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Some Oxygen-Containing Heterocycles as Liquid Scintillator Solutes

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Derivatives of dibenzofuran, dibenzo-*p*-dioxin, and xanthene have been screened as liquid scintillator solutes. The first of these appears to offer the most promise. The results suggest that methoxy derivatives increase the relative pulse height.

Continuing our general survey¹ of aromatic systems as liquid scintillator solutes, we have prepared and screened a few selected heterocycles containing oxygen as the only hetero atom (Table I). The compounds tested have many of the desirable properties of good solutes, and a remarkable variety is available by extension of the synthetic methods employed.

TABLE I
PRIMARY-SOLUTE RELATIVE PULSE HEIGHTS

No.	Compound	Relative Pulse Height
1.	Dibenzofuran	0.10
2.	3-Dimethylaminodibenzofuran ^a	0.79
3.	4,6-Dimethoxydibenzofuran ^b	0.24
4.	2,8-Dimethoxydibenzofuran ^c	0.27
5.	2-Hydroxy-8-methoxydibenzofuran ^c	0.21
6.	2,8-Diaminodibenzofuran ^d	0.14
7.	2-Methoxy-3-carbomethoxydibenzofuran ^e	0.13
8.	2,2'-Bidibenzofuran ^f	0.14
9.	6,6'-Dimethoxy-2,2'-bidibenzofuran ^f	0.46
10.	Tri-4-dibenzofurylcarbinol ^d	0.13
11.	1,2,3,4-Tetrahydro-6-methoxy-4-oxobenzob[naphtho[1,2-d]furan ^e	<0.10
12.	1,2,3,4-Tetrahydro-7-methoxy-1-oxocycloocta[klm]dibenzofuran ^e	<0.10
13.	Dibenzo- <i>p</i> -dioxin ^g	<0.10
14.	2-Phenyldibenzo- <i>p</i> -dioxin ^h	0.40
15.	1,1'-Bidibenzo- <i>p</i> -dioxin ^h	0.15
16.	2,2'-Bidibenzo- <i>p</i> -dioxin ^h	0.59
17.	1-(2-Dibenzo- <i>p</i> -dioxinyl)-1,2-diphenylethanol ^h	<0.10
18.	2-(α -Phenylstyryl)dibenzo- <i>p</i> -dioxin ^h	<0.10
19.	Spiro(fluorene-9,9'-xanthene) ⁱ	<0.10
20.	Spiro(9,10-dihydroanthracene-9,9'-xanthene) ⁱ	<0.10
21.	9,9'-Spirobixanthene ⁱ	<0.10
22.	2-Biphenyl phenyl ether ^j	0.16
23.	4-Biphenyl phenyl ether ^j	0.16
24.	2-Biphenyl 4-biphenyl ether ^j	<0.10

^a W. H. Kirkpatrick and P. T. Parker, *J. Am. Chem. Soc.*, **57**, 1123 (1935). ^b H. Gilman and L. C. Cheney, *J. Am. Chem. Soc.*, **61**, 3149 (1939). ^c H. Gilman, J. Swiss, H. B. Willis, and F. A. Yoeman, *J. Am. Chem. Soc.*, **66**, 798 (1944). ^d J. Swislow, *Iowa State Coll. J. Sci.*, **14**, 92 (1939). ^e S. Avakian, doctoral dissertation, Iowa State College, Ames, Iowa, 1944. ^f H. B. Willis, *Iowa State Coll. J. Sci.*, **18**, 98 (1943). ^g H. Gilman and J. J. Dietrich, *J. Am. Chem. Soc.*, **79**, 1439 (1957). ^h See Experimental. ⁱ R. G. Clarkson and M. Gomberg, *J. Am. Chem. Soc.*, **52**, 2881 (1930). ^j Kindly supplied by Dow Chemical Co.

(1) For leading references see: H. Gilman, E. A. Weipert, T. Soddy, and F. N. Hayes, *J. Org. Chem.*, **22**, 1169 (1957).

