

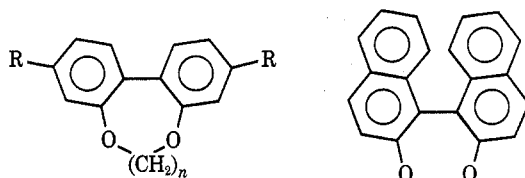
The Synthesis of Some 2,2'-Dioxa-Bridged Biphenyls and 1,1'-Binaphthyls^{1a}

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In the course of a study involving the synthesis and evaluation as liquid scintillator solutes of a number of bridged *p*-quaterphenyls of the type 1 it was necessary to prepare a number of 2,2'-bridged biphenyls (2). The 2,2'-bridged 1,1'-binaphthyls (3) were also of interest to us as scintillators and their synthesis is reported here along with the biphenyl derivatives (2).



1, R = C₆H₅; n = 1, 2, 3, 4
2a, R = H; n = 1
b, R = H; n = 2
c, R = H; n = 3
d, R = H; n = 4

3a, n = 1
b, n = 2
c, n = 3
d, n = 4

The dioxepins (a), dioxocins (b), dioxonins (c), and dioxecines (d) in the biphenyl series (2) and 1,1'-binaphthyl series (3) were each obtained from 2,2'-dihydroxybiphenyl (4) and 1,1'-bi-2-naphthol (5), respectively. In each case, depending on the desired number of methylenes in the bridge, a solution of methylene iodide, 1,2-dibromoethane, 1,3-dibromopropane, or 1,4-dibromobutane in anhydrous *N,N*-dimethylformamide (DMF) was added to a heated mixture of the appropriate dihydroxy compound and potassium carbonate in anhydrous *N,N*-dimethylformamide to yield the following: dibenzo[*d,f*][1,3]dioxepin (2a), 6,7-dihydrodibenzo[*e,g*][1,4]dioxocin (2b), 7,8-dihydro-6*H*-dibenzo[*f,h*][1,5]dioxonin (2c), 6,7,8,9-tetrahydrodibenzo[*g,i*][1,6]dioxecine (2d), dinaphtho[2,1-*d*:1'-2'-*f*][1,3]dioxepin (3a), 4,5-dihydrodinaphtho[2,1-*e*:1'-2'-*g*][1,4]dioxocin (3b), 5,6-dihydro-4*H*-dinaphtho[2,1-*f*:1':2'-*h*][1,5]dioxonin (3c), and 4,5,6,7-tetrahydrodinaphtho[2,1-*g*:1':2'-*i*][1,6]dioxecine (3d). See Table I.

Thus, the yields of the bridged ethers in the biphenyl

(1) (a) From the dissertation presented by J. Ernest Simpson to the graduate faculty of the University of New Mexico in partial fulfillment of the requirements for the degree of Doctor of Philosophy. This investigation was supported in part by a Research Grant from the Division of Biology and Medicine of the U. S. Atomic Energy Commission, Contract No. AT(29-2)-915. (b) Graduate Research Assistant, June 1963 to August 1967. (c) Work performed under the auspices of the U. S. Atomic Energy Commission.

TABLE I
DIOXA-BRIDGED BIPHENYLS AND BINAPHTHYLS^a

Compd	Time ^f	Temp, °C	Yield, %	Mp, °C
2a	1.0 (18)	80-90	56	36.5-37.5 (reported ^g 35-36)
2b	2.5 (16)	90-100	38	97.8 ^b (reported ^{g,h} 98)
2c	5.0 (15)	100-110	53	72.5-73.5 ^b (reported ^g 67-69)
2d	6.0 (14)	75-80	38	109-110 ^c (reported ^g 110-111)
3a	1.0 (4)	100-110	52	178.5-179.5 ^d
3b	7.0 (14)	75-85	7	197-198.5 ^d (reported ⁱ 196-197)
3c	3.0 (18)	80-90	49	272.5-273.5 ^e
3d	3.0 (18)	80-90	76	256.5-257.5 ^e

^a Analytical samples of all of the compounds reported here gave satisfactory analytical data ($\pm 0.4\%$ for C and H). All products were chromatographed in benzene or cyclohexane-benzene over Woelm neutral activity grade I alumina prior to recrystallization. ^b Recrystallization solvent was petroleum ether (bp 30-60°). ^c Recrystallization solvent was petroleum ether (bp 60-90°). ^d Recrystallization solvent was cyclohexane-benzene. ^e Recrystallization solvent was benzene. ^f Time of addition of halide in hours (time of heating in hours after addition). ^g D. W. Allen, P. N. Braunton, I. T. Millar, and J. C. Tebby, *J. Chem. Soc. C*, 3454 (1971). ^h O. Diels and A. Bibergeil, *Ber.*, **35**, 302 (1902). ⁱ M. R. Fosse, *Bull. Soc. Chim. Fr.*, **19**, 611 (1898).

series (2) were superior to those reported recently² in which the diol was treated with sodium hydroxide and the appropriate dihalide in aqueous dimethyl sulfoxide. In all cases the biphenyl derivatives 2a-2d obtained in our work had physical properties and ultraviolet absorption spectra essentially identical with those reported.^{2,3} The compounds 3a, 3c, and 3d are new compounds and the dioxocin 3b had physical properties in agreement with those previously reported.⁴

Experimental Section

All melting points were taken in Pyrex capillary tubes in a Hoover-Thomas melting point apparatus and are uncorrected. Ultraviolet absorption spectra were taken in cyclohexane solution and were run on a Cary Model 14 spectrophotometer.

General Procedure.—The preparation of dibenzo[*d,f*][1,3]dioxepin (2a) is described in detail, and the synthesis of the other compounds was carried out in a similar fashion.

Dibenzo[*d,f*][1,3]dioxepin (2a).—A solution of 2.95 g (0.011 mol) of methylene iodide in 35 ml of DMF was added dropwise over 1.0 hr to a stirred mixture of 1.86 g (0.01 mol) of 2,2'-dihydroxybiphenyl (4), mp 108-110°, and 3.04 g (0.022 mol) of anhydrous potassium carbonate in 50 ml of DMF maintained between 80 and 90°. After the reaction mixture has been heated for an additional 18 hr, it was poured into water and extracted with ether, and the ether layer was washed with 5% sodium hydroxide and water. The ether layer was dried (K₂CO₃), the solvent was removed on a steam bath, and the residue was chromatographed from a 10:1 cyclohexane-benzene solution through a Woelm alumina column (neutral activity, grade I). Removal of the solvent left an oil which solidified upon cooling; after several unsuccessful crystallization attempts, the solid was evaporatively distilled (90°, 0.05 Torr) yielding 1.1 g (56% yield) of dibenzo[*d,f*][1,3]dioxepin (2a) as a colorless solid, mp 36.5-37.5°.

Registry No.—2a, 220-11-1; 3a, 188-35-2; 3c, 38896-36-5; 3d, 38896-37-6; 4, 1806-29-7.

(2) D. W. Allen, P. N. Braunton, I. T. Millar, and J. C. Tebby, *J. Chem. Soc. C*, 3454 (1971).

(3) P. N. Braunton, I. T. Millar, and J. C. Tebby, *J. Chem. Soc., Perkin Trans. 2*, 138 (1972).

(4) M. R. Fosse, *Bull. Soc. Chim. Fr.*, **19**, 611 (1898).