*Some Products formed from Phenolic Inhibitors during the Autoxidation of Cumene. Part II.**

By (MISS) M. E. HEY and WILLIAM A. WATERS.

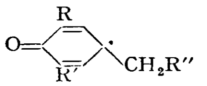
[Reprint Order No. 6214.]

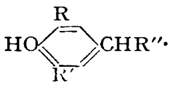
Representative 2 : 4 : 6-trialkylphenols have been oxidised with air in cumene solution. The only products which could be isolated are those derived from substituted 4-hydroxybenzyl radicals (II), *e.g.*, 4-hydroxyaryl ketones and 4 : 4′-dihydroxydibenzyl derivatives, and not products derived from aryloxy-radicals (I).

IN Part I,* Moore and Waters reported that, whereas autoxidising cumene brought about conversion of *p*-cresol, 2 : 4-xylen-1-ol, and 2 : 6-xylen-1-ol into dihydroxydiphenyl derivatives, mesitol, 2-*tert.*-butyl-4 : 6-dimethylphenol and 2 : 6-di-*tert.*-butyl-4-methylphenol gave dihydroxydibenzyl derivatives (III; R, R′ = Me or Bu^t, R″ = H). Attention was drawn to this evidence of autoxidative chain-breaking by 2 : 4 : 6-trialkylphenols, owing to formation of 4-hydroxybenzyl radicals (II) (reaction 2) instead of the expected mesomeric aryloxy-radicals (I) (reaction 1):

$$\text{(1)}\quad \text{Ph}\cdot\text{CMe}_2\cdot + \text{HO}\cdot\text{Ar} \longrightarrow \text{Ph}\cdot\text{CHMe}_2 + \cdot\text{O}\cdot\text{Ar}$$

$$\text{(2)}\quad \text{Ph}\cdot\text{CMe}_2\cdot + \text{HO}\cdot\text{C}_6\text{H}_2\text{R}_2\cdot\text{CH}_3 \longrightarrow \text{Ph}\cdot\text{CHMe}_2 + \text{HO}\cdot\text{C}_6\text{H}_2\text{R}_2\cdot\text{CH}_2\cdot$$

(I) 

 (II)

Since 4-*n*-alkyl-2 : 6-di-*tert.*-butylphenols are particularly good inhibitors of the autoxidation of hydrocarbon oils (Wasson and Smith, *Ind. Eng Chem.*, 1953, **45**, 197) it was of interest to examine the extent to which such phenols gave products derived from radical (II).

To facilitate somewhat the isolation of products, and to allow direct comparison with Bickel and Kooyman's observations (*J.*, 1953, 3211) on the oxidation of trialkylphenols with cumene hydroperoxide, cobalt phthalate has been substituted for ferric stearate as the metallic-salt catalyst and the autoxidation, effected by air at 80—100°, has been initiated by a little cumene hydroperoxide. As shown in the annexed Table, 4-ethyl-2 : 6-dimethylphenol resembled mesitol in giving a dibenzyl derivative (III; R = R′ = R″ = Me)

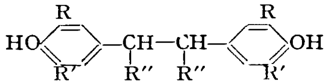
---

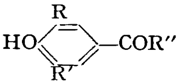
* This investigation continues that of *J.*, 1954, **243**, which is considered as Part I.

whilst with the other compounds examined the *para*-side-chains were oxidised rather more completely to give the hydroxy-ketones (IV), accompanied in one case by a little of the corresponding methanol. Oxidation of the phenols was never complete (recoveries 20—40%) and the yields of purified oxidation products were only about 2%, but apart from dark polymeric material no appreciable quantities of other products could be isolated from autoxidised mixtures so that a good percentage of each phenol seemed to have been destroyed completely.

