was distilled under reduced pressure to give 96 g. of crude product. Distillation through a 9″ stainless steel helices-packed column gave 23 g. (77%) of bis-(3,3,4,4,5,5,5-heptafluoropentyl)-diethoxysilane,[1] 4.4 g. (2.9%) of tetrakis-(3,3,4,4,5,5,5-heptafluoropentyl)-silane[1] and 55 g. of recovered 3,3,4,4,5,5,5-heptafluoropentyltriethoxysilane.

3,3,4,4,5,5,5-Heptafluoropentylmethyldiethoxysilane. A.—Two hundred and thirty-six ml. (1 *N*, 0.236 mole) of methylmagnesium bromide solution was added during 1 hr. to 85 g. (0.236 mole) of 3,3,4,4,5,5,5-heptafluoropentyltriethoxysilane in 236 ml. of ether. The solution was refluxed for five hours and the ether distilled, the final pot temperature being 100°. Benzene, 150 ml., was added and distillation continued until the temperature of the distillate was 77.5°. The residual mixture was cooled, centrifuged, and the precipitate washed with two 20-ml. portions of benzene. On fractional distillation there was obtained 47.5 g. (61%) of 3,3,4,4,5,5,5-heptafluoropentylmethyldiethoxysilane, b.p. 92° (42 mm.), $n^{20}\text{D}$ 1.3502.

B.—Methyltriethoxysilane (43.4 g., 0.236 mole) was heated to 93–95° and 84 ml. (1.195 *N*, 0.1 mole) of 3,3,-4,4,5,5,5-heptafluoropentylmagnesium bromide was added during 1.5 hr. The solution was stirred 1.5 hr. at 95° and then the liquid was decanted from a gummy residue and combined with the "flashed off" ether collected during the run. The residue was washed with benzene and the solutions combined. Ether and benzene were removed by distillation through an 8″ Vigreux column first at atmospheric pressure and then at 100 mm. The residual mixture was rectified through the 3′ glass spiral packed Todd column to give 19.8 g. (60%) of 3,3,4,4,5,5,5-heptafluoropentylmethyldiethoxysilane, b.p. 76.5° (23.5 mm.), $n^{20}\text{D}$ 1.3521, and 25.5 g. of recovered methyltriethoxysilane. The 3,3,4,4-5,5,5-heptafluoropentylmethyldiethoxysilane was rectified through a 3′ stainless steel helices packed column to give a product, b.p. 75.9° (23 mm.), $n^{20}\text{D}$ 1.3511. An infrared spectrum of this compound was identical with that of the product from methylmagnesium bromide and 3,3,4,4,5,5,5-heptafluoropentyltriethoxysilane.

Anal. Calcd. for $C_{10}H_{17}O_2F_7Si$: C, 36.40; H, 5.15; F, 40.30. Found: C, 36.42, 36.58; H, 5.56, 5.76; F, 39.92, 40.02.

3,3,3-Trifluoropropyltrimethoxysilane.—An ether solution of 3,3,3-trifluoropropylmagnesium chloride (0.641 mole) was added dropwise to 1280 g. (8.42 moles) of methyl silicate[5] at 90 ± 5°, during 3 hours, during which time 400 ml. of ether was stripped off through an 18″ column. Two liters of pentane were added, the solution was stirred and refluxed to remove the ether, cooled to 0°, and filtered with suction. Rectification of the filtrate after removal of pentane gave 638 g. of recovered methyl silicate and 131 g. (94%) of 3,3,3-trifluoropropyltrimethoxysilane, b.p. 79.8–80.5° (87 mm.), $n^{20}\text{D}$ 1.3547, d^{20}_4 1.137.

Anal. Calcd. for $C_6H_{13}O_3F_3Si$: C, 33.03; H, 5.97; F, 26.15. Found: C, 32.96; H, 5.93; F, 26.25.

Bis-(3,3,3-trifluoropropyl)-dimethoxysilane.—3,3,3-Trifluoropropylmagnesium chloride (0.29 mole) in ethyl ether was added to 155 g. (0.71 mole) of 3,3,3-trifluoropropyltrimethoxysilane at 100° initially, then gradually falling to 70° as the reaction proceeded. Pentane (2 l.) was added and the ether was stripped out. This was followed by the addition of 120 g. (0.79 mole) of methyl silicate to complex the magnesium methoxy chloride. The suspension was filtered, the pentane removed, and the residue rectified. There was obtained 68 g. (82%) of bis-(3,3,3-trifluoropropyl)-dimethoxysilane, b.p. 100.5° (57 mm.), $n^{20}\text{D}$ 1.3531, d^{20}_4 1.256.

