In a typical experiment the mould was cultivated in 20 ml. of synthetic medium[4] containing 300 microcuries of radioactive sulfur as sulfate.[5] Vegetative inoculum was used. After three days incubation at 26° on a rotatory shaker (300 r.p.m., stroke 1.5 cm.) the mycelium was filtered off, washed thrice with 5 ml. of cold water and homogenized in cold dilute hydrochloric acid (*p*H 2). The insoluble cell material was centrifuged off and the supernatant deproteinized according to Sevag, *et al.*[6]

One-dimensional paper chromatograms were made of this extract using as solvents propanol-water (70/30, v./v.),[7] *t*-butyl alcohol-formic acid-water (70/15/15, v./v.),[8] and propanol-water-diethylamine (85/15/3, v./v.).[9] Autoradiographs revealed besides a strong spot of sulfate a second one with R_f value 0.52, 0.45 and 0.23, respectively, on Whatman paper no. 1 in the above mentioned solvents. Weaker spots due to oxidized glutathione, methionine and unidentified compounds were observed.

The substance having R_f 0.45 in *t*-butyl alcohol-formic acid-water was eluted from chromatograms on paper cylinders and again chromatographed using as solvent propanol-water. This gave one radioactive zone with R_f 0.52. After elution the sulfur compound was characterized as follows: it passed columns of Dowex-50 (H^+-form) and Amberlite IRA-400 (OH^--form) and did not move on paper electrophoresis at *p*H 5.6 or 8.5 (except for electroendosmosis). Hydrolysis with 1 *N* HCl for 15 minutes at 100° gave radioactive sulfate, which was identified by paper chromatography and paper electrophoresis.

Radioactive choline sulfate synthesized from $H_2S^{35}O_4$ and choline chloride[10] behaved exactly in the same manner. Chromatography of the compound from the mycelial extract and the synthetic choline sulfate together gave only one radioactive spot in the three solvents used.

It is worth noting that choline sulfate is not retained by a strong acid or basic ion exchanger although it has a negative and a positive charge. Apparently one group prevents the other one from attachment to the ion exchanger.

The insoluble cell material left after the extraction with dilute hydrochloric acid was treated with hot 5% trichloroacetic acid (TCA). In this extract we found as sulfur compound sulfate only and no trace of methionine. This latter substance was of course detected in hydrolysates of the insoluble residue left after the TCA extraction.

Although we did find some methionine in our first mycelial extract, the quantities are much less than those reported by Gordon, *et al.*[1] This might be due to the different method used in making the extracts.

---

(4) F. G. Jarvis and M. J. Johnson, This Journal, **69**, 3010 (1947).

(5) Sometimes the sulfur content was lowered, but this makes not much qualitative difference in the sulfur compounds produced.

(6) M. G. Sevag, D. B. Lackman and J. Smolens, *J. Biol. Chem.*, **124**, 425 (1938).

(7) B. Pernis and Ch. Wunderly, *Biochim. Biophys. Acta*, **11**, 209 (1953).

(8) R. J. Block, *Anal. Chem.*, **22**, 1327 (1950).

(9) R. R. Redfield, *Biochim. Biophys. Acta*, **10**, 344 (1953).

(10) E. Schmidt and W. Wagner, *Ann.*, **337**, 54 (1904).

KON. NED. GIST- EN SPIRITUSFABRIEK
DELFT, THE NETHERLANDS

Redistribution of Et_4Si and Pr_4Si[1]

BY P. D. GEORGE, L. H. SOMMER AND F. C. WHITMORE[2]

RECEIVED OCTOBER 13, 1954

The random redistribution of organic groups in certain metal alkyls upon heating with anhydrous aluminum chloride has been well established, particularly in the case of lead alkyls.[3] The redistribution of Et_4Si and Pr_4Si has also qualitatively been demonstrated[4]; however a number of the products were not identified, and it was not possible to conclude whether isomerization of propyl groups had occurred.

