Polyaddition Reaction of Diphenylsilane to Difunctional Unsaturated Compounds. II

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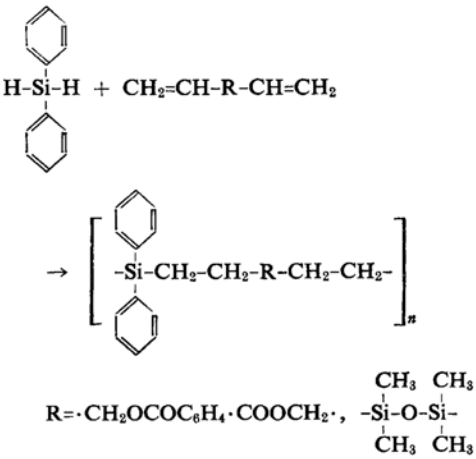
Several literatures have been published on the addition reaction of silicon hydrides to a number of olefines using peroxide, ultraviolet light, γ-rays or platinum catalysts.

In 1947, L. H Sommer reported that *n*-octyltrichlorosilane was prepared by the addition reaction of 1-octene with trichlorosilane in the presence of a small amount of diacetyl peroxide catalysts at 50~63°C[1,2]. This addition reaction was also carried out using γ-rays from a 30 kilocurie Co^{60} source at room temperature in an almost quantitative yield[3].

The addition reaction of trichlorosilane to styrene was first carried out by C. A. Burkhard in the presence of peroxide catalysts, resulting in the formation of only non-volatile telomeric products[4]. W. S. Wagner and coworkers succeeded in the preparation of β-phenylethyltrichlorosilane by the above mentioned addition reaction using platinized charcoal as the catalyst at 200°C[5]. S. Nozakura reported the formation of α- and β-trichlorosilylethylbenzene by the same reaction using tetrapyridine nickel chloride as the catalyst at 160°C[6]. The platinum catalyzed addition reaction of methyldichlorosilane with methyl methacrylate was carried out by L. H. Sommer and coworkers in the preparation of α-methyl-β-methyldichlorosilyl propionate[7].

The addition reaction of methyldichlorosilane with vinyl acetate was studied by J. L. Speier and coworkers in the preparation of 2-methyldichlorosilylethyl acetate[8]. L. Goodman reported similar reactions of various silanes (phenylsilane, methyldiethoxysilane, trichlorosilane or methyldichlorosilane to allyl acetate[9]. J. W. Curry and coworkers have recently described the polymerization of certain silanes having an unsaturated organic group and a hydrogen on the same silicon atom[10,11].

In the previous paper, we have reported the result of the polyaddition reaction of diphenylsilane with diallyl phthalate or methyldisiloxane in the presence of a small amount of platinum black[12].



By these reactions carried out in sealed glass tubes, new polymers containing silicon were obtained in good yield. As a continuation of the experiment, the present paper deals with a new synthetic method of polymers which can be generally applied to the polyaddition reaction of diphenylsilane with various difunctional unsaturated compound (diallyl adipate, divinyl adipate, tetramethylene dimethacrylate, divinylbenzene and hexadiene).

Our first work was to examine the polyaddition reaction of diphenylsilane with diallyl phthalate using platinum black as the catalyst. As the extension of this work, the effect of various catalysts (i. e. platinum black, chloroplatinic acid, benzoyl peroxide, *tert*-butyl hydroperoxide, and azobisisobyturonitrile) has been studied. The results are shown in Table I.

Platinum catalysts were more effective than other catalysts. The effect of the irradiation of γ-ray or ultraviolet light in this reaction was hardly recognized at room temperature.

