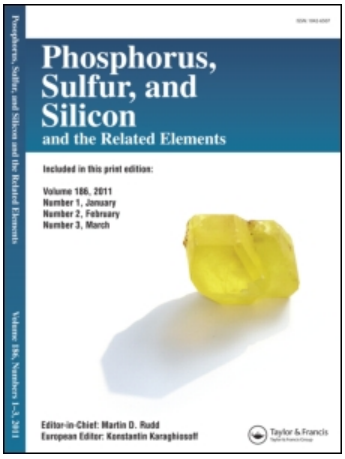

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SYNTHESIS AND CHARACTERIZATION OF (2,5-DIMETHYL-3,4-DIPHENYL)PHENYL SILICON COMPOUNDS

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SYNTHESIS AND CHARACTERIZATION OF (2,5-DIMETHYL-3,4-DIPHENYL)PHENYL SILICON COMPOUNDS

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(2,5-dimethyl-3,4-diphenyl)phenyl-triethoxysilane (DDPTES) and (2,5-dimethyl-3,4-diphenyl)phenyl-heptamethylcyclotetrasiloxane (DDPHMCTS) were synthesized by Diels-Alder reaction of 2,5-dimethyl-3,4-diphenylcyclopentadienone (DDCP) with vinyl-triethoxysilane (VTES) and vinyl-heptamethylcyclotetrasiloxane (VHMCTS) respectively. The structures of these two products have been characterized by IR, ^{1}HNMR and elemental analysis.

Key words: (2,5-Dimethyl-3,4-diphenyl)phenyl-triethoxysilane; (2,5-dimethyl-3,4-diphenyl)Phenyl-heptamethylcyclotetrasiloxane; Diels-Alder reaction

INTRODUCTION

Some organosilicon compounds containing polyphenylphenyl and condensed rings have been synthesized by Diels-Alder reaction of vinylsilane with 2,3,4,5-tetraphenylcyclopentadienone.[1,2] However, compounds containing (dimethyl-diphenyl)phenyl have not been reported previously. The synthesis and characterization of the organosilicon compounds which have both aromatic and aliphatic groups in the same molecule would be interesting in polymeric and synthetic organic chemistry.

Vinyl-triethoxysilane (VTES) and vinyl-heptamethylcyclotetrasiloxane (VHMCTS) was chosen as the dienophile and 2,5-dimethyl-3,4-diphenylcyclopentadienone (DDPC) as the diene to conduct Diels-Alder reactions. As a result, (2,5-dimethyl-3,4-diphenyl)phenyl-triethoxysilane (DDPTES) and (2,5-dimethyl-3,4-diphenyl)phenyl-heptamethylcyclotetrasiloxane (DDPHMCTS) have been obtained.

EXPERIMENTAL

General. Melting points were determined on an X_4 melting point apparatus and were uncorrected. IR spectra were taken in the region of 400–4000 cm^{-1} with a Nicolet-50X spectrometer. UV spectra were recorded on a UV240 spectrophotometer with 0.4% (V/V) product solution in chloroform. ^{1}HNMR spectra were carried out on a FX90Q spectrometer (using $CDCl_3$ as solvent and $CHCl_3$ as internal standard). Elementary analysis were performed by the Institute of Elementary Organic Chemistry, Nankai University.

Materials. 2,5-dimethyl-3,4-diphenylcyclopentadienone (DDCP) was prepared according to the procedure outlined previously.[3] Vinyl-triethoxysilane and diphenyl ether were obtained from the commercial sources and were purified before use. Vinyl-heptamethylcyclotetrasiloxane (VHMCTS) was prepared according to a literature method[1] and distilled before use with a high efficiency fractionator (Perkin. Elmer, U.S.A.) to obtain 54–56°C/8 mmHg fraction. The thermometer was uncorrected.

Synthesis of (2,5-dimethyl-3,4-diphenyl)phenyl-triethoxysilane (DDPTES). 2.60 g (0.01 mol) of DDCP, 3.81 g (0.02 mol) of VTES and 40 ml diphenyl ether were introduced into a round bottom flask equipped with a mechanical stirrer, a reflux condensor connected to a drying tube of calcium chloride, a nitrogen inlet tube and a thermometer. At room temperature, the color of the mixture was milky white, while upon heating with stirring under an atmosphere of dry nitrogen it turned red. After the red mixture was refluxed for half an hour a light yellow solution was produced. Heating was continued for 3 h until the reaction was completed. After evaporating the diphenyl ether under reduced pressure, the residual liquid was chromatographed on an Al_2O_3 column using a mixture of petroleum ether and dichloromethane as the developing agent. The viscous liquid was separated by removal of the volatiles and was dried in a vacuum dryer at 80°C/1 mmHg for 6 h obtaining 3.30 g DDPTES (78.8%). Elemental analysis, found C, 73.95, H, 7.68% ($C_{26}H_{32}O_3Si$ requires C, 74.28, H, 7.61%). UV_{max} was 250 nm ($CHCl_3$ used as a solvent and reference). The main peaks in the IR (film) were 3056, 2964, 1596, 957, 700.