Anal. Calcd. for $C_8H_{14}O_2SiF_6$: C, 33.75; H, 4.93; F, 40.2. Found: C, 33.79; H, 5.08; F, 39.84.

3,3,3-Trifluoropropylmethyldimethoxysilane.—A 1-liter, 3-necked flask was equipped with a Tru-bore stirrer, a 500-ml. dropping funnel and a 18 × 450 mm. glass helices-packed column. The column was in turn fitted with a partial take-off head and a 500-ml. receiver. The entire equipment was flame dried and swept with purified nitrogen just before use. With constant stirring, a freshly prepared ether solution (236 ml., 0.286 mole) of the Grignard reagent of 3,3,3-trifluoro-1-chloropropane was added dropwise to 365 g. (2.68 moles) of methyltrimethoxysilane[5] in the flask during 3 hr. The reaction mixture was maintained at 80–90° and the ether was distilled continuously. When no more ether distilled, the reaction mixture was cooled to room temperature and diluted with 300 ml. of dry pentane. After stirring and settling, the mixture was filtered into an ice-cold flask. The precipitate was washed twice with pentane. The pentane solution and the filtrate were then combined and fractionated in a glass helices-packed Todd column. When the solvent and most of the methyltrimethoxysilane had distilled, the crude 3,3,3-trifluoropropylmethyltrimethoxysilane was combined with those obtained from the two other batches started with 0.446 and 0.228 mole of the Grignard reagent. Upon further fractionation, 120 g. (61.9%) of 3,3,3-trifluoropropylmethyldimethoxysilane, b.p. 96.5–96.8° (251 mm.), $n^{20}\text{D}$ 1.3576, d^{20}_4 1.0954, was obtained.

Anal. Calcd. for $C_6H_{13}O_2F_3Si$: C, 35.62; H, 6.48; F, 28.20. Found: C, 35.37; H, 6.52; F, 28.08.

3,3,3-Trifluoropropylmagnesium Chloride.—A 500-ml. flask was charged with 15 g. (0.613 mole) of magnesium turnings, flame dried, and cooled under nitrogen atmosphere. A mixture of 73 g. (0.55 mole) of 3,3,3-trichloro-1-chloropropane[6] and 200 ml. of anhydrous ether was placed in the dropping funnel. The reaction was initiated by adding a few crystals of iodine to 20 ml. of the mixture in the flask. When the reaction started, the flask was immersed in a ice-water-bath and the rest of the chloride was added with constant stirring during 4 hours; when the addition was complete the reaction mixture was left stirring overnight. Two milliliters of the Grignard reagent was hydrolyzed with excess standard hydrochloric acid, titrated with standard sodium hydroxide using phenolphthalein as indicator, and was found to be 1.82 *N;* yield 82.3%. In one instance, when no ice-bath was used, decomposition of the Grignard reagent produced 1,1-difluorocyclopropane, b.p. −16°, mol. wt., 81 (Dumas). *Anal.* Calcd. for cyclo-$C_3F_2H_4$: C, 46.20; H, 5.13; F, 48.75. Found: C, 45.97; H, 4.91; F, 48.49. The infrared spectrum differs considerably from that of 1,1-difluoropropene.

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Determination of the Number of Nitro Groups in Aliphatic Polynitro Compounds[1]

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During the work of assigning the structure of an unusual polynitro compound,[2] it was found that maximal intensity measurements in the infrared on the anti-symmetric stretching bands of the nitro group gave reliable values in aliphatic compounds for the absorbance per nitro group. While the absorbance of the band maximum per centimeter of a one molar solution in chloroform varied between 400 and 550 (one exception) still there was never any doubt among the compounds measured (Table I) whether one, two, three or four nitro groups were present. The presence of a nitroso group in the molecule, of course, should not interfere with the determination since the nitroso group does not absorb in the 6.3 μ region.[3]

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[1] Work supported in part by Office of Ordnance Research Contract DA-19-020-ORD-592 at Brown University.

[2] J. S. Belew, C. E. Grabiel and L. B. Clapp, THIS JOURNAL, **77**, 1110 (1955).

