# Nonoxidative Routes to Quinones[1,2]

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On heating 1,4-dimethallyloxy-2,3,5,6-tetramethylbenzene (1) to 200° duroquinone (2) and 5,6-dimethallyl-2,3,5,6-tetramethyl-2-cyclohexene-1,4-dione (3) were obtained in 21 and 42% yields, respectively. On heating 4-methallyloxy-2,3,5,6-tetramethylphenol (5) and 1-benzyloxy-4-methallyl-2,3,5,6-tetramethylbenzene (6) to 200° about 68 and 84% yields, respectively, of 2 were obtained in addition to isobutene and 2-methyl-4-phenyl-1-butene. Thus a new nonoxidative method of preparation of certain quinones is at hand. The last step in the proposed mechanism involves the formation of an intermediate which breaks down *via* a cyclic mechanism to give the second carbonyl group of the quinone and an unsaturated hydrocarbon. Similarly allyldimethylcarbinol and 1-allylcyclohexanol yield acetone and cyclohexanone, respectively (together with propene), on heating to 290°.

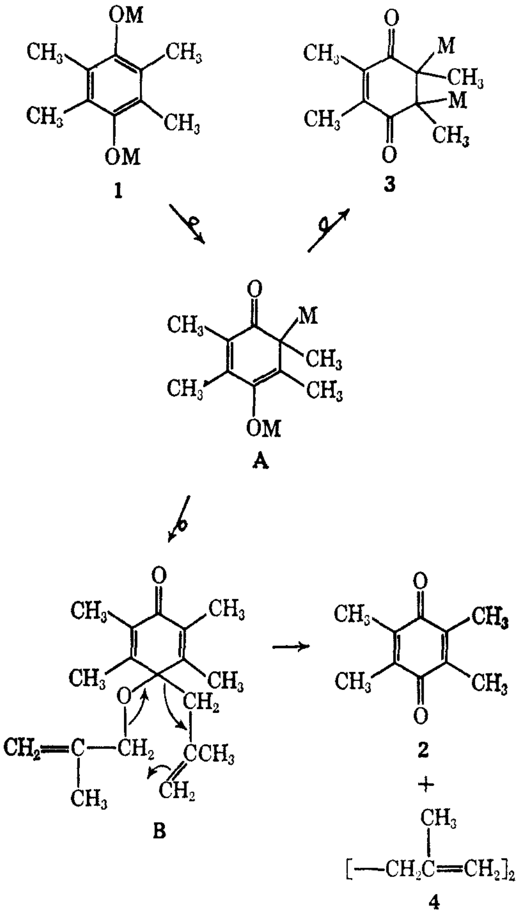
As pointed out previously[3] only four of the fifteen possible phenanthrenequinones are known. Also only three (the 1,2, 1,4, and 2,6 isomers) of the six possible naphthalenequinones are known. Since many hydroquinones corresponding to the unknown quinones are known, oxidative attempts to prepare the corresponding quinones have probably been made but not reported because of failure. Accordingly we initiated a program to develop what might be termed "nonoxidative" methods to prepare quinones. By nonoxidative methods we mean methods which do not require the use of conventional oxidants.

Our first successful result was obtained when 1,4-dimethallyloxy-2,3,5,6-tetramethylbenzene (1) yielded 21% duroquinone (2) on heating to 200°. In addition, a 42% yield of 5,6-dimethallyl-2,3,5,6-tetramethyl-2-cyclohexene-1,4-dione (3) was obtained. These results are explained as shown in Scheme I.[4]

The rearrangement of 1 to A represents the first step in a Claisen rearrangement.[5] Further shift of the methallyl group to the *para* position affords B which then undergoes pyrolysis into duroquinone (2) and dimethallyl (4). The last step represents another cyclic no-mechanism reaction and will be discussed further below. To show that the methallyl group can migrate to the *para* position in durene derivatives, 1-methallyloxy-2,3,5,6-tetramethylbenzene was shown to rearrange to 4-methallyl-2,3,5,6-tetramethylphenol in high yield on heating.

