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

Studies in Organosilicon Chemistry. XXXVIII. Further Studies in Sila-Organic Polysulfides

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Chlorination of methyltrichlorosilane results in the formation of chloromethyltrichlorosilane from which triethylchloromethylsilane and tri-*n*-propylchloromethylsilane can be prepared by the action of the proper Grignard reagent. Sodium hydrosulfide reacts with each of the last two compounds to form the corresponding mercaptans. These mercaptans, as well as trimethylsilylmethyl mercaptan, form addition compounds (2:1 mole ratio) with mercuric chloride. Sodium sulfide reacts with trimethylchloromethylsilane and triethylchloromethylsilane to form the respective sulfides. Each sulfide adds methyl iodide giving the corresponding sulfonium iodide while bis(trimethylsilylmethyl) sulfide adds mercuric iodide in a 1:1 mole ratio. The action of iodine on sodium trimethylsilylmethyl mercaptide and on sodium triethylsilylmethyl mercaptide results in the formation of the corresponding disulfides. Infrared absorption spectra are presented for triethylchloromethylsilane, tri-*n*-propylchloromethylsilane, trimethylsilylmethyl mercaptan, triethylsilylmethyl mercaptan, tri-*n*-propylsilylmethyl mercaptan, bis(trimethylsilylmethyl) sulfide, bis(triethylsilylmethyl) sulfide, bis(trimethylsilylmethyl)-methylsulfonium iodide, bis(triethylsilylmethyl)methylsulfonium iodide, bis(trimethylsilylmethyl) disulfide, and bis-(triethylsilylmethyl) disulfide. Ultraviolet absorption spectra have been examined for bis(trimethylsilylmethyl) disulfide and for bis(triethylsilylmethyl) disulfide.

The investigation was directed toward the preparation and study of mercaptans, sulfides, and polysulfides containing the trialkylsilylmethyl unit and certain of their derivatives, partly by the use of procedures already investigated and partly by methods which are new. A short bibliography has already appeared in a recent contribution by Minklei, Decker, and Post,[1b] summarizing work carried out by Gilman and co-workers[2–6] and by Burkhard,[7] Noller and Post,[8] Cooper[9] and by Marvel and Cripps.[10]

Sodium trimethylsilylmethyl mercaptide has been treated with iodine with the subsequent formation of bis(trimethylsilylmethyl) disulfide. Bis-(trimethylsilylmethyl) methylsulfonium iodide has been synthesized by the addition of methyl iodide to bis(trimethylsilylmethyl) sulfide. Mercuric iodide adds to the last named compound to form an additional product in 1:1 molar ratio. Trimethylsilylmethyl mercaptan also forms a 2:1 molar ratio addition compound with mercuric chloride. These reactions are presented in completion of the work previously reported by Minklei, Decker, and Post.[1b] The corresponding ethyl homologs have also been prepared.

By similar procedures tri-*n*-propylchloromethylsilane and tri-*n*-propylsilylmethyl mercaptan have been prepared as well as the 2:1 addition product of the latter with mercuric chloride.

These compounds, with the exception of the mercuric halide addition products, were examined using an infrared spectroscope to provide a basis for comparing and establishing structures and to support their chemical identification.

The infrared bands have been analyzed and a comparison has been made with data found in Bellamy.[11]

A Baird Atomic recording spectrophotometer was used to record all spectral measurements. Liquid samples were examined using fixed thickness cells. When the samples were solid they were prepared as Nujol mulls and examined between rock salt plates without a spacer. No compensating solvents or plates were used in the reference beam.

The ultraviolet absorption spectra were determined for bis(trimethylsilylmethyl) disulfide and bis(triethylsilylmethyl) disulfide. These spectra were measured with a Beckman Model D K-2 spectrophotometer, using iso-octane as the solvent. The concentration of the solutions which were examined was about 0.002*M*.

Bis(trimethylsilylmethyl) disulfide showed a minimum at 244 mμ and a maximum at 262 mμ. For bis(triethylsilylmethyl) disulfide the figures were 244 mμ and 257 mμ, respectively. These properties essentially agree with previously published data

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(1b) A. O. Minklei, Q. W. Decker, and H. W. Post, *Rec. trav. Chim.*, **76**, 187 (1957).

