pyridinium bromide (II) produced 1,3-pentadiene. Both dienes were identified as the tetrabromo derivatives.

Experimental

Preparation of the Bis-pyridinium Salts.—Dry pyridine was added to a solution of the dihalide in absolute methanol in slight excess of two moles of pyridine to one of the dihalide. The solution was allowed to stand for two days and the methanol distilled. The solid which crystallized was removed by filtration, washed with ether and recrystallized from absolute ethanol and ether or acetone. A quantitative yield of the salts was obtained.

The bis-pyridinium salt I of tetramethylene dibromide melted at 237–239° (lit.[2] m.p. 239°) after drying for one hour at 100° under reduced pressure.

Anal. Calcd. for $C_{14}H_{18}Br_2N_2$: Br, 42.74. Found: Br, 42.35.

The bis-pyridinium salt II of pentamethylene dibromide melted at 193–195° after drying as above.

Anal. Calcd. for $C_{15}H_{20}Br_2N_2$: Br, 41.18. Found: Br, 41.14.

The Thermal Decomposition of the Salts.—The bis-pyridinium salt was heated by a Woods metal-bath at 230–270° in a distilling flask connected through a trap at 0° to a receiver immersed in an acetone–Dry Ice-bath. A higher temperature increased the speed of the decomposition, but the distillate became contaminated with pyridine hydrobromide. The solid which remained in the distilling flask after the reaction was complete was recrystallized from absolute methanol and ether and melted at 212–215°; lit.[3] m.p. for pyridine hydrobromide, 213°.

Anal. Calcd. for C_5H_6BrN: Br, 49.94. Found: Br, 50.65.

Pyridine hydrobromide was recovered in quantitative yield from the decomposition of both salts.

The distillate (0.9 g.) from the decomposition of 10 g. of I was distilled into a solution of chloroform and bromine. After removal of the excess solvent, the solid was recrystallized from low-boiling petroleum ether yielding 3.1 g. (36% from I) of 1,2,3,4-tetrabromobutane, m.p. 115–116.8°; lit.[4] m.p. 118–119°. A mixed melting point with an authentic sample showed no depression.

Redistillation of the products from the decomposition of 39 g. of II yielded 5 g. (73% assuming 1,3-pentadiene) of a fraction boiling at 41–44°, n^{21}_{D} 1.4310; lit.[5] b.p. 43–44°, n^{20}_{D} 1.4314.

In order to prove the location of the double bonds, the diene was converted to the tetrabromo derivative by treatment with bromine in carbon tetrachloride. After recrystallization from ethanol, 1,2,3,4-tetrabromopentane melted at 113.4–114.4°; lit.[5] m.p. 114°.

---

(3) I. M. Heilbron, "Dictionary of Organic Compounds," Vol. III, Oxford University Press, New York, N. Y., 1938, p. 553.

(4) I. M. Heilbron, ref. 3, p. 672.

(5) L. E. Schniepp and H. H. Geller, THIS JOURNAL, **67**, 54 (1945).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NEW HAMPSHIRE
DURHAM, NEW HAMPSHIRE

Reaction of Grignard Reagents with Alkoxysilanes at Elevated Temperatures

BY E. T. MCBEE, C. W. ROBERTS, G. F. JUDD AND T. S. CHAO

RECEIVED SEPTEMBER 13, 1954

The first fluorine-containing difunctional silane, bis-(3,3,4,4,5,5,5-heptafluoropentyl)-diethoxysilane, was prepared in this Laboratory[1] by treating ethyl silicate with 3,3,4,4,5,5,5-heptafluoropentylmagnesium bromide. Subsequent work indicated that large quantities of this compound could not be obtained efficiently by this procedure. Appreciable quantities of tetrakis-(3,3,4,4,5,5,5-heptafluoropentyl)-silane and tris-(3,3,4,4,5,5,5-heptafluoropentyl)-ethoxysilane were obtained with small yields of 3,3,4,4,5,5,5-heptafluoropentyltriethoxysilane. Since tetrasubstitution occurred preferentially under the original reaction conditions, it seemed reasonable that a higher temperature and a high concentration of the alkoxysilane would produce the monosubstituted product exclusively. This has been realized, both with fluorine-containing and non-fluorine-containing Grignard reagents. Methylmagnesium bromide, with a fifteen-fold excess of ethyl silicate gave a 68% yield of methyltriethoxysilane, whereas at the temperature of refluxing ether and a 2.38 mole ratio of reactants, only 12% of the product was obtained. 3,3,3-Trifluoropropylmagnesium chloride reacted with methyl silicate to give 95% of the monosubstituted product.

