

## HYDROGEN CHLORIDE CLEAVAGE OF SOME UNSYMMETRICAL SILICON-SUBSTITUTED DIORGANOMERCURY COMPOUNDS

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### INTRODUCTION

Whitmore and Sommer<sup>1</sup> studied the cleavage of unsymmetrical diorganomercurials of the type  $(\text{CH}_3)_3\text{SiCH}_2\text{HgR}$  ( $\text{R} = \text{CH}_3$ ,  $n\text{-C}_6\text{H}_{13}$  and  $\text{C}_6\text{H}_5$ ) by hydrogen chloride in ethanolic solution and showed that the ease of cleavage of groups from the mercury atom decreased in the order  $\text{C}_6\text{H}_5 > (\text{CH}_3)_3\text{SiCH}_2 > \text{CH}_3 > n\text{-C}_6\text{H}_{13}$ . Seyferth<sup>2</sup> investigated the cleavage reaction of (trimethylsilyl)methyl-substituted tin compounds  $[(\text{CH}_3)_3\text{SiCH}_2]_2\text{SnR}_2$  ( $\text{R} = \text{CH}_3$ ,  $\text{CH}_2 = \text{CH}$ ,  $n\text{-C}_4\text{H}_9$  and  $\text{C}_6\text{H}_5$ ) by several acidic reagents. Again, he observed that the  $(\text{CH}_3)_3\text{SiCH}_2$  group was cleaved more easily than methyl and n-butyl groups if hydrogen chloride was used as cleavage agent.

In connection with studies of effects of silyl substituents, especially organo-disilanyl groups, on the reactivity at the adjacent carbon atom, it was of interest to investigate the competitive hydrogen chloride cleavage of unsymmetrical diorganomercury compounds containing silyl groups. We report here the results obtained for the relative ease of cleavage of the groups,  $(\text{CH}_3)_3\text{SiCH}_2$ ,  $(\text{CH}_3)_3\text{SiSi}(\text{CH}_3)_2\text{CH}_2$ ,  $\text{C}_2\text{H}_5(\text{CH}_3)_2\text{SiSi}(\text{CH}_3)_2\text{CH}_2$ ,  $[(\text{CH}_3)_3\text{Si}]_2\text{CH}$ ,  $(\text{CH}_3)_3\text{CSi}(\text{CH}_3)_2\text{CH}_2$  and  $\text{CH}_3$ , from mercury by hydrogen chloride in ethanol.

### RESULTS AND DISCUSSION

Silicon-substituted organomercury compounds prepared in this study are listed with some of their physical properties in Table 1. All of them but (I), (II) and (IV) are new compounds. (Silylmethyl)mercuric chlorides (I)–(V) are snow-white crystals, while all the diorganomercurials (VI)–(XVI) are colorless liquids with the exception of compound (XV) which is a low-melting, white crystalline substance. All of them are surprisingly thermally stable; the diorganomercurials could be distilled under reduced pressure without any change and the (silylmethyl)mercuric chlorides could be successfully subjected to gas-chromatographic analysis.

The preparation of each of these compounds was generally accomplished by the reaction of an appropriate Grignard reagent with an appropriate mercuric chloride in diethyl ether. Always, yields were satisfactory. Preparation routes, yields and mercury analyses for new compounds are listed in Table 2.

The unsymmetrical diorganomercurials (VI)–(XIV) were treated with a saturated ethanolic solution of hydrogen chloride. In each case, a mixture of crystals of two possible organomercuric chlorides was obtained. It was dissolved in benzene and

analyzed by gas chromatography. Relative yields of two products in each case are listed in Tables 3 and 4.

