until a spot becomes so thin as to be colorless or "black" when it usually breaks.

The higher fatty acids dissolve in cold concentrated sulfuric acid to give soap-like solutions. They are soap-like in that they foam and give bubble-films of great stability. This can be demonstrated as follows:

Into a 125-ml. Erlenmeyer flask place about 0.02 g. of stearic acid, keeping the neck of the flask clean, and pour in 20 ml. of 95% sulfuric acid. Seal the neck of the flask with an oxygen torch. The stearic acid solution is colorless when pure, and darkens slowly only after many days. (Apparently there is no sulfonation of the stearic acid at first. Experiments indicate that the fatty acid is recovered when the sulfuric acid is poured into water.)

When the flask is shaken the solution foams, giving a foam which persists for an hour or more. Occasionally a horizontal film remains across the flask out of contact with other bubbles. Such a horizontal film sometimes remains permanent for days, making it possible to observe the changes which occur.

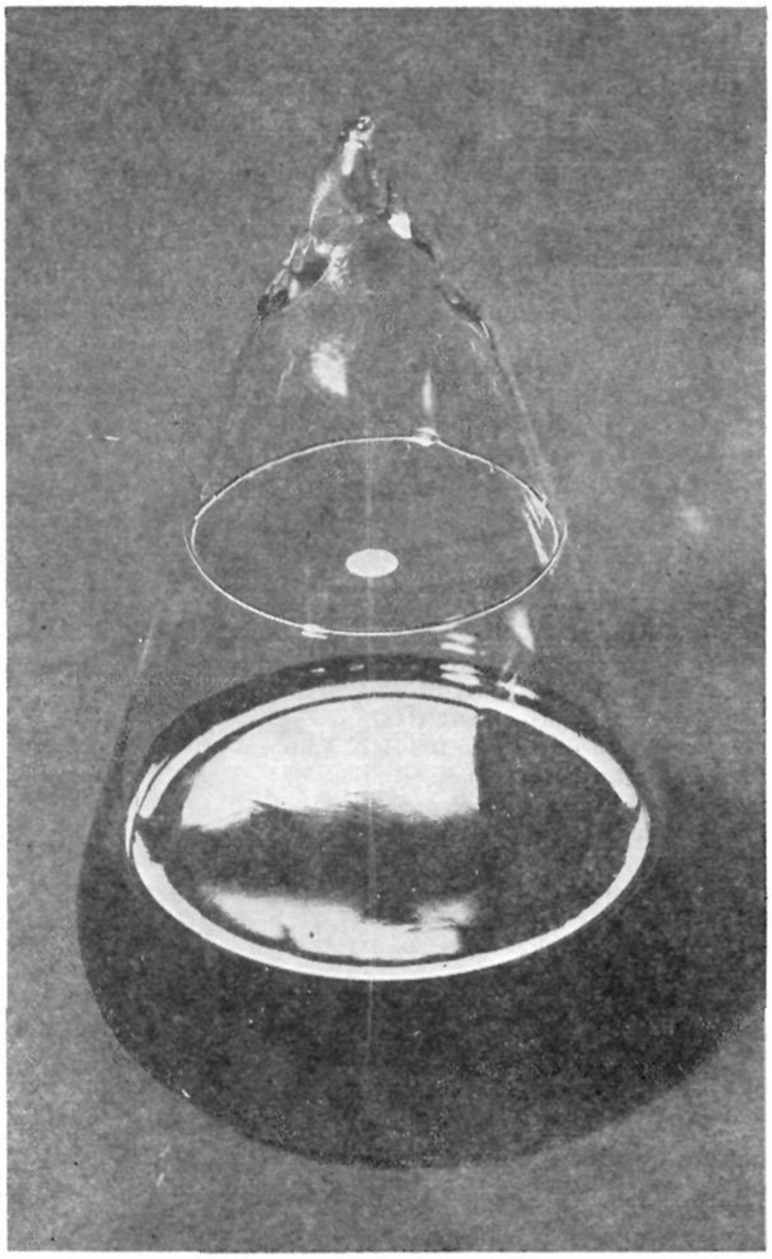

Fig. 1.—A black "soap" film of stearic acid in sulfuric acid and its suspended droplet.

