ISSN 1070-3632, Russian Journal of General Chemistry, 2007, Vol. 77, No. 1, pp. 55–61. © Pleiades Publishing, Ltd., 2007. Original Russian Text © E.A. Chernyshev, Z.V. Belyakova, L.K. Knyazeva, N.N. Khromykh, 2007, published in Zhurnal Obshchei Khimii, 2007, Vol. 77, No. 1, pp. 61–67.

Hydrosilylation of Allyl Glycidyl Ether with Triethoxysilane

E. A. Chernyshev, Z. V. Belyakova, L. K. Knyazeva, and N. N. Khromykh

State Research Institute of Chemistry and Technology of Organoelement Compounds, sh. Entuziastov 38, Moscow, 111123 Russia Fax: 007 (495)6731323 e-mail: eos2004@inbox.ru

Received June 6, 2006

Abstract—Hydrosilylation of allyl glycidyl ether with triethoxysilane in presence of Speier's catalyst leads to triethoxy(3-glycidoxypropyl)silane and triethoxy(2-glycidoxy-1-methylethyl)silane and is accompanied by isomerization of allyl glycidyl ether and cleavage of the oxirane ring and the ether bond. An effect of admixtures in allyl glycidyl ether on the process is revealed. Some other hydrosilylation catalysts and additives to Speier's catalyst are studied.

DOI: 10.1134/S1070363207010082

Hydrosilylation of allyl glycidyl ether leads mainly to triethoxy(glycidoxypropyl)silane which is used as a finishing material in glass-reinforced plastics industry. It is known [1–6] that hydrosilanes react with glycidoxy-containing unsaturated compounds by the double bond without cleavage of the oxirane ring. At the same time, epoxide ring opening in hydrosilylation of allyl glycidyl ether with hydroxysilanes of the general formula H[Si(MeR)O]_nSiMeRH (R = CH=CH₂, CH₂CH₂Cl, Ph; n = 1-5] in presence of H₂PtCl₆ at 100°C has been reported [7]. At 40°C, the reaction proceeds exclusively by the double bond. It is also known that hydrosilylation of allyl glycidyl ether gives mainly triethoxy(3-glycidoxypropyl)silane. Our research into hydrosilylation of allyl glycidyl ether with triethoxysilane in presence of Speier's catalyst showed that the substance isolated by vacuum distillation of the reaction mixture contains more than 98% of triethoxy(3-glycidoxypropyl)silane (I), 0.5% of triethoxy(2-glycidoxy-1-methylethyl)silane (II), and 0.5% of (3-allyloxypropyl)triethoxysilane (III) or IV). The rest is triethylglycidoxysilane (V) and unidentified admixtures [scheme (1)].

In some samples, equally small amounts of hexaethoxydisiloxane, unsymmetrical pentaethoxy(3glycidoxypropyl)disiloxane (VI), and tetraethoxy-(3-glycidoxypropyl)(hydroxy)disiloxane (VIa) were found. The latter may be formed by partial hydrolysis.



$$H_{2}C - CHCH_{2}O(CH_{2})_{3}Si(OEt)_{2}OSi(OEt)_{3} + H_{2}O \longrightarrow H_{2}C - CHCH_{2}O(CH_{2})_{3}Si(OEt)_{2}OSi(OEt)_{2}OH + EtO.$$
(5)

The first fraction obtained by vacuum distillation of the reaction mixture contained mainly unreacted allyl glycidyl ether and also 10% of glycidyl propenyl ether, 6-7% of tetraethoxysilane, 1-2% of compound **V**, and hexaethoxydisiloxane.

The results obtained show that the main reaction is hydrosilylation [reaction (1)] leading to formation of product I and a little isomer II is accompanied by side reactions of cleavage of the oxirane ring [reaction (2)] and the ether bond [reaction (3)].

It is evident that the occurrence of side reactions has almost no effect on the yield of the product. The presence in the reaction mixture of a significant amount of glycidyl propenyl ether allowed us to suggest that the hydrosilylation reaction is decelerated by a side process, allyl-propenyl isomerization [reaction (6)], which is known to accompany hydrosilylation of other allyl ethers, specifically allyl phenyl ether [8].

$$H_{2}C-CHCH_{2}OCH_{2}CH=CH_{2}$$

$$\longrightarrow H_{2}C-CHCH_{2}OCH=CHCH_{3}.$$
(6)

The amount of glycidyl propenyl ether in the reaction mixture was evaluated chromatographically.