TABLE I  
SILICON-SUBSTITUTED ORGANOMERCURY COMPOUNDS

| No.    | Compound   | B.p.<br>(°C/mm) | M.p.<br>(°C) | $n_D^{20}$ | $d_4^{20}$ |
|--------|--|-----------------|--------------|------------|------------|
| (I)    | $(CH_3)_3SiCH_2HgCl^a$                           |                 | 76-76.5      |            |            |
| (II)   | $(CH_3)_3SiSi(CH_3)_2CH_2HgCl^b$                 |                 | 69.5-70      |            |            |
| (III)  | $C_2H_5(CH_3)_2SiSi(CH_3)_2CH_2HgCl$             |                 | 55-56        |            |            |
| (IV)   | $(CH_3)_3CSi(CH_3)_2CH_2HgCl^c$                  |                 | 88           |            |            |
| (V)    | $[(CH_3)_3Si]_2CHHgCl$                           |                 | 90-91        |            |            |
| (VI)   | $(CH_3)_3SiSi(CH_3)_2CH_2HgCH_2Si(CH_3)_3$       | 90/3            |              | 1.5010     | 1.3766     |
| (VII)  | $C_2H_5(CH_3)_2SiSi(CH_3)_2CH_2HgCH_2Si(CH_3)_3$ | 101/3           |              | 1.5040     | 1.3621     |
| (VIII) | $(CH_3)_3CSi(CH_3)_2CH_2HgCH_2Si(CH_3)_3$        | 84/3            |              | 1.4924     | 1.4166     |
| (IX)   | $[(CH_3)_3Si]_2CHHgCH_2Si(CH_3)_3$               | 90/3            |              | 1.4920     | 1.3527     |
| (X)    | $(CH_3)_3SiCH_2HgCH_3$                           | 53/12           |              | 1.5000     | 1.8691     |
| (XI)   | $(CH_3)_3SiSi(CH_3)_2CH_2HgCH_3$                 | 56/3            |              | 1.5136     | 1.5786     |
| (XII)  | $C_2H_5(CH_3)_2SiSi(CH_3)_2CH_2HgCH_3$           | 57/3            |              | 1.5129     | 1.5193     |
| (XIII) | $(CH_3)_3CSi(CH_3)_2CH_2HgCH_3$                  | 57/3.5          |              | 1.5041     | 1.6580     |
| (XIV)  | $[(CH_3)_3Si]_2CHHgCH_3$                         | 50/3            |              | 1.4970     | 1.5417     |
| (XV)   | $[(CH_3)_3Si]_2CH_2Hg$                           | 108/4           | 35           |            |            |
| (XVI)  | $[(CH_3)_3SiCH_2]_2Hg$                           | 61/3            |              | 1.4886     | 1.5074     |

<sup>a</sup> Ref. 1: m.p. 76°. <sup>b</sup> Ref. 3: m.p. 69-70°. <sup>c</sup> Ref. 4: m.p. 82-83°. The present sample was believed to be highly pure on the basis of gas-chromatographic data.

TABLE 2  
PREPARATIVE ROUTES, YIELDS AND MERCURY ANALYSES FOR NEW ORGANOMERCURY COMPOUNDS

| No.    | Formula              | Prepared from | Yield <sup>a</sup><br>(%) | Hg <sup>b</sup> (%) |        |
|--------|----------------------|---------------|---------------------------|---------------------|--------|
|        |                      |               |                           | Found               | Calcd. |
| (III)  | $C_7H_{19}ClHgSi_2$  | c             | 49                        | 50.58               | 50.73  |
| (V)    | $C_7H_{19}ClHgSi_2$  | d             | 72                        | 50.15               | 50.73  |
| (VI)   | $C_{10}H_{23}HgSi_3$ | e             | 84                        | 45.60               | 46.31  |
| (VII)  | $C_{11}H_{30}HgSi_3$ | f             | 72                        | 45.21               | 44.86  |
| (VIII) | $C_{11}H_{29}HgSi_2$ | g             | 89                        | 47.95               | 48.09  |
| (IX)   | $C_{11}H_{30}HgSi_3$ | h             | 79                        | 44.16               | 44.86  |
| (X)    | $C_8H_{14}HgSi$      | i             | 81                        | 65.58               | 66.24  |
| (XI)   | $C_8H_{20}HgSi_2$    | j             | 80                        | 55.72               | 55.57  |
| (XII)  | $C_9H_{22}HgSi_2$    | k             | 62                        | 53.61               | 53.49  |
| (XIII) | $C_9H_{20}HgSi$      | l             | 86                        | 58.69               | 58.16  |
| (XIV)  | $C_9H_{22}HgSi_2$    | m             | 75                        | 53.40               | 53.49  |
| (XV)   | $C_{14}H_{29}HgSi_4$ | n             | 77                        | 38.00               | 38.62  |
| (XVI)  | $C_9H_{22}HgSi_2$    | o             | 92                        | 53.16               | 53.49  |

