[Contribution from the Mallinckrodt Chemical Laboratory, Harvard University]

REACTIONS OF DIBROMOALKANES WITH LITHIUM METAL

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A recent communication reported the first preparation of alkyldilithium compounds and their use in the synthesis of silicon-containing spiranes (1). To determine the generality of the formation of alkyldilithium compounds, the authors have studied the action of lithium metal in ether on a series of polymethylene dibromides. Stable solutions of organodilithium compounds were obtained only when the bromine atoms were separated by at least four carbon atoms (Table I). The reactions of polymethylene dihalides with lithium thus parallel closely their reactions with magnesium, since stable Grignard reagents can be prepared from dihalides only when the halogen atoms are equally remote (2).

To form the solutions of dilithium compounds, the dihalides were added to lithium shot in diethyl ether, usually below 0°. The solutions obtained were treated with excess trimethylchlorosilane. After removal of the lithium salts, fractional distillation of the reaction products then gave volatile silicon compounds whenever an organolithium compound was present in the original solution. In this way three new bis-(trimethylsilyl)alkanes were obtained. These compounds are colorless oils with faint pleasant odors; their properties are given in Table II.

No volatile silicon-containing products were obtained from 1,2-dibromoethane or 1,3-dibromopropane under any conditions, or from dibromomethane under normal circumstances. However, when dibromomethane and trimethylchlorosilane were added simultaneously to lithium shot at $-25°$, a very small yield of bis-(trimethylysilyl)methane was obtained, implying the formation of an unstable methylenedilithium compound in solution. This also has a parallel in the corresponding Grignard reaction; it has been shown that diiodomethane and magnesium react in ether to give a small amount of methylenebis-(magnesium iodide) (3). Magnesium reacts with 1,2-dibromoethane to give ethylene (4), and with 1,3-dibromopropane to give principally cyclopropane (5).

The dilithium compound from 1,10-dibromodecane was identified by treatment with methanol and distillation of the resulting *n*-decane, instead of by preparing a trimethylsilyl derivative.

The infrared spectra of the three bis-(trimethylsilyl)alkanes in chloroform solution were obtained using a Baird automatic recording infrared spectrophotometer. The positions of the absorption bands are given in Table III. As would be expected from the close structural similarity of these compounds, the spectra are nearly identical.

EXPERIMENTAL

Combustion analyses were carried out by Dr. S. M. Nagy and his associates at the M. I. T. Microanalytical Laboratories. Eastman organic chemicals were used except where specified.

TABLE I

Reactions of Dibromides With Lithium

DIBROMIDE	DILITHIUM COMPOUND	ISOLATED AS	YIELD, %
$BrCH_2Br$	Unstable	$(CH_3)_3SiCH_2Si(CH_3)_3$	6
$Br(CH_2)_2Br$	None	—	—
$Br(CH_2)_3Br$	None	—	—
$Br(CH_2)_4Br$	Stable	$(CH_3)_3Si(CH_2)_4Si(CH_3)_3$	63
$Br(CH_2)_5Br$	Stable	$(CH_3)_3Si(CH_2)_5Si(CH_3)_3$	68
$Br(CH_2)_6Br$	Stable	$(CH_3)_3Si(CH_2)_6Si(CH_3)_3$	42
$Br(CH_2)_{10}Br$	Stable	$CH_3(CH_2)_8CH_3$	71

TABLE II

Bis-(trimethylsilyl)alkanes, $(CH_3)_3Si(CH_2)_nSi(CH_3)_3$

n	B.P., °C.	MM.	n_D^{25}	d_D^{25}	MOLECULAR REFRACTION	
					Calc'd	Found
4	199	748	1.4244	0.763	67.69	67.77
5	216	760	1.4278	0.768	72.32	72.47
6	109.5	16	1.4298	0.772	76.95	77.09

