late was redistilled on a 20-plate spinning band column. When triphenylborane was employed, *n*-heptane was used as a solvent.

Preparation of $RB[N(CH_3)_2]_2$ *compounds.* The butylboroxines, (0.033 mole) were allowed to react with 0.1 mole of trisdimethylaminoalane at 75° for 1 hr. The reaction mixture was distilled under high vacuum keeping the pot temperature below 70°. The crude product was purified as above. When *n*-butylboroxine was employed, the reactants were placed in the pot of the spinning band column and heated to 50° for 15 min. The product was then distilled directly from the reaction mixture under vacuum. The pot temperature was maintained at 50–55° in an effort to minimize the disproportionation of the product.

Preparation of $\phi B[N(CH_3)_2]_2$. Diethyl phenyl boronate (0.1 mole) was allowed to react with trisdimethylaminoalane (0.05 mole) for 1 hr. at 85–90°. Distillation under high vacuum separated the crude product from the reaction mixture. Purification was accomplished by distillation on a 20-plate spinning band column. The reaction of ethyl diphenyl borinite (0.2 mole) with the alane (0.1 mole) was performed in the same manner.

Preparation of $B[N(CH_3)_2]_3$. Lithium aluminum hydride (0.22 mole) was dissolved in 400 ml. of ether in a 3-neck flask equipped with a stirrer, condenser, and a nitrogen purge. Solid trimethylammonium chloride (0.2 mole) was slowly added. After reaction was complete, gaseous dimethylamine was passed into the mixture for approximately 2 hr. Then 0.15 mole of tri-*n*-butylborate in 200 ml. of ether was added. The mixture was refluxed 1 hr. and filtered. The ether was distilled from the filtrate until a pot temperature of 50–55° was obtained. The system was evacuated and the product distilled under high vacuum into a −80° trap. It was necessary to heat the residue at 100° for several hours to obtain good yields. The crude product was purified by distillation on a 20 plate spinning band column.

Preparation of $RBHN(CH_3)_2$ *compounds.* Trimethylamine-*s*-butylborane or trimethylamine-*t*-butylborane, 8 g., was added slowly to 5 g. of trisdimethylaminoalane. After the addition was complete, the mixture was warmed slowly to 70° and heated for 0.5 hr. The products were distilled directly out of the reaction mixture under vacuum. Under these conditions trimethylamine-*n*-butylborane produced bisdimethylamine-*n*-butylborane and other products expected from the disproportionation of the bisaminoborane.

The reaction employing an excess of the borane did produce a low yield of the desired material. A 0.12-mole sample of the borane was allowed to react with 0.04 mole of trisdimethylaminoalane in 10 ml. of hexane. The mixture was refluxed for 15 min. and the volatile components were removed under high vacuum at ambient temperature. They were then distilled at atmosphere pressure on a Holtzmann column.

NMR spectra. The B^{11} NMR spectra of the compounds prepared were obtained on the neat liquids with a Varian Model V4300 B spectrometer operating at 12.8 megacycles.

Molecular weight determinations. The apparent molecular weights of some of the compounds were determined cryoscopically in benzene. The apparatus and the method of preparation of the solutions were described previously.[5]

Acknowledgment. The author wishes to thank Mr. R. D. Strahm for the analyses and Mrs. C. P. Haney for the NMR spectra. The work was performed under contract number DA-01-021-ORD-784.

HUNTSVILLE, ALA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY AT IOWA STATE UNIVERSITY]

The Synthesis of Some Organosilicon Compounds, Particularly Those Containing Halophenyl Groups

HENRY GILMAN, RICHARD D. GORSICH, AND BERNARD J. GAJ

Received August 14, 1961

A series of organosilicon compounds containing halophenyl groups has been obtained by treating the appropriately substituted chlorosilanes with *m*-fluorophenyl-, *m*-chlorophenyl-, and *p*-chlorophenyllithium. Several new compounds having either the $R_3Si(CH_2)_nSiR_3$, $R_3SiC_6H_4SiR_3$, or $R_3SiC_6H_4C_6H_4SiR_3$ structure have been prepared.

