TABLE I

THE COMPOSITION OF CUPRIETHYLENEDIAMINE INITIALLY AND AT THE END OF AN ELECTROPHORESIS RUN

Cupriethylenediamine solution	Cu, g./l.	N, g./l.
Initial	6.35	5.64
Anode chamber after 1300 minutes	6.25	5.51
Cathode chamber after 1300 minutes	5.37	5.90

A descending boundary quite different from the preceding in appearance was obtained with hydrolyzed cotton cellulose. Shown in Fig. 2 are initial and 1,352 minute boundaries for a hydrocellulose produced by autoclaving mercerized Empire cotton fiber with 0.5 *N* aqueous hydrochloric acid for 2 hours at 120°; the intrinsic viscosity of this preparation was 0.52 in cuprammonium. The descending boundary developed two peaks, corresponding to mobilities of 0.57 and 0.91 × 10^{-5} sq. cm./volt/sec. Not only the mobilities of the peaks but the distribution of material appears to be different from those of the methanolyzed sample.

Fig. 2.—The initial and 1352-minute descending boundaries for hydrolyzed cotton cellulose; 0.5% concentration in 0.1 *N* cupriethylenediamine solution: current, 30.5 ma.; field strength, 2.97 v./cm.

In an attempt to enhance the rate of anodic migration of the hydrocellulose the reducing end groups of the above preparation were oxidized at 0° with sodium hypoiodite solution buffered to *p*H 10.6, conditions favorable for producing end-group carboxyls. Titration of the acid form of the oxidized material showed the presence of 0.061 mole of carboxyl per gram. This oxidized hydrocellulose, subjected to electrophoresis, gave a descending boundary pattern (Fig. 3) similar to the preceding one; but the mobilities of the two components were greater, 0.71 and 0.99 × 10^{-5} sq. cm./volt/sec., respectively.

Purified Empire cotton fiber, after methanolysis for 96 hours at 15° in methanol containing 0.5 *N* hydrogen chloride, gave a methanolyzed cellulose having an intrinsic viscosity of 1.45 in cuprammonium solution. Two hundred and fifty milligrams of this material was dissolved in 10 ml. of the stock cupriethylenediamine solution and diluted to 50 ml. giving a solution 0.2 molar in copper. This solution was run against solvent of the same concentration and the boundaries were photographed initially and after 2,760 and 4,200 minutes. The descending boundaries are shown in Fig. 4; the mobilities of the slow and fast moving components were calculated to be 0.72 and 0.80 × 10^{-5} sq. cm./volt/sec., respectively.

Native cotton cellulose does not remain dissolved in cupriethylenediamine upon dilution to 0.1 molar copper concentration. However, celluloses having intrinsic viscosities as great as 2.88 in A.C.S. cuprammonium were run successfully with the 0.1 molar cupriethylenediamine. Runs made with 0.2 molar cupriethylenediamine solution yielded results essentially the same as those obtained with the 0.1 molar solvent; hence it is possible that even less degraded celluloses can be investigated with the stronger solvent.

Fig. 3.—The initial and 1400-minute descending boundaries for hypoiodite oxidized hydrolyzed cotton cellulose; 0.5% concentration in 0.1 *N* cupriethylenediamine solution: current, 30 ma.; field strength, 3.01 v./cm.

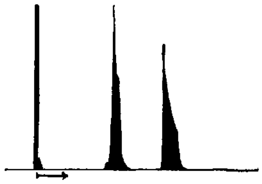

Fig. 4.—The initial, 2760-minute and 4200-minute descending boundaries for a methanolyzed native cotton cellulose; 0.5% concentration in 0.2 *N* cupriethylenediamine solution: current, 30 ma.; field strength 1.74 v./cm.

In the seven other experiments not reported in detail there are indications that increasing ethylenediamine concentration may increase the rate of cellulose migration; also that the mobilities may increase slightly during the course of a run. The latter may be due to oxidative degradation occurring during the experiment, since no particular precautions have yet been employed to exclude air from the system. It should be mentioned that δ and ϵ boundaries were not observed in any of these experiments.

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Alkyliodosilanes: Methyl, Propyl, Butyl and Amyl

BY HERBERT H. ANDERSON

Six new alkyliodosilanes—methyltriiodosilane, dimethyldiiodosilane, *n*-propyltriiodosilane, *i*-propyltriiodosilane, *n*-butyltriiodosilane and *n*-amyltriiodosilane prepared by the Ruff method[1] are described. Some information concerning the reaction of aniline with a variety of silicon halides and pseudo halides is also presented.

