emitted from one reaction such as step 5. In the former case, a little absorbed light in the initiating step will introduce a few carriers which upon entering the branched chain will have relatively enormous effects. The fact that boron hydrides decompose when exposed to ultraviolet light is in favor of such a postulate. However, a few experiments made in a spherical quartz bulb under irradiation from a mercury arc failed to produce any marked effect on the rate of disappearance of luminescence. Also pentaborane shows no marked absorption of light in the ultraviolet. The light observed in this reaction was in the visible, bluish in color; however, there is no reason to suppose that this is the only wave length emitted. There must be a whole series of rapid oxidative steps subsequent to that indicated in equation (6), each of which may emit its own characteristic wave length. Thus while equation (6) represents the rate-controlling oxidation and hence the rate of production of light it is quite possible that a whole series of frequencies actually is emitted. In the latter case, if the reaction emitting and absorbing light were the reversible equilibrium shown by equation (5), then the time dependence of luminosity has the correct form. Furthermore, in this case, it is unnecessary to assume light absorption in the initiating step, 4. The difficulty encountered here is that the intermediate, Y, would have to be in equilibrium with the light emitted. Also solution of the equations indicates that the explosion limit expression, 2, should depend on the luminosity.

The work presented and discussed in this paper is admittedly far from complete and many points need further investigation before a definite mechanism can be proposed. However, the author believes that the current interest in the boron hydrides warrants presentation of the data as a stimulus to future investigation of this interesting reaction.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BLACKBURN COLLEGE]

Alkyliodosilanes: Ethyl Series and Monododecyl

BY HERBERT H. ANDERSON,* DONALD L. SEATON AND RICHARD P. T. RUDNICKI

This paper describes four alkyliodosilanes: new ethyltriiodosilane, diethyldiiodosilane, triethyliodosilane and new monododecyltriiodosilane. Triethyliodosilane is prepared through a Grignard reaction, while the other three are made from the appropriate alkylchlorosilane and aniline, followed by hydrogen iodide. Phosphorus triiodide and tetraethoxysilane when heated furnish ethyl iodide rather than ethoxyiodosilanes. **Even distillation at low pressure does not yield methoxyiodosilanes or ethoxyiodosilanes after treating an alkoxychlorosilane first with aniline and later with hydrogen iodide.**

Whitmore and co-authors had already prepared trimethyliodosilane.[1] Moreover, the existence of all three iodofluorosilanes[2] indicated the stability of all three ethyliodosilanes, now confirmed herein.

Preparation of Alkyliodosilanes.—In the Whitmore method[2] trimethylchlorosilane and the phenyl Grignard reagent yield trimethylphenylsilane, which then reacts with iodine to give trimethyliodosilane and iodobenzene. However, the boiling point of 189° for iodobenzene is too close to that of triethyliodosilane, 193°, for use of an analogous reaction between triethylphenylsilane and iodine.

Ethyltriiodosilane, diethyldiiodosilane and dodecyltriiodosilane were prepared by the Ruff[3] method, wherein he converted trichlorosilane ultimately into triiodosilane. Aniline reacted with the halosilane in a benzene solution; after filtering and washing of the precipitated anilinium chloride, anhydrous hydrogen iodide was passed into the resultant benzene solution; anilinium iodide precipitated and the desired iodosilane was left in benzene solution; distillation followed.

Our chief precautions were: the use of 2.30 mols of aniline per mol of chlorine in the original alkylchlorosilane, with occasional agitation and storage for 20 hours; after filtering anilinium chloride, to test a small portion of filtrate with fresh aniline to check completeness of precipitation; a five-hour passage of gaseous hydrogen iodide[4] into the filtrate, using a system provided with ground joints or closely fitting rubber connections, and also provided with three bulbs containing phosphorus pentoxide; protected filtration of the anilinium iodide and a second passage of hydrogen iodide to check completion of precipitation; all distillations, including that of the solvent benzene, in equipment with ground joints; the chief physical measurements on the day of final purification of each compound; distillation finally in the presence of copper powder.