We are reporting the synthesis and physical constants for a number of organosilicon compounds and one organogermanium compound. The tetrasubstituted silanes listed in Tables I and II were prepared by treating either *m*-fluorophenyl-, *m*-chlorophenyl-, or *p*-chlorophenyllithium with the appropriate chlorosilane or silicon tetrachloride. The halophenyllithium compounds were obtained *via* the halogen-metal interconversion reaction[1] employing *n*-butyllithium and the proper bromochloro- or bromofluorobenzene in diethyl ether. The equations depicting the synthesis of di(*m*-fluorophenyl)diphenylsilane illustrate the general procedure used:

$$n\text{-}C_4H_9Li + m\text{-}FC_6H_4Br \xrightarrow{-40^\circ} n\text{-}C_4H_9Br + m\text{-}FC_6H_4Li$$

$$2\ m\text{-}FC_6H_4Li + Cl_2Si(C_6H_5)_2 \longrightarrow (m\text{-}FC_6H_4)_2Si(C_6H_5)_2 + 2LiCl$$

In Table III are listed eight new compounds having either the $R_3Si(CH_2)_nSiR_3$, $R_3SiC_6H_4SiR_3$, or $R_3SiC_6H_4C_6H_4SiR_3$ structure. The first six were prepared by the reaction of 1,2-ethylenebis-, *m*-phenylenebis-, and *p*-phenylenebis(trichlorosilane) with an organometallic compound; benzylmagnesium chloride was employed in the synthesis of the tribenzylsilyl derivatives, and alkyllithium compounds were used for the trialkylsilyl types.

$$6\ RLi + Cl_3SiCH_2CH_2SiCl_3 \longrightarrow R_3SiCH_2CH_2SiR_3 + 6LiCl$$

---

(1) For a general discussion and bibliography on the halogen-metal interconversion reaction, see R. G. Jones and H. Gilman in *Organic Reactions*, **Vol. VI**, R. Adams, ed., John Wiley and Sons, Inc., New York, 1951, pp. 339–366.

TABLE I

COMPOUNDS PREPARED FROM *m*-FLUOROPHENYLLITHIUM

Compound $R = m\text{-}FC_6H_4$	M.P.	B.P. (mm.)	Yield, %	Si Calcd.	Si Found
$RSi(C_6H_5)_3$	207–208[a]		51	7.92	7.68, 7.75
$R_2Si(C_6H_5)_2$	195–196[b]		26	7.53	7.67, 7.53[c]
$R_3SiC_6H_5$	191.5–193[d]		51	7.14	7.04, 7.22
R_4Si	196–197[e]		62	6.87	6.67, 6.64
$R_3Si(CH_2)_{11}CH_3$	35–37[f]	197–198 (0.02)[g]	62	5.81	5.68, 5.81
$R_3Si(CH_2)_{15}CH_3$	36–38[h]	214–217 (0.05)	71	5.21	5.21, 5.29[i]
$R_3Si(CH_2)_{17}CH_3$	38–40[j]	234–235 (0.08)	71	4.95	5.07, 4.99

[a] Crystallized from glacial acetic acid. [b] Crystallized from petroleum ether (b.p. 60–70°). [c] *Anal.* Calcd. for $C_{24}H_{18}F_2Si$: C, 77.39; H, 4.87. Found: C, 77.44, 77.54; H, 4.79, 4.77. [d] Crystallized from dioxane. [e] Crystallized from petroleum ether (b.p. 77–115°). [f] Crystallized on long standing. [g] n^{20}_D 1.5358. [h] Crystallized on cooling to 10°. [i] *Anal.* Calcd. for $C_{34}H_{45}F_3Si$: C, 75.80; H, 8.42. Found: C, 75.96, 76.17; H, 8.42, 8.39. [j] Crystallized on cooling to 0°.

