[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Organic Reactions with Silicon Compounds.[1] II. The Reaction of Silicon Tetrafluoride with the Grignard Reagent

BY J. A. GIERUT, F. J. SOWA AND J. A. NIEUWLAND

In an attempt to prepare a very pure quality of tetraethylsilicane by the reaction of silicon tetrachloride with ethylmagnesium halides, Jaeger and Dykstra[2] substituted silicon tetrafluoride for silicon tetrachloride. Silicon tetrafluoride was not treated with any alkylmagnesium halide other than the ethyl compound.

It was the purpose of this investigation to study the reaction of ethyl, propyl, butyl and amyl magnesium halides with silicon tetrafluoride.

The reaction was vigorous in ether solution and was completed within one hour. Instead of the expected product, however, the reaction went practically all to the trialkylsilicyl fluorides. The reaction may be represented as

$$SiF_4 + 3RMgX \longrightarrow R_3SiF + 3MgXF \qquad (1)$$

When ethylmagnesium bromide was used about one half of the reaction proceeded as in equation (1) and about half proceeded to give tetraethylsilicane. With propyl, butyl and amyl magnesium halides the reaction proceeded practically completely according to equation (1).

Flood[3] recently prepared triethylsilicyl fluoride by the reaction of diethylsilicon oxide with sulfuric acid and sodium or ammonium fluoride. He noted that this triethylsilicyl fluoride was quite stable toward hydrolysis with respect to the corresponding bromide. The same observation was noted in this investigation and in addition the tripropyl- and especially the tributyl- and triamylsilicyl fluorides were particularly inactive. The latter two compounds would react further neither with the Grignard reagent under the conditions of this reaction nor with metallic sodium in liquid ammonia solution.

Using alkyl chlorides in the preparation of the Grignard reagent seemed to give better yields of trialkylsilicyl fluorides than did the corresponding alkyl bromides.

Experimental Part

Preparation of Trialkylsilicyl Fluorides.—Since the procedure for the preparation of the various trialkylsilicyl fluorides was quite uniform, the description will be presented only for the triamylsilicyl fluoride preparation.

One mole of amylmagnesium chloride was prepared in a 2-liter, three-necked flask. The flask was fitted with a reflux condenser, inlet tube which extended to the bottom of the flask and a mechanical stirrer. When silicon tetrafluoride was passed into the well stirred ether solution of the amylmagnesium chloride, a reaction took place immediately as the ether began to reflux. When the solution was saturated with silicon tetrafluoride two layers appeared. The upper layer was clear while the lower layer was gray and turbid. Silicon tetrafluoride was passed in for a short time after the layers appeared.

At this point the procedure was varied for a number of different experiments.

The above contents were refluxed on a water-bath, in a series of runs, for periods of one, two and one-half, five and ten hours. The upper layer was decanted. The lower ether insoluble layer was washed thoroughly with anhydrous ether and the ether portion added to the supernatant liquid.

After the ether was removed by distillation the contents were carefully fractionated. Practically all of the product boiled at 267° (745 mm.). A small (usually about 5 g.) fraction below this point and a small fraction (about 6 g.) above 267° was collected. The yield of the principal fraction was 50 g. The time of reflux did not vary this yield. The main fraction was proved to be triamylsilicyl fluoride.

A second series of runs was made in which the quantity of amylmagnesium chloride was varied. In one run 0.75 mole of amylmagnesium chloride was treated as above. After the solution was saturated with silicon tetrafluoride a second portion of 0.25 mole of amylmagnesium chloride was added and refluxed. The yield was 50 g. (57.6%) as before.

When 0.5 mole of amylmagnesium chloride was used with subsequent addition of a second 0.5 mole of the Grignard reagent, a yield of only 22 g. (25.3%) was obtained.

A third run was made by the same procedure and 0.25 mole of amylmagnesium chloride was used in the beginning with the second addition of 0.75 mole. The yield was less than 10%.

Subjecting butyl chloride and bromide to the first procedure above, the main fraction boiled at 224° (745 mm. and was proved to be tributylsilicyl fluoride. The yield of this fraction from the butyl chloride and butyl bromide run was 51 g. (70.0%) and 46.0 g. (63.2%), respectively.

Propyl bromide by a similar procedure gave tripropylsilicyl fluoride (62%) while in the case of ethyl bromide about an equal quantity of tetraethyl silicane (b. p. 153°, $n^{25}D$ 1.4255, $d^{25}{}_{25}$ 0.7769) and triethylsilicyl fluoride[3] were formed.

Table I gives the physical properties of the trialkylsilicyl fluoride.

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[1] For previous paper see Gierut, Sowa and Nieuwland, THIS JOURNAL, **58**, 786 (1936).

[2] Jaeger and Dykstra, *Z. anorg. Chem.*, **143**, 233 (1925).

