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Organosilicon Epoxy-compounds

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The review deals with methods for the synthesis of monomeric organosilicon epoxy-compounds and some of their reactions. The possibility of employing these compounds for the synthesis of organosilicon polyepoxides is demonstrated and some of their properties are described.
The bibliography includes 46 references.

CONTENTS

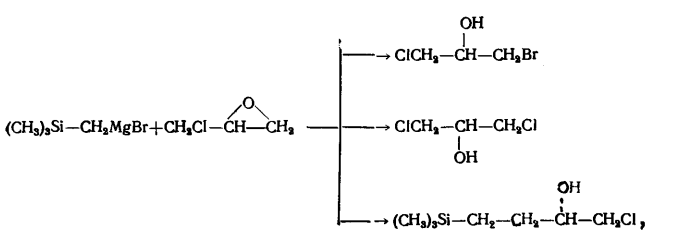
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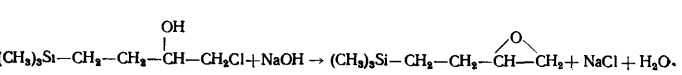
1. INTRODUCTION

Organosilicon polymers have found many applications in industry in view of their thermal stability and good dielectric properties. However, owing to their low mechanical strength and poor adhesion to glass and metals, the scope of their applications is significantly restricted. Materials formed on the basis of epoxy-resins are known to have a very high strength and satisfactory adhesion characteristics. Therefore at the present time much attention is being devoted to the synthesis of monomeric organosilicon compounds containing heterofunctional groups, particularly epoxy-groups, in the side chain at the silicon atom. Among the methods described for the synthesis of organosilicon epoxy-compounds, several trends may be distinguished.

2. DEHYDROHALOGENATION OF ORGANOSILICON CHLOROHYDRINS

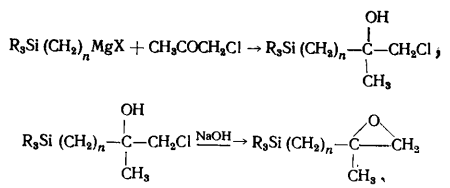
A widely employed method of synthesising epoxyalkanes is based on the dehydrohalogenation of halogenohydrins in the presence of alkaline agents. The first epoxysilylalkane was obtained by the interaction of the corresponding Grignard reagent with epichlorohydrin and subsequent dehydrohalogenation. The reaction resulted in a large amount of side products together with the desired substance:





The yields of the organosilicon chlorohydrins and of the corresponding epoxide did not exceed 25–30%.

The possibility of obtaining the halogenohydrin by the reaction of the Grignard reagent derived from the halogenoalkylsilane with monochloroacetone has been demonstrated[2]. The unambiguous course of this reaction makes it possible to obtain epoxides in high yields according to the scheme:



Ethynylepoxides have been obtained in this way[3,4].

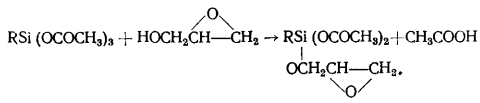
The attempt to obtain an epoxide from $R_2Si(OH)-CHCl-CH_3$ was unsuccessful[2]. Sodium hydroxide hydrolysed the Si–C bonds, while in the presence of calcium hydroxide the initial compound underwent no changes.

A method based on the addition of silanes to unsaturated halogenohydrins has also been used to synthesise organosilicon halogenohydrins. When trialkylsilanes react with $\delta\epsilon$-unsaturated halogenohydrins in the presence of H_2PtCl_6, products resulting from both addition to the multiple bond and dehydrocondensation are formed. The reaction of silanes with $\gamma\sigma$-unsaturated halogenohydrins yields only dehydrocondensation products[5,6].

3. REACTIONS OF FUNCTIONAL GROUPS AT THE SILICON ATOM WITH EPOXY-COMPOUNDS

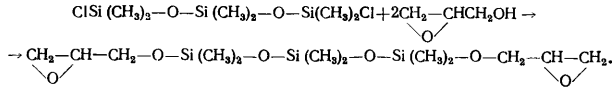
Tetra-alkoxysilanes (for example, tetraethoxysilane) or poly(silyl ethers) containing lower alkoxy-groups (methoxy-, ethoxy-) undergo complete or partial transetherification with glycidol *in vacuo* at a low temperature in the presence of transetherification catalysts (alkoxides)[7]. The compounds obtained readily harden on heating with maleic anhydride, forming polymers with satisfactory physicomechanical properties[8,9].

