Yu. V. Zeifman, E. G. Abduganiev, E. M. Rokhlin, and I. L. Knunyants

Hexafluoroacetone oxime (I) is a readily available compound that can be obtained by various methods [1-7]. It is a good solvent for various polymers [8, 9] and for this reason can be used when studying their properties, and also for the preparation of glues. Oxime (I) has well-defined acid properties ($pK_a = 6.0$) [10, 11] and gives stable adducts with weak bases like CH_3CN , $C_2H_5OC_2H_5$, CH_3COCH_3 , etc. [8].

Some of the reactions of (I) were studied: hydrolysis with H_2SO_4 [2], oxidation under the influence of CrO_3 , H_2O_2 in HF [12], or N_2O_5 [4], and chlorination [4, 7]. The oxime (I) formed in the hydrogenation of 2-nitroperfluoropropane is converted to 2-amino-2-hydroperfluoropropane under more drastic conditions [7]. Some of the O-substituted derivatives of oxime (I) were obtained. Reaction with C_2H_5I in the presence of alkali leads to the O-ethyl oxime (II) [13]. The vinylation of divinylmercury gave the O-vinyl oxime (III) [14]. The addition product (IV) is formed from oxime (I) and perfluoroisobutylene in the presence of triethylamine [15]. Finally, the phosphorylation of oxime (I) gives the O-phosphoryl derivatives (V) [13, 16, 17]



The reaction of oxime (I) with diethyl fluorophosphate gives the 1:1 adduct, which was assigned the structure of a complex that is formed via hydrogen bonding [13].

The present paper is devoted to the preparation of some other O-substitute derivatives of oxime (I) and a study of the properties of these compounds.

The acylation of (I) is easily accomplished using benzoyl chloride, p-toluenesulfonyl chloride or phenyl isocyanate in the presence of pyridine. Here the corresponding O-acyl derivatives are formed, and specifically the benzoyl (VI), tosyl (VII) and phenylcarbamoyl (VIII) derivatives

 $(CF_3)_2C = \text{NOH} \xrightarrow{C_6H_6N} (CF_3)_2C = \text{NOCOC}_6H_5 \quad (VI)$ $(I) \xrightarrow{P-CH_3C_6H_4SO_6CI} (CF_3)_2C = \text{NOSO}_2C_6H_4CH_3-p \quad (VII)$ $(CF_3)_2C = \text{NOCNHC}_6H_5 \quad (VIII)$ 0

O, N-Bis(trimethylsilyl) acetamide reacts with oxime (I) under mild conditions in the absence of bases



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The thus obtained O-trimethylsilyl oxime (IX) is also formed from oxime (I) and $(CH_3)_3SiCl$ in pyridine, but in this case the isolation of the pure product (IX) is associated with difficulties. The O-triphenylsilyl derivative (X) was obtained from the lithium salt of hexafluoroacetone oxime (XI), which is formed by the reaction of butyllithium with (I). The reaction of salt (XI) with diethyl sulfate leads to the formation of the O-ethyl oxime (II)



It is known that the oximes of α -halo-ketones when reacted with bases are converted to nitrosoolefins [18]. It might be expected that salt (XI) when heated will decompose to form 2-nitrosoperfluoropropylene. However, only tar formation was observed on heating salt (XI) in nitrobenzene. We were also unable to observe the formation of the nitrosoolefin from other derivatives of oxime (I) when they were heated, either alone or in the presence of CsF or BF₃ etherate. It should be mentioned that the O-acyl oximes (VI) and (VII), in contrast to the corresponding derivatives of the unfluorinated oximes [19], are very stable and do not undergo the Beckmann rearrangement.

At the same time, the electrophilic reactivity of benzoyl oxime (VI) and tosyl oxime (VII) is easily detected. The acyl-oxygen bond is cleaved when the benzoyl derivative is reacted with NH_3 ; oxime (I) and benzamide are formed

 $\begin{array}{ccc} (CF_3)_2 C = NO - CC_6H_5 \xrightarrow{NH_3} (CF_3)_2 C = NOH + C_6H_5CONH_2 \\ \parallel \\ (VI) & O & (I) \end{array}$

In the case of the tosyl derivative (VII) the attack by the nucleophilic agent is directed to the carbon atom of the azomethine group, and bis(trifluoromethyl)diazirdine (XIIa) is obtained as a result, evidently via cyclization of the intermediately formed geminal derivative (XIII). The O-tosyl oximes of trifluoroacetone (XIV) and trifluoroacetophenone (XV)* react in a similar manner



A similar reaction for the preparation of pentamethylenediaziridines from cyclohexanone oxime O-sulfate and either ammonia or methylamine was described previously [20].

