(1) One category comprises the interaction between two π-bond systems as in butadiene or vinyl ketones. Here, the π-orbitals overlap the center C–C single bond and increase its charge density and bond strength. In consequence, both of the adjacent double bonds (or unsaturated groups) lose charge and the bond strengths (and basicities of carbonyl groups) decrease. For conjugated carbonyl compounds, as the polarizability of the adjacent group increases the π-orbital overlap increases and the oxygen basicity also increases due to a greater release of charge to the carbonyl group (or possibly less charge is withdrawn from the carbonyl group since even acetophenone and methyl vinyl ketone are less basic than acetone).

(2) Conjugation, as in amides where an electron-donating atom is attached to a π-electron system: If no unoccupied orbitals are energetically available on this atom, then the only type of π-orbital overlap which can occur is by the donation of the lone pair of electrons into a molecular orbital extending over the donating atom and the adjacent unsaturated group. The force constants of the N—C bond and the C=O bond increase as did the central C—C bond in conjugated ketones, but the carbonyl basicity increases.

(3) Conjugation, as in thiolesters, where an electron-receiving atom is attached to a π-electron system: In this case, the group molecular orbital is set up by a pπ–dπ-orbital overlap allowing a certain amount of electron drift from the carbonyl bond into the sulfur orbitals thus decreasing the force constant of C=O, but increasing that of C—S. This markedly lowers the carbonyl basicity but not as effectively as does a single halogen.

Acknowledgment.—We gratefully acknowledge the help of Gil Berezin in synthesizing some of the sulfur compounds and the help of Mrs. Ethel Rightmire in preparing the graph and in obtaining spectra.

PITTSBURG, CALIF.

[COMMUNICATION NO. 2044 FROM THE KODAK RESEARCH LABORATORIES]

The Introduction of *n*-Alkyl Groups into Phenols and Hydroquinones

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Acylation of *n*-alkylhydroquinones and *n*- and *sec*-alkylphenols proceeds in the presence of boron trifluoride without isomerization of the alkyl groups. Reduction of the carbonyl groups (or of their Grignard reaction products) furnishes di- and tri- *n*- (or *sec*-)alkyl products.

Dialkylphenols[1] and dialkylhydroquinones[2-4] with alkyl groups of 3 to 18 carbon atoms are used in color photography. Properties such as melting point, solubility, diffusivity and resistance to aerial oxidation of the side chains vary with the nature of the side chains, and *n*-alkyl derivatives could be expected to offer advantages.

While the number of known alkylphenols and alkylhydroquinones is considerable, few authentic derivatives with two (or more) *n*-alkyl groups have been prepared. Direct alkylation has resulted in mixtures of isomers which differ in the location of the aliphatic chain on the ring and in the structure of the chain itself.[5] Acylation in the presence of catalysts such as aluminum chloride[5,6] (Friedel–Crafts, Fries), followed by reduction of the ketones, yields mono-*n*-alkylphenols[7] and mono-*n*-alkylhydroquinone dialkyl ethers.[8-12] Cruickshank and Robinson[8] have prepared 2-*n*-amyl-5-*n*-octylhydroquinone by such reactions; the yield and difficulties in isolation and characterization of the product discouraged us from using a similar route for the preparation of larger amounts. Moreover, it was verified that acylation of 4-*n*-alkylphenols and of their ethers with aluminum chloride catalyst results in extensive isomerization of the *n*-alkyl groups. For example, 4-*t*-amylphenol was isolated from a reaction involving 4-*n*-amylphenol, and mass spectrographic examination revealed isomerization of the amyl group of 4-*n*-amylanisole during an acylation reaction with $AlCl_3$ at 0°.

The desired di-*n*-alkyl compounds become readily available when boron trifluoride is used as an acylation catalyst[13,14]; ring acylations by aliphatic acids proceed without isomerization of normal chains in the starting materials and reduction yields di-*n*-alkylphenols and hydroquinones, respectively. A variety of di- and tri-*n*-alkylphenols has been made with smooth reactions. The mildness of the catalyst has also permitted acylation of *sec*-alkylphenols, without isomerization.

The synthesis of hydroquinone derivatives was

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(1) J. R. Thirtle and A. Weissberger, U. S. Patent 2,835,579 (1958).

(2) P. W. Vittum and L. S. Wilder, *U. S.* Patent 2,360,290 (1944).

(3) A. Loria, J. R. Thirtle and A. Weissberger, U. S. Patent 2,728,659 (1955).

(4) J. R. Thirtle, P. W. Vittum and A. Weissberger, U. S. Patent 2,732,300 (1956).

(5) C. A. Thomas, "Aluminum Chloride in Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1941.

(6) A. H. Blatt, in Vol. I of Adams, "Organic Reactions," J. Wiley and Sons, Inc., New York, N. Y., 1942, pp. 342–369.

(7) W. J. Close, B. D. Tiffany and M. A. Spielman, THIS JOURNAL, **71**, 1265 (1949); G. Sandulesco and A. Girard, *Bull. soc. chim. France*, [4] **47**, 1300 (1930).

(8) J. H. Cruickshank and R. Robinson, *J. Chem. Soc.*, 2064 (1938).

(9) T. Kurado and M. Wada, *Sci. Papers Inst. Phys. Chem. Research* (*Tokyo*), **34**, 1740 (1938).

(10) M. Asano and Z. Hase, *J. Pharm. Soc. Japan*, **60**, 650 (1940).

(11) A. H. Cook, I. M. Heilbron and F. B. Lewis, *J. Chem. Soc.*, 659 (1942).

(12) D. Wasserman and C. R. Dawson, THIS JOURNAL, **72**, 4994 (1950).

(13) D. Kästner, "Newer Methods of Preparative Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1948, pp. 249–313.

(14) W. M. McLamore, THIS JOURNAL, **73**, 2221, 2225 (1951).

TABLE I

2-*n*-ACYLHYDROQUINONES

2-*n*-Acyl group	Yield, %	M.p., °C.	Recrystn. solvent	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
COC_2H_5	59	97–98[a]	Dil. EtOH then CH_3CCl_3	65.1	65.6	6.0	6.2
COC_7H_{15}[b]	69	84.5–86.0[c]	Dil. methanol	71.2	71.5	8.5	8.3
$COC_{15}H_{31}$	50	106–107[d]	EtOH then CCl_4	75.9	75.7	10.3	10.4
$COC_{17}H_{35}$[b]	85	108–110[e]	Acetic acid then EtOH	76.6	76.6	10.6	10.9

[a] Lit. 92°; A. Goldzweig and A. Kaiser, *J. prakt. Chem.*, [2] **43**, 86 (1891). [b] Preparation described in this paper. [c] Lit.[8] 86°. [d] Lit.[10] 103–104°. [e] Lit.[10] 106–108.5°.

TABLE II

2-*n*-ALKYLHYDROQUINONES

2-*n*-Alkyl group	Yield, %	M.p., °C.	Recrystn. solvent	Method	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
C_3H_7	39[a]	91.5–92.0[b]	Water	Pd–C	71.1	71.4	7.9	8.7
C_8H_{17}[c]	86	96.5–98.0	Dil. acetic acid then petr. ether	Pd–C	75.7	75.5	9.9	10.0
$C_{16}H_{33}$	58	112.5–113.5[d]	Ligroin–benzene	Pd–C	79.0	80.2	11.4	11.2

[a] Reduction of 2-allylhydroquinone using Raney nickel gave a 90% yield. [b] Lit. 86°; T. B. Johnson and W. W. Hodge, THIS JOURNAL, **35**, 1014 (1913). [c] Preparation described in this paper; see also refs. 3 and 21. [d] Lit.[10] 110–111°.