The poor yield of quinone 2 may be explained by assuming that the hypothetical intermediate A is readily converted irreversibly into 3. Pure 3 is recovered essentially unchanged when heated under similar conditions. This new nonoxidative route[6] to duroquinone suffers from the fact that methallylation of durohydroquinone affords the bismethallyl ether 1 in 39% yield at best as larger amounts (59%) of 3 are obtained (see Experimental Section).

SCHEME I



To see if higher yields of duroquinone (2) could be obtained by a variation of the above route, the monomethallyl ethers 5, 6, and 7 were prepared (see Experimental Section) and heated. High yields of 2 were obtained in the cases of 5 and 6 but only tars were obtained with 7 (Scheme II). The successful results are explained by a path similar to that shown above for pyrolysis of 1 with one main difference. Because there is only one methallyl group in 5 and 6, no compound such as 3 can be formed irreversibly.

The preparation of 5 by alkylation of durohydroquinone with methallyl chloride proved complicated. Only about 18% pure 5 could be obtained. In addi-

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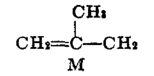
[1] This work was taken from the Ph.D. thesis presented by F. W. H., June 1968, to The Ohio State University.

[2] This work was supported by Grant 5552 from the National Science Foundation. A nonoxidative route means that no external oxidant is used and hence the quinone produced is not subject to further oxidation.

[3] M. S. Newman and R. L. Childers, *J. Org. Chem.*, **32**, 62 (1967)

[4] In all formulas M represents methallyl, while letters A, etc., represent nonisolated hypothetical intermediates.



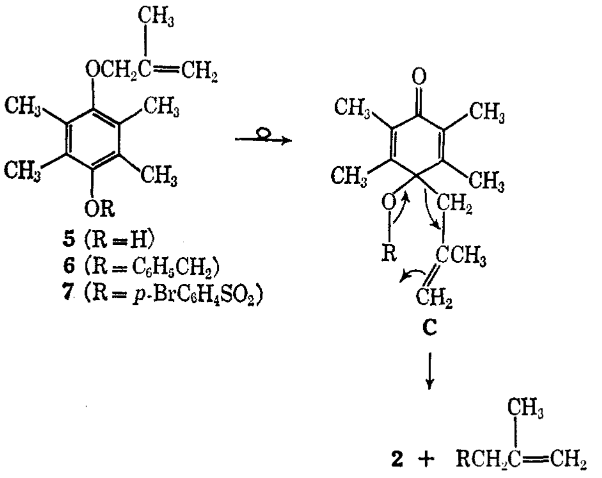
$$\begin{array}{c}\mathrm{CH_3}\\ |\\ \mathrm{CH_2{=}C{-}CH_2}\end{array}$$

M

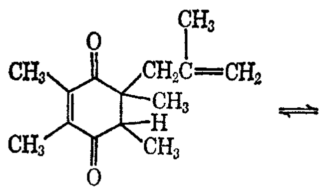
[5] For a recent review of the Claisen rearrangement, consult S. J. Rhoads in "Molecular Rearrangements," P. de Mayo, Ed., John Wiley & Sons, Inc., New York, N. Y., 1959, p 655.

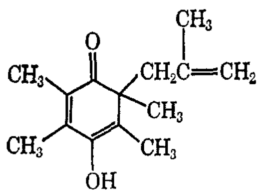
[6] This route is really an intramolecular oxidation–reduction process in which the quinone represents the oxidized product and the diolefin (4) the reduced product. It is called a nonoxidative route because no external oxidant is used and hence the quinone produced is not subject to further oxidation.

