precedence that the decreased rate on going from water to a less polar solvent is due to a decrease in entropy, and a case has also been made that this process may be accompanied by a decrease in activation energy.[12]

Experimental Section

The kinetic determinations and all inorganic materials were as described before. The benzene was a research grade sample of the Phillips Petroleum Co. (99.91 mole%), which was redistilled several times during the investigation. All solutions were made up at the temperatures of the kinetic runs. Changes in volume were determined for each temperature and appropriate corrections were applied. Special care was taken to minimize volatility loss of benzene during the preparation of the solutions. The benzene was added to the solution containing the other reagents at room temperature from a specially calibrated pipet. The mixture was then thoroughly shaken and placed in the thermostat for several minutes to affect complete solution of benzene. After a few minutes the flask was cooled to 35°, a bromine–bromide solution was added quickly, and the solution was transferred to eight or ten test tubes. The sealed test tubes were placed in the thermostat and allowed to come to temperature. After 15 min one test tube was withdrawn for the determination of 0 time and cooled in ice, and a 10-ml sample was analyzed for bromine as usual. Reactions were allowed to go to at least 50% completion, and all runs were conducted at least in duplicate. A vpc analysis of a completed run indicated that the product consisted of 99.5% of bromobenzene.[13] Rate constants were determined from second-order plots by the least-square method. The slopes rarely had an error of more than 2.5%. Although the precision within one kinetic run was always good, duplicate runs showed greater scatter than in aqueous acetic acid, possibly because of some unavoidable loss of benzene during the preparation of the solutions.

A value of 0.072 mole $l.^{-1}$ was obtained for the equilibrium constant K at 50° by extrapolation from literature data at lower temperatures, while for 25° the value of 0.0594 from the same source was taken.[14] From the literature data, a value of 1.45 kcal $mole^{-1}$ was obtained for $\Delta H°$, which agrees with the earlier value of 1.5 kcal $mole^{-1}$.[11]

Registry No.—Benzene, 71-43-2.

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Magnetic Anisotropy of the Oximido Group. Additional Proof of Greater Deshielding from Proximity of the Hydroxyl Group

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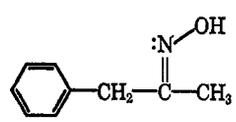
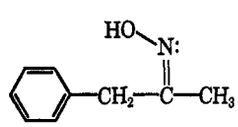
In a recent communication[2] we have reported the observation of a large difference in the geometrical dependence of the deshielding effect of the oximido group on the two sides of the functional group. For example, in 4-*t*-butylcyclohexanone oxime the difference in chemical shifts of the equatorial and axial hydrogen on a given α carbon is 1.68 ppm while on the other α carbon the difference is only 0.43 ppm, when measured in deuteriochloroform. This observation confirms the conformational dependence of chemical shifts of α hydrogens in aliphatic aldoximes proposed by Karabatsos, *et al.*[3] This conformational dependence provides a logical explanation for the known phenomenon[4] that in the nmr spectra of mixtures of isomeric *syn* and *anti* oximes of methyl ketones there is usually a significant difference in the chemical shifts of the α-methylene hydrogens in the two isomers, but little difference, if any, in the chemical shifts of the methyl groups.

Regarding the relative deshielding effects of the hydroxyl group and the unshared pair of electrons on the nitrogen of the oximido group, Karabatsos and co-workers[3] have given evidence that the largest deshielding results from the proximity of the hydroxyl group. Other investigators[4-8] have presented evidence which leads to the same conclusion. Recently, Saitô and co-workers[9-12] have come to the conclusion that the greatest deshielding effect is caused by the unshared pair of electrons on the nitrogen.

We now present additional experimental proof, from the characterization of *anti*- and *syn*-benzyl methyl ketoxime by a Beckmann rearrangement, of a greater deshielding by the proximity of the hydroxyl group of the oximido group than by the proximity of the unshared pair of electrons on the nitrogen.



anti-benzyl methyl ketoxime (I)



syn-benzyl methyl ketoxime (II)

Oxime formation of phenyl-2-propanone by standard methods in pyridine or aqueous sodium hydroxide solution[13] yielded a mixture of I and II in ratio of about 2 to 1 as analyzed by nmr. The spectrum of the mixture in carbon tetrachloride gives a single peak at τ 8.24[14] for the combined signals of the methyl groups of the two isomers, and two signals in ratio of 2:1 at τ 6.55 and 6.30, respectively, attributed to the α-methylene hydrogens of the *anti* and *syn* isomers. The signals of aromatic hydrogens overlap to give a single peak at τ 2.85. In pyridine at 60 Mc the signals of

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(14) Chemical shifts were seen to vary slightly with changes in concentration.

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 CCl_4 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.

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.

(15) Chemical shifts in pyridine follow: CH_3, τ 8.09, and CH_2, τ 6.39, for I; and CH_3, τ 8.16, and CH_2, τ 6.05, for II.

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(18) The chemical shifts have a slight concentration dependence.

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.

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