PERFLUORO-tert-BUTYL ISOCYANATE

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The reactions of perfluoroalkyl isocyanates, containing fluorine atoms in series with the isocyano group, are complicated by the presence of the unstable $-CF_2$ -NH grouping in the addition products [1]. In the case of α -hydroperfluoroisopropyl isocyanate this group is absent, but the presence of a tertiary hydrogen atom in series with the trifluoromethyl groups makes dehydrofluorination reactions possible (see [2]).

The present paper is devoted to a study of the previously unknown perfluoro-tert-butyl isocyanate (I), which is devoid of both fluorine and hydrogen atoms in the α -position to the isocyano group. Isocyanate (I) easily reacts with water, alcohol, and amines to respectively give perfluoro-tert-butylamine (II),* urethan (III), and substituted ureas (IVa, b)



The perfluoro-tert-butyl and perfluoropropyl isocyanates react with triethylamine similarly to the sulfonyl isocyanates [5], and give betaines (Va, b)

$$\mathbf{R}_{f}\mathbf{N}=\mathbf{C}=\mathbf{O}+(\mathbf{C}_{2}\mathbf{H}_{5})_{\mathbf{3}}\mathbf{N}\rightarrow \qquad \begin{array}{c} \mathbf{R}_{p}\mathbf{N}=\mathbf{O}\\ \mathbf{\Theta}\\ \mathbf{N}(\mathbf{C}_{2}\mathbf{H}_{5})_{\mathbf{3}} \end{array} \qquad \begin{array}{c} \mathbf{A} \ \mathbf{R}_{f}=\mathbf{C}_{\mathbf{3}}\mathbf{F}_{7}\\ \mathbf{B} \ \mathbf{R}_{f}=(\mathbf{C}\mathbf{F}_{8})_{\mathbf{3}}\mathbf{C} \end{array}$$

The cycloaddition reactions of isocyanates to activated multiple bonds lead either to cyclodimers or their decomposition products. Reactions with ketene and α -oximes belong to cyclodimerization reactions of the first type. Isocyanate (I) reacts with ketene in the same manner as does perfluoropropyl isocyanate [1], with the formation of perfluoro-tert-butyl-2,4-azetidinedione (VI), which with aniline gives malonic acid derivatives (VII)



The reaction of fluorinated isocyanates with α -oximes was previously unknown. It proved that the perfluoropropyl and perfluoro-tert-butyl isocyanates, similarly to unfluorinated isocyanates [6, 7], react with α -oximes in the presence of tetraethylammonium bromide at 180° to give 2-oxazolidones (VIIIa, b)

 $\begin{array}{cccc} \mathbf{R}_{f}\mathbf{N}{=}\mathbf{C}{=}\mathbf{O}+\mathbf{C}\mathbf{H}_{2}{-}\mathbf{C}\mathbf{H}_{2}\rightarrow\mathbf{R}_{f}\mathbf{N}{-}\mathbf{C}{=}\mathbf{O} & a \ \mathbf{R}_{f}{=}(\mathbf{C}\mathbf{F}_{3})_{3}\mathbf{C} \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & & \\ & & & &$

*Due to its low basicity, perfluoro-tert-butylamine does not give the urea with isocyanate (I), which is inherent to isocyanates in general, including α -hydroperfluoroisopropyl isocyanate [3] and hexafluoro-tert-butyl isocyanate [4].

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No.7, pp.1481-1486, July, 1971. Original article submitted August 20, 1969.

© 1972 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. All rights reserved. This article cannot be reproduced for any purpose whatsoever without permission of the publisher. A copy of this article is available from the publisher for \$15.00. Reactions with dimethylformamide or triphenylphosphine phenylimine belong to the second type of cycloaddition reactions. Perfluoro-tert-butyl isocyanate reacts with dimethylformamide to give N-per-fluoro-tert-butyl-N',N'-dimethylformamidine (IX) as the end product; the reaction goes with greater difficulty than in the case of α -hydroperfluoroisopropyl isocyanate [3]

$$(CF_3)_{3}CN = C = O + H - C \begin{pmatrix} O \\ & | \\ N(CH_3)_2 \end{pmatrix} \rightarrow \begin{bmatrix} (CF_3)_{3}CN - C = O \\ & | \\ (CH_3)_2NC - O \\ & | \\ H \end{bmatrix} \xrightarrow{-CO_2} (CF_3)_{3}CN = C \begin{pmatrix} H \\ N(CH_3)_2 \end{pmatrix}$$

