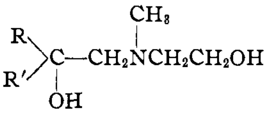
TABLE I

N-METHYLDIETHANOLAMINES



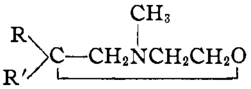
$$\begin{array}{c}\qquad\qquad\ \ CH_3\\ R\diagdown\qquad\qquad |\\ \quad C—CH_2NCH_2CH_2OH\\ R'\diagup\ |\quad\\ \ \ OH\end{array}$$

R	R'	Yield, %	B.p., °C.	B.p., Mm.	$n^{20}{}_D$	$d^{20}{}_{20}$	Formula	Nitrogen, %[a] Calcd.	Nitrogen, %[a] Found
C_6H_5	H	89.9[b]	152	0.9	1.5365	1.090	$C_{11}H_{17}O_2N$	7.18	7.45[c]
C_6H_5	C_6H_5	85	M. p. 110–111				$C_{17}H_{21}O_2N$	5.17	5.33
$C_6H_5CH_2$	H	85[d]	154	0.1	1.5271	1.065	$C_{12}H_{19}O_2N$	6.70	6.66[e]

[a] Analyses for nitrogen were performed by the micro Dumas method. [b] The styrene oxide was added dropwise to the methylethanolamine with the temperature kept below 45°. [c] Calcd. MR_D, 56.45; neut. equiv., 195. Found: MR_D, 55.89; neut. equiv., 193. [d] The conditions were the same as in (*b*). The intermediary 1-phenyl-2,3-epoxypropane was prepared by the dehydrohalogenation of 3-chloro-1-phenyl-2-propanol, which was kindly furnished by J. B. Honeycutt, Jr. A ring closure procedure described by H. Gilman, C. S. Sherman, C. C. Price, R. C. Elderfield, J. T. Maynard, R. H. Reitsema, L. Tolman, S. P. Massie, Jr., F. J. Marshall and L. Goldman, THIS JOURNAL, **68**, 1291 (1946), was utilized and the yield was 66%. See also E. Fourneau and M. Tiffeneau, *Compt. rend.*, **140**, 1596 (1905), for the preparation of this epoxide. [e] Calcd.: MR_D, 61.07. Found: MR_D, 60.58.

TABLE II

2-SUBSTITUTED-4-METHYLMORPHOLINES



$$\begin{array}{c}\qquad\qquad\ \ CH_3\\ R\diagdown\qquad\qquad |\\ \quad C—\underbrace{CH_2NCH_2CH_2O}\\ R'\diagup\end{array}$$

R	R'	Yield, %	B.p. °C.	B.p. Mm.	$n^{20}{}_D$	$d^{20}{}_{20}$	Formula	Nitrogen, %[a] Calcd.	Nitrogen, %[a] Found
C_6H_5	H	62[b]	115–118	0.5–0.8	1.5279	1.026	$C_{11}H_{15}ON$	7.91	9.16[c]
$C_6H_5CH_2$	H	32[d]	93–97	0.1	1.5239	1.021	$C_{12}H_{17}ON$	7.33	7.67[e]
C_6H_5	C_6H_5	71	M. p. 76–77				$C_{17}H_{19}ON$	5.53	5.52

[a] Analyses for nitrogen were performed by the micro Dumas method. [b] After the dropwise addition of the β-phenyl-N-methyldiethanolamine to the 70% sulfuric acid (the molar ratio of amine to acid was 1 to 3), the mixture was heated at 135–155° for 5.5 hours. [c] Calcd. MR_D, 52.84; neut. equiv., 177. Found: MR_D, 53.14; neut. equiv., 174. [d] Same as in (*b*) except that the mixture was heated at 140–150° for 4 hours. [e] Calcd.: MR_D, 57.46. Found: MR_D, 57.33. The picrate was prepared in 95% ethanol, m.p. 172–173.5°. Calcd. for $C_{18}H_{20}O_8N_4$: N, 13.33. Found: N, 13.09.