Scheme II



tion, about the same amount of **1** and larger amounts (*ca.* 45%) of a compound we believe to be 6-methallyl-2,3,5,6-tetramethyl-2-cyclohexene-1,4-dione (**8**) were obtained. The latter compound was isolated from the Claisen's alkali-insoluble fraction of the reaction products. The infrared (ir) spectrum of **8** (run neat between salt plates) showed a very weak OH band at about 3 $\mu$, but on heating the intensity of this band increases. We believe the OH band is due to the enolic modification, **8a**. The nmr spectrum in carbon tetrachloride shows one $CH_3$ group as a doublet [$\delta$ 1.08 ($J$ = 6 cps)] which fits structure **8**. On pyrolysis at 180°, **8** yielded duroquinone in high yield.


8


8a

When the R group in **5** and **6** was methyl or ethyl, no pyrolysis to **2** took place as the ethers were recovered unchanged. In the pyrolysis of **6** to **2** and 2-methyl-4-phenyl-1-butene, the last step (*e.g.*, C when R = benzyl) represents a new variant of the cyclic process described[7] in that a carbon–oxygen, rather than a hydrogen–oxygen, bond is broken and a carbon–carbon bond (rather than a carbon–hydrogen) bond is formed.

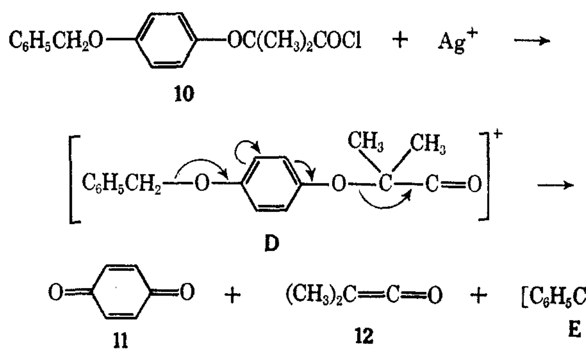
The last step in the pyrolysis of **5** to **2** and olefin is comparable with the formation of heptaldehyde and undecylenic acid by pyrolysis of ricinoleic acid.[8a] A complete discussion of this type of reaction (when R = H in C) and examples of its scope have been provided.[8a] The main difference is that in our work the intermediate C is hypothetical, whereas in the cases mentioned[7,8] definite compounds were used as starting materials. Two additional examples are provided herein by the pyrolysis of allyldimethylcarbinol and 1-allylcyclohexanol to acetone and cyclohexanone (plus propene).

In the pyrolysis of the monomethylallyl ether **5** a 27% yield of durohydroquinone (**9**) was obtained in addition to a 68% yield of quinone **2**. The formation of **9** may have been due to homolytic cleavage of the methallyl oxygen bond. Such fragmentations have been observed before in studies of the Claisen rearrangement.[9] However, the formation of quinone **2** from **1** was not affected by the presence of free-radical trapping agents, such as an aryl mercaptan, and hence the mechanism outlined for **1** seems likely to be correct.

Thus, one method for preparing quinones without the use of an external oxidant is at hand. However, this route is only applicable to molecules in which the Claisen rearrangement to allylphenol types is prohibited because of appropriate substitution.[5] Therefore, we have attempted to find another route which would be more generally useful. Although our efforts in this area are not complete, a preliminary report of such a route seems in order because of success, even though the yields were low.

On treatment of a solution of $\alpha$-*p*-benzyloxyphenoxyisobutyryl chloride (**10**) in acetronitrile with a solution of silver tetrafluoroborate in acetonitrile, a 10% yield of *p*-benzoquinone (**11**) was obtained. This result may be explained by postulating that silver ion first removes the chlorine by forming silver chloride and the oxocarbonium ion (D). The latter decomposes to yield a phenylcarbonium ion (E), dimethylketene (**12**), and **11** as shown in Scheme III.

Scheme III



The formation of **12** was confirmed by passing a stream of nitrogen through the reaction mixture into cooled methanol. A 60% yield of methyl isobutyrate was obtained. The fate of E is not known at present. Considerable amounts of tarry materials are formed and may possibly arise from reaction of E with **10**, **11**, and **12**. We hope to improve this nonoxidative route by structural modifications of **10** so that a carbonium ion more stable than E be produced. Alternately, the inclusion of a substance in the reaction medium which would react effectively with the carbonium ion formed (E or another ion) might allow greater yields of quinones to be obtained.

