1000 cm.$^{-1}$ and Δ_2 in the range 3000–10,000 cm.$^{-1}$ then are consistent with the $^4A_{2g}$ ground state for $R_2Co(MNT)_2$ and the $^1A_{1g}$ ground state for $R_2Ni(MNT)_2$.

The electronic spectrum of $R_2Co(MNT)_2$ in the solid or in DMF solution shows a band at 12,500 cm.$^{-1}$ (ϵ = 69), assigned to the $^4A_{2g} \rightarrow {}^4E_g{}^{(1)}$ ($xz, yz \rightarrow z^2$) transition. This gives Δ_3 = 9,500 cm.$^{-1}$. The next band, a shoulder indicative of a maximum at 15,000 cm.$^{-1}$ ($\epsilon \cong 200$), is assigned $^4A_{2g} \rightarrow {}^4E_g{}^{(2)}$ ($xz, yz \rightarrow xy$), giving Δ_2 = 5,500 cm.$^{-1}$, in agreement with the value assumed above for Δ_2. The bands at higher energies are much more intense and probably are due to charge transfer transitions.

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SYNTHESES OF 5-TRIFLUOROMETHYLURACIL AND 5-TRIFLUOROMETHYL-2′-DEOXYURIDINE[1]

Sir:

We wish to report the syntheses of 5-trifluoromethyluracil (VI) ("trifluorothymine") and its deoxyriboside 5-trifluoromethyl-2′-deoxyuridine (VII) which was done in connection with the interest of this laboratory in fluorinated pyrimidines. Replacement of the hydrogen atom of carbon-5 of uracil by fluorine gives 5-fluorouracil,[2] which is incorporated into ribonucleic acid,[3] and inhibits the growth of murine and human tumors as a result of the inhibition of thymidylate synthetase[4] by 5-fluoro-2′-deoxyuridine-5′-monophosphate.[5] Replacement of the same hydrogen atom by chlorine, bromine, or iodine leads to compounds[6] that are incorporated into deoxyribonucleic acid in place of thymine, presumably because of the similarity in sizes of these atoms and the methyl group of thymine. We considered, therefore, that similar effects might be produced by the replacement of the methyl group of thymine by a trifluoromethyl group, which would also have a similar size.

Other trifluoromethylpyrimidines have been prepared recently by Inoue, Saggiomo and Nodiff[7] and by Barone,[8] but the trifluoromethyl group has not been introduced into the crucial 5 position of a pyrimidine.

Trifluoromethylacrylonitrile[9] (I) dissolved in ethanol and saturated with hydrogen bromide at 5° gave β-bromo-α-trifluoromethylpropionamide (II) in 75% yield, m.p. 101–103°. (*Anal.* Calcd. for $C_4H_5NOF_3Br$: C, 21.84; H, 2.29; N, 6.36; F, 25.91. Found: C, 21.99; H, 2.39; N, 6.52; F, 25.77.) Condensation of this bromoamide with a 2 to 4 molar excess of urea in aqueous dioxane at 90° gave the monosubstituted urea (III) in *ca.* 30% yield, m.p. 169–171° (*Anal.* Calcd. for $C_5H_8N_3F_3O_2 \cdot C_2H_5OH$: C, 34.29; H, 5.72; N, 17.14; F, 23.24. Found: C, 33.87; H, 5.18; N, 17.27; F, 23.64). On refluxing this compound in 5 *N* hydrochloric acid, hydrolysis of the amide group first occurred, then cyclization giving the dihydropyrimidine (IV) in 60% yield m.p. 203–205° dec. (*Anal.* Calcd. for $C_5H_5N_2O_2F_3$: C, 33.00; H, 2.77; N, 15.38; F, 31.30. Found: C, 33.11; H, 2.81; N, 15.20; F, 31.26). Treatment of (IV) in acetic acid under reflux with one mole of bromine gave the bromohydropyrimidine (V) in 70% yield, m.p. 218–221° dec., which on heating in dimethylformamide[10] for 1 hour at 140° gave 5-trifluoromethyluracil (VI) in 85% yield, m.p. 239–241° *dec.* (*Anal.* Calcd. for $C_5H_3N_2F_3O_2$: C, 33.35; H, 1.68; N, 15.55; F, 31.65. Found: C, 33.75; H, 1.92; N, 15.40; F, 31.96), pK_a (water) 7.35, (method of Shugar and Fox[11]) Ultraviolet absorption spectra, in 0.1 *N* hydrochloric acid λ_{max} 257 mμ, ϵ molar 7050; in pH 7.0 buffer, λ_{max} 257 mμ, ϵ molar 6830; in pH 8.1 buffer λ_{max} 279, ϵ molar 6900; R_f, butanol/water, 86/14 v./v. ascending 0.79; butanol/acetic acid/water, 50/20/30 v./v., descending 0.80; ethyl acetate/methyl alcohol/water/*n*-heptane, 10/6/5/3 v./v., upper phase[12] 0.76.