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(9) G. D. Cooper, *J. Am. Chem. Soc.*, **76**, 3713 (1954).

(10) C. S. Marvel and H. N. Cripps, *J. Polymer Sci.*, **9**, 52 (1952).

(11) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, New York (1954).

TABLE I

PHYSICAL PROPERTIES

	B.P.	Mm.	n_{D}^{25}	D_4^{25}	Yield, %
$(C_2H_5)_3SiCH_2Cl$	116	100	1.4452[a]	0.9020	65.0
$(n\text{-}C_3H_7)_3SiCH_2Cl$	117	20	1.4502[b]	0.8899	28.3
$[(CH_3)_3SiCH_2S]_2$	82	1	1.4874[c]	0.9147	57.8
$(C_2H_5)_3SiCH_2SH$	110	50	1.4678	0.8750	50.7
$[(C_2H_5)_3SiCH_2]_2S$	111	0.8	1.4771	0.8802	76.0
$[(C_2H_5)_3SiCH_2S]_2$	122	0.02	1.5020	0.9334	53.3
$(n\text{-}C_3H_7)_3SiCH_2SH$	89	3	1.4676	0.8614	66.7

[a] Literature: n_{D}^{20} 1.4480.[13] [b] Literature: n_{D}^{20} 1.4530.[14] [c] Literature: n_{D}^{25} 1.4906.[1]

TABLE II

MELTING POINTS, SULFUR COMPOUNDS

	M.P.	Yield, %
$([(CH_3)_3SiCH_2]_2SCH_3)^{+}(I)$—	147	90
$[(CH_3)_3SiCH_2]_2S,HgI_2$	63	20
$([(CH_3)_3SiCH_2SH]_2\cdot Hg)^{++}2(Cl)$—	142	—
$([(C_2H_5)_3SiCH_2]_2SCH_3)^{+}(I)$—	145	69
$([(C_2H_5)_3SiCH_2SH]_2\cdot Hg)^{++}2(Cl)$—	105	—
$([(n\text{-}C_3H_7)_3SiCH_2SH]_2\cdot Hg)^{++}2(Cl)$—	135	—

TABLE III

CHARACTERISTIC INFRARED ABSORPTION BANDS[a]

Compounds	CH (stretching)	CH (def.) C—CH₃	CH (def.) —(CH₃)₃	CH (def.) —CH₂—	Ethyl Group	Propyl Group	Si—C	Si—CH₃, Si—CH₂—	S—H	C—Cl
$(C_2H_5)_3SiCH_2Cl$	3.4	7.1	—	6.8	9.8 10.4	—	13.0	8.1	—	13.6
$(n\text{-}C_3H_7)_3SiCH_2Cl$	3.4	7.1	—	6.8	—	9.9 11.1	13.0	8.3	—	13.4
$(CH_3)_3SiCH_2SH$	3.4	7.1	7.2	—	—	—	11.7	8.0	3.9	—
$(C_2H_5)_3SiCH_2SH$	3.4	7.1	—	6.8	9.8 10.3	—	13.5	8.1	3.9	—
$(n\text{-}C_3H_7)_3SiCH_2SH$	3.4	7.1	—	6.8	—	9.9 11.1	13.3	8.3	3.9	—
$[(CH_3)_3SiCH_2]_2S$	3.4	7.1	7.2	—	—	—	11.7	8.0	—	—
$[(C_2H_5)_3SiCH_2]_2S$	3.4	7.1	—	6.8	9.8 10.3	—	13.5	8.1	—	—
$([(CH_3)_3SiCH_2]_2SCH_3)^{+}(I)^{-}$	3.5[b]	7.1[b]	7.3[b]	6.9[b]	—	—	11.8	8.0	—	—
$([(C_2H_5)_3SiCH_2]_2SCH_3)^{+}(I)^{-}$	3.5[b]	7.0[b]	7.2[b]	6.8[b]	9.8 10.1	—	13.2	8.0	—	—
$[(CH_3)_3SiCH_2S]_2$	3.4	7.1	7.2	—	—	—	11.9	8.1	—	—
$[(C_2H_5)_3SiCH_2S]_2$	3.4	7.1	—	6.8	9.8 10.3	—	13.4	8.1	—	—

[a] Measured in microns. [b] Nujol interference.

on alkyl polysulfides not containing a silicon structure.[12]

EXPERIMENTAL

Di-(trimethylsilylmethyl mercaptyl) mercuric chloride. Trimethylsilylmethyl mercaptan (0.5 cc.) was added to 2 cc. of ethanol, and a 10% solution of mercuric chloride in the same solvent was added until precipitation ceased. The precipitate, di-(trimethylsilylmethyl mercaptan) mercuric chloride, was filtered, washed with ethanol and dried in air, m.p. 142°.

