ysis of *o*-tolyl ethyl xanthate by this method,[5] the yield obtained in our experiments was not more than 37%, based on the starting material, *o*-toluidine.

2,6-Dimethylthiophenol. Application of the lithium aluminum hydride reduction described above using 60.5 g. (0.5 mole) of 2,6-dimethylaniline as the starting material yielded 59.4 g. (86% overall) of colorless 2,6-dimethylthiophenol, b.p. 111° (25 mm.), n_D^{25} 1.5712, d^{25} 1.038.

Anal. Calcd. for $C_8H_{10}S$: S, 23.20; Found: S, 23.03.

When the crude 2,6-xylyl ethyl xanthate was hydrolyzed in the conventional manner,[2] the yield was 34 g. (49%) based on 60.5 g. (0.5 mole) of 2,6-dimethylaniline.

2,6-Dimethylphenyl disulfide. A solution of 6.9 g. (0.05 mole) of 2,6-dimethylthiophenol, in 15 ml. of ethanol, was treated with 6.7 g. (0.026 mole) of iodine. Upon stirring, the mixture became warm and the disulfide rapidly precipitated. The mixture was cooled and the disulfide was collected by filtration and washed with cold 80% ethanol, yielding 6.65 g. (97%) of light yellow crystals. After three recrystallizations from 80% ethanol, white needles weighing 5.3 g. (77%) were obtained.

Anal. Calcd. for $C_{16}H_{18}S_2$: S, 23.37; Found 23.13.

2,6-Dimethylphenyl 2,4-dinitrophenyl sulfide. A 2,4-dinitrophenyl sulfide was prepared from 2,6-dimethylthiophenol by treating an alcoholic solution of the thiol, containing an equivalent amount of sodium hydroxide solution, with an equimolar quantity of 2,4-dinitrochlorobenzene dissolved in alcohol. After recrystallization from ethanol, yellow needles were obtained which melted at 124.5–125°.

Anal. Calcd. for $C_{14}H_{12}O_4N_2S$: C, 55.25; H, 3.97. Found: C, 55.59; H, 4.01.

o-Phenylthiophenol. When 51.5 g. (0.25 mole) of finely ground *o*-aminobiphenyl hydrochloride was used as the starting material, and the crude xanthate cleaved with lithium aluminum hydride, 39.0 g. (84%) of *o*-phenylthiophenol was obtained, b.p. 105° (0.5 mm.), n_D^{25} 1.6403, d^{25} 1.076.

Anal. Calcd. for $C_{12}H_{10}S$: S, 17.21; Found: S, 16.94.

Alkaline hydrolysis of the crude xanthate prepared from 51.5 g. (0.25 mole) of *o*-aminobiphenyl hydrochloride yielded 9.8 g. (21%) of *o*-phenylthiophenol boiling at 104–105° (0.5 mm.).

o-Phenylthiophenol disulfide.[6] Oxidation with iodine of a crude sample of *o*-phenylthiophenol, prepared by the alkaline hydrolysis of *o*-biphenyl ethyl xanthate, gave the disulfide in 23% yield (based on the original amine). When an aqueous, alkaline solution of *o*-phenylthiophenol (prepared by alkaline hydrolysis of the xanthate for 24 hr. and worked up in the usual way[2]) was treated with equivalent quantities of 3% hydrogen peroxide or ammonium persulfate, the disulfide was obtained directly in 55 and 58% yields, respectively. It precipitated upon standing and was recrystallized from acetone to give pale yellow plates, m.p. 115.5–116°.

Anal. Calcd. for $C_{24}H_{18}S_2$: C, 77.80; H, 4.89; S, 17.31. Found: C, 77.52; H, 5.07; S, 17.21.

o-Biphenyl 2,4-dinitrophenyl sulfide. Treatment of an alkaline alcoholic solution of the above thiol with 2,4-dinitrochlorobenzene produced a yellow solid which, after recrystallization from ethanol, yielded yellow needles, m.p. 132.5–133°.

Anal. Calcd. for $C_{18}H_{12}O_4N_2S$: C, 61.35; H, 3.43. Found: C, 61.58; H, 3.46.