[3] N. B. Colthup, *J. Optical Soc. Am.*, **40**, 397 (1950).

TABLE I

MAXIMAL EXTINCTION COEFFICIENTS FOR THE 6-μ NITRO BAND

Compound	Band, μ	$E_{\max}$[a]	No. of nitro groups	$E_{\max}$ per nitro group
2,5,5-Trinitro-3-aza-4-oxa-2-hexene[2,5]	6.30 6.40	1060 550	2 1	530 550
2-Chloro-5,5-dinitro-3-aza-4-oxa-2-hexene[2,6]	6.30	860	2	430
2,2,3,3-Tetranitrobutane	6.30	1600	4	400
3,3,4,4-Tetranitrohexane	6.31	1620	4	405
2,2-Dinitropropane[7,8]	6.40	993	2	496
Ethanenitrolic acid[9]	6.44	365	1	365
N-Acetylethanenitrolic acid	6.41	439	1	439

[a] Absorbance per centimeter for a 1 *M* solution in chloroform, slit width 0.050 μ.

The two tetranitro compounds, 2,2,3,3-tetranitrobutane and 3,3,4,4-tetranitrohexane, are not reported in the literature. The compound[4] bearing the name 2,2,3,3-tetranitrobutane has been assigned the structure 2,5,5-trinitro-3-aza-4-oxa-2-hexene.[2,5] The structure of 2,2,3,3-tetranitrobutane was confirmed by synthesis from two starting compounds, dimethylglyoxime and 2,3-dinitro-2-butene, followed by reduction to 2,3-diaminobutane. Rearrangements in the two syntheses and the reduction seems unlikely.

Experimental[10]

Infrared Spectra.—Infrared spectra were measured on a double beam recording spectrometer, a modified Perkin-Elmer model 12B using a sodium chloride prism. For solutions in chloroform, matched cells in which one contained only solvent gave spectra free of solvent bands. The $E_{\max}$ given in Table I is the absorbance of the band maximum per centimeter in one molar solution, calculated from the formula $E_{\max} = \log (I_0/I)CL$ for a spectral slit width of 0.050 μ.

2,2,3,3-Tetranitrobutane. A. From Dimethylglyoxime.—Six grams of dimethylglyoxime (recrystallized from glacial acetic acid) was added slowly to 25 ml. of fuming nitric acid (sp. gr. 1.5) previously cooled to 5°. The reaction mixture was allowed to stand one-half hour in the cooling bath and then 25 ml. of fuming sulfuric acid (containing 30% sulfur trioxide) was added dropwise with stirring so that the temperature did not rise above 10°. After 15 minutes the red solution was poured into crushed ice and allowed to stand overnight. The white waxy solid was collected, washed with water and dried; yield 1.51 g. (12%), m.p. 159° dec. An analytical sample was prepared by recrystallization from dilute ethanol, followed by sublimation at 90° (0.5 mm.), m.p. 162.2–163.0° dec.

Anal. Calcd. for $C_4H_6N_4O_8$: C, 20.18; H, 2.54; N, 23.52. Found: C, 20.52; H, 2.76; N, 23.39.

B. **From 2,3-Dinitro-2-butene.**—One gram of 2,3-dinitro-2-butene[11] in a Carius tube was covered with 2 ml. of liquid nitrogen dioxide (dried by passing through phosphorus pentoxide on glass wool) at −77°. The tube was sealed and heated to 85° for 75 hours. Hexane was added after allowing the excess nitrogen dioxide to boil away and upon cooling white crystals of 2,2,3,3-tetranitrobutane precipitated. The crystals were washed with cold hexane and dried. Sublimation at 90° (0.4 mm.) gave 0.51 g. (31%) of pure 2,2,-3,3-tetranitrobutane, m.p. 159–160° dec.; mixed m.p. with the product from (A) above, no depression.

Reduction of 2,2,3,3-Tetranitrobutane.—Catalytic reduction of 2,2,3,3-tetranitrobutane in absolute ethanol with Adams catalyst under one atmosphere of hydrogen gave a 70% yield of 2,3-diaminobutane, isolated as the hydrochloride. The diamine was identified by converting the hydrochloride to the known dibenzamide, m.p. 295–297°.[12]

3,3,4,4-Tetranitrohexane.—By adding nitrogen dioxide to 3,4-dinitro-3-hexene[11] using the method just described (B, above) white waxy crystals of 3,3,4,4-dinitrohexane were obtained in 32% yield, m.p. 106.0–107.0°.

