H
8a,b, R = $COOCH_3$, R′ = H
9a,b, R = H, R′ = CH_3

The reactions of DTBU with several quinones were often complex. The first adducts of eq 9, for example, may enter into further cycloaddition with DTBU or aromatize. These products, starting quinone and the two primary adducts, contributed in varying degrees to isolation problems. For these reasons it was often necessary to convert the first adducts to simpler derivatives to demonstrate adduct formation, e.g., 2-methylnaphthoquinone (**10**) in eq 10 and the anthraquinones (**12, 14**) of eq 11. In



(10)



11a, R = H
13a, R = OH
12, R = H
14, R = OH

(11)

this way we were able to establish conditions for cycloadditon and identify some of the interesting adducts.

Products derived from *E,Z*- and *E,E*-DTBU were obtained from three naphthoquinones. In some cases ^1H NMR spectra for each were taken on the pure product; in others they had to be taken on the desired compound in the presence of an isomer, a known precursor or a known derivative. These data are collected in Table IV.

Stereochemistry. As indicated in Table II the isomers of DTBU may lead to one or more stereoisomeric products; with unsymmetrical dienophiles even more are possible. For reactions 7 and 8 the structural assignments were straightforward and probably unequivocal. On the other hand, where there were two or more possible products arising from any of the DTBU isomers, our characterizations of structure must be uncertain. It will be interesting to examine to what extent NMR data can resolve questions of configuration and conformation in such adducts.

Although maleic anhydride adducts of *E,Z* isomers are

Table IV. ^{1}H NMR Data of Isomeric Dihydronaphthoquinones Formed from *E,Z*- and *E,E*-DTBU[13,a]

ring site	7a[b]	8a[c]	9a[c]	7b[c]	8b[c]	9b
			Chemical Shifts			
2 (or CH_3)	6.65	6.67	1.96	6.66	6.71	1.96
3	6.79	6.80	6.65		6.63	6.50
5	4.87	4.82	4.12	4.15	4.54	4.10[c,d]
6	5.78	5.73	5.95	5.76	5.74	5.75
7	5.97	6.02	5.78		5.74	
8	4.14	4.58	4.86		4.01	4.12[c,d]
9	3.27	3.76	3.17	3.28	3.76	3.22[c,e]
10 (or $COOCH_3$)	3.19	3.74	3.30		3.79	3.26[c,e]
5 (OBu)	1.01	1.01	0.96	1.13	1.05	1.09
8 (OBu)	1.26	1.17	1.22		1.12	1.10
			Coupling Constants			
2,3	10.2	10.3	1.4		10.3	1.45
5,6	3.85	4.4	5.2		2.3	0
6,7	10.0	10.2	10.1			0
7,8	5.2	5.1	4.2			0
8,9	3.8			4.0	5.4	5-6
9,10	6.4		6.6			8.1
5,10	3.8		4.1	4.0		5-6
6,?			1.6			
7,?		1.3				
5,8						5.0

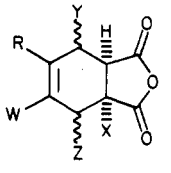
[a] Spectra taken in $CDCl_3$ at 300 MHz. Chemical shifts (ppm) or coupling constants (*J*, Hz) for designated ring substitutions are shown. [b] Assignments may be interchanged in pairs: 2,3; 5,8; 6,7; 9,10. [c] Equivalent or almost equivalent positions: 5,8; 6,7; 2,3 or 9,10. [d] Undecoupled shows *ca.* 4 peaks. Decoupled (from δ_5,δ_8) shows 2 peaks. [e] Uncoupled shows *ca.* 6 peaks. Decoupled (from δ_9,δ_{10}) shows 4 peaks.

Table V. ^{1}H NMR *J* Values (Hz) for [4 + 2] Adducts of 1,3-Dienes with Maleic-type Anhydrides[a]

compd	R	W	X	Y	Z	$J_{1,2}$	$J_{1,6}$	$J_{1,6'}$	$J_{2,3}$	$J_{2,3'}$	$J_{3,4}$	$J_{5,6}$	$J_{1,3}$ $J_{2,6}$	ref
2	H	H	H	*t*-BuO	*t*-BuO		4.7		4.7		~0.8	~0.8	2.1	*b*
15	MeO	Me	H	PhS	H	10.0	5.8		5.8	10.0				15a
16	H	Me_3SiO	H	MeO	H		4.2		5.1	10.7		6.4		15b
17	H	Me_3SiO	H	MeO	Me	10.8				9.5		6.1		15b
18[c]	H	H	H	NHQ	H		2.6					5.6		15c
19[c]	H	H	H	NHQ	Et	9.6	5.9		6.8		0	0		15c
20	H	H	Ph	AcO	AcO		8.0				2.0	2.0		15e
21	Me	H	COOMe	H	H		7.1	2.5			6.3			15f
22	H	H	H	Me	Me_3Si	9	7				6			4a
23	H	H	H	Me_3Si	Me_3Si		4		4					4a
24[d]	MeO	H	H	H	MeO				6.37		3.94	10.71 5.76	2.22	4c

