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ORGANOSILICON COMPOUNDS
X*. PREPARATION OF CYCLIC ORGANOSILICON COMPOUNDS CONTAINING *O*-SILYL-SUBSTITUTED ENOLS**

ROSHDY M. ISMAIL
Zentrallaboratorium, Dynamit Nobel Aktiengesellschaft, Troisdorf (Germany)

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O-Silyl-substituted enols were first prepared by Gilman and Clark[1]. Other papers describe the reactions of alkylhalosilanes with sodium enolates of carbonyl compounds, *e.g.* West[2] and Hance and Hauser[3]. The reaction of halosilanes with α-trialkylstannylketones to give *O*-silyl-substituted enols have also been described by Baukov *et al.*[4]. Krüger and Rochow prepared different *O*-silyl-substituted enols by the reaction of enolates and chlorosilanes at low temperatures. They used sodium-bis(trimethylsilyl)amide as an intermediate in the preparation of the enolates required[5].

We have described, in an earlier paper, the reactions of chlorosilanes with hydroxyphenyl compounds containing other reactive groups such as 2-hydroxypyridine[6-8].

This paper reports on the reaction of dichlorosilanes with hydroxy compounds that have the carbonyl groups in the β-position as we have found that some types of *O*-silyl-substituted enols can be easily prepared by the reaction of dichlorosilanes with carbonyl groups that are in the β-position to a hydroxy group. A cyclic organo compound results. This reaction takes place at temperatures of about 80°, although

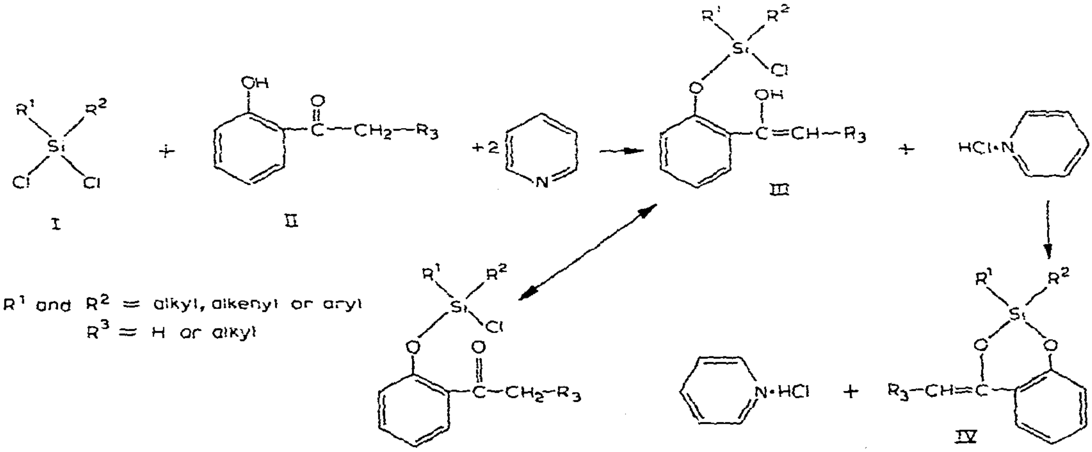

Fig. 1. Reaction of diorganodichlorosilane with hydroxy compounds containing carbonyl groups in the β-position.

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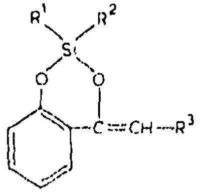
[*] For part IX see ref. 9.

[**] Dedicated to Dr. Gerhard Bier on the occasion of his 50th birthday.