Preparation of Compounds.—Our earlier paper[2] describes the synthetic process in detail; the equations are illustrative

$$RSiCl_3 + 6C_6H_5NH_2 \longrightarrow RSi(HNC_6H_5)_3 + 3C_6H_5NH_3Cl \downarrow$$

$$RSi(HNC_6H_5)_3 + 6HI \longrightarrow RSiI_3 + 3C_6H_5NH_3I \downarrow$$

A similar set of equations is valid for dimethyldiiodosilane. The method is not suitable for preparing trialkyliodosilanes.

***n*-Propyltriiodosilane.**—On mixing 43 g. of *n*-propyltrichlorosilane, 170 ml. of aniline and 250 ml. of benzene, there was spontaneous warming from 25 to 68°, and much precipitation took place. The material was processed as described earlier[2] to yield 44 g. of *n*-propyltriiodosilane.

***i*-Propyltriiodosilane.**—An initial temperature rise of only 16°, accompanied by only slight precipitation, occurred when 17 g. of *i*-propyltrichlorosilane, 64 ml. of aniline and 100 ml. of benzene were mixed. Even after three days the precipitate was small; the addition of another 25 ml. of aniline and another period of two days did not force the reaction more than one third of the way to completion, and it was necessary to reflux the mixture two hours to produce proper precipitation. The mixture was allowed to cool overnight, and processed as usual to give 14 g. of *i*-

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

(2) H. H. Anderson, D. L. Seaton and R. P. T. Rudnicki, THIS JOURNAL, **73**, 2144 (1951).

TABLE I

PROPERTIES OF NEW COMPOUNDS

Compound	B.p., °C.	d^{20}_4	Mol. wt. (Dumas) Found	Mol. wt. (Dumas) Calcd.	I, % Found		I, % Calcd.	Distillation range °C. uncor.	Distillation range Mm.
Me_2SiI_2	170 ± 1	2.203	306	312	81.5	81.8	81.3	168.0–168.5	760
$MeSiI_3$	229 ± 1	2.946	401	424	89.4	90.4	89.8	123.5–124.5	69
SiI_4	290[6]	...	...		..	..		....	
n-$PrSiI_3$	268 ± 2	2.552	461	452	84.6	83.6	84.3	142–143	20
i-$PrSiI_3$	267 ± 2	2.563	436	452	83.3	84.1	84.3	135–136	12
n-$BuSiI_3$	284 ± 2	2.400	450	466	81.2		81.5	151–152	12
n-$AmSiI_3$	299.5 ± 2	2.311	495	480	79.5		79.5	151–152	12

propyltriiodosilane, accompanied by 4 g. of a tarry by-product probably produced by hydrolysis.

Dimethyldiiodosilane.—Application of the standard process to 130 g. of purified dimethyldichlorosilane yielded 150 g. of dimethyldiiodosilane. Unless precautions are taken to exclude water this product may be contaminated by cyclic dimethylsiloxanes[3] which boil from 133° upward.

Other Alkyliodosilanes.—For each mole of chlorine in the alkylchlorosilane 2.30 moles of aniline was used; in the first stage the excess of aniline need not be great, but it is advisable to check its presence after filtration; in the reaction with hydrogen iodide it is advisable to filter the supposedly complete precipitate and then pass hydrogen iodide in again for a few minutes. Throughout this work equipment with ground joints was used. All six compounds were distilled in the presence of copper powder and stored in sealed tubes with a small amount of copper powder; yields averaged 60%.

Chemical Properties.—There is much variation in the vigor and in the rate of hydrolysis. In each case the compound was shaken with an equal volume of water at 25°, with the following results: methyltriiodosilane reacts vigorously, with spattering; dimethyldiiodosilane reacts vigorously, but without spattering; n-propyltriiodosilane reacts slowly at first, although vigorously after two minutes; n-butyltriiodosilane reacts vigorously after two minutes; n-amyltriiodosilane does not hydrolyze as easily as the others, and a self-filling micropipet[4] could be used in the analysis; i-propyltriiodosilane reacts quite mildly, with a temperature rise of approximately 10° only. Steric effects may be responsible for the differences between the n-propyl and the isopropyl derivatives. All six alkyliodosilanes react rapidly with ethanol, without any precipitation. The vapors of these compounds are somewhat inflammable at temperatures above the boiling points.