Anal. Calcd. for $C_8H_{24}Cl_2HgS_2Si_2$: Si, 10.9; C, 18.8; H, 4.7. Found: Si, 10.6; C, 18.2; H, 4.6.

Bis(trimethylsilylmethyl)methylsulfonium iodide. Following the general method of Cooper,[15] bis(trimethylsilylmethyl) sulfide 6.2 g. (0.03 mol.) was thoroughly mixed with methyl iodide 8.6 g. (0.06 mol.) and allowed to stand in the dark for 20 hr. A precipitate formed within 10 min. and was ultimately filtered, washed with dry cyclohexane, and dried in air, to yield an orange-yellow powder, 9.4 g. (0.2 mol.); m.p. 147°; yield 90.0%.

Anal. Calcd. for $C_9H_{25}IS\ Si_2$: Si, 16.1; S, 9.2; I, 36.4. Found: Si, 15.9; S, 9.0; I, 36.2.

Bis(trimethylsilylmethyl) sulfide mercuric iodide. Following the method of Linnemann[16] bis(trimethylsilylmethyl) sulfide 2.1 g. (0.01 mol.) was thoroughly mixed with mercuric iodide 4.0 g. (0.009 mol.) and allowed to stand 12 hr. The mixture was added to 25 cc. of hot ethanol, brought to a boil, filtered, and the filtrate cooled in ice. The resulting crystals, bis(trimethylsilylmethyl) sulfide mercuric iodide,

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(12) Q. W. Decker and H. W. Post, *J. Org. Chem.*, **22**, 145 (1957).

(13) V. Ponomarenko and V. Mironov, *Doklady Akad. Nauk S.S.S.R.*, **94**, 485 (1954).

(14) V. Mironov, *Doklady Akad. Nauk S.S.S.R.*, **108**, 266 (1956).

(15) G. D. Cooper, U. S. Patent **2,719,165**, Sept. 27, 1955.

(16) E. Linnemann, *Ann.*, **120**, 61 (1861).

were filtered, washed with absolute ethanol, and dried in air 2.0 g. (0.003 mol.); m.p. 63°; yield, 20.0%.

Anal. Calcd. for $C_8H_{22}I_2HgS\ Si_2$: Si, 8.5; S, 4.85. Found: Si, 8.5; S, 4.8.

Bis(trimethylsilylmethyl) disulfide. The general procedures here were taken from the work of McAllan *et al.*[17] Sodium hydroxide 4.7 g. (0.117 mol.) and potassium iodide 0.32 g. (0.0019 mol.) were placed in a 500 cc. three-neck flask equipped with a reflux condenser, a mercury-sealed mechanical stirrer, and dropping funnel. With stirring, 20 cc. of water was added until all solids dissolved. Trimethylsilylmethyl mercaptan 14.0 g. (0.117 mol.) in 200 cc. of dioxane was added slowly with stirring and cooling. After the addition was complete and the system had returned to room temperature, iodine was added 14.8 g. (0.058 mol.) in small portions, with stirring. After about 75% of the iodine had been added, discoloration of the system ceased and the remainder was added in one portion. After 2 hr. of refluxing, the mixture was once again colorless, and after cooling, was poured into 500 cc. of water, the crude product separated and was dried overnight over calcium chloride. Darkening of the crude product was observed, which could have been caused by a reversal of the reaction, so the product was placed over solid sodium hydroxide for several hours, decanted, and fractionated. Bis(trimethylsilylmethyl) disulfide 8.0 g. (0.033 mol.) was isolated, b.p. 82° (1 mm.); n_D^{25} 1.4874, lit.,[1] 1.4906; D_4^{25} 0.9147, lit.,[1] 0.9203; yield 57.8%.