TABLE 1

CYCLIC ORGANOSILICON COMPOUNDS OF THE GENERAL FORMULA



Compound	R^1	R^2	R^3	Yield (%)	B.p. (°C/mm)	n_D^{20}	Formula	Mol. wt.	Analysis	C	H	Si
Methylvinyl(styryldioxy-α,2)silane	CH_3–	CH_2=CH–	–H	85	79/0.4	1.5461	$C_{11}H_{12}O_2Si$	204.3	calcd. found	64.7 64.64	5.89 6.25	13.72 13.5
Dimethyl(styryldioxy-α,2)silane	CH_3–	CH_3	–H	91	80/0.2	1.5371	$C_{10}H_{12}O_2Si$	192.3	calcd. found	62.5 62.32	6.25 6.01	14.58 14.5
Diphenyl(styryldioxy-α,2)silane	C_6H_5	C_6H_5	–H	95		1.6118	$C_{20}H_{16}O_2Si$	316.4	calcd. found	75.9 75.70	5.07 5.2	8.86 8.8
Methylvinyl(β-methylstyryldioxy-α,2)silane	CH_3–	CH_2=CH–	–CH_3	84	88/0.9	1.5454	$C_{12}H_{14}O_2Si$	218.3	calcd. found	66.1 66.25	6.42 6.35	12.84 12.9
Dimethyl(β-methylstyryldioxy-α,2)silane	CH_3–	–CH_3	–CH_3	90	80/0.2	1.5358	$C_{11}H_{14}O_2Si$	206.3	calcd. found	64.1 64.25	6.8 6.63	13.59 13.4
Diphenyl(β-methylstyryldioxy-α,2)silane	C_6H_5	C_6H_5	–CH_3	96		1.6026	$C_{21}H_{18}O_2Si$	330.5	calcd. found	76.4 76.7	5.46 5.31	8.49 8.6
Methylvinyl(β-ethylstyryldioxy-α,2)silane	CH_3–	CH_2=CH–	–CH_2CH_3	88	87/0.5	1.5362	$C_{13}H_{16}O_2Si$	232.4	calcd. found	67.2 67.1	6.90 6.9	12.06 12.2
Dimethyl(β-ethylstyryldioxy-α,2)silane	CH_3–	CH_3–	–CH_2CH_3	92	81/0.5	1.5296	$C_{12}H_{16}O_2Si$	220.3	calcd. found	65.4 76.3	7.27 7.39	12.73 12.81
Diphenyl(β-ethylstyryldioxy-α,2)silane	C_6H_5	C_6H_5	–CH_2CH_3	97		1.5747	$C_{22}H_{20}O_2Si$	344.5	calcd. found	76.7 76.3	5.81 5.9	8.14 8.16

earlier workers used low temperatures between −50 and −70°. Isolation of the enolates is unnecessary since the Si–Cl group reacts directly with the carbonyl group to give high yields of the *O*-silyl-substituted enols.

It was found that first, one chlorine atom of the dichlorosilane reacts with the hydroxy group and then the second reacts with the enol form of the carbonyl group (III) to produce the cyclic compound (IV), Fig. 1. The same cyclic compound can also be prepared by a two-step reaction in which 1 mole of dichlorosilane (I) reacts with 2 moles of the keto-hydroxy compound (II).

For example, the reaction of 1 mole of dimethyldichlorosilane with 2 moles of 2-hydroxyacetophenone gave, in the first step, dimethylbis(acetophenoxy-2)silane (V), which produces on distillation the cyclic compound (VI) and 1 mole of 2-hydroxyacetophenone, see Fig. 2.