Similarly, by the polyaddition reaction of diphenylsilane with diallyl adipate was also prepared a linear polyaddition product in a

1) L. H. Sommer et al., *J. Am. Chem. Soc.*, **69**, 188 (1947).
2) L. H. Sommer et al., ibid., **70**, 484 (1948).
3) L. C. Anderson et al., ibid., **80**, 1737 (1958).
4) C. A. Burkhard et al., ibid., **69**, 2687 (1947).
5) W. S. Wagner et al., *Ind. Eng. Chem.*, **45**, 367 (1953).
6) S. Nozakura., This Bulletin, **29**, 784 (1956).
7) L. H. Sommer et al., *J. Am. Chem. Soc.*, **79**, 2764 (1957).
8) J. L. Speier et al., ibid., **79**, 974 (1957).
9) L. Goodman et al., ibid., **79**, 3073 (1957).
10) J. W. Curry, ibid., **78**, 1689 (1956).
11) J. W. Curry et al., *J. Org. Chem.*, **23**, 1219 (1958).
12) K. Kojima, This Bulletin, **31**, 663 (1958).

TABLE I. POLYADDITION OF DIPHENYLSILANE WITH DIALLYL PHTHALATE

Catalyst (mol.)	React. time (hr.)	Temp. (°C)	Yield (%)	Mol. wt.
Pt-black, $2 \cdot 10^{-4}$	50	110~20	76	2390
Chloroplatinic acid, $2 \cdot 10^{-6}$	〃	〃	73	2060
Benzoyl peroxide, $2 \cdot 10^{-4}$	〃	〃	60	955
tert-Butyl hydroperoxide, $2 \cdot 10^{-4}$	〃	〃	67	765
Azobisisobutyronitrile, $2 \cdot 10^{-4}$	〃	〃	69	775

In these experiments, 0.02 mol. of diphenylsilane and 0.02 mol. of diallyl phthalate were used.

76% yield. The molecular weight of this polyadduct was 1400.

In the polyaddition reaction of diphenylsilane with divinyl adipate using platinum black as catalyst, however, the linear polyaddition product was obtained in 34% yield and the other polyadduct was a highly branched (or a cross-linked) polymer. The molecular weight of the linear polymer was 1660. The combination ratio of divinyl adipate and diphenylsilane of the branched polymer was 4 : 1.

The reaction of diphenylsilane with tetramethylene dimethacrylate did not produce a linear high polymer, but gave a low molecular weight adduct (mol. wt. 460) in 37% yield and a branched polymer (combination ratio, tetramethylene dimethacrylate 2 moles : diphenylsilane 1 mole).

When diphenylsilane and divinylbenzene were heated at 120°C in the presence of Pt-black, the highly branched polymer and low molecular weight adducts were obtained. The molecular weight of this low-adduct was 440. The combination ratio of branched polymer was diphenylsilane 1 mol. : divinylbenzene 18 mol.

In the addition reaction of diphenylsilane with hexadiene using platinum black catalyst, the low molecular weight adduct (mol. wt. 685) was only obtained in a 43% yield.

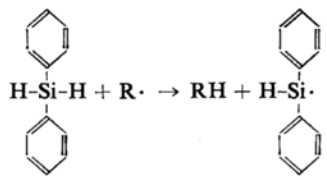
The mechanism of the addition reaction of silicon hydride to olefinic compounds catalyzed by platinum is not clear yet. But it has been asserted, that the addition reaction of silicon hydride to alkene using peroxide catalyst is a free radical chain reaction[1]. The proposed mechanism for the reaction is

$$R\cdot + HSi\equiv \rightarrow RH + \equiv Si\cdot$$

$$RCH{=}CH_2 + \equiv Si\cdot \rightarrow R\dot{C}H{-}CH_2Si\equiv$$

$$R\dot{C}HCH_2Si\equiv + HSi\equiv \rightarrow RCH_2CH_2Si\equiv + \equiv Si\cdot$$

In this paper, the reaction of diphenylsilane with difunctional unsaturated compound to form the linear high molecular weight polymer was predominant.