Hydrosilylation of allyl glycidyl ether with triethoxysilane, 60°C, [Pt] 1.3×10^{-4} M. Reaction conditions: (1) allyl glycidyl ether was added to a mixture of triethoxysilane with Speier's catalyst; (2) 1/5 of the reagent mixture was mixed with Speier's catalyst and then the rest mixture was added; and (3) triethoxysilane was added to a mixture of allyl glycidyl ether with Speier's catalyst.

The structure of by-products was established by means of GC–MS. The mass spectrum of compound **II**, unlike that of **I**, contains an $(M - \text{EtO} - \text{C}_3\text{H}_6)^+$ ion peak at m/z 191 (20.9%). We showed previously [9] that the loss of propylene is characteristic of (β -amino-isopropyl)triethoxysilane. In the mass spectrum of compound **III** [or **IV**], the principal peaks relate to the $(M - \text{OEt})^+$ (m/z 233, 4.5%), $(M - \text{OEt} - \text{C}_2\text{H}_4\text{O})^+$ (m/z 189, 22.7%), $(M - \text{OEt} - \text{C}_3\text{H}_4\text{O})^+$ (m/z 177, 63.6%), and $(M - \text{OEt} - \text{AllOAll})^+$ ions (m/z 135, 100%).

Evidence for the formation of compound V is provided by the preparation of compound Ia by disproportionation of products I and V.

$$\mathbf{I} + \mathbf{V} \longrightarrow \mathbf{Ia} + \mathrm{Si}(\mathrm{OEt})_4.$$

The mass spectrum of product Ia, by contrast to that of I, contains $Si^+(OEt)_2(OCH_2CHCH_2O (m/z 191, 13.6\%))$ and $Si^+H(OEt)(OCH_2CHCH_2O (m/z 147, 100\%))$ ion peaks.

In the mass spectrum of compound VI, all principal peaks are shifted by 134 [(EtO)₂SiO] to larger mass numbers compared to compound I; the base peak belongs to $[Si(OEt)_2OSi(OEt)_3]^+$, *m/z* 297. The base peak in the mass spectrum of compound VIa relates to the $[Si(OEt)_2OSi(OEt)_2OH]^+$ ion with *m/z* 269 (100%). In the spectrum recorded with high signal amplification, $[(C_2H_3O)CH_2OCH_2CHCH_2(CH_3) \cdot Si(OEt)_2OSi(OEt)(OCH=CH_2)]^+$ (*m/z* 337), [337 – (C₃H₆)]⁺ (*m/z* 295), and [337 – (C₂H₄)₂]⁺ (*m/z* 281) ion peaks are observed.

The hydrosilylation of allyl glycidyl ether with triethoxysilane involves, as a rule, an induction period followed by a step (15–60 min) with a relatively high reaction rate. The adduct content in this period 40– 50%. The reaction is then decelerated and to bring it to completion requires additional heating for 1–5 h. A characteristic kinetic curve is presented in the figure. We showed that upon pretreatment of the catalyst with triethoxysilane or allyl glycidyl ether the induction period is shorter or absent; therewith, in the first case the reaction rate is higher (see figure, curves 2 and 3, respectively). With freshly distilled allyl glycidyl ether, the reverse situation is observed (Table 1).

This fact prompted us to reveal possible admixtures in allyl glycidyl ether and study their influence on the reaction pathway. GLC showed that commercial allyl

Characterictic of allyl glycidyl ether	Method of synthesis ^a	Temperature, °C	Time, h	Yield of product I, %
Commercial, 97%	b	115–120	2.5	0
The same	The same	123-128	5	50.0
The same	С	123-128	5	61.0
Freshly distilled, 98%	b	70-90	1.5	78.9
The same	С	70–90	1.5	65.5

Table 1. Effect of the quality of allyl glycidyl ether and order of reagent mixing on the yield of product I

^a see Experimental.

