migration of a methyl rather than the neopentyl group in the rearrangement step.

In the distillation of the crude neopentyl alcohol evidence was seen for two by-products (b.p. 81 and 106°) which were not identified. The absence of *t*-amyl alcohol (b.p. 101.8°) was established, however, indicating that the degradation of the hydroperoxide did not occur *via* a neopentylcarbonium ion mechanism, which would undoubtedly result in the formation of some of this alcohol.[9] Yields of distilled neopentyl alcohol were about 40%, based on DIB.

If it is assumed that most of the DIB used up in the process must have been converted initially to hydroperoxide, then it is obvious that only about one-half of the hydroperoxide decomposes according to the mechanism which produces neopentyl alcohol.

Experimental Procedure.—Hydrogen peroxide (30%) (160 g.) was treated with 350 g. of cold sulfuric acid (95%) with vigorous stirring, the temperature being maintained below 25° by an ice-bath. After addition was complete and the temperature of the acid solution had fallen to 5°, DIB (112.2 g. 1 mole) was added over a one-hour period (only one-fourth was added during the first half-hour); the temperature was maintained at 6–8°. After one hour of further stirring, the temperature rose to 10° and after another 20 minutes to 20°. The temperature remained at 20° for 10 minutes and then rapidly returned to 10°. (Caution: The temperature should not be allowed to rise above 25° as there is danger of the reaction becoming uncontrollable; at about 40° the contents may be sprayed or blown from the flask. Vigorous stirring and good cooling are essential.) At this point, the reaction was considered complete, and a drop of the reaction mixture when added to a potassium iodide–glacial acetic acid solution liberated little if any iodine. The product was filtered, cold, on a sintered glass funnel with suction to remove the crystalline acetone peroxide. The lower acid layer of the filtrate was then run into cracked ice (100 g.) and water (350 g.). The neopentyl alcohol concentrate which formed (70.0 g.) was removed. To the diluted acid layer was added an equal volume of a saturated ammonium sulfate solution, and the resulting solution then was extracted with ether. The ether extracts were combined with the alcohol concentrate, the ethereal solution washed with sodium carbonate solution, dried over anhydrous sodium sulfate, and concentrated.

The crude neopentyl alcohol was distilled on a small (1.2 × 30 cm.) helices-packed column at atmospheric pressure. Hot water was circulated through the take-off condenser during distillation to prevent crystallization of the neopentyl alcohol (b.p. 110–111°; lit. 110–111°,[10,11] 111° (730 mm.)[12]); 37.0 g., or a yield of 42% based on the DIB, was obtained. The neopentyl alcohol was redistilled and a heart-cut of the distillate was twice sublimed at 0.5 mm. and room temperature to obtain a prime sample (m.p. 54.5–55.5°, lit.[11] 55–56°).

The organic layer (10.5 g.) remaining from the original reaction mixture and containing mostly DIB was now washed with aqueous sodium carbonate and dried over anhydrous sodium sulfate. After removal of the unreacted DIB by distillation, a 2,4-dinitrophenylhydrazone derivative was prepared from the residue. This was shown to be identical with the same derivative prepared from an authentic sample of methyl neopentyl ketone by its melting point (100.5 to 101.5°, lit.[13] 101–102°); a mixed melting of the two derivatives showed no depression.

The crystalline acetone peroxide (27.2 g.) isolated from the reaction mixture by filtration, was washed thoroughly with water, then with a small amount of alcohol and finally with benzene. Upon sublimation *in vacuo* at room temperature, a crystalline material having a melting point of 132–133° was obtained (lit. for acetone peroxide, m.p. 132–133°,[5] 132°[14]).

Acknowledgment.—Thanks go to Dr. Kenneth W. Greenlee for his continual interest and ready coöperation in extending the facilities of the American Petroleum Institute Research Project 45.

---

[9] F. C. Whitmore, THIS JOURNAL, **54**, 3274 (1932).

[10] H. Adkins and R. E. Burks, Jr., *ibid.*, **70**, 4174 (1948).

[11] A. Scattergood, W. H. Miller and J. Gammon, Jr., *ibid.*, **67**, 2150 (1945).

[12] L. H. Sommer, H. D. Blankman and P. C. Miller, *ibid.*, **76**, 803 (1954); appeared since the work presently described was completed.

[13] H. Baldock, N. Levy and C. W. Scaife, *J. Chem. Soc.*, 2627 (1949).

[14] A. Rieche and K. Koch, *Ber.*, **75B**, 1016 (1942).

