*Journal of Organometallic Chemistry*
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

# THE REACTION OF BIS(TRIMETHYLSILYL)MERCURY AND BIS(TRIMETHYLGERMYL)MERCURY WITH ORGANIC DIBROMO COMPOUNDS. AN EXAMPLE OF A MOLECULAR *cis*-1,2-ELIMINATION

S. W. BENNETT, C. EABORN, R. A. JACKSON, AND (IN PART) R. W. WALSINGHAM
*School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ (Great Britain)*

(Received October 1st, 1970)

## SUMMARY

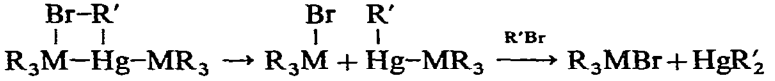
Bis(trimethylsilyl)mercury and bis(trimethylgermyl)mercury react with organic 1,2-dibromo compounds to give the corresponding alkene, along with mercury and trimethylbromosilane or trimethylbromogermane. The removal of two bromine atoms from *erythro*- and *threo*-2,3-dibromo-4-methylpentane by bis(trimethylgermyl)mercury is stereospecifically *cis*, suggesting a one stage molecular mechanism for this elimination.

1,3-Dibromopropane reacts with the mercurials to give cyclopropane, but attempts to convert *o*-xylylene dibromide into 1,2-dihydrobenzocyclobutene were unsuccessful.

---

## INTRODUCTION

Group IVB mercurials of the type $(R_3M)_2Hg$ [(I), M = Si, Ge] react thermally with many organic halides R'Hal to give the organomercurials $R'HgMR_3$ or $R_2'Hg$ (or their decomposition products), along with the organometallic halides $R_3MHal$. These are probably molecular four-centre reactions (1)[1].



$$R_3\overset{\overset{\displaystyle Br-R'}{|\quad\;|}}{M-Hg}-MR_3 \longrightarrow R_3\overset{\overset{\displaystyle Br}{|}}{M} + \overset{\overset{\displaystyle R'}{|}}{Hg}-MR_3 \xrightarrow{R'Br} R_3MBr + HgR_2' \qquad (1)$$

Aliphatic 1,2 and 1,3 dibromides react differently, as described below.

## RESULTS AND DISCUSSION

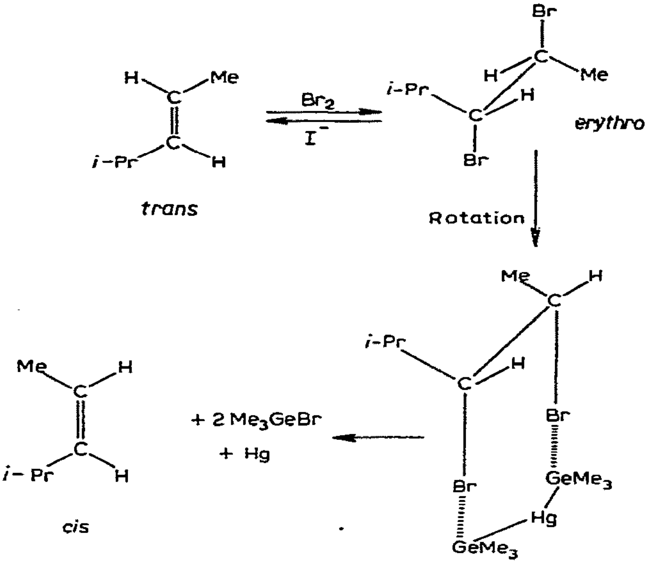
### *Reactions of bis(trimethylsilyl)mercury and bis(trimethylgermyl)mercury with 1,2-dibromides*

We have found that bis(trimethylsilyl)mercury reacts with 1,2-dibromoethane at room temperature to give a quantitative yield of mercury and ethylene, along with trimethylbromosilane. Bis(trimethylgermyl)mercury reacts with 1,2-dibromoethane at −20° to give quantitative yields of mercury, ethylene and trimethylbromogermane. The reaction with 1,2-dibromopropane gives corresponding products quantitatively, but requires 2 h at 80°. Bis(trimethylgermyl)mercury[2], bis(triphenylsilyl)mercury[3], and bis(triphenylgermyl)mercury[4] have also been shown to react with 1,2-dibromoethane in this manner.

