properties with those of the corresponding hydrazone of the by-product. A mixture of the two hydrazones showed no depression in the melting point.

DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE
AMES, IOWA

The Addition of Triphenylsilylpotassium to *trans*-Stilbene

BY HENRY GILMAN AND T. C. WU

RECEIVED JULY 31, 1952

Incidental to a study of the properties of organosilicon-metallic compounds, we have observed that triphenylsilylpotassium adds to *trans*-stilbene to give β-triphenylsilyl-α,β-diphenylethylpotassium which on hydrolysis yields triphenyl-α,β-diphenylethylsilane [I].

$$(C_6H_5)_3SiK + C_6H_5CH{=}CHC_6H_5 \longrightarrow$$

$$(C_6H_5)_3SiCH(C_6H_5)CH(C_6H_5)K \xrightarrow{H_2O}$$

$$(C_6H_5)_3SiCH(C_6H_5)CH_2(C_6H_5) \quad (I)$$

The yield of pure [I] was 55% when a solution of 3.6 g. (0.02 mole) of *trans*-stilbene in 50 ml. of benzene was added to a triphenylsilylpotassium suspension prepared[1] by cleaving 5.2 g. (0.01 mole) of hexaphenyldisilane with sodium-potassium alloy in ether, after removing the excess alloy by amalgamation. During the addition of *trans*-stilbene to the triphenylsilylpotassium the mixture changed in color from brownish-tan to deep brownish-red. After stirring the reaction mixture for 30 minutes at room temperature hydrolysis was effected by the slow addition of water. The organic layer was dried over sodium sulfate and the solvents were removed by distillation. The residue was recrystallized three times from petroleum ether (b.p. 60–70°) to give 4.8 g. (55%) of colorless granular crystals melting at 135–136°. *Anal.* Calcd. for $C_{32}H_{28}Si$: Si, 6.37. Found: Si, 6.40, 6.41. In another experiment the triphenylsilylpotassium suspension was added to the benzene solution of *trans*-stilbene to give a 39% yield of pure [I]. A like yield was obtained under these latter conditions when the reaction time was 24 hours.

This reaction which indicates a high order of reactivity of organometallic compounds is being extended to other organosilicon-metallic[2] compounds and other unsaturated systems like those containing the azomethylene, azo and carbonyl groups.

[1] H. Gilman, T. C. Wu, H. A. Hartzfeld, G. A. Guter, A. G. Smith, *J. J.* Goodman and S. *H.* Eidt, THIS JOURNAL, **74**, 561 (1952).

[2] It will be interesting to observe whether related high orders of reactivity will be shown by other types having the generalized formula R_nMM' where M is a metal or metalloid and where M' is an alkali or alkaline earth metal.

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AMES, IOWA

Decaethylcyclopentasiloxane

BY DALLAS T. HURD AND ROBERT C. OSTHOFF

RECEIVED SEPTEMBER 4, 1952

In the course of preparing a series of diethylsiloxanes, we have observed that the cyclic pentamer, *i.e.*, decaethylcyclopentasiloxane, is a solid. This was not anticipated; the minimum in the melting points of the known cyclic dimethylsiloxanes occurs with the pentamer and the observed melting points of the cyclic trimer and tetramer compounds are lower in the diethyl series than in the dimethyl series as shown in Table I.

TABLE I

MELTING POINTS OF CYCLIC DIORGANOSILOXANES

No. of Si atoms	M.p., °C. Dimethyl series[1]	Diethyl series
3	65	14
4	17.5	−50
5	−38	38
6	− 3	
7	−26	
8	31.5	

Attempts to obtain cyclic diethylsiloxanes beyond the pentamer compound were not successful (*v.i.*).

The cyclic pentamer of diethylsiloxane was studied in some detail. The compound is a soft transparent solid having the consistency of a very soft wax. It did not exhibit any liquid flow at room temperature and a sharp impression made in the soft solid with a needle showed no evidence of closure over a period of a week at normal room temperature. The material could, however, be extruded under slight pressure.

It is well known that molecules with near spherical symmetry can rotate (hindered) in the solid state and that this strongly affects the physical properties of such substances.[2] In particular, the heat and entropy of fusion are low, the melting point anomalously high and the phase between the melting and solid state transition points is clear (frequently isotropic) and of a waxy texture. It is believed that the physical properties of several of the siloxanes studied here are affected by the aforementioned molecular rotation in the solid state. For example, the freezing point of decaethylcyclopentasiloxane is very sensitive to impurities; this implies a high freezing point depression constant and hence a low heat of fusion. Decaethylcyclopentasiloxane is a clear solid near the melting point. Evidence of solid state transition points, although not specifically sought in this study, has been observed with various silicone compounds.[3] A definite first-order transition at −17.30° has been found in octamethylcyclotetrasiloxane (m.p. 17.538°), which has a low heat of fusion.[4]

Anal. Calcd. for decaethylcyclopentasiloxane: Si, 27.50; C, 47.00; H, 9.87; mol. wt., 511. Found: Si, 27.46; C, 46.8; H, 9.80; mol. wt. (from cryoscopic measurements in cyclohexane), 495.

The measured physical properties are summarized in Table II.

[1] E. G. Rochow, "Chemistry of the Silicones," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1951, p. 185.

[2] W. O. Baker and C. P. Smyth, *Ann. N. Y. Acad. Sci.*, **XL**, 447 (1940).

[3] Private communication from S. W. Kantor of this Laboratory, 1952.

[4] This investigation has been carried out by John D. Hoffman of this Laboratory and will be published in detail in the near future.