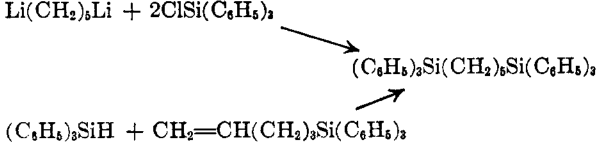
TABLE II

COMPOUNDS PREPARED FROM *m*- OR *p*-CHLOROPHENYLLITHIUM

Compound[a]	M.P.	B.P. (mm.)	Yield, %	n^{25}_D	d^{25}	MR[b] Calcd.	MR[b] Found	Si Calcd.	Si Found
$RSi(C_6H_5)_3$	156–157[c]		78					7.57	7.63 7.46
$R_2Si(C_6H_5)_2$	110–111[c]		80					6.92	6.92 6.75
$R_3SiC_6H_5$	87.5–89[c]		43					6.38	6.44 6.43
R_4Si	148–149[d]		43					5.92	5.96 5.97
$R_3Si(CH_2)_{11}CH_3$		229–230 (0.086)	78.5					5.28	5.21 5.07
$R_3Si(CH_2)_{15}CH_3$		240–241 (<0.01)	65.8	1.5579	1.078	173.7	175.9	4.78	4.76 4.85
$R_3Si(CH_2)_{17}CH_3$		250–255 (0.04)	87.4	1.5595	1.035	183	183.5	4.56	4.32 4.52
$R_3'Si(CH_2)_{15}CH_3$		246–251 (0.03)	65.6	1.5530	1.071	173.7	175.7	4.78	4.88 4.89
$R_3'Si(CH_2)_{17}CH_3$		255–262 (0.001)	76.8	1.5558	1.075	183	183.4	4.56	4.46 4.53

[a] R = *m*-ClC_6H_4; and R′ = *p*-ClC_6H_4. [b] Molecular refractions were calculated using the bond refraction values of A. I. Vogel, W. T. Cresswell, and J. Leicester, *J. Phys. Chem.*, **58**, 174 (1954); A. I. Vogel, W. T. Cresswell, G. H. Jeffery, and J. Leicester, *J. Chem. Soc.*, 514 (1952). [c] Crystallized from ethanol. [d] Crystallized from petroleum ether (b.p. 77–115°).

The last two compounds listed in Table III were prepared from 1,5-pentamethylenedilithium or 3,3′-biphenylenedilithium and chlorotriphenylsilane. 1,5-Pentamethylenedilithium was prepared in accordance with the procedure of West and Rochow[2]; while, a halogen-metal interconversion reaction between 3,3′-dibromobiphenyl and *n*-butyllithium was used to prepare the biphenylene compound. 1,5-Pentamethylenebis(triphenylsilane) was also synthesized from triphenylsilane and 4-pentenyltriphenylsilane according to a reported procedure.[3] It is interesting to note that this reaction, initiated with benzoyl peroxide, gave a 65% yield of 1,5-pentamethylenebis(triphenylsilane), as compared to a 48% yield obtained by use of the dilithium reagent.



$$Br(CH_2)_5Br + 4Li \longrightarrow Li(CH_2)_5Li + 2LiBr$$

$$Li(CH_2)_5Li + 2ClSi(C_6H_5)_3 \longrightarrow (C_6H_5)_3Si(CH_2)_5Si(C_6H_5)_3$$

$$(C_6H_5)_3SiH + CH_2{=}CH(CH_2)_3Si(C_6H_5)_3 \longrightarrow (C_6H_5)_3Si(CH_2)_5Si(C_6H_5)_3$$

The effect of long-chain alkyl groups on melting points in these compounds is as expected. All of the products containing such groups are either liquids or low-melting solids. Particularly noteworthy, however, is the low melting point of 1,2-ethylenebis(tri-*n*-hexadecylsilane). This compound, although having a molecular weight of approximately 1500, melts at 48°. To our knowledge, there are only two other nonpolymeric tetrasubstituted silanes containing only carbon, hydrogen, and silicon which have comparable molecular weights, namely, *p*-biphenylenebis(tri-*n*-hexadecylsilane)

---

[2] R. West and E. G. Rochow, *J. Org. Chem.*, **18**, 1739 (1953).

[3] H. Merten and H. Gilman, *J. Am. Chem. Soc.*, **76**, 5798 (1954).

[4] D. Miles, doctoral dissertation, Iowa State University, 1957.

TABLE III

COMPOUNDS HAVING THE $R_3Si—R'—SiR_3$ SKELETON[a]

Compound	M.P.	B.P. (mm.)	Yield, %	Si Calcd.	Si Found
1,2-Ethylenebis(tribenzylsilane)[b]	136–137[c]		81	8.89	8.95, 8.90
1,2-Ethylenebis(tri-2-ethylhexylsilane)[d]		215–220 (0.04)	54	7.35	7.52, 7.58
1,2-Ethylenebis(tri-*n*-hexadecylsilane)[d]	43–45[e]		75	3.91	3.83, 3.81
m-Phenylenebis(tribenzylsilane)[f]	155–157[g]		16	8.27	8.35, 8.26
m-Phenylenebis(tri-*n*-decylsilane)[h]		285–288 (0.03)[i]	58	5.73	5.59, 5.76
p-Phenylenebis(tri-*n*-decylsilane)[h]		290–294 (0.07)	20[j]	5.73	5.94, 5.86
1,5-Pentamethylenebis(triphenylsilane)[k]	145–146[l]		48	9.53	9.70, 9.48
3,3′-Biphenylenebis(triphenylsilane)[m]	221–223[n]		69	8.37	8.06, 8.07

