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Synthesis of Fluorinated Diisocyanates

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Fluorinated diisocyanates of the general structure $OCN(CH_2)_2(CF_2)_n(CH_2)_2NCO$ were prepared from α,ω-diiodoperfluoroalkanes by insertion of ethylene into the CF_2–I bond, displacement of the iodo groups with azide, reduction of the resulting azide groups to amines, and phosgenation of the diamine.

Perfluorinated diisocyanates, $OCN(CF_2)_nNCO$, have been prepared by the Curtius rearrangement of perfluorinated diacyl azides[1] or by a modified Lossen rearrangement involving pyrolysis of the silyl esters of perfluorohydroxamic acids.[2] These diisocyanates, however, are extremely sensitive to moisture and form polyurethanes that are hydrolytically and thermally unstable.

Fluorinated diisocyanates in which the isocyanate functionality is separated from the fluorinated segment by one intervening methylene group, $OCNCH_2(CF_2)_nCH_2NCO$, were prepared by either phosgenation of $\alpha,\alpha,\omega,\omega$-tetrahydroperfluoroalkylene diamines[1] or by the Curtius rearrangement of $\alpha,\alpha,\omega,\omega$-tetrahydroperfluorodiacyl azides.[3] Hollander and co-workers observed that $\alpha,\alpha,\omega,\omega$-tetrahydroperfluoroalkylene diisocyanates, in particular hexafluoropentamethylene diisocyanate, existed as dimers, and attempts to prepare high molecular weight polymers from this diisocyanate were unsuccessful; low melting solids or oils were obtained.[1]

The present work is concerned with the preparation of fluorinated diisocyanates with two intervening methylene groups, $OCNCH_2CH_2(CF_2)_nCH_2CH_2NCO$. These diisocyanates are expected to be comparable in reactivity with aliphatic isocyanates and should be useful for preparation of fluorinated condensation polymers, such as poly(urethanes) and poly(ureas).[4]

α,ω-Diiodoperfluoroalkanes (**1a–c**) are available from the telomerization of tetrafluoroethylene with iodine[5] and have been converted to ethylene adducts **2a–c** in high yields.[6] Displacement of the iodo groups with azide, reduction of azide groups to amines, and phosgenation of the diamine gave $OCNCH_2CH_2(CF_2)_nCH_2CH_2NCO$ (Scheme I).

Scheme I[a]

$$\underset{\mathbf{1a-c}}{I(CF_2)_nI} + CH_2{=}CH_2 \xrightarrow{180\ °C}$$

$$\underset{\mathbf{2a-c}}{ICH_2CH_2(CF_2)_nCH_2CH_2I} \xrightarrow[\text{DMSO/25 °C}]{NaN_3}$$

$$\underset{\mathbf{3a-c}}{N_3CH_2CH_2(CF_2)_nCH_2CH_2N_3} \xrightarrow[\substack{Pd(OH)_2\\ CH_3OH/\Delta}]{NH_2NH_2}$$

$$\underset{\mathbf{4a-c}}{H_2NCH_2CH_2(CF_2)_nCH_2CH_2NH_2} \xrightarrow[\text{2. }COCl_2]{\text{1. HCl}}$$

$$\underset{\mathbf{6a-c}}{OCNCH_2CH_2(CF_2)_nCH_2CH_2NCO}$$

[a] Key: a, $n = 4$; b, $n = 6$; c, $n = 8$.

Monofunctional fluorinated amines $R_fCH_2CH_2NH_2$ were previously prepared by the reaction of $R_fCH_2CH_2I$ with ammonia[7] or by a two-step procedure[8] involving reaction of $R_fCH_2CH_2I$ with sodium azide followed by reduction of the azide. Our attempts to prepare 1,8-diamino-1,1,2,2,7,7,8,8-octahydroperfluorooctane (**4a**) by the Gabriel synthesis[9] or by the reaction of the iodo compound with ammonia gave mainly HI elimination products. Consequently, fluorinated diamines were prepared by the two-step approach involving diazides.

Displacement reactions of **2a–c** with sodium azide in 98% DMSO/water gave the diazides **3a–c** in 92–98% yields. High yields of **3a** were obtained in 98% DMSO/water or 95% acetonitrile/water. In DMSO/water, the reaction proceeded at room temperature and reached completion in 4 h, whereas in acetonitrile/water, 16 h at reflux were needed. In moist alcoholic solvents, such as diethylene glycol, *tert*-butyl alcohol, *sec*-butyl alcohol, and isopropyl alcohol, high temperatures (82–120 °C) and long reaction periods (48–60 h) were needed to reach completion. In DMF, elimination competed with displacement and the product was contaminated with ca. 10% of $CH_2{=}CH(CF_2)_4CH{=}CH_2$ and $N_3CH_2CH_2(CF_2)_4CH{=}CH_2$.

