jected to identical glc–mass spectrometry analyses. The recovered chloride was found to consist of 52% 10-*1*-d_2 and 48% rearranged material, 10-*2*-d_2.

Analysis of the 1-phenyl-2-*p*-tolylethane fraction was based on the corrected relative intensities of the *m/e* 105 ($CH_3C_7H_6$) and 107 ($CH_3C_7H_4D_2$) peaks. For reference, 9-*1*-d_2 and 9-*2*-d_2 were subjected to identical glc–mass spectrometry analyses. The product was found to consist of 47% 9-*1*-d_2 and 53% 9-*2*-d_2.

Friedel–Crafts Reaction of 1,1-Dideuterio-2-*p*-tolylethyl Chloride (10-*1*-d_2) with Benzene at 7°. Analysis of the Starting Material and Product during the Reaction.—A mixture of 2.09 g (0.011 mol) of 10-*1*-d_2, 0.457 g (0.0034 mol) of $AlCl_3$, 1.385 g of *p*-dichlorobenzene (internal standard for glc analyses, inert), and 300 ml of benzene were stirred at 7° for approximately 1.5 hr. Periodically, 50-ml samples were removed, subjected to the usual work-up conditions, and separated into starting material and product by preparative glc. Mass spectral analyses were performed on these samples as well as on appropriate reference materials by Morgan–Schaffer Corp., Montreal, Canada, using a Hitachi RMU-6 mass spectrometer. The results are reported in Table I.

Registry No.—**1**, 694-87-1; **2**, 622-24-2; 10-*1*-d_2, 34403-01-5; phenyl 2-methylbenzyl ketone, 5033-67-0; phenyl 3-methylbenzyl ketone, 34403-03-7; phenyl 4-methylbenzyl ketone, 2430-99-1; 1-phenyl-2-*o*-tolylethane, 34403-05-9; 1-phenyl-2-*m*-tolylethane, 34403-06-0; 1-phenyl-2-*p*-tolylethane, 14310-20-4; α,α-dideuteriobenzyl chloride, 33712-34-4; α,α-dideuterio-*p*-methylbenzyl chloride, 33712-36-6.

Acknowledgments.—We are indebted to Professor Neil McKelvie, Professor Frank Brescia, and Mr. Sidney Liebgold for their kind assistance.

Dealkylation of Di-*tert*-butylhalo-1,4-benzoquinones

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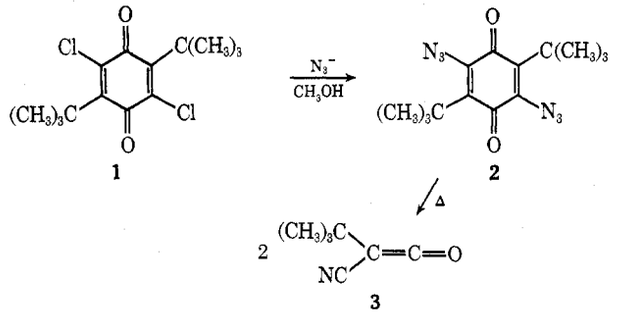
3-Chloro- and 3-bromo-2,5-di-*tert*-butyl-1,4-benzoquinone as well as 3-chloro-2,6-di-*tert*-butyl-1,4-benzoquinone react with anhydrous hydrohalic acids, resulting in dealkylation. This is a synthetically useful reaction for the preparation of 2,3-dihalo-5-*tert*-butyl-1,4-benzoquinones, specifically the 2,3-dichloro-2,3-dibromo-, 3-bromo-2-chloro, and 2-bromo-3-chloro isomers. The mechanism of this dealkylation involves an initial oxidation–reduction yielding the corresponding hydroquinones and molecular halogen. Electrophilic substitution by the halogen then results in elimination of the *tert*-butyl cation.

Recently the synthesis of 2,5-dichloro-3,6-di-*tert*-butyl-1,4-benzoquinone (**1**) was described.[1] This compound upon treatment with sodium azide gives the corresponding 2,5-diazido-3,6-di-*tert*-butyl-1,4-benzoquinone (**2**) which can be pyrolytically cleaved to *tert*-butylcyanoketene (**3**).[2] During our early attempts to synthesize the dichloroquinone **1**, some very interesting de-*tert*-butylation reactions were discovered. These dealkylation reactions are of synthetic utility and can be used to conveniently prepare 2,3-dichloro- (**13**), 2,3-dibromo- (**16**), 3-bromo-2-chloro- (**14**), and 2-bromo-3-chloro-5-*tert*-butyl-1,4-benzoquinone (**15**), from the readily available 2,5- and 2,6-di-*tert*-butyl-1,4-benzoquinones.



The mechanism of these dealkylation reactions is of interest and suggests that the "1,4 addition" of HCl and HBr to certain quinones is not a simple addition, but instead may involve an initial oxidation–reduction to the hydroquinone and molecular halogen followed by electrophilic substitution (halogenation) of the hydroquinone.

(1) H. W. Moore and W. Weyler, Jr., *J. Amer. Chem. Soc.*, **93**, 2812 (1971).

(2) H. W. Moore and W. Weyler, Jr., *ibid.*, **92**, 4132 (1970).

