

## THE ELECTROCHEMICAL REDUCTION OF ORGANOSILICON COMPOUNDS

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(Received January 12th, 1968)

### SUMMARY

The electrochemical reduction of phenyltrimethylsilane was studied in both a divided and an undivided cell. In the undivided cell, phenyltrimethylsilane was reduced cleanly to (1,4-dihydrophenyl)trimethylsilane, but, in the divided cell, considerable cleavage of the carbon-silicon bond occurred. A similar cleavage was observed for (phenylethynyl)trimethylsilane even in the undivided cell. The presence of isopropanol influenced the nature of the products in the latter case.

### INTRODUCTION

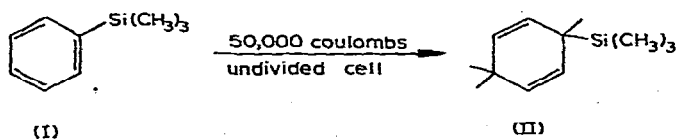
Earlier work from this Laboratory<sup>1</sup> demonstrated that phenyltrimethylsilane, diphenyldimethylsilane and triphenylmethylsilane, when dissolved in ethylamine, would react with lithium metal. Later it was established<sup>2</sup> that lithium metal, dissolved in ethylamine, was a general reducing medium for aromatic ring systems.

A recent modification<sup>3,4</sup> of this method showed that aromatic compounds could be reduced electrochemically to either dihydro- or tetrahydroaromatics by passing an electric current through a solution of the aromatic compound and lithium chloride dissolved in methylamine.

These observations suggested that organosilicon compounds could be reduced electrochemically. To investigate this possibility, several selected organosilicon compounds were prepared and reduced in the electrochemical cells described by Benkeser and Kaiser<sup>3</sup>.

### RESULTS AND DISCUSSION

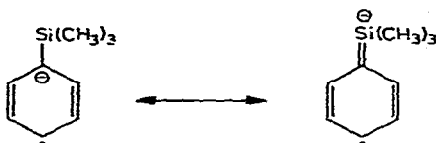
Phenyltrimethylsilane (I) was reduced by passing 50,000 coulombs of electricity through a solution of lithium chloride dissolved in methylamine. The product isolated in 76% yield was (1,4-dihydrophenyl)trimethylsilane (II). Identification of this compound was made on the basis of its distinctive NMR spectrum.



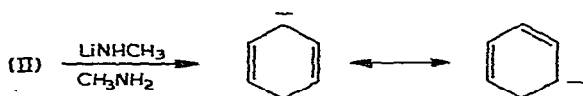
On the basis of dipole moment studies<sup>5</sup> and  $\sigma$  constant determinations<sup>6</sup>, the trimethylsilyl group is generally considered to exert a small electron-releasing inductive effect. Therefore, it might have been predicted that phenyltrimethylsilane would give rise to (2,5-dihydrophenyl)trimethylsilane, since electron donating substituents like alkyl have been shown to produce 2,5-dihydroaromatics in the electrochemical reduction<sup>3</sup>.

For example, tert-butylbenzene (the carbon analog of phenyltrimethylsilane) is reduced to 2,5-dihydro-tert-butylbenzene<sup>4</sup> in an "undivided" cell.

However, such was not the case with phenyltrimethylsilane, since the 1,4-dihydro product formed instead. A possible explanation is that the intermediate radical anion resulting from a 1,4-reduction is stabilized by back-bonding of the carbanion with the silicon atom. Similar resonance structures for phenyltrimethylsilane and phenylsilane have been proposed<sup>5,6,7</sup>. Because of the stabilization afforded this radical-anion intermediate, the activation energy for the reaction leading to compound (II) may well be less than that leading to the 2,5-dihydro product.