The 5-trifluoromethyluracil was converted quantitatively to 5-carboxyuracil in 20 minutes at room temperature in 1.0 *N* sodium hydroxide, and in 24 hours in 0.1 *N* sodium bicarbonate. The lability of the trifluoromethyl group in alkali may prove to be of some interest for chemical mutagenesis since it could be converted to a carboxyl group under conditions which would not degrade deoxyribonucleic acid.

5-Trifluoromethyl-2′-deoxyuridine (VII) has been prepared using a nucleoside phosphorylase preparation[13] from Ehrlich ascites cells, and 2-deoxy-α-D-ribose-1-phosphate. The deoxyribonucleoside was separated from the unconverted 5-trifluoromethyluracil by electrophoresis on paper in borate buffer pH 9.2, and purified by paper chromatography using a butanol/formic acid/water, 77/10/13 v./v., descending solvent system. It was obtained in an over-all yield of 8.2% m.p. 169–172°.

(*Anal.* Calcd. for $C_{10}H_{11}N_2O_5F_3$: C, 40.55; H, 3.73; F, 19.24. Found: C, 40.50, H, 4.15; F, 18.95.) Ultraviolet absorption spectra, in 0.01 *N* hydrochloric acid, λ_{max} 260 mμ, ϵ molar 9590, in 0.01 *N* sodium hydroxide, λ_{max} 260 mμ, ϵ molar 6250; R_f butanol/formic acid/water, 77/10/13 v./v., descending 0.72, ethyl acetate/methanol/water/*n*-heptane 10/6/5/3 v./v. descending 0.62.

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[1] This work was supported in part by a grant (C-2832) from the National Cancer Institute, National Institutes of Health, U. S. Public Health Service, and a training grant (CRTY-5002) from the National Institutes of Health, U. S. Public Health Service.

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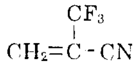
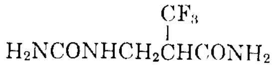


$CH_2{=}\overset{CF_3}{C}\text{-}CN$

I

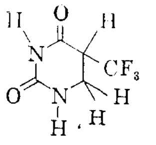
$BrCH_2\overset{CF_3}{C}HCONH_2$

II

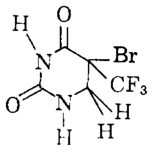


$H_2NCONHCH_2\overset{CF_3}{C}HCONH_2$

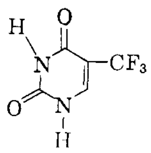
III



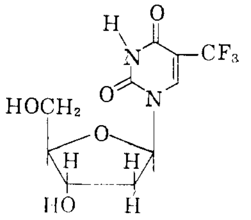
IV



V



VI



VII

NOTE ADDED IN PROOF.—5-Trifluoromethyl-5-hydroxy-5,6-dihydrouracil has been prepared recently by P. W. Feit, *Arch. der Pharmazie*, **295**, 321 (1962). Attempts to convert this dihydrouracil derivative to 5-trifluoromethyluracil were unsuccessful.

Preliminary studies have shown 5-trifluoromethyluracil to be mutagenic to bacteriophage T4[14]; further chemical and biological studies are being carried out with these compounds, and full details of these experiments will be published at a later date.

[14] Dr. Hubert Gottschling, personal communication.

[15] American Cancer Society Professor of Oncology.

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RECEIVED JULY 13, 1962

NEW CLASSES OF HIGH MOLECULAR WEIGHT BORON SULFIDES

Sir:

We have discovered two new classes of high molecular weight boron gases comparable to but considerably more numerous than the boron hydrides. These substances were obtained by vaporization from a slightly sulfur-rich, glassy B_2S_3 sample and were identified by mass spectrometry. One class consists of boron sulfides, and the other appears to contain boron, sulfur, and a third element or radical.