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[5] E. Bourgeois, *Rec. trav. chim.*, **18**, 447 (1899).

[6] Prepared by Dr. L. Ergener in these laboratories.

Some Azo Derivatives of 9-Ethylcarbazole

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Since the first azo dye containing the carbazole nucleus was reported in 1888[1] a large number of dyes and pigments incorporating the carbazolylazo group have been prepared by the dyestuff industry. Cohn[2] and Freudenberg[3] give good accounts of the carbazole dyes while the more extensive coverages of Grimmel,[4] Lubs,[5] and Venkataraman[6] include carbazole derivatives in conjunction with other compounds making up the various classes of dyes.

The incentive for the preparation of 9-ethylcarbazole dyes was the reports by Farr[7,8] and Kruger[9,10] on the use of boron-containing compounds in brain tumor therapy. Kruger[10] used boronic acid azo dyes prepared by Snyder[11,12] in place of the borax used previously. We wished to synthesize carbazole derivatives which contained both the azo linkage and a boronic acid group. Two possibilities of preparing the desired compounds were considered. One was coupling diazotized aminobenzeneboronic acids, prepared by Johnson and coworkers,[13,14] with 9-ethylcarbazole and the other was condensing diazotized 3-amino-9-ethylcarbazole with hydroxybenzeneboronic acids.[14,15] Prior to use of the boron compounds range-finding experiments were performed with more readily available amines and phenols and we are now reporting the results of those experiments.

Diazotized 2,4-dinitroaniline and *p*-nitroaniline were sufficiently reactive to couple with 9-ethyl-

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[1] Ger. Patent **46,438**.

[2] G. Cohn, "Die Carbazolgruppe," Georg Thieme, Leipzig.

[3] W. Freudenberg, in R. C. Elderfield, *Heterocyclic Compounds*, Vol. 3, John Wiley and Sons, Inc., New York, N. Y., 1952, pp. 291–341.

[4] H. W. Grimmel, in H. Gilman, *Organic Chemistry, An Advanced Treatise*, Vol. 3, John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 243–391.

[5] H. A. Lubs, *The Chemistry of Synthetic Dyes and Pigments*, Reinhold Publishing Corp., New York, N. Y., 1955.

[6] K. Venkataraman, *The Chemistry of Synthetic Dyes*, Academic Press, Inc., New York, N. Y., 1952.

[7] L. E. Farr, W. H. Sweet, J. S. Robertson, C. G. Foster, H. B. Locksley, D. L. Sutherland, M. L. Mendelsohn, and E. E. Stickley, *Am. J. Roentgenol. Radium Therapy Nuclear Med.*, **71**, 279 (1954).

[8] L. E. Farr, J. S. Robertson, and E. E. Stickley, *Proc. Nat. Acad. Sci.*, **40**, 1087 (1954).

[9] P. G. Kruger, *Proc. Nat. Acad. Sci.*, **26**, 181 (1940).

[10] P. G. Kruger, *Radiation Research* **3**, 1 (1955).

[11] H. R. Snyder and C. R. Weaver, *J. Am. Chem. Soc.*, **70**, 232 (1948).

[12] H. R. Snyder and S. L. Meisel, *J. Am. Chem. Soc.*, **70**, 774 (1948).

[13] W. Seaman and J. R. Johnson, *J. Am. Chem. Soc.*, **53**, 711 (1931).

[14] F. R. Bean and J. R. Johnson, *J. Am. Chem. Soc.*, **54**, 4415 (1932).

[15] D. R. Swayampati, unpublished studies.

carbazole while *o*-nitro- and *o*- and *p*-bromoaniline gave diazonium salts which have not as yet been successfully coupled with the heterocycle. Diazotized *p*-aminobenzoic acid, likewise, has not yet been condensed with 9-ethylcarbazole. Since the C_3 position is the carbon atom with the greatest electron density in the carbazole system the azo derivatives were assigned the structures 3-(2,4-dinitrophenylazo)- and 3-(*p*-nitrophenylazo)-9-ethylcarbazole, respectively. The infrared spectra also supported these structures.

