

THE PREPARATION AND REACTIONS OF AN OPTICALLY-ACTIVE SILYL-MERCURIAL

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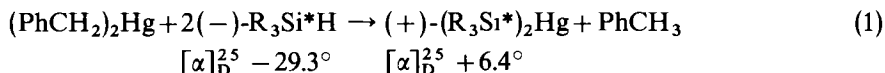
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SUMMARY

(-)-Bis [methyl(1-naphthyl)phenylsilyl]mercury, $(-)-(R_3Si^*)_2Hg$, $[\alpha]_D^{25} - 19.2^\circ$, has been obtained in high yield, but optically impure, from interaction of di-tert-butylmercury and (+)- R_3Si^*H ; the specific rotation, $[\alpha]_D$, of the optically-pure compound is estimated to be $> 200^\circ$. Cleavage with lithium aluminium hydride gives (+)- R_3Si^*H , $[\alpha]_D^{25} + 2.8^\circ$, and cleavage with 1,2-dibromoethane followed by reduction of the initially produced (+)- R_3Si^*Br gives (-)- R_3Si^*H , $[\alpha]_D^{25} - 2.4^\circ$. UV photolysis of the mercurial gives the disilane $(-)-(R_3Si^*)_2$, $[\alpha]_D^{25} - 5.2^\circ$; the value of $[\alpha]_D^{25}$ for the optically pure disilane is thought to be $> -70^\circ$. It is suggested that the configuration is predominantly retained at silicon in the formation and all three cleavages of the $(-)-(R_3Si^*)_2Hg$.

INTRODUCTION

The first preparation¹ of an optically-active silylmercurial was carried out by heating dibenzylmercury with $(-)-R_3Si^*H$ [where $R_3Si^* = Me(1-C_{10}H_7)PhSi$] at 130° for 4 h, according to eqn. (1).



Unchanged starting materials, together with some dibenzyl and mercury had to be sublimed from the product by heating under vacuum at 135° for a further 4 h, and since it was found that almost complete racemization of the mercurial occurred during 4 h at 150° , it was clear that the observed specific rotation of $+6.4^\circ$ represented a low optical purity. Nevertheless it was possible to carry out some stereospecific reactions¹.

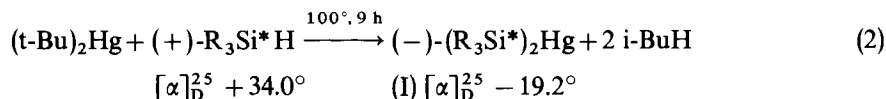
We describe below a somewhat improved preparation [actually of the enantiomer with the negative rotation, since (+)- R_3Si^*H was used as starting material], and also the stereochemical results of some decompositions.

RESULTS AND DISCUSSION

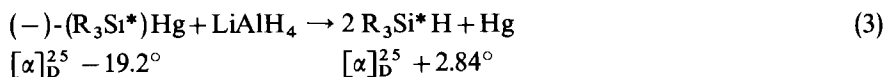
An attempt was made, using (+)- R_3Si^*H , to improve the preparation from

dibenzylmercury by use of a lower reaction temperature (*viz.* 120°) but IR analysis showed that all the residual (+)-R₃Si*H could not be satisfactorily removed at this temperature.

Use of di-*tert*-butylmercury² enabled a lower reaction temperature to be used. Initially a reaction and sublimation temperature of 100° was used, with a 2/1 mol ratio of silane to mercurial, and the results of different choices of reaction and sublimation temperatures are shown in Table 1. It will be seen that the rotation becomes more negative as unchanged (+)-R₃Si*H is sublimed out, and reaches a negative maximum, but then decreases as the (-)-(R₃Si*)₂Hg racemizes. Better results were obtained with a 1/1 mol ratio of silane to mercurial, since it was easier to sublime out residual di-*tert*-butylmercury than residual (+)-R₃Si*H; a maximum negative specific rotation of -19.2° was then obtained after a 3 h reaction time combined with a 6 h sublimation time (see Table 1). The product, (I), obtained in this way according to eqn. (2), was a bright yellow-green solid, of m.p. 55-58°, and the IR spectrum showed that no significant amount of (+)-R₃Si*H remained in it.