The relative pulse heights (RPH) of the limited number of dibenzo-*p*-dioxin derivatives screened are low and seem to reflect a suspected generalization, *i.e.*, values will always be higher for compounds having a direct union of two aromatic rings than for those in which the rings are joined through an oxygen atom. The biphenyl linkage in dibenzofuran will presumably make all of its derivatives superior to corresponding dibenzo-*p*-dioxin derivatives. This principle is remarkably evident when comparing 4-biphenyl phenyl ether (compound 23, RPH 0.16) and *p*-terphenyl (RPH 0.97). The generalization also appears to hold for preliminary work with carbazole and phenoxazine.

As previously noted¹ there is again a remarkably high response for the lone dimethylamino derivative tested (compound 2). In hopes of finding some reflection of this effect in structurally similar methoxy derivatives, a number of these compounds were also screened. The most remarkable (and as yet unexplainable) value obtained from the methoxy derivatives investigated is certainly that of compound 9 which gives a response so much higher than compound 8 (0.46 and 0.14, respectively). It is also noteworthy that all the methoxy derivatives tested give some response, although only compound 9 has more than two benzene rings. It would surely be unwarranted to generalize on the basis of so few examples, but these values are encouraging.

The fact that the values obtained from these methoxy derivatives are consistently good, along with the excellent values for dialkylamino derivatives, suggests that these groups result in a shortening of the lifetime of the excited state and thus provide a greater probability that fluorescence will occur before a radiationless transition.² The effect of methoxyl and dialkylamino groups on the lifetime of the excited state is not known with certainty, but all previous reports of solutes with substituent groups on an aromatic ring seem to indicate a rough parallel with the activation or deactivation of the aromatic system toward electrophilic substitution. Perhaps there is some significance in the fact that phenols and aryl amines give markedly lower values than the corresponding alkylated compounds.

(2) D. G. Ott, F. N. Hayes, E. Hansbury, and V. N. Kerr, *J. Am. Chem. Soc.*, **79**, 5448 (1957).

The dibenzo-*p*-dioxin derivatives reported herein are the first of these compounds screened as scintillators. The values recorded in Table I indicate that further work on this heterocycle is promising only in the case of the 2-substituted derivatives (compare, for example, compounds 15 and 16). Compound 18 would make it seem that any further aromatic systems should be linked directly to the heterocycle (see compound 14) rather than through a vinyl side chain.

Of some interest are the two general methods employed in the experimental section to prepare phenyl and styryl derivatives of heterocycles. Amino derivatives are converted by three relatively convenient steps to phenyl derivatives. The described modification of the Gomberg reaction obviates the isolation of intermediates and leads to a single isomer. The condensation of benzylmagnesium chloride with aromatic aldehydes or ketones, followed by dehydration of the resulting carbinol, gives good yields of styryl or β -substituted styryl derivatives. In this case also, isolation of the carbinol is unnecessary since dehydration by the Lucas reagent, as developed by Crawford and Nelson,³ can be effected conveniently using a benzene solution of the crude carbinol.

The values reported in Table I were measured in the pulse height analyzer previously described,⁴ and all were measured at a concentration of 3 g./l. in toluene except 6, 9, 10, 15, and 16 which, due to limited solubility, were measured as saturated solutions. All values are relative to 2,5-diphenyloxazole which is assigned the arbitrary value of 1.00.

EXPERIMENTAL⁵

1,1'-Bisdibenzo-p-dioxin. A mixture of 4.0 g. (0.015 mole) of 1-iododibenzo-*p*-dioxin⁶ and 4 g. of copper bronze was heated in an oil bath at 250° for 5 hr.⁷ After cooling, the reaction mixture was pulverized, extracted with hot benzene, and filtered. Concentration of the benzene followed by dilution with ethanol produced 0.9 g. of product melting at 215–218°. Further recrystallization from ethanol-benzene afforded 0.6 g. (22%) of white plates, m.p. 217–219°.

Anal. Calcd. for C₂₄H₁₄O₄: C, 78.69; H, 3.82. Found: C, 78.36, 78.50; H, 4.24, 4.28.