[a] See note in ref 13. [b] This study. [c] Q = $COCCl_3$. [d] $J_{5,6}$ *and* $J_{5,6'}$ and $J_{2,6}$ *or* $J_{2,6'}$ are given here.

known,[14] recent work on comparable adducts (**15–22**) does not include them,[4d,e,5,15] Indeed, where the stereochemistry



2, **15–24** (see Table V)

is discussed it is either assumed or demonstrated to be "endo"—in this context "all cis", *Z,Z*, or *Z,Z,Z* would be more precise terms. Thus, there is X-ray or chemical evidence for the all-cis structure for [4 + 2] adducts of maleic anhydride and 1,3-butadienes containing the following substituents: 1-methyl-4-trimethylsilyl (**22**),[4a] 1,4-ditrimethylsilyl (**23**),[4a] 1,4-diaryl,[5a] 2-methoxy-3-methyl-1-phenylthio (**15**),[15a] and 1-methoxy-3-trimethylsiloxy-4-phenylseleno.[15b]

The X-ray evidence indicates an "extended boat" conformation for two different examples closely related to these adducts.[15a,b] Here, one or the other pair of groups, i.e., 3,6 and 3′,6′, takes up "flagpole" or "bowsprit" orientations. Since there are two such "boats" in the all-cis series, namely "folded" and "extended",[15b] as well as many other possible conformations, there may be considerable uncertainty as to which conformation is favored. Of course, "the preference of the endo reaction mode in the cycloaddition process need not have any implications of conformational stability of the final product."[15b]

Several groups have associated NMR coupling constants with a particular conformation in the maleic anhydride adducts. The usual Karplus dependence of the vicinal coupling constant, *J* (Hz), on torsion angle (τ) is the basis for such structural assignments.[16] Note that in the *ideal boat* form there is complete eclipsing for certain vicinal protons as well as the flagpole groups so that $\tau_{1,2} = \tau_{4,5} = \tau_{3,6} = \tau_{3',6'} = 0°$, $\tau_{2,3} = \tau_{1,6} \simeq 55°$, $\tau_{2,3'} = \tau_{1,6'} \simeq 160°$, $\tau_{3',4}$

(14) Martin, J. G.; Hill, R. K. *Chem. Rev.* **1961**, *61*, 537.
(15) (a) Kozikowski, A. P.; Huie, E.; Springer, J. P. *J. Am .Chem. Soc.* **1982**, *104*, 2059. (b) Danishefsky, S.; Yan, C-F.; Singh, R. K.; Gammill, R. B.; McCurry, Jr., P. M.; Fritsch, N.; Clardy, J. *Ibid.* **1979**, *101*, 7001. (c) Overman, L. E.; Freerks, R. L.; Petty, C. B.; Clizbe, L. A.; Ono, R. K.; Taylor, G. F.; Jessup, P. J. *Ibid.* **1981**, *103*, 2816. (d) Eggelte, T. A.; de Koning, H.; Huisman, H. O. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 267. (e) Holbert, G. W.; Ganem, B. *J. Org. Chem.* **1976**, *41*, 1655. (f) Hall, Jr., H. K.; Nogues, P.; Rhoades, J. W.; Sentman, R. C.; Detar, M. *Ibid.* **1982**, *47*, 1451.

(16) (a) Bystrov, V. F. *Prog. Nucl. Magn. Reson. Spectrosc.* **1976**, *10*, 41. (b) Jankowski; K.; Bélanger, J; Söler; F.; Zamojski, A. *Org. Magn. Reson.* **1979**, *12*, 544. (c) Otter, A.; Mühle, H.; Neuenschwander, M.; Kellerhals, H. P. *Helv. Chim. Acta* **1979**, *62*, 1626.

$= \tau_{5,6'} \simeq 25°$, $\tau_{3,4} = \tau_{5,6} \simeq 90°$. (Models are invaluable here.) In view of the variability and dispersion of Karplus relations, the dual values of τ for every J over much of the range in τ, and the perturbing influences of structure, substituents, etc., it would appear that caution is in order when applying the Karplus criterion to conformationally mobile molecules.

Consider recent data recorded for maleic-type anhydride adducts (Table V). It has been argued cogently that the all-cis products **15**, **16**, and **17** have the *extended boat* conformation, because of the coupling constants $J \simeq 10$ and $J \simeq 5$–6 Hz that are indicative of $\tau \simeq 0°$ and 60°, respectively,[16] in such a boat.[15a,b] Compound **24** appears to belong in this group as well. The same criteria probably apply to the all-cis molecule **22**[4a] as well, but have inexplicably been used to relegate **19** to the folded boat conformation.[15c] As for the remaining adducts (**2**, **18**, **20**, **21**, **23**), it would appear that their conformations vary within this group and differ from the extended boat. In the case of **2**, the 300 MHz NMR spectrum appears to be too simple for the product expected from *E,Z*-DTBU on the basis of yield. That is, δ_3(Bu) = δ_6(Bu), $\delta_1 = \delta_2$, $\delta_3 = \delta_6$, and $\delta_4 = \delta_5$. On the basis of decoupling experiments, there appears to be a genuine coupling $J_{1,3}$ or $J_{2,6}$ = 2.1 Hz which is new for this group of compounds. Since "symmetric" isomers can be *Z,Z,Z*, *E,E,E*, *E,Z,E*, and *Z,E,Z*, the question of both configuration and conformation must remain open.

