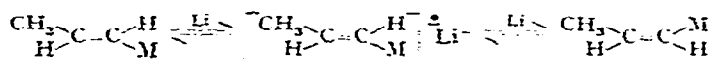


The reaction of the isomeric propenylmercuric bromides with metallic lithium*

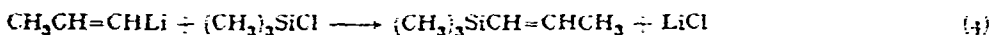
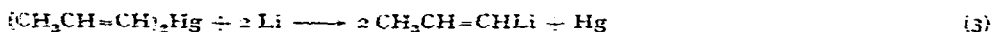
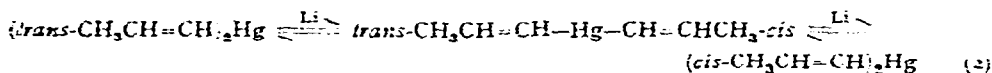
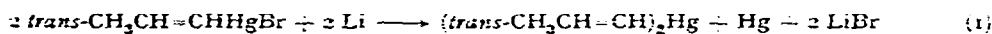
We have observed that the reaction of metallic lithium with either pure tetrapropenyltin isomer causes isomerization of propenyl groups attached to tin, as well as their partial cleavage to give propenyllithium¹. We find that a similar situation prevails with propenylmercury compounds. The R₂Hg/Li displacement reaction is well-known as a route to halogen-free organolithium compounds, and previous work of Nesmeyanov and coworkers² has shown that lithium will displace mercury from divinylmercury to give vinylithium in high yield. We chose to work with the propenylmercuric bromides rather than with the dipropenylmercury isomers.

trans-Propenylmercuric bromide reacted vigorously with an excess of metallic lithium (containing 1.1 % sodium) in ether when high speed stirring was used. Characterization of the lithium reagent formed with trimethylchlorosilane gave propenyltrimethylsilane (88 % *trans*, 12 % *cis*) in 64 % yield. More extensive isomerization occurred when *cis*-propenylmercuric bromide reacted with metallic lithium. The propenyltrimethylsilane obtained in this case (67 % yield) contained 60 % of the *trans* isomer and 40 % of the *cis*.

Our studies with the propenyl derivatives of carbon, silicon, germanium and tin have shown that lithium is capable of causing isomerization of propenyl groups attached to the latter three elements, most likely via a radical anion intermediate:



It appears that such isomerization also is possible with propenylmercury compounds. The probable course of the reactions studied is:

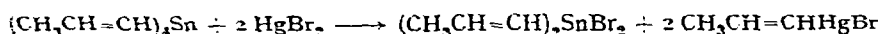


Reaction (4) does not involve a change in the configuration of the propenyl group³. Indirect evidence suggested that the displacement of a propenyl group by lithium from tin does not proceed with any change in configuration of the propenyl group being transferred¹, thus we assume that reaction (3) proceeds with retention of configuration of the propenyl groups. In view of our previous findings with propenyltin compounds¹, it is very probable that the isomerizations indicated by reaction (2) take place very readily. It is not known whether the "symmetrization" reaction (1) occurs with or without isomerization of propenyl groups. When the procedure for converting organomercuric halides to diorganomercurials which involves reduction of the former with sodium stannite was applied to the symmetrization of *cis*- and *trans*-propenyl-

* Part XXIII of the series "Vinyl derivatives of metals"; for Part XXII see ref. 1.

mercuric bromide, dipropenylmercury products with unchanged geometrical configuration were obtained⁴. Traylor and Winstein have presented evidence in favor of a radical mechanism for reductive symmetrization of RHgX with sodium stannite⁵, and thus, even if reaction (1) proceeds by a radical mechanism, retention of configuration may prevail. In view of these uncertainties, we cannot attribute with confidence our observed isomer ratios wholly to the process described by eqn. (2). It is clear, however, that propenyl group cleavage from mercury took place before an equilibrium ratio of *cis/trans* propenyl groups had been established. The lithium displacement route to propenyllithium using propenylmercury compounds appears to be quite acceptable from point of view of propenyl lithium yield, but has the drawback that isomerically pure reagents are not produced.

The propenylmercuric bromide isomers used in this study were prepared by cleavage of tetra-*cis*- and tetra-*trans*-propenyltin⁶ with mercuric bromide in ether:



We had previously shown that such cleavage of vinyltin compounds by mercuric halides led to formation of vinylmercuric halides in good yield⁷. Nesmeyanov and coworkers^{8,9} have reported that reactions of this type proceed with retention of the geometric configuration of the vinyl group transferred from tin to mercury. Our experiments have confirmed this.