Acetoxyalkylsilanes also react with glycidol[10] forming glycidyl derivatives of silanes as follows:



With decrease of the number of acetyl groups in alkylacetoxysilanes, their replacement by glycidyl residues becomes more difficult. Thus the acetoxy-groups in triacetoxymethylsilane and triacetoxyvinylsilane are fully replaced by glycidyl groups, while in diacetoxydimethyl- and diacetoxymethyl-silanes they are replaced only to the extent of 70–75%; in triacetoxytrimethylsilane no substitution takes place at all.

Yamamoto[11] and Martin[12] isolated glycidylsilanes after allowing chlorosiloxanes to react with glycidol in the presence of tertiary amines as catalysts:



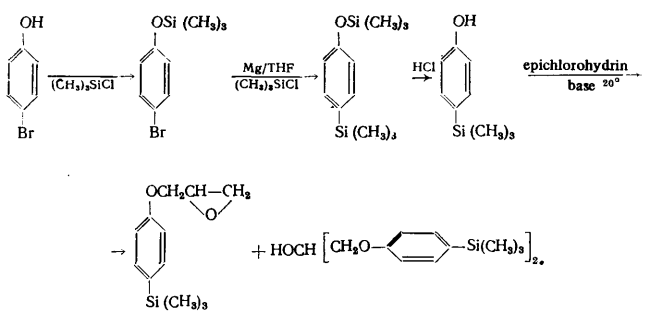
Rogers and Lewis[13] extended the scope of the synthesis of such silicon compounds. They suggested that glycidylsilanes be obtained by the reaction of glycidol or epichlorohydrin with organosilicon compounds containing not only halogeno-, alkoxy-, and acyloxy-groups at the silicon atom but also amino-, aryloxy-, and hydroxy-groups. The reaction is catalysed by alkali and is carried out at high temperatures. The resulting organosilicon epoxy-derivatives can be used as casting resins or for the preparation of laminated plastics.

Glycidylsilanes are hydrolytically and thermally unstable.

4. INTERACTION OF EPICHLOROHYDRIN WITH FUNCTIONAL GROUPS IN THE SIDE CHAIN AT THE SILICON ATOM

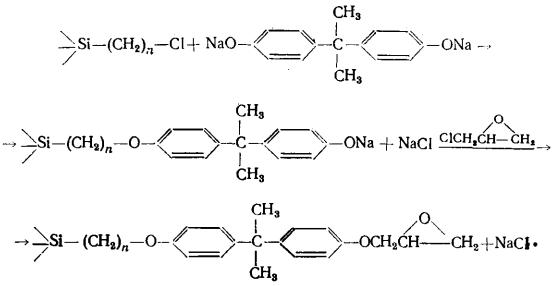
Aryl glycidyl ethers, obtained by the interaction of epichlorohydrin, aromatic hydroxy-compounds, and alkali, have become the main starting materials for the preparation of epoxy-resins. It was interesting to obtain the organosilicon analogues of such resins.

A report on the synthesis of glycidyl 4-trimethylsilylphenyl ether according to the following scheme has been published[14]:



Glycidyl 4-triphenylsilylphenyl ether has been synthesised in the same way[15].

Daniel[16] has proposed a convenient and simple method for the synthesis of interesting organosilicon derivatives of glycidol:



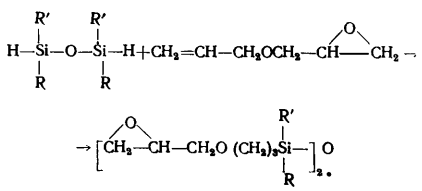
The initial organosilicon halides can be linear, cyclic or branched.

The polymers obtained from these monomers, which can be hardened by amines, are highly resistant to the action of chemical agents and have excellent adhesion properties and thermal stability. They are employed in engineering as insulating materials. Unfortunately the authors of this study do not quote quantitative estimates of the properties of the polymers.

