the methyl groups of the two isomers are separated by about 4 cps.[15] The major component (I)[16] was isolated by crystallization from petroleum ether. The nmr spectrum of pure I in carbon tetrachloride gave sharp singlets in the ratio 3:2:5 at τ 8.23, 6.56, and 2.83 for the methyl, methylene, and aromatic protons, respectively. The signal of the hydroxyl proton appeared at τ −1.63.

The isomeric oximes were characterized by comparison of the amides resulting from the Beckmann rearrangement of the pure major oxime and of the mixture of the two oximes with authentic samples of N-benzylacetamide (III) and N-methyl-2-phenylacetamide (IV). The Beckmann rearrangements were carried out by the method of Craig and Naik.[17] The major oxime yielded essentially one amide which was identical with authentic N-benzylacetamide (mixture melting point and nmr). The nmr spectrum of N-benzylacetamide in deuteriochloroform[18] gives a singlet for the methyl protons at τ 8.16, a doublet with separation of 5.8 cps at 5.74 for the methylene protons, and a singlet at 2.81 for the aromatic protons. The N–H proton gives a very broad signal in the region of the aromatic protons. The doublet of the methylene hydrogens results from coupling with N–H. With deuterium exchange the doublet collapses to a singlet at τ 5.74. The nmr spectrum of N-methyl-2-phenylacetamide in deuteriochloroform gives a doublet (separation of 4.8 cps) at τ 7.35 for the methyl protons, a singlet at 6.55 for the methylene protons, a singlet at 2.80 for the aromatic protons, and a very broad signal at about 3.2 for the N–H proton. Deuterium exchange caused a collapse of the doublet at τ 7.35 to a singlet.

The nmr spectrum of the amide obtained from the Beckmann rearrangement of the major oxime (I) matched that of N-benzylacetamide (III) exactly and the nmr spectrum of the rearrangement products of a mixture of the two oximes gave the singlet and doublet of III at τ 8.15 and 5.74, respectively, and the doublet and singlet of IV at 7.35 and 6.55, respectively. The aromatic hydrogens gave a single signal at τ 2.83. The ratio of the two amides was about the same as the ratio of the oximes in the starting mixture.

These results show that the proximity of the hydroxyl group in structure II causes a deshielding of the methylene protons of about 0.24 ppm (in CCl₄ and pyridine) in comparison to structure I where the OH is anti to the methylene protons.

Experimental Section

anti- and syn-Benzyl Methyl Ketoximes (I and II).—Phenyl-2-propanone was treated with hydroxylamine by the methods of Shriner, Fuson, and Curtin[13] in pyridine and in aqueous sodium hydroxide solution. Both methods yielded a liquid mixture of two ketoximes in the ratio ca. 2:1, as analyzed by nmr. Cooling the mixture caused precipitation of the major product, the anti-benzyl isomer (I), mp 69–71° after recrystallization from petroleum ether (bp 30–60°) (lit.[16] mp 68–70°). The identity of the major product was verified from its Beckmann rearrangement product. The syn-Benzyl methyl ketoxime II was not isolated in the pure form. Its identity was determined from the Beckmann rearrangement products of a mixture of I and II.

(15) Chemical shifts in pyridine follow: CH₃, τ 8.09, and CH₂, τ 6.39, for I; and CH₃, τ 8.16, and CH₂, τ 6.05, for II.
(16) P. W. Neber and A. v. Friedolsheim, Ann., 449, 109 (1926).
(17) J. Cymerman Craig and A. R. Naik, J. Am. Chem. Soc., 84, 3410 (1962).
(18) The chemical shifts have a slight concentration dependence.

Beckmann Rearrangement.—The Beckmann rearrangement was carried out by the method of Craig and Naik on the p-toluenesulfonate esters of the oximes. To a solution of 0.57 g (0.0038 mole) of the solid ketoxime (mp 69–71°) in 20 ml of acetone at 0° was added in succession 0.153 g (0.0038 mole) of sodium hydroxide in 1.9 ml of water and 0.73 g (0.0038 mole) of p-toluenesulfonyl chloride. The mixture was stirred at 0° for 10 min and the acetone was removed with a rotary evaporator at room temperature. The ester was taken up in benzene and the volume of benzene was reduced at room temperature with a rotary evaporator. The benzene solution was transferred to a column containing 20 g of neutral alumina, Brockmann activity I, and eluted with benzene and mixtures of benzene and increasing portions of moist chloroform. The combined fractions yielded 0.48 g of amide, mp 62.5–63.3° after recrystallization from hexane. The amide was identical (melting point, mixture melting point, and nmr spectrum) with a sample of N-benzylacetamide synthesized from benzyl amine and acetic anhydride. This establishes the structure of the ketoxime as anti-benzyl methyl ketoxime (I).