Isocyanate (I) reacts with triphenylphosphine phenylimine under mild conditions to give N-perfluoro-tert-butyl-N'-phenylcarbodiimide (X)

$$\begin{array}{c} CF_3CN = C = O \\ + \\ (C_6H_5)_3P = NC_6H_5 \end{array} \rightarrow \begin{bmatrix} (CF_3)_3CN = C - O \\ | \\ C_6H_5N - P(C_6H_5)_3 \end{bmatrix} \rightarrow (CF_3)_5CN = C = NC_6H_5 + (C_6H_5)_3PO \\ (X) \end{array}$$

Fluorine-containing isocyanates react both with enamines and with isonitriles, but we were unable to isolate the pure reaction products. Unstable hygroscopic addition products are formed in the case of the enamines, while tars are formed in the case of the isonitriles. But stable iminopyrrolidones (XIIa, b, c) were obtained when the isocyanates were reacted simultaneously with the enamine and cyclohexyl isonitrile. Apparently, the intermediately formed unstable betaine (XI), being a 1,4-bipolar compound (see [8]) enters into the reaction of α -addition to the isonitrile

In this connection the perfluoropropyl and α -hydroperfluoroisopropyl isocyanates react much more rapidly than does perfluoro-tert-butyl isocyanate. The unfluorinated isocyanates also react in the same manner with enamines and isonitriles [9].

As a result, perfluoro-tert-butyl isocyanate manifests a lower activity in certain reactions. Distinct proof of its lower reactivity is the competing reaction of equimolar amounts of perfluoropropyl isocyanate and perfluoro-tert-butyl isocyanate with 1 mole of alcohol. Here N-perfluoropropylethylurethan is formed exclusively. Since the electronegativity of the perfluoro-tert-butyl group (Taft constant $\sigma * = 2.8$ [10]) is not smaller than the electronegativity of the perfluoropropyl group, then the lower activity of perfluoro-tert-butyl isocyanate is evidently due to steric factors. The presence of the bulky perfluoro-tert-butyl group not only lowers the activity of the isocyanate, but it also imparts a certain uniqueness to the reaction products obtained from it (see [11]). For example, the properties of N-perfluoro-tert-butyl-N'-phenyl-carbodiimide proved to be unusual. A substituted urea could be obtained from it only under the influence of conc. H₂SO₄. When an aqueous dioxane solution of carbodiimide (X) is heated the urea is not formed, as is inherent to carbodiimides, but instead the guanidine (XIII). Apparently, the urea (IVa) is cleaved to ani-line, which then reacts with the next molecule of the carbodiimide

$$(CF_{3})_{3}CN = C = NC_{6}H_{5} \xrightarrow{H_{2}O} \left[(CF_{3})_{3}CNH_{1} \xrightarrow{I} C \longrightarrow NHC_{6}H_{5} \right] \xrightarrow{} \left[(CF_{3})_{3}CNH_{2} + C_{6}H_{5}NHC \xrightarrow{I} O \\ (X) \xrightarrow{I} O \xrightarrow{I} O \xrightarrow{I} C_{3}H_{5}NH_{2} + (X) \xrightarrow{} (CF_{3})_{3}CN = C \xrightarrow{I} O \xrightarrow{I}$$

Actually, aniline is formed when an aqueous dioxane solution of urea (IVa) is heated, while carbodiimide (X) easily reacts with aniline to give the same guanidine (XIII). Carbodiimide (X) reacts in a similar manner with alcohol, forming O-ethyl-N-phenyl-N'-perfluoro-tert-butylisourea (XIV)

$$(CF_{3})_{2}CN = C = NC_{6}H_{5} - | \underbrace{\begin{array}{c} C_{6}H_{6}NH_{2} \\ C_{2}H_{6}OH \end{array}}_{C_{2}H_{6}OH} (CF_{3})_{3}CN = C \underbrace{\begin{array}{c} NHC_{6}H_{5} \\ OC_{2}H_{5} \end{array}}_{OC_{2}H_{5}} (XIV)$$

The addition of alcohol and aniline to carbodiimide (X) probably takes place at the C = N group that is attached to the less electronegative radical, the same as in the case of unsymmetrical carbodiimides containing a sulforyl group [12].