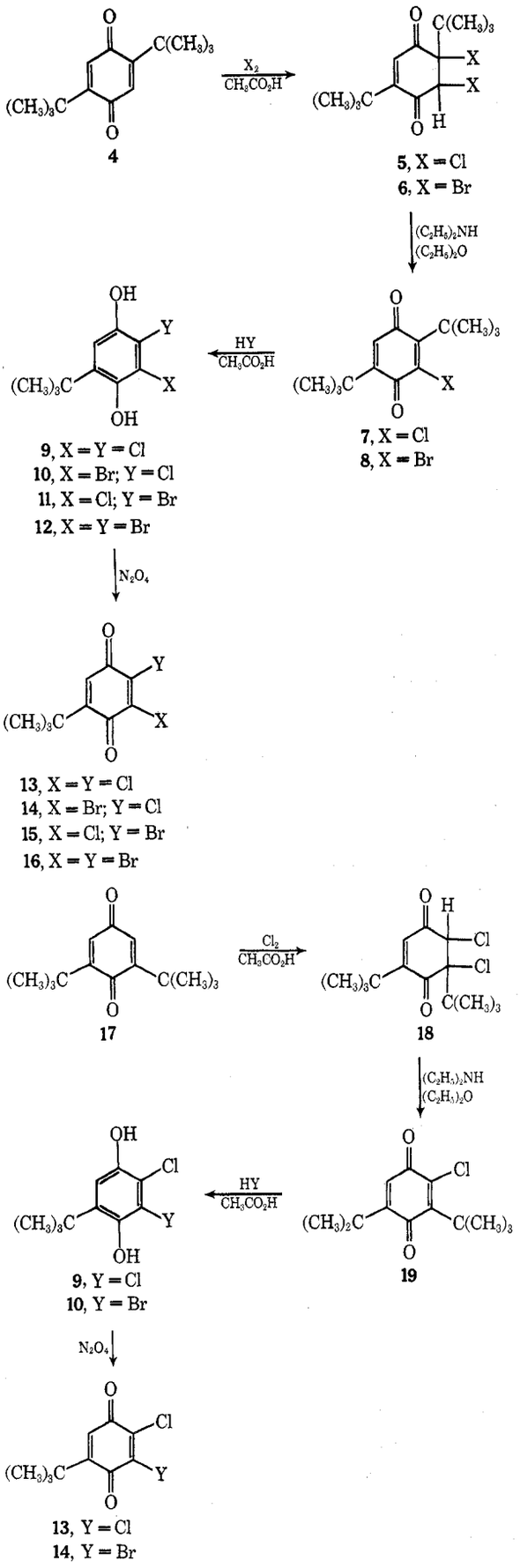
Synthetic Scope.—2,5-Di-*tert*-butyl-1,4-benzoquinone (**4**) was converted to its chloro and bromo derivatives **7** and **8** in high yield. These transformations were accomplished by an initial halogen addition to the carbon–carbon double bond to give the dihalo adducts **5** and **6**. These derivatives were then dehydrohalogenated upon reaction with diethylamine to the 3-halo-2,5-di-*tert*-butyl-1,4-benzoquinones **7** and **8**. Reaction of these haloquinones, 3-chloro-2,5-di-*tert*-butyl- (**7**) and 3-bromo-2,5-di-*tert*-butyl-1,4-benzoquinone (**8**) with anhydrous HCl in glacial acetic acid gave, respectively, 2,3-dichloro- (**9**) and 3-bromo-2-chloro-5-*tert*-butyl-1,4-benzoquinol (**10**). In completely analogous reactions, the monohalo-2,5-di-*tert*-butylquinones, **7** and **8**, were respectively converted to 2-bromo-3-chloro- (**11**) and 2,3-dibromo-5-*tert*-butyl-1,4-benzoquinol (**12**) upon reaction with anhydrous HBr. Oxidation of the above quinols with nitrogen oxides[3] gave the corresponding 2,3-dihalo-5-*tert*-butyl-1,4-benzoquinones, **13**–**16**.

2,3-Dichloro-5-*tert*-butyl-1,4-benzoquinone (**13**) and 3-bromo-2-chloro-5-*tert*-butyl-1,4-benzoquinone (**14**) were also obtained when 2,6-di-*tert*-butyl-1,4-benzoquinone (**17**) was converted to its monochloro derivative and then treated, respectively, with anhydrous HCl and HBr in glacial acetic acid. Oxidation of the resulting quinols gave the quinones in excellent yields.

Structural Assignments.—The structures of the 2,3-dihalo-5-*tert*-butyl-1,4-benzoquinones **13**–**16** are based upon both spectral (Table I) and chemical data. They all react with excess sodium azide to give the same diazide, 2,3-diazido-5-*tert*-butyl-1,4-benzoquinone (**20**),[4]

(3) L. Fieser and M. Fieser, "Reagents for Organic Synthesis," Vol. 1, Wiley, New York, N. Y., 1967, p 738.

(4) In general, azidoquinones are readily prepared by treating a dilute alcoholic solution of the corresponding halo-substituted quinone with aqueous sodium azide: H. W. Moore, H. R. Shelden, D. W. Deters, and R. J. Wikholm, *J. Amer. Chem. Soc.*, **92**, 1675 (1970).



thus showing the halogens in the four compounds to be in the same orientation. The monoazide, 3-azido-2-bromo-5-*tert*-butyl-1,4-benzoquinone (**21**), was obtained from 2,3-dibromo- (**16**) or 2-bromo-3-chloro-5-*tert*-butyl-1,4-benzoquinone (**15**) upon treatment with 1 equiv of sodium azide. This monoazide underwent the known[5] thermal rearrangement of azidoquinones to give 2-bromo-2-cyano-4-*tert*-butyl-1,3-cyclopentenedione (**22**), which shows a vinyl proton absorption at 7.08 ppm in its nmr spectrum. The fact that this cyclopentene **22** has a vinyl proton rules out 2-azido-5- or 6-bromo-6- or 5-*tert*-butyl-1,4-benzoquinone as possible structures for the monoazidoquinone **21**, since it is known that the substituent adjacent to the azide function in the azidoquinone is found at the sp^3 2 position of the 1,3-cyclopentenedione.

Rearrangement of the monoazidoquinone **21** to the butenolide **23** in concentrated sulfuric acid also aided in its structural assignment. The vinyl proton absorption in the nmr spectrum of the butenolide appears at 7.34 ppm. This is in agreement with structure **23**, while has its alkene proton β to the carbonyl.[6] Consideration of the mechanism of this known[4] acid catalyzed rearrangement reveals that the substituent in the 5 position of a 2-azido-1,4-benzoquinone is located at the β position in the butenolide. As a result, the only reasonable structure for the butenolide **23** precursor is 2-bromo-3-azido-5-*tert*-butyl-1,4-benzoquinone (**21**). These results strongly imply that the halo substituents in the quinones **13–16** are in an adjacent 2,3 orientation. This assignment was confirmed by the independent syntheses of 2,3-dibromo-5-*tert*-butyl-1,4-benzoquinone (**16**) starting from *tert*-butyl-1,4-benzoquinone (**31**) as described later.