The sample, prepared at 700° by the reaction of hydrogen sulfide with elemental boron in silica tubing, followed by flushing with hydrogen and helium to remove most of the excess sulfur, was heated to 300–500° in a graphite Knudsen cell in a Nuclide Analysis Associates 12 inch, 60° magnetic field mass spectrometer having a resolution of about 1000. Ions were formed by impact with 70-volt electrons.

The spectrum consists of clusters of lines which we shall call bands, using spectroscopic notation. The lines arise from the individual isotopic species of a particular chemical formula. The bands have been observed repeatedly and extend to masses higher than 800. Prominent intervals between bands are 11, 32, and 17 (and others by combination) and correspond to the addition of a boron atom, a sulfur atom, and the third element or radical. Although the most intense bands in the spectrum arise from $B_2S_3^+$, the sum of the intensities at higher masses is about twice the intensity of $B_2S_3^+$. The bands decrease in intensity through the 200–300 mass range but increase to a maximum in the 400–500 range.

The ion species in the first class which have been identified are $B_2S_3^+$, $B_2S_4^+$, $B_2S_5^+$, $B_3S_3^+$, $B_3S_4^+$, $B_3S_5^+$, $B_3S_6^+$, $B_4S_6^+$, $B_4S_7^+$, $B_4S_8^+$, $B_5S_6^+$, $B_5S_7^+$, $B_5S_8^+$, $B_5S_9^+$, $B_6S_9^+$, $B_6S_{10}^+$, $B_6S_{11}^+$, $B_7S_{10}^+$, $B_7S_{11}^+$, $B_7S_{12}^+$, $B_7S_{13}^+$, $B_8S_{12}^+$, $B_8S_{13}^+$, $B_8S_{14}^+$, $B_8S_{15}^+$, $B_9S_{13}^+$, $B_9S_{14}^+$, $B_9S_{15}^+$, $B_{10}S_{15}^+$, $B_{10}S_{16}^+$, and $B_{10}S_{17}^+$.

The third component in the second series of compounds has not been firmly identified, but the mass interval of 17 suggests that it is OH. On this basis the observed bands in this system could arise from the ions $B_3S_5OH^+$, $B_3S_6OH^+$, $B_4S_6OH^+$, $B_4S_7OH^+$, $B_5S_8OH^+$, $B_5S_9OH^+$, $B_6S_9OH^+$, $B_6S_{10}OH^+$, $B_7S_{11}OH^+$, $B_8S_{12}OH^+$, $B_8S_{13}OH^+$, $B_8S_{14}OH^+$, $B_9S_{15}OH^+$, $B_9S_{16}OH^+$, $B_{10}S_{15}OH^+$, $B_{10}S_{16}OH^+$, $B_{11}S_{17}OH^+$, and $B_{11}S_{18}OH^+$.

The mass associated with each peak up to about 800 was unambiguously obtained by counting individual lines in numerous spectra. Positive identification of a band was accomplished by comparing the observed relative line intensities with those computed on an IBM 650 computer from the normal isotopic abundance of boron and sulfur.

The boron sulfide species appeared to diminish in comparison with those in the second class as the sample was progressively vaporized. The species containing the most sulfur for a given number of boron atoms also appeared to fall in comparison with those containing less sulfur, in conformity with the suspected congruent vaporization of B_2S_3.

The appearance of such a complex spectrum suggests extensive fragmentation of a larger molecule, but both the change of the relative intensities with time and the spectra obtained with lower energy electrons indicate the presence of many parent species.

The important boron sulfide ions listed above have S/B ratios slightly greater than 1.5 which, when considered in light of the sulfur-rich character of the sample, suggests that the parent molecules may be equilibrium species.

Boron and its compounds exhibit a wide variety of structural and bonding types. It is possible that the large molecules may form boron chains, nets, or icosahedra as are found in the borides. Possibly structures similar to the boron hydrides may be found. More likely, the structures involve rings of alternate boron and sulfur atoms as in $(HBS_2)_3$[1] and perhaps sulfur rings and chains.

The complexity of the molecules in the gas phase suggests the possibility of similar complexity in the liquid phase which may account for the great tendency of boron sulfide samples to form glasses.

Acknowledgments.—We are pleased to acknowledge the generous support of the U. S. Atomic Energy Commission (Contract AT(11-1)-1140), the

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