We turn now to the adducts of the *p*-benzoquinones (Table IV). Büchi models indicate the two extended boats and respectable skew boats among other conformations. Judging by the "high" value of the coupling constants for the alkene proton pairs in **7a**, **8a**, **8b**, and **9a**, it would appear that $\tau_{1,2} \approx \tau_{6,7} \approx 0°$. Near coplanarity at these centers allows, but *does not* require, $\tau_{9,10} \approx 0°$. Distortion of the bridge from coplanarity to $\tau \approx 20$–30° would accommodate $J_{9,10} \simeq 6.5$ Hz in these compounds and lead to orientations of the *tert*-butoxy groups that were between the flagpole–bowsprit limits. (If an appropriate Karplus relation were available, torsion angles could be specified more closely.) For obvious structural reasons fewer J values are available in the **7**–**9b** series.[13] If anything, those we see are consistent with the conformation suggested for **7**–**9a**, although somewhat more bowsprit in the *tert*-butoxy groups and more flagpole in the 5,8-hydrogens are perhaps indicated by $J_{8,9}$ and $J_{5,6}$ (Table IV).

The preceding approach could, in principle, be applied to the conformations of certain other dihydroquinones, e.g., 2,9-dimethyl-8-(trimethylsilyl)-5,8-dihydro-1,4-naphthoquinone or 2,10-dimethyl-5-(trimethylsilyl)-5,8-dihydro-1,4-naphthoquinone.[4a] In view of the continuing interest in these molecules,[17] it is probable that, as J values become available, more refined applications of the Karplus equation to conformation would become practical.

Experimental Section

General. All boiling points and melting points are uncorrected. Melting points were determined on a Fisher-Johns apparatus. Organic liquids were dried over magnesium sulfate, unless otherwise specified. All of the cycloadditions with DTBU were carried out under nitrogen. Infrared spectra were determined with Pye Unicam 3-300 or Perkin-Elmer Model 337 spectrometers in KBr or as films on NaCl plates. NMR spectra were obtained in a Varian T60 spectrometer with tetramethylsilane as internal standard and in a Nicolet 300-Mhz spectrometer (the T60 data will be given, unless otherwise specified). Mass spectra were taken at ca. 70 eV in a Varian MAT CH7 instrument. Since the mass spectra of the DTBU products often lacked the parent peak (M^+), these may be omitted. Silica (60–200 mesh) was used in column chromatography. EM silica gel (60 Å, PF 254) on 20 × 20 cm^2 plates was used for preparative thin layer chromatography (TLC). Silica on plastic sheet (Eastman) or on glass slides was used for TLC. Elemental analyses were performed by Micro-Tech Laboratories, Skokie, Il.

1,4-Di-*tert*-butoxy-2-butyne. 2-Methylpropene (ca. 30 mL) was collected at −78 °C. After 1,4-dihydroxy-2-butyne (10 g, 0.116 mol), dichloromethane (50 mL), and 10 drops of concentrated sulfuric acid were added, the suspension was stirred at 30–40 °C for ca. 10 h when most of the solid had dissolved. Remaining solid was filtered off. The filtrate was poured into excess aqueous potassium carbonate (10%), which was then extracted with chloroform. The extract was washed with water, dried, and evaporated. Distillation of the residual oil gave the diether (15.7 g, 68%): bp 77–78 °C (1 mm); IR (NaCl) 2975, 1460, 1385, 1360 cm^{-1}; NMR ($CDCl_3$) δ 1.20 (s, 18 H), 4.04 (s, 4 H); MS, *m/e* 198 (M^+).

Two other routes to 1,4-di-*tert*-butoxy-2-butyne gave lower yields of product, but modifications may improve these syntheses. 1,4-Dihydroxy-2-butyne (860 mg, 10 mmol), *tert*-butyl chloride (2.77 g, 30 mmol), potassium carbonate (4.14 g, 30 mmol), and benzene (30 mL) were heated at reflux temperature for 7 h. Workup yielded an oil (100 mg) whose NMR spectrum indicated a mixture of starting alcohol and product, ca. 1:1 by the peak areas of the CH_2 groups.

1,4-Dihydroxy-2-butyne (430 mg, 5 mmol), *tert*-butyl alcohol (3 mL), and *p*-toluenesulfonic acid (5–10 mg) were heated at reflux temperature for 20 h. Workup yielded the diether (460 mg, 47%). In some preparations the product contained some starting dihydroxybutyne.

