

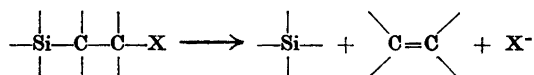
## On Diethyl Trimethylsilylmethylhalogenomalonates

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The diethyl trimethylsilylmethylchloro- and bromomalonates have been prepared and the chemical properties of the bromo compound have been studied in some detail. It has been allowed to react with aqueous base, ethanolic base, diethyl sodiomalonate, and bromine, and subjected to pyrolysis. In the first three reactions it has been found that  $\beta$ -elimination is wholly or partially absent, whereas in the last two reactions  $\beta$ -elimination occurs.

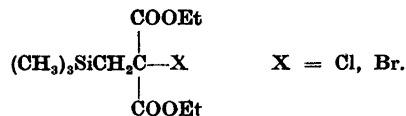
Organosilicon compounds in which a halogen atom is situated on the carbon atom  $\beta$  to the silicon atom have received much attention<sup>1-13</sup>. Their most important chemical property is the so-called  $\beta$ -elimination which occurs more or less readily under the influence of various reagents (alcoholic bases, aqueous alkali, water, methyl magnesium bromide, bromine, silver nitrate, anhydrous aluminium chloride, and heat alone) according to the formula



A few general rules of the influence of structure upon  $\beta$ -elimination have been established.

1. Electronegative substituents, *e. g.*, halogen, situated on the silicon atom give an increased rate of the reaction<sup>6</sup>.
2. The  $\beta$ -elimination is hindered by alkyl substituents on the  $\beta$  carbon atom<sup>11,13</sup>.
3. The order of reactivity of the  $\beta$  halogen is  $\text{I} > \text{Br} > \text{Cl}$ <sup>13</sup>.
4.  $\beta$ -Halovinylsilanes do not undergo  $\beta$ -elimination<sup>9</sup>.

This communication is a report of the preparation and the investigation of some chemical properties of the chloro and bromo derivatives of diethyl trimethylsilylmethylmalonate (I).



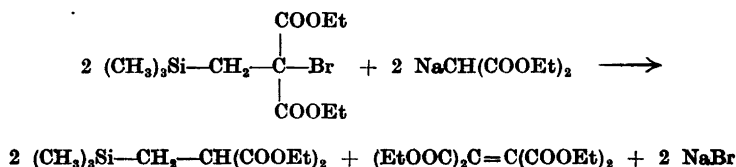
I

This type of  $\beta$ -haloalkylsilanes is substituted by two carboethoxy groups on the  $\beta$ -carbon and it was of interest to investigate if the presence of these groups has any remarkable influence on the  $\beta$ -elimination reaction. No  $\beta$ -haloalkylsilane simultaneously containing functional groups other than halogen on the  $\beta$ -carbon atom has hitherto been investigated.

When diethyl trimethylsilylmethylmalonate was boiled with an excess of sulphuryl chloride the chloroester (I),  $X = Cl$ , was obtained in a 62 % yield. The corresponding bromoester was prepared by adding one mole of bromine dropwise with stirring to one mole of diethyl trimethylsilylmethylmalonate. The reaction was started by adding a few ml of bromine and heating the mixture to 40–50°. When the reaction once had begun each new drop of bromine reacted almost instantaneously. The stirring had to be very efficient to avoid partially high bromine concentrations in the reaction mixture (see below).

Diethyl trimethylsilylmethylbromomalonate was quite stable towards aqueous bases. Thus, it could be boiled with 10 % aqueous potassium hydroxide without being affected. However, when treated with 10 % ethanolic potassium hydroxide, in which the compound was soluble, the bromine atom was rapidly split off as bromide ion and there were formed small amounts of hexamethyldisiloxane together with an alkali-soluble silicon-containing polymer. The minute amount of hexamethyldisiloxane formed and the fact that the polymer contained silicon indicated that  $\beta$ -elimination was only a side-reaction under these conditions. The nature of the polymer was not further investigated.