EXPERIMENTAL METHOD

The ¹⁹F NMR spectra (ppm from CF₃COOH) were taken on a Hitachi spectrometer (56.4 MHz) using CF₃COOH as the external standard, while the NMR spectra (δ , ppm) were taken on a Perkin-Elmer R-12 spectrometer using TMS as the external standard. The IR spectra were taken on a UR-20 instrument as KBr pellets.

Hexafluoroacetone O-Benzoyloxime (VI). With cooling, 3.5 g of hexafluoroacetone oxime (I) was added to 25 ml of absolute pyridine, followed by the addition of 2.6 g of benzoyl chloride. After 2 days the mixture was poured into cooled HCl solution (1:5), and the oil obtained was extracted with ether and then dried over MgSO₄. Distillation gave 4.45 g (81%) of compound (VI), bp 220-222°, 59-60° (5 mm), up 34-35° (from heptane). Found: C 42.2; H 1.7; F 39.7%. C₁₀H₅F₆NO₂. Calculated: C 41.9; H 1.7; F 40.0%. Infrared spectrum (ν , cm⁻¹): 1665 (C=N), 1810 (OC=O). ¹⁹F NMR spectrum (in CCl₄): -11.5 (CF₃, quadruplet), -14.0 (CF₃, quadruplet), J_{F-F} 6.5 Hz. Benzoyloxime (VI) remains unchanged when refluxed for many hours in a dry N₂ stream.

*Compounds (XIV) and (XV) were obtained by the acylation of the corresponding oximes.

Hexafluoroacetone O-(p-Toluenesulfonyl)oxime (VII). To a stirred solution of 18 g of p-toluenesulfonyl chloride in 50 ml of absolute pyridine was added in drops, with cooling, 17.8 g of oxime (I). The mixture was stirred for 30 min, allowed to stand for 5 days, and then poured into 900 ml of strongly cooled HCl solution (1:5). The precipitate was washed with water and then dried in vacuo over P_2O_5 . We obtained 24 g (75%) of sulfonyloxime (VII), mp 88-90° (from heptane). Found: C 36.1; H 2.2; N 4.5%. $C_{10}H_7$ $^{\circ}F_6NO_3S$. Calculated: C 35.7; H 2.3; N 4.2%. Infrared spectrum (ν , cm⁻¹): 1650 (C=N). ¹⁹F NMR spectrum (in CH₃CN): -10.8 (CF₃, quadruplet), -13.7 (CF₃, quadruplet), J_{F-F} 6.8 Hz.

Tosylate (VII) remains unchanged when refluxed with BF_3 etherate. p-Toluenesulfonyl fluoride is formed when tosylate (VII) is heated with CsF in absolute dimethylformamide.

1,1,1-Trifluoroacetone O-(p-Toluenesulfonyl)oxime (XIV). Similar to compound (VII), (XIV) was obtained from 1,1,1-trifluoroacetone oxime [21] in 65% yield, mp 68-69° (from CCl₄). Found: C 42.3; H 3.5; F 20.1%. C₁₀H₁₀F₃NO₃S. Calculated: C 42.6; H 3.6; F 20.3%. Infrared spectrum (ν , cm⁻¹): 1670 (C=N). ¹⁹F NMR spectrum (in CCl₄): -7.7 (CF₃, singlet).