The Beckmann rearrangement was also carried out under identical conditions on a sample of a mixture of the two isomeric ketoximes in the ratio ca. 2:1. The nmr spectrum of the product of the Beckmann rearrangement showed the presence of two amides in the ratio ca. 2:1. The spectrum of the major component was identical with the spectrum of N-benzylacetamide, described above, and the spectrum of the minor component was identical with the nmr spectrum of an authentic sample of N-methyl-2-phenylacetamide synthesized from phenylacetic acid.

Nmr spectra were determined with a Varian A-60 spectrometer at 37°. Melting points were determined with a Fischer-Johns apparatus.

Registry No.—I, 10048-64-3; II, 10048-65-4.

Pentafluoroguanidine

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The direct fluorination of nitrogen compounds has been reviewed by Tedder[1] and also by Hoffman and Neville.[2] A procedure involving the direct fluorination of silver cyanide diluted with fluorspar used by Ruff and Giese[3] has been modified recently by Davis and Groves[4] for the fluorination of urea, thiourea, guanidine, and melamine using alkali metal fluorides as the diluent.

In this Note we report the preparation of pentafluoroguanidine, $(F_2N)_2C{=}NF$, by this technique. Guanidine monohydrofluoride mixed with a large amount of sodium fluoride was fluorinated with an excess of 20–30% fluorine diluted with nitrogen. The gaseous product collected contained a mixture of low-boiling products from which pentafluoroguanidine was isolated by vapor phase chromatography (25%).

Pentafluoroguanidine is an extremely explosive, colorless liquid below its boiling point, −1.1 ± 0.6°, determined from vapor pressure measurements in a mercury-free system. From these data, the following Antoine equation was computed.

(1) J. M. Tedder, "Advances in Fluorine Chemistry," Vol. 2, M. Stacey, J. C. Tatlow, and A. G. Sharpe, Ed., Butterworth Inc., Washington, D. C., 1961, pp 104–137.
(2) C. J. Hoffman and R. G. Neville, Chem. Rev., 62, 1 (1962).
(3) O. Ruff and M. Giese, Ber., 69, 598,604 (1936).
(4) R. A. Davis and K. O. Groves, U. S. Patent 3,288,936 (1966).

$$\log P(\text{mm}) = 6.238 - \frac{689.39}{T(^\circ C.) + 206.44}$$

Trouton's constant and the heat of vaporization were 20.3 and 5.54 kcal/mole, respectively. The molecular weight found by gas density measurements is 148.5 (calcd, 149). The density of pentafluoroguanidine was found to be 1.51 g/ml at 0°.

The mass spectrum of pentafluoroguanidine showed a weak parent peak, relative intensity 0.88, at m/e 149. The major fragment, relative intensity 100, m/e 97, was assigned to $NF_2C=NF^+$ which results from loss of NF_2 from the parent molecule. Other major peaks with relative intensities greater than 10 were as follows (mass, ion, relative intensity): 14, N^+, 18; 26, CN^+, 16; 28, N_2^+, 23; 31, CF^+, 87; 33, NF^+, 70; 40, CN_2^+, 10; 45, CNF^+, 12; 50, CF_2^+, 12; 52, NF_2^+, 59; 59, CN_2F^+, 22; 64, CNF_2^+, 37; and 78, $CN_2F_2^+$, 76.

The infrared absorption spectrum of pentafluoroguanidine in the gas phase shows a weak intensity band at 6.15 assigned to $C=N$ stretch, a medium–weak band at 8.21, a medium band at 7.46, and strong bands at 10.10 and 11.03 μ assigned to the NF_2 groups. The 11.03 band has a shoulder at 10.65 μ.