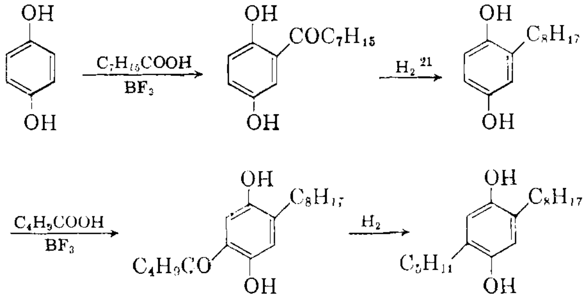
studied in greater detail than that of phenols and is therefore discussed first.

The isomeric status of the side chains in the phenols and the hydroquinones was established by the identity of products obtained by alternate routes (see Discussion) and by mass spectrometry.[15] The mass spectrometer was of the 60° sector type[16] equipped with a heated inlet system[17] which operated at 230°. This instrument successfully analyzed di- and trialkylphenols and dialkylhydroquinone ethers; the di-*n*-alkylhydroquinones were, however, insufficiently volatile.

The spectra contain peaks attributable to the parent compound and to the parent minus certain fragments split off in the ionization chamber. Fragmentation of alkylbenzenes is known to occur with greatest ease between the α- and β-carbon atoms of the alkyl chain,[18] so that a molecule containing a *n*-alkyl chain will reveal a major peak corresponding to loss in the chain of all except the α-CH_2. We have confirmed that this is also the pattern in alkylphenols, anisoles and hydroquinone ethers. A molecule containing a *sec*-alkyl chain, where R and CH_3 are attached to the α-carbon, will give a major peak corresponding to loss of the R group. The peak corresponding to loss of the α-methyl group is insignificant in size. Thus, 2,4-di-*n*-amylphenol gives peaks corresponding to mass 234 (the ionized molecule itself), mass 177 (loss of C_4H_9), mass 120 (loss of two C_4H_9 fragments) and mass 121 (loss of C_4H_9 and of C_4H_8, the latter through hydrogen rearrangement). The peak at mass 191, corresponding to a loss of C_3H_7, was only 1% in size, compared to the principal peak at mass 177.

4-*n*-Amyl-2-*sec*-amylphenol gives, among others, peaks corresponding to mass 234 (the ionized molecule), mass 191, the largest peak in the spectrum (loss of C_3H_7) and mass 177 (loss of C_4H_9 from the *n*-amyl chain).

Hydroquinones. 2,5-Di-*n*-alkylhydroquinones.—Cruickshank and Robinson's synthesis of 2-*n*-amyl-5-*n*-octylhydroquinone required eight steps, starting with hydroquinone dimethyl ether, valeryl chloride and aluminum chloride in carbon disulfide,[8] and was complicated by ether cleavages in each acylation step (see also refs.[9,10]), and by a tedious purification of the product. Cook, Heilbron and Lewis,[11] and Wasserman and Dawson,[12] preparing monoalkylhydroquinones, avoided ether cleavage by working at lower temperatures and with solvents such as tetrachloroethane. These modifications gave us a 24% yield of 2-*n*-amyl-5-*n*-octylhydroquinone in five steps as a waxy solid melting at 104–106° with some prior softening,[19] while acylation of hydroquinone with the corresponding acids in the presence of BF_3 yielded, in four steps, 32% of 2-*n*-amyl-5-*n*-octylhydroquinone melting at 106.5–107°. A no-solvent technique developed later in this program would probably increase the yield.[20]



Tables I–IV list the various hydroquinone derivatives prepared.[22]

Absence of isomerization in the final product was demonstrated by the fact that identical products

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(15) The authors are grateful to D. W. Stewart and G. P. Happ for this assistance.

(16) A. O. Nier, *Rev. Sci. Inst.*, **18**, 398 (1947); R. L. Graham, A. L. Harkness and H. G. Thode, *J. Sci. Instruments*, **24**, 119 (1947).

(17) V. J. Caldecourt, *Anal. Chem.*, **27**, 1670 (1955).

(18) F. H. Field and J. L. Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions," Academic Press, Inc., New York, N. Y., 1957, p. 175.

(19) We first assumed the product to be a mixture attributable to isomerization of the side chains by aluminum chloride. However, mass spectrometric examination of the intermediate, 2-amyl-5-octylhydroquinone dimethyl ether, refutes this assumption.

(20) See Experimental—Stearoylhydroquinone.

(21) Reductions were catalyzed by palladium-on-charcoal or by copper chromite. The authors thank J. L. R. Williams for suggesting the latter catalyst; see J. L. R. Williams, *J Org. Chem.*, **22**, 772 (1957).

(22) In many of the preparations, no attempt was made to work out maximum yields.

TABLE III

5-ACYL-2-*n*-ALKYLHYDROQUINONES

2-*n*-Alkyl	5-Acyl	Yield, %	Recrystn. solvent	M.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
C_8H_{17}	C_4H_9CO[a]	65	Petroleum ether	59–60	74.5	74.8	9.8	10.0
C_8H_{17}	$C_7H_{15}CO$[a]	70	Cyclohexane	82–83	75.9	76.2	10.3	10.6
CH_3	$C_{15}H_{31}CO$	69	Dil. ethanol	94–94.5	76.3	76.1	10.6	10.7
C_3H_7	$C_{15}H_{31}CO$	56	EtOH then ligroin	76.5–77.5	76.9	76.9	10.8	10.9
$C_{16}H_{33}$	C_2H_5CO	50	Ligroin then EtOH	93–94	76.9	76.9	10.8	10.6
$C_{12}H_{25}$	$C_{11}H_{23}CO$	37	Ligroin	88–90	78.2	77.9	11.4	11.3

[a] Preparation described in this paper; see also ref. 3.

TABLE IV

2,5-DI-*n*-ALKYLHYDROQUINONES

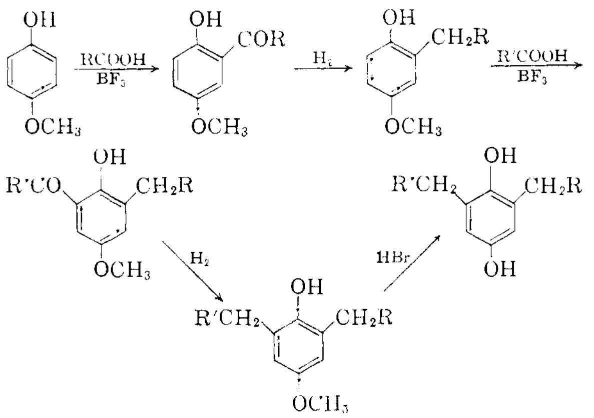
2-*n*-Alkyl	5-*n*-Alkyl	Yield, %	M.p., °C.	Recrystn. solvent	Method	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
C_8H_{17}	C_5H_{11}[a,b]	82	106.5–107	Ligroin	$CuCrO_2$	78.1	78.3	11.0	11.4
C_8H_{17}	C_8H_{17}[a]	90	109.5–110.5	Dil. HAc then cyclohexane	Pd–C	79.0	79.1	11.4	11.5
CH_3	$C_{16}H_{33}$	83	127–128	Acetic acid	Pd–C	79.3	79.1	11.6	11.4
C_3H_7	$C_{16}H_{33}$[c]	50	110–111	Benzene–heptane	Pd–C	79.8	80.1	11.7	11.5
C_3H_7	$C_{16}H_{33}$[d]	83	110–111	Benzene–cyclohexane	$CuCrO_2$	..	..	..	..
$C_{12}H_{25}$	$C_{12}H_{25}$	76	108–109.5	Acetic acid	Pd–C	80.7	80.3	12.2	11.8

[a] Preparation described in this paper; see also ref. 3. [b] Ref. 8 gave no data, but reported the quinone to melt at 65°; the quinone prepared from this material melts at 65°, also. [c] From 2-*n*-hexadecyl-5-propionylhydroquinone. [d] From 2-palmitoyl-5-*n*-propylhydroquinone.