 $\underline{\omega}, \underline{\omega}, \underline{\omega}$ -Trifluoroacetophenone O-(p-Toluenesulfonyl)oxime (XV). In a similar manner, (XV) was obtained from $\underline{\omega}, \underline{\omega}, \underline{\omega}$ -trifluoroacetophenone oxime [22] in 80% yield, mp 103-104° (from heptane). Found: C 52.6; H 3.4; F 16.8%. C₁₅H₁₂F₃NO₃S. Calculated: C 52.5; H 3.5; F 16.6%. Infrared spectrum (ν , cm⁻¹): 1650 (C=N). ¹⁹F NMR spectrum (in CH₃CN): -10.5 (CF₃, singlet). Toxyloxime (XV) remains unchanged when refluxed with excess BF₃ etherate.

Hexafluoroacetone O-Phenylcarbamoyloxime (VIII). A mixture of 1.8 g of oxime (I), 1.03 g of phenyl isocyanate and 2 drops of pyridine was kept for 2 weeks at ~ 20°C, after which it was dissolved in absolute benzene and refluxed for 5 h. The solution was cooled and treated with heptane. The precipitate contained 1.6 g (57%) of (VIII), mp 88-90° (from CCl₄). Found: C 40.0; H 2.0; F 37.9%. $C_{10}H_6F_6N_2O_2$. Calculated: C 40.0; H 2.0; F 38.1%. Infrared spectrum (ν , cm⁻¹): 1650 (C=N), 1765 (OC=O), 3270 (NH). ¹⁹F NMR spectrum (in C_6H_5CN): -11.7 (CF₃, quadruplet), -16.8 (CF₃, quadruplet), J_{F-F} 5.8 Hz. When refluxed in benzonitrile, (VIII) decomposes with the formation of diphenylurea.

<u>Hexafluoroacetone-O-(Trimethylsilyl)oxime (IX)</u>. To 11.2 g of O,N-bis(trimethylsilyl)acetamide [23], with stirring and cooling (~ 0°), was added 8.0 g of oxime (I) in drops. The obtained mixture was heated in vacuo (100 mm), and the distillate was repeatedly distilled. We obtained 6.42 g (71.5%) of trimethylsilyl-oxime (IX), bp 88-89°. Found: C 29.2; H 3.4; F 44.4; Si 12.0%; mol. wt. 253 (mass-spectrometrically). $C_{6}H_{9}F_{6}NOSi$. Calculated: C 28.4; H 3.5; F 45.1; Si 11.7%. Infrared spectrum (ν , cm⁻¹): 1630 (C=N). ¹⁹F NMR spectrum: -10.0 (CF₃, quadruplet), -12.3 (CF₃, quadruplet), J_{F-F} 6.9 Hz. NMR spectrum: 0.29 ppm upfield from (CH₃)₄Si (singlet).

Lithium Salt of Hexafluoroacetone Oxime (XI). In a dry argon atmosphere, to 9.8 g of oxime (I) in 10 ml of absolute benzene was carefully added in drops, with cooling, a solution of an equivalent amount of butyllithium in 45 ml of absolute benzene. The benzene was vacuum-distilled. The residue represented 10 g of salt (XI) as a white powder. ¹⁹FNMR spectrum (in CH_3CN): -14.7 (CF_3 , quadruplet), -13.8 (CF_3 , quadruplet), J_{F-F} 4.8 Hz.

Hexafluoroacetone O-(Triphenylsilyl)oxime (X). To a solution of 4.2 g of oxime (I) in 4 ml of absolute benzene, with cooling and stirring, in an argon stream, was carefully added a solution of an equivalent amount of butyllithium in 22 ml of absolute benzene. To the obtained solution was gradually added a solution of 6.2 g of $(C_{6}H_{5})_{3}$ SiCl in 15 ml of absolute benzene, the mixture was refluxed for 1.5 h, the precipitate was filtered, the filtrate was evaporated, hexane was added to the residue, the obtained precipitate was separated, and the solvent was distilled from the hexane solution. Vacuum-distillation gave 3.9 g (42%) of triphenylsilyloxime (X), bp 108-110° (0.001 mm). Found: C 58.5; H 3.7; F 24.3; N 3.4; Si 6.0%; mol. wt. 439 (mass-spectrometrically). $C_{21}H_{15}F_{6}NOSi$. Calculated: C 57.5; H 3.4; F 25.9; N 3.1; Si 6.3%. ¹⁹F NMR spectrum (in CCl₄): -12.4 (CF₃, quadruplet), -14.4 (CF₃, quadruplet), J_{F-F} 7.4 Hz. NMR spectrum (in CCl₄): $\delta_{C_{6}H_{5}}$ 6.9-7.3 (multiplet).