EXPERIMENTAL

<u>Perfluoro-tert-butyl Isocyanate (1)</u>. To a solution of 10 g of activated NaN₃ in 20 ml of water and 40 ml of m-xylene was added in drops, with ice cooling and stirring, 28 g of perfluoropivaloyl fluoride [13]. The cooled mixture was stirred for 1 h, and then it was stirred at room temperature for 4 h. The xylene layer was separated, washed with water, and dried first over MgSO₄ and then over Na. The dried azide solution was slowly heated up to 90°C, and on conclusion of N₂ evolution the obtained isocyanate was dis-tilled. It was purified by distillation through a column. We obtained 13 g (48%) of (I) with bp 45°; n_D^{19} 1.2895. Found: C 23.13; F 65.10; N 5.36%. C₅F₉NO. Calculated: C 22.98; F 65.51; N 5.36%. Infrared spectrum (ν , cm⁻¹): 2285 vs (N = C = O).

<u>Perfluoro-tert-butylamine (II)</u>. To a mixture of 10 ml of diglyme and 0.5 ml of water was added 5 g of (I) in drops. The reaction mixture was stood at room temperature for 4 h and the reaction product was distilled off. We obtained 2.4 g (54%) of (II) with bp 56-57°; $n_D^{21.5}$ 1.2815. From [10]: bp 56.5-57°; n_D^{20} 1.2795. The passage of dry HCl into an ether solution of (II) gave a precipitate of the hydrochloride with mp 71-75°. From [10]: mp 76-77°.

<u>N-Perfluoro-tert-butyl-O-ethylurethan (III)</u>. Excess absolute alcohol was added in drops, with cooling, to a solution of 0.5 g of (I) in 5 ml of absolute ether. We obtained 0.5 g (85%) of (III) with mp 36-41° (sub-limation). Found: C 27.17; H 1.99; F 55.24%. $C_7H_6F_9NO_2$. Calculated: C 27.36; H 1.95; F 55.70%.

From a mixture of equimolar amounts of isocyanate (I) and perfluoropropyl isocyanate with 1 mole of alcohol was exclusively formed N-perfluoropropylurethan, which was identified by GLC; urethan (III) was not detected in the reaction products.

<u>N-Perfluoro-tert-butyl-N'-phenylurea (IVa)</u>. To a solution of 1 g of (I) in 5 ml of absolute ether was added in drops, with cooling, a solution of 0.35 g of aniline in 5 ml of absolute ether. We obtained 1.2 g (88%) of (IVa) with mp 212-213° (decompn.) (from 50% alcohol). Found: C 37.27; H 1.90; F 48.33; N 7.65%. $C_{11}H_7F_9N_2O$. Calculated: C 37.28; H 1.97; F 48.30; N 7.90%.

A mixture of 0.3 g of carbodiimide (X) and 1 ml of conc. H_2SO_4 was allowed to stand at room temperature for 1 h. The addition of water gave a precipitate from which was obtained 0.2 g of crystals, with mp 209-211°, identical with the compound obtained in the preceding experiment.

<u>N-Perfluoro-tert-butyl-N',N'-dimethylurea (IVb)</u>. With cooling in ice and stirring, excess $(CH_3)_2NH$ was passed into a solution of 1 g of (I) in 15 ml of absolute ether. After 10 h (0°) the precipitate was recrystallized from a mixture of benzene and hexane to give 0.95 g (81%) of (IVb) with mp 88-89°. Found: F 56.27; N 8.92%. $C_7H_7F_9N_2O$. Calculated: F 55.68; N 9.15%.

Reaction of Perfluoropropyl Isocyanate with Triethylamine. To 8.4 g of perfluoropropyl isocyanate at 0°, with stirring, was added in drops 4.1 g of $(C_2H_5)_3N$. The mixture was allowed to stand at room temperature for 1 h and then it was distilled. We obtained 8 g (72%) of (Va) (as hygroscopic crystals) with bp 59° (250 mm) and mp ~30°. Found: C 38.99; H 5.19; N 9.11%. $C_{10}H_{15}F_7N_2O$. Calculated: C 38.46; H 4.80; N 8.97%. Infrared spectrum (ν , cm⁻¹): 1765 (vs).

Reaction of Perfluoro-tert-butyl Isocyanate with Triethylamine. To 1 g of isocyanate (I) in 3 ml of absolute ether was added in drops, at 0° and with stirring, 0.26 g of $(C_2H_5)_3N$ in 2 ml of ether. The precipitate was filtered. We obtained 0.56 g (45%) of (Vb) as quite volatile hygroscopic crystals with mp 39-41° (decompn.).

