

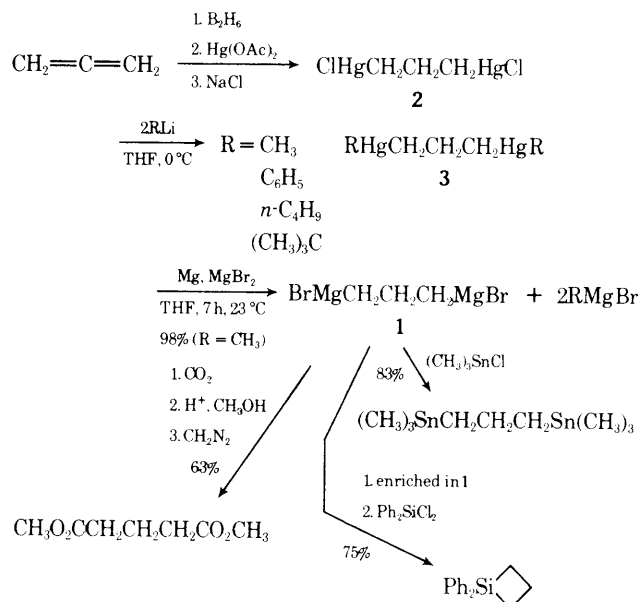
### Propane-1,3-di(magnesium halide)<sup>1</sup>

Sir:

Metallo-cyclic compounds are intermediates in a number of interesting metal-catalyzed reactions.<sup>2</sup> A useful method for preparing authentic metallocycles having rings of five or more members for mechanistic studies is the reaction of a metal halide with an alkane- $\alpha,\omega$ -dimagnesium or -dilithium reagent. It has not been possible to prepare four-membered metallocycles—metallocyclobutanes—by this procedure, since the requisite dimagnesium or dilithium reagents have not been available: reaction of 1,3-dihalopropanes with magnesium or lithium yields primarily cyclopropane, and does not generate propane-1,3-dimetals compounds.<sup>3,4</sup> We report here a preparation of propane-1,3-di(magnesium halide) (**1**), and illustrate its usefulness in the preparation of metallocyclobutanes by syntheses of 1,1-dimethyl- and 1,1-diphenylsilylacetylene (Scheme I).

Hydroboration-mercuration<sup>5</sup> of allene gave propane-1,3-di(mercury(II) chloride) (**2**). Attempts to convert **2** directly to **1** by transmetalation<sup>6</sup> with magnesium, or to propane-1,3-dilithium by reaction with lithium, produced only an unreactive, insoluble mixture of polymeric dialkylmercury

Scheme I. Preparation, Isolated Yields, and Reactions of Propane-1,3-di(magnesium halide) (**1**) and Related Compounds



compounds. To prevent the formation of these compounds on exposure of the propane-1,3-dimercury(II) moiety to magnesium, **2** was first treated with 2 equiv of an organolithium reagent, RLi, and converted to *soluble* dialkylmercury reagents (**3**).<sup>7,8</sup> Treatment of **3** with magnesium powder in THF containing magnesium bromide (prepared in situ by reaction of magnesium with 1,2-dibromoethane) yielded a mixture of **1** and monofunctional organomagnesium reagents, RMgX.

The composition of these mixtures of organomagnesium reagents was assayed by addition of an excess of trimethyltin chloride, and GLC examination of the resulting organotin compounds. In a typical reaction sequence carried through using methyl lithium to convert **2** to **3** (R = CH<sub>3</sub>), the organotin compounds detected were (GLC yields, %, based on **2**): (CH<sub>3</sub>)<sub>3</sub>SnCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Sn(CH<sub>3</sub>)<sub>3</sub> (98), (CH<sub>3</sub>)<sub>4</sub>Sn (100), CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Sn(CH<sub>3</sub>)<sub>3</sub> (2), CH<sub>2</sub>=CHCH<sub>2</sub>Sn(CH<sub>3</sub>)<sub>3</sub> (<1). Control experiments established that the conditions used in these assays converted *n*-decylmagnesium bromide to *n*-decyltrimethyltin quantitatively. The presence of **1** was confirmed by isolation of dimethyl glutarate in 63% yield following carbonation and esterification, and by preparation of 1,1-dimethylsilylacetylene in 66% yield (GLC), and 1,1-diphenylsilylacetylene in 75% yield (isolated) following reaction with the appropriate diorganosilicon dihalides (Scheme I).<sup>9</sup>