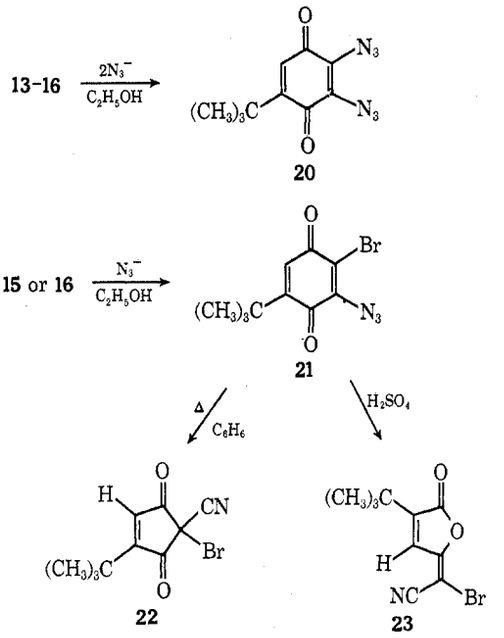
The nmr spectra of the 2,3-dihalo-5-*tert*-butyl-1,4-benzoquinones **13–16** are also in accord with their

TABLE I
SPECTRAL PROPERTIES OF NEW COMPOUNDS

Compd	Mp, °C	Ir, cm^{-1}	Nmr, ppm from TMS
5	127–128	1710, 1620	1.25 (9) s, 1.33 (9) s, 4.55 (1) s, 6.21 (1) s
6	112–113	1700, 1620	1.28 (9) s, 1.45 (9) s, 4.85 (1) s, 6.30 (1) s
7	Oil	1680, 1660, 1550	1.30 (9) s, 1.48 (9) s, 6.51 (1) s
8	Oil	1675, 1650, 1550	1.26 (9) s, 1.46 (9) s, 6.43 (1) s
13	89–89.5	1670, 1660, 1580	1.31 (9) s, 6.68 (1) s
14	81–83	1680, 1660, 1580	1.31 (9) s, 6.71 (1) s
15	77–78	1670, 1660, 1570	1.31 (9) s, 6.76 (1) s
16	90–91	1680, 1665, 1575	1.31 (9) s, 6.76 (1) s
18	118–118.5	1685, 1620	1.15 (9) s, 1.46 (9) s, 4.71 (1) d, J = 1.8 Hz, 6.61 (1) d, J = 1.8 Hz
19	Oil	1670, 1550	1.29 (9) s, 1.49 (9) s, 6.50 (1) s
20	104–106	2120, 1670, 1600	1.31 (9) s, 6.50 (1) s
21	71–74	2110, 1660, 1560	1.30 (9) s, 6.77 (1) s
22	91–92	2230, 1700, 1575	1.38 (9) s, 7.08 (1) s
23	102–104	2220, 1780, 1620	1.32 (9) s, 7.34 (1) s
27	167–168	3268, 3333 (sh)	1.25 (9) s, 6.67 (1) s, 6.94 (1) s, 7.32–7.92 (12) m
31	104–107	1700, 1610	1.28 (9) s, 4.60 (2) s, 6.33 (1) s

(5) H. W. Moore, W. Weyler, Jr., and H. R. Shelden, *Tetrahedron Lett.*, 3947 (1969).

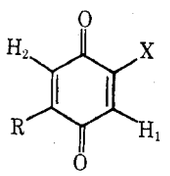
(6) The chemical shifts of vinyl protons in the β positions of known γ-cyanoalkylidine-$\Delta^{\alpha,\beta}$-butenolides occur in the range 7.30–7.42 ppm, while those in the α position appear at 4.00–5.67 ppm. See ref 4.



assigned structures. The chemical shifts of the vinyl protons in these compounds appear in the range 6.68–6.75 ppm. This is in good accord with the nmr spectra of other alkylhalo-1,4-benzoquinones having a vinyl proton adjacent to the alkyl substituent (Table II).

TABLE II[a]

