tion of the phenylurethan is proof of the secondary alcohol being the compound.

The Phenylurethan of 1,4-Dimethyl-3-(propanol-2)-carbostyril.—This derivative was prepared as described by Shriner and Fuson.[7] The compound was recrystallized from carbon tetrachloride. The m. p. was 178–179°.

Anal. Calcd. for $C_{21}H_{22}N_2O_3$: N, 8.00. Found: N, 8.28, 7.93.

Summary

1. Several N-methyl-α-alkylacetoacetanilides have been prepared by condensation of N-methylacetoacetanilide with the corresponding alkyl halide.

2. Ring closure of the N-methyl-α-alkylacetoacetanilides with concentrated sulfuric acid resulted in the formation of the 1,4-dimethyl-3-alkylcarbostyrils.

3. N-Methyl-α-allylacetoacetanilide when subjected to the sulfuric acid treatment gave the hydrated product, 1,4-dimethyl-3-(propanol-2)-carbostyril.

GREENCASTLE, INDIANA RECEIVED JANUARY 23, 1948

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[7] Ref. 6, p. 136.

[CONTRIBUTION FROM SOUTHERN REGIONAL RESEARCH LABORATORY[1]]

Trimethylsilylcellulose

BY H. A. SCHUYTEN, J. W. WEAVER, J. DAVID REID AND J. F. JURGENS

Silicon tetrachloride and aryl- and alkylhalosilanes react easily and rapidly with organic hydroxyl groups,[2,3,4] to yield hydrogen chloride and silicic esters. A number of patents have been issued dealing with the treatment of cellulose with organosilicon halides to impart water repellency.[5,6,7] In one case[5] a surface reaction either with adsorbed moisture or with hydroxyl groups of the cellulose was postulated. However, the amount of product formed was too small to be measured or analyzed. Jullander[8] has studied the reaction of silicon tetrachloride with nitrocellulose and reports the formation of gels due to cross linkage. The present investigation concerns the reaction of some organo-silanes with cellulose, particularly to obtain trimethylsilylcellulose.

It was found that halosilanes will react with cellulose in the presence of pyridine to form relatively stable compounds. The reaction will take place slowly at room temperature and rapidly at reflux temperatures. A group substitution as high as 2.75 trimethylsilyl groups per glucose unit was attained with cotton linters (Fig. 1). With partially substituted cellulose acetate, the total substitution approached 3.0 (Table I).

TABLE I

REACTIONS OF ALKYLCHLOROSILANES WITH CELLULOSE ACETATE

Reagent	Acetyl groups per glucose Before	After	Mole ratio Silane: Cell-OAc	Silyl groups per glucose by Weight	%Si	Total groups
$(CH_3)_3SiCl$	2.30	2.24	2.79	0.69	0.65	2.89–2.93
$(C_2H_5)_3SiCl$	2.30	2.24[a]	4.08	.66	.58	2.82–2.90
$(CH_3)_3SiCl$	2.90	2.87	4.86	.16	.14	3.01–3.03

[b] Assumed.

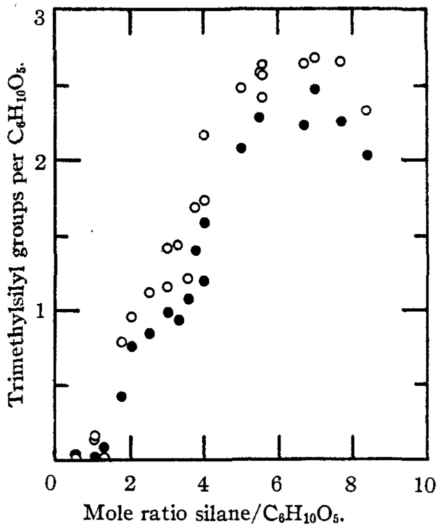

Fig. 1.—Change in trimethylsilyl substitution of cellulose with change in mole ratio of reactants: ○, calculated from gain in weight; ●, calculated from silicon content.