A free radical mechanism for these reactions appears unlikely, since they occur in the dark, and are clean, giving no indication of the formation of dimerization or disproportionation products of possible radical intermediates, but the most compelling evidence that the reactions are molecular in nature is provided by the *cis* stereospecificity of the elimination, as established below for *erythro*- and *threo*-2,3-dibromo-4-methylpentane.

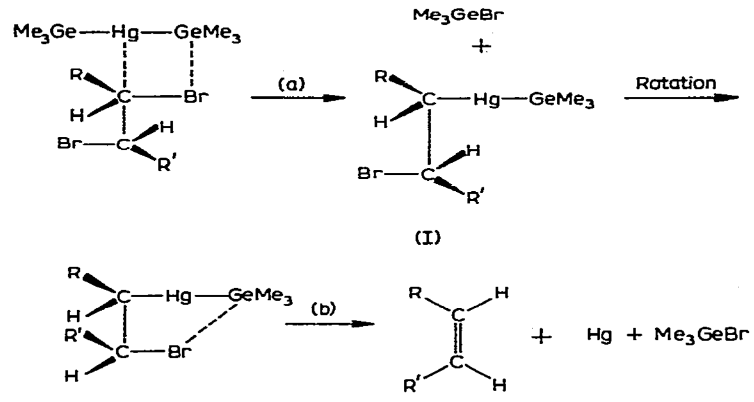
*Reaction of bis(trimethylgermyl)mercury with 2,3-dibromo-4-methylpentane.*

We prepared *erythro*- and *threo*-2,3-dibromo-4-methylpentane from *trans*- and *cis*-4-methyl-2-pentene, respectively, by addition of bromine, a reaction which is normally stereospecifically *trans*[5]. Our assignment of stereochemistry was checked by debromination of the dibromide back to the olefin by iodide ions: this reaction, which is also stereospecifically *trans*[6], gave back the original olefin from each dibromide. Bis(trimethylgermyl)mercury however reacts with the *erythro* dibromide to give 98% of the *cis*-olefin; the *threo* isomer correspondingly gives 96% of the *trans*-olefin, thus demonstrating the *cis* nature of this elimination. These reactions are illustrated for the *erythro* dibromide in the scheme below:

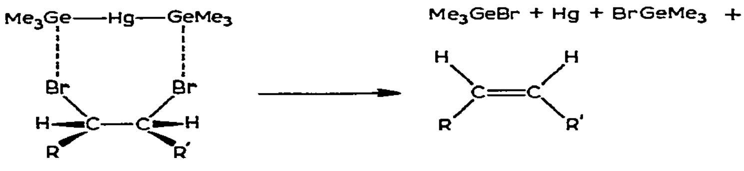


The *cis* stereospecificity of this reaction provides strong evidence for a molecular mechanism, which could be either a two-stage [as in reaction (2)] or a concerted process (3).

The concerted process would lead to *cis* elimination; so probably would the two-stage process, provided (as is likely[7]) that the first stage (2a) proceeded with retention of configuration at the carbon centre involved. Rotation about the central C–C bond in the intermediate (I) would be rapid, and thus reaction (2b) would be able to compete efficiently with reactions of (I) with other molecules. We favour the con-



(2)



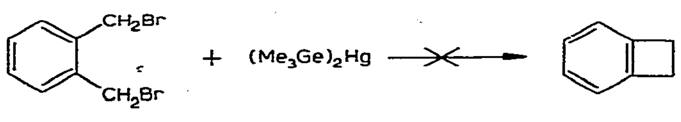
(3)

certed mechanism (3) because these reactions of the mercurials are so fast compared with those involving mono-bromides[1c] or 1,3-dibromides, but we note that rate enhancement might also arise in the two-stage process (2) if some carbonium ion character were developed at $C_\alpha$, in which case anchimeric assistance from the $\beta$-bromine atom would be possible.