The preparation of **10** was accomplished by routine methods as described in the Experimental Section.

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(7) R. T. Arnold and G. Smolinsky, *J. Org. Chem.*, **25**, 129 (1960).

(8) (a) C. D. Hurd, "The Pyrolysis of Carbon Compounds," the Chemical Catalog Co., Inc., (Reinhold Publishing Corp.), New York, N. Y., 1929, p 164. (b) R. T. Arnold and G. Smolinsky, *J. Amer. Chem. Soc.*, **81**, 6443 (1959); **82**, 4918 (1960). (c) R. T. Arnold and G. Metzger, *J. Org. Chem.*, **26**, 5185 (1961).

(9) Pyrolysis of allyl-2,6-dimethyl-4-phenyl phenyl ether yielded 75% parent phenol instead of the expected out-of-the-ring Claisen product: A. Nickon and B. R. Aaronoff, *ibid.*, **29**, 3014 (1964).

## Experimental Section[10]

**1,4-Dimethallyloxy-2,3,5,6-tetramethylbenzene (1).**—To 400 ml of a stirred, cooled solution of 41 g of durohydroquinone (1,4-dihydroxy-2,3,5,6-tetramethylbenzene)[11] in dimethylformamide (DMF) under nitrogen was added 12 g of sodium hydride. After the deep red reaction mixture was stirred for 3 hr, 50 g of freshly distilled methallyl chloride was added and the mixture heated on a steam bath for 8 hr. The solution was poured into 2 l. of 10% HCl; the product was taken into $CHCl_3$ and worked up as usual. The crystalline residue was recrystallized from methanol to yield 27 g (39%) of **1**, mp 83–84°.

*Anal.* Calcd for $C_{18}H_{26}O_2$: C, 78.8; H, 9.5. Found: C, 78.9; H, 9.5.

Several attempts at methallylation in ethanol, benzene, and ethanol–DMF at temperatures ranging from 25° to reflux did not increase the yield of **1**.

**5,6-Dimethallyl-2,3,5,6-tetramethyl-2-cyclohexene-1,4-dione (3).**—The mother liquors from the above **1** were removed and the yellow residue was chromatographed over silica gel, using 9:1 hexane–benzene as eluent. Distillation of the main fraction yielded 40 g (59%) of **3** as a yellow oil, bp 108–110° (0.1 mm).

*Anal.* Calcd for $C_{18}H_{26}O_2$: C, 78.8; H, 9.5. Found: C, 78.9; H, 9.7.

Spectral data (ir and nmr) were consistent with **3** but do not distinguish between *meso* and racemic forms.

**4-Methallyloxy-2,3,5,6-tetramethylphenol (5).**—To a stirred cooled solution of 82 g of 1,4-dihydroxy-2,3,5,6-tetramethylbenzene in 400 ml of DMF was added 2.4 g of NaH under nitrogen. After stirring for 3 hr, 27 g of methallyl chloride was added in one portion. Stirring at reflux was continued for 8 hr. After pouring on 1 l. of 10% HCl, the product was extracted with benzene. The combined benzene extracts were washed with Claisen's alkali. The alkaline extract afforded 4.0 g (18% calculated on 0.1 mol as 100%) of **5**, mp 121–122° after recrystallization from Skellysolve C (petroleum ether, bp 90–97°). This product proved identical with the **5** prepared by the alternate route described below.

*Anal.* Calcd for $C_{14}H_{20}O_2$: C, 76.4; H, 9.1. Found: C, 76.1; H, 9.1.