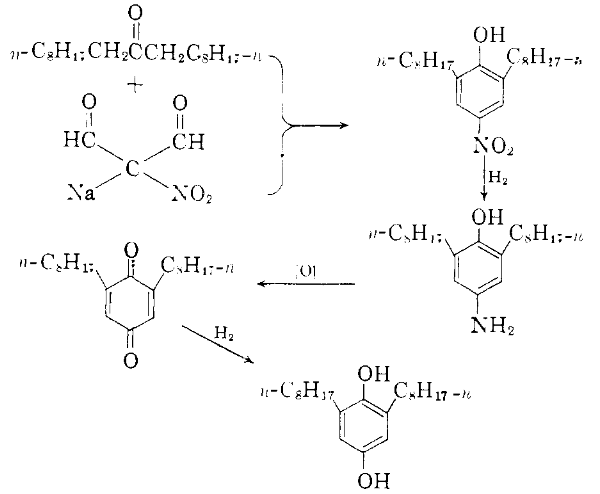
are obtained if the acyl groups are introduced in the reverse order. For example, 2-hexadecyl-5-propylhydroquinone prepared *via* 2-hexadecyl-5-propionylhydroquinone is identical with that prepared *via* 2-palmitoyl-5-propylhydroquinone.

A rigorous proof that 2-alkylhydroquinones or their ethers acylate in the 5-position has not been reported. It is given by the fact that the dialkylhydroquinones obtained ultimately, after acylation of monoalkylhydroquinones, differ (see Experimental) from the corresponding 2,6-dialkylhydroquinones and 2,3-dialkylhydroquinones prepared by unequivocal reactions.

2,6-Di-*n*-alkylhydroquinones.—A synthesis of 2,6-di-*n*-alkylhydroquinones is based on observation that acylation of phenol ethers in the *o*-position, with BF_3 as a catalyst, required forcing conditions,[13] while phenols are more readily acylated to products that include *o*-derivatives. It is therefore expected that 4-methoxyphenol would undergo acylation preferentially in the 2-position, and that 2-alkyl-4-methoxyphenol should be acylated in the 6-position.[23] This was confirmed by the identity of the di-*n*-octylhydroquinone prepared by this sequence



with the product of the sequence



This again demonstrates that, under the conditions described, little or no isomerization occurs in boron trifluoride-catalyzed acylations.

The substituted 4-methoxyphenols prepared are listed in Table V and 2,6-di-*n*-alkylhydroquinones in Table VI.

2,3-Di-*n*-alkylhydroquinones.—2,3-Dialkylhydroquinones, other than 2,3-dimethyl- and 2,3-diallylhydroquinone,[24] have not been reported in the literature. However, Baker and Lothian[25] prepared a potential intermediate, 2-acetyl-3-allylhydroquinone, the structure of which was proved by Cruickshank and Robinson.[8] We have made use of Baker and Lothian's method to prepare 2-*n*-hexadecyl-3-*n*-propylhydroquinone. The product differs from those obtained by procedures chosen to yield the corresponding 2,5- and 2,6-isomers.

Phenols.—2,4-Di-*n*-alkylphenols were prepared under conditions similar to those used in the alkyl-

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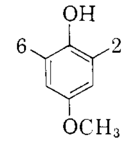
(23) Cruickshank and Robinson[8] prepared 6-octanoyl-2-amyl-4-methoxyphenol by an aluminum chloride-catalyzed acylation.

(24) L. F. Fieser, W. P. Campbell and E. M. Fry, THIS JOURNAL, 61, 2206 (1939).

(25) W. Baker and O. M. Lothian, *J. Chem. Soc.*, 274 (1936).

TABLE V

4-METHOXYPHENOLS



2-Position	6-Position	Yield, %	M.p., °C.	Recrystn. solvent	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
COC_7H_{15}	H[a,b]	55	42.5–44	Methanol	72.0	71.7	8.8	9.0
$COC_{16}H_{31}$	H	47	57.5–59	Ethanol	76.2	76.2	10.5	10.4
$COC_{17}H_{35}$	H	46	59.5–61.5[c]	Ethanol	76.9	76.9	10.8	11.0
C_8H_{17}	H[a]	88	43.5–5.5[d]	Methanol	76.3	75.7	10.2	10.0
$C_{16}H_{33}$	H	60	69.5–70.5	Acetic acid	79.3	79.6	11.5	11.4
$C_{18}H_{37}$	H	63	72–73.5[e]	Dil. HAc then ligroin	79.8	79.9	11.7	11.6
C_8H_{17}	$C_7H_{15}CO$[a,f]	43	31–32[g]	Ethanol	76.2	76.4	10.5	10.3
CH_3	$C_{16}H_{31}CO$[4]	37	66–67	Ethanol	76.6	77.0	10.9	10.9
$C_{16}H_{33}$	C_2H_5CO	54	65.4–66.5	Acetic acid	77.3	77.6	10.9	11.1
C_8H_{17}	C_8H_{17}[a]	89	39–41[h]	....	79.3	79.6	11.5	11.4
CH_3	$C_{16}H_{33}$[4]	76	70–71.5	Ethanol	79.5	79.1	11.6	11.2
$C_{16}H_{33}$	C_3H_7	59	61–62	Acetic acid	80.0	80.1	11.8	11.2

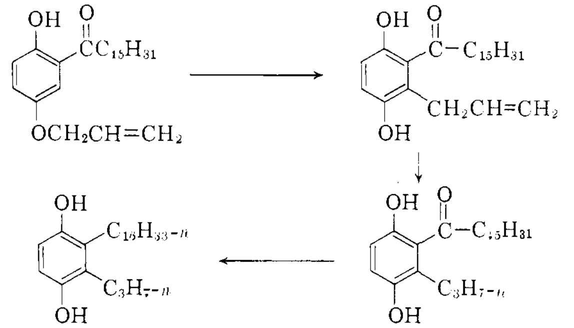
[a] Preparation described in this paper; see also ref. 3. [b] Also formed by action of diazomethane on 2-caprylylhydroquinone and by BF_3-catalyzed Fries rearrangement of *p*-methoxyphenyl caprylate (see Experimental). [c] Lit.[10] 63–64°. [d] B.p. 187–191° (10 mm.). [e] Lit. 73–75°. [f] Rearrangement of the caprylate of 4-methoxy-2-*n*-amylphenol using BF_3 as the catalyst, gave a 59% yield (see Experimental). [g] B.p. 195–205° (1 mm.). [h] B.p. 190–200° (1 mm.).

TABLE VI

26-DI-*n*-ALKYLHYDROQUINONES

2-Position	6-Position	Yield, %	M.p., °C.	Recrystn. solvent	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
C_8H_{17}	C_8H_{17}[a]	64	81.5–82.5	1:1 ligroin–petr. ether	79.0	79.1	11.4	11.3
CH_3	$C_{16}H_{33}$[4]	76	93.5–94.5	2:1 ligroin–petr. ether	79.3	79.6	11.5	11.2
$C_{16}H_{33}$	C_3H_7	44	74–75	Dil. MeOH	79.8	79.9	11.7	11.3

[a] Preparation described in this paper; see also ref. 3.