Some cleavages of the Si-Hg bonds of (I) were examined. Thus (I) reacted with lithium aluminium hydride to give back the (+)-R₃Si*H in high yield, with a rotation indicating that the configuration at silicon had been retained to the extent of 54% in the Walden cycle [see eqn. (3)]. It is known that lithium aluminium hydride cleavage of certain silyl-platinum complexes occurs with a high degree of stereo-



specificity³, and if the assumption is made that this is also the case with the mercurial

TABLE 1

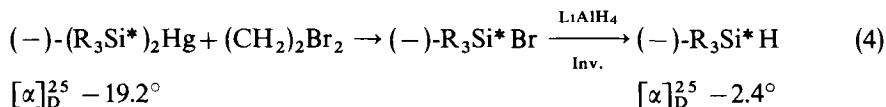
VALUES OF $[\alpha]_{\text{D}}^{25}$ FOR (-)-(R₃Si*)₂Hg AFTER VARIOUS TIMES OF REACTION AND SUBLIMATION

(+)-R ₃ Si*H/(<i>t</i> -Bu) ₂ Hg, 2/1				(+)-R ₃ Si*H/(<i>t</i> -Bu) ₂ Hg, 1/1			
Reaction time (h)	Sublim time (h)	Total time (h)	$[\alpha]_{\text{D}}^{25}$ (°)	Reaction time (h)	Sublim time (h)	Total time (h)	$[\alpha]_{\text{D}}^{25}$ (°)
0	0	0	+21 ^a	0	0	0	+15 ^a
2	4	6	+1.26	3	3	6	-10.6
2	7½	9½	-12.2	3	6	9	-19.2
5	9	14	-7.16				
5	13	18	-3.92				

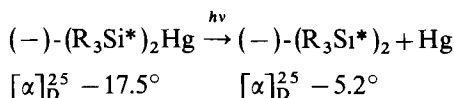
^a Calcd

(I), it follows that the optically-pure $(-)-(R_3Si^*)Hg$ would have an $[\alpha]_D^{25}$ value of $-19.2 \times 34/2.84$, *i.e.* -230° , a value which is reasonably consistent with the thermal racemization data in Table 1.

Treatment of (I) with 1,2-dibromoethane gives $(-)-R_3Si^*Br$, which on lithium aluminium hydride reduction gives the $(-)-R_3Si^*H$ with $[\alpha]_D^{25} -2.4^\circ$ [eqn. (4)]. (The negative rotation of the hydride is to be expected since the reduction of the bromide involves inversion at silicon⁴.) The value of the rotation implies that the stereospecificity of the cleavage by 1,2-dibromoethane is much the same as that in the cleavage by lithium aluminium hydride.



UV irradiation of (I), $[\alpha]_D^{25} -17.5^\circ$, in cyclohexane gives the disilane, $(-)-(R_3Si^*)_2$, and mercury in high yield [eqn. (5)].



From our general knowledge of the behaviour of silyl-mercurial compounds^{1,5}, we suspect that all three cleavages studied proceed with predominant retention at silicon, which implies that (I) is also formed with retention of configuration at silicon, as previously suggested¹. The cleavages by lithium aluminium hydride and 1,2-dibromoethane probably involve multi-centre molecular processes, and that by light probably involves initial liberation of free R_3Si^* radicals, which are known to be capable of retaining their configuration⁶. A multi-centre process within a photo-excited molecule is also conceivable for reaction (5), but either this or a process involving free radicals would be most unlikely to give inversion at *both* silicon atoms, and thus we conclude that the $(-)-(R_3Si^*)_2$, in spite of its negative rotation, has the same configuration about the silicon atoms as that in $(+)-R_3Si^*H$. Consistent with