<sup>a</sup> Yields are based on employed amounts of mercuric chlorides. <sup>b</sup> Mercury analyses were carried out according to the techniques by Whitmore and Sabatzki<sup>5</sup>. <sup>c</sup>  $(C_2H_5)(CH_3)_2SiSi(CH_3)_2CH_2MgCl$  and  $HgCl_2$  (see EXPERIMENTAL). <sup>d</sup>  $[(CH_3)_3Si]_2CH_2Hg$  and  $HgCl_2$  (see EXPERIMENTAL). <sup>e</sup>  $(CH_3)_3SiCH_2MgCl$  and  $(CH_3)_3SiSi(CH_3)_2CH_2HgCl$ . <sup>f</sup>  $(CH_3)_3SiCH_2MgCl$  and  $(C_2H_5)(CH_3)_2SiSi(CH_3)_2CH_2HgCl$ . <sup>g</sup>  $(CH_3)_3SiCH_2MgCl$  and  $(CH_3)_3CSi(CH_3)_2CH_2HgCl$ . <sup>h</sup>  $(CH_3)_3SiCH_2MgCl$  and  $[(CH_3)_3Si]_2CHHgCl$ . <sup>i</sup>  $CH_3MgBr$  and  $(CH_3)_3SiCH_2HgCl$ . <sup>j</sup>  $CH_3MgBr$  and  $(CH_3)_3SiSi(CH_3)_2CH_2HgCl$ . <sup>k</sup>  $CH_3MgBr$  and  $(C_2H_5)(CH_3)_2SiSi(CH_3)_2CH_2HgCl$ . <sup>l</sup>  $CH_3MgBr$  and  $(CH_3)_3CSi(CH_3)_2CH_2HgCl$ . <sup>m</sup>  $CH_3MgBr$  and  $[(CH_3)_3Si]_2CHHgCl$ . <sup>n</sup>  $[(CH_3)_3Si]_2CHMgCl$  and  $HgCl_2$  in tetrahydrofuran (see EXPERIMENTAL). <sup>o</sup>  $(CH_3)_3SiCH_2MgCl$  and  $(CH_3)_3SiCH_2HgCl$ .

TABLE 3

CLEAVAGE OF  $RHgCH_2Si(CH_3)_3$  COMPOUNDS BY HYDROGEN CHLORIDE IN ETHANOL

| No.    | R                                  | Products (mole %)    |         |
|--------|------------------------------------|----------------------|---------|
|        |                                    | $(CH_3)_3SiCH_2HgCl$ | $RHgCl$ |
| (VI)   | $(CH_3)_3SiSi(CH_3)_2CH_2$         | 44                   | 56      |
| (VII)  | $(C_2H_5)(CH_3)_2SiSi(CH_3)_2CH_2$ | 41                   | 59      |
| (VIII) | $(CH_3)_3CSi(CH_3)_2CH_2$          | 28                   | 72      |
| (IX)   | $[(CH_3)_3Si]_2CH$                 | 28                   | 72      |
| (X)    | $CH_3$                             | 18                   | 82      |

TABLE 4

CLEAVAGE OF  $RHgCH_3$  COMPOUNDS BY HYDROGEN CHLORIDE IN ETHANOL

| No.    | R                                  | Products (mole %) |            |
|--------|------------------------------------|-------------------|------------|
|        |                                    | $RHgCl$           | $CH_3HgCl$ |
| (X)    | $(CH_3)_3SiCH_2$                   | 18                | 82         |
| (XI)   | $(CH_3)_3SiSi(CH_3)_2CH_2$         | 19                | 81         |
| (XII)  | $(C_2H_5)(CH_3)_2SiSi(CH_3)_2CH_2$ | 26                | 74         |
| (XIII) | $(CH_3)_3CSi(CH_3)_2CH_2$          | 30                | 70         |
| (XIV)  | $[(CH_3)_3Si]_2CH$                 | 36                | 64         |