On reaction with diethyl sodiomalonate the bromoester behaved like other alkylbromomalonic esters<sup>14</sup>, *i. e.*, diethyl trimethylsilylmethylmalonate and tetraethyl ethylenetetracarboxylate were formed according to the formula



No traces of products which could have resulted from a  $\beta$ -elimination could be detected. The relative stability of (I) against  $\beta$ -elimination in the above reaction might be ascribed to the tendency of dissociating into a positive bromine ion and a negative diethyl trimethylsilylmethylmalonate ion<sup>15</sup>.

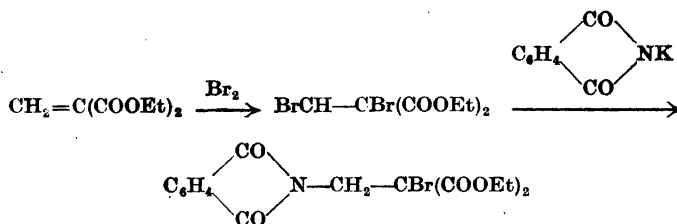


This ion is stable under the conditions employed.

Decomposition of I by heat occurred at 190–200° with the formation of trimethylbromosilane and diethyl methylenemalonate.

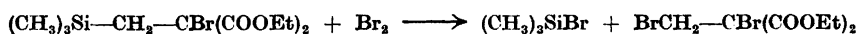


The diethyl methylenemalonate was identified by addition of bromine and reaction of the resulting dibromoester with potassium phthalimide<sup>16</sup>.



The product did not depress the melting point of an authentic sample.

Diethyl trimethylsilylmethylbromomalonate reacted with bromine with the formation of trimethylbromosilane and diethyl bromomethylbromomalonate according to



The last-mentioned compound was identified as before.

Preliminary experiments in order to brominate the free trimethylsilylmethylmalonic acid were not successful, as the bromination product was very unstable and decomposed rapidly on standing. Likewise the bromination of  $\beta$ -trimethylsilylpropionic acid gave decomposition products, among which trimethylbromosilane could be identified. The residue was probably a complex mixture of polybrominated propionic acids.

#### EXPERIMENTAL

*Chlorination of diethyl trimethylsilylmethylmalonate.* In a 100 ml flask equipped with a reflux condenser and a dropping funnel there was placed 24.6 g (0.1 mole) of diethyl trimethylsilylmethylmalonate. A few ml of freshly distilled sulphuryl chloride were added and the solution was heated to 60°. When the reaction had started as indicated by the evolution of hydrogen chloride the rest of the sulphuryl chloride (total amount 13.5 g) was added during a period of 30 minutes. The reaction was completed by heating at 70–80° for two hours. Then excess sulphuryl chloride and dissolved gases were evaporated under reduced pressure at room temperature and at last the residue was fractionated *in vacuo*. From this was obtained 17.3 g (0.062 mole) of diethyl trimethylsilylmethylchloromalonate, b. p. 131–133°/11 mm,  $n_D^{20}$  1.4463,  $d_4^{20}$  1.0553. (Found: C 47.1; H 7.6; Cl 12.4; Si 10.0;  $r_D$  0.2528. Calc. for  $\text{C}_{11}\text{H}_{21}\text{O}_4\text{Cl}$  Si: C 47.1; H 7.5; Cl 12.6; Si 10.0;  $r_D$  0.2516.)