5. ADDITION OF SILANES TO UNSATURATED EPOXY-COMPOUNDS

Silanes add to the double bonds of epoxyolefins in the same way as to other unsaturated compounds, in the presence of peroxide or platinum catalysts. The addition takes place under relatively mild conditions and the epoxy-group remains unchanged[17]. This reaction is applicable to silanes, alkoxysilanes, acyloxysilanes, and siloxanes, but not to chlorosilanes.

The attempt to isolate[18] $\alpha\omega$-bisepoxides after the reaction of allyl glycidyl ether with HRR'SiOSiR'RH in the presence of 0.1 *N* H_2PtCl_6 solution yielded polymeric products, probably as a result of the rupture of the epoxy-ring. It proved possible to obtain a bisepoxide of this kind by the following reaction using Pt/C containing 20% Pt as a catalyst:



By employing various epoxyolefins, it is possible to obtain a wide variety of organosilicon epoxides. In particular, Plueddemann and Fanger[17] obtained such compounds by the interaction of silanes with the monoepoxy-derivative of butadiene, allyl glycidyl ether, the monoepoxy-derivative of limonene, the monoepoxy-derivative of vinylcyclohexene, and 2-allylphenyl glycidyl ether. Other workers synthesised aminoepoxy-siloxanes[18–20], chlorine-containing organosilicon epoxides[21], and unsaturated organosilicon epoxy-derivatives[22]. Polymeric products derived from the latter can be obtained not only as a result of the opening of the epoxy-ring but also via the multiple bond.

Plueddemann[23] isolated individual cyclic, branched, and linear glycidylpropylsiloxanes containing less than six units. When these siloxanes hardened, it was found that cyclic polyepoxysilanes exhibit the highest hardness,

thermal stability, and impact strength. The Martens thermal stability of the polymers of lower epoxysilanes is lower than that of the usual epoxy-resins, but that of the higher polymeric epoxy-silanes is higher.

Epoxy-siloxanes synthesised by the addition of silanes have been recommended as active solvents for casting and adhesive epoxy-resins (in particular epoxynovolac resins[24]), as components of phenolic[25], alkyd, and polyester resins[26] to impart to them a higher thermal stability, as modifying agents for silicone resins to improve their adhesion and mechanical properties, and for other purposes. In 1958, epoxy-compounds of this kind were produced in France on an industrial scale[26].

6. OXIDATION OF UNSATURATED SILICON COMPOUNDS

Organosilicon epoxy-compounds with the smallest organic groups can be obtained by oxidising a multiple bond. The Prilezhaev epoxidation of silylolefins by peracids has been described. Organic peracids are electrophilic agents, the rate of reaction with such acids increasing appreciably as the nucleophilic properties of the olefin are enhanced following the substitution of the hydrogen atoms at the double bond by electron donating groups[27]. The silicon atom linked to the unsaturated aliphatic group should facilitate its oxidation by peracids.

Wende and Gesierich[28] showed that allyltriphenylsilane interacts with perbenzoic acid at a higher rate than the analogous carbon compound 1,1,1-triphenylbut-3-ene. The authors explained the increase of the rate of reaction by the negative charge on the double bond induced by the silicon atom. Under the same conditions, the vinylsilicon derivative reacts with a peracid (peracetic[17] and perbenzoic[28]) much more slowly than the allyl derivative.

In organosilicon compounds where the double bond is separated from the silicon atom by more than two carbon atoms, the silicon atom has no effect on the oxidation of the unsaturated group[17]. Organosilicon compounds containing two unsaturated groups[28] are oxidised faster than those containing one unsaturated group.

A study of the epoxidation of dimethyldivinylsilane with perbenzoic acid established[29] that the first vinyl group is oxidised much faster; the amount of monoepoxide formed is 5–6 times greater than that of the diepoxide.

In the oxidation of tetravinyldisiloxane, the first two vinyl groups are readily oxidised, while the third and particularly the fourth group are oxidised much more slowly.

