

COMMUNICATIONS TO THE EDITOR

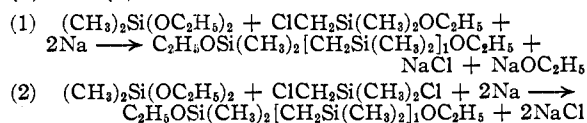
THE USE OF SODIUM IN THE PREPARATION OF METHYLENE-LINKED SILANES

Sir:

The use of sodium in the preparation of compounds of the type $\text{ASi}(\text{CH}_3)_2[\text{CH}_2\text{Si}(\text{CH}_3)_2]_n\text{B}$ has been investigated. These compounds have been made wherein the A and/or B may be methyl, chloride, or ethoxy. The compounds where both A and B are methyl groups have been tentatively called "silahydrocarbons."

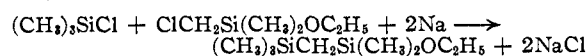
Compounds of the above type where A and B are methyl groups may be prepared from reactions of materials such as $(\text{CH}_3)_3\text{SiCl}$, $\text{CH}_3[(\text{CH}_3)_2\text{SiCH}_2]_n\text{Cl}$ and sodium. This reaction gives products of the type formula $(\text{CH}_3)_3\text{Si}[\text{CH}_2\text{Si}(\text{CH}_3)_2]_n\text{CH}_3$. Yields of these reactions are 65–70% of the desired product. Two of these compounds also have been prepared by reacting $(\text{CH}_3)_3\text{SiCl}$ and $(\text{CH}_3)_2\text{SiCl}_2$ with $(\text{CH}_3)_3\text{SiCH}_2\text{MgCl}$.¹

The preparation of compounds where both A and B are ethoxy groups may be carried out by (1) and (2) as follows.



In (2) it appears that NaOC_2H_5 is formed and reacts with the $\text{ClSi}(\text{CH}_3)_2\text{SiCH}_2(\text{CH}_3)_2\text{OC}_2\text{H}_5$ to give $\text{C}_2\text{H}_5\text{OSi}(\text{CH}_3)_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OC}_2\text{H}_5$.

The preparation of compounds where A is a methyl group and B is ethoxy is easily effected by a reaction such as



This reaction gives yields of 75–80% of the desired product and smaller amounts of higher members. The subsequent preparation of higher members of this series is best achieved by conversion of the ethoxy group to the chloride by reaction with acetyl chloride or benzoyl chloride and the reaction of the chloride with $\text{ClCH}_2\text{Si}(\text{CH}_3)_2\text{OC}_2\text{H}_5$ and sodium. In this way materials of the type $(\text{CH}_3)_3\text{Si}[\text{CH}_2\text{Si}(\text{CH}_3)_2]_n\text{OC}_2\text{H}_5$ may be produced.

The reaction of either the ethoxy materials or the chloride-ended materials with Grignard reagents will give the corresponding "silahydrocarbons." The monofunctional ethoxy and chloride compounds also may be hydrolyzed to give materials of the type $[(\text{CH}_3)_3\text{Si}[\text{CH}_2\text{Si}(\text{CH}_3)_2]_n]_2\text{O}$ while hydrolysis of the difunctional compounds gives cyclic materials with the type formula $[(\text{CH}_3)_2\text{SiCH}_2]_n\text{Si}(\text{CH}_3)_2\text{O}$. Two cyclic materials with formulas $[(\text{CH}_3)_2\text{SiCH}_2\text{Si}(\text{CH}_3)_2\text{O}]_m$

(1) Whitmore, Sommer, Goldberg and Gold, *THIS JOURNAL*, **69**, 980 (1947).

$\text{O}]_2$ and $(\text{CH}_3)_2\text{Si}[\text{CH}_2\text{Si}(\text{CH}_3)_2]_2\text{O}$ have been isolated and identified.

A typical experiment in this series of reactions involves the following procedure: 800 g. of toluene and 4 moles of sodium were placed in a flask and heated to 110° with vigorous stirring. A mixture of 2 moles of $(\text{CH}_3)_3\text{SiCl}$ and 2 moles of $\text{ClCH}_2\text{Si}(\text{CH}_3)_2\text{OC}_2\text{H}_5$ was added at such a rate that the temperature was maintained at 110° . The materials were then filtered and distilled. Distillation gave 1.57 moles of $(\text{CH}_3)_3\text{Si}[\text{CH}_2\text{Si}(\text{CH}_3)_2]_1\text{OC}_2\text{H}_5$, b. p. 160° at 740 mm., n_D^{25} 1.4148, d_4^{25} 0.8060, a yield of 78.5%. *Anal.* Calcd. for $\text{C}_8\text{Si}_2\text{H}_{22}\text{O}$: Si, 29.5; C, 50.55; *MRD*, 59.15. Found: Si, 29.65; C, 50.6; *MRD* 58.9. Similar experiments have produced the compounds indicated up to n values of 4.

There is a good reason for using $\text{ClCH}_2\text{Si}(\text{CH}_3)_2\text{OC}_2\text{H}_5$ rather than $\text{ClCH}_2\text{Si}(\text{CH}_3)_2\text{Cl}$ in these reactions. The reaction of $\text{ClCH}_2\text{Si}(\text{CH}_3)_2\text{Cl}$ with other molecules like itself is so rapid that the simpler members of the series are very difficult to isolate. The products of the reaction of several molecules of $\text{ClCH}_2\text{Si}(\text{CH}_3)_2\text{Cl}$ and sodium are materials with high molecular weights and with the basic unit $[\text{Si}(\text{CH}_3)_2\text{CH}_2]_n$ predominating in the molecule.

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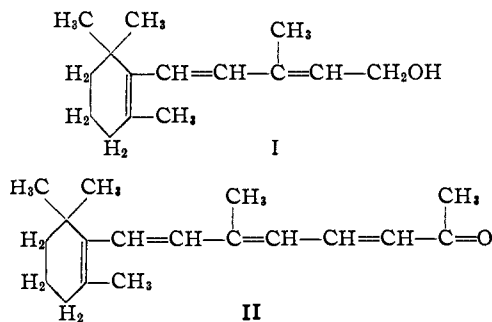
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A NEW SYNTHESIS OF 1-(2',6',6'-TRIMETHYL-CYCLOHEXEN-1'-YL)-3-METHYLHEXA-1,3,5-TRIEN-7-ONE (C_{18} KETONE)

Sir:

The C_{18} ketone (II)¹ is an important intermediate in the synthesis of "vitamin A acid" and vitamin A itself. Recently we have synthe-



(1) (a) Arens and van Dorp, *Nature*, **157**, 190 (1946); *Rec. trav. chim.*, **65**, 338 (1946); (b) Heilbron, Jones and O'Sullivan, *Nature*, **157**, 485 (1946); *J. Chem. Soc.*, 868 (1946); (c) Karrer, Jucker and Schick, *Helv. Chim. Acta*, **29**, 704 (1946).