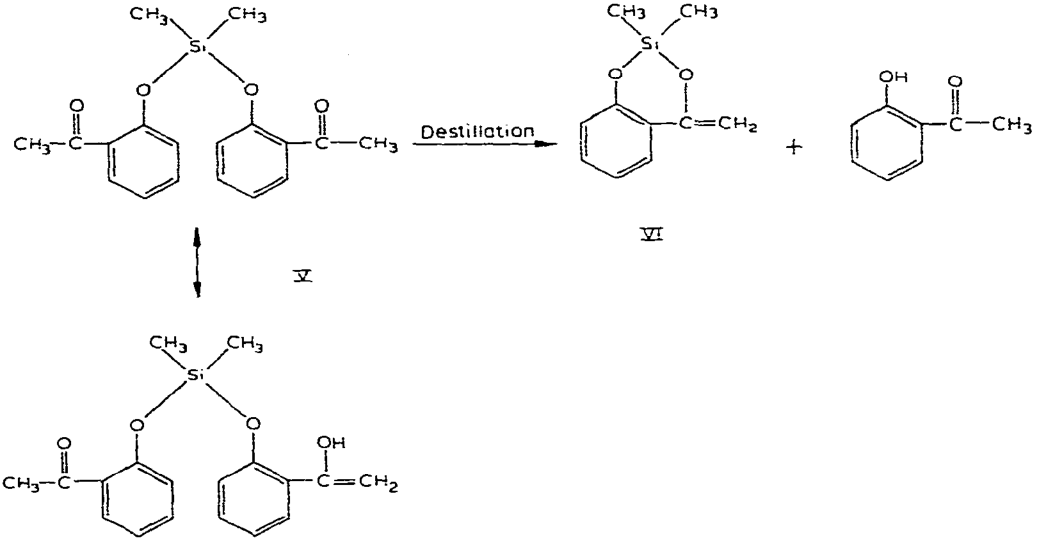


Fig. 2. Reaction of dimethyldichlorosilane with 2-hydroxyacetophenone.

All cyclic compounds prepared in this work are hydrolytically unstable. Hydrolysis yields the original carbonyl compound and siloxane.

Table 1 gives the physical properties and analysis of the compounds prepared.

EXPERIMENTAL

In general, the reactions were carried out as follows: a diorganodichlorosilane of formula I was added dropwise with stirring to a benzene solution of the carbonyl compound of formula II and the stoichiometric amount pyridine. The reaction mixture was then boiled for about 5 h. The precipitated pyridinium salt was removed by filtration and the solvent distilled. The product was then purified by distillation.

(*a*) *Methylvinyl(styryldioxy-α,2)silane*

A solution of 64 g (0.4 mole) of methylvinyldichlorosilane in 20 ml of ether was added dropwise to a solution of 54.4 g (0.4 mole) of 2-hydroxyacetophenone dissolved in 100 ml ether and 64 g of pyridine. After the addition was complete, the reaction mixture was refluxed for 5 h, then filtered with exclusion of moist air. After removal of the solvent by distillation, the residue remaining was fractionally distilled, b.p./0.4 mm, 79°, n_D^{20} 1.5461, yield 85%. (Found: C, 64.64; H, 6.25; Si, 13.5. $C_{11}H_{12}O_2Si$ calcd.: C, 64.7; H, 5.89; Si, 13.7%.)

(*b*) *Dimethylbis(acetophenoxy-2)silane*

25.8 g (0.2 mole) of dimethyldichlorosilane were added dropwise to a solution of 54.4 g (0.4 mole) of 2-hydroxyacetophenone dissolved in 100 ml ether and 32 g of pyridine. After the addition was complete, the reaction mixture was refluxed for 5 h and then filtered from the pyridinium salt. After the complete removal of the solvent by distillation, the residue remaining was dimethylbis(acetophenoxy-2)silane, n_D^{20} 1.5466. (Found: C, 65.53; H, 6.12; Si, 8.37. $C_{18}H_{20}O_4Si$ calcd.: C, 65.8; H, 6.1; Si, 8.54%.)

Distillation of dimethylbis(acetophenoxy-2)silane under vacuum first produces 2-hydroxyacetophenone, b.p./1 mm 85°, n_D^{20} 1.5597, yield 25.5 g, then the cyclic compound, dimethyl(styryldioxy-α-2)silane b.p./0.3 mm 80°, n_D^{20} 1.5371, yield 35 g. (Found: C, 62.32; H, 6.01; Si, 14.5. $C_{10}H_{12}O_2Si$ calcd.: C, 62.5; H, 6.25; Si, 14.58%.)