[3] Flood, THIS JOURNAL, **55**, 1735 (1933).

The trialkylsilicyl fluorides were very stable and did not respond to the action of sodium in liquid ammonia and therefore could not be analyzed by the sodium–liquid ammonia[4] method.

The fluorine was qualitatively determined in each compound by oxidation with chromic acid in sulfuric acid solution to silicon tetrafluoride which was passed into aniline[5] to form a solid addition compound.

TABLE I

PROPERTIES AND ANALYSES OF TRIALKYLSILICYL FLUORIDES

Trialkyl-silicyl fluorides	B. p., °C. (745 mm.)	$n^{25}\text{D}$	d^{25}_4	Yield, %	Carbon, % Calcd.	Carbon, % Found
Ethyl[3]	109	1.3900	0.8354	45.0	53.66	52.50
Propyl	175	1.4107	.8339	62.0	61.28	60.93
Butyl	224	1.4250	.8372	70.1	65.97	65.96
Amyl	267	1.4305	.8389	57.6	69.10	69.10

The compounds were analyzed quantitatively for carbon by a modified Chalmer's[6] method which is a wet combustion method. The results of this analysis are given in Table I.

Summary

A study was made of the reaction between silicon tetrafluoride and ethyl, propyl, butyl and amylmagnesium halides.

Three new trialkylsilicyl fluorides were prepared.

The fluorine atom in trialkylsilicyl fluorides is very inactive, much less reactive than the corresponding bromide or chlorides.

The reaction between alkylmagnesium halides and silicon tetrafluoride is completed in less than one hour.

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[4] Vaughn and Nieuwland, *Ind. Eng. Chem., Anal. Ed.*, **3**, 274 (1931).

[5] Comey and Jackson, *Am. Chem. J.*, **10**, 166 (1888).

[6] Chalmer, *Ind. Eng. Chem., Anal. Ed.*, **4**, 1 (1932).

NOTRE DAME, INDIANA RECEIVED MARCH 5, 1936

[CONTRIBUTION FROM KENT AND GEORGE HERBERT JONES CHEMICAL LABORATORIES, UNIVERSITY OF CHICAGO]

Lactones in Liquid Ammonia

BY J. W. E. GLATTFELD AND DUNCAN MACMILLAN[1]

In an earlier article[2] the authors described the preparation of aldonic and saccharinic acid amides in liquid ammonia. In the procedure employed it was found that the lactones of sugar acids were readily ammonolyzed and gave quantitative yields of the amides. Experiments with lactones of the other types indicated that not all lactones show this property. This suggested that further study might contribute to an understanding of the lactone bond. It seemed desirable that the work be done on a quantitative basis, and under anhydrous conditions. For this purpose a system capable of evacuation was constructed, as shown in the figure.

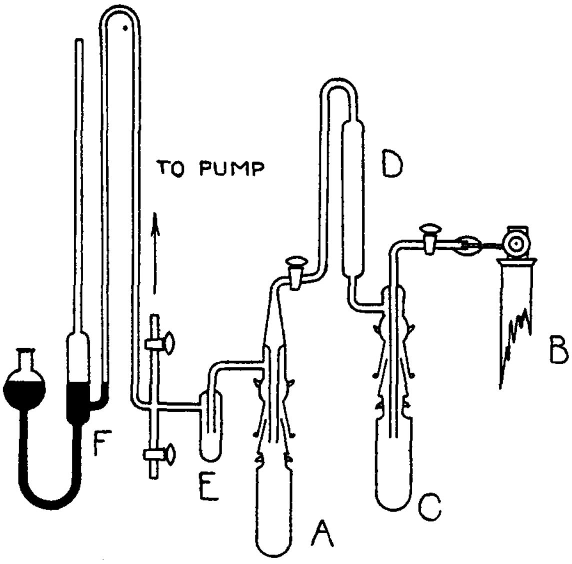

Fig. 1.

Since the same procedure was used in all cases, a general description may be given. A quantity of the material to be studied was placed in a weighed tube (A), the open end of which was the inner cone of a ground-glass joint; the joint was greased and the tube placed in the line. The system was evacuated to a pressure of 10^{-4} mm. with a mercury vapor pump. The tube was then detached, the joint cleaned with ether, and the tube weighed, after which it was again placed in the line and evacuated. Ammonia was then condensed from a small tank (B) into a tube (C) which contained sodium metal, over which the ammonia was allowed to stand until the blue color became permanent. The ammonia was then distilled through a column (D) packed with glass wool, into the reaction tube (A). The purpose of the glass wool was to remove small amounts of

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[1] The material in this article will be used by Duncan Macmillan as a part of his dissertation for the degree of Doctor of Philosophy in the University of Chicago.

[2] Glattfeld and Macmillan, THIS JOURNAL, **56**, 2481 (1934).