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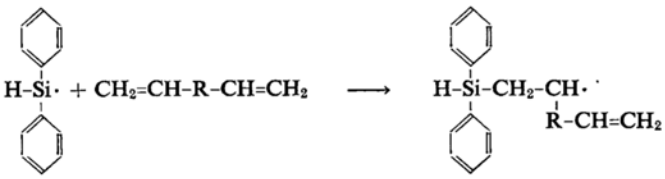

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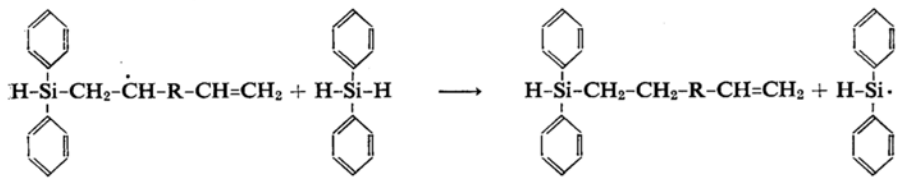

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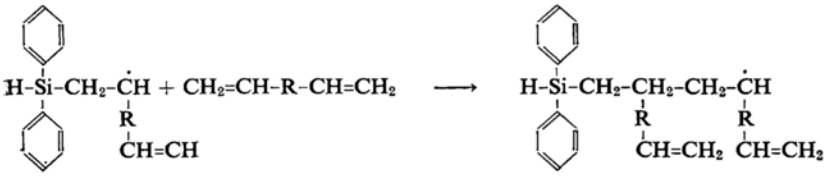

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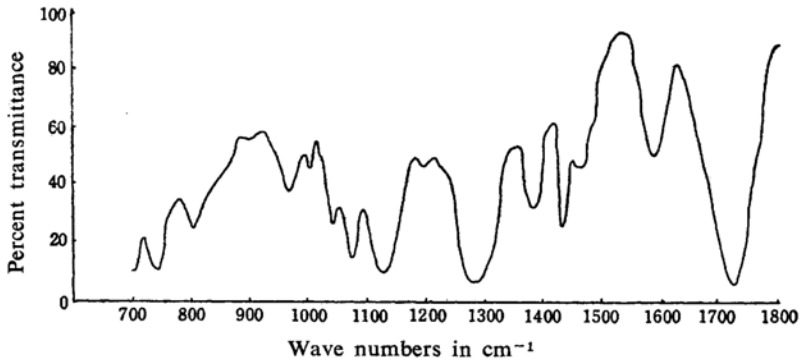

Fig. 1. Infrared spectrum of adduct of diphenylsilane with diallyl phthalate.

But in some cases, it was found that the second reaction shown in Eq. 4 also took place.

This reaction is responsible for the formation of branched polymer and a strong competitor for the normal addition reaction 3. In case of diallyl phthalate, diallyl adipate and hexadiene, only the reaction 3 can proceed. Theerfore it gave linear products only. But, in the case of divinyl adipate, tetramethylene dimethacrylate and divinylbenzene, branched polymers were obtained together with linear polymers.

The addition reaction of silicon hydrides to some unsaturated compounds has been shown to yield two isomers by other investigators[9,13,14]. The addition compound of trichlorosilane to acrylonitrile could be either $NCCH_2CH_2SiCl_3$ (α-adduct) or $NCCH(CH_3)SiCl_3$ (β-adduct).

But, in the case of platinum catalyzed reaction, the addition reactions of silicon hydrides to vinyl acetate and to methyl methacrylate have been shown to yield β-adducts, and the addition to allyl acetate has been shown to yield γ-adducts.

By analogy, the addition compounds of diphenylsilane with each of divinyl adipate, and tetramethylene dimethacylate are presumed to be mainly β-adducts, and the adduct of diallyl phthalate are γ-adduct. But, it was shown, that the infrared absorption spectra of the addition compounds obtained in this work were identical in all important respects with that of the mixture of them.

In the isolation of the polymer, it was found, thats ome volatile by-products are also obtained from the reaction mixture. In the case of tetramethylene dimethacrylate, the volatile product was obtained in considerable quantities, and the yielded gas was identified as propylene and propane by gas-chromatography. But the mechanism of the production of propylene and propane is indistinct.