**Durenequinone (2).**—This quinone, mp 109–110°, was prepared from durene[12] as described.[13] Reduction to durohydroquinone, mp 230–233°, was carried out quantitatively as described.[11]

**4-(Methallyloxy)-2,3,5,6-tetramethylphenol (5).**—As poor yields of **5** were obtained in attempts to monoalkylate durohydroquinone, a synthetic route from 2,2′,3,3′,5,5′,6,6′-octamethylbenzophenone was studied.

To a stirred suspension of 268 g of $AlCl_3$ in 1 l. of $CS_2$ was added a solution of 120 g of phosgene in 500 ml of cold $CS_2$ while the temperature was held at 0–10° (1 hr). After being stirred at 5° for 4 hr and at 25° for 14 hr the mixture was poured into 2 l. of 10% HCl. After a conventional work-up the neutral fraction was recrystallized three times from methanol to yield 83 g (35%) of octamethylbenzophenone,[14] mp 161.0–161.5°.

To a cooled solution prepared from 65 g of acetic anhydride, 30 g of concentrated $H_2SO_4$ and 25 g of 30% $H_2O_2$ was added 22.9 g of the above ketone. The mixture was held at 5° for 2 hr and then diluted with water. The crude solid ester thus obtained was heated at reflux for 8 hr with a solution of 10 g of KOH in 60 ml of alcohol and 15 ml of water. After acidification with HCl, the products were taken into ether–benzene. Extraction with 10% $NaHCO_3$ solution removed the carboxylic acid. After removal of solvent, 10.4 g (57% from ester) of durenol was obtained as a solid, mp 121–122°.[15,16] Durenol was converted into 4-aminodurenol, mp 176–178°, in 94% yield as described.[17]

To a rapidly stirred solution of 15.6 g of 4-aminodurenol in 100 ml of DMF at 5–10° under nitrogen was added 2.4 g of sodium hydride in portions during 15 min. After stirring at 20–25° for 30 min, 12 g of methallyl chloride was added. After 4 hr at reflux, the mixture was poured into 400 ml of 10% NaOH and the products were isolated in the usual way after extraction with $CHCl_3$. Chromatography over silica gel (benzene) provided 5.0 g (25%) of product least strongly absorbed (probably an N,O-dimethallylated product not further studied except to show that a secondary amino hydrogen was present) and 14.5 g (68%) of a primary amine. Since the latter was sensitive to air, an ethereal solution was treated with hydrogen chloride to yield colorless crystals, mp 222–223°, of the hydrochloride of 4-amino-1-methallyloxy-2,3,5,6-tetramethylbenzene.

*Anal.* Calcd for $C_{14}H_{22}ClNO$: C, 65.7; H, 8.5; N, 5.7. Found: C, 65.6; H, 8.6; N, 5.5.

A cold solution (*ca.* 5°) of 19 g of the above salt and 15 ml of isoamyl nitrite in 200 ml of 50% acetic acid was slowly added to a boiling solution of 50 g of $K_2SO_4$ and 25 g of $H_2SO_4$ in 200 ml of water in a flask equipped with a large-bore condenser as much gas was evolved. The cooled mixture was worked up as usual (benzene–ether) to yield 10.5 g (55%) of **5**, mp 116–118°.

*Anal.* Calcd for $C_{14}H_{20}O_2$: C, 76.4; H, 9.1. Found: C, 76.6; H, 9.1.

**4-Ethoxy-1-methallyloxy-2,3,5,6-tetramethylbenzene.**—Methallylation in DMF of 4.0 g of 4-ethoxy-2,3,5,6-tetramethylphenol[18] yielded 2.2 g (44%) of pure 4-ethoxy-1-methallyloxy-2,3,5,6-tetramethylbenzene, mp 53.5–55.0° (recrystallized from methanol).

*Anal.* Calcd for $C_{16}H_{24}O_2$: C, 77.4; H, 9.7. Found: C, 77.6; H, 9.7.

Essentially the same procedure[18] was used to prepare 4-methoxy-2,3,5,6-tetramethylphenol, mp 111–112°, in high yield from trimethyl phosphite and durenequinone.