Phenol oxidised	Products isolated
4-Ethyl-6 : 6-dimethylphenol	4 : 4'-Dihydroxy-α : α' : 3 : 5 : 3' : 5'-hexamethyldibenzyl
2 : 6-Di-*tert*.-butyl-4-ethylphenol	3 : 5-Di-*tert*.-butyl-4-hydroxyacetophenone 2 : 6-Di-*tert*.-butyl-4-2'-hydroxyethylphenol (trace)
2-*tert*.-Butyl-4-ethyl-6-methylphenol	3-*tert*.-Butyl-4-hydroxy-5-methylacetophenone
2 : 6-Di-*tert*.-butyl-4-propylphenol	3 : 5-Di-*tert*.-butyl-4-hydroxypropiophenone
4-Benzyl-2 : 6-dimethylphenol	4-Hydroxy-3 : 5-dimethylbenzophenone

(III)





(IV)

For 2 : 4 : 6-trialkylphenols, substituted in the 4-position by methyl or *tert*.-butyl, there is considerable experimental evidence to indicate that some free-radical-producing agents, such as benzoyl peroxide (Cosgrove and Waters, *J.*, 1951, 388), acetyl peroxide (Wessely and Schinzel, *Monatsh.*, 1953, **84**, 425), lead tetra-acetate (*idem, ibid.*), and alkyl hydroperoxides (Campbell and Coppinger, *J. Amer. Chem. Soc.*, 1952, **74**, 1469; Bickel and Kooyman, *loc. cit.*) and one-electron-abstracting reagents such as alkaline ferricyanide (Cook and Woodworth, *J. Amer. Chem. Soc.*, 1953, **75**, 6242; Müller and Ley, *Chem. Ber.*, 1954, **87**, 922) can yield aryloxy-radicals with chemical reactivity indicative of structure (I). However, with 2 : 6-dialkyl-4-methylphenols only a very slight change in reaction conditions is needed to produce instead 4 : 4'-dihydroxydibenzyl derivatives (III) or stilbenequinones, indicative of the formation and subsequent dimerisation of isomeric but not mesomeric radicals (II). All our present work indicates that autoxidation of the 2 : 4 : 6-trialkylphenols occurs by way of substituted benzyl radicals (II). It has been suggested (Wessely and Schinzel, *loc. cit.*) that derivatives of (II) are formed from those of (I) by molecular rearrangement, but the occurrence of such rearrangements has been established only under conditions of heterolysis: to explain the formation of dimers (III) in this way one would have to suppose that the change (I) ⟶ (II) is also a favourable homolytic hydrogen transfer.

Now it is significant that the products which have been isolated from the 2 : 4 : 6-trialkylphenols listed above are structurally similar to those which can be obtained by autoxidation of the corresponding 1 : 3 : 5-trialkylbenzenes. In view of the small yields of isolated products it is possible therefore that the oxidations established by this work are side reactions (reaction 2) in which the strictly hindered phenolic group is not concerned, and that the concurrent oxidation, *via* (I), has proceeded more extensively, leading to the complete breakdown of much of the original phenol.

It was not possible to isolate any 4-hydroxy-3 : 5-dimethylbenzophenone after direct reaction between 4-benzyl-2 : 6-dimethylphenol and cumene hydroperoxide. This affords some support for the view that the side-chain oxidation is effected, as shown (reaction 2), by the cumyl radical, Ph·CMe$_2$·, and not by the cumylperoxy, Ph·CMe$_2$·O·O·, or cumyloxy, Ph·CMe$_2$·O·, radicals which have been shown to yield derivatives of radical (I) (Bickel and Kooyman, *loc. cit.*).

EXPERIMENTAL

2 : 6-Di-*tert*.-butyl-4-ethyl- and -4-propyl-phenol were prepared by Fries rearrangement of phenyl acetate and phenyl propionate, reduction of the resulting *p*-ketones by the Huang-Minlon method, and then exhaustive butylation with *iso*butene (Stevens, *Ind. Eng. Chem.*, 1943, **35**, 655). 4-Benzyl- and 4-ethyl-2 : 6-dimethylphenol were prepared in a similar way from 2 : 6-xylen-1-ol; 2-*tert*.-butyl-4-ethyl-6-methylphenol had been prepared similarly in the laboratory of the Coal Tar Research Association.