The unsymmetrical dialkylmercury compounds (**3**) could be isolated. For preparative reactions, however, isolation was not necessary: when a suspension of 1.0 equiv of **2** and 30 equiv (a large excess) of magnesium powder in THF was treated in sequence with 2.0 equiv of an organolithium reagent and 2.0 equiv of 1,2-dibromoethane, and the resulting mixture allowed to stir for 7 h at room temperature, **1** was generated in yields that depended on the structure of the organolithium reagent used (yield of **1**, %, based on **2**): CH<sub>3</sub>Li (98), C<sub>6</sub>H<sub>5</sub>Li (95), *n*-C<sub>4</sub>H<sub>9</sub>Li (80), (CH<sub>3</sub>)<sub>3</sub>CLi (60). For most preparative work, **3** (R = CH<sub>3</sub>) was the most convenient material with which to work. The preparation of **1** by this procedure is necessarily accompanied by the formation of 2 equiv of monofunctional Grignard reagent (RMgX). For further reactions with monofunctional substrates, use of this mixture presented little difficulty, since the products were easily separated. For metallocyclobutane formation, however, it was desirable to use a solution of **1** which contained less RMgX. Two techniques produced solutions which were enriched in **1**. In the first, addition of diethyl ether to the reaction mixture in THF resulted in the separation into two phases, with **1** concentrated in the lower. Removal of the upper layer, solution of the lower layer

in THF, and repetition of this procedure several times resulted in solutions in which the ratio of **1** to RMgX was greater than 9:1. A disadvantage of this procedure is that only 10–20% of the available **1** is recovered. The second procedure involved treating the initially formed mixture of organomagnesium reagents with additional **1** and subsequent transmetalation of the resulting mixture of diorganomercury compounds. With this method 30-mmol quantities of **1** can be prepared routinely in solutions in which the ratio of **1** to RMgX is ca. 2:1. Attempts to produce more homogeneous solutions of **1** with this process are frustrated by increasingly slow transmetalation rates and decreased yields of **1**.<sup>10</sup> Utilization of these two techniques in combination permits the preparation of useful quantities (5–10 mmol) of **1** in solutions containing no more than ca. 20 mole % of this quantity of monofunctional Grignard reagents.

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**Supplementary Material Available.** Experimental procedures for the preparation of **1** and **2** (4 pages). Ordering information available on any current masthead page.

## References and Notes

- (1) Supported by the National Science Foundation, Grant MPS74-20946.
- (2) For recent references, see T. J. Katz and R. Rothchild, *J. Am. Chem. Soc.*, **98**, 2519 (1976); J. X. McDermott, J. F. White, and G. M. Whitesides, *ibid.*, **98**, 6521 (1976); J. X. McDermott, M. E. Wilson, and G. M. Whitesides, *ibid.*, **98**, 6529 (1976); R. H. Grubbs, P. L. Burk, and D. D. Carr, *ibid.*, **97**, 3235 (1975); C. P. Casey and T. J. Burkhardt, *ibid.*, **96**, 7808 (1974); E. L. Muetterties, *Inorg. Chem.*, **14**, 951 (1975); R. Noyori, I. Umeda, H. Kawachi, and H. Takaya, *J. Am. Chem. Soc.*, **97**, 812 (1975).
- (3) (a) E. Mueller, Ed., "Methoden der Organischen Chemie" (Houben-Weyl), Vol. 13/2a, Georg Thieme Verlag, Stuttgart, 1973, pp 97–106; (b) I. T. Millar and H. Heaney, *Q. Rev., Chem. Soc.*, **11**, 109 (1957); (c) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances", Prentice Hall, New York, N.Y., 1954, pp 34–35; (d) R. West and E. G. Rochow, *J. Org. Chem.*, **18**, 1739 (1953).
- (4) A patent claim for the formation of 1,3-dilithiopropane from 1,3-dichloropropane and lithium metal is based only on a low yield of titratable organolithium reagent, and contained no evidence for the formation of dilithium reagent: K. C. Eberly, U.S. Patent 2 947 793 (1960); *Chem. Abstr.*, **55**, 382 (1961).
- (5) H. C. Brown and R. C. Larock, *J. Am. Chem. Soc.*, **92**, 2467 (1970).
- (6) (a) Reference 3a, Vol 13/2b, 1974, pp 277–281; (b) Reference 3a, pp 202–205; (c) F. R. Jensen and J. A. Landgrebe, *J. Am. Chem. Soc.*, **82**, 1004 (1960).
- (7) **CAUTION:** Although we have not explicitly checked for volatile alkylmercury species in these reactions, disproportionation of compounds **3** will certainly generate them. All reactions involving organomercury compounds should be conducted in a good hood, and contact with solutions or vapor avoided.
- (8) Reference 6a, pp 234–236.
- (9) Silacyclobutane chemistry has been reviewed by R. Damrauer, *Organomet. Chem. Rev., Sect. A*, **8**, 67 (1972).
- (10) Thermal instability apparently limits the length of time that solutions of **1** can be manipulated without decrease in purity. Qualitative observation suggests that storage of **1** in THF at ambient temperature for 7 days converts ca. 50% of it to a mixture of allyl- and *n*-propylmagnesium halides.

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