ether, 2.8 g. of an almost colorless gum whose structure was not investigated. The partly crystalline dithiol acid was purified by vacuum sublimation followed by recrystallization from petroleum ether; yield 2.13 g. (41% from the gum), m.p. 59–61°. A mixture melting point with a sample isolated from asparagus juice showed no depression.

β,β′-Diisothiouroniumisobutyric Acid Dihydroiodide.—A solution of 1.70 g. (0.005 mole) of β,β′-diiodoisobutyric acid was added to a solution of 0.76 g. (0.01 mole) of thiourea in 30 ml. of acetone and refluxed for 30 minutes. About half of the acetone was distilled off and benzene was added to precipitate an oil which readily crystallized; yield, quantitative. For analysis, it was recrystallized from water, m.p. 160–163° dec.

Anal. Calcd. for $C_6H_{14}I_2N_4O_2S_2$: C, 14.6; H, 2.87; N, 11.4. Found: C, 15.0; H, 3.02; N, 11.3.

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The Structures of the Diterpenoid Alkaloids Laurifoline and Cuauchichicine. Nomenclature Alteration

BY CARL DJERASSI, C. R. SMITH, A. E. LIPPMAN, S. K. FIGDOR AND J. HERRAN

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We have recently reported[1] the isolation and structure elucidation of a new diterpenoid alkaloid, named laurifoline, from the Mexican tree *Garrya laurifolia* Hartw. It has now been called to our attention by Prof. M. Tomita of the University of Kyoto that the name "laurifoline" has been used already by him for an aporphine-like alkaloid isolated[2] from *Cocculus laurifolius* DC. In view of the priority of the Japanese workers and in order to avoid any confusion in the alkaloid literature, we propose that the name of our alkaloid[1] be changed to "garryfoline."

(1) C. Djerassi, C. R. Smith, A. E. Lippman, S. K. Figdor and J. Herran, THIS JOURNAL, **77**, 4801 (1955).
(2) M. Tomita and F. Kusuda, *Pharm. Bull. (Japan)*, **1**, 1 (1953).

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The Pyrolysis of Trifluoromethyl Sulfur Pentafluoride and its Reaction with Perfluoropropylene

BY RICHARD DRESDNER

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The pyrolysis of CF_3SF_5, trifluoromethyl sulfur pentafluoride, and its reaction with C_3F_6, perfluoropropylene, have been investigated. The experiments were carried out at temperatures between 425 and 518°. The only products found when CF_3SF_5 was heated, under the conditions outlined, were C_2F_6, perfluoroethane, and SF_4, sulfur tetrafluoride. When CF_3SF_5 and C_3F_6 were heated together at elevated temperatures, a series of fluorocarbons was isolated and identified.

Experimental

Apparatus.—The experiments were carried out in a closed system at approximately atmospheric pressure. The gases to be pyrolyzed or reacted were condensed air-free into a valved 1600-cc. stainless steel container. They were allowed to come to equilibrium at room temperature. The flow rate of the gases through the system was observed by their passage through a small bubbler containing a few cc. of dibutyl phthalate. The gas flow was controlled by the settings on the container valve and the stopcock on a liquid air cooled condenser-collector at the end of the system. The reactor was made from a 0.5″ i.d. nickel tube 18″ long and filled with extruded nickel packing. The reaction zone was wrapped with 0.25″ copper wire and heated in a Hoskins furnace. The reaction temperatures were noted with a 22-gauge chromel–alumel thermocouple placed at the center of the reaction zone. The temperatures at the surface of the reactor at equilibrium were 2 to 5° higher than those observed inside the unpacked tube.

Conditions.—All experiments were carried out at approximately atmospheric pressure. The average mass flow rates were held between 0.20 and 0.40 g./min. Temperatures were maintained within ±3° of the reported values.