[a] R′ is a difunctional hydrocarbon group. [b] Prepared from 1,2-ethylenebis(trichlorosilane) and benzylmagnesium chloride. [c] Crystallized from petroleum ether (b.p. 60–70°), then from ethyl acetate. [d] Prepared from 1,2-ethylenebis(trichlorosilane) and the appropriate organolithium compound. [e] Crystallized from a mixture of carbon tetrachloride and ethanol after reduced pressure distillation. [f] Prepared from *m*-phenylenebis(trichlorosilane) and benzylmagnesium chloride. [g] Crystallized from ethyl acetate. [h] Prepared from the phenylenebis(trichlorosilane) and the appropriate organolithium compound. [i] n^{20}_D 1.4811, d^{20}_4 0.863, MR_D Calcd. for $C_{66}H_{130}Si_2$: 323.6. Found: 323.8. [j] In addition, 10.2 g. of decane was obtained from the reaction using 0.11 mole of *n*-decyllithium and 0.015 mole of the chlorosilane. [k] Prepared from 1,5-pentamethylenedilithium and chlorotriphenylsilane. [l] From ethanol–ethyl acetate. [m] Prepared from 3,3′-biphenylenedilithium and chlorotriphenylsilane. [n] From aqueous dioxane.

and tetrakis(*p*-tribenzylsilylphenyl)silane.[5] The former compound was isolated as a slightly impure liquid, while the latter, is a solid melting at 159°, and is crystallizable from petroleum ether (b.p. 60–70°). Here also, the pronounced tendency of long-chain alkyl groups to lower the melting points is exemplified.

It is evident from Tables I and II that the *m*-fluorophenyl group shows a much lesser tendency to contribute toward a melting point lowering, than does the *m*-chlorophenyl group. All of the tetrasubstituted silanes listed in Table I, containing the *m*-fluorophenyl moiety, are solids at room temperature. The corresponding compounds containing the *m*-chlorophenyl group (Table III) are either lower melting or are liquids at room temperature. Apparently, this difference is partially due to the smaller atomic radius of fluorine as compared to chlorine.

EXPERIMENTAL[6]

m-Fluorophenyllithium. To a rapidly stirred solution of 0.05 mole of *n*-butyllithium[7] in 170 ml. of diethyl ether was slowly added a solution of 8.75 g. (0.05 mole) of *m*-bromofluorobenzene in 95 ml. of the same solvent, while maintaining the temperature below −45°. When the addition was complete, the mixture was stirred at −40° for 20 min. and then carbonated. The usual work-up for carbonation reactions involving extraction of the organic layer with sodium bicarbonate, boiling to expel the organic solvent, acidification with concd. hydrochloric acid and crystallization from water gave 4.5 g. (65%) of *m*-fluorobenzoic acid, m.p. 123–124°; reported[8] m.p. 124°.

In a second reaction employing 0.05 mole of *n*-butyllithium and 8.0 g. (0.046 mole) of *m*-bromofluorobenzene, the mixture was allowed to warm to room temperature after stirring at −40° for *ca.* 20 min. Upon attaining room temperature, the mixture continued to evolve heat and eventually began to reflux. When refluxing subsided (25 min.), Color Test II[9] was negative and Color Test I[10] was positive. Following carbonation and work-up of the aqueous layer, the crude acid was crystallized from water to give 2.36 g. (37%) of *m*-fluorobenzoic acid, m.p. 122–123°.

Di(m-fluorophenyl)diphenylsilane. A solution of 0.12 mole of *m*-fluorophenyllithium in 200 ml. of diethyl ether was added slowly to a stirred solution of 12.7 g. (0.05 mole) of dichlorodiphenylsilane in 80 ml. of the same solvent. The mixture was stirred at room temperature for 8 hr. and then refluxed for 2 hr. Subsequent to hydrolysis, separation of the layers, and removal of the solvent from the organic layer, the crude product was dissolved in petroleum ether (b.p. 60–70°) and decolorized with Norit A. From this solution there was obtained 4.8 g. (26%) of di(*m*-fluorophenyl)-diphenylsilane, m.p. 195–196°.