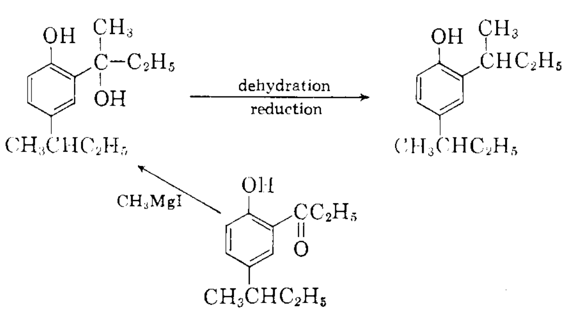


hydroquinone syntheses but at somewhat higher acylation temperatures to avoid contamination of the ketones by esters. In the case of 2,4-di-*n*-amylphenol, a repetition of the acylation and reduction yielded 2,4,6-tri-*n*-amylphenol.

The 4-*n*-alkylphenols used as starting materials were obtained by reduction of the corresponding ketones. The ketones were prepared by acylation of phenol in the presence of aluminum chloride in excess to avoid formation of the 2-isomer.[7] An excess of boron trifluoride cannot be maintained since only little more than the theoretical amount is absorbed by the reaction mixture[26] and, therefore, more or less of the *o*-derivatives result. However, 4-decanoylphenol was isolated in fairly good yield from a BF_3-catalyzed reaction which most likely also yielded some of the 2-isomer. As with the hydroquinones, the absence of isomerization by BF_3 was confirmed mass spectrometrically and by comparison of products; *e.g.*, 4-*n*-decyl-2-*n*-propylphenol, obtained from 4-*n*-decyl-2-propionylphenol, is identical with the material obtained from 4-*n*-decyl-2-allylphenol. Table VII lists *n*-alkylphenols and their intermediates.

The *n*-alkyl groups, as compared to the *t*-groups, can have a marked influence on tendency to crystallize and on melting points of derivatives. 2,4-Di-*n*-amylphenol does not freeze at −40°, while its *t*-isomer freezes at 25.8°. It gives an α-naphthylurethan melting at 104.5° and an aryloxyacetic acid melting at 65°, while the corresponding *t*-isomers melt at 133.5 and 126°, respectively.

The failure of boron trifluoride to isomerize *n*-alkyl chains also applies to *sec*-chains and has made possible the preparation of authentic *sec*-alkylphenols. Thus, *p*-*sec*-butylphenol has yielded 2,4-di-*sec*-butylphenol and 2,4,6-tri-*sec*-butylphenol, the mass spectra of which follow the pattern predicted for *sec*-alkyl derivatives and show no evidence



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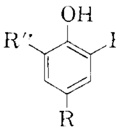
(26) Boron trifluoride etherate might aid in maintaining an excess of catalyst, but we did not examine this possibility.

TABLE VII

POLY-*n*-ALKYLPHENOLS AND INTERMEDIATES

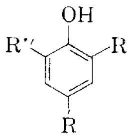


R	R'	R''	M.p. or b.p., °C. (mm.)	Yield, %	n^{25}D	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
CH_3	COC_9H_{19}	H	145 (1)	67	1.5110	77.9	78.3	9.9	9.9
C_5H_{11}	$COCH_3$	H	145–148 (7)	87	1.5249	75.7	75.8	8.8	8.9
C_5H_{11}	COC_3H_7	H	185–192 (16)	88	1.5180	76.9	76.5	9.4	9.6
C_5H_{11}	COC_4H_9[a]	H	122–127 (1)	77	1.5144	77.4	77.0	9.7	9.3
C_5H_{11}	COC_7H_{15}	H	172–175 (1.5)	66	1.5067	78.6	78.1	10.4	10.4
C_5H_{11}	COC_8H_{17}	H	143–145 (1)	73	1.5048	78.9	79.0	10.6	10.4
C_5H_{11}	$COC_{11}H_{23}$	H	189–194 (2)	66	1.5000	79.7	80.3	11.0	11.3
$C_{10}H_{21}$[b]	COC_2H_5	H	161–165 (1)	81	1.5072	78.6	78.6	10.4	10.8
COC_9H_{19}	CH_3	H	72.5–74[c]	73	....	77.8	77.7	10.0	10.0
$COC_{17}H_{35}$	CH_3	H	72–73[d]	86	....	80.2	80.6	11.3	11.2
CH_3	$C_{10}H_{21}$	H	125–128 (1)	82	1.4995	82.2	82.6	11.3	11.4
C_5H_{11}	C_5H_{11}[a,e]	H	110 (0.5)	82	1.5017	82.0	82.4	11.1	11.3
C_5H_{11}	C_8H_{17}	H	150–161 (0.06)	76	1.4981	82.6	82.4	11.6	12.0
C_5H_{11}	C_9H_{19}	H	149–151 (1)	86	1.4953	82.7	83.1	11.8	11.4
$C_{10}H_{21}$	CH_3	H	138–141 (1)	93	1.5008	82.2	82.1	11.3	11.2
$C_{10}H_{21}$	C_3H_7[f]	H	149–154 (1)	83[g]	1.4966	82.5	82.9	11.7	11.6
$C_{18}H_{37}$	CH_3	H	61–62[c]	88	....	83.3	83.3	12.3	12.2
C_5H_{11}	C_5H_{11}	COC_4H_9	140–145 (1)	91	1.5071	79.2	79.4	10.8	10.7
C_5H_{11}	C_5H_{11}	C_5H_{11}[h]	148–151 (1)	85	1.4945	82.8	82.4	11.9	11.9

[a] Preparation described in this paper. [b] 4-Decanoylphenol and 4-*n*-decylphenol are described in the Experimental. [c] From ligroin. [d] From *n*-heptane. [e] α-Naphthylurethan, m.p. 104–104.5° (see Experimental). [f] α-Naphthylurethan, m.p. 87–88°. [g] Hydrogenation of the corresponding allyl intermediate was effected in 81% yield (see Experimental). [h] α-Naphthylurethan, m.p. 76–79°.

TABLE VIII

BRANCHED-CHAIN ALKYLPHENOLS AND INTERMEDIATES



R	R'	R''	M.p. or b.p., °C. (mm.)	Yield, %[a]	n^{25}D	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
C_5H_{11}	$CH_3CHC_3H_7$[b,c]	H	157–159 (7)	91	1.5019	82.0	81.7	11.2	11.1
$CH_3CHC_2H_5$	COC_2H_5	H	134–137 (6)	71	1.5251	75.7	76.2	8.8	8.8
$CH_3CHC_2H_5$	$CH_3CHC_2H_5$[d]	H	86–89 (1)	84.5	1.5056	81.4	81.9	10.8	10.5
C_5H_{11}	$CH_3CHC_6H_{13}$[e]	H	123–128 (1)	60.5	1.4961	82.5	82.1	11.7	11.6
CH_3	$CH_3CHC_{10}H_{21}$[g]	H	140–141 (1)	35	1.4970	82.5	82.9	11.7	11.8
$CH_3CHC_2H_5$	$CH_3CHC_2H_5$	COC_2H_5	106–109 (1)	67	1.5153	77.8	78.1	10.0	10.1
$CH_3CHC_2H_5$	$CH_3CHC_2H_5$	$CH_3CHC_2H_5$	95–98 (1)	73	1.4964	82.4	82.9	11.5	11.5

[a] From the ketone, the intermediate *sec*-alcohols were dehydrated and the resulting alkene hydrogenated without characterization; see also ref. 22. [b] Preparation described in this paper. [c] α-Naphthylurethan, m.p. 83–84°. [d] α-Naphthylurethan, m.p. 87–88°. [e] α-Naphthylurethan, m.p. 70.5–72°. [f] Mechanical loss encountered. [g] α-Naphthylurethan, m.p. 81–83°.

for isomerization. The branched alkylphenols prepared are listed in Table VIII.