Diazides **3a–c** were reduced to diamines **4a–c** by conventional hydrogenation[10,11] or by the hydrazine-mediated catalytic-transfer hydrogenation.[12] Either procedure afforded fluorinated diamines **4a–c** in ca. 60% yield. Catalytic transfer hydrogenation, however, can be conducted in normal glassware at atmospheric pressure.[12] Reduction of **3a** with lithium aluminum hydride, sodium borohydride, titanium (III) chloride, or triphenylphosphine by standard procedures[10,13–16] gave complex mixtures.

Diamines **4a–c** were converted to diisocyanates **6a–c** in 55–85% yield by reacting a slurry of the dihydrochloride salts **5a–c** in *o*-dichlorobenzene with phosgene at 135 °C.

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(1) (a) Hollander, J.; Trischler, F. D.; Gosnell, R. B. *J. Polym. Sci: Part A-1* **1967**, *5*, 2757. (b) Hollander, J.; Trischler, F. D.; Harrison, E. S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1967**, *8*, 1149. (c) Hollander, J. In *High Polymers*; Wall, L., Ed.; Wiley-Interscience: New York, 1972; Vol XXV, Chapter 6, 195.

(2) Middleton, W. J. *J. Org. Chem.* **1984**, *49*, 4541.

(3) Takakura, T.; Yamabe, M.; Kato, M. *J. Fluorine Chem.* **1988**, *41*, 173.

(4) Ulrich, H. *J. Polymer Sci., Part D: Macromol. Rev.* **1976**, *11*, 93.

(5) Bedford, C. D.; Baum, K. *J. Org. Chem.* **1980**, *45*, 347.

(6) (a) Baum, K.; Bedford, C. D.; Hunadi, R. J. *J. Org. Chem.* **1982**, *47*, 2251. (b) Knunyants, I. L.; Khrlakyan, S. P.; Zeifman, Yu. V.; Shokina, V. V. *Izv. Akad. Nauk SSR, Ser. Khim.* **1964**, *2*, 384.

(7) (a) Takao, H.; Hitoshi, H. Japan Kokai JP 77,118,406 1977 (*Chem. Abstr.* 1978, 88, 61965f). (b) Foulletier, L.; Jean, P. L. U.S. 4,059,629 1977 (*Chem. Abstr.* 1978, 88, 169572r).

(8) Rondestvedt, C. S.; Thayer, G. L. *J. Org. Chem.* **1977**, *42*, 2680.

(9) (a) Gibson, M. S.; Bradshaw, R. W. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 919. (b) Sheehan, J. C.; Bolhofer, W. A. *J. Am. Chem. Soc.* **1950**, *72*, 2786. (c) Landini, D.; Rolla, F. *Synthesis* **1976**, 389. (d) Soai, K.; Ookawa, A.; Kato, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1671.

(10) (a) Scriver, E. F. V.; Turnbull, K. *Chem. Rev.* **1988**, *88*, 321. (b) Boyer, J. H.; Canter, F. C. *Chem. Rev.* **1954**, *54*, 1. (c) Hudlicky, M., In *Reduction in Organic Chemistry*; Halsted Press: New York, 1984; 69.

(11) (a) Corey, E. J.; Nicolaou, K. C.; Balanson, R. D.; Machida, Y. *Synthesis* **1975**, 590. (b) Mungall, W. S.; Greene, G. L.; Heavner, G. A.; Lestinger, R. L. *J. Org. Chem.* **1975**, *40*, 1659.

(12) Malik, A. A.; Preston, S. B.; Archibald, T. G.; Cohen, M. P.; Baum, K. *Synthesis* **1989**, 450.

(13) (a) Boyer, J. H. *J. Am. Chem. Soc.* **1951**, *73*, 5865. (b) Bose, A. K.; Kistner, J. F., Farber, L. *J. Org. Chem.* **1962**, *27*, 2925.