2,2'-Bisdibenzo-p-dioxin. A mixture of 4.0 g. (0.015 mole) of 2-iododibenzo-*p*-dioxin⁸ and 5 g. of copper bronze was

(3) H. M. Crawford and H. B. Nelson, *J. Am. Chem. Soc.*, **68**, 134 (1946).

(4) F. N. Hayes, D. G. Ott, V. N. Kerr, and B. S. Rogers, *Nucleonics*, **13**, No. 12, 38 (1955).

(5) All melting points are uncorrected.

(6) J. J. Dietrich, doctoral dissertation, Iowa State College, Ames, Iowa, 1957.

(7) D. A. Shirley, *Preparation of Organic Intermediates*, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 122.

(8) H. Gilman and J. J. Dietrich, *J. Am. Chem. Soc.*, **79**, 1439 (1957).

heated at 240–250° for 4 hr.⁷ After cooling, the reaction mixture was pulverized, extracted with hot benzene, and chromatographed on alumina. The eluate was concentrated and diluted with ethanol to produce 0.7 g. of product melting at 225–230°. One further recrystallization from glacial acetic acid afforded 0.6 g. (22%) of white plates melting at 227–230°.

Anal. Calcd. for C₂₄H₁₄O₄: C, 78.69; H, 3.82. Found: C, 78.40, 78.49; H, 4.08, 4.07.

2-Phenyldibenzo-p-dioxin. Nitrous fumes⁹ were slowly bubbled through a solution consisting of 4.0 g. (0.016 mole) of 2-acetamidodibenzo-*p*-dioxin,⁶ 130 ml. of glacial acetic acid, and 20 ml. of acetic anhydride at 10° for 2.5 hr.¹⁰ The yellow-green solution was poured into a liter of ice water, and the precipitated yellow solid was filtered off. This solid was air dried and then stirred for 8 hr. with 200 ml. of dry benzene. After 8 hr. at room temperature, the solution was warmed for 1 hr. and the bulk of the benzene distilled. The concentrated benzene solution was chromatographed on alumina and the eluate was evaporated. Two recrystallizations of the residue from ethanol produced 0.7 g. (16%) of white plates, m.p. 108–110°. The infrared spectrum showed bands characteristic of 1,2,4 trisubstitution, 1,2 disubstitution, and monosubstitution.

Anal. Calcd. for C₁₈H₁₂O₂: C, 83.08; H, 4.61. Found: C, 82.64, 82.71; H, 4.64, 4.72.

1-(2-Dibenzo-p-dioxinyl)-1,2-diphenylethanol. An excess of benzylmagnesium chloride was added to a stirred solution of 5.76 g. (0.02 mole) of 2-benzoyldibenzo-*p*-dioxin⁶ in 100 ml. of diethyl ether over a period of 15 min. After addition, which caused gentle reflux, the reaction mixture was refluxed for 2 hr. and then hydrolyzed with saturated ammonium chloride. The ether layer was separated, dried over sodium sulfate, and evaporated. The residual 6 g. of crude material was recrystallized three times from ethanol-water to give 4.5 g. (60%) of white needles, m.p. 141–142°.

Anal. Calcd. for C₂₆H₂₀O₂: C, 82.10; H, 5.26. Found: C, 82.12, 82.15; H, 5.22, 5.48.

2-(α -Phenylstyryl)dibenzo-p-dioxin. A mixture of 3.5 g. (0.009 mole) of 1-(2-dibenzo-*p*-dioxinyl)-1,2-diphenylethanol, 45 ml. of benzene, and 15 ml. of Lucas reagent was refluxed for 2 hr. The benzene layer was separated and washed with dilute sodium carbonate solution. Evaporation of the benzene left an oil which solidified when boiled with petroleum ether (b.p. 60–70°). Three recrystallizations of this material from ethanol-water afforded 1.1 g. (33%) of white needles, m.p. 123–125°.

Anal. Calcd. for C₂₆H₁₈O₂: C, 86.18; H, 4.97. Found: C, 86.18, 86.19; H, 4.83, 5.08.

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(9) J. Haworth and D. Hey, *J. Chem. Soc.*, 361 (1940).

(10) W. E. Bachman and R. A. Hoffman, *Org. Reactions*, **II**, p. 249 (1949).