We have not succeeded in obtaining satisfactory products in BF_3-catalyzed acylations of *p*-*t*-alkylphenols; *p*-*t*-amylphenol generally yielded much low-boiling material. The excessive degradation of a *t*-alkyl group in the presence of aluminum chloride[27] has been reported, and such degradation seems to occur even in the presence of the milder BF_3.

Experimental

Typical preparations are described. Most of the others were effected in *sym*-tetrachloroethane or 1,2-dichloroethane under the time and temperature conditions described. Late in the program it was found that no solvent may be required if the reaction mixture forms a melt at a reasonable temperature. The preparation of 2-stearoylhydroquinone illustrates such a case.

Hydroquinones. 2-*n*-Stearoylhydroquinone.—A mixture of 11 g. (0.1 mole) of hydroquinone and 28.4 g. (0.1 mole) of stearic acid was stirred at 75–80° while boron trifluoride was passed in during 1.5 hr., a total of 11.7 g. (0.17 mole) being absorbed. The mixture was stirred for 0.5 hour on a steam-bath, then was heated to 140° during 45 min. and held at 140° for one hour. The mixture was cooled to 110° and poured with stirring into 300 ml. of 5% sodium carbonate. Stirring was continued while the mixture was heated to boiling, the gray solid softening and turning yellowish-green and resolidifying. The solid was collected and dried, giving 35.5 g. (94.5%), m.p. 103–108° (softens at 85°). Recrystallization from 350 ml. of 95% alcohol gave 32.0 g. (85%) of yellow-tan crystals, m.p. 108–110° (partly melts and resolidifies at 91°).

2-*n*-Caprylylhydroquinone.—A mixture of 220 g. (2 moles) of hydroquinone, 433 g. (3 moles) of *n*-caprylic acid

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[27] R. A. Smith, This Journal, **59**, 899 (1937); R. A. Smith and C. J. Rodden, *ibid.*, **59**, 2353 (1937).

and 500 ml. of 1,2-dichloroethane[28] was treated with gaseous boron trifluoride, the temperature being kept at 50–55° by adjusting the rate of flow. The addition was continued until 250 g. (3.7 moles) had been absorbed (3 hr.). The reaction mixture was allowed to stand overnight, then was heated for 5–6 hr. on a steam-bath. The mixture was poured into a solution of 615 g. (7.5 moles) of sodium acetate in 3100 ml. of water and stirred vigorously for 30 to 40 min. The organic layer was allowed to settle and the supernatant aqueous layer was removed as much as possible by suction. The 1,2-dichloroethane layer was washed twice with 2 to 3 liters of water, with stirring and decanting. Finally, the 1,2-dichloroethane and some of the excess caprylic acid was steam distilled. The residue, which crystallized on cooling, was collected on a funnel, sucked down and pressed fairly free of water and adhering oil. The remaining oil was washed away with portions of petroleum ether totaling 500 ml. The crude product, yellow crystals, weighed 361 g. (76.5%) and melted at 84–86°. Recrystallization from 1800 ml. of 80% methanol (Darco) gave 327 g. (69%) of bright-yellow crystals, m.p. 84.5–86°.

2-*n*-Octylhydroquinone.—To a slurry of 2 g. of 10% palladium-on-charcoal catalyst in 200 ml. of glacial acetic acid was added 23.6 g. (0.1 mole) of 2-*n*-caprylylhydroquinone. Hydrogen was admitted through a fritted glass tube, a slight pressure being maintained in the reaction flask. With vigorous stirring for about 20 hr. reduction was complete. The catalyst was filtered off and the pale yellow filtrate made colorless by treatment with small amounts of zinc dust (2–3 g.). The zinc dust was filtered off and the filtrate was diluted with 250 ml. of hot water and cooled to 0°. The white solid was collected, washed with water and dried. A residual oily material was washed off with petroleum ether, leaving 19 g. (86%) of slightly off-white product, m.p. 96.5–98°.

This reduction has been effected similarly in a Parr reduction apparatus or at higher temperatures and pressures with copper chromite as the catalyst.[21]

2-*n*-Caprylyl-5-*n*-octylhydroquinone.—A mixture of 111 g. (0.5 mole) of 2-*n*-octylhydroquinone, 108 g. (0.75 mole) of *n*-caprylic acid and 250 ml. of 1,2-dichloroethane was treated with boron trifluoride at such a rate that the temperature was maintained at 40–45°. When about 62 g. (0.9 mole) of boron trifluoride had been absorbed, which required about 1.25 hr., the addition was stopped and the reaction mixture was left at room temperature overnight (16–20 hr.).

The flask was then heated on the steam-bath for 6 hr., cooled to room temperature and poured, with stirring, into a solution of 140 g. (1.7 moles) of sodium acetate in 1260 ml. of water. The mixture was stirred at room temperature for about 30 min.

The organic layer was separated and the aqueous layer extracted with two 500-ml. portions of ether. The ether extracts and the dichloroethane solution were combined, washed once with 250 ml. of water and then with four 250-ml. portions of 5% sodium carbonate solution. The dark, yellow-brown solution became light-yellow on treatment with the carbonate. It was finally washed with 500 ml. of water and dried over magnesium sulfate.

The filtered solution was concentrated under reduced pressure to a volume of about 300 ml.; 600 ml. of petroleum ether was added and the mixture was cooled to 0°. The precipitate was filtered off, washed free of dark, oily material with petroleum ether, and dried in the air to give 115 g. of yellow crystals, m.p. 82–83°.

A second crop of 13 g. was obtained by concentrating the combined filtrate and washings to dryness and crystallizing the dark, oily residue from 300 ml. of petroleum ether.

The combined crops (128 g.) were recrystallized from 640 ml. of cyclohexane, and the filtered solution was cooled overnight at about 5°. The precipitate was filtered off, washed with a little cold cyclohexane and then with three 100-ml. portions of petroleum ether. After drying in the air, 122 g. (70%) was obtained as light-yellow crystals, m.p. 82–83°, with slight softening at 80°.

2,5-Di-*n*-octylhydroquinone.—2-*n*-Caprylyl-5-*n*-octylhydroquinone (69.6 g.) was reduced under the conditions just described for 2-*n*-octylhydroquinone. The crude product, m.p. 104–109°, was recrystallized from ten volumes of cyclohexane, giving 60 g. (90%) in the form of white plates melting at 109.5–110.5°.

2-*n*-Octyl-5-*n*-valerylhydroquinone.—A mixture of 22.2 g. (0.1 mole) of 2-*n*-octylhydroquinone, 15.3 g. (0.15 mole) of *n*-valeric acid and 50 ml. of *sym*-tetrachloroethane was treated with gaseous boron trifluoride, and the temperature was kept at 40–50° by adjusting the rate of flow. After 13 g. (0.19 mole) of boron trifluoride had been absorbed, the mixture was allowed to stand overnight, then was heated on a steam-bath for 6 hr. The mixture was poured into a solution of 30 g. of sodium acetate in 250 ml. of water, stirred for 0.5 hour and separated. The organic layer was diluted with 250 ml. of ether and extracted with four 50-ml. portions of 5% sodium carbonate, then washed with 50 ml. of water. The organic layer was dried over sodium sulfate and concentrated *in vacuo* to an oil which crystallized on dilution with 100 ml. of low-boiling petroleum ether, followed by chilling at 0° overnight. The crystals were collected and washed at 0° with petroleum ether, giving 19 g., m.p. 59–60°. Recrystallization from 11 volumes of petroleum ether and work-up of filtrates gave 19.8 g. (65%), m.p. 59.5–60°.