From figures given in both tables, it can be seen that the  $(CH_3)_3SiCH_2$  is cleaved most easily of all the organosilicon groups studied, which interestingly undergo cleavage more readily than the methyl (methyl is known to be cleaved most easily of all alkyl groups under similar conditions). Although we at present have no available data that permit us to directly compare the ease of cleavage among the three organosilicon groups other than  $(CH_3)_3SiCH_2$ , on the basis of the results in Tables 3 and 4 it seems not unreasonable to assume that the ease of cleavage of the groups decreases in the order:  $(CH_3)_3SiCH_2 > (CH_3)_3SiSi(CH_3)_2CH_2 > (C_2H_5)(CH_3)_2SiSi(CH_3)_2CH_2 > (CH_3)_3CSi(CH_3)_2CH_2 \sim [(CH_3)_3Si]_2CH > CH_3$ .

Whitmore and Sommer<sup>1</sup> attributed the greater ease of cleavage of  $(CH_3)_3SiCH_2$  relative to that of methyl to the higher electronegativity of that group, in which the silicon atom behaves as an electron sink because of its electronic unsaturation. On the other hand, Seyferth<sup>2</sup> suggested that the ready cleavage of the  $(CH_3)_3SiCH_2$  group by hydrogen chloride from  $[(CH_3)_3SiCH_2]_2SnR_2$  is caused by the positive inductive effect of the  $(CH_3)_3Si$  group at one side and of the trialkylstannyl group at another, which should make the methylene carbon linking the silicon and tin atoms more negative than other  $\alpha$ -carbons, hence more susceptible to electrophilic cleavage. He also showed that the size of the attacking reagent was the crucial factor in the cleavage of compounds containing hindered groups such as (trimethylsilyl)methyl, since only methyl and n-butyl cleavage occurred in the reaction of  $[(CH_3)_3SiCH_2]_2SnR_2$  ( $R = CH_3$  and  $n-C_4H_9$ ) with iodine.

The results for relative ease of cleavage obtained in the present study seem to be fairly well explained in terms of both positive inductive and steric effects of organosilicon substituents on the carbon atom linked to mercury. Thus, although the

$(\text{CH}_3)_3\text{SiSi}(\text{CH}_3)_2$  group is expected to be somewhat more electron-donating than the  $(\text{CH}_3)_3\text{Si}$ , the  $(\text{CH}_3)_3\text{SiSi}(\text{CH}_3)_2\text{CH}_2$  is cleaved with slightly lesser ease than the  $(\text{CH}_3)_3\text{SiCH}_2$ , probably because of larger steric effect of the former relative to that of the latter. More bulky groups  $(\text{CH}_3)_3\text{CSi}(\text{CH}_3)_2\text{CH}_2$  and  $[(\text{CH}_3)_2\text{Si}]_2\text{CH}$  undergo cleavage with much more difficulty than the  $(\text{CH}_3)_3\text{SiCH}_2$  does.

## EXPERIMENTAL

### *Preparation of organomercury compounds*

Since all organomercury compounds listed in Table 1 were prepared in the usual method, as summarized in Table 2, only a few examples are given for the detailed description of synthesis.