*Bromination of diethyl trimethylsilylmethylmalonate.* In a 250 ml flask equipped with an efficient stirrer, a reflux condenser, and a dropping funnel 98.4 g (0.4 mole) of diethyl trimethylsilylmethylmalonate was heated with a few ml of bromine to ca. 40°. The reaction soon began and the bromine colour disappeared. Bromine (a total of 64 g = 0.4 mole) was then added so slowly that the solution never assumed more than a faint brown colour. The stirring was rapid to avoid partially too high bromine concentrations. The hydrogen bromide evolved was absorbed in alkali. After the gas evolution had ended the reaction mixture was washed twice with water, once with saturated sodium carbonate solution, and with water again. After drying with anhydrous calcium chloride the product was fractionated under reduced pressure. From this was obtained 99.0 g (0.304 mole) of diethyl trimethylsilylmethylbromomalonate, b. p. 118–120°/4 mm,  $n_D^{20}$  1.4597,  $d_4^{20}$  1.2033, a yield of 76%. (Found: C 40.4; H 6.5; Br 24.6; Si 8.5;  $r_D$  0.2275. Calc. for  $\text{C}_{11}\text{H}_{21}\text{O}_4\text{BrSi}$ : C 40.6; H 6.5; Br 24.6; Si 8.6;  $r_D$  0.2261.)

*Reactions of diethyl trimethylsilylmethylbromomalonate.* A. With aqueous base. 3.25 g of the bromo compound (0.01 mole) was boiled for 30 minutes with 20 ml of 10% aqueous

potassium hydroxide. Only traces of bromide ion could be detected in the aqueous layer after cooling and extraction with ether. The ether solution was dried with anhydrous calcium chloride and gave upon distillation nearly all the starting material in recovery.

*B. With ethanolic base.* To a solution of 6.7 g (0.12 mole) of potassium hydroxide in 3 ml of water and 10 ml of ethanol was added 6.5 g (0.02 mole) of diethyl trimethylsilylmethylbromomalonate. The mixture was gradually heated and suddenly a violent reaction occurred. The flask was cooled in ice water, when necessary. At last the solution was heated under reflux for three hours, after which time it was acidified with hydrochloric acid and 50 ml of water was added. The organic layer was taken up in ether and the ether solution washed thoroughly with water to remove ethanol. After drying with anhydrous sodium sulphate fractionation gave 0.2 g of hexamethyldisiloxane, b. p. 99°,  $n_D^{20}$  1.3774, a 12 % yield. None of the other lowboiling products contained silicon. The residue (3.3 g) was a very viscous, alkali-soluble polymer, which on titration with standard alkali solution showed an equivalent of 172. The silicon content was 10.5 %, corresponding to 62 % of the silicon present in the starting material.

*C. With diethyl sodiomalonate.* In a 25 ml three-necked flask equipped with a stirrer, a reflux condenser, and a dropping funnel 0.46 g (0.02 mole) of sodium was dissolved in 10 ml of absolute ethanol, followed by 3.2 g (0.02 mole) of diethyl malonate. 6.50 g (0.02 mole) of the bromoester was added cautiously. This was followed by refluxing for one hour, after which time the mixture was slightly acidified with glacial acetic acid and the ethanol distilled off. The residue was poured into 20 ml of water and worked up as usual. From this was obtained 3.0 g of diethyl trimethylsilylmethylmalonate (0.012 mole) and 1.8 g of tetraethyl ethylenetetracarboxylate (0.0057 mole), m. p. after recrystallization from ligroin 52–53°, mixed m. p. with an authentic specimen 52–53°<sup>17</sup>.

The diethyl trimethylsilylmethylmalonate was identified by conversion into its diamide according to the method of Russell<sup>18</sup>. The authentic compound which was prepared from diethyl trimethylsilylmethylmalonate prepared otherwise melted at 161–162°. It contained one mole of water of crystallization which was removed by heating the compound before being analyzed in air at 110° for 20 hours. (Found C 45.5; H 8.7; Si 14.9; Calc. for  $C_7H_{16}O_2N_2Si$ : C 45.6; H 8.7; Si 14.9.)

*D. Decomposition by heat.* In a 25 ml flask equipped with a short column and a thermometer reaching into the flask there was placed 8.1 g (0.025 mole) of diethyl trimethylsilylbromomalonate. The flask was slowly heated. When the temperature of the liquid reached 190° the compound began to decompose and a liquid distilled over, b. p. 75–77°. It was redistilled and was found to be trimethylbromosilane, b. p. 78–80°, 3.0 g, a yield of 79 %. (Found: Br 52.0. Calc. for  $C_3H_7BrSi$ : Br 52.2.)