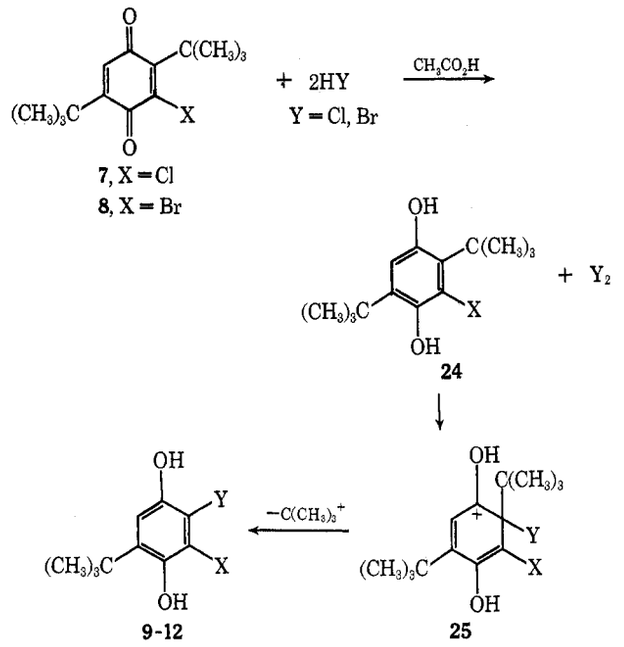
CHEMICAL SHIFTS OF VINYL PROTONS OF ALKYLHALOQUINONES



R	X	H_1	H_2
$(CH_3)_3C$–	Cl	6.88	6.68
$(CH_3)_3C$–	Br	7.10	6.65
CH_3	Cl	6.98	6.73
CH_3	Br	7.25	6.75

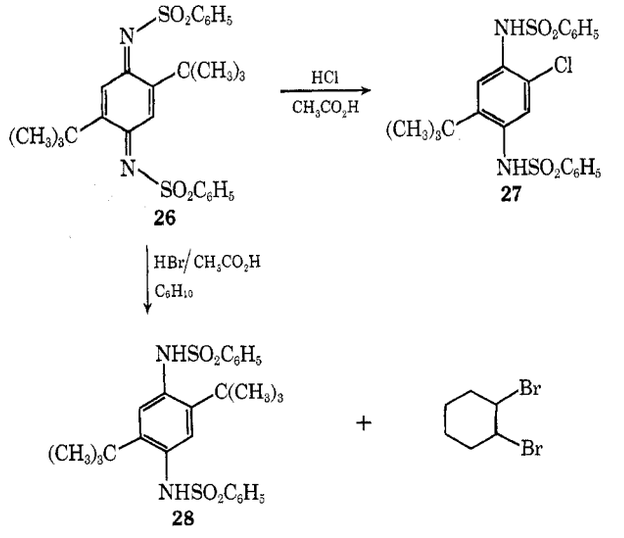
[a] All spectra were obtained for solution of the quinone in CCl_4 solvent.

Mechanism.—The above mechanism is suggested for the de-*tert*-butylation described here. The first step involves an oxidation–reduction to give the hydroquinone **24** and molecular halogen. The hydroquinone then undergoes electrophilic substitution (halogenation) *via* the σ complex **25** to give the hydroquinones **9–12**, which were isolated after N_2O_4 oxidation as the quinones, **13–16**. Data which are consistent with the above mechanism follow. (1) Reaction of 3-bromo-2,5-di-*tert*-butyl-1,4-benzoquinone (**8**) with anhydrous HBr in glacial acetic acid in the presence of excess cyclohexene gave 1,2-dibromocyclohexane (92%) and 3-bromo-2,5-di-*tert*-butyl-1,4-benzoquinol (**24**) (90%). This is in good accord with the first step of the proposed mechanism in which bromine is a product. This oxidation–reduction reaction is of course very dependent upon a balance of redox potentials. This is illustrated by the fact that 2,5-di-*tert*-butyl-1,4-benzoquinone (**4**) does not react with anhydrous HCl in glacial acetic acid. However, this quinone **4** does oxidize anhydrous HBr to bromine under



the same conditions. Substitution of a halogen on the quinone **4** to give **7** or **8** apparently increases their oxidation potential to the point where both hydrohalic acids are oxidized.

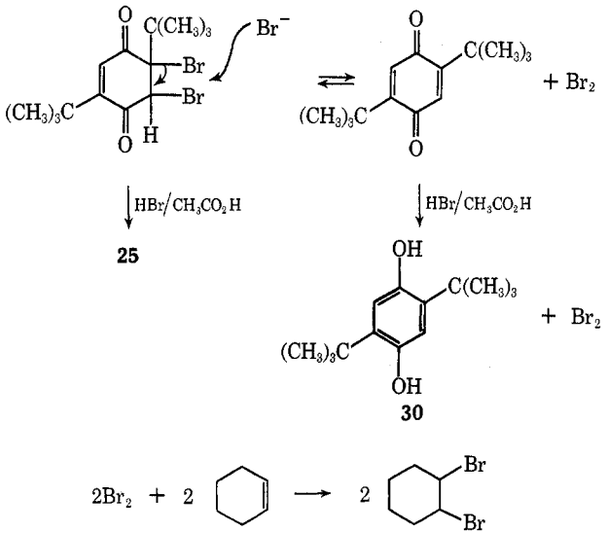
Quinonedibenzenesulfonimides appear to be better oxidizing agents than the corresponding quinones.[7] As a result, one might expect 2,5-di-*tert*-butyl-1,4-benzoquinonedibenzenesulfonimide (**26**)[8] to undergo de-*tert*-butylation upon reaction with HCl in glacial acetic acid. Indeed, such a transformation is readily accomplished. Compound **26** is converted to 5-chloro-2-*tert*-butyl-1,4-benzoquinonedibenzenesulfonamide (**27**) (75%). In addition, when **26** is treated with anhydrous HBr in glacial acetic acid in the presence of excess cyclohexene the reduced diamide **28** and dibromocyclohexane are formed in nearly quantitative yields.



The above transformation of **6** → **12** is not so straightforward as indicated in the preceding reaction scheme. For example, when **6** is treated with anhydrous HBr in glacial acetic acid in the presence of excess cyclohexene, 1,2-dibromocyclohexane (170%, based upon **6** as the

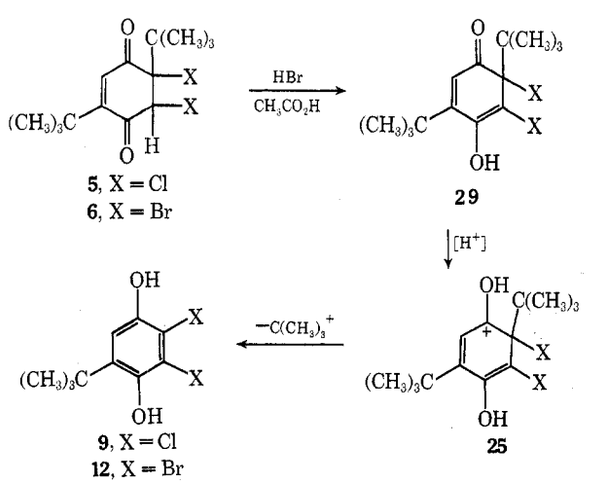
(7) R. Adams and W. Reifschneider, *Bull. Soc. Chim. Fr.*, 23 (1958).
(8) I. Baxter and I. A. Mensah, *J. Chem. Soc. C*, 2604 (1970).

limiting reagent) and 2,5-di-*tert*-butyl-1,4-benzoquinol (**30**) (86%) was formed. Such a transformation can be envisaged as depicted below.