Experimental

General comments. All reactions were carried out under an atmosphere of argon or prepurified nitrogen. Melting points are uncorrected. The tetrapropenyltin compounds were prepared as described in a previous paper of this series⁶. Lithium wire containing 1.1% sodium was purchased from the Lithium Corp. of America, trimethylchlorosilane from Dow Corning Corp.

*Cleavage of tetra-*trans*-propenyltin with mercuric bromide.* A solution of 17.8 mmoles of tetra-*trans*-propenyltin in 30 ml of diethyl ether was added to 35.5 mmoles of mercuric bromide and two ml of tetrahydrofuran. The mixture was heated at reflux for 48 h under argon, cooled to 0°, and the liquid layer decanted. The precipitated solid was washed with ether to give 10.4 g (100%) of *trans*-propenylmercuric bromide. A sample of this material, after two recrystallizations from acetone, had m.p. 120–121.5°. A mixed m.p. with authentic material prepared by the reaction of *trans*-propenyllithium with mercuric bromide⁸ was not depressed. After the ether was removed from the liquid layer by rotary evaporation, the residue was dissolved in 20 ml of petroleum ether and filtered. Fractional distillation then gave 5.8 g of liquid product, b.p. 66–70°/0.1 mm (90% yield). The forerun of this product was contaminated with traces of *trans*-propenylmercuric bromide, which sublimed and condensed on the cold finger of the still head. The tail fraction had n_D^{20} 1.5754; Nesmeyanov et al.⁸ report n_D^{20} 1.5790, b.p. 128–129°/10 mm for di-*trans*-propenyltin dibromide. The infrared spectrum of this product was identical with that of tetra-*trans*-propenyltin in the 3500 to 800 cm^{-1} region.

*Cleavage of tetra-*cis*-propenyltin with mercuric bromide.* The procedure followed was identical to that used in the cleavage of the *trans* isomer, 3.7 g (13.1 mmoles) of tetra-*cis*-propenyltin being added to 26.2 mmoles of mercuric bromide in 30 ml of ether. The yield of crude product was 7.5 g (89%), which after two recrystallizations

from petroleum ether had m.p. 62.5–63.5°. A mixed m.p. with authentic material prepared by the organolithium route according to Nesmeyanov et al.⁸ showed no depression. After the ether was distilled off from the decanted ether layer, the liquid residue (4.5 g) was partially distilled, giving 2.5 g (53%) of di-*cis*-propenyltin dibromide, b.p. 90–94°/0.3 mm, n_D^{20} 1.5852. This product was contaminated with *cis*-propenylmercuric bromide, which sublimed and crystallized on the cold finger as the di-*cis*-propenyltin dibromide was being distilled. Nesmeyanov et al.⁸ report for the latter: b.p. 122–123°/10 mm, n_D^{20} 1.5818.

Reaction of metallic lithium with trans-propenylmercuric bromide. In a 200 ml, three-necked Morton flask, equipped with a high speed stirrer, reflux condenser, addition funnel and protected by an argon atmosphere, was placed 1.4 g (0.2 g-atom) of sliced lithium wire (1.1% sodium content) and 25.6 mmoles of *trans*-propenylmercuric bromide in 100 ml of diethyl ether. When stirring was started, a vigorous reaction commenced almost immediately and continued for about 15 min. The stirring was continued for an additional 2 h. To the mixture then was added 27.7 mmoles of trimethylchlorosilane. When this addition was complete, the mixture was heated at reflux for 2 h. The mixture then was filtered through a sintered glass filter and the filtrate was fractionally distilled to give 1.9 g (64%) of propenyltrimethylsilane, b.p. 87–90°. Gas chromatography (silver nitrate column⁸ at 52°, 14 p.s.i. helium) showed the isomer ratio to be 88% *trans*, 12% *cis*.

Reaction of lithium with cis-propenylmercuric bromide. The procedure followed was identical to that used in the previous experiment, 27.7 mmoles of *cis*-propenylmercuric bromide being added to 0.22 g-atom of lithium wire (1.1% sodium content) in 100 ml of ether; 37 mmoles of trimethylchlorosilane was added to the reaction mixture. Fractional distillation gave propenyltrimethylchlorosilane (40% *cis*, 60% *trans*) in 67% yield.

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