An additional factor in these displacement reactions is the complexing or adsorption of the products by magnesium ethoxy bromide. This loss of the silanes was lessened by adding excess ethyl silicate, which preferentially complexed with the magnesium salts.

Experimental[2]

Methyltriethoxysilane.—Methylmagnesium bromide (0.499 mole) was added dropwise over two hours to 1560 g. (7.5 moles) of ethyl silicate maintained at 105 ± 3°; the ether was removed as the reaction proceeded. The precipitate formed during the reaction was removed by filtration at 0°, and rectification of the filtrate through a 3′ Heli-grid-packed Todd column gave 2.7 g. (5.27%) of dimethyldiethoxysilane,[3] b.p. 111°, n^{20}_{D} 1.3829, and 60 g. (67.5%) of methyltriethoxysilane, b.p. 143–146°, n^{20}_{D} 1.3829. When this reaction was conducted at the temperature of refluxing ether, only 12% of methyltriethoxysilane was produced.

Dimethyldiethoxysilane.—Methylmagnesium bromide (107 ml., 0.1 mole) was added dropwise during 1.5 hr. to 43.4 g. (0.238 mole) of methyltriethoxysilane maintained at 93 ± 15° in a 250-ml. 3-necked flask fitted as described in the previous experiment. Ether was removed by distillation, benzene was added, and 14.9 g. of solid was removed by centrifugation. Rectification of the filtrate through a 3′ glass spiral-packed Todd column gave 11.2 g. (76%) of dimethyldiethoxysilane, b.p. 69.5° (179 mm.), n^{29}_{D} 1.3824.[4]

3,3,4,4,5,5,5-Heptafluoropentyltriethoxysilane.—A solution of 150 ml. (0.50 *N*, 0.075 mole) of 3,3,4,4,5,5,5-heptafluoropentylmagnesium bromide in ether was added dropwise during 3 hr. to 156 g. (0.75 mole) of ethyl silicate at 95–130°; the ether was stripped off through an 18″ glass helices-packed column during the addition. The suspension was cooled in an ice-bath and filtered by suction, the flask being cooled in Dry Ice; the pentane was removed, and the residue rectified to give 19 g. (71%) of 3,3,4,4,-5,5,5-heptafluoropentyltriethoxysilane, b.p. 47° (3 mm.), n^{20}_{D} 1.211.

Anal. Calcd. for $C_{11}H_{19}O_3SiF_7$: C, 36.70; H, 5.29; F, 36.90. Found: C, 36.83; H, 5.37; F, 36.78.

There also was obtained 18.8 g. (12.3%) of tetrasubstituted silane and 111.8 g. of recovered ethyl silicate.[1]

Bis-(3,3,4,4,5,5,5-heptafluoropentyl)-diethoxysilane.—One hundred and twenty-five milliliters (0.45 *N*, 0.0565 mole) of 3,3,4,4,5,5,5-heptafluoropentylmagnesium bromide solution was added dropwise over three hours to 103 g. (0.29 mole) of 3,3,4,4,5,5,5-heptafluoropentyltriethoxysilane maintained at 95–105°. A white solid separated as the ether was stripped through an 18″ glass helices-packed fractionating column. Pentane (500 ml.) was added to precipitate the solid, the solution was filtered, and the liquid

---

(1) O. R. Pierce, E. T. McBee and R. E. Cline, THIS JOURNAL, **75**, 5618 (1953).

(2) Microanalyses were done by Mrs. C. S. Yeh, Purdue University, and the Clark Microanalytical Laboratory, Urbana, Ill.

(3) W. Simpson, British Patent 635,726 (1950).

(4) R. R. McGregor and E. L. Warrick, U. S. Patent 2,380,057 (1945).

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[3] 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.

Acknowledgment.—The authors wish to express their appreciation to the Materials Laboratory, Wright Air Development Center, Dayton, Ohio, for their financial support of this work.

---

[5] D. F. Peppard, W. G. Brown and W. C. Johnson, THIS JOURNAL, **68**, 73 (1946).

[6] E. T. McBee, H. B. Hass, R. M. Thomas, W. G. Toland and A. Truchan, *ibid.*, **69**, 945 (1947).

DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
WEST LAFAYETTE, INDIANA

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

BY CHARLES E. GRABIEL, DONALD E. BISGROVE AND LEALLYN B. CLAPP

RECEIVED MARCH 12, 1954

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]

---

[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).