Analytical data for this compound and for others prepared by this general procedure are listed in Table I. The tetrasubstituted silanes containing long-chain alkyl groups and *m*-fluorophenyl groups were prepared similarly. These compounds, however, were purified by reduced pressure distillation.

Tetra(m-fluorophenyl)germane. This compound was prepared from 8.0 g. (0.037 mole) of germanium tetrachloride and 0.178 mole of *m*-fluorophenyllithium in *ca.* 300 ml. of diethyl ether. The usual work-up gave 4.1 g. (25%) of product, m.p. 194–195°, after crystallization from petroleum ether (b.p. 60–70°).

Anal. Calcd. for $C_{24}H_{16}F_4Ge$: Ge, 16.03. Found: Ge, 16.11, 15.91.

The compounds listed in Table II were prepared in an analogous manner except that *m*-chlorophenyllithium[11] or

---

(5) H. Gilman and O. Marrs, *J. Org. Chem.*, **25**, 1194 (1960).

(6) Melting points and boiling points are uncorrected. The solvents used for the preparations and reactions of organometallic compounds were sodium-dried. All reactions involving organometallic compounds and chlorosilanes were carried out under an atmosphere of dry, oxygen-free nitrogen in oven-dried glassware. The infrared spectra of all compounds reported herein are compatible with the assigned structures.

(7) H. Gilman, J. A. Beel, C. C. Brannen, M. W. Bullock, G. E. Dunn, and L. S. Miller, *J. Am. Chem. Soc.*, **71**, 1499 (1949).

(8) A. F. Holleman, *Rec. trav. chim.*, **25**, 330 (1906).

(9) H. Gilman and J. Swiss, *J. Am. Chem. Soc.*, **62**, 1848 (1940).

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

(11) H. Gilman and S. M. Spatz, *J. Am. Chem. Soc.*, **66**, 621 (1944).

p-chlorophenyllithium[12] was employed instead of *m*-fluorophenyllithium.

1,2-Ethylenebis(tribenzylsilane). Benzylmagnesium chloride, prepared from 25.3 g. (0.20 mole) of benzyl chloride and 4.86 g. (0.20 g.-atom) of magnesium turnings in 200 ml. of diethyl ether, was added to a stirred solution of 5.9 g. (0.02 mole) of 1,2-ethylenebis(trichlorosilane)[13] in 55 ml. of diethyl ether. The mixture was refluxed for 12 hr., after which most of the solvent was distilled and replaced by xylene. Subsequent to refluxing at 100° for 50 hr., the mixture was hydrolyzed with 5% hydrochloric acid. Filtration gave 10.9 g. of crude product which was combined with 0.7 g. of similar material obtained by removal of the solvent from the dried organic layer. Three crystallizations of this solid from petroleum ether (b.p. 60–70°) and one crystallization from ethyl acetate afforded 10.2 g. (81%) of colorless crystals, m.p. 136–137°.

The first six compounds listed in Table III were prepared by a similar procedure from 1,2-ethylenebis-,[13] *m*-phenylenebis-,[13] or *p*-phenylenebis(trichlorosilane).[13] The compounds having long-chain alkyl groups, however, employed alkyllithium compounds which were prepared by a procedure similar to that used for *n*-butyllithium.[7]

4-Pentenyltriphenylsilane. The 4-pentenyllithium was prepared in 56% yield from 8.0 g. (0.054 mole) of 1-bromo-4-pentene in 70 ml. of diethyl ether and 0.9 g. (0.13 g.-atom) of lithium wire in 60 ml. of the same solvent at −30°.

A solution of 7.38 g. (0.025 mole) of chlorotriphenylsilane in 60 ml. of diethyl ether was added to this reagent at −30°. Subsequent to stirring at 0° for 15 min. and at room temperature for 11 hr., the mixture was hydrolyzed and worked up in the usual manner. Reduced pressure distillation at 155–157° (0.15 mm.), followed by crystallization from ethanol cooled by an ice bath, gave 5.6 g. (67%) of 4-pentenyltriphenylsilane, m.p. 45–46°.

Anal. Calcd. for $C_{23}H_{24}Si$: Si, 8.54. Found: Si, 8.61, 8.55.