TABLE III

Infrared Absorption[a] of the Bis-(trimethylsilyl)alkanes, $(CH_3)_3Si(CH_2)_nSi(CH_3)_3$

n = 4	n = 5	n = 6	INTENSITY
2920	2920	2920	s
2380	2380	2370	w
1925	1930	1935	w
1715	1720	1700	w
1615	1617	1615	w
1450	1460	1456	m
1412	1414	1412	s
1354	1362 1340	1346	w
1298	1298	1294	m
1250	1252	1250	s
1148	1150		s
1087	1081	1085	w
1054			w
	1042		w
1006	1012		m
	985		m
964		968	w
		902	m
860	862	864	s
839	841	837	s

[a] Frequencies in cm^{-1}; intensities as indicated: s, strong; m, medium; w, weak.

The reaction vessel was a 500-ml. flask fitted with a dropping funnel, a mercury-sealed Hershberg type stirrer, and a reflux condenser. During the reactions, a positive pressure of dry nitrogen was maintained on the system through the condenser.

Lithium shot. The required quantity of lithium metal was heated in a flask with mineral oil until the metal was completely melted. A few drops of oleic acid were added, and the flask was closed with a glass stopper and was shaken vigorously until the lithium had cooled well below its melting point (6). The resulting shot were filtered off on glass cloth, washed with purified petroleum ether, and added immediately in a stream of nitrogen to the reaction vessel, in which 150 ml. of anhydrous ethyl ether (Mallinckrodt) had already been placed.

1,4-Bis-(trimethylsilyl)butane. Lithium shot was prepared as described above from 5.0 g. (0.7 mole) of lithium. A solution of 28 g. (0.13 mole) of 1,4-dibromobutane in 100 ml. of anhydrous ether was placed in the dropping funnel. The reaction flask was cooled to 0° in a Dry Ice-acetone bath, and about 3 ml. of the dibromide solution was added. Reaction was initiated by vigorous stirring. The temperature was then lowered to $-10°$ and the remaining dibromide was added dropwise over two hours, with continued stirring. After completing the addition, the reaction mixture was stirred for 30 minutes at 10°. The flask was then cooled to $-15°$ and a solution of 27 g. (0.25 mole) of trimethylchlorosilane was added dropwise. The mixture was then allowed to warm to room temperature and to stand overnight.

After excess lithium metal had been dissolved by the addition of ethanol, the reaction mixture was poured into water. The organic layer was separated, washed well with water, and dried over calcium chloride. The ether was removed on a steam-bath and the residue was distilled fractionally through a 40-cm. helix-packed column. After the removal of hexamethyldisiloxane (b.p. 101°) the product distilled at 197–200°. The yield was 16.5 g. (63%). The product was allowed to stand over solid sodium hydroxide for several days and was purified by redistillation.

Anal. Calc'd for $C_{10}H_{26}Si_2$: C, 59.31; H, 12.94.
Found: C, 59.44; H, 12.70.

1,5-Bis-(trimethylsilyl)pentane. Using 1,5-dibromopentane, lithium shot, and trimethylchlorosilane, this compound was prepared in the same way as 1,4-bis-(trimethylsilyl)-butane. The product distilled at 215–216.5° and redistillation was found to be unnecessary.

Anal. Calc'd for $C_{11}H_{28}Si_2$: C, 61.02; H, 13.03.
Found: C, 61.45; H, 12.98.

1,6-Bis-(trimethylsilyl)hexane. This compound was prepared from 1,6-dibromohexane (Halogen Chemical Co.) by the same sequence of reactions used in the two previous preparations. This dihalide reacted slowly with lithium and the reaction was difficult to initiate. The product was distilled under reduced pressure from a modified Claisen flask, allowed to stand for several weeks over sodium hydroxide, and redistilled.

Anal. Calc'd for $C_{12}H_{30}Si_2$: C, 62.51; H, 13.12.
Found: C, 62.82; H, 12.99.

