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
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The Addition of Triphenylsilylpotassium to *trans*-Stilbene

BY HENRY GILMAN AND T. C. WU

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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].

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

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

$$(C_6H_5)_3SiCH(C_6H_5)CH_2(C_6H_5) \quad \text{(I)}$$

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.

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(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.

DEPARTMENT OF CHEMISTRY
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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]	M.p., °C. 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.

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(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.

TABLE II

PHYSICAL PROPERTIES OF DECAETHYLCYCLOPENTASILOXANE

Melting point, °C.	38–39
Boiling point, °C.	167.5 at 1 mm.
$n^{20}\mathrm{D}$ (solid)	1.4408
Density, g./ml.	0.968 at 20°
$MR\mathrm{D}$ (obsd.)	139.3
(calcd.)	139.5[5]

The authors determined the dipole moment of this siloxane in benzene solution at 20°. Dielectric constant measurements were carried out at 1,000 cycles using a Schering bridge.[6,7] The observed data are listed in Table III.

TABLE III

DATA FOR THE EVALUATION OF THE DIPOLE MOMENT OF DECAETHYLCYCLOPENTASILOXANE AT 20° IN BENZENE SOLUTION

Mole fraction of solute C_2	Dielectric constant ϵ	Density d	Total molar polarization of solution $P_{1,2}$ cm.³	Total molar polarization of solute P_2, cm.³
0.0871	2.29 ± 0.02	0.8819	39.53	173.5
.0651	2.29	.8809	36.32	173.9
.0370	2.28	.8803	32.06	170.5
.0277	2.28	.8781	30.68	168.9
.0194	2.28	.8779	29.46	166.9
			$P_{2\infty}$ =	162

If 5% of the molar refraction is allowed for the atomic polarization, the dipole moment of the cyclic pentamer (calculated according to the method of Smyth[8]) is found to be 0.88 ± 0.25 *D*. It is interesting that this value is somewhat smaller than the dipole moment of the corresponding methyl compound, 1.35.[9]

Attempts were made to isolate the cyclic hexamer compound following the separation of the trimer, tetramer and pentamer compounds from the mixture of diethyl siloxanes obtained by the hydrolysis of diethyldichlorosilane, but when the distillation pot temperature was raised above that necessary for the separation of the pentamer, the higher diethylsiloxanes were cracked thermally and only the cyclic trimer and tetramer could be collected. Since the thermal rearrangement process in organopolysiloxanes is very sensitive to, and catalyzed by, traces of acid or base, it may be possible to isolate the cyclic hexamer and higher compounds if a rigorous purification of the mixed diethylsiloxanes is made prior to the actual distillation.

We are grateful to Dr. F. E. Luborsky of the Research Laboratory for his measurements of dielectric constants and to Dr. John D. Hoffman for his assistance and helpful suggestions.

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[5] E. L. Warrick, THIS JOURNAL, **68**, 2455 (1946).

[6] R. M. Fuoss, *ibid.*, **59**, 1703 (1937).

[7] D. J. Mead and R. M. Fuoss, *ibid.*, **61**, 2048 (1939).

[8] C. P. Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Co. (Reinhold Publ. Corp.), New York, N. Y., 1931.

[9] R. O. Sauer and D. J. Mead, THIS JOURNAL, **68**, 1794 (1946).

Podophyllotoxin from *Juniperus* Species; Savinin

BY JONATHAN L. HARTWELL, JAMES M. JOHNSON, DOROTHEA B. FITZGERALD AND MORRIS BELKIN

RECEIVED AUGUST 11, 1952

In the course of a survey of the conifers for possible damaging effect against Sarcoma 37 in mice, it was found[1] that aqueous suspensions of the dried needles of certain junipers caused hemorrhage and necrosis in this tumor. A search for the components responsible for this activity was instituted, using successive fractionation with different solvents and chromatography, and following the distribution of biological activity in the fractions by quantitative bioassay with mice bearing Sarcoma 37.[2] In this way crystalline podophyllotoxin (one of the tumor-damaging components of podophyllin) was isolated from all the junipers listed (Table I), and from one of these (savin) a new substance called savinin, inactive toward tumors, was also obtained.

The occurrence of podophyllotoxin reported here is interesting in being the first report of this substance in anything but a plant of the *Podophyllum* genus.

Experimental[3]

Fractionation of Savin.—Since savin was the product on which most of the present work was done, the fractionation finally adopted for this material is given. The other species of juniper were treated in similar fashion, and gave a similar distribution of activity. The successive fractions were extracted at room temperature with the different solvents by shaking a few minutes in stoppered flasks until further treatment failed to remove additional material, and the solvents were evaporated off at room temperature; in cases where the extract was gummy, further extraction was facilitated by breaking up the gum with a stirring rod or triturating it in a mortar with the new solvent.

Extraction of the dried ground needles with acetone yielded 17% of a soluble fraction containing essentially all the biological activity. Ligroin treatment of the acetone-soluble fraction removed an inactive soluble part, leaving 47% insoluble containing practically all the activity. Chromatography on activated alumina of an absolute ethanol solution of the ligroin-insoluble fraction, and successive elution with absolute ethanol, 70% ethanol and water gave correspondingly, three cuts from the filtrate. These represented 38, 31 and 11%, respectively, of the original fraction chromatographed, while an estimated 20% remained on the tower. Essentially all the biological activity appeared in the first cut. Treatment of the first cut with ethyl acetate removed 9% of an insoluble, inactive fraction. Extraction of the soluble part with xylene gave 92% of a soluble fraction containing most of the activity. Fractional evaporation of the xylene solution gave a succession of several crops of crystals called A, B, C, D, E and F in yields (based on the original savin) of 0.145, 0.015, 0.043, 0.090, 0.013 and 0.013%, respectively. Fractions A, B and C had similar melting points and high biological activity, while fractions D, E and F had similar melting points and low biological activity. The mother liquor, after separation of the crystals, still had biological activity.

Podophyllotoxin.—Fractions A, B and C were combined (0.20% yield) and recrystallized from benzene yielding colorless needles, m.p. 111° (softens 107°) and having a second m.p. of 185°, $[\alpha]^{21}\mathrm{D}$ −123° (*c* 1.03, chloroform). This was identified as podophyllotoxin (m. p. of anhydrous form 183.4°, $[\alpha]^{20}\mathrm{D}$ and anhydrous form −132°[4]). Acetyla-

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[1] D. B. Fitzgerald, M. Belkin, M. D. Felix and M. K. Carroll, to be published in *J. Natl. Cancer Inst.*, **13**, Feb. (1953).

[2] J. Leiter, V. Downing, J. L. Hartwell and M. J. Shear, *ibid.*, **10**, 1273 (1950).

[3] Melting points in this paper were taken on the Hershberg apparatus and are corrected values.

[4] J. L. Hartwell and A. W. Schrecker, THIS JOURNAL, **73**, 2909 (1951).