Physical Properties.—All six alkyliodosilanes are colorless mobile liquids. However, they tend to foam during the measurement of the boiling point, which could therefore be determined to one degree only. Because of the ease of hydrolysis, the determination of density was difficult in the usual pycnometer,[4] notably so with the monomethyl derivative. Only triiodofluorosilane and diiododifluorosilane[5] are more difficult to handle.

Analyses.—The method of analysis previously used[2] consisting of solution in excess ethanolic sodium hydroxide solution and back-titration with acid was suitable. All molecular weights were determined by the Dumas method.[6]

Further Study of the Ruff Method.—To establish some of the limitations of the Ruff aniline method,[1] a number of small-scale tests were carried out in benzene solution. Aniline reacts rapidly with $SiCl_4$, $SiBr_4$, $MeSiBr_3$ and $MeSiI_3$, fairly rapidly with $Si(NCO)_4$, n-$BuSi(NCO)_3$ and n-$PrSi(NCS)_3$, the criterion being 40% completion within an hour; aniline and $(C_6H_5)_2Si(NCO)_2$ gave considerable reaction after 15 hours; Et_3SiCl did not react[2] in a clean-cut fashion; aniline and $Et_2Si(NCS)_2$, or $Et_3Si(NCS)$ or $(EtO)_4Si$ did did not react at all.

CARLINVILLE, ILLINOIS RECEIVED JUNE 15, 1950

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[3] M. J. Hunter, J. F. Hyde, E. L. Warrick and H. J. Fletcher, THIS JOURNAL **68**, 667 (1946).

[4] H. H. Anderson, *Anal. Chem.*, **20**, 1241 (1948). See Figs. 2, 4.

[5] H. H. Anderson, THIS JOURNAL, **72**, 2091 (1950).

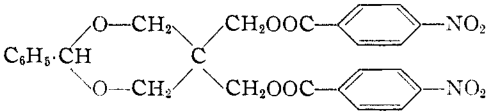
[6] (Added in proof) Since submission of this paper, C. Eaborn, *J. Chem. Soc.*, 3084 (1950) has described Me_2SiI_2 as boiling at 170.0°. The method herein is shorter.

An Unusual Orthoester of Pentaerythritol

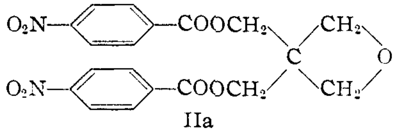
BY ERNST D. BERGMANN, ELIAHU BOGRACHOV AND S. PINCHAS

When benzylidenepentaerythritol di-p-nitrobenzoate (I) is treated with 4-nitrophenylhydrazine or 2,4-dinitrophenylhydrazine and hydrochloric acid in glacial acetic acid, the nitrated phenylhydrazone of benzaldehyde separates and a second crystalline compound is formed, which has not the expected composition of pentaerythritol di-(p-nitrobenzoate),[1] but contains one mole of water less.

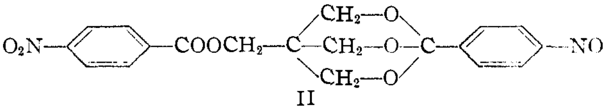
Infrared analysis revealed the absence of free hydroxyl groups, boiling formic acid, acetyl chloride and acetic anhydride caused no reaction, and also the Zerewitinoff analysis gave a negative result. The formula (IIa) of a substituted trimethylene oxide is incompatible with the negative response to acetyl chloride, as Derick and Bissell[1a] have shown trimethylene oxide to yield γ-chloropropyl acetate with this reagent. The infrared spectrum led to the conclusion that the product was an ortho-ester (II); the spectrum is not in accord with (IIa).



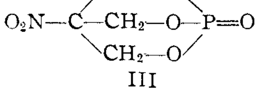
I



IIa



II



III

The spectrum (Fig. 1) shows four absorption bands, at 1178, 1118, 1103 and 1048 cm.$^{-1}$, characteristic of the C–O–C–O–C grouping, *e. g.*, in acetals.[2] In intensity, the third band exceeds even the very high absorption coefficient of the third

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[1] Diesters of pentaerythritol (but not containing nitro-groups in the acid radicals) are known: Barth and Burrell, U. S. Patent 2,356,745 (*C. A.*, **39**, 223 (1945)); Orthner and Freyss, *Ann.*, **484**, 131 (1930).

[1a] Derick and Bissell, THIS JOURNAL, **38**, 2478 (1916).

[2] Anderson and Seyfried, *Anal. Chem.*, **20**, 998 (1948); Boekelheide, *et al.*, THIS JOURNAL, **71**, 3303 (1949); E. Bergmann and Pinchas, *Rec. trav. chim.*, **70**, in press (1951).