2-*n*-Amyl-5-*n*-octylhydroquinone.—A 325-ml. high-pressure bomb was charged with 15.3 g. (0.05 mole) of 2-*n*-octyl-5-*n*-valerylphenol, 50 ml. of methanol and 2 g. of copper chromite catalyst. Shaking under 102–136 atm. of hydrogen at 150–160° resulted in complete reduction within 0.5 hour. The catalyst was filtered off and washed with methanol and the filtrate was concentrated to dryness. After standing at 0° overnight, the residue was dissolved in 200 ml. of high-boiling ligroin, and gave 12.0 g. (82.3%) of fine colorless crystals, m.p. 106.5–107°.

2-*n*-Caprylyl-4-methoxyphenol. (A) By Direct Acylation.—Boron trifluoride was passed into a mixture of 124 g. (1.0 mole) of *p*-methoxyphenol, 216 g. (1.5 moles) of *n*-caprylic acid and 300 ml. of dry tetrachloroethane for a period of about 4 hr. The reaction mixture was allowed to stand overnight at room temperature and was then heated on a steam-bath for about 3 hr. When cool, the mixture was poured into 130 g. of sodium acetate in 2 liters of water, with stirring. The layers were separated and the water layer extracted with ether. The ether extract was combined with the tetrachloroethane, washed thoroughly with water and concentrated under reduced pressure. The product was collected at 195° (10 mm.) (yield 181.5 g.). Recrystallization from about 600 ml. of methanol gave 137 g. (55%), m.p. 42.5–44°.

(B) By the Fries Rearrangement.—4-Methoxyphenyl *n*-caprylate, b.p. 137–140° (1 mm.), was prepared in 85% yield by reaction of *p*-methoxyphenol and *n*-caprylyl chloride in ethyl ether containing pyridine. *Anal.* Calcd. for $C_{15}H_{22}O_3$: C, 72.0; H, 8.8. Found: C, 72.4; H, 8.9.

A solution of 83 g. (0.33 mole) of 4-methoxyphenyl *n*-caprylate in 200 ml. of *sym*-tetrachloroethane was saturated with boron trifluoride and allowed to stand for 6 hr. while additional boron trifluoride was permitted to escape at a slow rate. Following 5 hr. of heating on a steam-bath, the reaction mixture was poured into water and neutralization effected with potassium carbonate. The organic material was extracted into ethyl ether and the product isolated by concentration of the extract and vacuum distillation. The 65 g. of oil obtained at 180–185° (10 mm.) partly crystallized. The oily unreacted ester contaminant was removed by recrystallization from methanol which yielded 27 g. (32.6%) of 2-*n*-caprylyl-4-methoxyphenol, m.p. 44–46°.

4-Methoxy-2-*n*-octylphenol.—Three portions of 2-*n*-caprylyl-4-methoxyphenol, totaling 170 g., were hydrogenated. For each, approximately 170 ml. of glacial acetic acid, 10–12 g. of 10% palladium-on-charcoal and hydrogen at 2–2.7 atm. were used. The reduction was performed in a Parr hydrogenation apparatus at room temperature and was completed overnight. The catalyst was filtered off and the filtrate poured into a large volume of water. The organic material was extracted into ether, and the ether layer was neutralized with sodium bicarbonate, washed with water, dried over sodium sulfate and concentrated. The product, 141 g. (88%), was collected at 187–190° (10 mm.).

2-*n*-Caprylyl-4-methoxy-6-*n*-octylphenol. (A) By Direct Acylation.—Eighty grams (0.34 mole) of 4-methoxy-2-*n*-octylphenol was dissolved in 150 ml. of dry tetrachloroethane, 65 g. (0.45 mole) of *n*-caprylic acid was added, and boron trifluoride was passed in for about 6 hr. The mix-

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(28) Some of the procedures described here specify *sym*-tetrachloroethane. 1,2-Dichloroethane is equally effective as a solvent and is reputed to be less toxic.

ture was heated on a steam-bath for about 5 hr. and then, on cooling, was poured into a large quantity of water, treated with excess sodium carbonate, and washed thoroughly with water, ether being added as a diluent. The solution was concentrated and the forerun removed up to b.p. 240° (10 mm.). The product, 79 g. (64%), was collected at 195–205° (1 mm.). Crystallization from 95% alcohol gave 52.5 g. (42.5%), m.p. 30–31°.

(B) **By the Fries Rearrangement.**—4-Methoxy-2-*n*-octylphenyl *n*-caprylate, b.p. 170–180° (1 mm.), was prepared in 83% yield by reaction of 4-methoxy-2-*n*-octylphenol and *n*-caprylyl chloride in ethyl ether containing pyridine. *Anal.* Calcd. for $C_{23}H_{38}O_3$: C, 76.2; H, 10.5. Found: C, 76.4; H, 10.4. Rearrangement of 188 g. under the conditions described for 2-*n*-caprylyl-4-methoxyphenol gave 110 g. (59%), m.p. 31–32°.

2,6-Di-*n*-octyl-4-methoxyphenol.—Three portions totaling 167 g. (0.46 mole) of 2-*n*-caprylyl-4-methoxy-6-*n*-octylphenol were reduced catalytically in a Parr hydrogenation apparatus. Each portion was dissolved in about 250 ml. of glacial acetic acid and used approximately 15 g. of 10% palladium-on-charcoal with hydrogen at 30–40 p.s.i. Reduction occurred quite slowly (*ca.* 20 hr.) and slight warming was required. After the catalyst was filtered off, the filtrate was poured into a large quantity of water and extracted with ether. The ether extract was neutralized with sodium carbonate, washed with water, dried over sodium sulfate and concentrated. The product, 142 g. (88.5%), which was collected at 190–200° (1 mm.), melted at 39–41°.

2,6-Di-*n*-octylhydroquinone.—Twenty-five grams of 2,6-di-*n*-octyl-4-methoxyphenol was hydrolyzed by refluxing in a mixture of 400 ml. of glacial acetic acid and 80 ml. of hydrobromic acid (48%) for approximately 24 hr. When cool, the reaction mixture was poured into at least twice its volume of water and chilled under running water for a few hours. The solid was filtered off and the sticky material was slurried carefully in the funnel with ice-cold petroleum ether, most of the color and stickiness being removed by this procedure. The product was recrystallized from a mixture of approximately 215 ml. of ligroin (b.p. 90–120°) and 215 ml. of low-boiling petroleum ether, giving 15.5 g. (64%) melting at 81.5–82.5°.

2,6-Di-*n*-octylhydroquinone. Cyclization Procedure.—10-Nonadecanone was prepared as described by R. R. Briese and S. M. McElvain, THIS JOURNAL, **55**, 1697 (1933), and sodium nitromalonaldehyde by the method of H. B. Hill and J. Torrey, Jr., *Am. Chem. J.*, **22**, 89 (1899). The condensation of these reactants was effected as described by H. B. Hill, *ibid.*, **24**, 1 (1900), giving 2,6-di-*n*-octyl-4-nitrophenol, m.p. 75–76°. Reduction by hydrogen and Raney nickel gave 4-amino-2,6-di-*n*-octylphenol, which was not isolated but oxidized by lead tetraacetate, following the directions of E. C. S. Jones and J. Kenner, *J. Chem. Soc.*, 1842 (1931), giving 2,6-di-*n*-octylquinone, m.p. 57–60°. The latter was reduced by zinc and acetic acid to 2,6-di-*n*-octylhydroquinone, m.p. 82–83°.