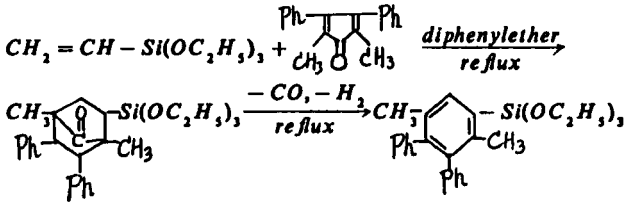
^{1}HNMR 2.08, 2.21 (6H-CH_3 in phenyl), 6.80–7.30 (11H, m, phenyl), 3.8–4.0 [6H, q, —$Si(OCH_2CH_3)_3$], 1.20–1.40 [9H, t, —$Si(OCH_2CH_3)_3$].

Synthesis of (2,5-dimethyl-3,4-diphenyl)phenyl-heptamethyl cyclotetrasiloxane (DDPHMCTS). 2.60 g (0.01 mol) of DDCP, 3.08 g (0.01 mol) of VHMCTS and 40 ml diphenyl ether were introduced into round bottom flask with the same equipment as DDPTES. The synthetic procedure was the same as that of DDPTES.

The yield of the final product was 3.96 g (73.4%). Elementary analysis: Found C, 60.43, H, 7.10%; $C_{27}H_{38}O_4Si_4$ requires C, 60.17, H, 7.11%. UV_{max} was 250 nm ($CHCl_3$ used as a solvent and reference). The main peaks in the IR (film) were 3052, 2962, 1599, 1260, 1072, 847, 809. ^{1}HNMR 0.18 (21H, m, $SiCH_3$), 2.10, 2.23 (6H, Ph-CH_3), 6.90–7.40 (11H, m, Ph).

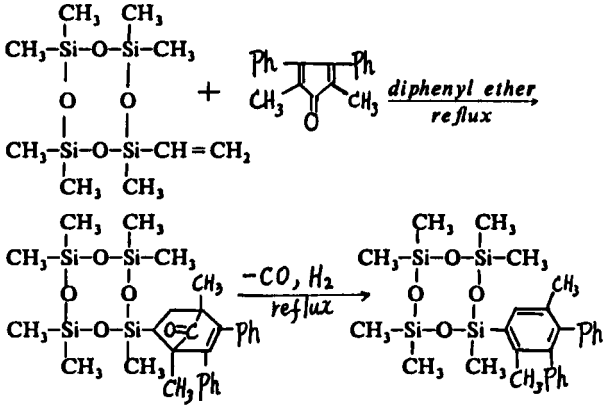
RESULTS AND DISCUSSION

Two compounds above were prepared as follows:



D–A addition product **Aromatization product**

SCHEME I



D–A addition product **Aromatization product**

SCHEME II

The similar reactions in the literature[1,2] are either in a sealed tube at high temperature or in α-chloronaphthalene as a solvent in open vessel at reflux temperature. However, in this paper diphenyl ether was used to replace α-chloronaphthalene as a solvent in open vessel at reflux temperature. It is an efficient solvent for the Diels-Alder reaction of vinylsilane with 2,5-dimethyl-3,4-diphenylcyclopentadienone. The experimental results demonstrated that not only some Diels-Alder reactions can be carried out but also the reaction products can be continuously aromatized into (2,5-dimethyl-3,4-diphenyl)phenyl silicon compounds. We have once used tetrahydronaphthalene as solvent for the reactions mentioned above. The results obtained demonstrated that only part of Diels-Alder products were aromatized into (2,5-dimethyl-3,4-diphenyl)phenyl silicon compounds. Diphenyl ether is cheaper and less toxic than α-chloronaphthalene.

Since (2,3,4,5-tetraphenyl)phenyl-triethoxysilane has been adopted as a cross linker[4] on room-curable silicone rubber (RCSR) and VHMCTS has been used as monomer[5] of polysiloxane, we can assume that DDPTES and DDPHMCTS could be of use in silicone chemistry.

REFERENCES

1. JianHua Chen, ShengYu Feng and ZuoDong Du, *Chem. J. Chinese Univ.*, **7,** 1150 (1986).
2. ZuoDong Du and Shang Yin, *Acta Polym. Sinico*, **6,** 422 (1988).
3. Japp and Meldrum, *J. Chem. Soc.*, **79,** 1036 (1901).
4. ZuoDong Du and JianHua Chen, *Polym. Commn., (China)*, 174 (1981).
5. ZuoDong Du, *Chem., Research and Application, (Chinese)*, **2** (1990).