Consideration of the mesomeric and inductive effects of the various substituents on the aniline molecule explains the results, although the reason for the failure of *o*-nitrobenzenediazonium chloride to couple is uncertain. Since the results indicate that a diazonium salt must be at least as reactive as *p*-nitrobenzenediazonium chloride to couple with 9-ethylcarbazole it is believed that the simple, unsubstituted, diazotized aminobenzeneboronic acids may not be sufficiently reactive to couple with the carbazole derivative. The most readily available aromatic aminoboronic acid is *m*-aminobenzeneboronic acid[13] in which the electron-withdrawing boron atom is not situated so as to increase the positive character of a diazonium group. Furthermore, the inductive effect of a boronic acid function would act so as to increase the electron density of the benzene ring thus inhibiting coupling.

Diazotized 3-amino-9-ethylcarbazole was reacted with phenol, 2-naphthol, and *o*-hydroxybenzeneboronic acid anhydride.[15] The reaction product from phenol was a fluffy yellow solid which did not analyze correctly for 3-(*p*-hydroxyphenylazo)-9-ethylcarbazole or for a disazo compound. The infrared spectrum, however, contained a band at 6.4μ which is indicative of a N=N bond and which was found in the spectra of the other azo derivatives prepared in this study. 2-Naphthol and 9-ethylcarbazole-3-diazonium chloride gave maroon needles of 3-(2-hydroxy-1-naphthylazo)-9-ethylcarbazole. The addition of diazotized 3-amino-9-ethylcarbazole to an alkaline solution of *o*-hydroxybenzeneboronic acid anhydride gave a progressive color change. The only products obtained after attempted purification by crystallization or chromatography were tars and oils.

In unpublished studies by other workers in these laboratories benzenediazonium chloride and monosubstituted benzenediazonium chlorides have been coupled with *o*-hydroxybenzeneboronic acid anhydride.

EXPERIMENTAL[16]

3-(2,4-Dinitrophenylazo)-9-ethylcarbazole. The diazonium salt solution prepared from 3.7 g. (0.02 mole) of 2,4-dinitroaniline and nitrosylsulfuric acid solution[17] was filtered into a stirred solution of 3.9 g. (0.02 mole) of 9-ethylcarbazole in 150 ml. of ethanol and 10 ml. of a 10% aqueous sodium hydroxide solution. Stirring was continued for 10 hr. and the resulting red solid was filtered off and air-dried. Repeated recrystallizations from glacial acetic acid gave 0.6 g. (0.7%) of maroon needles melting at 214–215° (dec.).

Anal. Calcd. for $C_{20}H_{15}N_5O$: N, 18.46%. Found: N, 18.68, 18.57%.

3-(p-Nitrophenylazo)-9-ethylcarbazole. The diazonium salt solution prepared in the usual manner from 1.4 g. (0.01 mole) of *p*-nitroaniline and hydrochloric acid was filtered into a stirred solution of 1.95 g. (0.01 mole) of 9-ethylcarbazole in 50 ml. of glacial acetic acid which had been cooled to 14°. After 30 min. 16.0 g. (0.2 mole) of anhydrous sodium acetate was added slowly and stirring was continued for 5 hr. The orange solid was separated and recrystallized twice from glacial acetic acid (Norit-A) to give 0.05 g. (1.4%) of reddish needles melting at 183–184°. Further recrystallization did not raise the melting point.

Anal. Calcd. for $C_{20}H_{16}N_4O_2$: N, 16.27%. Found: N, 16.10, 16.19%.

Reaction of diazotized 3-amino-9-ethylcarbazole with phenol. The diazonium salt solution from 2.1 g. (0.01 mole) of 3-amino-9-ethylcarbazole and hydrochloric acid was filtered into 0.94 g. (0.01 mole) of phenol, 2.9 g. (0.072 mole) of sodium hydroxide, and 3.8 g. (0.036 mole) of anhydrous sodium carbonate in 50 ml. of water which had previously been cooled to 1°. Stirring was continued for 6 hr. and the mixture, which contained no precipitate, was acidified with 3*N* hydrochloric acid while being stirred in an ice bath to give a black solid. A hot ethanolic solution of the washed solid was treated with Norit-A, filtered, and cooled, but gave no solid product. The solution was poured into water to give a dark oil which was separated from the aqueous phase. Dissolution in benzene, treatment with Norit-A, and cooling gave 1.6 g. (50.8%) of yellow fibrous material melting over the range 127–141° with darkening. Two recrystallizations from benzene (Norit-A) gave 0.25 g. (7.9%) of a yellow solid melting 130–132° (dec.). Analysis of the compound gave precise results for nitrogen content which were not, however, in accord with the calculated amount of nitrogen for either the monoazo derivative or the disazo derivative.