of product was obtained by low temperature crystallization,[9] m.p. 54–55° and the mixed m.p. with 1,1-diphenylethylene oxide was 33–36°. Two-tenths gram of the product was refluxed with 10 ml. of 25% potassium hydroxide in methanol for one hour. The mixture was cooled and diluted with water. A small amount of neutral compound precipitated, m.p. 69–70°. The same compound, as shown by m.p. and mixed m.p., was obtained when the oxidation product (m.p. 54–55°) was treated with semicarbazide hydrochloride and sodium acetate in dilute ethanol. The structures of the oxidation product and of its hydrolysis product are under investigation.

β,β-Diphenyl-N-methyldiethanolamine.—Nine grams (0.12 mole) of methylethanolamine[10] containing 1 ml. of water was stirred while 13 g. (0.066 mole) of 1,1-diphenylethylene oxide was added portionwise. The mixture was heated on the steam-bath overnight and the resulting oil solidified on cooling. Crystallization from a mixture of petroleum ether (b.p. 60–70°) and absolute ethanol gave 15.3 g. of the product. The N-methyldiethanolamines prepared are listed in Table I.

2,2-Diphenyl-4-methylmorpholine.—In a 250-ml. 3-necked flask equipped with a stirrer, solid addition funnel and condenser set for downward distillation was placed 5 ml. of 70% sulfuric acid. To the well-stirred, ice-cold acid was added portionwise 5.4 g. (0.02 mole) of β,β-diphenyl-N-methyldiethanolamine. The mixture was heated on the steam-bath for three hours upon completion of the addition. It was made basic with sodium hydroxide, and the basic solution extracted with ether. The ether extract was washed with water and dried over anhydrous sodium sulfate. The solvent was removed and the residue solidified on cooling. A single crystallization from dilute ethanol gave 3.6 g. of pure white product. Slight modifications in the preparation of the other substituted morpholines are given in the footnotes to Table II.

Acknowledgment.—The authors are grateful to Burt Hofferth for assistance. They also wish to express their appreciation to Parke, Davis and Company for arranging for the pharmaceutical tests, details of which will be published elsewhere.

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Cleavage of the Silicon–Silicon Bond in Hexaphenyldisilane

BY HENRY GILMAN AND T. C. WU

It is well known that hexaarylethanes dissociate into triarylmethyl radicals and react readily with halogens, oxygen and alkali metals.[1] It has also been shown that the central metal–metal bonds of hexaphenyldilead,[2] hexamethylditin[3] and hexaphenyldigermanium[4] can be cleaved with sodium in liquid ammonia. However, attempts to cleave the silicon–silicon bonds in some hexasubstituted disilanes by sodium in liquid ammonia,[5] lithium in ethylamine,[5] and iodine[6] or oxygen[6,7] in boiling xylene have been reported to be unsuccessful. Kipping,[8] after treating some hexasubstituted disilanes with aqueous or alcoholic alkali and with concentrated sulfuric acid, found that the silicon–silicon bonds of the disilanes were intact. The organometallic compounds of silicon have been made from

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[9] The technique is described by H. Adkins and R. H. Gillespie, *Org. Syntheses*, **29**, 81 (1949).

[10] Generously supplied by the Carbide and Carbon Chemical Corporation, New York.

[1] See Chapter by W. E. Bachmann in H. Gilman, "Organic Chemistry, An Advanced Treatise," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 585 ff.

[2] L. S. Foster, W. M. Dix and I. J. Gruntfest, THIS JOURNAL, **61**, 1685 (1939).

[3] C. C. Kraus and W. V. Sessions, *ibid.*, **47**, 2361 (1925).

[4] C. A. Kraus and L. S. Foster, *ibid.*, **49**, 462 (1927).

[5] C. A. Kraus and W. K. Nelson, *ibid.*, **56**, 195 (1934).

[6] H. Gilman and G. E. Dunn, *ibid.*, **73**, 3404 (1951).

[7] W. Schlenk, J. Renning and G. Racky, *Ber.*, **44**, 1178 (1911).