#### *(2-Ethyltetramethyldisilanyl)methylmercuric chloride (III)*

In a 500-ml three-necked flask there was prepared in the usual way a Grignard solution from 30 g (0.15 mole) of 1-(chloromethyl)-2-ethyltetramethyldisilane<sup>6</sup> and 3.6 g (0.15 g-atom) of magnesium in 100 ml of dry ether. To the solution was added dropwise and with cooling 41 g (0.15 mole) of mercuric chloride suspended in 100 ml of ether over a 20-min period. After being refluxed for 10 h, the reaction mixture was hydrolyzed with dilute sulfuric acid. The organic layer was separated and ether was removed by distillation initially at atmospheric pressure on a steam bath, but later *in vacuo* at room temperature. To the residue was added 300 ml of ethanol and the mixture was refluxed for 1 h. To the resulting solution was added 50 ml of water. After overnight 38 g of crude crystals were obtained. Recrystallization from 200 ml of 90% aqueous ethanol gave 29 g (49% yield) of compound (III).

#### *Bis(trimethylsilyl)methylmercury (XV)*

To a stirred solution of 81 g (0.3 mole) of mercuric chloride in 100 ml of tetrahydrofuran was added with cooling a Grignard solution, prepared from 61 g (0.31 mole) of bis(trimethylsilyl)chloromethane<sup>3</sup> and 7.2 g (0.30 g-atom) of magnesium turnings in 100 ml of tetrahydrofuran, over a 30-min period. After completion of the addition, the reaction mixture was heated to gentle reflux for 6 h, and then hydrolyzed with cooling. The resulting organic layer was separated and the aqueous phase was extracted with about 100 ml of ether. All the organic layers were combined and worked up in a similar manner to that described above to give 60 g (77% yield) of white crystals of compound (XV), which could be distilled at  $107-108^\circ/4$  mm without decomposition.

#### *[Bis(trimethylsilyl)methyl]mercuric chloride (V)*

A mixture of 20 g (0.039 mole) of compound (XV), prepared in the preceding paragraph, with 10.5 g (0.039 mole) of mercuric chloride in 50 ml of absolute ethanol was heated to reflux for 5 h. When it was cooled, 28 g of crystals of compound (V) was obtained. Recrystallization from 85% aqueous ethanol gave 22 g (72% yield) of the pure sample.

### *Cleavage reactions of unsymmetrical diorganomercurials*

In a 25-ml flask equipped with a reflux condenser a given amount of a diorgano-

mercurial was admixed at 0° with a given volume of ethanol previously saturated with dry hydrogen chloride. The mixture was frequently shaken for 10 min at this temperature and then heated to gentle reflux for 5 min. At this point, the mixture was cooled again to 0° and treated with the same volume of water as that of ethanol used. The resulting crystals were collected by filtration, dried in a desiccator overnight. About 0.1 g of the crystals was dissolved in benzene and analyzed by gas chromatography. Table 5 summarizes amounts of diorganomercurials and ethanol used, and crystals obtained.

TABLE 5  
RESULTS OF CLEAVAGE OF DIORGANOMERCURIALS

| Compound |     | Ethanol<br>(ml) | Crystals<br>(g) |
|----------|-----|-----------------|-----------------|
| No.      | (g) |                 |                 |
| (VI)     | 3   | 8               | 2.2             |
| (VII)    | 3   | 8               | 2.4             |
| (VIII)   | 3   | 8               | 2.4             |
| (IX)     | 3   | 8               | 2.2             |
| (X)      | 3   | 8               | 2.6             |
| (XI)     | 3   | 8               | 2.4             |
| (XII)    | 1.5 | 3               | 1.3             |
| (XIII)   | 2   | 3               | 1.7             |
| (XIV)    | 2   | 5               | 1.7             |

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#### SUMMARY

Several silicon-substituted unsymmetrical diorganomercurials were prepared and their cleavage reaction by hydrogen chloride in ethanol was investigated. The ease of cleavage of groups from mercury under the conditions used decreases in the order:  $(\text{CH}_3)_3\text{SiCH}_2 > (\text{CH}_3)_3\text{SiSi}(\text{CH}_3)_2\text{CH}_2 > (\text{C}_2\text{H}_5)(\text{CH}_3)_2\text{SiSi}(\text{CH}_3)_2\text{CH}_2 > (\text{CH}_3)_3\text{CSi}(\text{CH}_3)_2\text{CH}_2 \sim [(\text{CH}_3)_3\text{Si}]_2\text{CH} > \text{CH}_3$ .

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