**Tetrahedron Letters No.38, pp. 3355-3359, 1965. Pergamon Press Ltd.
Printed in Great Britain.**

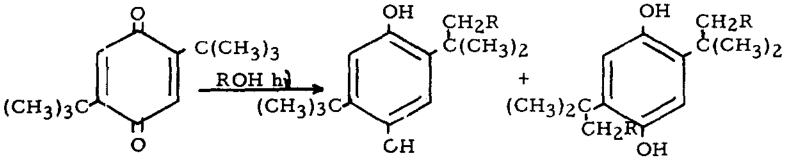
THE STRUCTURES OF THE PHOTOCHEMICAL DECOMPOSITION PRODUCTS OF 2,5-DI-t-BUTYL-p-BENZOQUINONE

Alexander T. Shulgin and Herbert O. Kerlinger
Western Research Laboratories
The Dow Chemical Company
Walnut Creek, California

(Received 29 May 1965; in revised form 30 July 1965)

A recent publication(1) has described the photochemical decomposition of 2,5-di-t-butylbenzoquinone in alcoholic media. The reported products were, in addition to the corresponding hydroquinone, a mono-ethoxy and a diethoxy- derivative, as well as phenolic products of unassigned structure. As these quinols, purportedly 3-ethoxy-2,5-di-t-butylhydroquinone and 3,6-diethoxy-2,5-di-t-butylhydroquinone, would be of value in the study of intramolecular hydrogen bonding, the syntheses described were repeated. Indeed, the irradiation of a saturated solution of 2,5-di-t-butylbenzoquinone(I) in anhydrous ethanol led to the formation of a mono- and a di-ethoxylated hydroquinone with properties agreeing in every particular with those described. In addition, a mono-basic phenolic product was isolated, described below.

The above ethers, although microanalytically and titratively proper, displayed nuclear magnetic resonance (N.M.R.) spectra incompatible with the suggested structures. There was a consistent presence of two aromatic ring hydrogens, as well as a decrease in number of methyl groups with a corresponding appearance of methylene groups. This suggested that these products may represent chain ethoxylation rather than nuclear ethoxylation and should be represented by IIc and IIIb.



I

II

R =
a. H
b. OCH_3
c. OC_2H_5
d. $O\text{-}i\text{-}C_3H_7$

III

R =
a. OCH_3
b. OC_2H_5

To simplify the N.M.R. assignments, the above process was paralleled employing methanol as solvent for I. A monomethoxyhydroquinone (mp. 197°, diacetate mp. 107°) and a dimethoxy counterpart (mp. 211°, diacetate mp. 109°) were readily isolated from the irradiation reaction residue, due to the insolubility of the latter in dimethylsulfoxide. The spectral data are shown in the accompanying table, and clearly indicate that methoxylation has occurred on the *t*-butyl group. The *gem*-dimethyl group resulting from alkoxylation in each of three distinct alcohols, is in every instance shifted some 0.2 ppm *up field* from the position of the unsubstituted *t*-butyl group. Infrared absorption spectra were obtained for each of these materials in dilute CCl_4 solutions. The presence

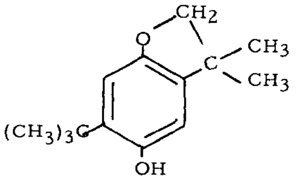
Table

	IIa	IIb	IIIa	IIc	IIIb	IId	IV	V
$-C(C\underline{\underline{H}}_3)_3$	1.38 (18)	1.39 (9)	--	1.37 (9)	--	1.41 (9)	1.40 (9)	--
$-C(C\underline{\underline{H}}_3)_2CH_2R$	--	1.19 (6)	1.18 (12)	1.18 (6)	1.24^{b}	1.23^{b}	1.47 (6)	1.45 (12)
$-C(CH_3)_2C\underline{\underline{H}}_2R$	--	2.70 (2)	2.75 (4)	2.70 (2)	2.80 (4)	2.70 (2)	2.98 (2)	2.96 (4)
ArH	6.69 (2)	6.42 (1) 6.90 (1)	6.60 (2)	6.39 (1) 6.92 (1)	6.67 (2)	6.42 (1) 6.97 (1)	6.57 (1) 6.79 (1)	6.60 (2)
OR	--	3.27 (3)	3.25 (6)	1.22 (3)^{c} 3.50 (2)^{e}	1.24^{c} 3.53 (4)^{e}	1.17^{d} 3.95 (1)^{f}	--	--
OH^{g}	4.49 (2)	4.67 (1) 8.30 (1)	8.33 (2)	5.02 (1) 8.32 (1)	8.42 (2)	4.97 (1) 8.78 (1)	4.68 (1)	--
ν OH anti	3649	3650	--	3648	--	3648	3649	--
free	3611	3617	--	3616	--	3618	3616	--
bonded	--	3314	3307	3308	3310	3287	--	--