[8] F. S. Kipping, *J. Chem. Soc.*, **119**, 647 (1921).

reactions of triphenylbromosilane[9] or triphenylgermanyltriethylsilane[6] with lithium in ethylamine, and from phenylisopropyltriphenylsilane with sodium–potassium alloy in ethyl ether by a very attractive procedure recently described by Benkeser and Severson.[10]

We have now found that hexaphenyldisilane can be cleaved smoothly with sodium–potassium alloy in ethyl ether to give triphenylsilylpotassium which reacts readily with bromobenzene and trimethylchlorosilane to give tetraphenylsilane and 1,1,1-triphenyl-2,2,2-trimethyldisilane, respectively.

$$(C_6H_5)_3SiSi(C_6H_5)_3 \xrightarrow[\text{ether}]{\text{Na-K}} 2(C_6H_5)_3SiK$$

$$(C_6H_5)_3SiK + C_6H_5Br \longrightarrow (C_6H_5)_4Si + KBr$$

$$(C_6H_5)_3SiK + (CH_3)_3SiCl \longrightarrow (C_6H_5)_3SiSi(CH_3)_3 + KCl$$

We have also been able to show that hexaphenyldisilane can be cleaved with potassium in hot *n*-butyl ether. On the other hand, sodium dispersion did not seem to react with hexaphenyldisilane in boiling xylene or in refluxing dioxane. Also, 40% sodium amalgam did not cleave hexaphenyldisilane in ethyl ether. Since triphenylsilylpotassium can be prepared in a high yield from hexaphenyldisilane and sodium–potassium alloy, it may be of promise as an intermediate for the synthesis of other organosilicon compounds which have hitherto been either difficult or impossible of preparation. Also, we have observed, incidental to these studies, that triphenylsilylpotassium can be prepared in highly satisfactory yields by the reaction of triphenylchlorosilane and sodium–potassium alloy in ethyl ether.

Experimental

All reactions before hydrolysis were carried out in a dry, oxygen-free atmosphere of nitrogen. The melting points are uncorrected.

Hexaphenyldisilane.—Hexaphenyldisilane was prepared from triphenylchlorosilane with sodium in boiling xylene by the modified procedure recently described.[6]

Tetraphenylsilane from Triphenylsilylpotassium and Bromobenzene.—To 1.6 g. (0.0031 mole) of hexaphenyldisilane in 50 ml. of anhydrous ether was added 1 ml. of sodium–potassium alloy (1:5). This mixture was stirred vigorously at room temperature for 16 hours. A light yellow color appeared at the end of the first hour. Later this color changed to brown, and finally a dark brown precipitate was formed. One gram (0.0064 mole) of bromobenzene dissolved in 20 ml. of anhydrous ether was added rapidly to the stirring mixture. A small amount of heat was evolved. After 15 minutes, water was added carefully (in a nitrogen atmosphere) to destroy the unreacted alloy. The colorless precipitate thus formed was filtered by suction and dried. The crude yield of product melting at 228–231° was 2.0 g. (96%). One recrystallization raised the melting point to 233–235°; no depression of m.p. resulted from admixture with an authentic specimen of tetraphenylsilane.

1,1,1-Triphenyl-2,2,2-trimethyldisilane from Triphenylsilylpotassium and Trimethylchlorosilane.—To 3.0 g. (0.0058 mole) of hexaphenyldisilane in 70 ml. of anhydrous ether was added 1.5 ml. of sodium–potassium alloy. The mixture was stirred 20 hours at room temperature. Then 1.6 g. (0.015 mole) of trimethylchlorosilane dissolved in 20 ml. of anhydrous ether was added rapidly to the reaction mixture. The black precipitate which had formed dissolved almost instantaneously. The colorless, clear liquid was decanted from the excess alloy and was hydrolyzed with water. The ethereal solution was separated and dried over anhydrous sodium sulfate. Removal of the ether gave 3.3 g. (86%) of practically colorless crystals melting at 101–104°. One crystallization from 95% ethanol gave 2.9 g. (75%) of colorless needles melting at 107–108° (lit.[10] 103–104°).