The successful reduction of alkylbenzenes in a "divided" cell<sup>3</sup> to monoolefins suggested that phenyltrimethylsilane might be reduced in a similar fashion to (trimethylsilyl)cyclohexenes. To test this, phenyltrimethylsilane was reduced by passing a current of 50,000 coulombs through the "divided" electrolytic cell<sup>3</sup>. Cleavage of the carbon-silicon bond occurred under these conditions, however. The products isolated from the reduction, following hydrolysis, were hexamethyldisiloxane (37%), cyclohexene (36%) and cyclohexane (5%). It has been shown<sup>4</sup> that the major function of the cell divider in such cases is to prevent the immediate neutralization of lithium methylamide which forms in the cathode compartment during the reduction. Possibly the (1,4-dihydrophenyl)trimethylsilane, which also forms at the cathode, undergoes nucleophilic attack by the lithium methylamide on the silicon atom to yield the resonance-stabilized cyclohexadiene carbanion. Protonation of this carbanion by solvent would lead to the more stable 1,3-cyclohexadiene, which could be reduced further, in a 1,4-fashion, to cyclohexene and ultimately to cyclohexane.



Next we turned our attention to the reduction of (phenylethynyl)trimethylsilane in the "undivided" cell. Despite the passage of sufficient current to reduce only double bond, the major product of the reduction was ethylbenzene. However, when the reduction was carried out in the presence of isopropanol, the ethylbenzene was virtually eliminated and considerable quantities of (2-phenylethyl)trimethylsilane were formed. Considerable quantities of phenylacetylene (see Table 1) were formed both in the presence and absence of isopropanol, however, indicating that extensive cleavage of the carbon-silicon bond was occurring in both cases.

TABLE 1

PRODUCTS FROM THE ELECTROCHEMICAL REDUCTION OF (PHENYLETHYNYL)TRIMETHYLSILANE IN AN UNDIVIDED ELECTROLYTIC CELL

Compounds	Yield <sup>a</sup> (%) <sup>b</sup>
$C_6H_5C_2H_5$	38 (1)
$C_6H_5C\equiv CH$	47 (34)
$C_6H_5(CH_2)_2Si(CH_3)_3$	13 (31)
$C_6H_5C\equiv CSi(CH_3)_3$	— (23)
2,5-Dihydro-cyclo- $C_6H_7(CH_2)_2Si(CH_3)_3$	— (7)

<sup>a</sup> Values are the average of several individual reductions. <sup>b</sup> The first value listed is for the runs *without* isopropanol; the values in parentheses were obtained in the presence of isopropanol.

It was demonstrated that methylamine alone does not cause carbon-silicon bond cleavage of (phenylethynyl)trimethylsilane under the conditions of the reduction. When lithium chloride was added to the methylamine, a small amount of cleavage was observed\*, but the magnitude was insufficient to explain the rather extensive cleavages noted in Table 1.

A possible explanation which occurs to us is that (phenylethynyl)trimethylsilane is being reduced to a radical anion, which, in the absence of isopropanol, decomposes into the phenylacetylide carbanion and a silicon radical species. The phenylacetylide carbanion is then protonated by solvent and the phenylacetylene thus formed is reduced in part to ethylbenzene\*\*. With isopropanol present, the radical anion may be protonated *before* cleavage of the carbon-silicon bond can occur and thus lead ultimately to (2-phenylethyl)trimethylsilane.

Since very little ethylbenzene is formed in the presence of isopropanol, despite the formation of appreciable amounts of phenylacetylene, it would seem that the latter must be forming *after* the actual reduction has occurred. It is clear from Table 1 that a considerable amount of unchanged (phenylethynyl)trimethylsilane remains in the reaction mixture after the reduction is completed (23% recovery is realized). It is conceivable that, during the work-up process which involves a slow evaporation of solvent, cleavage of some of this (phenylethynyl)trimethylsilane to phenylacetylene could be occurring. In partial support of this hypothesis was the observation that *extensive* cleavage of (phenylethynyl)trimethylsilane to phenylacetylene is brought about by lithium chloride in the presence of methylamine and isopropanol. The mechanism by which the isopropanol increases the rate of silicon-carbon bond cleavage under these conditions was not investigated\*\*\*.