Trimethylsilylcellulose is stable in dry air at room temperature but at elevated temperatures or in the presence of atmospheric moisture will decompose slowly. The compound is insoluble in the usual organic solvents and in mixtures of solvents such as are used in dissolving cellulose acetate and other cellulose derivatives.

Materials.—The trimethylchlorosilane used was commercial grade and the acetoxysilanes were prepared according to the method of

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted. Presented at the Southwestern Regional Meeting, Houston, Texas, September, 1947.

[2] J. J. Ebelman, *Compt. rend.*, **18**, 1202; **19**, 398 (1844).

[3] M. N. Kalinin, *Compt. rend. acad. sci. URSS*, **26**, 365 (1940).

[4] G. Martin, *J. Chem. Soc.*, **105**, 2860 (1914).

[5] W. I. Patnode, U. S. Patent 2,306,222 (Dec. 22, 1942).

[6] British Thomson-Houston Co., British Patent 575,696 (Feb. 28, 1946).

[7] J. F. Hyde, U. S. Patent 2,413,050 (Dec. 24, 1946).

[8] I. Jullander, "Studies of Nitrocellulose," Almqvist and Wiksells Boktryckeri-A.-B., Stockholm, 1945, or H. K. Lewis and Co., Ltd., London, pp. 109–117.

Schuyten, Weaver and Reid.[9] Other silanes were prepared by the usual methods.

Analyses.—All silicon analyses were carried out by fusion of the silylcellulose in a Parr bomb followed by the usual gravimetric procedure. Ashing before fusion was impractical because of loss of silicon as trimethylsilanol or similar compounds.

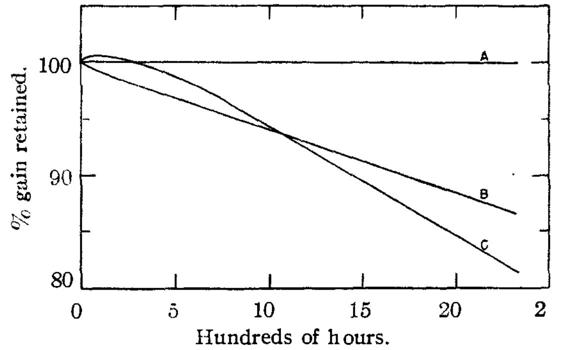

Fig. 2.—Deterioration of trimethylsilylcellulose: A, desiccated (P_2O_5); B, heated (105°); C, conditioned (see text).

Experimental

Trimethylsilylcellulose.—Two grams of oven-dried, low-viscosity cotton linters was suspended in a small amount of anhydrous pyridine in a 500-ml., round-bottom flask provided with a reflux condenser and mercury-sealed stirrer. Trimethylchlorosilane was added from a stock solution in anhydrous pyridine containing 0.05 g. of silane per ml. of solution. The mole ratio of silane per glucose unit of cellulose was varied as indicated in Fig. 1 and the total volume of pyridine was adjusted to 250 ml. The mixture was refluxed and after about one hour the cellulose assumed a dispersed and almost invisible condition. This was undoubtedly due to the nearly identical refractive indices of the compound and pyridine.

After three hours the mixture was cooled and filtered. Washing was done on different runs with both organic solvents and with water; no apparent difference in results were obtained. The samples were vacuum-dried and weighed. Trimethylsilyl group substitution was calculated from gain in weight by

$$\text{Groups} = \frac{\text{Gain in wt.} \times 162.1}{\text{Sample wt.} \times 72.16}$$

and from silicon content by

$$\text{Groups} = \frac{\%\ \text{Si} \times 162.1}{2806 - (72.16 \times \%\ \text{Si})}$$

Other monofunctional group substitutions may be calculated by inserting (group weight—1.008) in place of 72.16.

The correlation of results obtained by these two methods is reasonably good. The difference between results may be due to retention of solvent; it is difficult to remove the last traces of material of this type from cotton.

Other Silanes.—Various other silanes were employed with similar results as recorded in Table II.