TABLE 2

ORD DATA

Compound	Solvent	Concn. (g/100 g)	nm	$[\alpha]_D^{25}$ ($^\circ$)	$10^{-2} [M]^{25}$
$(-)-(R_3Si^*)_2Hg$, (I)	Cyclohexane	3.0	589	-17.5	-1.22
			578	-18.5	-1.28
			546	-20.6	-1.43
			436	-43	-2.99
			365	+19.6	+1.36
$(-)-(R_3Si^*)_2$	Benzene	1.3	589	-5.2	-0.26
			578	-0.094	-0.046
			546	-0.47	-0.024
			436	+3.3	+0.16
			365	+113	+5.58

this is the observation that the $(-)-(R_3Si^*)_2$ gives a positive plain dispersion curve (see Table 2), as do most R_3Si^*X compounds having the same configuration as $(+)-R_3Si^*H$ ^{3,7}. It is noteworthy that if we are correct in our suggestion that the correct value for the rotation of the $(-)-(R_3Si^*)_2Hg$ is in the region of 230° , the observed value of $[\alpha]_D^{25}$ for $(-)-(R_3Si^*)_2$, obtained from $(-)-(R_3Si^*)_2Hg$ of $[\alpha]_D^{25} - 17.5^\circ$, indicates that the value of $[\alpha]_D^{25}$ for optically pure $(-)-(R_3Si^*)_2Hg$ would be at least -70° .

Limited ORD data for $(-)-(R_3Si^*)Hg$, listed in Table 2 (which were obtained on a sample with less than the highest rotation observed) as interpreted in Fig. 1, suggest that there is a weak negative Cotton effect centred at the UV absorption maximum of 387 nm. The apparent negative plain dispersion curve may arise from a positive plain curve with the negative Cotton effect imposed upon it. There are no ORD curves for optically active R_3Si^*X compounds which can usefully be correlated with that in Fig. 1, which thus cannot be taken either to confirm or to contradict the suggestion that the configuration about both silicon atoms in $(-)-(R_3Si^*)_2Hg$ is the same as that about the silicon atom of $(+)-R_3Si^*H$.

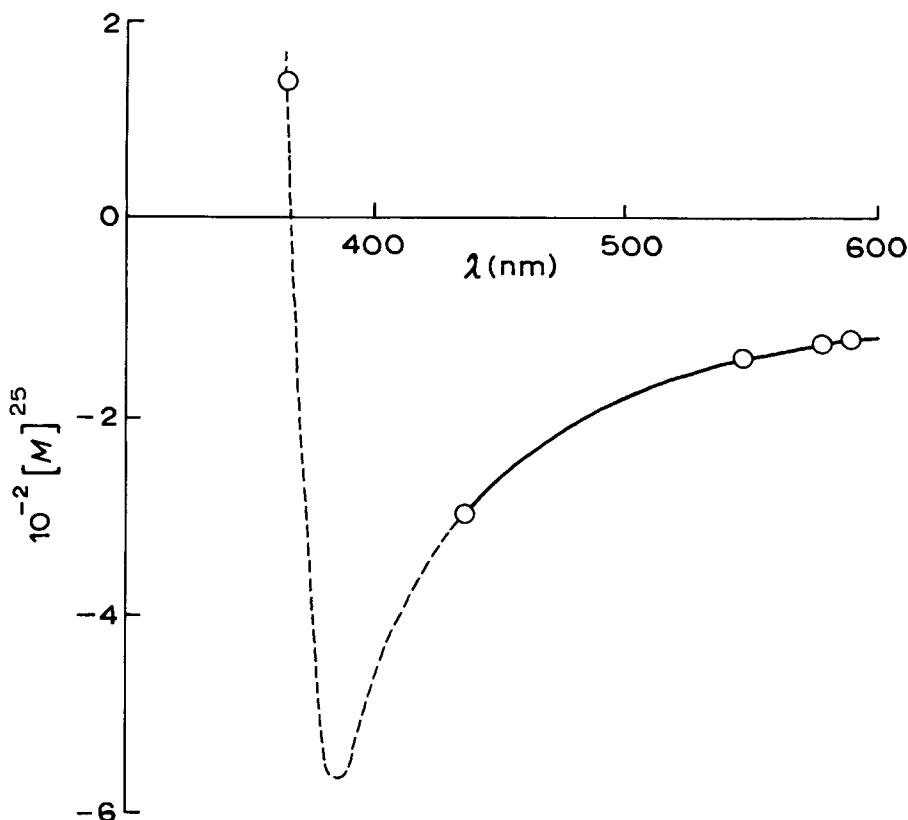


Fig. 1. ORD curve for $(-)-[Me(1-C_{10}H_7)PhSi]_2Hg$ from 589 to 365 nm. (The broken line represents only a diagrammatic interpolation.)