1,4-Di-*tert*-butoxy-1,3-butadiene (DTBU). A solution of 1,4-di-*tert*-butoxy-2-butyne (9.9 g, 0.05 mol) and potassium *tert*-butoxide (2.5 g) in dimethyl sulfoxide (50 mL) (which had been stored over molecular sieves) was heated under a nitrogen atmosphere at 75–80 °C for 3 h. The solution was cooled to ca. 25 °C, poured into water (100 mL), and treated with ether. The ether layer was washed with brine, dried, and evaporated. The remaining oil was distilled under nitrogen to give liquid DTBU (6.3 g, 64%), which solidified on storage at ca. 5 °C: bp 77–78 °C (0.9 mm); IR (NaCl) 1650, 1605, 1260 cm^{-1}; NMR ($CDCl_3$, 300 MHz) of *E,E* δ 1.28 (s, 18 H), 5.60 (dd, 2 H, J = 8.5, 2.8 Hz), 6.39 (dd, 2 H, J = 8.5, 2.8 Hz); NMR ($CDCl_3$, 300 MHz) of *E, Z*, δ 1.29 (s, 9 H), 1.295 (s, 9 H), 5.03 (dd, 1 H, J = 10.9, 6.2 Hz), 5.99 (ddd 1 H, J = 12.1, 11.0, 0.9 Hz) 6.54 (d, 1 H, J = 12.3 Hz), 6.05 (d, 1 H, J = 6.3 Hz); NMR ($CDCl_3$, 300 MHz) of *Z,Z* δ 1.305 (s, 18 H) 5.49 (dd, 2 H, J = 3.7, 1.2 Hz), 6.14 (dd, 2 H, 2 H, J = 3.7, 1.2 Hz); MS, *m/e* 198 (M^+). Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.73; H, 11.11. Found: C, 72.14; H, 10.84.

It is worth noting that when the isomerization was carried out at 90–100 °C, the yield of DTBU decreased to ca. 30%. Moreover, DTBU turns light yellow and becomes somewhat viscous on exposure to air. The ease with which oxygen was absorbed by DTBU showed up in an unsatisfactory initial elementary analysis (not given) and in the analysis reported above for carbon, which was somewhat low. A third sample, which was given no special care in handling, gave the following interesting result. Anal. Calcd for DTBU·O_2 or $C_{12}H_{22}O_4$: C, 62.60; H, 9.56. Found: C, 60.28; H, 8.87.

Unlike DMBU, which appears to decompose,[2] TLC of DTBU on silanized silica gel (Whatman KC_{18}) with a solvent consisting of 1:1 aqueous sodium chloride (0.5 M) and methanol yielded three spots with R_f values 0.10, 0.24, and 0.35. A single attempt to separate DTBU by liquid chromatography on a Waters Model 440 instrument with a μBondapack CN column and water: MeOH: Et_2NH = 45: 55: 0.05 as solvent was unsuccessful.

GC analysis of the isomers in our DTBU sample on a SCOT SE30 glass capillary column (25 m) at 80 °C indicated three well-resolved peaks. The retention times (min) were *Z,Z*, 10.1; *E,Z*, 11.1; *E,E*, 13.4. The relative concentrations taken from the peak areas are given in Table I. With regard to the analysis, we regard NMR integrals in the alkene region as most susceptible to error, because of peak overlap; the NMR integrals of the *tert*-butoxy groups and the integrals of the GC peaks were well separated.

(17) (a) Kraus, G. A.; Taschner, M. J. *J. Org. Chem.* **1980**, *45*, 1174. (b) Rozeboom, M. D.; Tegmo-Larsson, I-M.; Houk, K. N. *Ibid.* **1981**, *46*, 2333.

1,4-Diacetoxy-1,4-di-*tert*-butoxy-2-butene. This product was obtained instead of the desired adduct between DTBU and 3,6-pyridazinedione. DTBU (198 mg, 1 mmol) and maleic hydrazide (112 mg, 1 mmol) were stirred in acetonitrile (10 mL) at ca. 25 °C, while lead tetraacetate (443 mg, 1 mmol) was gradually added. After 2 h, the mixture was evaporated and the residue extracted with ether. The extract was dried and evaporated to leave an oil, which was subjected to a short-pass distillation (ca. 1 mm). The distillate (250 mg, 79%) had IR (NaCl) 1730, 1240, cm^{-1}; NMR ($CDCl_3$) 1.33 (s, 18 H), 2.08 (s, 6 H), 5.72 (s, 2 H), 6.38 (s, 2 H). Anal. Calcd for $C_{16}H_{28}O_6$: C, 60.76; H, 8.86. Found: C, 60.74; H, 8.72.

In a second attempt to effect the cycloaddition, silver(I) oxide was used as the oxidant—over 94% of the starting DTBU was recovered.

