

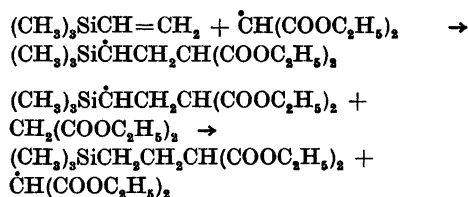
## The Addition of Diethylmalonate to Trimethylvinylsilane

KJELL WETTERLIN\*

Department of Organic Chemistry, Chemical Institute, University of Lund, Sweden

Sommer *et al.*<sup>1</sup> have described the reaction between diethylmalonate and different halogenosilanes with the exception of  $\beta$ -halogenosilanes as these compounds give rapid  $\beta$ -eliminations involving silicon in the alkaline medium they used. Allen *et al.*<sup>2</sup> published in 1961 a new method for the preparation of alkylated malonic esters. They added diethylmalonate to suitable olefins in the presence of peroxide.

As the addition of mercapto compounds to vinylsilanes gives, for the main part,  $\beta$ -addition products, it is conceivable that the addition of malonic ester to trimethylvinylsilane, in the presence of a catalytic amount of peroxide, could give alkylated malonic esters, which could not be prepared in the standard way owing to the  $\beta$ -elimination.



Malonic ester was reacted with trimethylvinylsilane in the presence of peroxide, and a product was isolated that, according to the analyses, could be diethyl trimethylsilylethylmalonate. As the addition theoretically could give two isomeric products (diethyl  $\alpha$ -trimethylsilylethylmalonate and diethyl  $\beta$ -trimethylsilylethylmalonate) the product has been investigated gas chromatographically. This showed that only one of the two possible isomers was formed. For identification, the product was hydrolyzed and decarboxylated. The IR-spectrum of the decarboxylation product was identical with that of  $\gamma$ -trimethylsilylbutyric acid.<sup>3</sup> The S-benzylthiuronium

salts of the decarboxylation product and of the  $\gamma$ -trimethylsilylbutyric acid were prepared. The mixed melting point was determined, but no melting point depression could be found. This indicates that the  $\beta$ -compound has been formed at the addition, which is confirmed by the NMR-spectrum of the compound, where signals from one CH-group and two CH<sub>2</sub>-groups could be identified (the CH<sub>2</sub>-groups in the ester groups uncounted) which excludes the structure of the  $\alpha$ -compound.

*Experimental.* Diethyl  $\beta$ -trimethylsilylethylmalonate. 6.0 g (0.06 mole) trimethylvinylsilane, 285.0 g (1.8 mole) diethylmalonate and 0.3 g di-*tert*-butylperoxide were introduced in an ampoule, which was sealed and heated in a steel bomb to 110° for 103 h. The malonic ester was distilled off through a short column and the residue fractionated *in vacuo*. The yield of crude diethyl  $\beta$ -trimethylsilylethylmalonate was 7.9 g (51 %) b.p. 55–60°/0.001 mm,  $n_D^{25}$  1.4303  $d_4^{25}$  0.9567. (Found: C 55.0; H 9.1; Si 10.6. Calc. for C<sub>12</sub>H<sub>24</sub>O<sub>4</sub>Si: C 55.3; H 9.3; Si 10.8). 6.0 g (0.2 mole) of the ester was hydrolyzed by boiling for 18 h with 10 % ethanolic potassium hydroxide. The ethanol was distilled off and the residue acidified with diluted hydrochloric acid. After extraction with ether, the ether solution was dried with anhydrous magnesium sulphate, the ether was evaporated, and the residue decarboxylated by heating to 190–200° for 10 min. The yield was 1.6 g (35 %). The S-benzylthiuronium salt of the decarboxylation product was prepared<sup>4</sup> and recrystallized from ethanol m.p. 133–134°. The S-benzylthiuronium salt of authentic  $\gamma$ -trimethylsilylbutyric acid had the melting point 134.5–135.5°. The mixed melting point of these two salts was 133–134°. (The melting points were determined with a Kofler melting point microscope.)

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\* Present address: Draco AB., Pob. 242. Lund 1, Sweden.