Anal. Calcd. for $C_8H_{22}S_2Si_2$: M.R., 74.4; Mol. Wt., 238.57. Found: M.R., 75.04; Mol. Wt., 237.9 (cryoscopic in benzene).

Triethylchloromethylsilane. This procedure also was adapted from the results of Mironov.[14] Ethylmagnesium bromide 159.6 g. (1.2 mol. in about 1000 cc. of anhydrous ether) was treated with an ethereal solution of 73.5 g. (0.4 mol.) of chloromethyltrichlorosilane at a rate sufficient to induce refluxing about 2 hr. The system was refluxed for an additional 5 hr. after all of the chlorosilane compound had been added. Most of the ether was then removed and the crude reaction mixture refluxed at 85° for 10 hr. Chilled dilute hydrochloric acid was added to the reaction mixture and the aqueous layer separated and extracted twice with 200 cc. of ether. Distillation of the combined organic layers removed the solvent. The residue was dried over calcium chloride for 12 hr. and fractionated giving triethylchloromethylsilane, 43.0 g. (0.26 mol.); b.p. 116° (100 mm.); n_D^{25} 1.4452, n_D^{20} 1.4480 (lit.)[14]; D_4^{25} 0.9020, D_4^{20} 0.9101 (lit.)[14]; yield 65.0%.

Anal. Calcd. for $C_7H_{17}ClSi$: M.R., 48.9. Found: M.R., 48.7.

Triethylsilylmethyl mercaptan. This compound was prepared following a modified method previously recorded by Cooper.[18] Potassium hydroxide 9.5 g. (0.17 mol.) and 75 cc. of absolute ethanol were placed in a 250 cc. three-neck flask, with stirrer, dropping funnel and reflux condenser protected by a calcium chloride tube and were saturated with hydrogen sulfide for 3 hr. Triethylchloromethylsilane 19.0 g. (0.12 mol.) in 25 cc. of absolute ethanol was added during 1 hr. with stirring and refluxing. Hydrogen sulfide was bubbled through the system during the addition and refluxing period which was an additional hr. The precipitate was centrifuged and the organic layer decanted. The solid was washed twice with ethanol and again centrifuged for 2 min. The organic layer and washings were freed from solvent by distillation and the residue dried over calcium sulfate for 4 hr. Fractionation yielded 9.5 g. (0.06 mol.) of triethylsilylmethyl mercaptan, b.p. 110° (50 mm.); n_D^{25} 1.4678; D_4^{25} 0.8750; yield 50.7%.

Anal. Calcd. for $C_7H_{18}SSi$: Si, 17.3; S, 19.6; M.R., 51.55. Found: Si, 17.4; S, 19.5; M.R., 51.60.

Bistriethylsilylmethyl sulfide was also isolated, 1.7 g. (0.006 mol.) about a 10% yield, b.p. 149° (4 mm.).

Di(triethylsilylmethyl mercaptyl) mercuric chloride. This compound, m.p. 105°, was prepared by the same method as that used in the preparation of di(trimethylsilylmethyl mercaptyl) mercuric chloride.

Anal. Calcd. for $C_{14}H_{36}Cl_2HgS_2Si_2$: Si, 9.4; C, 28.2; H, 6.1. Found: Si, 8.9; C, 27.5; H, 5.8.

Bistriethylsilylmethyl sulfide. This compound also was prepared by a modification of the method reported by Cooper.[9] Triethylchloromethylsilane 16.5 g. (0.1 mol.) was added with stirring, to 130 cc. of ethanol in a flask equipped as in the preparation of the corresponding mercaptan. Sodium sulfide 7.0 g. (0.009 mol.) in 25 cc. of warm water was added over 1 hr. with heating and stirring, and the system was stirred and refluxed for 4 hr. To facilitate separation of the organic layer, the mixture was poured into 400 cc. of water and the water layer extracted with 300 cc. of ether. Combined organic layer and extractions were distilled to remove solvent and the residue dried overnight over 5 g. of calcium chloride. Fractionation yielded 11.0 g. (0.04 mol.) of bis(triethylsilylmethyl) sulfide, 76.0% yield; b.p. 111° (0.08 mm.); n_D^{25} 1.4771; D_4^{25} 0.8802.