1,2-Dicyano-3,6-di-*tert*-butoxycyclohex-4-ene (1a). DTBU (198 mg, 1 mmol), (*E*)-1,2-dicyanoethene (78 mg, 1 mmol), and *p*-xylene (10 mL) were heated at reflux temperature for 17 h. The solution was evaporated and the residue was purified by column chromatography (silica gel) with ether–petroleum ether (1:3). A fraction of DTBU (45 mg, 23%) rich in *Z,Z* isomer was recovered. A later eluate gave **1a**, which was recrystallized from ether and *n*-hexane as white leaflets (50 mg, 18%): mp 192–193 °C; IR (KBr) 2220 cm^{-1}; NMR ($CDCl_3$) δ 1.25 (s, 18 H), 2.92 (dd, 2 H, $J \simeq 6$, 3 Hz), 4.25 (dd, 2 H, $J \simeq 6$, 3 Hz). Anal. Calcd for $C_{16}H_{24}N_2O_2$: C, 69.57; H, 8.69. Found: C, 69.89; H, 8.82.

In a second experiment under similar conditions, purified material that showed one spot on a TLC plate was shown to consist of at least two compounds by NMR (300 MHz).

3,6-Di-*tert*-butoxycyclohex-4-ene-1,2-dicarboxylic Anhydride (2). After DTBU (396 mg, 2 mmol), maleic anhydride (98 mg, 1 mmol), and acetonitrile (5 mL) were heated at reflux for 1 h, the solution was evaporated. The residue was purified by preparative TLC with ether–petroleum ether (1:1). The product crystallized from ether and *n*-hexane as white needles (100 mg, 33%): mp 123–124 °C; IR (KBr) 1860, 1780 cm^{-1}; NMR (300 MHz, $CDCl_3$) δ 1.26 (s, 18 H), 3.38 (dd, 2 H, J = 4.7, 2.1 Hz), 4.25 (dd?, 2 H, J = 4.7, 2.0, ~0.8 Hz), 5.91 (d?, 2 H, $J \simeq 0.8$ Hz). This spectrum appears to be that of structure **2b** rather than **2a**.[13] Anal. Calcd for $C_{16}H_{24}O_5$: C, 64.86; H, 8.11. Found: C, 64.88; H, 8.07.

1,2-Dicarbethoxy-3,6-di-*tert*-butoxy-1,2,3,6-tetrahydropyridazine (3a). DTBU (198 mg, 1 mmol) and diethyl azodicarboxylate (87 mg, 0.5 mmol) were heated at 90–100 °C for 5 h. The oily residue in ether–petroleum ether (1:1) was purified by preparative TLC, followed by a short-path vacuum distillation (ca, 1 mm). Though **3a** (84 mg, 45%) solidified in the refrigerator, it could not be crystallized from *n*-hexane: IR (NaCl) 1740, 1720, 1700 cm^{-1}; NMR ($CDCl_3$) δ 1.30 (s, 18 H), 1.30 (t, 6 H, 7 Hz), 3.83–4.43 (br s, 4 H), 5.70 (br s, 4 H); MS, m/e 372 (M^+). Anal. Calcd for $C_{18}H_{32}N_2O_6$: C, 58.06; H, 8.60. Found: C, 57.72; H, 8.54.

1,2-Dibenzoylbenzene (4). DTBU (198 mg, 1 mmol) (*E*)-1,4-diphenyl-1,4-dioxo-2-butene (118 mg, 0.5 mmol), and magnesium bromide[2] (50 mg) were heated at 150–160 °C for 24 h. The black product was taken up in ether–petroleum ether (1:1) and purified by TLC to yield yellow **4**. This was recrystallized from acetone–petroleum ether as light yellow platelets (22 mg, 8%) with mp 143–144 °C and spectral properties identical with those previously reported.[2]

(*E*)- and (*Z*)-3,6-Di-*tert*-butoxy-1,1,2,2-tetracyanocyclohex-4-ene (5a,b). A solution of DTBU (396 mg, 2 mmol) and TCNE (128 mg, 1 mmol) in benzene (10 mL) was heated at reflux for 5 h. (For anyone seeking evidence of charge transfer in Diels–Alder processes,[5b] it may be of interest that the color of this solution, which started out green, gradually disappeared in ca. 1 h.) The solution was evaporated and the residual solid, **5a**, was recrystallized from methanol as colorless needles (140 mg, 43%): mp 160–161 °C; IR (KBr) 1370, 1060 cm^{-1}; MS, m/e 311 $(M - 15)^+$, 255 $(M - 15 - 56)^+$. Anal. Calcd for $C_{18}H_{22}O_2N_4$: C, 66.26; H, 6.75. Found: C, 65.92; H, 6.80.

In a second experiment on the same scale but run for 3 h, the residue obtained by evaporation was purified by preparative TLC with a solvent consisting of ether–petroleum ether (2:3). The top (highest R_f) band yielded DTBU (45 mg, 11%). The second band yielded **5a** (216 mg, 66%). The third band yielded **5b** (21 mg, 6.4%) from ether–petroleum ether: mp 168–169 °C; IR (KBr) 1375, 1075 cm^{-1}; MS, m/e similar to **5a**. Anal. Calcd for $C_{18}H_{22}O_2N_4$: C, 66.26; H, 6.75. Found: C, 65.90; H, 6.73.