The F^{19} nmr spectrum ($CFCl_3$ as reference) showed bands broadened by nitrogen coupling at ϕ -42.3, -46.9, and -20.2 in an area ratio of approximately 2:2:1. The bands at ϕ -42.3 and -46.9 are attributed to the NF_2 groups syn and $anti$ to the $=NF$ at -20.2.

Pentafluoroguanidine is a very reactive compound. It reacts rapidly with mercury and must be handled in a mercury-free system. It hydrolyzes rapidly even at room temperature. Within 1 hr it partially hydrolyzes to form N_2F_4, CO_2, N_2, and HF. It may be stored, however, for long periods of time in dry glass containers without decomposition. On heating, pentafluoroguanidine began to undergo a slow exothermic decomposition at about 205° which became rapid at 265°. Pentafluoroguanidine is a very explosive material in the gas, liquid, or solid state. Explosions were readily initiated by shock and spark and sometimes by liquid–solid or solid–liquid phase transitions. When the material was exploded, the following reaction was shown to occur stoichiometrically.

$$(F_2N)_2C=NF \longrightarrow CF_4 + 1.5N_2 + 0.5F_2$$
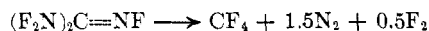
Experimental Section

Caution!—Pentafluoroguanidine is an extremely explosive compound in the gas, liquid, and solid state. It has been manipulated routinely in a mercury-free vacuum line with Freon-12 slush baths at -130 to $-145°$. Liquid nitrogen baths freeze the product and explosions often occurred during freezing and melting. It was standard practice to use adequate shielding and protective equipment and to keep the sample size below 0.5 g.

Preparation of $(F_2N)_2C=NF$.—Guanidine monohydrofluoride (5 g, 72 mmoles) was mixed with 50 g of sodium fluoride which had been dried at 110°. The mixture was charged into a three-necked, 1-l. monel flask fitted with a stirrer and gas inlet and outlet. The flask was immersed in an ice bath and stirred while 20–30% fluorine diluted with nitrogen was introduced into the flask at a total gas flow rate of 200 to 400 ml/min for 3 hr. The crude product was collected from the effluent stream in a glass U trap cooled to the range of -130 to $-145°$ with a Freon-12 slush bath. When approximately 0.5 ml of crude product was collected in the U trap, the trap was removed and additional product was collected in a second and third trap, etc.

First-stage purification of the product to a 60–80% purity was achieved by codistillation[5] using a 10-mm copper column packed with fluorine-treated 40–60 mesh magnesium beads. Further purification to a 99+% purity was achieved either by repeated codistillation or by vapor phase chromatography using Dow Corning FS1265 fluorosilicone oil on a Chromosorb packed column. The yield of purified pentafluoroguanidine varied considerably from 10 to 25%.

Infrared Spectra.—The infrared data were obtained wth a Perkin-Elmer Model 137B spectrophotometer. The cell had a 2.5-cm path length and NaCl windows.

Mass Spectrum.—The mass spectrum was obtained on a Consolidated 21-103 spectrometer with inlet at room temperature and an ionizing voltage of 70 v.

Vapor Pressure.—The vapor pressure was measured in a mercury-free system from -80 to $-2°$.

Nmr Spectrum.—The nmr spectrum was obtained on an instrument described by Baker and Burd.[6]

Registry No.—Pentafluoroguanidine, 10051-06-6.

(5) G. H. Cady and D. P. Siegwarth, *Anal. Chem.*, **31**, 618 (1959).
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Chemiluminescent Reactions of Tetracyanoethylene and Trichloroacetyl Chloride with Hydrogen Peroxide. A Suggested Mechanistic Relationship

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While chemiluminescence has been observed from a considerable variety of chemical reactions,[1] only a few such reactions are known to provide moderate light intensities and emission lifetimes consistent with quantum yields above 1×10^{-2} einstein mole^{-1}.[2,3] The mechanism of light production is incompletely understood even in these relatively efficient chemiluminescent systems, but it has been recognized that such reactions require the presence or the formation of a fluorescent compound as well as the essentially

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(3) M. M. Rauhut, B. G. Roberts, and A. M. Semsel, *J. Am. Chem. Soc.*, **88**, 3604 (1966).