We undertook to examine this redistribution reaction in greater detail because of its possible utility in synthesizing mixed tetraalkylsilanes and because of the growing importance of redistribution reactions in silicone technology.[5]

It has been found that, just as with lead alkyls,[3b] the reaction does indeed proceed without appreciable isomerization. This was established by carefully separating the redistribution products and independently synthesizing the expected products for a direct comparison of refractive indexes and infrared spectra.

$$Et_4Si + Pr_4Si \xrightarrow{AlCl_3} Et_4Si + PrSiEt_3 + Pr_2SiEt_2 + Pr_3SiEt + Pr_4Si$$

Fractional distillation of the redistribution product from equimolar amounts of tetraethylsilane and tetra-*n*-propylsilane gave three major boiling point plateaus and two less well-defined plateaus corresponding to the five tetraalkylsilanes expected. This was of little significance with regard to possible isomerization because the literature showed that *n*-propyl- and isopropylsilane isomers boil within 1° of each other. Refractive index proved to be a satisfactory criterion; isopropylsilanes have refractive indexes 0.003 unit per isopropyl group higher than their *n*-propyl isomers. Infrared spectra provided a more sensitive criterion; it was found that *n*-propylsilanes show a characteristic absorption at 7.50 μ which is not exhibited by isopropyl compounds while the latter show a characteristic absorption at 11.37 μ which is not exhibited by *n*-propyl compounds. The refractive indexes and the infrared spectra of the redistribution products were the same as those of the authentic compounds prepared by conventional methods. No evidence for isopropyl derivatives was found even in the interfractions. These results show that no appreciable, *i.e.*, less than 3–5%, isomerization occurred.

Experimental

Di-*n*-propyldiethylsilane.—The intermediate di-*n*-propyldichlorosilane,[6] b.p. 170° at 730 mm., was prepared conventionally in 35% yield from silicon tetrachloride and *n*-propylmagnesium bromide in ether. Addition of an ether solution of 0.94 mole of the dichlorosilane to 3.5 moles of ethylmagnesium bromide was followed by distillation of the ether, heating of the residue at 100° for 16 hours, hydrolysis of the residue, and distillation of the liberated ether. The crude product was washed twice with cold concentrated sulfuric acid, then with water, dilute ammonium hydroxide and finally water again. After being dried with anhydrous sodium sulfate, the crude product was fractionally distilled, and there was obtained 110 g. (0.64 mole, 68% yield) of di-*n*-propyldiethylsilane, b.p. 185–186° at atmospheric pressure, $n^{20}D$ 1.4338–41. The product was freed of an aromatic odor with activated alumina, and the following

---

(1) Paper 46 in a series on organosilicon compounds. For paper 45, W. D. English and L. H. Sommer, This Journal, **77**, 170 (1955).

(2) Deceased.

(3) (a) G. Calingaert and H. A. Beatty, This Journal, **61**, 2748 (1939); (b) G. Calingaert, H. A. Beatty and H. Soroos, *ibid.*, **62**, 1099 (1940); (c) G. Calingaert, H. Soroos and H. Shapiro, *ibid.*, **62**, 1104 (1940); for a general treatment of redistribution reactions see G. Calingaert and H. A. Beatty in Gilman's "Organic Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 1806–1826.

(4) G. Calingaert, H. Soroos and V. Hnizda, This Journal, **62**, 1107 (1940).

(5) (a) R. O. Sauer and E. M. Hadsell, *ibid.*, **70**, 3590 (1948); (b) P. D. Zemany and F. P. Price, *ibid.*, **70**, 4222 (1948); (c) R. O. Sauer, U. S. Patent 2,647,136 (July 28, 1953); (d) A. J. Barry and J. W. Gilkey, U. S. Patent 2,647,912 (August 4, 1953).

(6) A. Bygden, Inaugural Dissertation, Uppsala, Sweden, 1916; *C. A.*, **14**, 1974 (1920).

properties were determined[7]: d^0 0.7907, d^{20} 0.7764, n^{20}_D 1.4339, b.p. 89.8° (30 mm.), b.p. 109.6° (66 mm.), b.p. 124.4° (115 mm.), b.p. 148.0° (248 mm.), b.p. 163.0° (383 mm.), b.p. 187.4 (731 mm.), calculated b.p. 189.3° (760 mm.), infrared spectrum #2054.

Anal. Calcd. for $C_{10}H_{24}Si$: C, 69.66; H, 14.03; *MR*D,[8] 58.06. Found: C, 71.0; H, 14.4; *MR*D, 57.83.

