

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 azeotrope⁷ 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

(CH₃)₃SiF, (CH₃)₂SiF₂, CH₃SiF₃.—These compounds were prepared in a three-necked flask by adding the corresponding chlorosilane⁸ 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) ₃ SiCl	1.00	0.81	(CH ₃) ₃ SiF	0.49 +17 49 ^a
(CH ₃) ₂ SiCl ₂	2.00	1.49	(CH ₃) ₂ SiF ₂	.57 + 3 38 ^b
CH ₃ SiCl ₃	2.00	4.00	CH ₃ SiF ₃	.80 -30 40 ^a

^a Yield based on the chlorosilane. ^b Yield based on zinc fluoride.

ZnF₂ + Azeotrope.—A sample of 559 g. of the azeotrope formed between SiCl₄ and (CH₃)₃SiCl was placed in a 1-liter three-necked flask, and 93.2 g. of dried ZnF₂ (equivalent to the (CH₃)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 SiCl₄ as SiCl₄ and 83.7% of the (CH₃)₃SiCl as (CH₃)₃SiF.

(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.

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RECEIVED APRIL 29, 1946

The Isomerization of Dicyclohexyl¹

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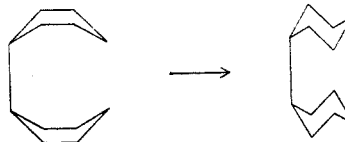
R. Ya. Levina and co-workers reported³ that treatment of dicyclohexyl with aluminum chlo-

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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. Loshkomoinkov, *J. Gen. Chem. U. S. S. R.*, **7**, 341 (1937).

ride 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 multi-component 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 reported⁴ to give a mixture of products containing dicyclohexyl and 2,2'-dimethyldicyclopentyl and that 2,2'-dimethyldicyclopentyl has also been reported⁵ 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

(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).

conditions at total reflux gave a column efficiency of over 100 plates. About 10% of the distillate boiled below 200°. This included some material boiling at 119–121° which had a refractive index of n_D^{20} 1.4250 (probably dimethylcyclohexane).⁴ The main fraction (A) was collected over 0.2° range and after some intermediate fractions, a second large fraction (C) was collected at a higher temperature. The properties of these fractions and some pertinent data of the Russian workers are given in Table I.

TABLE I
ISOMERIZATION OF DICYCLOHEXYL

	% Yield	B. p., °C. 750 mm. press.	n_D^{20}	d_4^{20}
Russian workers				
Dicyclohexyl		234	1.4807	0.8840
Isomerized main fraction	75	217–219	1.4663	.8592
Present authors				
Dicyclohexyl		238	1.4696	
Isomerized fraction A	23	215.5–215.7	1.4629	.8512
Isomerized fraction C	8	222–225	1.4701	.8644

Fraction A, containing 885 g. of material, on cooling to 0° partly solidified. The crystalline material was separated (189 g.) and the index of refraction of the filtrate was n_D^{20} 1.4631. Cooling the filtrate to –10° gave a second crop of crystals (96 g.) which was separated by filtration. The mother liquor still had an index of refraction of n_D^{20} 1.4631 and now had a density of d_4^{20} 0.8516. The combined solid material was recrystallized several times from methanol until a constant melting point was reached. The properties of this compound, presumed to be 2,2'-dimethyldicyclopentyl,^{4,5} were accurately determined. *Anal.*⁶ Calcd. for $C_{12}H_{12}$: C, 86.66; H, 13.34. Found: C, 86.6; H, 13.4; melting point 45.5–45.7° (cor.); boiling point (760) 216.9° (cor.); n_D^{20} 1.4500; n_D^{60} 1.4463. The density and refractive index of this compound in pure dodecane were determined at 20° at different concentrations. The straight-line plot, extrapolated to 100% 2,2'-dimethyldicyclopentyl, gave n_D^{20} 1.4595 and d_4^{20} 0.8492.⁷ The infra-red absorption spectrum of the solid is given in Fig. 1.⁸

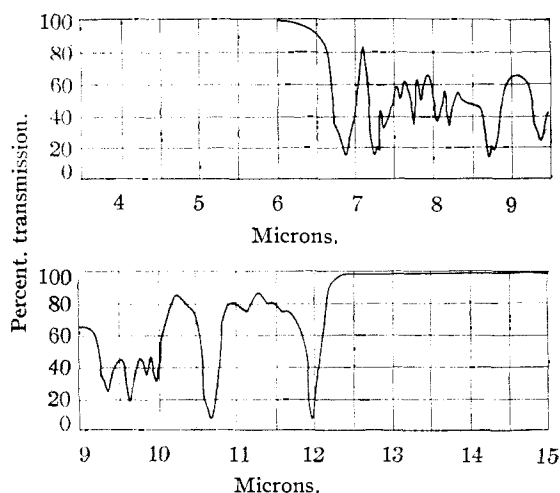


Fig. 1.—Infra-red absorption spectrum: 2,2'-dimethyldicyclopentyl as solid; cell length, 0.1 mm.