DEPARTMENT OF CHEMISTRY
THE OHIO STATE UNIVERSITY
COLUMBUS 10, OHIO

The Preparation of Tetra-*t*-butoxysilane and Tri-*t*-butoxyfluorosilane

BY J. FRANKLIN HYDE AND JAMES W. CURRY

RECEIVED JANUARY 15, 1955

Previously reported attempts to synthesize tetra-*t*-butoxysilane have not been successful, or at least have not been fully documented.[1] Ridge and Todd[2] treated silicon tetrachloride with the various isomeric butyl alcohols and found that the yield of tetralkoxysilane is nil when *t*-butyl alcohol is used. They showed that *t*-butyl chloride and silica are the products of this reaction. This behavior appears to be characteristic of tertiary alcohols,[3] the result being that *t*-alkoxysilanes cannot be prepared by the normal, unmodified procedure involving alcoholysis of chlorosilanes.[4]

Miner and co-workers treated silicon tetrachloride with *t*-butyl alcohol in the presence of pyridine and isolated di-*t*-butoxydichlorosilane as the product of the reaction.[5,6] They then subjected this compound to the action of additional *t*-butyl alcohol, again in the presence of pyridine, and obtained tri-*t*-butoxychlorosilane. Under these conditions they were unable to cause replacement of the fourth chlorine atom by the *t*-butoxy group.

Backer and Klasens[7] obtained tri-*t*-butoxychlorosilane from sodium *t*-butoxide and silicon tetrachloride in refluxing petroleum ether. When they treated the tri-*t*-butoxy compound with an excess of sodium *t*-butoxide in a sealed tube for 15 hours at 170°, they found the reaction products to be sodium tri-*t*-butoxysilanolate and hexa-*t*-butoxydisiloxane. They were unable to isolate any tetra-*t*-butoxysilane. The only product which could be identified by Hyde and Kookootsedes[8] when they

---

[1] H. Breederveld and H. I. Waterman, *Rec. trav. chim.*, **72**, 166 (1953). In this paper there is a very brief mention of the successful synthesis of tetra-*t*-butoxysilane from tri-*t*-butoxybromosilane and sodium *t*-butoxide. However, physical data and a complete description of the synthesis were not reported. NOTE ADDED IN PROOF.—After this manuscript had been submitted for publication, it was learned that Breederveld and Waterman had published recently their synthesis of tetra-*t*-butoxysilane (H. Breederveld and H. I. Waterman, *Rec. trav. chim.*, **73**, 871 (1954)).

[2] D. Ridge and M. Todd, *J. Chem. Soc.*, 2637 (1949).

[3] W. Gerrard and A. H. Woodhead, *ibid.*, 519 (1951).

[4] D. C. Bradley, R. C. Mehrotra and J. W. Wardlaw, *ibid.*, 4204 (1952).

[5] G. W. Pedlow, Jr., and C. S. Miner, Jr. (to Minnesota Mining and Manufacturing Co.), U. S. Patents 2,566,364 and 2,566,365, September 4, 1951.

[6] C. S. Miner, Jr., L. A. Bryan, R. P. Holysz, Jr., and G. W. Pedlow, Jr., *Ind. Eng. Chem.*, **39**, 1368 (1947).

[7] H. J. Backer and H. A. Klasens, *Rec. trav. chim.*, **61**, 500 (1942).

[8] J. F. Hyde and G. J. Kookootsedes, unpublished data.

treated silicon tetrachloride with sodium *t*-butoxide under various conditions was tri-*t*-butoxychlorosilane.

While other investigators have been able to effect the attachment of a fourth *t*-butoxy group to silicon only after considerable effort, they have been able to synthesize, with comparative ease, several tri-*t*-butoxyalkoxysilanes from the monochlorosilane and the sodium alkoxides of sterically less hindered alcohols. Thus, Backer and Klasens[7] have synthesized tetralkoxysilanes in which the fourth group is ethoxy or isopropoxy, and Breederveld and Waterman[1] have prepared similar compounds containing 1-ethylpropoxy and cyclohexyloxy groups.

The successful synthesis of tetra-*t*-butoxysilane reported herein depended upon the unique behavior exhibited by silicon tetrafluoride toward alcohols.[9] Contrary to the marked reactivity shown by other silicon halides, silicon tetrafluoride dissolves readily in all of the lower alcohols at room temperature with but slight evidence of reaction.[10,11] Unstable complexes of the type $SiF_4 \cdot 4ROH$[12] are evidently formed, which decompose when heated, liberating some silicon tetrafluoride.

The method of synthesis was similar to that used by Klippert[13] for the preparation of tetraethoxysilane, namely, the reaction of silicon tetrafluoride with a sodium alkoxide. In order to obtain a high yield of the fluorine-free product, it was found necessary to use a smaller excess of silicon tetrafluoride, and to reflux the reaction mixture for an extended period of time once the addition of the gaseous fluoride had been completed. Unless these conditions were employed, tri-*t*-butoxyfluorosilane became the major product of the reaction, although the total over-all yield of both products was lower. It is possible to account for the preponderance of the monofluorinated product under the less favorable conditions by assuming that the excess silicon tetrafluoride reacts with the tetra-*t*-butoxysilane present in the reaction mixture. A similar interaction is known to occur when tetraethoxysilane is treated with silicon tetrafluoride.[11]

The hydrolytic behavior of the monofluorinated material seemed interesting. The Si–F linkage was only partially hydrolyzed initially by 0.1 *N* sodium hydroxide, but when the alcoholic solution of the compound was allowed to stand overnight in the presence of excess dilute alkali, complete hydrolysis took place. It is likely that this effect can be accounted for, at least in part, by steric factors.