*Anal.* Calcd for $C_{11}H_{16}O_2$: C, 73.4; H, 8.9. Found: C, 73.2; H, 8.8.

Methallylation of the methoxy compound afforded of pure 4-methoxy-1-methallyloxy-2,3,5,6-tetramethylbenzene, mp 40–41° after crystallization from methanol. The analytical sample was sublimed.

*Anal.* Calcd for $C_{15}H_{22}O_2$: C, 77.0; H, 9.4. Found: C, 77.2; H, 9.4.

**1-Benzyloxy-4-methallyloxy-2,3,5,6-tetramethylbenzene (6).**—A solution of 4.4 g of **5** in 50 ml of DMF was stirred with 0.5 g of sodium hydride for 4 hr after which 2.5 g of benzyl chloride was added. The mixture was kept at room temperature for 8 hr and then at 100° for 4 hr. After pouring into 250 ml of 10% KOH solution, the mixture was extracted with benzene. After the usual work-up, recrystallization of the residue from methanol afforded 5.1 g (82%) of **6**, mp 82–83° (analytical sample sublimed).

*Anal.* Calcd for $C_{21}H_{26}O_2$: C, 81.3; H, 8.3. Found: C, 81.3; H, 8.1.

**1-*p*-Bromophenylsulfonyloxy-4-methallyloxy-2,3,5,6-tetramethylbenzene (7).**—The preparation of **7** from **5** was effected essentially as described[19] in 95% yield to yield **7** as a colorless solid, mp 114–115° after crystallization from ethanol.

*Anal.* Calcd for $C_{20}H_{23}BrO_4S$: C, 54.8; H, 5.2; Br, 18.2. Found: C, 55.0; H, 5.3; Br, 17.9.

**Methallylation of Durenol.**—To a stirred refluxing suspension of 60 g of durenol and 28 g of KOH in 100 ml of benzene and 200 ml of ethanol was added 68 g of methallyl chloride. After the mixture was heated for 8 hr, 300 ml of Claisen's alkali was added and the mixture was cooled. The alkaline layer was separated from the benzene layer and twice extracted with 100-ml portions of benzene. After the usual work-up, distillation of the product in the benzene layer yielded 14.0 g (17.5%) of 1-methallyloxy-2,3,5,6-tetramethylbenzene, bp 92–94° (0.4 mm), and 27.1 g

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(10) All melting points were taken on a Fisher-Johns apparatus. Microanalyses were by the Galbraith Laboratories, Knoxville, Tenn. Nmr spectra for all new compounds were obtained on a Varian A-60 spectrometer and are reported in the thesis of F. W. H. The phrase "worked up in the usual way" means that an organic layer (usually ether–benzene) of the reaction products was washed with portions of Claisen's alkali and/or dilute hydrochloric acid, followed by saturated salt solution The organic layer was then filtered through a cone of anhydrous $MgSO_4$ and concentrated on a rotary evaporator. The Claisen's alkali was prepared by dissolving 35 g of KOH in 25 ml of water, cooling, and diluting with 100 ml of methanol.

(11) L. I. Smith and A. Dobrovolny, *J. Amer. Chem. Soc.*, **48**, 1420 (1926).

(12) We thank the Esso Research and Engineering Co., Baytown, Texas, for a generous gift of durene which was purified by recrystallization from ethanol.

(13) L. I. Smith in "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1943, p 254.

(14) H. Galenkamp and A. C. Faher, *Rec. Trav. Chim.*, **77**, 850 (1958). See also R. R. Rekker and W. T. Nauta, *ibid.*, **77**, 714 (1958).

(15) G. Lejeune, M. Sy, and A. Cheutin, *Bull. Soc. Chim. Fr.*, 1073 (1957), report mp 117–120°.

(16) A. Barnsworth, U. S. Patent 2,864,871 (1958).

(17) L. I. Smith and W. M. Schubert, *J. Amer. Chem. Soc.*, **70**, 2656 (1948).