\* Recently it was shown<sup>8</sup> that (phenylethynyl)trimethylsilane was cleaved to phenylacetylene by alcoholic solutions of various sodium or potassium halides.

\*\* It has been shown (unpublished work from this Laboratory) that phenylacetylene is reduced cleanly to ethylbenzene under conditions of this experiment.

\*\*\* It was not the purpose of this research to investigate the mechanism of silicon-carbon bond cleavage in any of the reductions we are reporting. Hence, any statements made above bearing on this point are to be viewed as purely hypotheses. It remains for future experimentation to establish or disprove their validity.

## EXPERIMENTAL SECTION

*Reduction of phenyltrimethylsilane in an undivided electrolytic cell*

Phenyltrimethylsilane<sup>9</sup> (0.1 mole) was reduced in the "undivided" electrolytic cell described previously<sup>3</sup>. The cell was charged with 34.0 g (0.8 mole) of lithium chloride and 900 ml of anhydrous methylamine. The solution was electrolyzed by passing a current of 2 amp through the system for 7 h (50,000 coulombs). At the end of this time, solvent was allowed to evaporate and the residue hydrolyzed by the slow addition of water. The organic material was extracted with ether and the ethereal extracts were dried over calcium sulfate. After solvent removal, the product (11.5 g, 76%) was distilled; b.p. 168–169°. Analysis by VPC (20 ft. 25%, Carbowax 1540 column; 135°) showed that the product consisted of (1,4-dihydrophenyl)trimethylsilane (92%) and starting material (8%). The compound had NMR absorption (chloroform internal standard) at  $\delta$  5.6 (4 H, multiplet), 2.74 (2H, multiplet), 2.27 (1 H, multiplet) and 0.13 (9 H, singlet). (Found: C, 71.28; H, 10.63; Si, 18.25. C<sub>9</sub>H<sub>16</sub>Si calcd.: C, 70.98; H, 10.59; Si, 18.43 %.)

*Reduction of phenyltrimethylsilane in a divided electrolytic cell*

Phenyltrimethylsilane was reduced in a "divided" electrolytic cell previously described<sup>3</sup>. The half cells were each charged with lithium chloride (17.0 g 0.4 mole) and 450 ml of methylamine. Phenyltrimethylsilane (15 g, 0.1 mole) was placed in the cathode compartment. Current was passed through the cell for 7 h (50,000 coulombs, 2 amp). The solvent was allowed to evaporate through water condensers and the residue in each half cell was hydrolyzed by the slow addition of water. The aqueous solutions were combined and extracted with ether. Distillation of the residue following the customary work-up yielded 8.3 g of a product boiling at 85–168°. Analysis by VPC (15 ft. 20% Carbowax 20 M column; 140° and 20 ft. 20% FFAP column; 120°) showed the product consisted of hexamethyldisiloxane (37%), cyclohexane (5%), cyclohexene (36%), two unknown compounds (16%) and phenyltrimethylsilane (7%).

*Reduction of (phenylethynyl)trimethylsilane in an undivided electrolytic cell*

In a 500 ml three-neck flask fitted with a dry ice condenser and two (2 by 5 cm) platinum electrodes were placed lithium chloride (17.0 g, 0.4 mole) and 400 ml of methylamine. (Phenylethynyl)trimethylsilane<sup>10</sup> (8.8 g, 0.05 mole) was reduced by passing a current of 2 amp through the system for 80 min (9,650 coulombs). Upon completion of the reduction, the solvent was allowed to evaporate through a water condenser and the residue was hydrolyzed. Following the usual work-up, there was obtained 5.8 g of product (b.p. 140–200°) upon distillation. Analysis by VPC (12 ft. 20% silicone oil, 710 column; 180°) showed that the product consisted of approximately 20% hexamethyldisiloxane and 80% reduction products; the composition of the latter is presented in Table 1.