Trimethylsilylcellulose Acetate.—Samples of cellulose acetate were dissolved in pyridine and treated as above. The products were soluble in the solvent and were precipitated by pouring into cold water. They were then filtered and washed with water, vacuum-dried, weighed and analyzed. The number of acetyl groups per glucose unit showed little change. The results are given in Table I.

Formation of Trimethylsilylcellulose at Room Temperature.—A sample of cotton linters was treated with trimethylchlorosilane in a mole ratio of 5.58 for four-hundred hours at room temperature. The gain in weight of the cellulose was equivalent to 1.73 groups substitution as compared to 2.53 groups with a similar mole ratio when refluxed for three hours in the pyridine mixture.

TABLE II

REACTIONS OF VARIOUS SUBSTITUTED SILANES WITH CELLULOSE

Reagent	Weight cellulose, g.	Mole ratio[a]	Gain in weight, g.	Si, %	Silyl groups per glucose by weight	Silyl groups per glucose by %, Si
$(C_2H_5)_3SiCl$	2.154	6.06	2.007	11.55	1.32	1.27
$(CH_3)_2SiCl_2$	1.786	5.84	0.202	2.47	[b]	[b]
n-$C_8H_{17}SiCl_3$	1.960	4.01	0.030	1.33	[b]	[b]
$CH_3Si(OAc)_3$	1.904	3.95	0.080	1.16	[b]	[b]

[a] Ratio of moles of silane to glucose unit. [b] Not calculated because of the possibility of cross linkage.

Decomposition of Trimethylsilylcellulose.—Trimethylsilylcellulose may be decomposed by boiling with water or with dilute acid or base. No quantitative results were obtained but boiling with dilute acid yielded a volatile liquid product which burned and deposited silica and was assumed to be trimethylsilanol. Accordingly samples of trimethylsilylcellulose containing 2.6 trimethylsilyl groups per glucose unit were placed in open containers under three sets of conditions: (1) Desiccated over phosphorus pentoxide; (2) dried in an oven at 105°; and (3) conditioned at 70°F. (21.1°) and 65% relative humidity. The samples were weighed at intervals and the per cent. retention of added weight was plotted against time. The results are shown in Fig. 2. The inflection at the beginning of the curve for the conditioned sample is due to increase in moisture content at 65% relative humidity.

Solubility of Trimethylsilylcellulose.—A 0.1-g. sample of trimethylsilylcellulose (2.42 groups per glucose unit) was placed in 5 ml. of solvent in a small tube and tumbled on a wheel for twenty-four hours at room temperature. When the major portion of the material remained undissolved as determined by visual inspection, it was considered insoluble. In some cases (designated below by "sw") the sample particles showed a tendency to swell. No noticeable amount dissolved in the following solvents: acetone, benzene, carbon tetrachloride, chloroform, diethylformamide, ethyl acetate, ethyl alcohol, ethylene dichloride, ether (sw), methylene chloride, methyl ethyl ketone (sw), nitromethane, nitropropane, pyridine (sw), *s*-tetrachloroethane and xylene. The material was not soluble in the following mixtures: acetone (80%), ethanol (15%), ethyl acetate (5%) (sw); toluene (80%), ethanol (20%) (sw); ethylene dichloride (90%), methyl alcohol (10%); and benzene (66%), ethylene dichloride (34%) (sw).

Summary

Trimethylchlorosilane and other chloro- and acetoxysilanes react with cellulose to yield products which by gain in weight and silicon content show a group substitution as high as 2.75 groups per glucose unit. Determination of change in weight of samples of trimethylsilylcellulose over a period of time indicates that it is stable in dry air at room temperature but decomposes at elevated temperatures or in the presence of atmospheric moisture. It may be readily hydrolyzed with boiling water or with dilute acids or alkalies.

The halosilanes react only with the unreacted hydroxyl groups in partially substituted cellulose acetate.

These data indicate the formation of definite compounds of cellulose with substituted silanes.

NEW ORLEANS, LA.

RECEIVED FEBRUARY 2, 1947

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[9] H. A. Schuyten, J. W. Weaver and J. David Reid, THIS JOURNAL, **69**, 2110 (1947).