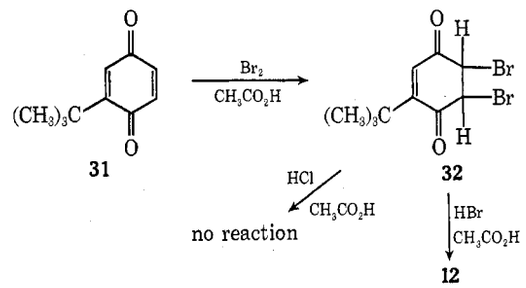


It is, of course, possible that **12** is formed from **6** *via* bromination of the hydroquinone **30**. However, such a reaction sequence is very unlikely for the conversion of the dichlorocyclohexenedione **5** to 2,3-dichloro-5-*tert*-butyl-1,4-benzoquinol (**9**) by the action of anhydrous HBr. For such a reaction sequence to be tenable, at best, a mixture of 2,3-dichloro-, 2,3-dibromo-, 2-bromo-3-chloro-, and 3-bromo-2-chloro-5-*tert*-butyl-1,4-benzoquinol would be anticipated. However, an 80% yield of **9** was obtained. As a result, for the dichloro derivative **5** the σ complex **25** may be generated directly.

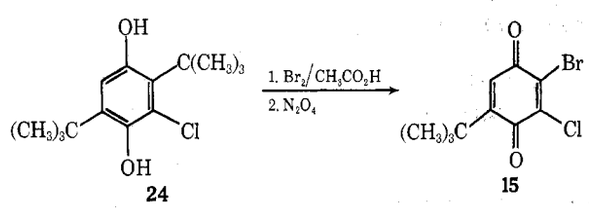
(2) Reaction of the dihalocyclohexenediones **5** and **6** with anhydrous HBr in glacial acetic acid gave, respectively, 2,3-dichloro-5-*tert*-butyl- (**9**) and 2,3-dibromo-5-*tert*-butyl-1,4-benzoquinol (**12**). These transformations presumably arise *via* the σ complex **25**. An acid-catalyzed tautomerism of **5** or **6** would give the dieneone **29**, which upon further protonation would yield the σ complex **25**. Interestingly, these transformations do not take place when **5** or **6** are subjected to the same reaction conditions employing anhydrous HCl as the acid. The fact that HCl is a weaker acid than HBr in acetic acid may account for this observation.



tert-Butyl-1,4-benzoquinone (**31**) reacts with molecular bromine in acetic acid to give the dibromo adduct **32**. This compound is analogous to compound **6** regarding its reactions with HCl and HBr in glacial acetic acid; *i.e.*, it is converted to **12** in the presence of anhydrous HBr but fails to react with anhydrous HCl.



(3) Reaction of 3-chloro-2,5-di-*tert*-butyl-1,4-benzoquinol (**24**) with excess bromine in acetic acid followed by nitrogen oxide gave 2-bromo-3-chloro-5-*tert*-butyl-1,4-benzoquinone (**15**) in excellent yield, thus establishing an analogy for step 2 in the general mechanism presented above.



Experimental Section

2,5-Di-*tert*-butyl-5,6-dichloro-1,4-cyclohexenedione (**5**).—A 100-g (0.45 mol) portion of 2,5-di-*tert*-butyl-1,4-benzoquinone (**4**) was suspended in 800 ml of glacial acetic acid. Chlorine gas was passed through this vigorously stirred mixture for 50 min. The reaction solution was then allowed to stand at ambient temperature for 4 hr. During this time a white, crystalline precipitate formed and was collected. The mother liquor was poured into water and the resulting white precipitate was collected and combined with the above. The product was dried *in vacuo* to give 127 g (98% yield) of 2,5-di-*tert*-butyl-5,6-dichloro-1,4-cyclohexenedione (**5**), mp 127–128°. The product was readily recrystallized from ether; however, this is not necesssry for the subsequent reactions reported here. It is necessary to avoid hydroxylic solvents and high temperatures (>50°) in the recrystallization; otherwise some dechlorination will result.

Anal. Calcd for $C_{14}H_{20}Cl_2O_2$: C, 57.73; H, 6.92; Cl, 24.35. Found: C, 57.78; H, 6.95; Cl, 24.45.

2,6-Di-*tert*-butyl-5,6-dichloro-1,4-cyclohexenedione (**18**).—A solution of 20 g (0.091 mol) of 2,6-di-*tert*-butyl-1,4-benzoquinone (**17**) in 150 ml of glacial acetic acid was treated with excess chlorine gas for 30 min. The reaction solution was then allowed to stand at ambient temperature for an additional 3 hr and then poured into water. The resulting white, crystalline solid was collected and recrystallized from ice-cold diethyl ether to give 26 g (98%) of **18**, mp 118–118.6°.

Anal. Calcd for $C_{14}H_{20}Cl_2O_2$: C, 57.73; H, 6.92; Cl, 24.35. Found: C, 57.86; H, 6.80; Cl, 24.55.

2,5-Di-*tert*-butyl-5,6-dibromo-1,4-cyclohexenedione (**6**).—A 10-g (0.045 mol) portion of 2,5-di-*tert*-butyl-1,4-benzoquinone (**4**) was dissolved in 50 ml of glacial acetic acid. A 7-g (0.046 mol) portion of bromine was added and the resulting solution was stirred at room temperature for 12 hr. The resulting light yellow solution was poured into water and the crystalline product was collected. Recrystallization from diethyl ether gave 17 g (97%) of the pale yellow product **6**, mp 112–113°.

Anal. Calcd for $C_{14}H_{20}Br_2O_2$: C, 44.23; H, 5.30; Br, 42.05. Found: C, 44.40; H, 5.34; Br, 41.84.

3-Chloro-2,5-di-*tert*-butyl-1,4-benzoquinone (**7**).—A solution of 118 g (0.41 mol) of 2,5-di-*tert*-butyl-5,6-dichloro-1,4-cyclo-

hexenedione (**5**) in 1200 ml of anhydrous diethyl ether was cooled to 12°. The solution was vigorously stirred while 30 g (0.41 mol) of diethylamine was slowly added over a period of 10 min. Addition of the base immediately resulted in the precipitation of diethylamine hydrochloride and the formation of a lemon-yellow reaction solution. The reaction mixture was extracted four times with water and dried over sodium sulfate, and the ether was removed *in vacuo* giving 103 g (99%) of **7** as a yellow oil. Vacuum distillation of a small sample gave the analytical sample.