The oxidations were carried out by blowing air at 80—100° into the purified phenol (10 g.), dissolved in cumene (400 ml.) containing cobalt phthalate (0·5 g.), cumene hydroperoxide (2 ml.) being added to initiate reaction. After the requisite time most of the cumene was distilled off; the remainder, in ether, was washed with dilute acid, then distilled in steam, and the involatile residue was dried and chromatographed through acid-washed alumina. Unchanged phenols were eluted with light petroleum–benzene, and the crystallisable products with benzene–ether or benzene–chloroform. Dark tar from which no pure products could be obtained remained on the column. The ketonic products all showed the characteristic Aryl-CO absorption band at 6·0—6·1 μ, and the methyl ketones gave positive iodoform reactions.

In 100 hr. 2-*tert*.-butyl-4-ethyl-6-methylphenol gave 0·4 g. of 3-tert.-*butyl-4-hydroxy-5-methylacetophenone*, m. p. 126° (from aqueous alcohol) (Found: C, 75·7; H, 8·5. $C_{13}H_{18}O_2$ requires C, 75·7; H, 8·7%).

In 72 hr. 2 : 6-di-*tert*.-butyl-4-ethylphenol (m. p. 44°) gave 0·21 g. of 3 : 5-*di*-tert.-*butyl-4-hydroxyacetophenone*, m. p. 148° [from light petroleum (b. p. 40—60°)] (Found: C, 77·5; H, 9·6. $C_{16}H_{24}O_2$ requires C, 77·4; H, 9·75%), and 0·1 g. of 2 : 6-*di*-tert.-*butyl-4-2′-hydroxyethylphenol*, m. p. 103° [from light petroleum (b. p. 40—60°)] [Found: C, 76·8; H, 10·5%; *M* (Rast), 223. $C_{16}H_{26}O_2$ requires C, 76·8; H, 10·4%; *M*, 250]. The latter product had no ketonic absorption bands, but had doubled hydroxyl bands at 2·93 and 3·18 μ.

In 100 hr. 2 : 6-*di*-tert.-*butyl-4-propylphenol*, b. p. 155°/15 mm. (Found: C, 82·1; H, 11·6. $C_{17}H_{28}O_2$ requires C, 82·3; H, 11·3%), gave 0·4 g. of 3 : 5-*di*-tert.-*butyl-4-hydroxypropiophenone*, m. p. 136° (from light petroleum) (Found: C, 77·6; H, 9·9. $C_{17}H_{26}O_2$ requires C, 77·8; H, 10·0%). After 48 hr. 4-ethyl-2 : 6-dimethylphenol, m. p. 37°, gave 0·47 g. of 4 : 4′-*dihydroxy-α : α′ : 3 : 5 : 3′ : 5′-hexamethyldibenzyl* which crystallised from benzene–ether in pale orange needles, m. p. 234° [Found: C, 80·4; H, 8·95%; *M* (Rast), 237. $C_{20}H_{26}O_2$ requires C, 80·5; H, 8·7%; *M*, 298]. The absorption spectrum, which showed no ketonic bands, very closely resembled that of 4 : 4′-dihydroxy-3 : 5 : 3′ : 5′-tetramethyldibenzyl (Moore and Waters, *loc. cit.*). No crystalline product was obtained when oxidation was prolonged to 100 hr.

In 100 hr. 4-benzyl-2 : 6-dimethylphenol, m. p. 67·5°, b. p. 195—200°/20 mm., gave 0·7 g. of 4-hydroxy-3 : 5-dimethylbenzophenone, m. p. and mixed m. p. 143° (Found: C, 79·7; H, 6·2. Calc. for $C_{15}H_{14}O_2$: C, 79·7; H, 6·2%); 5 g. of the unchanged phenol were recovered. No similar product was obtained when the 4-benzyl-2 : 6-dimethylphenol was boiled for 12 hr. in benzene with 4 mol. of cumene hydroperoxide and a trace of cobalt salt.

This work was carried out on behalf of the D.S.I.R. Road Tar Research Committee. We thank the Director of the Research Laboratory of the Coal Tar Research Association (Gomersal) for a gift of 2-*tert*.-butyl-4-ethyl-6-methylphenol.

THE DYSON PERRINS LABORATORY, OXFORD. [*Received, March 9th*, 1955.]