Radiation-induced Phenylation of *p*-Bromophenol in Aqueous Solution

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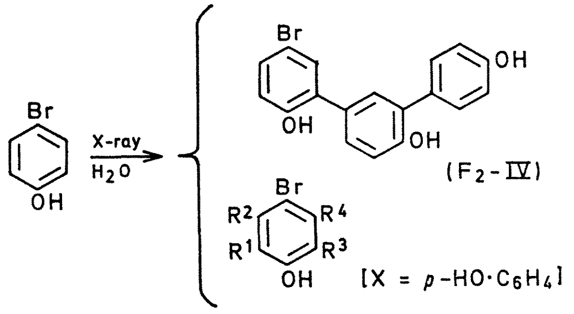
Summary New hydroxy-biphenyls and -terphenyls were formed by radiolysis of *p*-bromophenol in aqueous solution.

WHILE studying the γ-radiolysis of *p*-bromophenol in aqueous solution, we have observed the formation of new phenol oligomers. These oligomers may be formed by the arylation of *p*-bromophenol or of the dimeric product by aryl radical intermediates, resulting from the debromination of *p*-bromophenol by some radiolysis product(s) of water.[1] This communication deals with the identification of these oligomers, two asymmetric biphenyls and four terphenyls.

The *p*-bromophenol solution (25 mM) in triply distilled water was irradiated under nitrogen gas at room temperature with γ-rays from a ^{60}Co source; the total doses were 1·5 Mrad. From the ether extracts of the irradiated *p*-bromophenol solution, several phenolic fractions (Folin–Denis reagent positive) were separated by gradient elution chromatography in benzene–ethyl acetate. Fraction 1 was rechromatographed to give 5-bromo-2,4′-dihydroxybiphenyl (F_1-I); m.p. 134°; λ_{max} (EtOH) 224, 254, and 299 nm (log ϵ 4·3, 4·0, and 3·8). The structure assigned to (F_1-I) is supported by the n.m.r. spectrum of the methyl ether which showed the presence of two methoxy-groups (δ 3·75, 3H, s and 3·69, 3H, s) and three protons *ortho* to the methoxy-group (δ 6·71, 1H, d *J* 8 Hz and 6·81, 2H, d *J* 8 Hz). The structure was further confirmed by the synthesis of 5-bromo-2,4′-dimethoxybiphenyl[2] using the method of Hodgson *et al.*[3] The presence of 2-bromo-5,4′-dihydroxybiphenyl (F_1-II) in fraction 1 was evident from g.l.c. data on synthetic 2-bromo-5,4′-dihydroxybiphenyl silyl ether.[2]



	R^1	R^2	R^3	R^4
(F_1-I)	X	H	H	H
(F_1-II)	H	X	H	H
(F_2-I)	X	H	X	H
(F_2-II)	X	H	H	X
(F_2-III)	X	X	H	H

The methylated fraction 2 gave four peaks on g.l.c., and these products could be isolated by column chromatography. All these compounds have the same molecular formula $C_{21}H_{19}O_3Br$: $M = 399$ (from mass spectra). Trimethyl ethers of (F_2-I), (-II), and (-III) were assigned as *meta*-, *para*-, and *ortho*-terphenyls, respectively, in which C-4, C-2′, and C-4″ are substituted by methoxy-groups and C-5′ by a bromine atom. The trimethyl ether of (F_2-IV) is 5-bromo-2,4′,4″-trimethoxy-*m*-terphenyl. The evidence for the structures is as follows; (F_2-I) trimethyl ether (m.p. 94°): λ_{max} (EtOH) 263 and 302(sh)nm. (log ϵ 4·54 and 3·70); n.m.r. (CCl_4) δ 3·08, 3H, s and 3·84, 6H s ($ArOCH_3$), 6·88, 4H, d *J* 9 Hz (protons *ortho* to methoxy-groups), 7·49, 4H, d *J* 9 Hz (*ortho* coupling ArH), 7·35, 2H, s (isolated ArH); (F_2-II) trimethyl ether (m.p. 169—170°): λ_{max} (EtOH) 224(sh), 275, and 306 nm (log ϵ 4·32, 4·27, and 3·98); n.m.r. (CCl_4) δ 3·72, 3H, s, 3·77, 3H, s and 3·78, 3H, s ($ArOCH_3$), 6·78, 1H, s (isolated proton *ortho* to methoxy-group), 6·82, 2H, d *J* 9 Hz and 6·85, 2H, d *J* 9 Hz (protons *ortho* to methoxy-groups), 7·41, 1H, s (isolated ArH), 7·35, 2H, d *J* 9 Hz, and 7·28, 2H, d *J* 9 Hz (*ortho* coupling ArH); (F_2-III) trimethyl ether (m.p. 121—122°): λ_{max} (EtOH) 229, 239 (sh), 280, and 285 (sh) nm (log ϵ 4·44, 4·41, 3·93, and 3·90); n.m.r. (CCl_4) δ 3·68, 3H, s, 3·70, 3H, s, and 3·71, 3H, s ($ArOCH_3$), 7·53, 1H, d *J* 9 Hz (*ortho* coupling proton deshielded by bromine atom) and nine *ortho*-protons including four aromatic protons shielded by nonplanarity of benzene rings and five protons *ortho* to methoxy-group (δ 6·59, 2H, d *J* 9 Hz, 6·65, 2H, d *J* 9 Hz, 6·78, 1H, d *J* 9 Hz, 6·82, 2H, d *J* 9 Hz, and 6·87, 2H, d *J* 9 Hz); (F_2-IV) trimethyl ether (m.p. 130—131°): λ_{max} (EtOH) 223, 256, and 295 nm (log ϵ 4·47, 4·48, and 4·11); n.m.r. (CCl_4) δ 3·79, 3H, s and 3·83 6H, s ($ArOCH_3$), 6·80, 1H, d *J* 9 Hz, 6·89, 2H, d *J* 9 Hz, and 6·93, 1H, d *J* 9 Hz (aromatic protons *ortho* coupling to methoxy-groups); six other aromatic protons appeared at lower field than 7·0 p.p.m. The *ortho*-, *meta*-, and *para*-structures of the four terphenyls are in agreement with the u.v. spectroscopic data for *o*-, *m*-, and *p*-terphenyl, λ_{max} (EtOH) 237·5, 250·9 and 273·7 nm, respectively.[4]

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[1] M. Anbar, Z. B. Alfassi, and H. Bregman-Reisler, *J. Amer. Chem. Soc.*, 1967, **89**, 1263.
[2] T. Komiya, S. Kawakishi, H. Aoki, and M. Namiki, *Agric. and Biol. Chem.* (*Japan*), in the press.
[3] H. H. Hodgson and E. Marsden, *J. Chem. Soc.*, 1940, 208.
[4] N. D. Coggeshall and E. M. Lang, *J. Amer. Chem. Soc.*, 1948, **70**, 3283.