(6) Analysis by the Coal Analysis Section, Bureau of Mines, U. S. Dept. of the Interior.

(7) The authors wish to thank Mr. Irving Wender and Miss Mary C. Gray for the determination of many of the constants.

(8) This absorption spectrum was kindly determined by Dr. R. A. Friedel of this Laboratory.

Fraction C was redistilled and the properties of the middle cut were determined. These were as follows: *Anal.*⁸ Calcd. for $C_{12}H_{22}$: C, 86.66; H, 13.34. Found: C, 86.2; H, 13.2; n_D^{20} 1.4705; d_4^{20} 0.8683; boiling point (760) 224.4° (cor.). These properties are in good agreement with the following properties reported for 1-cyclohexyl-2-methylcyclopentane by Zelinskii and co-workers⁹: b. p. (744 mm.) 225.5–227°; n_D^{20} 1.4701; d_4^{20} 0.8680.

(9) Zelinskii, Shuikin and Fateev, *J. Gen. Chem. U. S. S. R.*, **2**, 671 (1932).

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RECEIVED AUGUST 5, 1946

Preparation of Vanillic Acid Amide from Vanillonitrile¹

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Common methods² such as the ammonolysis of methyl vanillate and cautious treatment of vanillonitrile with concentrated mineral acids³ have failed to give vanillic acid amide. This catalog of unsuccessful efforts includes treatment with mildly alkaline hydrogen peroxide,⁴ a reaction which serves to convert to the corresponding amides even highly hindered ortho substituted nitriles.

To obtain vanillic acid amide an indirect method was employed in which the nitrile was converted to vanillic acid *n*-butyl amido ester chloride. The latter compound was easily pyrolyzed to the amide in a reaction developed by Pinner⁵ for the synthesis of malonic ester amide.

Experimental⁶

Vanillin Oxime.—The compound was prepared in nearly quantitative yield using the procedure of Lach,⁷ modified by omitting the use of alcohol as part of the solvent. Recrystallized from water gave a m. p. 121–122.5°.

Acetovanillonitrile.—Vanillin oxime was converted to the acetylated nitrile by the method of Marcus.⁸ The product recrystallized from water and from aqueous ethanol melted at 110°; yield 94%.

Vanillonitrile.—This compound was prepared by dissolving acetovanillonitrile (48 g., 0.25 mole) in 150 cc. of concentrated hydrochloric acid at 60–70° and cooling immediately. The product deposited when the acid solution was poured into 1 liter of water, neutralized to pH 4–5 with sodium hydroxide and cooled. It was collected on a filter, washed with water and dried over barium oxide. The yield was 25–26 g. of white needles or 70% of the theoretical quantity, m. p. 86–87°.⁸

Vanillic Acid *n*-Butyl Amido Ester Chloride.—For preparation of the amido ester vanillonitrile (46 g., 0.31 mole) was dissolved in 150 cc. of anhydrous diethyl ether and absolute *n*-butanol (23 g., 0.31 mole) was added. The solution was cooled in an ice-salt-bath and saturated with

(1) Presented before the Organic Section, Northwest Regional Meeting of the A. C. S., October 29, 1945.

(2) Hickinbottom, "Reactions of Organic Compounds," Longmans, Green and Co., London, 1936, p. 250.

(3) Cold sulfuric acid more concentrated than 25 *N* sulfonates vanillonitrile as will be described in another communication.

(4) McMaster and Langreck, *THIS JOURNAL*, **39**, 103 (1917); McMaster and Noller, *J. Indian Chem. Soc.*, **12**, 652 (1935).

(5) Pinner, *Ber.*, **23**, 479 (1895).

(6) All melting points are uncorrected.

(7) Lach, *Ber.*, **16**, 1786 (1883).

(8) Marcus, *ibid.*, **24**, 3654 (1891).