Anal. Calcd for $C_{14}H_{19}ClO_2$: C, 66.00; H, 7.52; Cl, 13.92. Found: C, 66.12; H, 7.47; Cl, 13.88.

3-Chloro-2,6-di-*tert*-butyl-1,4-benzoquinone (**19**).—A solution of 23 g (0.08 mol) of 2,6-di-*tert*-butyl-5,6-dichloro-1,4-cyclohexenedione (**18**) in 100 ml of diethyl ether was cooled to 0° and 5.9 g (0.08 mol) of diethylamine was slowly added. Diethylamine hydrochloride immediately formed and the solution became yellow. After 10 min the reaction solution was extracted several times with water. The organic layer was then dried over sodium sulfate and the solvent was removed *in vacuo*, leaving 20.8 g of the orange oily quinone **19**. Vacuum distillation of this oil gave 10.6 g (51%) of the analytically pure quinone **19** as a yellow oil.

Anal. Calcd for $C_{14}H_{19}ClO_2$: C, 66.00; H, 7.52; Cl, 13.92. Found: C, 65.83; H, 7.45; Cl, 13.95.

3-Bromo-2,5-di-*tert*-butyl-1,4-benzoquinone (**8**).—A solution of 48 g (0.126 mol) of 2,5-di-*tert*-butyl-5,6-dibromo-1,4-cyclohexenedione (**6**) in 150 ml of diethyl ether was cooled to 10°. To this vigorously stirred solution was slowly added 9.2 g (0.126 mol) of diethylamine. The reaction mixture was washed four times with water and dried over sodium sulfate, and the solvent was removed *in vacuo*, giving 34 g (96%) of the quinone **8** as a yellow oil. Vacuum distillation of a small sample gave the analytical sample.

Anal. Calcd for $C_{14}H_{19}BrO_2$: C, 56.20; H, 6.40; Br, 26.71. Found: C, 56.41; H, 6.60; Br, 26.59.

2,3-Dichloro-5-*tert*-butyl-1,4-benzoquinone (**13**). **Method A.**—Anhydrous HCl was bubbled through a solution of 3 g (0.012 mol) of 3-chloro-2,5-di-*tert*-butyl-1,4-benzoquinone in 50 ml of glacial acetic acid for 30 min. The solution was allowed to stand at ambient temperature for 3 hr and then poured into water. The light yellow oily hydroquinone **9** was extracted into ether. This solution was dried and the solvent was removed *in vacuo*. Glc analysis of this oil showed it to be 86% of the hydroquinone **9**. This oily product was then dissolved in 25 ml of cold chloroform and approximately 3 ml of N_2O_4 was slowly added. The oxidation was complete after 10 min and the excess nitrogen oxides were removed by passing a stream of nitrogen through the reaction mixture for 15 min. The chloroform was dried and removed *in vacuo*, yielding a dark red solid. Recrystallization of this product from 95% ethanol produced 1.8 g (65%) of the quinone **13**, mp 89–89.5°.

Anal. Calcd for $C_{10}H_{10}Cl_2O_2$: C, 51.53; H, 4.32; Cl, 30.42. Found: C, 51.68; H, 4.32; Cl, 30.23.

Method B.—Anhydrous HBr was bubbled through a solution of 10.2 g (0.035 mol) of 2,5-di-*tert*-butyl-5,6-dichloro-1,4-cyclohexenedione (**5**) in 125 ml of glacial acetic acid for 30 min. The reaction solution was allowed to stand at ambient temperatures for an additional 12 hr and then poured into water, giving 10.2 g of the pale yellow hydroquinone **9**. This hydroquinone was oxidized with N_2O_4 as described above to give 7.25 g (80%) of 2,3-dichloro-5-*tert*-butyl-1,4-benzoquinone (**13**) after recrystallization. This compound was identical in all respects with that produced by method A.

Method C.—A 3-g (0.012 mol) portion of 3-chloro-2,6-di-*tert*-butyl-1,4-benzoquinone (**19**) was dissolved in 50 ml of glacial acetic acid. The solution was vigorously stirred while anhydrous HCl was passed through the solution for 45 min. The reaction solution was allowed to stand at room temperature for an additional 3 hr, and then poured into water. The resulting oily hydroquinone **9** was oxidized with N_2O_4 as described above. The resulting quinone **13** was recrystallized from ethanol to give 1.71 g (62%).

2-Chloro-3-bromo-5-*tert*-butyl-1,4-benzoquinone (**14**).—Anhydrous HCl was rapidly bubbled through a solution of 23 g (0.078 mol) of 3-bromo-2,5-di-*tert*-butyl-1,4-benzoquinone (**8**) in 200 ml of glacial acetic acid for 1 hr. The reaction solution was then poured into water and extracted four times with $CHCl_3$. The combined organic extracts were washed three times with water. The chloroform solution was then dried over anhydrous sodium sulfate and oxidized as described previously with N_2O_4. The chloroform was then removed *in vacuo* to give 18.1 g (85.7%) of the yellow, crystalline quinone **14**, mp 79–83°. This quinone was recrystallized from 95% ethanol to give 16 g (75%) of the pure quinone **14**, mp 81–83°.

Anal. Calcd for $C_{10}H_{10}BrClO_2$: C, 43.27; H, 3.63; Br, 28.81; Cl, 12.77. Found: C, 43.29; H, 3.72; Br, 28.91; Cl, 12.65.