NMR data for **5a** and **5b** are given in Table II.

The course of the above cycloaddition was also monitored by GC. DTBU (99 mg, 0.5 mmol), TCNE (64 mg, 0.5 mmol), 2,6-dimethoxytoluene (10 mg) as internal standard, and benzene (10 mL) were heated at reflux temperature. After 30 min, the *E,Z* and *E,E* isomers of DTBU had been totally consumed, while a substantial fraction of *Z,Z*-DTBU remained by GC analysis.

(*E*)- and (*Z*)-1,2-Dicarbomethoxy-3,6-di-*tert*-butoxycyclohexa-1,4-diene (6a,b). DTBU (693 mg, 3.5 mmol) and dimethyl acetylenedicarboxylate (650 mg, 4.5 mmol) were heated at 110–120 °C for 15 h and then evaporated at 60–70 °C (1 mm) to drive off starting materials; the distillate weighed 780 mg. (A longer reaction time of 15 h did not increase the conversion appreciably.) The residual oil was purified by preparative TLC with ether–petroleum ether (1:1). The upper band (highest R_f) yielded solid product (100 mg, 8%), presumably **6a**, which was recrystallized from ether–*n*-hexane as white needles: mp 98–99 °C; Ir (KBr) 1730, 1270 cm^{-1}; NMR ($CDCl_3$) δ 1.20 (s, 18 H), 3.73 (s, 6 H), 4.88 (d, 2 H, J = 1 Hz), 6.00 (d, 2 H, J = 1 Hz). Anal. Calcd for $C_{18}H_{28}O_6$: C, 63.53; H, 8.23. Found: C, 63.40; H, 8.16.

From the lower band, a mixture of product isomers (260 mg, 22%) was obtained in a ratio of **6a:6b** $\simeq$ 7:3 by NMR; MS, m/e 266 $(M - t\text{-BuOH})^+$, 210 $(266 - C_4H_8)^+$; NMR ($CDCl_3$) δ (peaks of the isomer of mp 98–99 °C are omitted) 1.20 (s), 3.73 (s), 4.61 (br s, 2 H), 5.85 (br s, 2 H).

Several derivatives of **6** were prepared. A mixture of **6** (214 mg, 0.6 mmol, isomeric ratio ca. 1:1) was stirred with potassium *tert*-butoxide (70 mg, 0.6 mmol) in Me_2SO (1 mL) at ca. 25 °C for 2 h. Workup yielded dimethyl 3-*tert*-butoxyphthalate as an oil (56 mg, 34%): IR (NaCl) 1738, 1720 cm^{-1}; NMR ($CDCl_3$) δ 1.40 (s, 9 H), 3.80 (s, 3 H), 3.86 (s, 3 H), 7.20–7.63 (m, 3 H).

A mixture of **6** (141 mg, 0.41 mmol), sodium hydroxide (100 mg), ethanol (1 mL), and water (1 mL) was heated at reflux temperature for 3 h, then cooled, acidified with 10% hydrochloric acid, and extracted with ether. The extract was washed, dried, and evaporated, leaving a residue that was purified by chromatography on silica gel. The chloroform eluate yielded a solid (60 mg, 62%), which was recrystallized from ether and *n*-hexane to yield needles of 3-*tert*-butoxyphthalic acid: mp 127–158 °C dec: IR (KBr) 1720, 1710, 1690 cm^{-1}; MS, m/e 238 (M^+), 237, 181, 164. Anal. Calcd for $C_{12}H_{14}O_5$: C, 60.50; H, 5.88. Found: C, 60.89; H. 6.13.

The product mixture of **6** (130 mg, 0.38 mmol, **6a:6b** $\simeq$ 7:3), *N*-bromosuccinimide (150 mg, 0.84 mmol), and carbon tetrachloride (10 mL) were heated at reflux temperature for 2 h and evaporated. The residue was extracted with ether. The ether solution was washed with brine, dried, and evaporated to yield dimethyl 3,6-di-*tert*-butoxyphthalate as an oil (100 mg, 78%), which decomposed on distillation (1 mm); IR (NaCl) 1750, 1730 cm^{-1}; NMR ($CDCl_3$) 1.38 (s, 18 H), 3.82 (s, 6 H), 7.03 (s, 2 H).

Dimethyl 3,6-Dihydroxyphthalate. Trifluoroacetic acid (2 mL) and dimethyl 3,6-di-*tert*-butoxyphthalate (100 mg, 0.29 mmol) were stirred at ca. 25 °C for 24 h and then evaporated. The residue was taken up in ether and was washed with aqueous sodium bicarbonate and brine. The ether solution, dried over magnesium sulfate and evaporated, gave solid dihydroxy diester (40 mg, 59%): mp 140–141 °C (lit.[18] mp 140–143 °C).