Triethyliodosilane could not be obtained by the Ruff method from the corresponding chloride, nor from triethylphenylsilane and iodine. It was prepared, in two sections, starting with a total of 120 g. of pure diethyldiiodosilane and 0.41 mol of ethylmagnesium iodide, in anhydrous ether. After standing for 12 hours, during which slight warming occurred, two ether layers were found, the lower of which crystallized in an ice-bath, and was magnesium iodide (with some ether). The crude product consisted of 16 ml. of tetraethylsilane and 9 ml. of triethyliodosilane; thereupon, further distillation several times yielded a final center fraction boiling at 191.5–192.5° uncorrected.

Chemical and Physical Properties.—Ethyltriiodosilane hydrolyzes the most rapidly and vigorously; diethyldiiodosilane hydrolyzes rapidly; triethyliodosilane hydrolyzes readily, although less so than the first two, yet much more easily than the corresponding isocyanate, triethylsilicon isocyanate. All three ethylsilicon iodides are colorless, mobile liquids which fume readily in moist air; dodecyltriiodosilane is colorless, but is somewhat more viscous and does not fume so readily. These four iodides may be kept colorless only in a sealed tube bearing some copper powder; even the determinations of density involved more than usual difficulty.[5] Measurements of refractive index in an Abbe refractometer were impossible in air of 70% humidity.

Analyses.—Many investigators have weighed samples of organosilicon halides and then titrated the available acidity; it has been found possible to use self-filling micropipets for the analysis of certain of these compounds *without weighing the samples*.[6] Several precautions are mandatory with the iodides, however; there is a tendency to lose acidity. A very-thin-walled, soft glass tube holding a weighed sample of the alkyliodosilane was placed in the neck

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(1) F. C. Whitmore and others, THIS JOURNAL, **70**, 433 (1948).

(2) H. H. Anderson, *ibid.*, **72**, 3091 (1950).

(3) O. Ruff, *Ber.*, **41**, 3738 (1908).

(4) To prepare anhydrous hydrogen iodide, one should use water and a mixture of phosphorus and iodine in the atomic ratio of one to five—equivalent to a hypothetical phosphorus pentaiodide, rather than our actual ratio of one to three, which could give traces of phosphonium iodide.

(5) H. H. Anderson, *Anal. Chem.*, **20**, 1241 (1948); see Fig. 2.

(6) H. H. Anderson, THIS JOURNAL, **71**, 1801 (1949). See Table II.

TABLE I

PROPERTIES OF NEW ALKYLIODOSILANES

Compound	°C.	d^{20}_4	Mol. wt. (Dumas) Found	Mol. wt. (Dumas) Calcd.	I, % Found	I, % Calcd.	Distillation range °C., uncor.	Distillation range Mm.
Et_4Si	153.7[a]	0.7662[b]	...	...	....		....	
Et_3SiI	193 ± 1	1.333	235	242	52.0, 52.8	52.4	191.5–192.5	760
Et_2SiI_2	221 ± 1	2.009	350	340	74.5, 74.9	74.6	149–150	102
$EtSiI_3$	251 ± 1	2.748	450	438	87.2, 86.3	86.9	112.5–113.5	10
SiI_4	290[c]	....	...		....		....	
$C_{12}H_{25}SiI_3$	389 ± 2	1.744	...		67.5	66.0	199–202	3

[a] R. N. Lewis and A. E. Newkirk, THIS JOURNAL, **69**, 701 (1947). Value listed. [b] F. C. Whitmore and others, *ibid.*, **68**, 475 (1946). [c] Value generally accepted.

of a special round-bottom flask of appropriate size, in which there was approximately double the theoretical equivalence of ethanolic sodium hydroxide solution; after closing the stopper, a special ground joint, the entire system was shaken most vigorously until the thin capsule holding the sample had shattered. In this method the excess of base reacted quite rapidly with the hydrogen iodide and thus prevented a reaction between ethanol and hydriodic acid. Thereupon the excess of base was titrated in the presence of a universal indicator, finally crushing the fragile soft glass tube completely just before the end-point. Because the alcoholysis product was insoluble in ethanol, the acidity from dodecyltriiodosilane could be approximated closely only after an extended period of extremely vigorous agitation.