1,5-Pentamethylenebis(triphenylsilane). a. *From 4-pentenyltriphenylsilane and triphenylsilane.* A mixture of 26 g. (0.10 mole) of triphenylsilane, 3.4 g. (0.01 mole) of 4-pentenyltriphenylsilane, 0.32 g. (0.0013 mole) of benzoyl peroxide, and 25 ml. of *n*-hexane was stirred at 80° for 20 hr., after which the excess triphenylsilane was distilled at 148–160° (0.7 mm.). A brown, gummy solid remained which was soluble in common organic solvents. Crystallization from a mixture of ethanol and methyl ethyl ketone gave 4.18 g. of product, m.p. 140–143°. Two additional crystallizations from an ethanol–ethyl acetate pair afforded 3.8 g. (65%) of pure product, m.p. 146–147°.

b. *From 1,5-pentamethylenedilithium and chlorotriphenylsilane.* To a solution of 1,5-pentamethylenedilithium (prepared from 20 g., 0.087 mole of 1,5-dibromopentane according to the procedure of West and Rochow[2]) in 180 ml. of diethyl ether was added, at −20°, 17.4 g. (0.059 mole) of chlorotriphenylsilane in 160 ml. of the same solvent. The mixture was allowed to warm to room temperature and to stir overnight. Hydrolysis and the usual work-up gave 8.4 g. (48%) of 1,5-pentamethylenebis(triphenylsilane), m.p. 145–146°. This product did not depress the melting point of the material obtained from the preceding experiment. Its analysis is reported in Table III.

3,3′-Biphenylenebis(triphenylsilane). A solution of 6 g. (0.019 mole) of 3,3′-dibromobiphenyl in 30 ml. of diethyl ether was added to 75 ml. of a stirred etherial solution of 0.038 mole of *n*-butyllithium at −30°. Subsequent to stirring at room temperature for 6 hr., and at reflux for 15 min., a solution of 11.3 g. (0.038 mole) of chlorotriphenylsilane in *ca.* 100 ml. of diethyl ether was added to the insoluble dilithium reagent. After refluxing for 45 min., 100 ml. of benzene was added and the mixture was distilled until the internal temperature reached 53°, at which temperature it was refluxed for 15 min. and then hydrolyzed. Filtration and recrystallization from a mixture of dioxane and water gave, in several crops, 8.85 g. (69%) of pure product, m.p. 221–223°.

Acknowledgment. This research was supported in part by the United States Air Force under Contract 33(616)-3510 monitored by the Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright-Patterson AFB, Ohio. Infrared spectra were obtained through the courtesy of Dr. V. A. Fassel of the Institute for Atomic Research, Iowa State University, Ames, Iowa.

AMES, IOWA

---

[12] H. Gilman, W. Langham, and F. W. Moore, *J. Am. Chem. Soc.*, 62, 2327 (1940).

[13] Kindly furnished by Linde Air Products.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

Fischer-Hepp Rearrangements of Substituted 9-Nitrosocarbazoles[1]

NATHAN L. DRAKE,[2] HANS J. S. WINKLER,[3] CHARLOTTE M. KRAEBEL,[4] AND TERRILL D. SMITH[5]

Received July 21, 1961

Nitrosation of 1-bromocarbazole by conventional procedures led to a rearranged and oxidized product rather than to 1-bromo-9-nitrosocarbazole. Of the possible isomers, 1-bromo-3-nitrocarbazole, was synthesized unequivocally and identified with a product of the rearrangement-oxidation. Similarly, 1-isopropyl-4-methylcarbazole was nitrosated to 1-isopropyl-4-methyl-9-nitrosocarbazole, which rearranged readily to a mixture of 1-isopropyl-2 (or 3)-nitro-4-methylcarbazole and 1-isopropyl-4-methyl-6 (or 7)-nitrocarbazole.

DISCUSSION

Difficulties in nitrosating 1-substituted carbazoles in the 9- position were observed incidental to a study of preparation of asymmetrically substituted *N*-picryl-9-aminocarbazyl free radicals.[6] Two

---

[1] From the theses submitted to the Graduate School of the University of Maryland in partial fulfillment of the requirements for the Ph.D. degree by H. J. S. Winkler (1959) and C. M. Kraebel (1959) and for the M. S. degree by T. D. Smith (1958).

[2] Deceased.

[3] P. L. Prof. G. Wittig, Org. Chem. Inst. d. Univ. Heidelberg, Tiergartenstrasse, Heidelberg.

[4] B. F. Goodrich Co. Research Center, Brecksville 41, Ohio, to whom correspondence should be addressed.

[5] Monsanto Chemical Co., St. Louis 2, Mo.