2-*n*-Hexadecyl-3-*n*-propylhydroquinone.—A mixture of 87 g. (0.25 mole) of 2-palmitoylhydroquinone, 30.3 g. (0.25 mole) of allyl bromide, 50 g. of anhydrous potassium carbonate and one liter of acetone was refluxed for 8 hr. and left overnight at room temperature. The reaction mixture was poured into 2 liters of water. The light-tan precipitate, difficult to filter, was extracted into ethyl ether (three 500-ml. portions). The ether extract was filtered, washed with water and dried over magnesium sulfate. Concentration left a dark-yellow residue which crystallized on cooling. The crude product was dissolved in 2 liters of boiling methanol and filtered while hot. The filtrate was cooled to 0° and the precipitate was collected and washed with a little ice-cold methanol, giving 66.2 g. (68%) of light crystalline powder, m.p. 57–58°, after slight softening at 54°. Recrystallization from 2 liters of methanol yielded 60 g. (62%) of 4-allyloxy-2-palmitoylphenol, m.p. 58–59°. *Anal.* Calcd. for $C_{25}H_{40}O_3$: C, 77.3; H, 10.3. Found: C, 77.5; H, 10.4.

In a flask fitted with an air condenser, thermometer and inlet for nitrogen was placed 59.5 g. (0.15 mole) of 4-allyloxy-2-palmitoylphenol. The flask was placed in an oil-bath electrically heated to 170°. The bath temperature was raised gradually to 223° during 80 min., the melt temperature during this interval rising from 139 to 218°. The bath was removed and the solid which formed on cooling was slurried with 100 ml. of petroleum ether and washed with petroleum ether on a funnel, giving 48 g. (81%) of light-yellow powder melting at 74–78° (softens at 62°). Recrystallization from *n*-heptane (no improvement in melting point) was followed by recrystallization from 1,1,1-trichloroethane, giving 37.7 g. (63%) of 3-allyl-2-palmitoylhydroquinone as a light-ivory crystalline powder, m.p. 77.5–78.5° (slight softening at 74°). *Anal.* Calcd. for $C_{25}H_{40}O_3$: C, 77.3; H, 10.3. Found: C, 77.7; H, 10.7.

A solution of 27.8 g. (0.072 mole) of 3-allyl-2-palmitoylhydroquinone in 200 ml. of absolute ethanol was shaken with Raney nickel under 2.7 atm. of hydrogen. Reduction was complete in a few minutes at room temperature. The catalyst was filtered off and the filtrate and washings were concentrated to dryness under reduced pressure. The residue was warmed with 100 ml. of petroleum ether, stirred thoroughly, then chilled to 0°. The product was collected and washed with petroleum ether, giving 26.8 g. (95.5%) of cream-colored crystalline powder, m.p. 67–68.5° (softens at 63°). Recrystallization from 200 ml. of ligroin gave 26 g. of 2-palmitoyl-3-*n*-propylhydroquinone, m.p. 67–68°. *Anal.* Calcd. for $C_{25}H_{42}O_3$: C, 76.9; H, 10.8. Found: C, 77.1; H, 10.9.

A mixture of 7.8 g. (0.02 mole) of 2-palmitoyl-3-*n*-propylhydroquinone, 4 g. of copper chromite catalyst and 60 ml. of absolute alcohol was shaken in a 110-ml. bomb under 140 atm. starting pressure of hydrogen. Reduction was complete in a few minutes at 140° (170 atm.), although shaking and heating were continued at 150–157° for one hour longer. The catalyst was filtered off and washed thoroughly with acetone and the filtrate and washings were concentrated to dryness under reduced pressure. The brown residue, 7.5 g., was dissolved in 100 ml. of hot glacial acetic acid, treated with zinc dust until no further lightening of color was noted and the solution filtered. The filtrate was heated again to boiling and water was added to the turbidity point. The product, which separated on cooling, was washed thoroughly with water, sucked dry, then washed with petroleum ether on the funnel, giving 6.8 g. (90%) of 2-*n*-hexadecyl-3-*n*-propylhydroquinone, m.p. 111–112.5° (softens at 103°). With the object of reaching maximum purity, the product was treated twice in methanol with 0.1 *N* sulfuric acid and zinc granules until a colorless solution resulted. The product eventually obtained was a light-tan powder melting at 112.5–113.5°. *Anal.* Calcd. for $C_{25}H_{44}O_2$: C, 79.8; H, 11.7. Found: C, 79.8; H, 12.0.

A mixture with 2-*n*-hexadecyl-5-*n*-propylhydroquinone (m.p. 110–111°) melted at 102.5–106.5° (softened under 100°).

When an attempt was made to reduce the carbonyl group in acetic acid with palladium-on-charcoal catalyst, the only product isolated is believed to be 2-(α-hydroxyhexadecyl)-3-propylhydroquinone, m.p. 74.5–76°. *Anal.* Calcd. for $C_{25}H_{44}O_3$: C, 76.5; H, 11.2. Found: C, 76.5; H, 11.7.

Phenols. 4-*n*-Decanoylphenol.—A mixture of 71 g. (0.75 mole) of phenol and 86 g. (0.5 mole) of *n*-decanoic acid was saturated with boron trifluoride (67 g., *ca.* 1 mole) during 1.5 hr. and the temperature was held at 20–25° by cooling. After standing for 18 hr., the reaction mixture was poured into a solution of 200 g. of sodium acetate in 1 liter of water. The mixture was stirred on a steam-bath for 0.5 hour and the oily layer was extracted into ligroin. The extract was washed with three 250-ml. portions of 5% sodium bicarbonate (ether was used to break the emulsion) and steam distilled to remove unreacted phenol. The residue, which partly solidified, was extracted into benzene, washed with 5% bicarbonate solution, then with water and concentrated, giving 95 g. of a brownish crystalline solid, m.p. 55–61°. Two recrystallizations from ligroin (seven volumes) gave 74.5 g. (60%) of colorless crystals, m.p. 62.5–63.5°. *Anal.* Calcd. for $C_{16}H_{24}O_2$: C, 77.4; H, 9.7. Found: C, 77.5; H, 9.8.

4-*n*-Decylphenol.—A mixture of 49.6 g. (0.2 mole) of 4-*n*-decanoylphenol, 20 g. of copper chromite catalyst and 105 ml. of absolute ethanol was shaken under hydrogen. At 140° and 150 atm., reduction was complete in 0.5 hour. The catalyst was filtered off and washed with acetone. The filtrate was concentrated to dryness, giving 47 g. (100%) of a colorless oil which crystallized to a white solid, m.p. 54–56°. Recrystallization from ligroin gave white crystals, m.p. 55–56.5°, in 85.5% yield. *Anal.* Calcd. for $C_{16}H_{26}O$: C, 82.0; H, 11.2. Found: C, 81.8; H, 10.8.

4-*n*-Amyl-2-*n*-valerylphenol.—A mixture of 82 g. (0.5 mole) of 4-*n*-amylphenol and 76 g. (0.75 mole) of *n*-valeric acid was cooled at 25–30° while 54 g. (0.79 mole) of boron trifluoride was absorbed during about 0.5 hour. The mixture stood for 15 min., then was heated by an electric mantle to 140° during 12 min., and was held at 140–150° for one hour.

The red-amber solution was poured into 250 g. of sodium acetate in 600 ml. of water. The organic layer was washed with 500 ml. of 5% sodium carbonate and 500 ml. of water and concentrated. Distillation gave 95 g. (77%), b.p. 122–127° (0.5 mm.).