### *1,3-Dibromopropane and o-xylylene dibromide*

Bis(trimethylsilyl)mercury and bis(trimethylgermyl)mercury both react with 1,3-dibromopropane to give $Me_3MBr$ (M=Si, Ge), cyclopropane, and mercury as major products. The reactions are slower than the corresponding reactions with 1,2-dibromoethane. The quantitative production of mercury, and the absence of propene indicate that this reaction is also a molecular process, involving only one molecule of 1,3-dibromopropane and one of the mercurial in the transition state.

Since 1,3-elimination of two bromine atoms from 1,3-dibromopropane occurred with the formation of a *sigma* bond between the 1- and 3-carbon atoms, it was hoped that *o*-xylylene dibromide might react to give 1,2-dihydrobenzocyclobutane, (II), which is somewhat difficult to prepare by other routes. The reaction of bis(trimethylgermyl)mercury with *o*-xylylene dibromide (5 h, 70°) gave trimethylbromogermane and mercury quantitatively. GLC analysis of the products showed the presence of a high-boiling compound, whose mass spectrum showed peaks at *m/e* 208 and *m/e* 132, corresponding to $C_{16}H_{16}^+$ and $C_{10}H_{12}^+$ respectively. This may have been 5,6,11,12-hydrodibenzo[*a,e*]cyclo-octene, a common by-product of the production of 1,2-dihydrobenzocyclobutene by other methods[8]. Smaller amounts of still higher boiling materials were formed, but no trace of the hoped for 1,2-dihydrobenzocyclobutene (II) was detected.



(II)

## EXPERIMENTAL

### *Erythro and threo-2,3-dibromo-4-methylpentane*

Bromine (16.0 g, 0.1 mole) was added dropwise to a cooled solution of *trans*-4-methyl-2-pentene (8.4 g, 0.1 mole) in chloroform (20 ml) at such a rate that the temperature of the reaction mixture did not rise above 5°. The colourless solution was refluxed for 1 h, after which fractionation yielded *erythro*-2,3-dibromo-4-methylpentane (nc) (21.0 g, 85%), b.p. 68–70°/7 mm, $n_D^{25}$ 1.5030. (Found: C, 29.5; H, 4.94. $C_6H_{12}Br_2$ calcd.: C, 29.7; H, 5.02%.) The *threo* isomer (nc) was prepared similarly from *cis*-4-methyl-2-pentene in 80% yield, b.p. 49–50°/1.6 mm, $n_D^{25}$ 1.5039. (Found C, 29.4; H, 5.01%.)

### *Debromination of erythro- and threo-2,3-dibromo-4-methylpentane with iodide ion*

*erythro*-2,3-Dibromo-4-methylpentane (2.5 g, 0.01 mole) was added to a warm solution of sodium iodide (7.5 g, 0.05 mole) in 1-propanol (75 ml) and water (25 ml), and the mixture was refluxed for 4 h. The solution was extracted with 30–40° petroleum ether, the extracts were dried over anhydrous magnesium sulphate, distilled, and the fraction b.p. 53–59°/755 mm was collected. GLC showed this fraction to comprise *trans*-4-methyl-2-pentene (98%) and *cis*-4-methyl-2-pentene (2%). The *threo*-dibromide, treated analogously, gave a mixture of *cis*-4-methyl-2-pentene (94%) and *trans*-4-methyl-2-pentene (6%).

