

enedioxy-1-bromobenzene, 1.1 g. (0.012 mole) of cuprous cyanide, and 1 ml. of anhydrous pyridine was heated under reflux for 15 hr. using an oil bath at 210–225°. The contents of the reaction flask were stirred thoroughly with dilute aqueous ammonia and then with 25 ml. of benzene, and the resulting mixture was filtered through a sintered glass funnel. After extracting the aqueous layer of the filtrate several times with benzene, all the benzene fractions were combined and were concentrated on the steam bath. Crystallization of the residue from aqueous alcohol gave slightly pink needles, which after drying, weighed 0.84 g. (57%).

Anal. Calcd. for $C_8H_5O_2N$: C, 65.30; H, 3.43. Found: C, 65.5; H, 3.5.

The melting point, 90–91°, of this product corresponds more closely to the reported m.p. 94–95° for 3,4-methylenedioxybenzoxonitrile (piperonylonitrile)¹² than to the m.p. 80° for 2,3-methylenedioxybenzoxonitrile.¹³

3,4-Methylenedioxy-1-bromobenzene treated with butyllithium followed by acetic anhydride. An ether solution (60 ml.) containing 0.064 mole of butyllithium was added over a 5-min. period to 12.8 g. (0.064 mole) of 3,4-methylenedioxy-1-bromobenzene. The reaction mixture was blanketed with nitrogen and was held at –35°. After swirling the mixture briefly it was allowed to stand at –35° for another 5 min. Acetic anhydride (15 ml.) was added rapidly to the cold solution, which was then allowed to come to room temperature and to stand at room temperature for 2 days. Volatile materials were removed by distillation on the steam bath at water-pump pressures. Distillation of the residual oil through a 6-inch Vigreux column furnished some starting material [1.2 g., b.p. 104–105° (9 mm.), n_D^{25} 1.5791], an intermediate fraction (2–3 ml.), and finally a viscous yellow oil, b.p. 170–175° (1 mm.). Decomposition was evident, especially during the last part of the distillation when the bath temperature was raised to 270°, and much residue remained in the flask. The yellow oil on standing deposited crystals (0.53 g.) with m.p. 90.5–101°. Chromatography of this material in benzene solution using an alumina column gave colorless crystals (0.33 g.), m.p. 91–93°. Recrystallization from absolute alcohol brought the melting point to 92–93°.

Anal. Calcd. for $C_{16}H_{12}O_4$: C, 71.63; H, 4.51. Found: C, 70.5; H, 4.3.

This compound, tentatively considered to be 1,1-bis-(3',4'-methylenedioxyphenyl)ethylene, absorbed bromine rapidly from a chloroform solution, contained no halogen, and showed absorption peaks at 299 $m\mu$ ($\log \epsilon$ 3.85) and 269 $m\mu$ ($\log \epsilon$ 3.83) in a 1×10^{-4} M alcoholic solution.

3,4-Methylenedioxy-1-bromobenzene treated with butyllithium followed by carbon dioxide. 3,4-Methylenedioxy-1-bromobenzene (14.1 g. or 0.070 mole) was treated as described above with 148 ml. of an ethereal solution containing 0.0705 mole of butyllithium. After a maximum exchange time of 10 minutes, the mixture was poured over a slurry of approximately 20 g. of crushed solid carbon dioxide in ether. The mixture was acidified with dilute hydrochloric acid, the ether layer was removed, and the aqueous layer extracted twice with ether. The combined ether solutions were dried over magnesium sulfate and then were warmed to remove solvent. Two crystallizations of the residual solid from 95% alcohol resulted in 7.0 g. (60%) of piperonylic acid, m.p. 226–227°. The melting point of this carbonation product admixed with authentic piperonylic acid was 225.8–227°.

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Some Derivatives of Biphenyl as Liquid Scintillator Solutes

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Received November 26, 1957

Previous studies of liquid scintillator solutes¹ have indicated the general principle that efficient solutes must contain three, and preferably four, aromatic rings linked to one another in chainlike fashion. We have screened a variety of compounds which may be regarded as derivatives of biphenyl in that each has only two distinct benzene rings joined directly (although some have fused rings as well). A few of these compounds have high relative pulse height values for such "small" molecules.

TABLE I
PRIMARY-SOLUTE RELATIVE PULSE HEIGHTS

No.	Compound	Relative Pulse Heights	Ref.
1.	2-Aminobiphenyl	0.16	^a
2.	4-Benzylbiphenyl	<0.10	^b
3.	2,2'-Dimethoxybiphenyl	0.14	^c
4.	4,4'-Dimethoxybiphenyl	0.20	^d
5.	2,2'-Dimethoxy-3,3'-dimethylbiphenyl	<0.10	^c
6.	3,4-Benzocoumarin	<0.10	^a
7.	N,N,N',N'-Tetramethylbenzidine	0.28	^a
8.	4,4'-Bistrimethylsilylbiphenyl	0.30	^e
9.	N-(4-Biphenyl)-aniline	0.63	^f
10.	N-(<i>o</i> -Phenyldiphenylmethyl)-aniline	0.13	^g
11.	2,3-Dimethoxyphenanthrene	0.14	^h
12.	2-Aminophenanthrene	0.23	ⁱ
13.	3-Aminophenanthrene	0.20	^j
14.	1,1'-Binaphthyl	0.87	^k
15.	2,2'-Binaphthyl	0.25	^l
16.	Perylene	0.24	^m