Materials.—Trifluoromethyl sulfur pentafluoride: this material was prepared by the electrochemical process.[1] The starting materials were a solution of $(CH_3)_2S$, dimethyl sulfide, in anhydrous HF.[2] The CF_3SF_5 was purified by fractionation and had a b.p. of −20.5° and a molecular weight of not less than 193 and not more than 196.

Perfluoropropylene.—This material was obtained from the Peninsular Chemical Research Co., Gainesville, Fla. It had a molecular weight of 150, b.p. −30°.

Results

Two trials were made to pyrolyze CF_3SF_5. The first was made at 450°, a flow rate of 0.40 g./min., and an average pressure of 760 mm. No products were recovered that were characterized as different from the starting material. The second trial was made at 500°, a flow rate of 0.20 g./min. and the same pressure as in trial 1. Two grams of C_2F_6 and 2 g. of SF_4 were isolated and identified and some 16 g. of starting material was recovered out of 21 g. of CF_3SF_5 passed through the system. The nickel packing was very slightly attacked during the second trial.

Five trials were made with CF_3SF_5 and C_3F_6. Generally, the unreacted starting materials were recovered from each trial and reused in the succeeding trial. The conditions and results of these trials are presented in Table I.

TABLE I

SUMMARY OF REACTIONS OF CF_3SF_5 AND C_3F_6 IN A NICKEL-PACKED REACTOR

C_3F_6, g.	CF_3SF_5, g.	Flow, g./m.	Temp., °C.	Mm.	Products in g. C_2F_6	SF_4	SM[a]	b. above −19°
17	21	0.29	425	735	Tr.	Tr.	37	1
16	20	.32	485	740	1	1	28	4
26	33	.28	512	760	1	13	15	17
60	75	.40	515	760	2	27	70	38
45	55	.28	518	740	1	27	25	47
					5	68		107

[a] Starting materials.

The products boiling above −19° were collected and fractionated in appropriate columns. The main fractions isolated and identified were 17 g. C_4F_{10}, 7 g. C_5F_{12}, 15 g. C_6F_{14} and 9 g. C_7F_{16}.

(1) J. H. Simons and co-workers, *J. Electrochem. Soc.*, **95**, 47 (1949).
(2) A. F. Clifford, H. K. El-Shamy, H. J. Emeléus and R. N. Haszeldine, *J. Chem. Soc.*, 2372 (1953).

Identification of Products.—C_4F_{10}: This material was recovered from fractionation at between −1° and 1°. It had a molecular weight of between 238 and 240; analysis showed the absence of sulfur.

C_5F_{12}: This material was recovered from fractionation and boiled between 29 and 31°. Its molecular weight was between 286 and 288. It did not show the presence of sulfur. The crude fraction had a melting point range above 10°. Nuclear magnetic resonance spectra were made on aliquots of the sample and from the relative intensity of the CF_3 peaks, it was concluded that the sample contained neo-C_5F_{12}, iso-C_5F_{12} and *n*-C_5F_{12}, crudely in the ratio 3:2:1.

C_6F_{14}: This material boiled between 57 and 59°. It had a molecular weight of between 338 and 340. It contained no sulfur. The refractive index, $n^{25}D$, was 1.2558.

C_7F_{16}: This material boiled between 82 and 83°. It had a molecular weight of 392. It contained no sulfur. The refractive index, $n^{25}D$, was 1.2685.

Six grams of product boiled above 83°, and appeared to be fluorocarbon material.

Although the attack on the nickel packing was not too serious even at 518°, one trial, essentially the same as the third trial in the table, was made with the reactor filled with 0.125″ NaF pellets. From this trial, 5 g. of C_4F_{10}, 2 g. of C_5F_{12} and 5 g. of C_6F_{14} were isolated and characterized. As only 3 g. of material boiled above 60°, no C_7F_{16} was isolated.