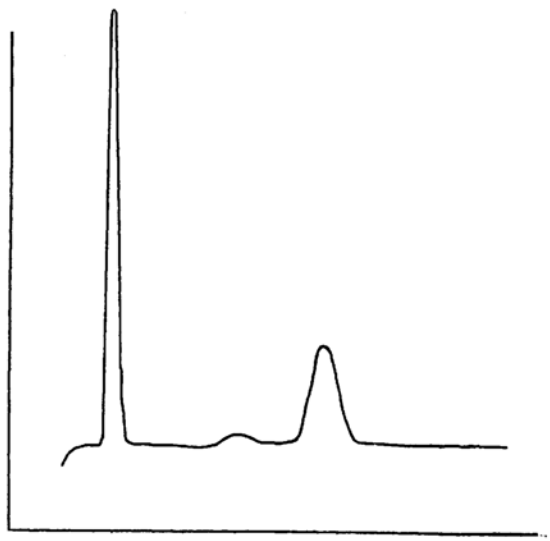

Fig. 2. Gas-chromatograph of the reaction by-products of diphenylsilane with tetramethylene dimethacrylate. Carrier gas, hydrogen; column dimethyl formamid-active charcoal.

Experimental

Materials.—Diallyl adipate[15] and divinyl adipate[16] were prepared by the published methods. Tetramethylene dimethacrylate was prepared by the ester interchange reaction of methyl methacrylate with 1,4-butanediol in the presence of sulfuric acid and hydroquinone[17]. Diallyl phthalate and divinylbenzene were commercial products. Hexadiene was prepared by the reaction of allyl bromide with metallic magnesium in ether[18]. Diphenylsilane was prepared from diphenyldichlorosilane by lithium

13) S. Nozakura et al., ibid., **29**, 322 (1956).
14) S. Nozakura et al., ibid., **29**, 326 (1956).
15) K. Kojima et al., *Reports of the Research Institute of Dental Materials, Japan.*, 8, 136, (1957).
16) K. Kojima et al., ibid., **9**, 38 (1958).
17) K. Kojima et al., ibid., **8**, 144 (1957).
18) L. Vanino, "Handbuch der Präparativen Chemie", Bd. 2, 7 (1937).

aluminum hydride by ordinary method[19]. Diphenyldichlorosilane was supplied by Shin-etu Chem. Co. and redistilled before being used.

Polyaddition of Diphenylsilane with Diallyl Phthalate.—*Method 1—Pt Black Initiation.*—Diallyl phthalate (4.92 g., 0.02 mol.), diphenylsilane (3.68 g., 0.02 mol.) and platinum black (0.03 g.) as catalyst were placed in a glass tube and the tube was sealed in nitrogen stream, and then heated at 110~120°C in an air oven for 50 hr. The reaction product was dissolved in 100 ml. benzene and reprecipitated by 200 ml. methanol. The precipitated material was separated and dried in a vacuum desiccator at 50°C for 7 days. Yield, 76%.

Found: Si, 5.34. Calcd. for $C_{26}H_{26}O_4Si$: Si, 5.83% mol. wt., 2390.

Method 2—Chloroplatinic Acid Initiation.—Under similar condition as described for Pt black initiation, chloroplatinic acid ($2\cdot10^{-5}$ mol.) in methanol solution, diphenylsilane (3.65 g.) and dially phthalate (4.92 g.) were heated and the product was reprecipitated. The average molecular weight of this polymer was found to be 2060. Yield 73%.

Method 3—Benzoyl Peroxide Initiation.—The mixture of diphenylsilane (3.68 g.), diallyl phthalate (4.92 g.) and benzoyl peroxide (0.005 g.) were heated in an air oven for 50 hr. at 110~20°C. The reaction gave a linear polymer of mol. wt. 954. Yield 60%.

Method 4—tert-Butyl Hydroperoxide Initiation.—Under similar condition as described above, 0.002 g. of *tert*-butyl hydroperoxide was used as the catalyst. The reaction gave a linear polymer of mol. wt. 765. Yield 67%.

Method 5—Azobisisobutyronitrile Initiation.—Under similar condition as employed in the preceding experiment, diphenylsilane (3.68 g.), diallyl phthalate (4.92 g.), and azobisisobutyronitril (0.003 g.) were traced to produce 5.81 g. of the linear polymer with 69% of theoretical yield. mol. wt. 774.