(14) (a) Soai, K.; Yokoyama, S.; Ookawa, A. *Synthesis* **1987**, 48. (b) Rolla, F. *J. Org. Chem.* **1982**, *47*, 4327. (c) Boyer, J. H.; Ellzey, S. E. *J. Org. Chem.* **1958**, *23*, 127.

(15) Stanovnik, B.; Tisler, M.; Polanc, S.; Gracner, M. *Synthesis* **1978**, 65.

(16) (a) Staudinger, H.; Hauser, E. *Helv. Chim. Acta.* **1921**, *4*, 861. (b) Zimmer, H.; Vaultier, M.; Knouzi, N.; Carrie, R. *Tetrahedron Lett.* **1983**, *24*, 763. (c) Horner, L.; Gross, A. *Liebigs Ann. Chem.* **1955**, *591*, 117. (d) Kozirara, A.; Osowska-Pacewicka, K.; Zawadzki, S.; Zwierzak, A. *Synthesis* **1985**, 202.

0022-3263/91/1956-3043$02.50/0

Direct displacement of **2a** with potassium cyanate[17] afforded mainly elimination products, whereas reaction of iminophosphorane **7a** with carbon dioxide[18] gave **6a** in <5% yield.[19]

$$\underset{\textbf{3a}}{N_3CH_2CH_2(CF_2)_4CH_2CH_2N_3} \xrightarrow[CH_2Cl_2]{Ph_3P}$$

$$[\underset{\textbf{7a}}{Ph_3P{=}NCH_2CH_2(CF_2)_4CH_2CH_2N{=}PPh_3}] \xrightarrow[\text{benzene}]{CO_2}$$

$$\underset{\textbf{6a}}{OCNCH_2CH_2(CF_2)_nCH_2CH_2NCO}$$

Experimental Section

^{1}H and ^{19}F NMR spectra were recorded on a 200-MHz AC 200 Bruker FT NMR spectrometer with $CDCl_3$ as a solvent. Chemical shifts are reported in ppm relative to TMS and $CFCl_3$. Infrared spectra were obtained on a Perkin-Elmer 700 spectrometer. Elemental analyses were conducted by Galbraith Laboratories, Knoxville, TN. (*Caution*. Organic diazides are potentially explosive and should be handled with care. Adequate safety shielding should be used.)

1,8-Diazido-3,3,4,4,5,5,6,6-octafluorooctane (3a). A mixture of 1,8-diiodo-3,3,4,4,5,5,6,6-octafluorooctane (3.0 g, 5.9 mmol), sodium azide (1.0 g, 15.4 mmol), DMSO (25 mL), and water (0.5 mL) was stirred at ambient temperature for 4 h. The reaction mixture was poured into water and extracted with diethyl ether (3×). The organic layer was washed with water (2×), 10% aqueous sodium sulfite solution (2×), water (3×), and brine, dried ($MgSO_4$), filtered, and stripped of solvent under reduced pressure to give 1.9 g (95%) of **3a**, a pale yellow oil. An analytical sample was bulb-to-bulb distilled at 90 °C (0.10 mmHg): ^{1}H NMR δ 3.43 (t, J = 7 Hz, 4 H) and 2.26 (tt, J = 16 and 7 Hz, 4 H); ^{19}F NMR δ −115.0 (4 F) and −128.8 (4 F); IR (neat) 2950, 2150, 1100–1300 cm^{-1}. Anal. Calcd for $C_8H_8F_8N_6$: C, 28.25; H, 2.37. Found: C, 28.12; H, 2.40.

1,10-Diazido-3,3,4,4,5,5,6,6,7,7,8,8-dodecafluorodecane (3b). The previous procedure with 1,10-diiodo-3,3,4,4,5,5,6,6,7,7,8,8-dodecafluorodecane gave a 98% yield of **3b**, a yellow oil: ^{1}H NMR δ 3.53 (t, J = 7.6 Hz, 4 H), 2.31 (tt, J = 7.6 Hz and 18.1 Hz, 4 H); ^{19}F NMR δ −114.2 (4 F), −122.0 (4 F), and −123.6 (4 F); IR (neat) 2150 cm^{-1}. The material was used without further purification in the synthesis of 1,10-diamino-3,3,4,4,5,5,6,6,7,7,8,8-dodecafluorodecane.