Experimental

Tetra-*t*-butoxysilane.—Sodium *t*-butoxide was prepared from 57.5 g. (2.50 gram atoms) of sodium and 1.5 l. of *t*-butyl alcohol, freshly dried by distillation from sodium metal.[14] The mixture was stirred under reflux for 20 hours, then cooled slightly to just below reflux temperature. Silicon tetrafluoride (1.50 moles) was prepared by a modification of the procedure of Hyde and Domicone.[11] To a mixture of 178.0 g. (1.00 mole) of ammonium fluosilicate and 30.0 g. (0.50 mole) of powdered silica contained in a lead reactor was added 222.0 g. (2.14 moles, 120 ml.) of 95% sulfuric acid, dropwise over a period of 6 hours. The gas so generated was passed through a Dry Ice trap and then into the hot, stirred solution of sodium *t*-butoxide. After the addition had been completed, the reaction mixture was stirred under reflux for 112 hours, then tested with *p*H paper and found to be neutral. After filtering to remove solid inorganic fluorides, the mixture was distilled at atmospheric pressure to recover the excess *t*-butyl alcohol. The residue was fractionally distilled under reduced pressure. Five fractions were obtained, each of which was refractionated carefully to afford tetra-*t*-butoxysilane, b.p. 105–105.5° (15 mm.), m.p. 56.5–57° (uncor.), yield 103.2 g. (51.6%). The infrared spectrum showed a band at 9.37 μ, characteristic of Si–O absorption. No Si–F absorption was noted.

Anal. Calcd. for $C_{16}H_{36}O_4Si$: C, 59.95; H, 11.32; Si, 8.75; mol. wt., 320.5. Found: C, 60.6; H, 11.7; Si, 8.76; mol. wt. (cryoscopic, in benzene), 330.4.

There also was obtained a small amount of impure tri-*t*-butoxyfluorosilane (see below), yield 9.0 g. (4.1%).

Tri-*t*-butoxyfluorosilane.—The same general procedure was used. Important variations involved the use of a larger excess of silicon tetrafluoride (0.75 mole for 1.00 mole of sodium *t*-butoxide) and the omission of the extended refluxing period following the addition of the silicon tetrafluoride. From the reaction mixture there was obtained tri-*t*-butoxyfluorosilane, b.p. 78.5–80.5° (15 mm.), n^{25}_{D} 1.3831, d^{25}_{4} 0.9054, yield 17.9 g. (20.2%). The infrared spectrum showed absorption bands at 9.25 and 11.35 μ, characteristic of Si–O and Si–F absorption, respectively.

Anal. Calcd. for $C_{12}H_{27}FO_3Si$: C, 54.10; Si, 10.53; F, 7.13; mol. wt., 266.4; MR_D, 68.51.[15] Found: C, 53.0; Si, 10.62; F, 7.00; mol. wt. (cryoscopic, in benzene), 272.3; MR_D, 68.66.

A lesser amount of impure tetra-*t*-butoxysilane was isolated also, yield 10.7 g. (13.4%).

Acknowledgments.—The authors wish to thank Mr. Arnold Kolb and Dr. Lee Smith for carrying out the analytical phases of this work.

DOW CORNING CORPORATION
MIDLAND, MICHIGAN

---

[9] W. Knop, *J. prakt. Chem.*, [1] **74**, 41 (1858).

[10] G. Tarbutton, E. P. Egan, Jr., and S. G. Frary, THIS JOURNAL, **61**, 2555 (1939).

[11] J. F. Hyde and J. J. Domicone, unpublished data.

[12] A. V. Topchiev and N. F. Bogomolova, *Doklady Akad. Nauk S.S.S.R.*, **88**, 487 (1953).

[13] L. Klippert, *Ber.*, **8**, 713 (1875).

[14] W. S. Johnson and G. H. Daub, in "Organic Reactions," Vol. 6, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 44.

[15] Calculated from bond refractivities listed in the following references: K. G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940), and A. I. Vogel, W. T. Cresswell and J. Leicester, *J. Phys. Chem.*, **58**, 174 (1954).

Regeneration of Sugars from Anilides and Sugar Acids from Phenylhydrazides[1]

BY G. W. HUFFMAN AND F. SMITH

RECEIVED JANUARY 6, 1955

The anilides of sugars and the phenylhydrazides of sugar acids have long been used for purposes of characterization and purification and not infrequently it becomes necessary to recover the parent sugar or sugar acid from these derivatives. Usually the recovery entails cleavage of the anilide or phenylhydrazide with dilute mineral acid followed by neutralization of the mineral acid, extraction of the base and finally isolation of the sugar or sugar acid.

It has been shown previously that acids acting in solution as catalysts for acetal formation can be replaced satisfactorily by insoluble acids in the form of cation exchange resins.[2–4]

---

[1] Paper No. 3298, Scientific Journal Series, Minnesota Agricultural Experiment Station.

[2] J. E. Cadotte, F. Smith and D. Spriestersbach, THIS JOURNAL, **74**, 1501 (1952).

[3] F. Smith and D. Spriestersbach, *ibid.*, **76**, 4191 (1954).

[4] W. H. Wadman, *J. Chem. Soc.*, 3051 (1952).