Anal. Calcd. for $C_{21}H_{24}Si_2$: Si, 16.88. Found: Si, 16.70.

Reaction of Potassium with Hexaphenyldisilane in *n*-Butyl Ether.—A mixture of 2.0 g. (0.0039 mole) of hexaphenyldisilane, 0.6 g. of potassium and 50 ml. of *n*-butyl ether was stirred at 80–90° for 30 hours. A light brown precipitate was formed. Trimethylchlorosilane (1.0 g., 0.0092 mole) dissolved in 20 ml. of anhydrous ether was added rapidly to the vigorously stirred mixture after the latter had been cooled to room temperature. The color of the reaction mixture changed to light gray at the conclusion of addition. After 45 minutes of stirring, water was added carefully (in a nitrogen atmosphere). A white precipitate melting at 360–362° was obtained by filtration. The weight of recovered starting material (mixed melting point) was 0.4 g. (20%). The ethereal solution from the hydrolyzed mixture was separated and dried over sodium sulfate. Removal of the ethers by distillation gave 1.8 g. (70%) of crystals melting at 97–102°. Two recrystallizations from 95% ethanol gave 1.2 g. (47%) of 1,1,1-triphenyl-2,2,2-trimethyldisilane which melted at 107 – 108°.

Attempted Reactions of Hexaphenyldisilane with Sodium Dispersion in Xylene and in Dioxane.—In the following three experiments attempts were made to cleave hexaphenyldisilane followed by the addition of ethyl iodide with the expectation of obtaining triphenylethylsilane.

A mixture of 2.86 g. (0.0055 mole) of hexaphenyldisilane and 0.72 g. (0.011 g. atom) of 35% sodium dispersion in tetrahydronaphthalene[11] was stirred vigorously in 70 ml. of dry xylene at the refluxing temperature for 5 hours. Then 3.4 g. (0.022 mole) of ethyl iodide dissolved in 10 ml. of xylene was added to the reaction mixture, and it was refluxed for another 5 hours. The mixture was hydrolyzed carefully (in a nitrogen atmosphere). The recovered hexaphenyldisilane (mixed melting point) obtained by filtration was 2.75 g. (96%).

A mixture of 2.4 g. (0.0046 mole) of hexaphenyldisilane and 1.21 g. (0.018 g. atom) of 35% sodium dispersion in tetrahydronaphthalene was refluxed in 70 ml. of pure dioxane for 66 hours. Then it was refluxed 7 hours after the addition of 2.9 g. (0.019 mole) of ethyl iodide dissolved in 15 ml. of dioxane. Following hydrolysis (in a nitrogen atmosphere) 2.1 g. (88%) of white solid melting at 357–360° was obtained; a mixed melting point determination with hexaphenyldisilane was not depressed.

Attempted Reaction of Hexaphenyldisilane and 40% Sodium Amalgam.—A mixture of 2.0 g. (0.0039 mole) of hexaphenyldisilane, 0.4 ml. of 40% sodium amalgam and 50 ml. of anhydrous ether was stirred at room temperature for 68 hours. A gray suspension was formed. A solution containing 5.4 g. (0.035 mole) of ethyl iodide in 20 ml. of ether was added rapidly to the reaction mixture. There was no appreciable heat effect or color change after the addition. After the reaction mixture had been stirred 2 hours, water was added carefully (in a nitrogen atmosphere). The resulting white suspension was decanted from the mercury and was filtered. The dry recovered hexaphenyldisilane (mixed melting point) melting at 359–361° weighed 2.0 g. (100%).

Other Methods of Preparation of Triphenylsilylpotassium.[12]—Although the cleavage of hexaphenyldisilane by sodium–potassium alloy gave a high yield of triphenylsilylpotassium, the starting material is not available commercially. We found that the same organometallic compound could be made from triphenylchlorosilane with the probable formation of hexaphenyldisilane as an intermediate. In this simple one-step process the triphenylsilylpotassium was also derivatized as 1,1,1-triphenyl-2,2,2-trimethyldisilane. Also, from some preliminary experiments, we found that triphenylethoxysilane could be cleaved by sodium–potassium alloy to give satisfactory yields of triphenylsilylpotassium.