Anal. Calcd. for $C_{20}H_{17}N_3O$ (monoazo deriv.): N, 13.32%. Calcd. for $C_{34}H_{28}N_6O$ (disazo deriv.): N, 15.66%. Found: N, 11.18, 11.25%.

3-(2-Hydroxy-1-naphthylazo)-9-ethylcarbazole. 9-Ethylcarbazole-3-diazonium chloride [from 2.1 g. (0.01 mole) of 3-amino-9-ethylcarbazole] was filtered into a cold stirred solution of 1.44 g. (0.01 mole) of 2-naphthol, 2.9 g. (0.072 mole) of sodium hydroxide, and 3.8 g. (0.036 mole) of anhydrous sodium carbonate in 50 ml. of water. Stirring was continued for 6 hr. with the internal temperature below 5° and for an additional 4 hr. while the mixture warmed to room temperature. The maroon solid was filtered off and washed with water; 3.05 g. (83.5%) melting over a range of 161–180°. One g. of the solid was chromatographed through 40.0 g. of a 1:2 Celite–silicic acid mixture using toluene as the eluant. The main fraction yielded 0.7 g. (19.1%) of maroon needles melting at 179–181°. Portions of the remaining crude product could not be recrystallized from benzene, ethanol, or petroleum ether (b.p. 60–70°) or from a mixture of these solvents.

Anal. Calcd. for $C_{24}H_{19}N_3O$: N, 11.79%. Found: N, 11.82, 11.98%.

Acknowledgment. We wish to thank Mr. Robert McCord of the Ames Laboratory of the Atomic Energy Commission for the infrared spectra.

Particular acknowledgment is made to the Division of Biology and Medicine of the United States Atomic Energy Commission under whose auspices

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[16] All melting points are uncorrected.

[17] S. V. Sunthankar and H. Gilman, *J. Org. Chem.*, **15**, 1200 (1950).

this work is being undertaken. Results of the biological tests will be reported by Dr. Otho E. Easterday of the Brookhaven National Laboratory.

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Phenyl and *p*-Trimethylsilylphenyl Compounds of Silicon, Germanium, and Tin

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We wish to report several new compounds of silicon, germanium, and tin, containing phenyl and *p*-trimethylsilylphenyl substituents (Table I) which have been synthesized by treatment of an appropriate chlorine compound with *p*-trimethylsilylphenyllithium.

$$2p\text{-}(CH_3)_3SiC_6H_4Li + (C_6H_5)_2SiCl_2 \longrightarrow [p\text{-}(CH_3)_3SiC_6H_4]_2Si(C_6H_5)_2 + 2LiCl$$

TABLE I

COMPOUNDS PREPARED FROM *p*-TRIMETHYLSILYLPHENYLLITHIUM

Reagent	Moles of RLi / Moles of the chlorine compound	Reaction Time, Hr.	Product	M.P., °C.	Yield, %	Formula	Analyses Element	Analyses Calcd.	Analyses Found
$(C_6H_5)_3SiCl$	1.2	8[a]	Triphenyl(*p*-trimethylsilylphenyl)silane	163–165[b]	83	$C_{27}H_{28}Si_2$	Si	13.8	13.5, 13.8
$(C_6H_5)_2SiCl_2$	2.3	1[a]	Diphenylbis(*p*-trimethylsilylphenyl)silane[c]	163.5–165[b]	86	$C_{30}H_{36}Si_3$	Si	17.5	17.4, 17.3
$SiCl_4$	6.3	12[d]	Tetrakis(*p*-trimethylsilylphenyl)silane	355–357[e]	77	$C_{36}H_{52}Si_5$	Si	22.4	22.3, 22.2
$GeCl_4$	5.3	12[f]	Tetrakis(*p*-trimethylsilylphenyl)germane	351–354[g]	49	$C_{36}H_{52}GeSi_4$	Si	16.8	17.1, 17.2
$SnCl_4$	4.5	12[a]	Tetrakis(*p*-trimethylsilylphenyl)tin	343–345[h]	58	$C_{36}H_{52}Si_4Sn$	Si Sn	15.7 16.6	15.5, 15.6 16.6, 16.0