2-Bromo-3-chloro-5-*tert*-butyl-1,4-benzoquinone (**15**).—Anhydrous HBr was bubbled through a solution of 5.4 g (0.012 mol) of 3-chloro-2,5-di-*tert*-butyl-1,4-benzoquinone (**7**) in 150 ml of glacial acetic acid for 30 min. The reaction solution was allowed to stand at room temperature for an additional 4 hr and then poured into water. The resulting pale yellow oily hydroquinone **11** was dissolved in 25 ml of chloroform and cooled to 0°. An excess, 8 ml, of N_2O_4 was slowly added and the solution was allowed to stand at ambient temperature for an additional 10 min. Nitrogen was vigorously bubbled through the reaction solution for 15 min to remove any excess N_2O_4 and the solvent was then removed *in vacuo*. The resulting red solid was recrystallized from 95% ethanol to give 3.7 g (64%) of the yellow crystalline quinone **15**, mp 77–78°.

Anal. Calcd for $C_{10}H_{10}BrClO_2$: C, 43.27; H, 3.63; Br, 28.81; Cl, 12.77. Found: C, 43.22; H, 3.60; Br, 28.81; Cl, 12.63.

2,3-Dibromo-5-*tert*-butyl-1,4-benzoquinone (**16**). **Method A.**—Anhydrous HBr was bubbled through a solution of 3.4 g (0.011 mol) of 3-bromo-2,5-di-*tert*-butyl-1,4-benzoquinone (**8**) in 50 ml of glacial acetic acid for 30 min. The reaction solution was allowed to stand at room temperature for an additional 3 hr and then poured into water. The resulting oily hydroquinone **12** was dissolved in 25 ml of chloroform and cooled to 0°. N_2O_4 (4 ml) was added slowly, resulting in a vigorous reaction which subsided after approximately 10 min. The excess N_2O_4 was then removed by passing a stream of nitrogen through the reaction solution for 15 min. The chloroform was removed *in vacuo* and the resulting red solid was recrystallized from 95% ethanol to give 2 g (55%) of the yellow quinone **16**, mp 90–91°.

Anal. Calcd for $C_{10}H_{10}Br_2O_2$: C, 37.30; H, 3.11; Br, 49.62. Found: C, 37.37; H, 3.07; Br, 49.53.

Method B.—Anhydrous HBr was passed through a solution of 2 g (0.005 mol) of 2,5-di-*tert*-butyl-5,6-dibromo-1,4-cyclohexenedione (**6**) in 50 ml of glacial acetic acid for 30 min. The reaction solution was allowed to stand at ambient temperature for an additional 1 hr and then poured into water. The oily hydroquinone **12** was then oxidized with N_2O_4 as described above to give 1 g (60%) of the purified quinone **16**.

Method C.—A solution of 9.0 g (0.027 mol) of 5,6-dibromo-2-*tert*-butyl-1,4-cyclohexenedione (**32**) in 100 ml of glacial acetic acid was treated with excess anhydrous HBr for 30 min. The reaction solution was then poured into water and the resulting oily hydroquinone **12** was extracted into chloroform. This product was then oxidized with excess N_2O_4 as described above to give 5.2 g (61%) of 2,3-dibromo-5-*tert*-butyl-1,4-benzoquinone (**16**) after recrystallization from 95% ethanol.

2,3-Diazido-5-*tert*-butyl-1,4-benzoquinone (**20**).—A solution of 4.2 g (15 mmol) of 2,3-dibromo-5-*tert*-butyl-1,4-benzoquinone (**16**) in 50 ml of acetone was treated with 2.0 g (30 mmol) of NaN_3 in 10 ml of water. The resulting deep red solution was stirred at ambient temperature for 20 min and then cooled to 0°, and 100 ml of 95% ethanol was added. The resulting fine red crystalline precipitate was collected, giving 2.85 g (77%) of **20**, mp 104–106°.

Anal. Calcd for $C_{10}H_{10}N_6O_2$: C, 48.78; H, 4.06; N, 34.14. Found: C, 48.92; H, 4.08; N, 33.77.

The same diazide **20** was prepared in a completely analogous manner starting with 2,3-dichloro- (**13**), 2-bromo-3-chloro- (**15**), or 3-bromo-2-chloro-5-*tert*-butyl-1,4-benzoquinone (**14**).

3-Azido-2-bromo-5-*tert*-butyl-1,4-benzoquinone (**21**).—A solution of 0.284 g (1 mmol) of 2-bromo-3-chloro-5-*tert*-butyl-1,4-benzoquinone in 10 ml of acetone was treated with 0.068 g (1.06 mmol) of NaN_3 in 5 ml of water. After 5 min the product precipitated as a red oil. The oil was dissolved in aqueous ethanol and then the solution was cooled to 0°. The resulting red precipitate was collected, giving 0.142 g (50%) of **21**, mp 71–74°.

Anal. Calcd for $C_{10}H_{10}BrN_3O_2$: C, 42.25; H, 3.52; N, 14.78. Found: C, 42.36; H, 3.55; N, 14.90.

The same azidoquinone **21** could be formed in 64% isolated yield starting with 2,3-dibromo-5-*tert*-butyl-1,4-benzoquinone (**16**).

2-Bromo-2-cyano-4-*tert*-butyl-1,3-cyclopentenedione (**22**).—A solution of 4.2 g (0.015 mol) of 3-azido-2-bromo-5-*tert*-butyl-1,4-benzoquinone (**21**) in anhydrous toluene was refluxed for 2 hr.

During this time nitrogen evolved and the color of the reaction solution changed from deep red to light orange. The solvent was then removed *in vacuo* and the resulting solid was recrystallized from cyclohexane and then sublimed to give 2.8 g (75%) of **22** as a light orange solid, mp 91–92°.

Anal. Calcd for $C_{10}H_{10}BrNO_2$: C, 46.87; H, 3.90; N, 5.46. Found: C, 46.78; H, 3.99; N, 5.48.

α-*tert*-Butyl-γ-cyanobromomethylene-$\Delta^{\alpha,\beta}$-butenolide (23).—3-Azido-2-bromo-5-*tert*-butyl-1,4-benzoquinone (**21**), 2 g (0.007 mol), was slowly (20 min) added to 40 ml of vigorously stirred cold (0–5°) concentrated sulfuric acid. The reaction solution became a deep blue upon addition of the azide and nitrogen slowly evolved. Upon disappearance of the color the solution was poured into ice water, causing the butenolide to precipitate, yield 1.55 g (86%), mp 102–104. Recrystallization from ether–petroleum ether (bp 30–60°) gave an analytical sample.