2,4-Di-*n*-amylphenol.—A small shaking autoclave was charged with 124 g. (0.5 mole) of 4-*n*-amyl-2-*n*-valerylphenol, 10 g. of copper chromite catalyst and hydrogen at 130 atm. Reduction started at 155° and 170 atm. and was complete in 0.5 hour, the temperature rising to 182° during the reaction. The reaction mixture was diluted with about 600 ml. of methanol and the catalyst was filtered off. The filtrate was concentrated, diluted with benzene and heated to codistil water. Distillation gave 96.5 g. (82%), b.p. 110° (0.5 mm.).

2,4-Di-*n*-amylphenyl N-(1-naphthyl)-carbamate.—A mixture of 2.34 g. (0.01 mole) of 2,4-di-*n*-amylphenol, 2.03 g. (0.012 mole) of α-naphthyl isocyanate and three drops of pyridine was heated on a steam-bath for 2 hr. Addition of 20 ml. of petroleum ether and stirring gave a solution from which 3.73 g. (93%) of the urethan, m.p. 101–102.5°, separated. Recrystallization from ethanol raises the melting point to 104–104.5°. *Anal.* Calcd. for $C_{27}H_{33}NO_2$: C, 80.4; H, 8.2; N, 3.5. Found: C, 80.2; H, 8.0; N, 3.8.

Allyl 4-*n*-Decylphenyl Ether.—A mixture of 23.4 g. (0.1 mole) of 4-*n*-decylphenol, 14.5 g. (0.12 mole) of allyl bromide, 20 g. of freshly ignited anhydrous potassium bromide and 200 ml. of anhydrous acetone was stirred under reflux for 7 hr. Dilution with an equal volume of water gave an oil which was extracted into petroleum ether (three 100-ml. portions). The extract was washed with 100 ml. of 2.5% sodium hydroxide; the emulsion was broken by adding a little methanol and more water. After several washings with alkali, then with water, the petroleum ether solution was dried over magnesium sulfate, filtered and concentrated, giving 25 g. of colorless oil. Vacuum fractionation gave 23.2 g. (85%) of product, b.p. 132–136° (1 mm.), $n^{25}D$ 1.4937. *Anal.* Calcd. for $C_{19}H_{30}O$: C, 83.2; H, 11.0. Found: C, 83.6; H, 10.6.

2-Allyl-4-*n*-decylphenol.—A small flask containing 22.5 g. (0.082 mole) of allyl 4-*n*-decylphenyl ether was heated in an oil-bath to 235° during one hour. An exothermic reaction raised the melt temperature to 244.5° while the bath remained at 238°. The bath was held at 238° for 15 min. longer and was then removed. Distillation of the melt gave 19.8 g., b.p. 140–150° (1 mm.). Refractionation yielded 17.2 g. (76%), b.p. 143–148° (1 mm.), $n^{25}D$ 1.5034. An amorphous white solid present in the distillation column may be evidence of polymerization.

4-*n*-Decyl-2-*n*-propylphenol.—A mixture of 17.1 g. (0.062 mole) of 2-allyl-4-decylphenol, 85 ml. of absolute ethanol and a small amount of Raney nickel catalyst was shaken under hydrogen at 2.7 atm. Reduction was complete in a few minutes. The catalyst was filtered off and the filtrate concentrated to an oil. The latter was fractionated twice, giving 13.9 g. (81%), b.p. 146–150° (1 mm.), $n^{25}D$ 1.4960.

The α-naphthylurethan prepared as just described melted at 87–88° after two crystallizations from *n*-heptane and one from ethanol. A mixed melting point with the urethan obtained from 4-*n*-decyl-2-*n*-propylphenol prepared *via* the propionyl compound was not depressed.

4-*n*-Amyl-2-(1-methyl)-butylphenol.—To 0.3 mole of methylmagnesium iodide in 120 ml. of ethyl ether was added 23.4 g. (0.1 mole) of 4-*n*-amyl-2-butyrylphenol in 120 ml. of ethyl ether during 20 min. The clear, gray-green solution was refluxed for 3 hr. longer, then poured into 500 ml. of ice. Following the addition of 70 ml. of 5 *N* sulfuric acid, the organic layer was separated and the aqueous layer extracted with two 100-ml. portions of ethyl ether. The ether solution was washed with water, dried over magnesium sulfate, and concentrated. The oil was dissolved in 200 ml. of benzene and the solution, following addition of 5 g. of anhydrous oxalic acid, refluxed under a Dean–Stark trap for 3 hr. The reaction mixture was washed with 100 ml. of water, 100 ml. of 5% sodium carbonate and four 100-ml. portions of water. Following concentration, the residue was vacuum distilled, giving 22.2 g. (95%) of 4-*n*-amyl-2-(1-methyl-1-butenyl)-phenol, b.p. 95–109° (1 mm.) mostly at 106–109°. The material was not purified further but immediately hydrogenated at 2.7 atm. in the presence of Raney nickel and ethanol. The filtrate was concentrated to an oil which was dissolved in 200 ml. of benzene and washed with 100 ml. of 5% hydrochloric acid and five 100-ml. portions of water. Fractional distillation gave 20.3 g. (91%) of product, b.p. 157–159° (7 mm.), $n^{25}D$ 1.5019. Equally good material was prepared *via* 4-*n*-amyl-2-*n*-butyrylanisole, b.p. 171–174° (6 mm.), $n^{25}D$ 1.5096. *Anal.* Calcd. for $C_{16}H_{24}O_2$: C, 77.4; H, 9.7. Found: C, 77.8; H, 9.6, prepared by methylation of 4-*n*-amyl-2-*n*-butyrylphenol, and 4-*n*-amyl-2-(1-methylbutyl)-anisole, b.p. 147–151° (6 mm.), $n^{25}D$ 1.4930. *Anal.* Calcd. for $C_{17}H_{28}O$: C, 82.2; H, 11.3. Found: C, 82.5; H, 11.2.

2,4-Di-*sec*-butylphenol and 2,4,6-tri-*sec*-butylphenol were prepared *via* the reaction of the keto-phenols with excess Grignard reagent, as just described, followed by hydrogenation.

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[CONTRIBUTION FROM THE SHELL DEVELOPMENT CO.]

The Use of Cupric and Ferric Chlorides in the Trapping of Radical Intermediates and the Synthesis of Alkyl Chlorides

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Alkyl radicals derived from di-*t*-butyl peroxide, *t*-butyl hydroperoxide, 2-tetrahydropyranyl hydroperoxide, 2,5-dimethyl-2,5-dihydroperoxyhexane and azo-bis-isobutyronitrile have been trapped by the use of metal halides such as ferric and cupric chlorides. In the trapping process, an alkyl radical is converted to the corresponding alkyl chloride. A mechanism involving one electron transfer through a chloride bridge is proposed.

Introduction

An area of considerable interest in free radical chemistry concerns the nature of primary and intermediate radical species. Since end products do not always conclusively establish the identity of an intermediate radical, much attention has been given to the chemical interception of such intermediates. The present work is concerned primarily with the capture of alkyl radicals in solution by the general process

$$R\cdot + \text{metal}^{n}(\text{chloride})_{n} \longrightarrow RCl + \text{metal}^{n-1}(\text{chloride})_{n-1}$$

This technique has recently been used for intercepting growing polymer chains,[1] and reported and interpreted for its use in homolytic addition to

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(1) C. H. Bamford, A. D. Jenkins and R. Johnston, *Proc. Roy. Soc. (London)*, **A239**, 214 (1957).