Anal. Calcd. for $C_{14}H_{34}SSi_2$: Si, 19.3; S, 11.0; M.R., 93.0. Found: Si, 19.3; S, 10.8; M.R., 93.4.

Bis(triethylsilylmethyl)methylsulfonium iodide. This compound was prepared in a manner similar to the corresponding trimethyl homolog; however, it was necessary to cool the reaction mixture in Dry Ice to induce precipitation. The product was filtered and washed three times with dry cyclohexane, 3.0 g. (0.0069 mol.); m.p. 145°; yield 69.0%.

Anal. Calcd. for $C_{15}H_{37}ISSi_2$: Si, 13.0; S, 7.4; I, 29.3. Found: Si, 13.0; S, 7.3; I, 29.0.

Bis(triethylsilylmethyl) disulfide. The method described previously for the preparation of bis(trimethylsilylmethyl) disulfide was followed here, using 6.0 g. (0.15 mol.) of sodium hydroxide, 0.5 g. (0.003 mol.) of potassium iodide, 12.0 g. (0.074 mol.) of triethylsilylmethyl mercaptan and 9.4 g. (0.037 mol.) of iodine. Bis(triethylsilylmethyl) disulfide was collected, 6.5 g. (0.02 mol.); b.p. 122° (0.02 mm.); n_D^{25} 1.5020; D_4^{25} 0.9334; yield 53.3%.

Anal. Calcd. for $C_{14}H_{34}S_2Si_2$: Si, 17.4; S, 19.9; M.R., 101.6. Found: Si, 17.3; S, 20.0; M.R., 102.0.

Tri-n-propylchloromethylsilane. The procedure followed closely that which lead to the synthesis of triethylchloromethylsilane, using 176.8 g. (1.2 mol.) of *n*-propylmagnesium bromide and 73.5 g. (0.4 mol.) of chloromethyltrichlorosilane. The crude reaction mixture was refluxed and stirred for 15 hr. at 35°. The temperature of this mixture then was increased to 105° for 30 hr., after the majority of the ether had been removed. Fractionation of the crude mixture yielded 23.3 g. (0.113 mol.) of tri-*n*-propylchloromethylsilane, b.p. 117° (20 mm.), 222–225° (749 mm.), lit.[14] 222° (733 mm.); n_D^{25} 1.4502, n_D^{20} (lit.[14]) 1.4530; D_4^{25} 0.8899, D_4^{20} (lit.[14]) 0.8919; yield 23.3%.

Anal. Calcd. for $C_{10}H_{23}ClSi$: Si, 13.55; Cl, 17.4; M.R., 62.8. Found: Si, 13.4; Cl, 17.3; M.R., 62.5.

Tri-n-propylsilylmethyl mercaptan. The compound was prepared in a manner similar to triethylsilylmethyl mercaptan, with 5.6 g. (0.10 mol.) of potassium hydroxide, hydrogen sulfide, and 15.0 g. (0.072 mol.) of tri-*n*-propylchloromethylsilane, giving 9.8 g. (0.048 mol.) of tri-*n*-propylsilylmethyl mercaptan, b.p. 89° (3 mm.); n_D^{25} 1.4676; D_4^{25} 0.8614; yield 66.7%.

Anal. Calcd. for $C_{10}H_{24}SSi$: Si, 13.7; S, 15.7; M.R., 65.5. Found: Si, 13.6; S, 15.5; M.R., 65.9.

Di(tri-n-propylsilylmethyl mercaptyl) mercuric chloride.

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(17) D. McAllan, T. Cullum, R. Dean, and F. Fidler, *J. Am. Chem. Soc.*, **73**, 3627 (1951).

(18) G. D. Cooper, *J. Am. Chem. Soc.*, **76**, 2500 (1954).

This compound, m.p. 135°, was prepared using a procedure analogous to the preparation of the two preceding mercuric chloride addition compounds.

Anal. Calcd. for $C_{20}H_{48}Cl_2HgS_2Si_2$: Si, 8.2; C, 35.3; H, 7.1. Found: Si, 7.9; C, 34.4; H, 6.6.

