carbon joined at once to a silicon atom and a carbonyl group provided added support for I by precluding the isomeric structure, methyl α-methyl-α-(triethylsilyl)propionate.

The α-methyl group thus influences the reaction in the direction of "normal" addition. It is interesting to note that both Speier *et al.*,[11] and Sommer *et al.*[12] obtained similar results with methyldichlorosilane and certain methacrylate esters.

EXPERIMENTAL[16–18]

Addition of triethylsilane to methyl methacrylate. A mixture of 20.0 g. (0.172 mole) of triethylsilane, 17.2 g. (0.172 mole) of methyl methacrylate, and 0.17 g. of a 0.06% platinum-on-carbon catalyst[7] was heated under reflux for a period of 115.5 hr., during which time the temperature rose from 97 to 150°. The reaction mixture was allowed to cool to room temperature, ether was added, and the catalyst was removed by filtration. (There remained in the reaction vessel 10.8 g. of a polymeric substance which was not further investigated.) The combined filtrate and ether washings were dried over anhydrous sodium sulfate, and the solvent was removed by distillation. Repeated fractionation of the liquid residue gave, ultimately, methyl α-methyl-β-(triethylsilyl)-propionate, b.p. 117–120° (23 mm.), n_{D}^{25} 1.4413–1.4421, yield 11.4 g. (30.6%). An analytical sample exhibited the following properties: b.p. 119.5–120° (23 mm.), n_{D}^{25} 1.4421, d_4^{25} 0.8905.

Anal. Calcd. for $C_{11}H_{24}O_2Si$: C, 61.05; H, 11.18; mol. wt., 216; MR_{D}, 64.48. Found: C, 60.90; H, 11.14; mol. wt. (Rast), 192; MR_{D}, 64.31.

The proton magnetic resonance spectrum was determined using the Varian Associates High Resolution Spectrometer (V-4300B), operated at 40 mc. and 9394.7 Gauss.

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[16] Boiling points are uncorrected.

[17] The microanalysis was performed by Dr. Adalbert Elek, Elek Microanalytical Laboratories, Los Angeles, Calif.

[18] The calculated molar refractivity was computed from bond refractivity values listed in the following references: A. I. Vogel, W. T. Cresswell, G. H. Jeffery, and J. Leicester, *Chem. & Ind.* (*London*), **1950**, 358; A. I. Vogel, W. T. Cresswell, and J. Leicester, *J. Phys. Chem.*, **58**, 174 (1954).

Some *N*-Arylated Heterocycles as Liquid Scintillator Solutes

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In order to gain some insight into the effect of the point of attachment of polyaryls on their efficiency as liquid scintillator solutes, a number of *N*-aryl heterocycles and related amines have been screened for this purpose (Table I). Although some of the values are out of line with closely related compounds, a few structural relationships are beginning to emerge.

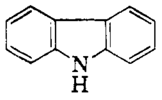
TABLE I

PRIMARY-SOLUTE RELATIVE PULSE HEIGHTS

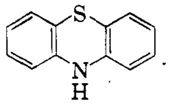
No.	Compound	Relative Pulse Heights
1.	4-Biphenylyldiphenylamine	0.39[a]
2.	Bis-4-biphenylylamine	0.95[a]
3.	Bis-4-biphenylylphenylamine	0.61[a]
4.	Tris-4-biphenylylamine	0.58[a]
5.	9-Phenylcarbazole	0.24[b]
6.	9-(4-Biphenylyl)carbazole	0.35[b]
7.	*p*-Bis(9-carbazolyl)benzene	0.27[b]
8.	4,4′-Bis(9-carbazolyl)biphenyl	0.93[b]
9.	Phenoxazine	<0.10[c]
10.	10-Phenylphenoxazine	<0.10[c]
11.	10-Benzylphenoxazine	0.10[c]
12.	10-(2-Bromophenyl)phenoxazine	<0.10[c]
13.	10-(4-Bromophenyl)phenoxazine	<0.10[c]
14.	10-(4-Biphenylyl)phenoxazine	<0.10[c]
15.	*p*-Bis-(10-phenoxazyl)benzene	<0.10[c]
16.	4,4′-Bis(10-phenoxazyl)biphenyl	<0.10[c]
17.	10-Allylphenothiazine	<0.10[d]
18.	10-Phenylphenothiazine	<0.10[e]
19.	10-Phenylphenothiazine-5-oxide	<0.10[d]
20.	10-Phenylphenothiazine-5,5-dioxide	<0.10[f]
21.	10-(*o*-Tolyl)phenothiazine	<0.10[g]
22.	10-(4-Biphenylyl)phenothiazine	<0.10[h]
23.	*p*-Bis-(10-phenothiazinyl)benzene	<0.10[h]