Within a few minutes bands of interference colors appear arranged in rings. Soon the rings contract and there remains a colorless or "black" film, too thin to show interference color. The colored rings finally disappear at the center, into a disk-shaped droplet suspended by the colorless film. Such films within this flask may be about two inches in diameter. In the course of a few days a film may travel slowly upward because of the conical shape of the glass wall. The suspended liquid disk swings with great freedom when the flask is moved. If the glass at the edge of the film is warmed at one spot, as by contact of a finger, little iridescent "droplets" with streamers push out from the edge and pass to the center, where they become absorbed into the colorless droplet. These minute colored "droplets" move with great ease under the influence of gravity, showing the fluidity of these films. The color changes in these films are sharply discontinuous, as in bubbles of soap in water. These "black" films resemble the extremely stable black films of soap with glycerol prepared by Sir James Dewar, which showed the same movement of droplets. One of his black bubbles was 40 cm. in diameter and weighed about 50 milligrams, making the average thickness 150 Å. The minimum black bubble thickness has been estimated as 50 Å. or two molecular layers.[1]

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(1) Sir James Dewar, "Soap Bubbles of Long Duration," *J. Franklin Inst.*, **188**, 713–749 (1919); N. K. Adam, "The Physics and Chemistry of Surfaces," 3rd ed., Oxford University Press, London, 1941.

WESTINGHOUSE RESEARCH LABORATORIES
EAST PITTSBURGH, PA.

RECEIVED JULY 22, 1946

Preparation of the Methylfluorosilanes

BY ARTHUR E. NEWKIRK

The use of zinc fluoride to replace, by fluorine, a chlorine atom attached to silicon has been reported by Schumb and Gamble[1] who made hexafluorodisilane from hexachlorodisilane, and by Emeleus and Wilkins[2] who made ethyl and phenyl fluorosilanes from the corresponding chlorosilanes.

In connection with the investigations of organosilicon compounds in this Laboratory, the methylfluorosilanes have been prepared from the corresponding chloride and zinc fluoride. This method is of interest in view of the discovery by Rochow[3] of a convenient method for the preparation of organohalosilanes. Although the fluorinated homologs may also be prepared by this direct method, it is not as convenient because of the difficulties in preparing the necessary organofluorine compounds.

Only the completely fluorinated compounds were obtained as products. Their boiling points were in good agreement with those reported by Pearlson, Brice and Simons,[4] and by Booth and his

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(1) Schumb and Gamble, THIS JOURNAL, **54**, 583 (1932).

(2) Emeleus and Wilkins, *J. Chem. Soc.*, 454 (1944).

(3) Rochow, THIS JOURNAL, **67**, 963 (1945).

(4) Pearlson, Brice and Simons, *ibid.*, **67**, 1769 (1945).

co-workers.[5,6] In the preparation of dimethyldifluorosilane an inflection on the distillation curve was obtained at +36° which might have been due to the presence of dimethylchlorofluorosilane.

Trimethylfluorosilane was also prepared by treating the silicon tetrachloride–trimethylchlorosilane azeotrope[7] with zinc fluoride. The silicon tetrachloride was not affected to an appreciable extent.

Trimethylfluorosilane hydrolyzed to a very slight extent on being bubbled through water, but in an aqueous solution of sodium hydroxide, hexamethyldisiloxane was formed rapidly.

Experimental

$(CH_3)_3SiF$, $(CH_3)_2SiF_2$, CH_3SiF_3.—These compounds were prepared in a three-necked flask by adding the corresponding chlorosilane[8] to technical zinc fluoride that had been dried at 110° for twenty-four hours and cooled to 30° in the flask. The gas that was evolved in each case was passed through a water-cooled reflux condenser (which returned some of the unreacted chlorosilane), to a trap cooled by a mixture of Dry Ice and acetone. After the initial rapid evolution of gas, the flask was heated until the reaction ceased. The contents of the trap were distilled through a low-temperature fractionating column to obtain the fluorosilanes. In each case, some hydrogen chloride distilled off first at −85° followed by the fluorosilane and then the unreacted chlorosilane. The details of the separate experiments are given in Table I.

TABLE I

Chlorosilane,	moles	ZnF_2, moles	Fluorosilane,	moles	B. p., °C.	Yield, %
$(CH_3)_3SiCl$	1.00	0.81	$(CH_3)_3SiF$	0.49	+17	49[a]
$(CH_3)_2SiCl_2$	2.00	1.49	$(CH_3)_2SiF_2$	.57	+ 3	38[b]
CH_3SiCl_3	2.00	4.00	CH_3SiF_3	.80	−30	40[a]

[a] Yield based on the chlorosilane. [b] Yield based on zinc fluoride.

