

methoxyl contents of the dark brown amorphous products were only a fraction of those of the original acids. That from ferulic acid contained 9.8% methoxyl after five minutes of oxidation, and after five hours of reaction the product from vanillic acid contained 6.5% methoxyl.

Methoxyl groups previously reported lost during the periodate oxidation of purified ammonium lignin sulfonate<sup>1</sup> have been identified as methanol in the volatile products of the oxidation, as measured by the colorimetric method described by Simmons.<sup>5</sup>

The evidence cited here indicates an attack upon the aromatic nucleus in the lignin sulfonic acids. The absence of any easily discernible stoichiometry and failure to isolate definite products precludes any ready interpretation for the course of the reaction, without further investigation. Such a study is being undertaken in this Laboratory.

(5) Simmons, *Analyst*, **37**, 16 (1912).

PULP MILLS RESEARCH PROJECT  
UNIVERSITY OF WASHINGTON  
SEATTLE 5, WASHINGTON

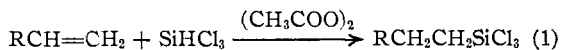
D. E. PENNINGTON  
D. M. RITTER

RECEIVED DECEMBER 16, 1946

#### PEROXIDE-CATALYZED ADDITION OF TRICHLOROSILANE TO 1-OCTENE

Sir:

The preparation of *n*-octyltrichlorosilane in 46% yield from silicon tetrachloride and *n*-octylmagnesium bromide has been reported.<sup>1</sup> We have now prepared this compound in excellent yield from 1-octene and trichlorosilane in the presence of diacetyl peroxide.



This new reaction of trichlorosilane is applicable to a wide variety of silicon hydrides and unsaturated compounds, and thus provides an important new synthesis for organosilicon compounds.<sup>2</sup>

Similar additions of chloroform and of bromoform to 1-octene and other olefins have been reported.<sup>3</sup>

1-Octene, 17.9 g., 0.16 mole, and trichlorosilane, b. p. 32°, 135.5 g., 1.0 mole, were placed in a three-necked flask with dropping funnel, thermometer, and a reflux condenser connected through a trap cooled in Dry Ice-acetone to a mercury seal of 20 cm. height. The system was swept with nitrogen for two hours, and the reaction mixture was heated to 45° under the slight extra pressure of the mercury. Crystalline diacetyl peroxide, 3 g., 0.025 mole, dissolved in 19.1 g., 0.17 mole, of 1-octene was then added during two hours. The mixture was heated at 50–63° for an additional nine hours.

After removal of excess trichlorosilane, the resi-

(1) Whitmore, Sommer, Di Giorgio, Strong, Van Strien, Bailey, Hall, Pietrusza and Kerr, *THIS JOURNAL*, **68**, 475 (1946).

(2) Cf. Rochow, "Introduction to the Chemistry of Silicones," John Wiley and Sons, New York, N. Y., 1946, pp. 18–30.

(3) Kharasch, Jensen and Urry, (a) *Science*, **102**, 128 (1945);

(b) *THIS JOURNAL*, **68**, 154 (1946).

due was distilled at reduced pressure and then redistilled at atmospheric pressure, giving 80.9 g. of clear colorless liquid, b. p. 231–232° at 728 mm., 99% yield.

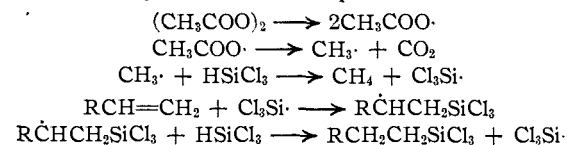
*Anal.* Calcd. for  $\text{C}_8\text{H}_{17}\text{SiCl}_3$ : Cl, 43.0. Found: Cl, 42.9, 43.0.

*n*-Octyltrichlorosilane from silicon tetrachloride and *n*-octylmagnesium bromide boils 233° at 731 mm.; 119° at 28 mm.<sup>1</sup>

Treatment of a portion of the product with ethanolic potassium hydroxide gave no hydrogen, indicating the absence of Si–H bonds.<sup>4</sup>

Reaction of the product, 24.8 g., 0.1 mole, with 0.35 mole of methylmagnesium bromide (using a procedure known to form the tetra-alkylsilane from *n*-octyltrichlorosilane)<sup>1</sup> gave 13.0 g. of *n*-octyltrimethylsilane, b. p. 201.5° at 733 mm.,  $n_D^{20}$  1.4242, 74% yield. Constants for this compound<sup>1</sup> are: b. p. 202° at 760 mm.,  $n_D^{20}$  1.4242. All the data thus conclusively confirm equation (1).

According to Kharasch,<sup>3</sup> the addition of chloroform to olefins is a free-radical chain reaction, initiated by free methyl radicals generated in the reaction mixture by decomposition of the peroxide. A similar free-radical mechanism applies to our reaction, especially in view of the lower bond energy of Si–H (75.1 kcal./mole) as compared to that of C–H (87.3 kcal./mole).<sup>5</sup> Thus the addition may involve the steps



This work is being continued.

Trichlorosilane and 1-octene at 47–54° with a weak ultra-violet source give a 24% yield of *n*-octyl trichlorosilane corresponding completely to the product of the peroxide-catalyzed reaction. (Added to proof January 13, 1947.)

(4) Cf. Sauer, Scheiber and Brewer, *ibid.*, **68**, 962 (1946).

(5) Cf. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1942, p. 53.

DEPARTMENT OF CHEMISTRY  
THE PENNSYLVANIA STATE COLLEGE  
STATE COLLEGE, PA.

L. H. SOMMER  
E. W. PIETRUSZA  
F. C. WHITMORE

RECEIVED DECEMBER 17, 1946

#### THE REACTION OF AMINOALKYL HALIDES WITH DIPHENYLACETONITRILE. THE STRUCTURE OF AMIDONE

Sir:

Recent reports have indicated an uncertainty of the structure of the new German analgesic drug Amidone, or No. 10820.<sup>1,2</sup>

In this Laboratory, the preparation of this new drug by the German procedure led to the finding that the reaction between diphenylacetoneitrile and 1-dimethylamino-2-chloropropane results in a mixture containing equal amounts of two isomeric

(1) Office of the Publication Board, Department of Commerce, Report PB-981, p. 96-A.

(2) Scott and Chen, *J. Pharmacol.*, **57**, 63 (1946).