

COMMUNICATIONS TO THE EDITOR

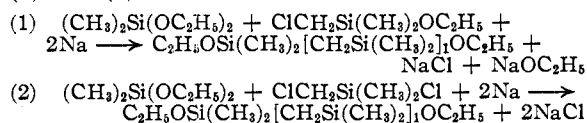
THE USE OF SODIUM IN THE PREPARATION OF METHYLENE-LINKED SILANES

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."

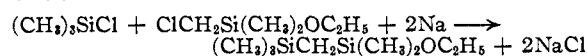
Compounds of the above type where A and B are methyl groups may be prepared from reactions of materials such as $(\text{CH}_3)_3\text{SiCl}$, $\text{CH}_3[(\text{CH}_3)_2\text{SiCH}_2]_n\text{Cl}$ and sodium. This reaction gives products of the type formula $(\text{CH}_3)_3\text{Si}[\text{CH}_2\text{Si}(\text{CH}_3)_2]_n\text{CH}_3$. 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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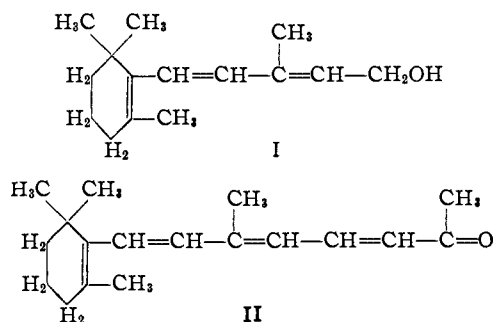
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RECEIVED AUGUST 15, 1947

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).

sized this ketone by the application of the Oppenauer oxidation² on β -ionylidene ethyl alcohol (I) which was prepared by the reduction of ethyl β -ionylidene acetate with lithium aluminum hydride.^{3,4}

Ethyl β -ionylidene acetate (b. p. 141–144° (2–3 mm.); n_D^{25} 1.5320; λ_{\max} 2850 Å., log ϵ 4.42) was prepared according to Karrer, *et al.*,⁵ by the Reformatsky condensation of β -ionone (n_D^{25} 1.5180) and ethyl bromoacetate. The intermediate hydroxy ester was dehydrated with *p*-toluene sulfonic acid in toluene. This ester (180 g.) was reduced in an ethereal solution at 0° with lithium aluminum hydride (32 g.) prepared essentially by the recently published method.³ The product (163 g.) was recovered after acidification with a mixture of ice and glacial acetic acid and fractionated under reduced pressure and the fraction (113.6 g.) boiling at 137–144° (4 mm.), collected and analyzed; n_D^{25} 1.5496; λ_{\max} 2740 Å., log ϵ 4.45.

Anal. Calcd. for $C_{15}H_{24}O$: C, 81.76; H, 10.98; unsaturation, 3 \bar{F} ; active hydrogen, 1.0. Found: C, 81.42; H, 10.92; unsaturation, 3.12, 3.17 (Pt) \bar{F} ; active hydrogen (Zerewitinoff), 0.99, 1.01, 1.02.

β -Ionylidene ethyl alcohol (44.8 g.) was dissolved in a mixture of thiophene-free benzene (1000 cc.) and purified acetone (400 cc.) and to the mixture was added 60 g. of freshly prepared aluminum *t*-butoxide and refluxed in nitrogen for forty-four hours. The mixture was cooled, hydrolyzed with 1 liter of water and filtered and the benzene layer separated from the filtrate, dried and the benzene removed under vacuum; yield of the crude product, 40 g. (active hydrogen, 0.55). This dark brown product was distilled under a high vacuum and the fraction (32 g.) distilling at 80–85° (10^{-4} – 10^{-5} mm.) collected and analyzed. Carbon and hydrogen showed the presence of about 10% ketol, so that the product was further dehydrated with 2% *p*-toluene sulfonic acid in toluene. The ketone was recovered and, after preliminary purification in petroleum ether and in methanol at –78°, was fractionated under high vacuum and the fraction (yellow oil, 24.5 g.) boiling at 80–82° (10^{-4} – 10^{-5} mm.) was collected and analyzed; n_D^{17} 1.5685; λ_{\max} 3330 Å., log ϵ 4.2.

Anal. Calcd. for $C_{18}H_{26}O$: C, 83.67; H, 10.14; unsaturation, 4.0 \bar{F} . Found: C, 83.67; H, 10.43; unsaturation, 4.15 \bar{F} .

The ketone had a negligible active hydrogen (Zerewitinoff) and gave a wine red color with antimony trichloride in chloroform. We expect to carry out a Reformatsky on this ketone, de-

(2) Batty, Burawoy, Harper, Heilbron and Jones, *J. Chem. Soc.*, 175 (1938).

(3) Finholt, Bond and Schlesinger, *THIS JOURNAL*, 69, 1199 (1947).

(4) Nystrom and Brown, *ibid.*, 69, 1197 (1947).

(5) Karrer, Salomon, Morf and Walker, *Helv. Chim. Acta*, 15, 878 (1932); Karrer, Morf and Schoepp, *ibid.*, 16, 557 (1933); Karrer, Ruegger and Solmssen, *ibid.*, 21, 448 (1938).

hydrate the hydroxy ester and reduce the final ester to vitamin A with lithium aluminum hydride.

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RECEIVED AUGUST 26, 1947

PHOSPHITE ISOMERIZATION IN THE SYNTHESIS OF THIOPHENE PHOSPHONIC ACIDS

Sir:

In view of the very poor yields heretofore attainable in the preparation of thiophene-substituted phosphonic acids,¹ the classical isomerization of alkylphosphites was tried in an attempt to make the compounds of this type more available for study.

Sodium dibutylphosphite (from 45 g. of dibutyl phosphite) was treated in hexane solution with 31 g. of α -chloromethylthiophene to give, after three hours of reflux, 71% yield of dibutyl α -thienylmethane phosphonate, b. p. 147–150° at 3 mm. Hydrolysis by boiling with hydrochloric acid, followed by evaporation and recrystallization of the residue from water, gave a substantially quantitative conversion of the ester to α -thienylmethane phosphonic acid, which formed yellowish plates; m. p. 108–109°. *Anal.* Calcd.: S, 16.3. Found: S, 16.46.

(1) Sachs, *Ber.*, 25, 1514 (1892).

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RECEIVED AUGUST 11, 1947

CARCINOGENESIS

Sir:

Concerning the excellent paper by L. F. Fieser and S. T. Putnam on the Oxidation of Carcinogenic Hydrocarbons in the May issue of *THIS JOURNAL*, I should like to suggest that peroxidation is more important than oxidation in determining their carcinogenicity. Since the ionization potential decreases with the number of conjugation centers, a simple electron transfer process involving the non-localized π electrons can readily occur with these hydrocarbons. This may be followed by a proton transfer resulting in the formation of a free-radical. This radical reacts with oxygen to form a peroxide free-radical capable of initiating a branched-chain, free-radical oxidation of intracellular nutrient material, thus increasing cell-metabolism and cell-growth. In the presence of trace quantities of such materials as chromium, iron, cobalt, arsenic, ascorbic acid, etc., the activation energy required for the decomposition of the hydroperoxides into free radicals may be low enough to accelerate tissue growth to the extent that it is entirely out of proportion to the growth rate of the normal surrounding tissues.

The hydroperoxides will increase until limited by the supply of arterial oxygen. Since they are a