### *Reaction of bis(trimethylgermyl)mercury with erythro- and threo-2,3-dibromo-4-methylpentane*

Bis(trimethylgermyl)mercury (0.52 g, 0.0012 mole) and *erythro*-2,3-dibromo-4-methylpentane (2 ml) were heated to 75° for 4 h, when the solution had become colourless and mercury (98%) had precipitated. GLC analysis showed the products to be *cis*-4-methyl-2-pentene (96%) and *trans*-4-methyl-2-pentene (2%), bromotrimethylgermane (94%), and a trace of hexamethyldigermoxane. The *threo*-dibromide (2 ml) reacted similarly with the mercurial (0.62 g, 0.0014 mole) in 2 h at 65° to give mercury (99%), *trans*-4-methyl-2-pentene (97%) and *cis*-4-methyl-2-pentene (1%), bromotrimethylgermane (95%) and a trace of hexamethyldigermoxane.

### *Reaction of bis(trimethylsilyl)mercury and bis(trimethylgermyl)mercury with o-xylylene dibromide*

Bis(trimethylgermyl)mercury (0.5 g, 0.0011 mole) was heated with *o*-xylylene dibromide (1.0 g, 0.004 mole) in benzene (2 ml). After 5 h at 70°, the mixture was colourless and mercury had been quantitatively precipitated, but no 1,2-dihydrobenzocyclobutene was detected in the reaction mixture. GLC showed the presence of bromotrimethylgermane (87%) and a high boiling compound, the mass spectrum of which showed peaks at *m/e* 208 and 132, corresponding to the ions $C_{16}H_{16}^+$ and $C_{10}H_{12}^+$ respectively. Bis(trimethylsilyl)mercury reacted similarly with *o*-xylylene dibromide to produce high yields of bromotrimethylsilane and the high-boiling product, along with a quantitative amount of mercury.

*Reaction of bis(trimethylgermyl)mercury with 1,2-dibromoethane*

1,2-Dibromoethane (0.90 g, 0.005 mole) was condensed onto bis(trimethylgermyl)mercury (0.52 g, 0.0012 mole) at −196° under vacuum. On warming to −20°, a vigorous reaction set in, gas was evolved, and mercury was precipitated. The reaction subsided after 10 min, and little further reaction occurred on warming to 30°. The volatile reaction products were distilled through a trap at −78° into a trap cooled by liquid nitrogen, leaving a mercury residue. GLC analysis of the contents of the −78° trap showed the presence of bromotrimethylgermane (0.0019 mole, 79%) and hexamethyldigermoxane (trace). The liquid nitrogen trap contained 0.0010 mole of a gas identified as ethylene by its molecular weight (28±2), its IR spectrum[9], and its mass spectrum which showed peaks at *m/e* 28 and 14 corresponding to $C_2H_4^+$ and $CH_2^+$, respectively.

*Reaction of bis(trimethylgermyl)mercury with 1,2-dibromopropane*

This reaction was carried out in a similar manner to the reaction with 1,2-dibromoethane, although heating for 1 h at 40° was necessary to complete the reaction. Mercury was recovered quantitatively. GLC analysis of the liquid products showed the presence of bromotrimethylgermane (90%) and hexamethyldigermoxane (trace). The gas evolved was identified as propene by its molecular weight (40±2), its IR spectrum[9,10] and its mass spectrum which showed peaks at *m/e* 42, 41, 40, 27, and 15 corresponding to the ions $C_3H_6^+$, $C_3H_5^+$, $C_3H_4^+$, $C_2H_3^+$ and $CH_3^+$, respectively.

*Reaction of bis(trimethylgermyl)mercury with 1,3-dibromopropane*

1,3-Dibromopropane (0.8 g, 0.004 mole) was condensed onto bis(trimethylgermyl)mercury (0.48 g, 0.0011 mole) at −196° under vacuum. No reaction took place until the temperature was raised to 50°, and completion of the reaction required 4 h at 80°. Work-up as in the reaction with 1,2-dibromoethane showed that mercury (quantitative) bromotrimethylgermane (0.0018 mole, 82%) and hexamethyldigermoxane (trace) had been formed, along with 0.0008 mole (73%) of a gas identified as cyclopropane by its mol.wt. (41±2), its IR spectrum[11], and its mass spectrum, which showed peaks at *m/e* 42, 41, 40, 39, and 14 corresponding to the ions $C_3H_6^+$, $C_3H_5^+$, $C_3H_4^+$, $C_3H_3^+$, and $CH_2^+$, respectively.