1,12-Diazido-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-hexadecafluorododecane (3c). The previous procedure with 1,12-diiodo-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-hexadecafluorododecane gave a 92% yield of **3c**, a pale yellow solid. An analytical sample was sublimed at 70 °C (0.5 mmHg): mp 60–64 °C; ^{1}H NMR δ 3.61 (t, J = 7.2 Hz, 4 H), 2.39 (tt, J = 7.2 and 18.2 Hz, 4 H); ^{19}F NMR δ −114.2 (4 F), −122.1 (8 F), −123.8 (4 F); IR (neat) 2150 cm^{-1}. Anal. Calcd for $C_{12}H_8F_{16}N_6$: C, 26.30; H, 1.60. Found: C, 26.68; H, 1.49.

1,8-Diamino-3,3,4,4,5,5,6,6-octafluorooctane (4a). Procedure A. A solution of hydrazine (1.1 g, 32 mmol) in methanol (5 mL) was added to a stirred mixture of 1,8-diazido-3,3,4,4,5,5,6,6-octafluorooctane (3.3 g, 9.7 mmol), Pearlman's catalyst (palladium hydroxide on carbon, 350 mg), and methanol (30 mL) under nitrogen. The mixture was heated under reflux for 16 h, cooled, and filtered through a pad of Celite. Solvent was evaporated, and the residue (2.4 g) was distilled to give 1.6 g (59%) of **4a**, a colorless oil: bp 93–95 °C (0.2 mmHg); ^{1}H NMR δ 2.89 (t, J = 6 Hz, 4 H), 2.10 (m, 4 H), 1.23 (s, 4 H, exchanges with D_2O); ^{19}F NMR δ −116.0 (4 F), −125.0 (4 F); IR (neat) 3400, 2950, 1000–1100 cm^{-1}. Anal. Calcd for $C_8H_{12}F_8N_2$: 33.34; H, 4.20; F, 52.74; N, 9.27. Found: C, 33.65; H, 4.49; F, 52.57; N, 9.53.

Procedure B. A solution of 1,8-diazido-3,3,4,4,5,5,6,6-octafluorooctane (3.1 g, 9.1 mmol) in methanol (25 mL) was hydrogenated over Pearlman's catalyst (350 mg) in a Parr hydrogenator under 35 psi of hydrogen. After 14 h, the reaction mixture was diluted with methanol and filtered through a pad of Celite. Solvent was evaporated under reduced pressure, and the residue was distilled to give 1.6 g (61%) of **4a**, a colorless oil. The product was identical in all respects with **4a** isolated in procedure A.

1,10-Diamino-3,3,4,4,5,5,6,6,7,7,8,8-dodecafluorodecane (4b). Reduction of 1,10-diazido-3,3,4,4,5,5,6,6,7,7,8,8-dodecafluorodecane by procedure A gave a 57% yield of **4b**. The product was purified by Kugelrohr distillation (110 °C (0.2 mmHg)): mp 35–38 °C; ^{1}H NMR δ 3.06 (t, 4 H), 2.25 (tt, 4 H), 1.29 (br s, 4 H, exchanges with D_2O); ^{19}F NMR δ −113.9 (4 F), −122.1 (4 F), −124.1 (4 F); IR (CH_2Cl_2) 3400, 3050, 2975, 1100–1300 cm^{-1}. Anal. Calcd for $C_{10}H_{12}F_{12}N_2$: C, 30.94; H, 3.12; F, 58.73; N, 7.22. Found: C, 30.83; H, 3.16; F, 58.96; N, 7.19.

1,12-Diamino-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-hexadecafluorododecane (4c). Reduction of 1,12-diazido-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-hexadecafluorododecane by procedure A gave a 58% yield of **4c**. An analytical sample was recrystallized from diethyl ether/hexane: mp 109–111 °C; ^{1}H NMR δ 3.05 (t, 4 H), 2.20 (m, 4 H), 1.33 (br s, 4 H, exchanges with D_2O); ^{19}F NMR δ −115.0 (4 F), −125.1 (4 F), −128.2 (8 F); IR (CH_2Cl_2) 3500, 2950, 1100–1000 cm^{-1}. Anal. Calcd for $C_{12}H_{12}F_{16}N_2$: C, 29.52; H, 2.48. Found: C, 29.72; H, 2.60.