Alkoxyiodosilanes.—Persistent attempts to convert methoxychlorosilanes or ethoxychlorosilanes by the Ruff method into the corresponding alkoxyiodosilanes never yielded any definite product which boiled at a fixed low pressure, such as 10 mm. Moreover, 100 g. of phosphorus triiodide and 40 g. of tetraethoxysilane upon heating furnished 15 g. of ethyl iodide, boiling at 72.5°, rather than an ethoxyiodosilane; triethoxyiodosilane should boil at approximately 200°. Despite all this, alkoxyiodosilanes may enjoy a limited stability at 30° or so.

Discussion

(1) Alkyliodosilanes are far more reactive toward water than are the alkylbromosilanes, alkylchlorosilanes and alkylfluorosilanes; this factor makes the handling and analysis of the iodine compounds the most difficult of all.

(2) Our boiling points for triethyliodosilane and diethyldiiodosilane are in good agreement with those of Eaborn, who lists 190.5° (744 mm.) and 220–221°, respectively.[7]

(3) All-in-all, the Ruff method[3] is probably the best for alkyltriiodosilanes and dialkyldiiodosilanes; it is shorter than the Eaborn process,[7] especially for dialkyldiiodosilanes.

(4) Other information regarding alkyliodosilanes has been submitted for publication. Alkylanilinosilanes are stable compounds; six are now (March, 1951) known, and will be described later. This information explains difficulties encountered in the Ruff process—especially with trialkylhalogenosilanes.

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[7] C. Eaborn, *J. Chem. Soc.*, 2760 (1949).

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Preparation and Physical Properties of a Series of *n*-Alkanes

BY ARTHUR K. DOOLITTLE AND ROLAND H. PETERSON

Ten *n*-paraffin hydrocarbons covering a molecular weight range of 72 to 900 were prepared by conventional synthetic methods. Most of the preparations were of high purity and their freezing points, refractive indices and densities (the last over the temperature range −10 to 300°) were carefully determined as criteria of their purity. The viscosities of the hydrocarbons were measured with great precision from −10 to 300° for the purpose of testing the validity of certain viscosity relationships over a greater range of temperature and molecular weights than heretofore possible. The results of this analysis will be published elsewhere. The estimation of the errors in viscosity measurements is discussed and a maximum probable error assigned to each viscosity measurement.

The studies here described were undertaken to appraise certain viscosity relationships for liquids over ranges of temperature and of molecular weights (in homologous series) greater than have been possible with data heretofore available. In order to provide the simplest conditions for the study of Newtonian flow, as free as possible from complications due to association and from uncertainties in regard to molecular weight and molecular weight distribution, the study was made with pure members of the homologous series of normal paraffins. Ten members of this series ranging from *n*-pentane (m = 72) to *n*-tetrahexacontane (m = 900) were synthesized, and their viscosities and densities measured with great accuracy at atmospheric pressure over a range of temperatures between −10 and 300°.

Preparation of Hydrocarbons

***n*-Pentane** was prepared by hydrogenolysis of pure hexanol-1 after the method of Adkins[1] wherein the alcohol is treated with hydrogen at 250° and 3000 p.s.i. in the presence of Raney nickel. In contrast to higher alcohols, very poor yields resulted unless an equal quantity of heptane was included in the bomb charge. Under these conditions 40% yields were realized. Distillation of several bomb charges yielded a liter of crude pentane which was refractionated after washing with concd. sulfuric acid. Heart cuts of identical densities (±0.00002 g./cm.^{3}) were retained for study.

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[1] H. Adkins, "Reactions of Hydrogen," University of Wisconsin Press, Madison, Wis., 1937, pp. 79–80.