The residue in the reaction flask was a dark oil with the characteristic odour of diethyl methylenemalonate, which was distilled at atmospheric pressure, b. p. 195–198°, 3.0 g, a yield of 70 %. For identification it was dissolved in 10 ml of carbon tetrachloride, 2.8 g of bromine was slowly added, the solvent was evaporated, and at last 3.2 g of potassium phthalimide was added. This mixture was heated at 150° for two hours, and then cooled. The solid mass was washed with water and finally recrystallized twice from ethanol, giving beautiful crystals, m. p. 135.5–136.5° undepressed on admixing with an authentic sample<sup>16</sup>.

*Reaction with bromine.* To 8.1 g (0.025 mole) of diethyl trimethylsilylmethylbromomalonate 4.0 g (0.025 mole) of dry bromine was slowly dropped. The mixture warmed and soon began to reflux. After standing for an hour the trimethylbromosilane formed was distilled over, b. p. 76–78°, 3.1 g, a yield of 81 %. It was redistilled over a small amount of red phosphorus in order to remove traces of bromine. (Found: Br 52.1. Calc. for  $C_3H_7BrSi$ : 52.2.)

The residue was distilled under reduced pressure. From this was obtained 6.7 g of diethyl bromomethylbromomalonate, b. p. 125–126/5 mm,  $n_D^{20}$  1.4838,  $d_4^{20}$  1.6268, a yield of 80 %. It was identified as in the foregoing experiment.

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## REFERENCES

1. Ushakov, S. N. and Itenberg, A. M. *J. Gen. Chem. S.S.S.R.* **7** (1937) 2495.
2. Sommer, L. H. and Whitmore, F. C. *J. Am. Chem. Soc.* **68** (1946) 485.
3. Sommer, L. H., Dorfman, E. Goldberg, G. M. and Whitmore, F. C. *J. Am. Chem. Soc.* **68** (1946) 488.
4. Sommer, L. H., Goldberg, G. M. and Whitmore, F. C. *J. Am. Chem. Soc.* **68** (1946) 1083.
5. Sommer, L. H., Bailey, D. L., Strong, W. A. and Whitmore, F. C. *J. Am. Chem. Soc.* **68** (1946) 1881.
6. Sommer, L. H., Bailey, D. L. and Whitmore, F. C. *J. Am. Chem. Soc.* **70** (1948) 2869.
7. Sommer, L. H., Tyler, L. J. and Whitmore, F. C. *J. Am. Chem. Soc.* **70** (1948) 2872.
8. Tyler, L. J., Sommer, L. H. and Whitmore, F. C. *J. Am. Chem. Soc.* **70** (1948) 2876.
9. Agre, C. L. *J. Am. Chem. Soc.* **71** (1949) 300.
10. Sommer, L. H., Bailey, D. L., Goldberg, G. M., Buck, C. E., Bye, T. S., Evans, F. J. and Whitmore, F. C. *J. Am. Chem. Soc.* **76** (1954) 1613.
11. Petrov, A. D. and Mironov, V. F. *Doklady Akad. Nauk S.S.S.R.* **75** (1950) 707.
12. Petrov, A. D. and Mironov, V. F. *Doklady Akad. Nauk S.S.S.R.* **80** (1951) 761.
13. Petrov, A. D. and Mironov, V. F. *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* (1952) 635.
14. Ruhemann, S. *Ber.* **26** (1893) 2356.
15. Fresenius, Ph. *Angew. Chem.* **64** (1952) 470.
16. Elks, F., Elliott, D. F. and Hems, B. A. *J. Chem. Soc.* **1944** 626.
17. Corson, B. B. and Benson, W. L. *Org. Syntheses, Coll. Vol. II*, p. 273.
18. Russell, P. B. *J. Am. Chem. Soc.* **72** (1950) 1853.

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