[a] J. Piccard, *Helv. Chim. Acta*, **7**, 789 (1924). [b] H. Gilman and J. B. Honeycutt, *J. Org. Chem.*, **22**, 226 (1957). [c] H. Gilman and L. O. Moore, *J. Am. Chem. Soc.*, **79**, 3485 (1957). [d] H. Gilman and D. A. Shirley, *J. Am. Chem. Soc.*, **66**, 888 (1944). [e] H. Gilman, P. R. Van Ess, and D. A. Shirley, *J. Am. Chem. Soc.*, **66**, 1214 (1944). [f] C. Finzi, *Gazz. chim. ital.*, **62**, 175 (1932). [g] H. Gilman, R. D. Nelson, and J. F. Champaigne, Jr., *J. Am. Chem. Soc.*, **74**, 4205 (1952). [h] See Experimental.

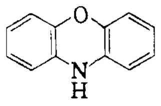
The three heterocycles under consideration, carbazole (I), phenothiazine (II) and phenoxazine (III), differ only in the manner of bridging two benzene rings bonded to the same nitrogen atom. Derivatives of the sulfur heterocycle, II, were expected to have poor values on the basis of a previous investigation,[1] and, in fact, gave no values at all; the corresponding oxidized derivatives (Compounds 19 and 20) also fail to respond. The phenoxazine derivatives give no measurable pulse height, but this may be a side effect attributable to the persistent color of these derivatives, which probably



I



II



III

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

results in some self-quenching.[2] It has been previously noted in the case of dibenzofuran and dibenzo-*p*-dioxin[3] that the direct union of two benzene rings in a heterocycle, provides a more efficient scintillator nucleus than the corresponding heterocycle with an oxygen bridge. This is clearly confirmed in the comparison of derivatives of I and II. The 9-aryl carbazoles give values ranging from 0.24 to 0.93 (Compounds 5 through 9) while exactly analogous phenoxazine derivatives (Compounds 10, 14, 15, and 16) all fail to respond within the sensitivity of the instrument. The amine related to Compounds 5 and 9, triphenylamine, has been reported[4] to have a very low value (about 0.06 on our scale), markedly lower than that of 9-phenylcarbazole. 4-Biphenylyldiphenylamine (Compound 1) on the other hand has a slightly higher value than the corresponding carbazole derivative (Compound 6).

The synthetic methods employed in the preparation of these compounds are listed in the footnotes to Table I and appear to be completely general. An extension of these methods may prove rewarding in view of the fact that Compound 8 with six benzene rings is soluble to the extent of about 5 g./l. in toluene. A number of promising scintillator solutes, notably 1,4-di[2-(5-phenyloxazolyl)]benzene and 2,5-di(4-biphenylyl)oxazole,[5] have been relegated to use as secondary solutes because of poor solubility in toluene.

The values reported in Table I were measured in the pulse height analyzer previously described,[1] and all were measured at a concentration of 3 g./l. in toluene except compound 16, which, due to limited solubility, was measured as a saturated solution. All values are relative to 2,5-diphenyloxazole which is assigned the arbitrary value of 1.00.