(*c*) *Diphenylbis(β-methylstyryldioxy-α,2)silane*

This was prepared from 45 g (0.3 mole) of 2-hydroxypropiophenone, 75.9 g (0.3 mole) of diphenyldichlorosilane and 48 g of pyridine in 300 ml dry benzene, n_D^{20} 1.5745, yield 97%. (Found: C, 76.3; H, 5.9; Si, 8.16. $C_{21}H_{18}O_2Si$ calcd.: C, 76.7; H, 5.81; Si, 8.14%.)

IR SPECTRA

The IR spectra of all the cyclic compounds prepared were similar. Typical $>C=O$ or $-OH$ frequencies are missing. Instead, the characteristic frequencies of the unsaturated groups appear: ν(C=C) 1648–1658 cm⁻¹. The compounds show also the typical absorption of the $>Si(CH_3)$ or $>Si(C_6H_5)_2$ groups, and in the range 1020–1050 cm⁻¹, a characteristic Si–O-absorption, see Fig. 3.

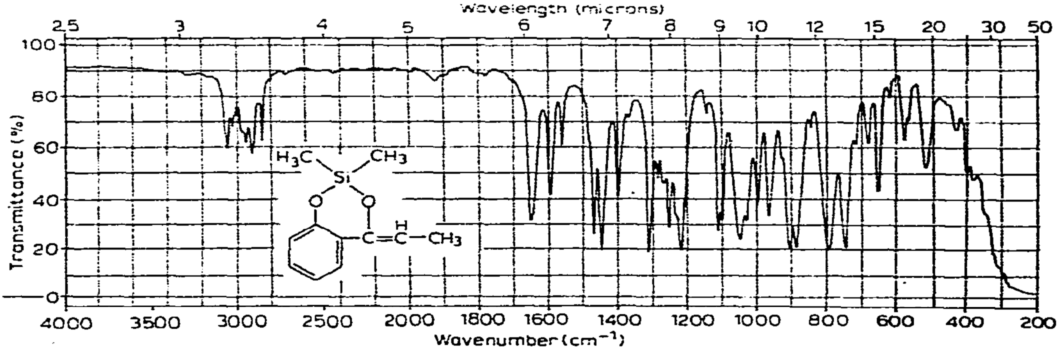


Fig. 3. IR-spectrum of dimethyl(β-methylstyryldioxy-α,2)silane.

ACKNOWLEDGEMENT

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SUMMARY

Cyclic organosilicon compounds containing *O*-silyl-substituted enols have been prepared by the reaction of diorganodichlorosilanes with carbonyl compounds having carbonyl groups in the β-position to a hydroxy group. The structures of the cyclic compounds prepared have been elucidated by analyses and IR spectroscopy.

REFERENCES

1 H. GILMAN AND R. N. CLARK, *J. Am. Chem. Soc.*, 69 (1947) 967.
2 R. WEST, *J. Org. Chem.*, 23 (1958) 1552; *J. Am. Chem. Soc.*, 80 (1958) 3246.
3 C. R. HANCE AND C. R. HAUSER, *J. Am. Chem. Soc.*, 75 (1953) 994.
4 J. I. BAUKOV, G. S. BURLACHENKO AND I. F. LUTSENKO, *J. Organometal. Chem.*, 3 (1965) 478.
5 C. R. KRÜGER AND E. G. ROCHOW, *J. Organometal. Chem.*, 1 (1964) 476.
6 R. M. ISMAIL, Australian Pat. 249690 (1966).
7 R. M. ISMAIL, French Pat. 1475896 (1967).
8 R. M. ISMAIL, *J. Organometal. Chem.*, 6 (1966) 663.
9 R. M. ISMAIL, *Kolloid-Zeitschrift, Z. Polymere*, in the press.