Anal. Calcd. for $C_6H_{10}N_4O_8$: C, 27.07; H, 3.79; N, 21.05. Found: C, 27.44; H, 3.95; N, 20.44.

The tetranitrohexane was identified by catalytic reduction to 3,4-diaminohexane in 70% yield and conversion to the dibenzamide, m.p. 330–332°.[12]

N-Acetylethanenitrolic Acid.[13,14]—The sodium ethanenitrolate prepared from 10.0 g. of ethanenitrolic acid[9] was added slowly with stirring to an ice-cold solution of 6.3 g. of acetyl chloride in 100 ml. of ether. After stirring for 45 minutes the sodium chloride was removed, the filtrate was washed with 20 ml. of saturated sodium bicarbonate solution and dried over calcium chloride. Part of the ether was removed in an atmosphere of nitrogen at reduced pressure. Upon adding hexane and cooling with a Dry Ice-bath, 5.64 g. (50%) of N-acetylethanenitrolic acid precipitated. Recrystallization from ether gave an analytical sample, m.p. 24.0–25.0°. Infrared spectrum (0.013 *M* solution in chloroform, μ): 5.58 (strong),[15] carbonyl; 6.01 (weak), C=N; 6.44, 7.44 (medium), nitro.

Anal. Calcd. for $C_4H_6N_2O_4$: C, 32.88; H, 4.14; N, 19.18. Found: C, 33.18; H, 4.29; N, 19.26.

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[4] A. J. Miller and H. Hunt, *J. Phys. Chem.*, **49**, 20 (1945).

[5] Or an alternate structure, 2,4,4-trinitro-3-aza-2-pentene 3-oxide.

[6] Or an alternate structure, 2-chloro-4,4-dinitro-3-aza-2-pentene 3-oxide.

[7] A value $E_{\max}$ 430 for 2,2-dinitropropane with a spectral slit width of 0.034 μ was obtained by Dr. John F. Brown, Jr., General Electric Co., Schenectady, N. Y. The authors are grateful to Dr. Brown for valuable talks in connection with this work.

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[9] V. Meyer, *Ann.*, **175**, 96 (1875); V. Meyer and E. J. Constam, *ibid.*, **214**, 329 (1882); H. Wieland, *ibid.*, **353**, 82 (1907).

[10] Melting points given to tenths of a degree are corrected. Analyses by S. M. Nagy, Microchemical Laboratory, Massachusetts Institute of Technology, Cambridge, Mass.

[11] E. M. Nygaard and T. T. Noland, U. S. Patent 2,396,282 March 12, 1946).

[12] L. B. Clapp, J. F. Brown, Jr., and L. Zeftel, *J. Org. Chem.*, **15**, 1043 (1950).

[13] P. Grammaticakis, *Compt. rend.*, **223**, 741 (1946); **224**, 1067 (1947). Grammaticakis has presented spectral evidence in the ultraviolet region on a number of oximes related to the compound under discussion which suggests that direct acylation of an oxime leads to N-acylation. Evidence from thermal decomposition and hydrolysis[14] leading to an O-acyl assignment in this ethanenitrolate derivative appears less reliable for the purpose of structure assignment. Grammaticakis suggested that N-acyl oximes are converted to O-acyl oximes during hydrolysis. See also infrared data below and footnote 15.

[14] V. Meyer, *Ber.*, **27**, 1600 (1894); J. U. Nef, *Ann.*, **280**, 284 (1894); L. W. Jones, *Am. Chem. J.*, **20**, 1 (1898).

[15] Interpretation of the position of the strong band found at a shorter wave length (5.58 μ) than would be expected in a normal ester carbonyl band (5.68–5.81 μ) in the light of recent work by E. J. Hartwell, R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, 1436 (1948), led the authors to conclude that the N-acyl structure assignment is more tenable than an O-acyl structure.

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The 2,4-Dinitrophenylhydrazones of Some Hindered Ketones

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The 2,4-dinitrophenylhydrazones of 2,6-dimethyl-, 2,4,6-trimethyl- and 2,6-dimethyl-4-*t*-butylacetophenones previously have not been reported. The general impression is probably that they cannot be made directly because of the steric effect of the *ortho*-situated methyl groups.[1] This impression must now be revised because the 2,4-

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