ZnF_2 + Azeotrope.—A sample of 559 g. of the azeotrope formed between $SiCl_4$ and $(CH_3)_3SiCl$ was placed in a 1-liter three-necked flask, and 93.2 g. of dried ZnF_2 (equivalent to the $(CH_3)_3SiCl$) was added with vigorous stirring. The other details were the same as described above. The products of the reaction were separated by fractional distillation. Unreacted azeotrope amounted to 34.4%. From the azeotrope that reacted, there was obtained 74.8% of the $SiCl_4$ as $SiCl_4$ and 83.7% of the $(CH_3)_3SiCl$ as $(CH_3)_3SiF$.

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(5) Booth and Martin, THIS JOURNAL, **68**, 2655 (1946).

(6) Booth and Suttle, *ibid.*, **68**, 2658 (1946).

(7) See Sauer, U. S. Patent 2,381,139, August 7, 1945.

(8) The author is indebted to Mr. W. J. Scheiber of this Laboratory for these samples.

RESEARCH LABORATORY
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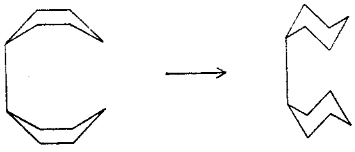
RECEIVED APRIL 29, 1946

The Isomerization of Dicyclohexyl[1]

BY MILTON ORCHIN[2] AND JULIAN FELDMAN[3]

R. Ya. Levina and co-workers reported[3] that treatment of dicyclohexyl with aluminum chloride at 100° gave, as a principal product, a fraction boiling at 217–219°. This product was regarded as *trans–trans* dicyclohexyl which resulted from the aluminum chloride induced, stereochemical isomerization of the *cis–cis* isomer



We have found that similar treatment of dicyclohexyl gives a mixture of isomers possessing about the same properties as those reported for the *trans–trans* dicyclohexyl. From this multicomponent mixture we were able to isolate 2,2′-dimethyldicyclopentyl and 1-cyclohexyl-2-methylcyclopentane.

The Russian workers passed their product boiling at 217–219° three times over a 20% platinum-on-charcoal catalyst at 310°. The aromatic material formed under these conditions was removed and the physical properties of the non-aromatic material compared with those of the original. After three more passes over the catalyst the physical properties of the non-aromatic portion were still approximately the same as those of the starting material. From this behavior they concluded that they were dealing with a single pure compound that was only slowly dehydrogenated to 2,6-dimethylnaphthalene. Our results indicate that the Russian workers were probably dealing with a mixture of isomers of closely related properties and that removal of one component or a fraction of it would not affect the physical properties they determined on the balance of the material. No freezing point data were given by these workers.

It is interesting to note that treatment of cyclohexane with aluminum chloride at 150° has been reported[4] to give a mixture of products containing dicyclohexyl and 2,2′-dimethyldicyclopentyl and that 2,2′-dimethyldicyclopentyl has also been reported[5] to result from the Friedel–Crafts reaction of cyclohexyl chloride with cyclohexane.[5]

Experimental

The dicyclohexyl was obtained from the Dow Chemical Co. and after purification had the properties indicated in Table I. It was treated in batches with aluminum chloride at about 100° for fifty hours with stirring in the manner described by the Russian workers. It was found that if a stream of dry hydrogen chloride gas was passed into the mixture, a five-hour heat treatment gave a product of the same character (boiling point-refractive index plot). Treatment of 3887 g. of dicyclohexyl with 1100 g. aluminum gave 3860 cc. of crude isomerized product. This was distilled through a three-foot heli-grid column. Similar fractions were combined and redistilled through a six-foot heli-grid packed column at a rate which under test

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[2] Organic chemist, Central Experiment Station, Bureau of Mines, Pittsburgh, Pa.

[3] R. Ya. Levina, Yu. K. Yur'ev and A. I. Loshkomoinikov, *J. Gen. Chem. U. S. S. R.*, **7**, 341 (1937).

(4) Ipatieff and Komarewsky, THIS JOURNAL, **56**, 1926 (1934). These authors also reported the presence of isobutane, methylcyclopentane, cyclohexane, and 1,3-dimethylcyclohexane.

(5) Nenitzescu and Ionescu, *Ann.*, **491**, 189 (1931).