<u>1-Perfluoro-tert-butyl-2,4-azetidinedione (VI)</u>. A mixture of 3 g of (I) and 1.5 ml of ketene was allowed to stand in a sealed ampul under ice cooling for 3-4 h, and then overnight at room temperature. After distilling off the unreacted isocyanate (1.54 g) we obtained 0.8 g (46%) of (VI) with mp 104-106° (from petro-leum ether, sublimation). Found: C 27.80; H 0.77; F 56.51; N 5.16%. $C_7H_2F_9NO_2$. Calculated: C 27.72; H 0.66; F 56.43; N 4.62%. Infrared spectrum (ν , cm⁻¹): ~1790 vs (C = O).

Reaction of 1-Perfluoro-tert-butyl-2,4-azetidinedione (VI) with Aniline. A solution of 0.6 g of (VI) and 0.55 g of aniline in 10 ml of anhydrous benzene was refluxed for 2 h. After distilling off the benzene,

the residue was washed with water. We obtained 0.7 g (89%) of the N-perfluoro-tert-butyl-N'-phenyldiamide of malonic acid (VII) with mp 115-117° (from petroleum ether). Found: C 39.30; H 2.31; F 43.00; N 7.35%. $C_{13}H_9F_9N_2O_2$. Calculated: C 39.39; H 2.27; F 43.18; N 7.07%. Infrared spectrum (ν , cm⁻¹): ~1690 s and 1720 vs (C=O).

A solution of 0.5 g of (VI) and 0.46 g of aniline in 5 ml of absolute o-xylene was refluxed for 6 h. From the precipitate was isolated 0.3 g of the dianilide of malonic acid with mp 223-225°. The mixed melting point with an authentic sample was not depressed. The dianilide of malonic acid was also obtained by re-fluxing a xylene solution of (VII) and aniline.

<u>3-Perfluoro-tert-butyl-2-oxazolidone (VIIIa)</u>. A mixture of 5.2 g of (I), 2 ml of ethylene oxide and 0.1 g of $(C_2H_5)_4$ NBr was heated in a metal ampul at 180° for 6 h. From the fraction, boiling at 65-70° (8 mm), by recrystallization was isolated 2.8 g (46%) of (VIIIa) with mp 44-46° (from petroleum ether, sub-limation). Found: C 27.62; H 1.41; F 56.25; N 4.34%. $C_7H_4F_9NO_2$. Calculated: C 27.54; H 1.21; F 56.04; N 4.59%. Infrared spectrum (ν , cm⁻¹): 1780 vs (C=O).

Under analogous conditions, from 6.3 g of perfluoropropyl isocyanate, 2 ml of ethylene oxide and 0.2 g of $(C_2H_5)_4NBr$ was obtained 1.5 g (20%) of 3-perfluoropropyl-2-oxazolidone (VIIIb) with mp 28-30° (from a mixture of ether and petroleum ether, sublimation). Found: C 28.40; H 1.68; F 51.94; N 5.30%. $C_6H_4F_7NO_2$. Calculated: C 28.23; H 1.56; F 52.15; N 5.49%. Infrared spectrum (ν , cm⁻¹): 1790 vs (C=O).

<u>N-Perfluoro-tert-butyl-N',N'-dimethylformamidine (IX)</u>. A mixture of 3 g of (I) and 0.85 g of absolute $HCON(CH_3)_2$ was heated under reflux on the steam bath for 20 h until the CO_2 evolution ceased. The mixture was dissolved in 5 ml of ether, washed with water, and dried over $MgSO_4$. The ether was distilled off, and the residue was vacuum-distilled. We obtained 1.5 g (46%) of (IX) with bp 78° (56 mm); n_D^{19} 1.3572. Found: C 28.44; H 2.44; F 58.20; N 9.88%. $C_7H_7F_9N_2$. Calculated: C 28.96; H 2.41; F 58.96; N 9.65%.

<u>N-Perfluoro-tert-butyl-N'-phenylcarbodiimide (X)</u>. To 6.8 g of triphenylphosphine phenylimine in 20 ml of absolute ether, with cooling to -78° , was added 5 g of (I). The mixture was allowed to stand in a sealed ampul at room temperature overnight. The obtained precipitate of triphenylphosphine oxide was filtered, the ether was distilled from the filtrate, and the residue was vacuum-distilled. We obtained 4.9 g (76%) of (X) with bp 76.5° (13 mm); n_D^{22} 1.4225. Found: C 38.89; H 1.40; F 50.30; N 8.62%. $C_{11}H_5F_9N_2$. Calculated: C 39.28; H 1.48; F 50.89; N 8.33%. Infrared spectrum (ν , cm⁻¹): 2170 vs (N = C = N).