Tri-*n*-propylethylsilane.—This compound was similarly prepared by reaction 166 g. (1.0 mole) of ethyltrichlorosilane with 3.8 moles of *n*-propylmagnesium bromide in one liter of ether. Fractional distillation of the dried crude product gave 94 g. (0.51 mole, 51% yield) of tri-*n*-propylethylsilane[9]; b.p. 202–202.5° at atmospheric pressure, n^{20}_D 1.4361–3. The product was freed of a pungent odor with activated alumina and decolorizing carbon and the following properties were determined[7]: d^0 0.7936, d^{20} 0.7795, n^{20}_D 1.4362, b.p. 104.8° (33 mm.), b.p. 129.0° (90 mm.), b.p. 151.4° (181 mm.), b.p. 164.4 (264 mm.), b.p. 179.4 (406 mm.), b.p. 202.2 (732 mm.), calculated b.p. 204.3° (760 mm.), infrared spectrum #2053.

Anal. Calcd. for $C_{11}H_{26}Si$: C, 70.87; H, 14.06; *MR*D,[9] 62.69. Found: C, 71.2; H, 14.4; *MR*D, 62.55.

Other Tetraalkylsilanes.—The other compounds needed in this investigation were well known[7] and were prepared by the Grignard reaction: tetraethylsilane, n^{20}_D 1.4269, infrared spectrum #2056; *n*-propyltriethylsilane, n^{20}_D 1.4313, infrared spectrum #2057; tetra-*n*-propylsilane, n^{20}_D 1.4384,[10] infrared spectrum #2055. Samples of triisopropylsilane and triisopropylphenylsilane were kindly loaned to us by Dr. Henry Gilman[11] for determination of their infrared spectra, #2589 and 2584, respectively.

Purification of Tetraalkylsilanes.—Many of the highly refined tetraalkylsilanes prepared during this and a previous investigation[7] possessed pungent, terpene-like odors. It was found possible to remove these odors by treatment with Norit A decolorizing carbon black; less effective were activated alumina and silica gel. $MeSiEt_3$ and Et_4Si retained a mild camphor odor through many treatments with absorbents. The pungent, terpene-like odors were apparently due to traces of decomposition products formed upon refluxing for several hours above about 150° in the presence of air; deodorized samples subjected to this treatment reacquired the pungent, terpene-like odor. This behavior was noted with $PrSiEt_3$, $BuSiEt_3$, $AmSiEt_3$, *n*-$C_6H_{13}SiEt_3$, *n*-$C_7H_{15}SiEt_3$, Pr_2SiEt_2, Pr_3SiEt and *n*-$C_7H_{15}SiMe_3$. Presence or absence of odors had no perceptible effects on physical properties.

Redistribution of Et_4Si and Pr_4Si.—In a 100-ml., round-bottom flask was placed 20.2 g. (0.14 mole) of tetraethylsilane and 30.1 g. (0.15 mole) of tetra-*n*-propylsilane together with 1.2 g. (0.009 mole) of C.P. anhydrous aluminum chloride. The reaction mixture turned yellow and then colorless during a five-hour reflux period at 175–180° after which it was found to have incurred no weight loss. The crude product was washed twice with water and dried over Drierite and anhydrous K_2CO_3. Fractional distillation in a Piros–Glover spinning band column gave the five products corresponding to Et_4Si, $PrSiEt_3$, Pr_2SiEt_2, Pr_3SiEt and Pr_4Si which by calculation from the distillation curve were obtained in 5, 24, 39, 26 and 7 mole % yields, respectively; these values agree well with those obtained previously both theoretically and experimentally.[4] The infrared spectra of many of the fractions, including some inter-fractions, were kindly determined by C. A. Hirt of the General Electric Research Laboratory with a Perkin-Elmer Recording Infrared Spectrophotometer. These were compared with the reference curves which were also determined by Mr. Hirt using 0.03-mm. cells, except for the isopropyl compounds which were done in 0.017–0.019 mm. cells. The infrared spectra of the redistribution products were the same as those of the reference compounds. None of the redistribution product fractions showed the absorption band at 11.37 μ characteristic of isopropylsilanes, even though it is a very strong band.

COLLEGE OF CHEMISTRY AND PHYSICS
THE PENNSYLVANIA STATE UNIVERSITY
STATE COLLEGE, PENNSYLVANIA

---

[7] The methods have been described: F. C. Whitmore, L. H. Sommer, P. D. George, W. A. Strong, R. E. Van Strien, D. L. Bailey, H. K. Hall, E. W. Pietrusza and G. T. Kerr, THIS JOURNAL, **68**, 475 (1946).