1,8-Diisocyanato-3,3,4,4,5,5,6,6-octafluorooctane (5a). Hydrogen chloride gas was bubbled into a stirred suspension of 1,8-diamino-3,3,4,4,5,5,6,6-octafluorooctane (25 g, 86.8 mmol) in *o*-dichlorobenzene (300 mL) at a rate of 10 mL/min for 1 h. Phosgene was then bubbled into the mixture and the temperature was raised gradually to 135 °C over 2 h. The formation of a homogeneous solution indicated completion of the reaction. Phosgene was flushed from the reaction mixture with argon, and the solvent was removed by distillation (30–32 °C/0.2 mmHg). The residue was distilled to give 25.4 g (86%) of **5a**, a colorless liquid: bp 110 °C (0.2 mmHg); ^{1}H NMR δ 3.66 (t, J = 6.9 Hz, 4 H), 2.40 (tt, J = 17.9 Hz and 6.9 Hz, 4 H); ^{19}F NMR δ −114.8 (4 F), −123.9 (4 F); IR (CH_2Cl_2) 3150, 3050, 2300, 1360–1100, 1020 cm^{-1}. Anal. Calcd for $C_{10}H_8F_8N_2O_2$: C, 35.29; H, 2.35; F, 44.71; N, 8.24. Found: C, 35.36; H, 2.44; F, 44.56; N, 8.12.

1,10-Diisocyanato-3,3,4,4,5,5,6,6,7,7,8,8-dodecafluorodecane (5b). Phosgenation of 1,10-diamino-3,3,4,4,5,5,6,6,7,7,8,8-dodecafluorodecane (5.0 g, 12.9 mmol) by the previous procedure gave a 80% yield of **5b**, a white waxy solid. An analytical sample was recrystallized from hexane: mp 30–31 °C; ^{1}H NMR δ 3.67 (t, J = 6.9 Hz, 4 H), 2.42 (tt, J = 18.0 Hz and 6.9 Hz, 4 H); ^{19}F NMR δ −114.8 (4 F), −122.1 (4 F), and IR (CH_2Cl_2) 3100, 3050, 2300, 1380–1110 cm^{-1}. Anal. Calcd for $C_{12}H_8F_{10}N_2O_2$: C, 32.74; H, 1.83; F, 51.79; N, 6.36. Found: C, 32.52; H, 1.81; F, 52.01; N, 6.45.

1,12-Diisocyanato-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-hexadecafluorododecane (5c). Phosgenation of 1,12-diamino-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-hexadecafluorododecane (4.1 g, 8.4 mmol) by the previous procedure gave a 55% yield of **5c**, a white waxy solid. An analytical sample was recrystallized from hexane: mp 86–88 °C; ^{1}H NMR δ 3.68 (t, J = 6.9 Hz, 4 H), 2.42 (tt, J = 18.0 Hz and 6.9 Hz, 4 H); ^{19}F NMR δ −114.9 (4 F), −122.3 (8 F), −124.1 (4 F); IR (CH_2Cl_2) 3100, 3050, 2350, 1420, 1340–1050, 900 cm^{-1}. Anal. Calcd for $C_{14}H_8F_{16}N_2O_2$: C, 31.13; H, 1.49; N, 5.19; F, 56.27. Found: C, 31.03; H, 1.47; N, 4.98; F, 56.38.

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[17] (a) Vodop'yanov, V. G.; Golov, V. G.; Dvoeglazova, N. P.; Ivanoc, M. G.; Mysin, N. I.; Gerega, V. F. *Žh. Obshch. Khim.* 1981, *51*(8), 1885. (b) Schaeffer, W. D. U.S. 3,017,420 1962. (c) Mc Master, A. L.; Park, L. U.S. 3,440,269 1969. (d) Argabright, P. A.; Rider, H. D.; Sieck, R. *J. Org. Chem.* 1965, *30*, 3317.

[18] (a) Molina, P.; Arques, A. A. *Synthesis* 1982, 596. (b) Tsuge, O.; Kanemasa, S.; Matsuda, K. *J. Org. Chem.* 1984, *49*, 2688.

[19] Iminophosphorane **7a** was prepared by the Staudinger reaction.[16] Triphenylphosphine (16.2 g, 61.8 mmol) was added to a solution of **3a** (10.1 g, 29.9 mmol) in dichloromethane (50 mL) and the mixture was stirred at room temperature for 3 h. Solvent was evaporated under reduced pressure to give 23.0 g (97%) of **7a**, a viscous oil: ^{1}H NMR ($CDCl_3$) δ 7.68–7.33 (m, 30 H), 3.39 (m, 4 H) and 2.32 (m, 4 H); ^{19}F NMR ($CDCl_3$) δ −114.2 (4 F), −124.3 (4 F). The material was reacted with carbon dioxide in refluxing benzene without further purification.