1,3-Dibromopropane and lithium. Reactions with lithium were carried out as described above, both in the usual way and with simultaneous addition of the trimethylchlorosilane and dibromopropane, at -30 and $-55°$. Even at the latter temperature, the dibromide reacts rapidly with lithium. When the reaction mixtures were worked up, no volatile organosilicon compound other than hexamethyldisiloxane could be isolated, although a small amount of oily residue was left after distillation.

1,2-Dibromoethane and lithium. One reaction was carried out at $-30°$ with the trimethylchlorosilane added simultaneously with the dibromoethane. The dibromide reacted rapidly with lithium shot at this temperature, but no product other than hexamethyldisiloxane was found.

Bis-(trimethylsilyl)methane. To 4.2 g. (0.60 mole) of lithium shot was added a mixture of 21 g. (0.12 mole) of dibromomethane and 12 g. (0.115 mole) of trimethylchlorosilane at $-25°$, under the conditions described above. From the reaction mixture was isolated 0.8 g. (6%)

of a liquid boiling at 132–135°, with n_D^{25} 1.4155. Bis-(trimethylsilyl)methane is reported to boil at 134°, and to have n_D^{20} 1.4172 (7, 8). When the same reaction was carried out at various temperatures adding first all the dibromomethane and then the trimethylchlorosilane, none of the product could be isolated.

1,6-Dilithiohexane and carbon dioxide. A dilithium reagent solution was prepared from 24.4 g. (0.10 mole) of 1,6-dibromohexane. Treatment with gaseous carbon dioxide gave a mixture from which was isolated 5.5 g. (32%) of suberic acid, m.p. 136°, along with an approximately equal quantity of polymeric material. Only a trace of volatile ketone was found.

A similar qualitative experiment showed that the principal product of carbonation of the lithium reagent obtained from 1,5-dibromopentane was cyclohexanone, with acidic and polymeric materials as minor products.

n-Decane from 1,10-dibromodecane. A lithium reagent solution was prepared from 20 g. (0.067 mole) of 1,10-dibromodecane (Matheson Co.). This dibromide reacts only slowly with lithium and the mixture required refluxing to start the reaction. The organolithium solution was treated with methanol and water, and the organic layer was fractionally distilled to give 6.8 g. (71%) of *n*-decane, b.p. 174°, n_D^{25} 1.4100 (9).

SUMMARY

The reactions of a series of polymethylene dibromides, [$Br(CH_2)_nBr$, where $n = 1$ through 6, and 10] with metallic lithium in ether have been investigated. All of the dibromides studied reacted with lithium, but only those with $n > 3$ gave stable organolithium compounds.

From the reactions of alkyldilithium compounds with trimethylchlorosilane, three new bis-(trimethylsilyl)alkanes have been prepared.

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REFERENCES

(1) WEST AND ROCHOW, *Naturwissenschaften*, **40**, 142 (1953).
(2) RUNGE, *Organometallverbindungen*, Wissenschaftliche Verlagsgesellschaft m. b. H., Stuttgart, 1944, pp. 251, 252, 518.
(3) EMSCHWILLER, *Compt. rend.*, **183**, 665 (1926); **188**, 1555 (1929).
(4) TISSIER AND GRIGNARD, *Compt. rend.*, **132**, 835 (1901).
(5) ZELINSKY AND GUTT, *Ber.*, **40**, 3049 (1907).
(6) BARTLETT, SWAIN, AND WOODWARD, *J. Am. Chem. Soc.*, **63**, 3229 (1941).
(7) SOMMER, GOLDBERG, GOLD, AND WHITMORE, *J. Am. Chem. Soc.*, **69**, 980 (1947).
(8) SOMMER, MITCH, AND GOLDBERG, *J. Am. Chem. Soc.*, **71**, 2746 (1949).
(9) SHEPARD, HENNE, AND MIDGLEY, *J. Am. Chem. Soc.*, **53**, 1948 (1931).