(18) F. Ramirez, E. H. Cohen, and S. Dershowitz, *ibid.*, **81**, 4338 (1959).

(19) S. E. Hazlet, *ibid.*, **60**, 399 (1938).

(24%) of 4-methallyl-1-methallyloxy-2,3,5,6-tetramethylbenzene, bp 114–116° (0.4 mm).

*Anal.* Calcd for $C_{14}H_{20}O$: C, 82.3; H, 9.8. Found: C, 82.1; H, 10.0. Calcd for $C_{18}H_{26}O$: C, 83.7; H, 9.9. Found: C, 83.5; H, 10.0.

From the above alkaline extracts there was obtained by chromatography over silica gel (5% ethyl acetate in benzene elution) 5 g (12%) of durenol and 21 g (27%) of 4-methallyl-2,3,5,6-tetramethylphenol. The latter was identified by conversion into the brosylate and comparison with a known sample, mp 144.5–146.0°, since the phenol was low melting.

*Anal.* Calcd for $C_{20}H_{23}BrO_3S$: C, 56.8; H, 5.5. Found: C, 56.8; H, 5.5.

**Ethyl 2-(4-Benzyloxyphenoxy)-2-methylpropanoate.**—A stirred solution of 100 ml of ethanol, 10.0 g of 4-benzyloxyphenol,[20] 10.0 g of ethyl α-bromoisobutyrate, and 2.8 g of potassium hydroxide was heated at reflux for 36 hr. Distillation of the neutral fraction yielded 8.1 g (55%) of desired ester, bp 167–170° (0.3 mm).

*Anal.* Calcd for $C_{19}H_{22}O_4$: C, 72.6; H, 7.0. Found: C, 72.3, H, 7.0.

Alkaline hydrolysis and recrystallization of the acid from 3:1 Skellysolve C–ethanol afforded **2-(4-benzyloxyphenoxy)-2-methylpropanoic acid**, mp 130.5–131.5°, in high yield.

*Anal.* Calcd for $C_{17}H_{18}O_4$: C, 71.4; H, 6.3. Found: C, 71.4; H, 6.2.

**2-(4-Benzyloxyphenoxy-2-methylpropanoyl Chloride (10).**—A mixture of 2.9 g of the above acid and 2.20 g of $PCl_5$ was magnetically stirred under dry nitrogen. After 30 min, the mixture liquefied. After further stirring for 90 min, the mixture was warmed to 60° and held under vacuum until all $POCl_3$ had been removed (absence of band at 7.75 $\mu$). This material was used in the following experiment. The analytical sample was held under a vacuum of 0.2 mm for 24 hr and sealed under nitrogen.

*Anal.* Calcd for $C_{17}H_{17}ClO_3$: C, 67.0; H, 5.6; Cl, 11.7. Found: C, 67.1; H, 5.6; Cl, 11.4.

**Quinone 11 from 10.**—A solution of 6.1 g of **10** and 4.0 g of silver tetrafluoroborate in 100 ml of dry acetonitrile was stirred at room temperature for 8 hr during which time the solution ranged from colorless at the start through red to black. After heating to reflux for 2 hr, the solution was poured into 300 ml of 10% hydrochloric acid. A benzene extract of the products was treated as usual and concentrated to dryness. Vacuum sublimation yielded 0.22 g (10%) of 1,4-benzoquinone, mp and mmp 115–117° with authentic sample. Essentially the same result was obtained when the reaction was run in 2:1 dimethyl resorcinol–acetonitrile.

**Pyrolysis Experiments.**—All pyrolyses were carried out under nitrogen in clean flasks which had been steamed and dried.