[a] Reaction carried out at 0 to 25°. [b] Recrystallized from absolute ethanol. A mixed melting point between these compounds was depressed.[c] A mixture of the *o*-, *p*- and *m*-isomers has been reported previously by H. A. Clark, U. S. Patent **2,507,515** [*Chem. Abstr.*, **45**, 2197 (1951)]; Brit. Patent **669,179** [*Chem. Abstr.*, **46**, 8894 (1952)].[d] Reaction carried out at reflux temperature. [e] Recrystallized from absolute ethanol–chloroform (2:1) and from absolute ethanol–methyl ethyl ketone (2:1). [f] The ether was distilled off and replaced by toluene at reflux temperature. [g] The crude product was freed from a less soluble impurity by extraction with a minimum volume of cold benzene, and then was recrystallized from benzene–absolute ethanol. [h] Recrystallized from absolute ethanol–benzene (1:1) and from petroleum ether (b.p. 100–120°).

The last three compounds (Table I), which differ only in the central atom, have nearly the same melting points. When these compounds are admixed in pairs the melting points are not depressed below those of the lower melting components. Presumably they constitute an isomorphic series. Similarly it has been reported[1] that mixtures of tetraphenylsilane and tetraphenylgermane show no depression in melting point, although mixtures of tetraphenylgermane and tetraphenyltin do show a slight depression.

EXPERIMENTAL[2]

Diphenylbis(p-trimethylsilylphenyl)silane. *p*-Trimethylsilylphenyllithium[3] was prepared by adding 22.9 g. (0.1 mole) of trimethyl(*p*-bromophenyl)silane[4] in 100 ml. of ether to 1.8 g. (0.26 g.-atom) of lithium in 140 ml. of ether during 90 min. under spontaneous reflux. The yield was 80%, determined by titration of the total base formed on hydrolysis. The excess lithium was removed by filtration. A solution of 8.85 g. (0.035 mole) of diphenyldichlorosilane in 100 ml. of ether was added during 30 min. at 0 to 5°. The mixture was allowed to warm to room temperature during 30 min., by which time Color Test I[5] was negative. After hydrolyzing the reaction mixture with cold dilute sulfuric acid, the ether layer was separated, dried over sodium sulfate, and distilled, leaving a residue, which after crystallization from absolute ethanol melted at 160–163.5° and weighed 14.4 g. (86%). A second recrystallization gave 13.5 g. (80%) of crystals, m.p. 162.5–164.5°. The analytical sample melted at 163.5–165°.

Anal. Calcd. for $C_{30}H_{36}Si_3$: Si, 17.5. Found: Si, 17.4, 17.3.

Elementary analyses. It has been observed in this laboratory that silicon analyses performed by the sulfuric acid digestion procedure[6] give erratically low results with com-

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(1) H. D. K. Drew and J. K. Landquist, *J. Chem. Soc.* 1480 (1935). It might be mentioned in this connection that Dr. T. C. Wu in this laboratory has observed that a mixture of all of the tetraphenyl derivatives of carbon, silicon, germanium, tin, and lead melted at 218–220°.

(2) Melting points are uncorrected. All operations involving organolithium compounds were carried out under an atmosphere of dry, oxygen-free nitrogen, in sodium-dried ethyl ether.

(3) Adapted from procedures kindly supplied by Dr. Horace W. Melvin of this laboratory.

(4) C. A. Burkhard, *J. Am. Chem. Soc.*, **68**, 2103 (1946); H. Gilman, H. W. Melvin, and J. J. Goodman, *J. Am. Chem. Soc.*, **76**, 3219 (1954).

(5) H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

(6) H. Gilman, B. Hofferth, H. W. Melvin, and G. E. Dunn, *J. Am. Chem. Soc.*, **72**, 5767 (1950).