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Preparation and Reactions of Methylenedimagnesium Dihalides

BY D. A. FIDLER, J. R. JONES, S. L. CLARK AND HUGO STANGE

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During the course of another investigation it became necessary to prepare methylenedimagnesium dihalides (methylene di-Grignards). Both the dibromide and diiodide had been prepared previously by Emschwiller from the corresponding methylene halide, but the conversion of the magnesium was only of the order of 11%.[1] Chang and Chao-Lun Tseng have confirmed the preparation

$$CH_2X_2 + 2Mg \longrightarrow CH_2(MgX)_2$$

of the diiodide but state that the maximum yield is 10%.[2] We have succeeded in preparing methylenedimagnesium dibromide and methylenedimagnesium diiodide with conversions of the magnesium as high as 54%. The yield of the di-Grignard has been as high as 73%. A small amount of coupling accompanies this reaction, leading to the formation of ethylene.

$$CH_2X_2 + Mg \longrightarrow {}^1/_2CH_2 = CH_2 + MgX_2$$

The reactivity of the methylene di-Grignard reagent was found to be exceptionally low. No reaction was observed when an ethereal solution of benzaldehyde was heated to reflux for three hours with the di-Grignard reagent. The benzaldehyde was recovered quantitatively as the semicarbazone. When an ethereal solution of benzoyl chloride was heated to reflux for one hour with the reagent, there also was no reaction and the benzoyl chloride was recovered quantitatively as benzoic acid. A similar reaction with acetyl chloride, followed by hydrolysis, resulted only in the recovery of solvent from the organic layer. These results are in agreement with Chang and Chao-Lun Tseng who report no reaction with acetone, benzophenone, Michler ketone or carbon dioxide.[2]

Experimental

Methylenedimagnesium Diiodide.—Five grams (0.21 g. atom) of magnesium was covered with anhydrous ethyl ether. While the ether was heated under reflux and the magnesium stirred, 28.0 g. (0.11 mole) of methylene iodide, diluted with ten times its volume of anhydrous ether, was added dropwise over a period of 4.5 hours. After an additional hour of stirring, the flask was cooled and two layers formed. Hydrolysis of the lower layer gave 790 ml. (S.T.P.) of methane as confirmed by its infrared spectrum.[3] The spectrum was recorded by the use of a 10-cm. cell at a gas pressure of approximately 760 mm. Gas which was collected in a cold trap (−196°) during the reaction was identified as ethylene by its vapor pressure.

The weight of unreacted magnesium indicated a 54% conversion of which 73% formed methylenedimagnesium diiodide while 27% went to the formation of ethylene. By decreasing the addition time of the methylene iodide to 1.5 hours, both the conversion and yield were reduced to 50%.

Methylenedimagnesium Dibromide.—The dibromide was prepared in the same manner as the diiodide. The addition of 19.0 g. (0.11 mole) of the methylene bromide solution required 15 minutes. Heating under reflux for three hours and the addition of a few crystals of iodine were necessary to initiate the reaction. In this case a 50% conversion of the magnesium was achieved, 58% of which formed methylenedimagnesium dibromide.

(1) G. Emschwiller, *Compt. rend.*, **183**, 665 (1926).

(2) D. Y. Chang and Chao-Lun Tseng, *Trans. Sci. Soc. China*, **7**, 243 (1932); *C. A.*, **26**, 5544 (1932).

(3) The lower-membered di-Grignard reagents are insoluble in ether, forming a lower layer. A. Kreuchunas, THIS JOURNAL, **75**, 3339 (1953), reports that the solubility increases with chain length and that the C_{10}-compound does not form a separate layer.

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The Effect of Liquid Ammonia on Proteins. I. Insulin

BY ERIC ELLENBOGEN

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In order to evaluate the use of non-aqueous solvents for tissue fractionation, preliminary experiments were carried out with the insulin–liquid ammonia system[1] employing samples of high potency insulin with known physical chemical properties. These experiments indicated that long exposures of insulin to liquid ammonia did not alter any physical chemical properties as judged by solubility, sedi-

(1) E. Ellenbogen, Abstr. 124th National Meeting, American Chemical Society, page 20 C, 1953.