**1,4-Dimethallyloxy-2,3,5,6-tetramethylbenzene (1).**—In a typical experiment 50.0 g of **1** was heated at 190–200° for 2 hr with a slow stream of nitrogen leading into a cooled solution of bromine in carbon tetrachloride. Purification of the reaction mixture by chromatography over silica gel using benzene–petroleum ether afforded 5.1 g (21%) of **2**, mp and mmp 110–111° with an authentic sample.[18] The second fraction was 20.4 g (42%) of **3**, identical in every respect with that prepared by methallylation of durohydroquinone. Only resinous material was obtained on further elution. Removal of solvent from the bromine–carbon tetrachloride trap yielded 15.0 g (19%) of colorless crystals, mp 95–98°. Recrystallization from methanol raised the melting point to 100.5–102.0° with little loss. This product proved essentially identical with a similar product prepared by addition of bromine to dimethallyl.[21]

*Anal.* Calcd for $C_8H_{14}Br_4$: C, 22.3; H, 3.3; Br, 74.4. Found: C, 22.3; H, 3.3; Br, 74.2.

When the above pyrolysis was carried out in the presence of equimolar 2-naphthalenethiol, a mixture was obtained from which a 25% yield of durohydroquinone, mp 231–233°, and a 45% yield of 2-naphthyl disulfide were isolated. When equal moles of **2** and 2-naphthalenethiol were heated at 200° for 2.5 hr, good yields (>50%) of durohydroquinone and 2-naphthyl disulfide,[22] mp 134–135°, were obtained.

**4-Methallyloxy-2,3,5,6-tetramethylphenol (5).**—Similarly, 22.0 g of **5** was heated at 200° for 20 min. A benzene solution of the products yielded 4.5 g (27%) of durohydroquinone, mp 231–233°. By sublimation of the remainder of the products was obtained 11.2 (68%) of **2**, mp 110–111°. From the carbon tetrachloride trap was isolated 7.5 g (35%) of 1,2-dibromo-2-methylpropane, bp 147–150°.

*Anal.* Calcd for $C_4H_8Br_2$: C, 22.2; H, 3.7; Br, 74.1. Found: C, 22.0; H, 3.7; Br, 74.0.

When the above pyrolysis was carried out for 20 min in the presence of 2-naphthalenethiol, essentially the same yields of products were obtained.

Pyrolysis of methyl and ethyl ethers of **5** resulted in recovery of the starting materials. Pyrolysis of the *p*-bromobenzenesulfonyl derivative of **5** yielded only tars.

**1-Methallyloxy-2,3,5,6-tetramethylbenzene.**—On heating 1-methallyloxy-2,3,5,6-tetramethylphenol at 200° for 2 hr there was isolated an 89% yield of the above 4-methallyl-2,3,5,6-tetramethylphenol, characterized[19] as the brosyl derivative by mp and mmp 144–146° and by ir and nmr spectra.

**Registry No.**—**1**, 19613-65-1; **3**, 19587-88-3; **5**, 19587-89-4; **6**, 19587-90-7; **7**, 19587-91-8; 4-ethoxy-1-methallyloxy-2,3,5,6-tetramethylbenzene, 19587-92-9; 4-methoxyl-2,3,5,6-tetramethylphenol, 19587-93-0; 4-methoxy-1-methallyloxy-2,3,5,6-tetramethylbenzene, 19587-94-1; 4-methallyl-1-methallyloxy-2,3,5,6-tetramethylbenzene, 19587-95-2; ethyl 2-(4-benzyloxyphenoxy)-2-methylpropanoate, 19587-96-3; 2-(4-benzyloxyphenoxy)-2-methylpropanoic acid, 17413-75-1; 1,2-dibromo-2-methylpropane, 594-34-3.

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[20] Crude 4-benzyloxyphenol (Aldrich Chemical Co.) was distilled [bp 155–159° (0.3 mm)] and the distillate was recrystallized from Skellysolve C to yield a solid, mp 123.0–124.5°.

[21] The authors thank Dr. K. Greenlee, Chemical Samples Co., Columbus, Ohio, for a generous gift of pure 2,5-dimethyl-1,5-hexadiene.

[22] H. R. Al-Kazimi, D. S. Tarbell, and D. Plant, *J. Amer. Chem. Soc.*, **77**, 2479 (1955).