We should point out that the results reported above are not quantitatively consistent with those previously obtained with (+)- $(R_3Si^*)_2Hg$; for example, from a sample of the (+)-mercurial with only one-third of the rotation of (I), the sample of $(-)-R_3Si^*H$ obtained by 1,2-dibromoethane cleavage and subsequent reduction had a higher rotation than that obtained similarly from (I). Our present work suggests that the sample of (+)- $(R_3Si^*)_2Hg$ used in the earlier work may contained some $(-)-R_3Si^*H$ impurity, though no doubt is cast on the main conclusions¹ reached by its use.

An attempt to make an optically-active germyl-mercurial by interaction of (+)-Et(1-C₁₀H₇)PhGeH with dibenzylmercury gave only racemic product, which is not surprising in view of the fairly ready racemization even of the (+)-hydride itself. No attempt was made to use di-tert-butylmercury, which should give somewhat better results.

EXPERIMENTAL

*Di-tert-butylmercury*²

This was prepared from mercuric chloride and tert-butylmagnesium chloride in tetrahydrofuran, and purified by elution in diethyl ether through an alumina column to give a solid of m.p. 58–60° (lit.² 56–58°). It decomposes slowly at room temperature, but samples can be conveniently purified after storage by sublimation (at 0.1 mmHg at a bath temperature of 80°).

Preparation of (-)-bis[methyl(1-naphthyl)phenylsilyl]mercury, (I)

Di-tert-butylmercury (1 g, 3.2 mmol) and (+)- R_3Si^*H , (0.77 g, 3.2 mmol), $[\alpha]_D^{25} + 34.0^\circ$, were transferred to a 50 ml round-bottom flask in a dry box. The flask was closed with a high vacuum stopcock, withdrawn from the box, and connected to a vacuum line so that the contents could be degassed. The flask was disconnected from the line, and the mixture was kept under vacuum for 3 h, with the flask totally immersed in an oil bath at 100°, light being carefully excluded with aluminium foil. The flask was cooled, and, still protected from light, was connected to a small sublimator in the dry box. The apparatus was then removed from the box and heated at 100° for 6 h under a pressure of 10^{-3} mmHg, with exclusion of light. The excess of di-tert-butylmercury and (+)- R_3Si^*H sublimed out during this time, and cooling of the flask gave bright yellow-green crystals of $(-)-R_3Si^*_2Hg$ (1.03 g, 95%), m.p. 55–58°, $[\alpha]_D^{25} - 19.2^\circ$ (c, 1.51 in degassed cyclohexane) (Found: C, 58.7; H, 4.4. C₃₄H₃₀HgSi₂ calcd.: C, 58.9; H, 4.1 %). The IR spectrum (Nujol mull) indicated that effectively all the (+)- R_3Si^*H , $\nu(Si-H)$ 2115 cm⁻¹, had been removed.

Reactions of (-)- $(R_3Si^)_2Hg$, (I)*

(i). A solution of (I) (0.10 g, 0.15 mmol), $[\alpha]_D^{25} - 19.2^\circ$, in degassed cyclohexane (5 ml) was added in the drybox to lithium aluminium hydride (0.01 g, 0.26 mmol) in diethyl ether. The flask was stoppered and kept at room temperature for 5 days, then 2 N hydrochloric acid (10 ml) was added, and the organic layer was separated, washed and dried (CaSO₄). Solvents were evaporated off, to leave an oil, which was eluted in 1/1 benzene/light petroleum (b.p. 40–60°) through a silica gel column (15 × 1.2 cm) to give (+)- R_3Si^*H (0.063 g, 90%), $[\alpha]_D^{25} + 2.84^\circ$ (c, 1.9 in cyclohexane);

the IR spectrum (liquid film) was identical with that of an authentic sample; $\nu(\text{Si-H})$ 2120 cm^{-1} .