A solution of 4.5 g. (0.0152 mole) of triphenylchlorosilane (Dow Corning, purified grade) in 80 ml. of anhydrous ether was added rapidly to a stirred mixture of 2 ml. of sodium–potassium alloy in 20 ml. of anhydrous ether. The mixture

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[9] C. A. Kraus and H. Eatough, THIS JOURNAL, **55**, 5008 (1933).

[10] R. A. Benkeser and R. G. Severson, *ibid.*, **73**, 1424 (1951).

[11] The authors wish to thank the Ethyl Corporation for the supply of sodium dispersion.

[12] The authors are grateful to Howard A. Hartzfeld and Julian B. Honeycutt for assistance from their current studies with these and related reactions.

turned dull gray gradually. After 36 hours of stirring, a black precipitate was formed. Trimethylchlorosilane (2.0 g., 0.018 mole) dissolved in 20 ml. of ether was added rapidly to the reaction mixture. Fifteen minutes later it was hydrolyzed carefully (in a nitrogen atmosphere). Removal of ether from the sodium sulfate-dried ethereal solution left 4.9 g. (97%) of pale yellow crystals melting at 95–101°. Two recrystallizations from 95% ethanol yielded 3.4 g. (67%) of colorless needles melting at 107–108°.

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A New Synthesis of 2-Chloro-7-nitrofluorene[1]

BY HELMUT R. GUTMANN AND FRANCIS E. RAY

The synthesis of 2-chloro-7-nitrofluorene has been reported by Courtot[2,3] and more recently by Schulman.[4] These investigators chlorinated fluorene in chloroform or carbon tetrachloride at 0–5° without a catalyst for 18 to 30 hours. This was followed by nitration of the crude 2-chlorofluorene in glacial acetic acid.

This method of chlorination has yielded, in our hands, mixtures which contained large amounts of unreacted fluorene. The compounds melted from 87–92° but showed a chlorine content of only 4.09%. The theory requires a chlorine content of 17.45% for 2-chlorofluorene melting at 96°. Nitration of the chlorinated products resulted in mixtures of 2-nitrofluorene and 2-chloro-7-nitrofluorene melting from 140–160° which were very difficult to purify.

It has now been found that 2-chloro-7-nitrofluorene can also be prepared by the chlorination, for 35 minutes, of 2-nitrofluorene in monochlorobenzene using iodine as a catalyst. Pure 2-chloro-7-nitrofluorene was obtained in 56% yield. 2-Amino-7-chlorofluorene was likewise available from the 2-chloro-7-nitrofluorene by reduction with zinc dust and calcium chloride in ethanol.[5]

Experimental

Preparation of 2-Chloro-7-nitrofluorene.—A sample of 24.5 g. of 2-nitrofluorene (0.12 mole), m.p. 158°, was suspended in 300 cc. of monochlorobenzene in a 2 l. three-necked flask fitted with a mechanical stirrer, a reflux condenser and a gas inlet tube. The flask was submerged in a boiling water-bath and the suspension stirred vigorously. When all of the 2-nitrofluorene had dissolved 0.5 g. of iodine was added to the solution. Fourteen grams of dry chlorine (0.2 mole) was passed into the reaction mixture in the course of 20 minutes. Hydrogen chloride was observed to evolve from the solution. After the addition of chlorine had been completed carbon dioxide was passed through the chlorine generator and the reaction flask for 15 minutes. The reaction vessel was removed from the boiling water-bath and allowed to stand at room temperature for 16 hours. The crystalline mass which had precipitated from the reaction mixture was collected on a Buchner funnel and washed with 10 cc. of cold monochlorobenzene. The yellow product melted from 237–239°. The mixed melting point of the compound with an authentic sample of 2-chloro-7-nitrofluorene, m.p. 235–238° (nitrogen, found 5.71; nitrogen, calcd. 5.70) was 237–238°. Courtot and Vignati[3] reported a melting point of 237° for 2-chloro-7-nitrofluorene. After the material had been dried in air for three days it weighed 16.5 g. which represents a yield of 56%.