Anal. Calcd for $C_{10}H_{10}BrNO_2$: C, 46.87; H, 3.90; N, 5.46; Br, 31.24. Found: C, 46.78; H, 3.87; N, 5.56; Br, 31.13.

Reaction of 3-Bromo-2,5-di-*tert*-butyl-1,4-benzoquinone (8) with HBr in the Presence of Cyclohexene.—3-Bromo-2,5-di-*tert*-butyl-1,4-benzoquinone (**8**) was dissolved in 20 ml of glacial acetic acid and 5 ml of cyclohexene. This solution was vigorously stirred at ambient temperature and saturated with anhydrous HBr. The solution immediately lightened in color and after 2 min it was quenched with water and extracted with diethyl ether. The ether extract was backwashed twice with water and then dried over anhydrous sodium sulfate. The solvent was then removed *in vacuo*, giving a light yellow oil. This oil was analyzed by gas chromatography using known standards of 1,2-dibromocyclohexane and 3-bromo-2,5-di-*tert*-butyl-1,4-benzoquinol, showing 0.337 g (92.5%) of the former and 0.404 g (90.5%) of the latter.

2-Chloro-5-*tert*-butyl-1,4-benzoquinonedibenzenesulfonamide (27).—Anhydrous HCl was bubbled through a solution of 180 mg (0.36 mmol) of 2,5-di-*tert*-butyl-1,4-benzoquinonedibenzenesulfonimide in 10 ml of glacial acetic acid for 4 min and the mixture was then allowed to stand at room temperature for 21 hr. The reaction solution was then poured into ice–H_2O and the resulting white precipitate (130 mg, 75%) was collected and washed with acetic acid, mp 162–166°. Recrystallization from acetone–ether gave the analytical sample.

Anal. Calcd for $C_{22}H_{23}ClN_2S_2O_4$: C, 55.17; H, 4.80; N, 5.85. Found: C, 55.22; H, 4.83; N, 5.98.

Reaction of 2,5-Di-*tert*-butyl-1,4-benzoquinonedibenzenesulfonimide with Anhydrous HBr in the Presence of Cyclohexene.—A suspension of 249 mg (0.52 mmol) of 2,5-di-*tert*-butyl-1,4-benzoquinonedibenzenesulfonimide (**26**) in 7 ml of glacial acetic acid and 4 ml of cyclohexene was treated with anhydrous HBr for 3 min. The reaction solution was then allowed to stand at ambient temperature for 7 hr. During this time the original yellow color disappeared and a white solid precipitated. The reaction solution was poured into water and basified with 1% NaOH. An ether extract of this mixture was analyzed by vpc, which showed 1,2-dibromocyclohexane. The basic solution was acidified with dilute HCl. The white solid (230 mg, 92%), mp 261–264°, was collected and recrystallized from acetone, giving pure 2,5-di-*tert*-butyl-1,4-benzoquinonedibenzenesulfonamide, mp and mmp 265–266°.

2-*tert*-Butyl-5,6-dibromo-1,4-cyclohexenedione (32).—A solution of 10 g (0.061 mol) of 2-*tert*-butyl-1,4-benzoquinone (**31**) was dissolved in 100 ml of glacial acetic acid. This solution was then treated with 9.7 g (0.061 mol) of bromine. The halogen was added over a period of 2 min. The bromine immediately reacted with the quinone, as evidenced by the disappearance of the bromine color. The reaction solution was then poured into water and the resulting precipitate was filtered to give 18.9 g (91%) of the dibromo derivative **32**, mp 103–106°. Recrystallization from diethyl ether gave 12.8 (61%), mp 104–106°.

Anal. Calcd for $C_{10}H_{12}Br_2O_2$: C, 33.63; H, 3.36; Br, 49.38. Found: C, 33.58; H, 3.42; Br, 49.27.

Reaction of 2,3-Dibromo-2,5-di-*tert*-butyl-1,4-cyclohexenedione (6) with HBr/CH_3CO_2H in the Presence of Cyclohexene.—2,3-Dibromo-2,5-di-*tert*-butyl-1,4-cyclohexenedione (**6**) (4.0 g, 0.0105 mol) was dissolved in 75 ml of glacial acetic acid and 10 ml of cyclohexene. Anhydrous HBr was slowly passed through the vigorously stirred solution for 45 min. The reaction was then quenched with water and extracted twice with ether. The combined ether extracts were washed with water, dried over anhydrous magnesium sulfate, and concentrated by removal of the solvent *in vacuo* to give 2.0 g (86%) of 2,5-di-*tert*-butyl-1,4-benzoquinol (**30**). This hydroquinone **30** was identified by comparison of its ir spectrum with that of an authentic sample as well as by a mixture melting point. The mother liquor contained 4.3 g (170%) of 1,2-dibromocyclohexane as determined by glc analysis.

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The Ortho Alkylation of Anisole

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Aluminum chloride catalyzed alkylation of anisole with a series of olefins and with γ-valerolactone is demonstrated to result primarily in the formation of ortho-substituted products. The extent of ortho alkylation is shown to be a function of solvent and of basic functionality in the alkylating agent.

The aluminum chloride catalyzed alkylation of aromatic compounds with olefins[2] and γ-lactones[3] is a well-documented reaction. Application of this reaction to anisole has generally been reported to result in a mixture of ortho and para isomers, with the para isomer predominating.[2] An unusual exception exists in the literature, however. This consists of a report that reaction of anisole with ethyl allylmalonate in the presence of $AlCl_3$ affords a product consisting of approximately 90% of the ortho isomer.[4] In view of this, we have carefully examined the isomer distribution produced on $AlCl_3$-catalyzed alkylation of anisole with a series of olefins and with γ-valerolactone (**7**). The results (Table I) demonstrate that, with all those alkylating agents studied, the ortho isomer is either the principal or nearly by exclusive alkylation product.

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