(ii). Degassed 1,2-dibromoethane (1 ml) was added to (I) (0.50 g, 0.72 mmole), $[\alpha]_{\text{D}}^{25} - 19.2^\circ$, in the dry box at room temperature. The mixture was shaken for 10 min, removed from the dry box and added to lithium aluminium hydride (0.1 g, 2.6 mmol) in degassed diethyl ether (10 ml). The mixture was stirred at room temperature for 30 min, and then treated with 2 *N* hydrochloric acid. Work up as in (i) gave (–)- $\text{R}_3\text{Si}^*\text{H}$ (0.29 g, 82%), $[\alpha]_{\text{D}}^{25} - 2.44^\circ$ (*c*, 2.8 in cyclohexane); the IR spectrum (liquid film) was identical with that of an authentic sample; $\nu(\text{Si-H})$ 2120 cm^{-1} .

(iii). A solution of (I) (0.96 g, 1.38 mmol), $[\alpha]_{\text{D}}^{25} - 17.5^\circ$, in degassed cyclohexane (20 ml) was sealed in a Pyrex glass ampoule, and irradiated with UV light from a medium pressure mercury arc lamp (Englehard Hanovia Model UVS 50/A) for 30 h. During this period, metallic mercury and a white solid were deposited at the base of the ampoule. The ampoule was opened, and most of the cyclohexane was removed by pipette. The residue was extracted with hot benzene ($2 \times 2 \text{ ml}$) to leave mercury (0.26 g, 94%), and evaporation of the benzene under reduced pressure left a white solid (0.68 g, 100%), m.p. $160\text{--}180^\circ$. This was recrystallized from benzene/pentane to give (–)-*sym*-dimethyl-*di*-1-naphthyldiphenylsilane, (–)- $(\text{R}_3\text{Si}^*)_2$, m.p. $204\text{--}207^\circ$, $[\alpha]_{\text{D}}^{25} - 5.2^\circ$ (*c*, 1.3 in benzene) (Found: C, 81.5; H, 6.8. $\text{C}_{34}\text{H}_{30}\text{Si}_2$ calcd.: C, 82.5; H, 6.1%). The proton NMR spectrum (in CDCl_3 , with TMS as internal standard) had the correct integration pattern, with τ values as follows: C_{10}H_7 and C_6H_5 , 2.4–3.2 (m); CH_3 , 9.95 (s).

Preparation of impure (\pm)-bis[ethyl(1-naphthyl)phenylgermyl]mercury

Dibenzylmercury (0.50 g, 1.31 mmol) and (+)-Et($1\text{-C}_{10}\text{H}_7$)PhGeH (1.61 g, 5.24 mmol), $[\alpha]_{\text{D}}^{25} + 15^\circ$, were placed in a vacuum sublimator in the dry-box. The sublimator was stoppered, withdrawn from the dry-box, and degassed on the vacuum line. The mixture was then heated at 120° for 6 h with protection from light. The sublimator was then cooled and replaced in the dry-box, and after 3 days at room temperature the mixture solidified. The stopper was replaced by a cold finger, and the sublimator was heated for 6 h at 120° at $5 \times 10^{-3} \text{ mmHg}$ with exclusion of light. Some impurities sublimed out, to leave a bright green solid, which was probably mainly (\pm)-[Et($1\text{-C}_{10}\text{H}_7$)PhGe] $_2$ Hg (0.7 g, 65%), m.p. $44\text{--}50^\circ$, $[\alpha]_{\text{D}}^{25} 0.0^\circ$ (*c*, 1.7 in degassed cyclohexane). The IR spectrum showed that it still contained some of the original germanium hydride, $\nu(\text{Ge-H})$ 2020 cm^{-1} (Nujol mull), and so the compound was not studied further.

ACKNOWLEDGEMENTS

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