[8] Calculated with bond refractions given by K. G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940), and by E. L. Warrick, THIS JOURNAL, **68**, 2455 (1946). Similar results may be obtained by the method of R. O. Sauer, *ibid.*, **68**, 954 (1946).

[9] A. D. Petrov and V. F. Mironov, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk*, **4**, 635 (1952); *C. A.*, **47**, 10471f (1953), and **48**, 4462h (1954). These workers obtained the compound from ethylmagnesium bromide and 2-bromopropyltri-*n*-propylsilane through a beta-elimination reaction; their product had b.p. 207–210 (748 mm.), n^{20}_D 1.4375, d^{20} 0.7824.

[10] This refractive index has not previously been reported. Used with d^{20} 0.7845 (S. Sugden and H. Wilkins, *J. Chem. Soc.*, 126 (1931)) it gives *MR*D 67.07 compared with calcd.[9] *MR*D 67.32.

[11] H. Gilman and R. N. Clark, THIS JOURNAL, **69**, 1499 (1947).

On the Sublimation of Amino Acids and Peptides

BY D. GROSS AND G. GRODSKY

RECEIVED NOVEMBER 16, 1954

Kempf,[1] Werner,[2] and Brown[3] have studied the sublimation of some amino acids. These reports, along with others,[4–6] however, have included little information on the recovery, extent of decomposition, diketopiperazine formation and change in optical rotation. In view of the possible ease of purification of some radioactive amino acids by sublimation, a large variety of amino acids was investigated for the mentioned properties. In the course of these studies it also was discovered that some peptides were capable of subliming with little decomposition.

Experimental

Chemicals.—The free amino acids and related compounds were commercial preparations which were chromatographically pure, and had optical rotations close to values[7–9] given in the literature. The peptides were obtained from the following sources: Mann Research Labs., N. Y., glycyl-L-leucine, DL-alanyl-DL-norvaline; Fischer Collection, University of California, L-alanyl-L-leucine, leucyl-alanine (configuration unknown); H. M. Chemical Co., California, glycyl-glycine; synthetic preparation, L-leucyl-glycine. All chromatographed as single spots, except leucyl-glycine. This was chromatographically identical to a known sample of leucyl-glycine (Mann Research Labs.), but had a trace of leucine which did not interfere with the determinations.

Apparatus and Methods.—The glass sublimation apparatus used had a 7 mm. gap distance between the flat bottom pot (4 cm. dia.) and the glass sleeve (2.5 cm. dia.) which fitted snugly on the water-cooled condenser. The sleeve made the apparatus convenient for manipulation and determination of yield. This size apparatus was convenient for 200 to 500 mg. of amino acid or peptide. The apparatus was heated in a clear oil-bath. A vacuum of 0.3 mm. was used. Sublimation was conducted usually 30–60° above the temperature at which a sublimate first was noted. Sublimation to completion usually took two to three hours, though the majority of the material sublimed in a shorter period. The sublimation temperature was determined in this apparatus whose temperature was raised approximately one degree per minute. The table records the initial sublimation temperature and the temperature at which the majority of the sublimate passed over quickly without decomposition.

---

[1] R. Kempf, *J. prakt. Chem.*, [II] **78**, 201 (1908).

[2] O. Werner, *Mikrochemie*, **I**, 33 (1923).

[3] J. Brown, *Trans. Roy. Soc. Canada*, Ser. III, **26**, 177 (1932).

[4] J. F. Scott, R. L. Sinsheimer and J. R. Loofbourow, *Science*, **107**, 302 (1948).

[5] R. Ostwald, P. R. Adams and B. M. Tolbert, THIS JOURNAL, **74**, 2425 (1952).

[6] E. Flynn, J. W. Hinman, E. L. Caron and D. O. Woolf, Jr., *ibid.*, **75**, 5867 (1953).

[7] S. Birnbaum, L. Levintow, R. Kingsley and J. Greenstein, *J. Biol. Chem.*, **194**, 455 (1952).

[8] D. Hamer and J. Greenstein, *ibid.*, **193**, 81 (1951).

[9] J. Gilbert, V. Price and J. Greenstein, *ibid.*, **180**, 473 (1949).