5,8-Di-*tert*-butoxy-5,8,9,10-tetrahydro-1,4-naphthoquinone (7a,b). DTBU (396 mg, 2 mmol) and *p*-benzoquinone (108 mg 1 mmol) were heated at 110 °C for 13.5 h. The resulting dark oil was dissolved in ether–petroleum ether (1:1) and partially purified by two or three cycles of preparative TLC. DTBU (54 mg, 14%) was recovered from the first band (highest R_f). From the second band **7a** was obtained as an oil (101 mg, 33%): IR (NaCl) 1675 cm^{-1}; MS, m/e no parent $C_{18}H_{26}O_4$ 306, 250 $(M - 56)^+$, 176 $(M - 56 - 74)^+$, 158 $(M - 74 - 74)^+$.

From the third band, **7b** was obtained as an oil (10 mg, 3.3%): IR (NaCl) 1680 cm^{-1}; MS, m/e no parent $C_{18}H_{26}O_4$ 306, 250 $(M - 56)^+$, 232 $(M - 74)^+$, 176 $(M - 56 - 74)^+$, 158 $(M - 74 - 74)^+$.

Neither of the isomers (**7**) could be prepared in sufficient purity for *satisfactory* elemental analysis—residual impurities were

(18) Ansell, M. F.; Nash, B. W.; Wilson, D. A. *J. Chem. Soc.* **1963**, 3028.

apparent both in the NMR spectra and on the TLC plates. Anal. Calcd for $C_{18}H_{26}O_4$ (**7a**): C, 70.56; H, 8.55. Found: C, 69.84; H, 8.12.

5,8-Di-*tert*-butoxy-5,8,9,10-tetrahydro-10-carbomethoxy-1,4-naphthoquinone (8a,b). To a stirred solution of DTBU (396 mg, 2 mmol) 2-carbomethoxy-1,4-hydroquinone (168 mg, 1 mmol) in benzene (10 mL and silver(I) oxide (462 mg, 2 mmol) were added in one portion. The suspension was stirred at ca. 25 °C for 46 hr and then diluted with ether and filtered. The filtrate was dried and evaporated and the residue taken up in ether–petroleum ether (1:1) for purification by preparative TLC.

The top band (highest R_f) gave white needles of **8a** (80 mg, 22%): mp 104–105 °C; IR (KBr) 1738, 1678 cm^{-1}; MS, m/e no 364 (M^+), 308 $(M - 56)^+$, 291 $(M - 73)^+$, 252 $(M - 56 - 56)^+$. Anal. Calcd for $C_{20}H_{28}O_6$: C, 65.93; H, 7.69. Found: C, 65.55; H, 7.58.

The next band gave white solid of almost pure **8b** (20 mg, 5.6%)—some small impurity peaks are omitted in Table IV; MS, m/e no 364 $(M)^+$, 308 $(M - 56)^+$, 291 $(M - 73)^+$, 252 $(M - 56 - 56)^+$.

5,8-Di-*tert*-butoxy-5,8,9,10-tetrahydro-2-methyl-1,4-naphthoquinones (9a,b) and 2-methyl-1,4-naphthoquinone (10). The following experiments describe conditions for incomplete reactions as well as those in which **9** was aromatized to **10**. Since it was difficult to separate starting material or **10** from the first adducts (**9**), yield figures may be omitted. DTBU (396 mg, 2 mmol), 2-methylhydroquinone (248 mg, 2 mmol), benzene (10 mL), and silver(I) oxide (693 mg, 3 mmol) were heated at reflux temperature for 26 h. The mixture was treated with ether and filtered, and the filtrate was evaporated. The residue was taken up in ether–petroleum ether (1:1) and purified by TLC. From the first band (highest R_f) DTBU (150 mg, 38%) was recovered. From the second band crude 2-methylbenzoquinone was obtained; on recrystallization from petroleum ether, pure product, mp 69 °C and identical with an authentic sample, was obtained.

In a second experiment DTBU (396 mg, 2 mmol) and 2-methylbenzoquinone (122 mg, 1 mmol) were heated at 110–120 °C for 15.5 h. The black solid product was purified by preparative TLC as described above. From the second band a yellow solid (98 mg) was obtained; its NMR spectrum indicated **9a** and **10** in the ratio of ca. 7:3. Note that the NMR peaks of both starting material and **10** could be assigned. This solid (57 mg) and pyridine (2 mL) were heated at reflux temperature for 2 h, evaporated, and treated with aqueous hydrochloric acid and ether. The ether layer was washed, dried, and evaporated to leave a yellow solid (33 mg) whose melting point, NMR ($CDCl_3$), and IR (KBr) were identical with those of an authentic sample of **10**.

The reaction conditions of the second experiment were now changed to heating at 75–85 °C for 16 h. The black product, which was purified by repeated preparative TLC, contained 2-methylbenzoquinone and small amounts of the adducts (**9**), each of which was obtained as an almost pure solid (ca. 30 mg). On the basis of the NMR spectrum of these products (Table IV), the peaks of both adducts could be assigned. Although the NMR spectrum appeared clean, the coupling patterns at $\delta \simeq 3.2$ and 4.1 were complex.