*Reaction of bis(trimethylsilyl)mercury with 1,2-dibromoethane*

A solution of 1,2-dibromoethane (0.95 g, 5.05 mmole) in benzene (2 ml) was added to bis(trimethylsilyl)mercury (1.51 g, 4.35 mmole). An exothermic reaction ensued, gas was evolved, and the mercurial was completely decomposed after 1 h, giving mercury quantitatively. The products, separated as above, included bromotrimethylsilane as a major component, together with unreacted 1,2-dibromoethane and traces of hexamethyldisilane and hexamethyldisiloxane. The gas was identified as ethylene (4.18 mmole, 96%) by its mol.wt. (28.6), its IR spectrum[9], and by its mass spectrum which showed major peaks at *m/e* 28 and 14 attributable to $C_2H_4^+$ and $CH_2^+$.

### *Reaction of bis(trimethylsilyl)mercury with 1,3-dibromopropane*

1,3-Dibromopropane (1.3 g, 6.25 mmole) was added to bis(trimethylsilyl)-mercury (2.09 g, 6.25 mmole). A gas was evolved immediately and mercury was precipitated, but heating at 100° for 6 h was required to complete the reaction. Analysis as above showed a quantitative recovery of mercury, a major amount of bromotrimethylsilane and 2.9 mmole (46 %) cyclopropane, identified by its mol.wt. (40.6), its IR spectrum[11], and its mass spectrum.

## ACKNOWLEDGEMENT

We thank the S.R.C. for Research Studentships (to S.W.B. and R.W.W.).

## REFERENCES

1 (a) C. Eaborn, R. A. Jackson and R. W. Walsingham, *J. Chem. Soc. C*, (1967) 2188;
(b) R. Fields, R. N. Haszeldine and R. E. Hutton, *J. Chem. Soc. C*, (1967) 2559;
(c) A. G. Beaumont, S. W. Bennett, C. Eaborn and R. A. Jackson, unpublished work.

2 N. S. Vyazankin, G. A. Razuvaev, S. P. Korneva, O. A. Kruglaya and R. F. Galiulina, *Proc. Acad. Sci. U.S.S.R.*, 158 (1964) 1002.

3 N. S. Vyazankin, O. A. Kruglaya, G. S. Kalinina and E. N. Gladyshev, *J. Gen. Chem. U.S.S.R.*, 38 (1968) 1544.

4 N. S. Vyazankin, V. T. Bychkov, O. V. Linzina and G. A. Razuvaev, *J. Gen. Chem. U.S.S.R.*, 39 (1969) 950.

5 A. McKenzie, *Proc. Chem. Soc.*, 27 (1911) 150; *J. Chem. Soc.*, (1912) 1196; B. Holmberg, *Svensk Kem. Tidskr.*, (1911) No. 5; for more recent references see E. L. Eliel, *Stereochemistry of Carbon Compounds*, McGraw Hill, New York, 1962, p. 355.

6 S. Winstein, D. Pressman and W. G. Young, *J. Amer. Chem. Soc.*, 61 (1939) 1645.

7 F. R. Jensen and B. Rickborn, *Electrophilic Substitution of Organomercurials*, McGraw-Hill, New York, 1968.

8 M. P. Cava and A. A. Deana, *J. Amer. Chem. Soc.*, 81 (1959) 4266.

9 R. S. Rasmussen and R. R. Brattain, *J. Chem. Phys.*, 15 (1947) 120.

10 W. A. Patterson, *Anal. Chem.*, 26 (1954) 823.

11 J. R. Lacher, C. H. Walden, K. R. Lea and J. D. Park, *J. Amer. Chem. Soc.*, 72 (1950) 331.