EXPERIMENTAL[6]

10-(4-Biphenylyl)phenothiazine. Twenty grams (0.10 mole) of phenothiazine, 35 g. (0.15 mole) of 4-bromobiphenyl, 12 g. (0.11 mole) of anhydrous sodium carbonate, and 1 g. of copper powder were stirred at 150–160° for 16 hr. After this period the temperature was raised to 200° where it was maintained for an additional 4 hr. Steam distillation of the mixture afforded 15 g. (43%) of unreacted 4-bromobiphenyl. The undistilled residue was extracted with benzene, and this solution was chromatographed on alumina and eluted with more benzene. Evaporation of the eluate left 29 g. of hard resinous solid, melting at 140–170°. Two crystallizations from an acetone-water pair afforded 20 g. (57.5%) of pale yellow powder, melting at 174–178°.

Anal. Calcd. for $C_{24}H_{17}NS$: S, 9.12. Found: S, 9.24, 9.37.

p-Bis(10-phenothiazinyl)benzene. Twenty-four grams (0.12 mole) of phenothiazine, 16.5 g. (0.05 mole) of *p*-diiodobenzene, 12 g. (0.11 mole) of anhydrous sodium carbonate, and 1 g. of copper powder were stirred at 200° for 12 hr. During this period it was necessary to scrape the sublimed *p*-diiodobenzene from the sides of the reaction vessel in order to return it to the reacting mass. After cooling to room temperature the solid was crushed and extracted with five 200-ml. portions of benzene. The benzene was removed and the residue was extracted with three 20-ml. portions of absolute ethanol to remove unreacted *p*-diiodobenzene and phenothiazine. The remaining material was chromatographed on alumina using benzene as solvent and eluant. Removal of the solvent from the eluate left 18 g. of material melting at 248–250°. Recrystallization from benzene gave 16.5 g. (70%), m.p. 253–255°.

Anal. Calcd. for $C_{30}H_{20}N_2S_2$: S, 13.57. Found: S, 13.70, 13.70.

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[2] For discussion of this phenomenon see (a) V. N. Kerr, F. N. Hayes, and D. G. Ott, *Intern. J. Appl. Radiation and Isotopes*, **1**, 284 (1957); (b) D. G. Ott, F. N. Hayes, E. Hansbury, and V. N. Kerr, *J. Am. Chem. Soc.*, **79**, 5448 (1957).

[3] H. Gilman, E. A. Weipert, J. J. Dietrich, and F. N. Hayes, *J. Org. Chem.*, in press.

[4] H. Kallman and M. Furst, *Nucleonics*, **8**, No. 3, 32 (1951).

[5] F. N. Hayes, D. G. Ott, and V. N. Kerr, *Nucleonics*, **14**, No. 1, 42 (1956).

[6] Melting points are uncorrected.

Rearrangement in the Reactions of *p*-Halotoluenes with Potassium Anilide[1]

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In recent years it has been shown that alkali amides in liquid ammonia[2–4] and refluxing piperidine[5,6] and organolithium compounds[7,8] react with non-activated aryl halides by the way of benzyne (I) intermediates. Strong bases and nucleophiles in liquid ammonia react with aryl halides in liquid

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[1] (a) Taken in part from the Ph.D. thesis of Franco Scardiglia, California Institute of Technology, 1957; (b) This research was supported in part by a grant from The Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of said fund.

[2] J. D. Roberts, D. A. Semenow, H. E. Simmons, Jr., and L. A. Carlsmith, *J. Am. Chem. Soc.*, **78**, 601 (1956).

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[4] J. D. Roberts, H. E. Simmons, Jr., L. A. Carlsmith, and C. W. Vaughan, *J. Am. Chem. Soc.*, **75**, 3290 (1953).

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[6] J. F. Bunnett and T. K. Brotherton, *J. Am. Chem. Soc.*, **78**, 6265 (1956).

[7] E. Jenny and J. D. Roberts, *Helv. Chim. Acta*, **38**, 1248 (1956).

[8] R. Huisgen and H. Rist, *Naturwiss.*, **41**, 358 (1954); *Ann.*, **594**, 137 (1955).