*Reduction of (phenylethynyl)trimethylsilane in an undivided electrolytic cell in the presence of isopropanol*

(Phenylethynyl)trimethylsilane (0.05 mole) was reduced in a 3-neck flask as described above. The flask was charged with 17.0 g (0.4 mole) of lithium chloride, 12 g (0.2 mole) of isopropanol and 400 ml of methylamine. The solution was electro-

lyzed by passing a current of 2 amp through the system for 80 min (9,650 coulombs). The usual work-up yielded 6.3 g of product boiling at 100–160°. Analysis by VPC (12 ft. 20% silicone oil, 710 column; 180°) showed that the product consisted of hexamethyldisiloxane (10–15%) and organic material (85–90%) having the composition listed in Table 1.

*Attempted cleavage of (phenylethynyl)trimethylsilane by methylamine*

(Phenylethynyl)trimethylsilane (5.0 g, 0.028 mole) was stirred in 200 ml of methylamine for 1 h. At the end of this time, the solvent was allowed to evaporate through a water condenser. The product was extracted with pentane and the solvent removed. Distillation of the residue yielded 4.6 g (92%) of product boiling at 215–218°. Analysis by VPC (12 ft. 20% silicone oil, 710 column), showed that the product consisted solely of (phenylethynyl)trimethylsilane (100%).

*Reaction of (phenylethynyl)trimethylsilane with lithium chloride*

(Phenylethynyl)trimethylsilane (4.4 g, 0.025 mole) was stirred for 70 min in a solution of lithium chloride (8.5 g, 0.2 mole) dissolved in 200 ml methylamine. The solvent was then allowed to evaporate and the residue was hydrolyzed with 100 ml of water. After the usual work-up, distillation yielded 3.5 g of a product boiling at 100–200°. Analysis by VPC (4 ft. Apiezon L column; 160°) showed that the product contained phenylacetylene (15%) and (phenylethynyl)trimethylsilane (85%).

*Reaction of (phenylethynyl)trimethylsilane with lithium chloride in the presence of isopropanol*

In a 200 ml three-neck flask fitted with a dry-ice condenser and a magnetic stirrer, (phenylethynyl)trimethylsilane (4.4 g, 0.025 mole) was stirred in a solution of lithium chloride (8.5 g, 0.2 mole), isopropanol (3 g, 0.05 mole) and 200 ml of methylamine for 70 min. After work-up and distillation there was obtained 3 g of product boiling at 100–200°. Analysis by VPC (4 ft. Apiezon L column; 160°) showed that the product, before distillation of the ethereal solution, contained phenylacetylene (77%) and (phenylethynyl)trimethylsilane (23%).

ACKNOWLEDGMENT

The authors wish to thank the Petroleum Research Fund of the American Chemical Society for its generous support of this program.

REFERENCES

- 1 R. A. BENKESER, R. E. ROBINSON AND H. LANDESMAN, *J. Amer. Chem. Soc.*, 74 (1952) 5699.
- 2 R. A. BENKESER, R. E. ROBINSON, D. M. SAUVE AND O. H. THOMAS, *J. Amer. Chem. Soc.*, 76 (1954) 631.
- 3 R. A. BENKESER AND E. M. KAISER, *J. Amer. Chem. Soc.*, 85 (1963) 2858.
- 4 R. A. BENKESER, E. M. KAISER AND R. F. LAMBERT, *J. Amer. Chem. Soc.*, 86 (1964) 5272.
- 5 J. D. ROBERTS, E. A. McELHILL AND R. ARMSTRONG, *J. Amer. Chem. Soc.*, 71 (1949) 2923.
- 6 R. A. BENKESER AND H. R. KRYSIAK, *J. Amer. Chem. Soc.*, 75 (1953) 2421.
- 7 J. E. BISSEY, *J. Chem. Educ.*, 44 (1967) 95.
- 8 C. S. KRAIHANZEL AND J. E. POIST, *J. Organometal. Chem.*, 8 (1967) 239.
- 9 F. C. WHITMORE *et al.*, *J. Amer. Chem. Soc.*, 70 (1948) 433.
- 10 A. D. PETROV, L. L. SHCHUKOVSKAYA AND YU. P. EGOROV, *Dokl. Akad. Nauk SSSR*, 93 (1953) 293.