1,4-Di-*tert*-butoxy-1,4-dihydro-9,10-anthraquinone (11a) and 9,10-Anthraquinone (12). DTBU (396 mg, 2 mmol) and 1,4-naphthoquinone (158 mg, 1 mmol, purity 90%) were heated at 110–120 °C for 16 h. The dark product was dissolved in ether–petroleum ether (1:1) and partially purified by preparative TLC, yielding a yellow solid (65 mg) in the second band. This consisted of **11a** and **12** in the ratio ~2.3:1 by NMR. For **11a**: NMR ($CDCl_3$) δ 0.070 (s, 9 H), 1.27 (s, 9 H), 3.28–3.57 (m, 2 H), 4.0–4.21 (m, 1 H), 4.88–5.0 (m, 1 H), 5.75–5.91 (m, 2 H), 7.45~8.38 (m).

9,10-Anthraquinone was obtained in a second experiment run on the same scale at 130 °C for 40 h. The dark product was then heated in pyridine (2 mL) at the reflux temperature for 4 h and evaporated. The residue was extracted with chloroform and the extract washed with hydrochloric acid (10%). The extract was dried and evaporated and the residue purified by preparative chromatography on silica gel with chloroform as eluant. The yellow needles of **12** had mp 278–279 °C and IR (KBr) and NMR (CF_3COOH-$CDCl_3$) spectra identical with those of an authentic sample.

1,4-Di-*tert*-butoxy-1,4-dihydro-5-hydroxy-9,10-anthraquinone (13a) and 1-Hydroxy-9,10-anthraquinone (14). DTBU (198 mg, 1 mmol) and 5-hydroxy-1,4-naphthoquinone (87 mg, 0.5 mmol) were heated at 120 °C for 21.5 h. The dark product was dissolved in ether–petroleum ether (1:1) and partially purified by preparative TLC, yielding a yellow solid (93 mg) consisting of **13a** and **14** in the ratio $\simeq$ 7:3 by NMR. This mixture was heated at reflux temperature with pyridine (2 mL) for 5 h. Workup yielded **14** as yellow needles (56 mg, 50%) from ether and *n*-hexane: mp 194–195 °C (lit.[19] mg 195–196 °C); IR (KBr) 1675, 1640 cm^{-1}; NMR ($CDCl_3$) δ 7.0–7.23 (m, 1 H), 7.43–7.83 (m, 5 H), 7.93–8.26 (m, 2 H); MS, m/e 224 (M^+).

By deletion of the peaks of **14**, the identification of the peaks of **13a** could be made as follows: NMR ($CDCl_3$) δ 0.73 (s, 9 H), 1.23 (s, 9 H), 3.13–3.63 (m, 2 H), 4.03–4.33 (s, 1 H), 4.93–5.13 (s, 1 H), 5.80–6.0 (m, 2 H).

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Registry No. **1**, 86528-04-3; **2**, 86528-05-4; **3a**, 86528-06-5; **4**, 1159-86-0; **5a**, 86528-07-6; **5b**, 86528-08-7; **6a**, 86528-09-8; **6b**, 86528-10-1; **7**, 86528-11-2; **8**, 86528-12-3; **9**, 86528-13-4; **10**, 58-27-5; **11a**, 86542-49-6; **12**, 84-65-1; **13a**, 86542-50-9; **14**, 129-43-1; (*E*,*E*)-DTBU, 86528-14-5; (*E*,*Z*)-DTBU, 86528-15-6; (*Z*,*Z*)-DTBU, 79989-51-8; *t*-$BuOCH_2C{\equiv}CCH_2OBu$-*t*, 79989-39-2; $Me_2C{=}CH_2$, 115-11-7; $HOCH_2C{\equiv}CCH_2OH$, 110-65-6; *t*-BuO(AcO)CHCH=CHCH(OAc)OBu-*t*, 86528-16-7; (*E*)-NCCH=CHCN, 764-42-1; EtOOCN=NCOOEt, 1972-28-7; (*E*)-PhCOCH=CHCOPh, 959-28-4; TCNE, 670-54-2; $MeOOCC{\equiv}CCOOMe$, 762-42-5; *tert*-butyl chloride, 507-20-0; *tert*-butyl alcohol, 75-65-0; maleic anhydride, 108-31-6; dimethyl 3-*tert*-butoxyphthalate, 86528-17-8; 3-*tert*-butoxyphthalic acid, 86528-18-9; dimethyl 3,6-di-*tert*-butoxyphthalate, 86528-19-0; *p*-benzoquinone, 106-51-4; 2-carbomethoxy-1,4-benzoquinone, 3958-79-0; 2-methyl-*p*-benzoquinone, 553-97-9; 1,4-naphthoquinone, 130-15-4; 9,10-anthraquinone, 84-65-1; 5-hydroxy-1,4-naphthoquinone, 481-39-0.

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