Hydrogen sulfide, solvents, and other reagents were purchased from the usual sources. *Spectro grade iso-octane* was purchased from Phillips Petroleum Company. All were found to possess satisfactory physical constants. Molecular refractions were calculated using the data of Warrick.[19]

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[19] E. L. Warrick, *J. Am. Chem. Soc.,* **68,** 2455 (1946).

[CONTRIBUTION FROM THE CHEMICAL DIVISION, DENVER RESEARCH INSTITUTE, UNIVERSITY OF DENVER]

Alkylpolyphenyls. I. 4'-Alkyl-*m*-terphenyls[1]

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A series of 4'-alkyl-*m*-terphenyls have been prepared for potential use as high temperature hydraulic fluids and lubricants. An improved synthesis of 4'-bromo-*m*-terphenyl has been developed.

In connection with a study on the preparation of potential hydraulic fluids and lubricants of high thermal stability and wide liquid range, the authors have prepared a number of alkylbiphenyls and alkylterphenyls. Compounds of the alkylpolyphenyl type were chosen for investigation as it was expected that the well established thermal stability of such "chain-type" aromatic structures as biphenyl and the terphenyls might also be found to some extent in their derivatives.

Although biphenyl and the terphenyls are rather high melting compounds, it is known, especially from the study of biphenyl derivatives, that the introduction of an alkyl group into the nucleus greatly extends the liquid range of the compound. While numerous alkylbiphenyls are known, only a very few alkyl terphenyls have been reported; however the information available for the biphenyls is sufficient to make certain correlations concerning the substitution of alkyl groups on the terphenyl nucleus.

A study of the alkylbiphenyls revealed that substitution of an alkyl group at any position in the molecule lowered the melting point of the parent compound, substitution in the 2- or 3-position producing much greater lowering than substitution in the 4-position. This same depression was postulated for substitution in the terminal nucleus of the terphenyl molecule and was confirmed by the few examples reported in the literature. It was further postulated that substitution in the inner ring of a terphenyl molecule should depress the melting point; however, a literature survey revealed only one such compound, 5'-methyl-*m*-terphenyl,[3] and this compound, perhaps because of its molecular symmetry, had a melting point of 130°, somewhat higher than that (87°) of *m*-terphenyl. It was also evident that increased symmetry of the substituted alkyl group would lead to an increased melting point for the corresponding alkyl derivative. For example, melting points have been reported for certain 2-alkylbiphenyls as follows: *n*-propyl, −11.26°[4]; isopropyl, 24.46°[4]; *n*-butyl, −9.65° and −13.71°[4]; isobutyl, glass;[5] *sec*-butyl, 8.12°[5]; and *tert*-butyl, 31–34°.[6] This trend has been confirmed by our work which shows that the normal alkyl derivatives generally have lower pour points than the branched alkyl derivatives.

In considering the terphenyls, the *ortho* and *meta* isomers are much more attractive starting materials, from the standpoint of providing derivatives of wide liquid range, than is the *para* isomer due to the much lower melting points of the first two isomers.

Among the alkylpolyphenyls which have been prepared in this laboratory are 2-, 3-, and 4-monoalkylbiphenyls; 2- and 3-monoalkyl-*o*-terphenyls; 2-, 3-, 4-, and 4'-monoalkyl-*m*-terphenyls and 2-, 3-, and 4-monoalkyl-*p*-terphenyls. Other alkylterphenyls have been prepared by the Friedel-Crafts reaction, which by its inherent nature usually gave products of indefinite composition. While the 2- and 3-substituted alkyl derivatives will be described in a subsequent publication, the 4'-alkyl-*m*-terphenyls are discussed in this communication.

The 4'-alkyl-*m*-terphenyl series was selected for the investigation of inner ring substitution due to the availability of 4'-bromo-*m*-terphenyl as a starting material. The bromination of *m*-terphenyl to give 4'-bromo-*m*-terphenyl has been re-

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[2] Denver Research Institute Fellow 1956–57.

[3] C. Gastaldi and F. Cherchi, *Gazz. Chim. Ital.,* **45,** 11, 251 (1915); *Chem. Abstr.,* **10,** 1637 (1916).

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