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OPTICALLY-ACTIVE BIS(METHYL-1-NAPHTHYLPHENYLSILYL)-MERCURY

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SUMMARY

(+)-Bis(methyl-1-naphthylphenylsilyl)mercury has been prepared, though probably in an optically impure state. Racemization without decomposition takes place at about 150°, and stereospecific cleavages of the Si–Hg bonds are possible.

INTRODUCTION

We describe below the preparation of (+)-bis(methyl-1-naphthylphenylsilyl)-mercury, probably not optically pure. This is the first example of an optically active silyl mercurial. A few exploratory studies have been carried out with it.

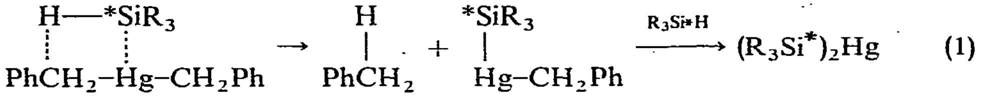
EXPERIMENTAL

(+)-Bis(methyl-1-naphthylphenylsilyl)mercury

Methyl-1-naphthylphenylsilane (2.5 g, 0.01 mole), $[\alpha]_D$ −29.3° (cyclohexane), was heated with dibenzylmercury (0.96 g, 0.0025 mole) at 130° for 4 h, after which unchanged starting materials, bibenzyl, toluene and mercury were sublimed off at 135° for 4 h, leaving bis(methyl-1-naphthylphenylsilyl)mercury as a brillant lemon-yellow solid, m.p. 72–76°, $[\alpha]_D$ +6.4° (dry and degassed cyclohexane). (Found: C, 57.9; H, 3.9; Hg, 27.8. $C_{34}H_{30}Si_2Hg$ calcd. C, 58.7; H, 4.35; Hg, 28.85%.) The mass spectrum showed a group of peaks in the parent-ion region, centred around *m/e* 695, the intensities being in good agreement with the combined isotope pattern of one mercury and two silicon atoms. The UV spectrum showed a weak absorption band at 387 nm, along with stronger absorptions between 245–280 and 320–340 nm. The neat mercurial decomposed at a noticeable rate at 190°, and rapidly at 300°. No apparent decomposition took place when the mercurial was heated under vacuum at about 150°, but the optical activity fell to about 10% of its initial value in 4 h. Photolysis of a 5% w/v solution of the mercurial ($[\alpha]_D$ +3.3°) in cyclohexane (Engelhard Hanovia UVS 500/A, 30 cm away, 10 h) caused complete decolourization of the solution, and precipitation of mercury (96%). The solution was laevorotatory the rotation corresponding to a value of $[\alpha]_D$ of −3° if the disilane had been formed in 100% yield. Likewise, when a 3.6% w/v solution of the mercurial ($[\alpha]_D$ +3.3°) in cyclohexane was allowed to come into contact with the air, decomposition took place immediately with precipitation of mercury, to give a solution with a rotation corresponding to a value of $[\alpha]_D$ of -5.1 if the disiloxane had been formed in 100% yield. Attempts to isolate the pure disiloxane were unsuccessful.

DISCUSSION

The reaction of methyl-1-naphthylphenylsilane with dibenzylmercury almost certainly involves four-centre processes, as in eqn. (1), involving predominant retention of configuration at silicon. (Compare the corresponding reaction involving triphenylsilane[1].) Even if triorganosilyl radicals were involved, as in eqn. (2), retention of configuration would be likely, since organosilyl radicals are known to be pyramidal[2]



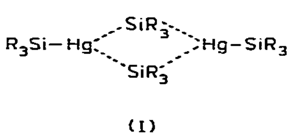
$$\underset{\text{PhCH}_2\text{–}\overset{\vdots}{\text{Hg}}\text{–CH}_2\text{Ph}}{\text{H}\text{—}{}^*\text{SiR}_3} \rightarrow \underset{\text{PhCH}_2}{\overset{\text{H}}{|}}\ \cdot + \underset{\text{Hg–CH}_2\text{Ph}}{\overset{{}^*\text{SiR}_3}{|}} \xrightarrow{\text{R}_3\text{Si*H}} (\text{R}_3\text{Si}^*)_2\text{Hg} \qquad (1)$$

$$(PhCH_2)_2Hg \xrightarrow{\Delta} PhCH_2^{\bullet} \xrightarrow{R_3Si*H} Ph_3CH_3 + R_3Si^{*\bullet} \xrightarrow{Hg(CH_2Ph)_2}$$

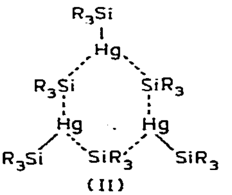
$$PhCH_2^{\bullet} + R_3Si^*\text{–}Hg\text{–}CH_2Ph \rightarrow R_3Si^*\text{–}Hg\text{–}{}^*SiR_3 \qquad (2)$$

and to retain their configuration in abstraction reactions[3]. Thus $(+)$–$(R_3Si^*)_2Hg$ probably has the same configuration as S-$(-)$-R_3Si^*H. Application of Brewster's Rules[4] (which have been shown to apply generally to optically active silicon compounds when atomic refractivities derived from organic compounds are used[4–6]) supports this conclusion. We calculate mercury to have an atomic refractivity of between 12 and 14, depending on the refractive index and density data used[7], but regardless of its exact value, the atomic refractivity of mercury is substantially greater than the group values for 1-naphthyl, phenyl, and methyl. Thus R_3Si^*H and $(R_3Si^*)_2Hg$ of the same configuration should have opposite signs of rotation, the least polarizable group (hydrogen) having been replaced by the most polarizable (mercury).

In view of the fairly rapid racemization of the mercurial at temperatures little above those used for its production, it is very unlikely that our sample was optically pure. This racemization without decomposition is interesting, since it represents a rare example of self-racemization of an optically active R_3Si^*X compound in the absence of negative ions or coordinating solvents (*cf.* ref. 12). Exchange of Me_3M groups ($M = Si$, Ge) in $(Me_3M)_2Hg$ is fairly rapid in solution at room temperature on a chemical[8], if not on an NMR[9] time scale, and NMR temperature-dependence studies[10] indicate an activation energy of only 11.3 kcal/mole for the exchange of trimethylsilyl groups between two bis(trimethylsilyl)mercury molecules. If these exchanges involve four-centre processes, as has been postulated[8,10], they would be expected to involve retention of configuration at silicon, but it is possible that at higher temperatures a minority of the exchanges involve a transition state such as (I) in which the Hg–Si–Hg



(I)



(II)

angle is greater than tetrahedral (approximating to a situation in which the leaving and entering groups both occupy equatorial positions in an sp^3 d-hybridized intermediate). These processes would involve inversion[11], and racemization would ultimately result. Other explanations are possible, however; for example, termolecular processes, such as (II), involving Hg–Si–Hg angles of *ca.* 120°, and thus inversion[11], may contribute at high temperatures in the neat liquid.

The only significance of the results of the photolysis and the exposure to air is that they show that cleavages of the Si–Hg bonds can occur stereospecifically. If the negative rotation of the solution obtained when optically-active mercurial is exposed to air arises mainly from the disiloxane $(-)$-$(R_3Si)_2O$, then the latter must have been formed from the initial hydride with overall retention of configuration at silicon. The negative rotation of the solution obtained on photolysis of the (+)-mercurial can be tentatively attributed to the disilane $(-)$-$Re_3Si^*Si^*R_3$, though acceptance of this suggestion must await isolation of the product. The disilane would probably be formed by combination of two $R_3Si^{*\bullet}$ radicals which had retained their configuration.

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