<u>Hydrolysis of Carbodiimide (X)</u>. A mixture of 1 g of (X), 5 ml of dioxane, and 1 ml of water was refluxed for 3 h until the CO₂ evolution ceased. To the reaction mixture was added 50 ml of water and the obtained precipitate was filtered. We obtained 0.6 g of N-perfluoro-tert-butyl-N',N"-diphenylguanidine (XIII) with mp 107-109° (from 50% alcohol). Found: C 47.81; H 2.96; F 40.63; N 9.80%. $C_{17}H_{12}F_{9}N_{3}$. Calculated: C 47.55; H 2.79; F 39.86; N 9.79%. Infrared spectrum (ν , cm⁻¹): 1650 s (C = N). 3470 s; 3480 s (NH).

<u>N-Perfluoro-tert-butyl-N',N"-diphenyl guanidine (XIII)</u>. A mixture of 0.28 g of (X) and 0.16 g of aniline was allowed to stand at room temperature for 3 days. We obtained 0.34 g (94%) of crystals with mp 106-107°, which were identical with the crystals obtained in the hydrolysis of (X).

<u>O-Ethyl-N-phenyl-N'-perfluoro-tert-butylisourea</u> (XIV). A mixture of 0.8 g of (X) and 2 ml of absolute ethanol was refluxed for 2 h. After distilling off the alcohol we obtained 0.87 g (87%) of (XIV) with bp 95-96° (8 mm). Found: C 40.13; H 2.61; F 44.24%. $C_{13}H_{11}F_{9}N_{2}O$. Calculated: C 40.84; H 2.88; F 43.72%.

<u>1-Perfluoro-tert-butyl-3,3-dimethyl-4-morpholino-5-cyclohexylimino-2-pyrrolidone (XIIc)</u>. To a solution of 0.7 g of isobutenylmorpholine and 0.55 g of cyclohexyl isonitrile in 5 ml of absolute petroleum ether at room temperature was added 1.3 g of isocyanate (I). The reaction mixture was allowed to stand at 5-10° for 30 days. The mixture was cooled to -78° and the obtained precipitate was filtered. We obtained 0.8 g (20%) of (XIIc) with mp 94-95.5° (from petroleum ether, sublimation). Found: C 47.05; H 4.88%. C₂₀ \cdot H₂₆F₉N₃O₂. Calculated: C 46.96; H 5.08%. Infrared spectrum (ν , cm⁻¹): 1690 vs (C=N); 1770 s (C=O).

 $\frac{1-\text{Perfluoropropyl-3,3-dimethyl-4-morpholino-5-cyclohexylimino-2-pyrrolidone (XIIa). In a similar manner, from 1.4 g of isobutenylmorpholine, 1.1 g of cyclohexyl isonitrile, and 2.1 g of perfluoropropyl isocyanate in 4 ml of absolute petroleum ether, after 16 h (20°), was obtained 1.7 g (37%) of (XIIa) with mp 82-84° (from alcohol, sublimation). Found: C 49.30; H 5.67; F 29.10; N 9.15%. C₁₉H₂₆F₇N₃O₂. Calculated: C 49.54; H 5.64; F 28.85; N 9.11%.$

 $\frac{1-(\alpha-\text{Hydroperfluoroisopropyl})-3,3-\text{dimethyl}-4-\text{morpholino}-5-\text{cyclohexylimino}-2-\text{pyrrolidone} (XIIb).}{\text{Pyrrolidone} (XIIb) was obtained under the same conditions as (XIIa), from α-hydroperfluoroisopropyl iso-cyanate in 53% yield; mp 134-135° (from hexane). Found: C 51.52; H 6.17; F 25.77; N 9.12%. C₁₉H₂₇F₆N₃O₂. Calculated: C 51.47; H 6.09; F 25.73; N 9.48%. Infrared spectrum (ν, cm⁻¹): 1690 vs (C = N); 1760 s (C = O).$

CONCLUSIONS

Perfluoro-tert-butyl isocyanate was synthesized and studied, and it was shown that it is less active in some reactions than are the perfluoropropyl and α -hydroperfluoroisopropyl isocyanates.

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