^a Commercially available. ^b K. Goldschiedt, *Monatsh.*, **2**, 433 (1881). ^c H. Gilman, J. Swiss, and L. C. Cheney, *J. Am. Chem. Soc.*, **62**, 1963 (1940). ^d F. Ullman and O. Lowenthal, *Ann.*, **332**, 67 (1904). ^e H. A. Cook (Dow Corning Ltd.), Brit. Patent **671,553** (1952); *Chem. Abstr.*, **47**, 4909 (1953). ^f J. Piccard, *Helv. Chim. Acta*, **7**, 789 (1924). ^g H. Gilman, J. E. Kirby, and C. R. Kinney, *J. Am. Chem. Soc.*, **51**, 2252 (1929). ^h H. Gilman and T. H. Cook, *J. Am. Chem. Soc.*, **62**, 2813 (1940). ⁱ W. E. Bachmann and C. H. Boatner, *J. Am. Chem. Soc.*, **58**, 857 (1936). ^j J. Schmidt, *Ber.*, **34**, 3553 (1901). ^k H. Gilman and C. G. Brannen, *J. Am. Chem. Soc.*, **71**, 658 (1949). ^l F. Ullman and R. Gilli, *Ann.*, **332**, 50 (1904). ^m J. Weitzenbock and R. Seer, *Ber.*, **46**, 1996 (1913).

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Previously tested hydrocarbons with a single phenyl-phenyl linkage include such compounds as biphenyl,^{1a} fluorene,^{1a} phenanthrene,^{1b} and pyrene^{1b} (0.10, 0.12, 0.16, and 0.21, respectively). Table I shows the remarkable value of 0.87 for 1,1'-binaphthyl along with 0.25 for 2,2'-binaphthyl and 0.24 for the closely related perylene. Some partially hydrogenated terphenyls and quaterphenyls having only two benzenoid nuclei also give surprisingly high values and will be reported later along with the corresponding aromatic compounds.

Included in Table I are a number of interesting functional derivatives of biphenyl. Among these are two solutes related to *p*-terphenyl (RPH 0.97^{1b}). Previously^{1e} we have reported a value of 0.16 for 4-biphenyl phenyl ether. In Table I Compound 2, in which the three rings are separated by a —CH₂— group, gives no response within the limits of our measuring system. Compound 9 with an —NH— function separating the rings shows a value of 0.63. The temptation to attribute this high value to resonance interaction between rings is discouraged by the low value of the corresponding oxygen compound. To date no theoretical explanation involving the hydrogen attached to the nitrogen separating the rings has been proposed, although there are other examples that lend appeal to this line of thought. Compare, for example, 4-biphenyldiphenylamine^{1f} (0.39) with Compound 9 and bis-4-biphenylamine^{1f} (0.95) with bis-4-biphenylphenylamine^{1f} (0.61). Even Compound 10, with little opportunity for any sort of interaction between the rings and the secondary amine function, affords a measurable response. In all of these cases consideration of the values of the oxygen analogs is discouraging in that the diaryl ethers have poor values and the phenolic hydroxyl group is known to be an undesirable function in all instances examined thus far.^{1b}

The encouraging results for the dimethylamino and methoxy derivatives tested (Compounds 3,4,5,7, and 11) seem to indicate that these functions give rise to enhanced scintillation in compounds which are otherwise poor solutes in spite of the fact that they have little, if any, effect on molecules which are otherwise good scintillators. The simple aminophenanthrenes are the first derivatives of this system reported, and the pulse heights (0.20 and 0.23) indicate good potential for this nucleus. Synthesis and examination of more complex derivatives will almost certainly be rewarding.

The values reported in Table I were measured in the pulse height analyzer previously described,^{1b} and all were measured at a concentration of 3 g./l. in toluene. All values are relative to 2,5-diphenyl-oxazole which is assigned the arbitrary value of 1.00.

Acknowledgment. This work was supported by the United States Atomic Energy Commission under Contract No. AT(11-1)-59. The authors are in-

debted to Drs. Wright H. Langham and Donald G. Ott of the Los Alamos Scientific Laboratory for their interest and helpful suggestions and to Elizabeth Hansbury and Vernon N. Kerr, also of the Los Alamos Scientific Laboratory, for technical assistance.

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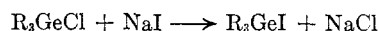
Some Compounds in the Tri-*n*-hexylgermane Series

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Received December 23, 1957

Because the information in the literature on the higher aliphatic germanium compounds¹ is meager, a study of such types has recently been initiated in this laboratory. The preparations and physical properties of some compounds of the tri-*n*-hexylgermane series are reported herein, including tetra-*n*-hexylgermane, phenyltri-*n*-hexylgermane, tri-*n*-hexylbromogermane, bis(tri-*n*-hexylgermanium) oxide, tri-*n*-hexylchlorogermane, tri-*n*-hexyliodogermane and tri-*n*-hexylgermane.

Tetra-*n*-hexylgermane was prepared by the reaction of germanium tetrachloride with an excess of *n*-hexyllithium. Tri-*n*-hexylbromogermane was obtained directly from germanium tetrachloride and 3.3 equivalents of *n*-hexylmagnesium bromide, although the product obtained by this method cannot be completely freed of di-*n*-hexyldibromogermane. The ready displacement by bromide ion of the chloride ion from the expected initial product, tri-*n*-hexylchlorogermane, finds a parallel in the preparation of the corresponding iodide from either the chloride or the bromide by the action of sodium iodide in acetone solution. The high rate



of reaction of trialkylhalogermanes compared to tertiary butyl halides in bimolecular nucleophilic displacement reactions can be partially ascribed to the relative unimportance of steric hindrance at the large central germanium atom. Also, germanium is less electronegative than carbon.² This suggests a polarization of the alkyl-germanium bonds which would tend to lower the electron density at the central atom thereby speeding S_N2 reactions.

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