<u>Hexafluoroacetone O-Ethyloxime (II)</u>. A mixture of 2.9 g of salt (XI) and 2.4 g of diethyl sulfate was slowly heated up to 80°, cooled, and 1.5 ml of condensate was distilled off at ~ 20° (150 mm) (into a trap, -78°). Redistillation gave 1.5 g (48%) of ethyloxime (II), bp 63-65° [13]. ¹⁹F NMR spectrum: -10.0 (CF₃, quadruplet), -11.5 (CF₃, quadruplet), J_{F-F} 5.6 Hz. NMR spectrum: δ_{CH_3} 0.8 (triplet), δ_{CH_2} 3.7 (quadruplet), J_{H-H} 7.0 Hz.

<u>Reaction of Hexafluoroacetone O-Benzoyloxime (VI) with Ammonia</u>. Benzoyloxime (VI) (4.13 g) was dissolved in excess liquid ammonia. The ammonia was evaporated, and 2.3 g (80%) of oxime (I) was distilled from the residue by heating to 100° (5 mm). The residue was recrystallized from benzene to give 1.55 g (89%) of benzamide.

3.3, Bis(trifluoromethyl)diaziridine (XIIa). Hexafluoroacetone O-(p-toluenesulfonyl)oxime (VII) (3.3 g) was distilled with stirring in liquid ammonia, after which the ammonia was slowly evaporated, and the residue was vacuum-sublimed (3-4 mm) into a trap (-78°). We obtained 1.62 g (91%) of diaziridine (XIIa), mp 78-80° (in a sealed capillary). The mixed melting point of (XIIa) and an authentic sample [24] is not depressed.

 $\frac{3-\text{Methyl}-3-\text{trifluoromethyldiaziridine (XIIb).}}{\text{toluenesulfonyloxime (XIV) in 85\% yield, mp 58-60°} (in a sealed capillary). Found: C 28.6; H 4.0; F 44.5\%. C_{3}H_{5}F_{3}N_{2}.$ Calculated: C 28.6; H 4.0; F 45.2\%. ¹⁹F NMR spectrum (in benzene): +1.1 (CF₃, singlet).

<u>3-Phenyl-3-trifluoromethyldiazirdine (XIIc).</u> A mixture of 7.0 g of ω, ω, ω -trifluoroacetophenone O-(p-toluenesulfonyl)oxime (XV), 20 ml of absolute ether and 3 ml (at – 78°) of liquid ammonia was kept in a sealed ampule for 12 h at ~ 20°, after which it was heated on the steam bath, the ammonia was distilled off, the precipitate was filtered, and the filtrate was evaporated in vacuo. From the residue by vacuum-sublimation (2-3 mm) was obtained 3.1 g (81%) of diaziridine (XIIc), mp 33–35°. Found: C 50.6; H 3.7; F 29.8%. $C_8H_7F_3N_2$. Calculated: C 51.1; H 3.7; F 30.3%. ¹⁹F NMR spectrum (in CCl₄): – 3.4 (CF₃, singlet). NMR spectrum (in CCl₄): $\delta_{C_6H_5} \sim$ 7.3 (multiplet), δ_{NH} 2.15 and 2.70 (AB system of nonequivalent H atoms, J 8.26 Hz); when heated in nitrobenzene, the signals from the NH protons gradually widen and merge into a broad singlet at 140–150°, but the original spectrum is restored on cooling.

A solution of 2.3 g of diaziridine (XIIc) in 5 ml of conc. H_2SO_4 was allowed to stand for 3 days (~ 20°), after which it was poured over ice, and extraction with ether gave 1.4 g (67%) of ω, ω, ω -trifluoroaceto-phenone, bp 50-51° (16 mm). Based on the GLC data, the compound is identical with an authentic specimen.

CONCLUSIONS

1. The O-acyl and O-silyl derivatives of hexafluoroacetone oxime were obtained.

2. The O-arylsulfonyl oximes of fluoro ketones readily give the corresponding substituted diaziridines when reacted with ammonia.

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