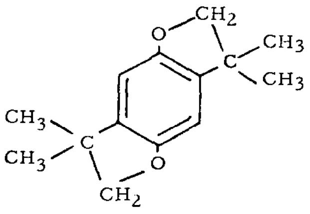
(a) The IR data employed dilute (ca. 5x10^{-3}M) solutions in CCl_4, in 1 cm cells, employing a Beckman IR-7 prism-grating spectrophotometer. All N.M.R. data are from solutions in $CDCl_3$, employing a Varian A-60 spectrograph; Resonances are given in ppm from internal TMS, and integrated intensities are included, where obtainable, parenthetically; (b) The gem-dimethyl resonance is superimposed on the methyl group of the OR, precluding integration; (c) center of triplet; (d) center of doublet; (e) center of quartet, (f) center of septet; (g) with the unsymmetric hydroquinones, the two OH's commerged to an intermediate value upon addition of trifluoroacetic acid.

or absence of a foreshortened ν_{OH} stretch (ca. 3650 cm^{-1}, adjacency to a t-butyl group), of a normal phenolic group (ca. 3610 cm^{-1}, adjacency to a hydrogen) or of an intramolecular hydrogen bond (ca. 3300 cm^{-1}, adjacency to an electronegative atom), agreed in each instance with the assigned structures (see Table).

Preparative gas liquid chromatography of the reaction mother liquors (SE-30 substrate on acid-washed chromasorb) resulted in the isolation of two additional components. These were independent of the identity of the alcohol employed. One of these was readily confirmed as being the previously detected(1) hydroquinone(IIa) corresponding to the starting quinone. The assignment of a dihydrobenzofuran structure (IV) to the second material followed from the various spectral data recorded. This structure was confirmed by the facile conversion with 47% HI, of either IIb, IIc, or IId, to IV (mp. 157°, monoacetate mp. 60°). Similar treatment of the dialkoxy analogs IIIa and IIIb led to the novel tetrahydrobenzodifuran V (mp. 128°).

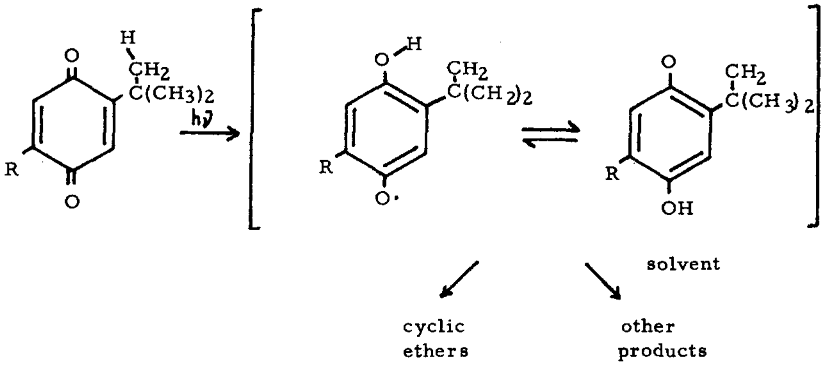


IV



V

A possible explanation for this attack on an aromatic t-butyl group may involve the abstraction of the t-butyl hydrogen



by the excited quinone oxygen to yield a semiquinone radical. This, then, may interact with its surroundings, or may tautomerize to give various products. An oxidation-reduction equilibrium between the various quinones and hydroquinones is essential to explain the introduction of a second alkoxy group. Support for these intermediates has been obtained from the observed participation of mono-*t*-butylbenzoquinone in these reactions, and the apparent inertness of the methyl counterpart (tolylquinone).

REFERENCES

1. J. Petránek and O. Ryba, *Chem. and Ind.* 225 (1965).