Preparation of 2-Amino-7-chlorofluorene.—The reduction of 16.5 g. of 2-chloro-7-nitrofluorene (0.068 mole), m.p. 237–239°, was carried out as described in reference 5 except that 0.5 g. of charcoal was included in the reaction mixture and the reaction time was 8 hours. The yield was 8.8 g. of 2-amino-7-chlorofluorene melting at 131.5–133.5°.

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[1] Our thanks are due to the Damon Runyon Memorial Fund for a grant that defrayed the cost of this work.

[2] Courtot, *Ann. chim.*, [10] **14**, 104 (1930).

[3] Courtot and Vignati, *Compt. rend.*, **184**, 1179 (1927).

[4] Schulman, *J. Org. Chem.*, **14**, 382 (1949).

[5] "Organic Syntheses," Coll. Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 448.

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RECEIVED FEBRUARY 12, 1951

Acylation Studies in the Thiophene and Furan Series.[1a] VIII. Mixed Melting Points of Some Homologous Acetylmethylthiophene Derivatives

BY HOWARD D. HARTOUGH[1b]

Steinkopf[2] has summarized the literature on the "isomorphic phenomena" exhibited by thiophene compounds. In this respect, Steinkopf creates the impression that mixed melting points cannot be relied upon in the thiophene series to distinguish between isomeric thiophene derivatives and cites many examples among the derivatives of halothiophenes to substantiate his postulation. The principal examples stressed[2] are the mixed melting points of the derivatives of the isomeric trichlorothiophenes studied by Steinkopf and Kohler.[3] They prepared some nineteen derivatives of 2,3,4-trichlorothiophene and of a compound *assumed* to be 2,3,5-trichlorothiophene and found that, in each case, the melting points of corresponding derivatives of these two materials were identical and the mixed melting point was the same. The investigators were able to distinguish between the isomeric derivatives by luminescence under light from a mercury-quartz lamp. This method appears spurious since the work of later investigators[4] showed that Steinkopf and Kohler were actually preparing derivatives of two individual samples of 2,3,4-trichlorothiophene.

Since Steinkopf's postulation[2] was felt to be misleading, the mixed melting points of the oximes, *p*-nitrophenylhydrazones, and semicarbazones of nine homologous acetylmethylthiophenes, 2-acetylthiophene and 2-acetyl-5-ethylthiophene have been determined. Among the oximes and *p*-nitrophenylhydrazones all nine acetylmethylthiophenes showed adequate mixed melting point depression. In one instance, the melting point of a mixture of the oximes of 2-acetyl-5-methylthiophene and 2-acetyl-5-ethylthiophene did not show depression. However, the semicarbazone and *p*-nitrophenylhydrazone derivatives showed adequate depression. These data are listed in Table I. The mixed melting point data on the semicarbazones are not complete since most of these materials decompose near their melting points. Thus mixture melting points normally are not so significant as in the other series

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[1] (a) Paper VII of this series, H. D. Hartough and A. I. Kosak, THIS JOURNAL, **70**, 867 (1948); (b) Hercules Experiment Station, Wilmington, Delaware.

[2] W. Steinkopf, "Die Chemie des Thiophens," Verlag von Theodor Steinkopf, Dresden and Leipzig, 1941, pp. 15–19.

[3] W. Steinkopf and W. Kohler, *Ann.*, **532**, 250 (1937).

[4] H. L. Coonradt, H. D. Hartough and G. C. Johnson, THIS JOURNAL, **70**, 2564 (1948), found that 2,3,4-trichlorothiophene arose from direct chlorination of thiophene. Steinkopf and Kohler[3] assumed this product to be 2,3,5-trichlorothiophene.