When epoxy-rings accumulate in the molecule, the stability of the compound diminishes.

The general characteristics of the epoxidation reaction hold for unsaturated siloxane derivatives. The introduction into the silane molecule of the electrophilic phenyl group decreases the reactivity of the vinyl group at the silicon atom; the bulky trimethylsilyl group has a similar effect. On the other hand, when the small electron-donating methyl group is present, the rate of epoxidation increases[30].

The rate of oxidation of silanes containing one unsaturated group by perbenzoic acid decreases in the following sequence: trimethylsilane > tripropylsilane > triethylsilane > tribenzylsilane > triphenylalkylenesilane[28].

Numerous studies have established[31] that the rate of reaction between peracids and olefins follows a second-order equation (the reaction is of first-order with respect to each component). Kinetic data for the oxidation of the vinyl group in silylolefins by perbenzoic acid[30] have shown that the reaction involving organosilicon compounds is also of second order and can be represented by the following kinetic equation:

$$-\frac{dx}{d\tau} = k\,(C_3H_5CO_3H)\ \text{(silyl olefin)}.$$

The rate constant depends on the number and nature of the substituents in the reacting molecule and on the strength of the acid oxidising the olefin[32].

The epoxidation of unsaturated silicon compounds by perbenzoic[33–36], perphthalic[37], 40% peracetic[17], and peroxytrifluoroacetic[38] acids has shown that peroxytrifluoroacetic acid is the best epoxidising agent. The oxidation with perbenzoic acid is as a rule carried out at 0–20°C over a period of several days.

The epoxidation of vinylsiloxanes with 40% peracetic acid in acetic acid is very slow and gives a very low yield of epoxy-derivatives (less than 20%). Temperature and time play an important role. On raising the temperature and reaction time, there is an increased contribution due to decomposition side reactions and the yield of the epoxy-product falls appreciably[38]. Therefore one must employ the most reactive peracid and the optimal reaction conditions must be determined.

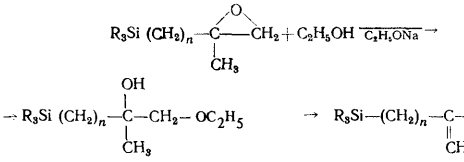
The reaction of unsaturated silicon compounds with perbenzoic acid takes place in chloroform and carbon tetrachloride much faster than in other solvents, but by employing a less active solvent (ether, tetrahydrofuran) it is possible to eliminate the side reactions.

Epoxy-organosiloxanes obtained by the oxidation of the vinyl group give rise to absorption bands in the infrared close to 758, 815, and 1138 cm^{-1}, which are characteristic of the epoxy-group[39]. Compounds of this class can be used as plasticisers, coatings, adhesives, and casting resins[39]. They are also suitable as agents imparting to coatings based on siloxanes an enhanced stability to wear[40].

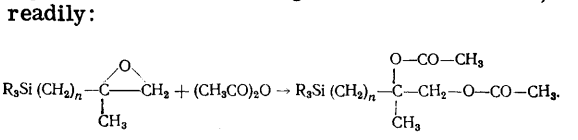
7. REACTIONS OF ORGANOSILICON EPOXY-COMPOUNDS

The epoxy-group in organosilicon compounds enters into its characteristic reactions with alcohols, phenols, acids, amines, and other compounds in the presence of appropriate catalysts[18,26,41].

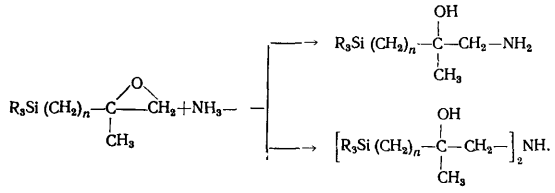
On treatment with alcohols in the presence of sodium alkoxides, organosilicon epoxy-compounds form ether-alcohols which are dehydrated on heating in the presence of $KHSO_4$ with formation of unsaturated organosilicon ethers[42]:



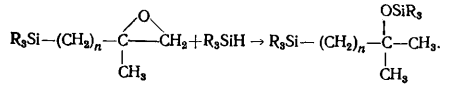
The reaction of epoxysilanes with acetic anhydride, resulting in the formation of organosilicon diacetates, takes place readily:



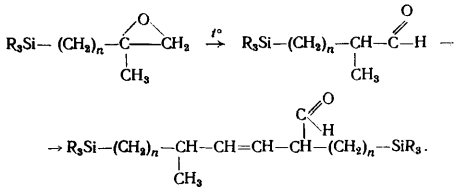
On prolonged refluxing of organosilicon epoxy-compounds with ammonia, organosilicon mono- and di-amino-alcohols are produced:



Organosilicon epoxy-compounds readily combine with silanes, forming an ether and not an alcohol[2]:

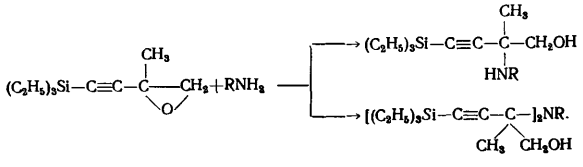


On prolonged heating up to the boiling point (at atmospheric pressure), organosilicon epoxy-compounds isomerise to aldehydes, which then undergo partial crotonic condensation[42]:

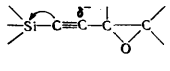


In order to assess the electronic influence of the silicon atom on the properties of the adjacent epoxy-group, a study was made of the reduction of a number of epoxyethylsilanes with lithium aluminium hydride[43]. In monosubstituted epoxides, the sterically more accessible carbon atom is usually subjected to hydride attack with formation of a secondary alcohol. When epoxyethylsilanes are reduced, a primary alcohol $R_3SiCH_2CH_2OH$ is formed unambiguously in a high yield. It would appear that steric factors should favour attack on the primary carbon atom in epoxyethylsilanes, but it has been established that in the reduction with lithium aluminium deuteride a primary alcohol is formed as a result of direct attack by the hydride ion on the carbon atom linked to silicon; this anomalous behaviour of epoxyethylsilanes can be explained by the electronic influence of the silicon atom on the epoxy-group.

The epoxy-ring of organosilicon ethynylepoxides[3], where the silicon atom is linked directly to a triple bond, is opened under the influence of aliphatic amines at the carbon atom linked directly to the triple bond (contrary to the Krasusskii rule):

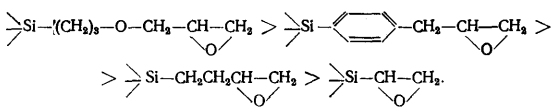


This phenomenon can be explained by a specific intramolecular interaction of the triple bond π electrons with the free *d*-orbital of the silicon atom, which leads to an enhanced polarisability of the C–O bond on the side of the more substituted carbon atom:

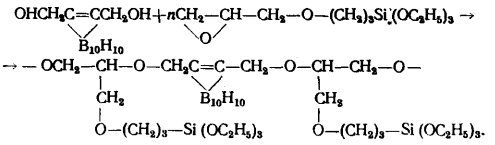


The proximity of the silicon atom lowers the reactivity of the epoxy-group in relation to the aromatic amine[44].

Organosilicon epoxy-compounds can be arranged in the following sequence in terms of their reactivity in the presence of the aromatic amine $H_2N-C_6H_4-OSi\equiv$ at 100°C:



Epoxy-organosilanes form optically active polymers[45] in the presence of a catalytic system comprising an organometallic compound and a complex-forming agent. A study of the migration polymerisation of triethoxyglycidylpropylsilane in the presence of bishydroxymethylcarborane showed[46] that in the first stage of the polymerisation the epoxy-groups interact with the hydroxy-groups of the carborane with formation of a linear polymer in accordance with the following scheme:



In the second polymerisation stage, where the content of epoxy-groups reaches a minimum, the ethoxy-groups are alcoholysed, the product changing from a viscous liquid to an elastic form.

In the absence of compounds with active hydrogen (amines, alcohols, etc.), the siloxane moiety of epoxy-organosilanes can undergo a rearrangement catalysed by alkali without the opening of the oxiran ring[17]. Alkoxysilyl groups can also be hydrolysed under mild conditions without the involvement of the epoxy-component of the molecule[17,26].

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