Method 6—^{60}*Co Initiation.*—Diphenylsilane (3.68 g.) and diallyl phthalate (4.92 g.) were charged in a glass tube. The tube was sealed in dry nitrogen atmosphere, and then exposed to ^{60}Co irradiation at room temperature for 150 hr. at a rate of $2.1\cdot10^{-5}$ r.e.p./hr. The molecular weight of this product was 600. Yield 9.8%.

Method 7—Ultraviolet Light Initiation.—The same mixture employed in the preceding experiment was exposed to ultraviolet light irradiation at room temperature for 150 hr. at 10170 c. d. by merucric lamp but the unreacted diphenylsilane and diallyl phthalate were recovered.

Polyaddition of Diphenylsilane with Diallyl Adipate.—A mixture of diphenylsilane (3.68 g.) and diallyl adipate (4.52 g., 0.02 mole) with 0.03 g. platinum black were heated for 50 hrs. at 120°C in a sealed glass tube. The product was dissolved in benzene and reprecipitated by methanol. The average molecular weight of this polymer was found to be 1400. Yield 68%.

Found: Si, 6.69. Calcd for $C_{24}H_{28}OSi$: Si, 6.84%.

Polyaddition of Diphenylsilane with Divinyl Adipate.—Divinyl adipate (3.96 g., 0.02 mole), diphenylsilane (3.68 g., 0.02 mole) and 0.03 g. platinum black as the catalyst were heated at 120°C for 50 hr. in a sealed glass tube. The product was dissolved in benzene and reprecipitated in methanol. The molecular weight of benzene-soluble polymer was 1660.

Found: Si, 7.12. Calcd. for $C_{22}H_{24}O_4Si$: Si, 7.38%. Yield 39%.

The benzene-insoluble polymer was found to be an adduct of diphenylsilane and divinyl adipate at the mole ratio of 1 : 4.

Found: Si, 3.32. Calcd. for 1 : 4 adduct: Si, 3.59%.

Polyaddition of Diphenylsilane with Tetramethylene Dimethacrylate.—Tetramethylene dimethacrylate (4.52 g., 0.02 mol.), diphenylsilane (3.68 g., 0.02 mol.) and 0.03 g. platinum black were heated for 50 hr. at 120°C in a sealed glass tube. The product was dissolved in benzene and reprecipitated by methanol. The low molecular weight addition product (benzene-soluble part) was obtained in a 37% yield. The average molecular weight of this polymer was found to be 460. A branched (or cross-linked) polymer was also formed and it has been cleared by Si analysis, that it was the addition product of diphenylsilane and tetramethylene dimethacrylate at the mole ratio of 1 : 2.

Found: Si, 4.18, Calcd. for 1 : 2 adduct: Si, 4.18%.

Polyaddition of Diphenylsilane with Divinylbenzene.—Divinylbenzene (2.60 g., 0.02 mol.), diphenylsilane (3.68 g., 0.02 mol.) and platinum black (0.03 g.) were charged in a glass tube. The tube was sealed under the atmosphere of nitrogen and heated in an air oven for 50 hr. at 125~130°C. The product was dissolved in benzene. The average molecular weight of the soluble product was 440. Yield 65%. The insoluble product was an addition product of diphenylsilane 1 mol. and divinylbenzene 18 mol.

Found: Si, 1.11. Calcd. for 1 : 18 adduct: Si, 1.10%.

Polyaddition of Diphenylsilane with Hexadiene. Hexadiene (1.64 g., 0.02 mol.), diphenylsilane (3.68 g. 0.02 mol.) and platinum black (0.03 g.) were charged in a glass tube, and the tube was sealed under the nitrogen atmosphere and heated in an air oven for 50 hr. at 110~120°C. Only the low molecular weight product (mol. wt. 685) was obtained in a 43% yield.

Found: Si, 9.87. Calcd for $C_{18}H_{22}Si$: Si, 10.78%.

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19) R. A. Benkeser et al., *J. Am. Chem. Soc.*, **74**, 648 (1952).