glycidyl ether may contains up to nine admixtures X_1-X_9 . Two of them (X₅ and X₆, 0.5–0.6% each) are present in a distilled product (purity ~98%). Their structure was established by GC-MS. The principal peaks in the mass spectrum of allyl glycidyl ether relate to the $C_{3}H_{5}^{+}$ (*m/z* 41, 100%) and $C_{3}H_{5}O^{+}$ (*m/z* 57, 82%). Under high-amplification conditions (the base peak is off-scale), m/z 114 (M⁺), 113 (M – H)⁺, and 95 $(M - H - H_2O)^+$ ion peaks are observed. In the mass spectrum of compound X₅, the principal peaks relate to the $C_3H_7O^+$ (*m/z* 59, 100%), $C_3H_7^+$ (*m/z* 43, 47%), $(M - CH_3)^+$ (*m/z* 101, 32%), and $(M - CH_3 - CH_3)^+$ H_2O)⁺ (*m*/z 83, 7%) ions. From these data it follows that compound X_5 is propyl glycidyl ether (VII). In the mass spectrum of the second admixture X_6 , the base peak belongs to the acryloyl cation CH₂CHC=O⁺ at m/z 55, and the intensities of all the other peaks vary within the range 1-4%. The mass spectrum of the same compound recorded under high-amplification conditions also contains $(M - H)^+$ $(m/z 127), (M - H - H)^+$ H₂O) (*m*/z 109), and (*M* – CH₃CO)⁺ (*m*/z 73) ions peaks, which corresponds to glycidyl acrylate (VIII). The formation of the latter can be explained by the oxidation of allyl glycidyl ether with atmospheric oxygen to a hydroperoxide (the process characteristic of ethers), followed by rearrangement [10].

$$O_2 + H_2C - CHCH_2OCH_2CH=CH_2$$

$$O'$$

$$H_2C - CHCH_2OCHCH=CH_2.$$

$$O'$$

$$OOH$$

Evidence for the oxidation of allyl glycidyl ether was obtained by a qualitative reaction with potassium iodide. Compound **VIII** was found in distilled allyl glycidyl ether just after a week. Upon prolonged handling (more than a year) at room temperature without protection from light, the content of glycidyl acrylate **VIII** in some samples reached 30%. Such allyl glycidyl ether was a viscous liquid with n_D^{20} 1.4679 (for freshly distilled sample, n_D^{20} 1.4545), evidently containing a polymeric arylate **VIII**. As known, boiling of allyl glycidyl ether at 155°C under a stream of air increases its refractive index to 1.4764 (conversion 50%) [11]. In a sample of allyl glycidyl ether containing 90.8% of the main substance, 2.9% of ether VII, and 2.3% of acrylate VIII after 48-h handling at room temperature, the content of ether VII increased to 4.6%, whereas the content of acrylate VIII decreased to 0.7%, evidently because of the formation of ether VII under these conditions.

Glycidyl acrylate **VIII** is probably formed by a radical reaction with C–H bond cleavage [12].

$$2R^{1}R^{2}HCOO^{-} \longrightarrow R^{1}R^{2}CO + R^{1}R^{2}HCOH + O_{2},$$

$$R^{1}=H_{2}C-CHCH_{2}O, R^{2}=CH=CH_{2}.$$

Both admixtures likely result from more intricate processes involving hydroperoxides. Hence, the presence of the ether **VII** admixture may be caused by initial oxidation of allyl glycidyl ether and subsequent reaction of the hydroperoxide with allyl glycidyl ether (for example, addition to the double bond [10] followed by rearrangement). The decreased content of acrylate **VIII** may be connected with its polymerization in the presence of alkali.

As freshly distilled allyl glycidyl ether contains very little other admixtures, they were not identified on this stage of the work.

The effect of admixtures **VII** and **VIII** on hydrosilylation is reflected in Table 2. As would be expected, ether **VII** has no effect on the reaction progress, while acrylate **VIII** decreases the yield of compound **I** from 78.6 to 60%. The hydrosilylation of freshly distilled allyl glycidyl ether with triethoxysilane in presence of Speier's catalyst and allyl methacrylate proceeds slower than in the absence of the latter additive. In the first case, to bring the reaction to completion requires heating for 5 h, while in the second, for 2 h. Obviously, Speier's catalyst reacts with allyl methacrylate to give an acrylate platinum

Content, %			Yield of
VII	allyl glycidyl ether	VIII	product I, %
0.67 4.56 3.22	98.1 97.3 91.2 92.2	0.17 0.72 1.44	78.6 70.6 64.5 60.0

Table 2. Effect of admixtures in allyl glycidyl ether on the yield of product I (synthesis time 1 h)

complex which is inactive in hydrosilylation. The same reason probably explains the decreased activity of Speier's catalyst in the reaction with undistilled allyl glycidyl ether. The platinum complex with allyl glycidyl ether, formed in the absence of acrylate **VIII**, exhibits a higher catalytic activity than the acrylate one. It was shown previously [13] that addition of allyl glycidyl ether accelerates hydrosilylation of allylamine due to formation of an olefin platinum complex. However, this complex is insufficiently selective and causes isomerization of allyl glycidyl ether on its hydrosilylation.

Searching for a more effective catalyst for hydrosilylation of allyl glycidyl ether, we tried some platinum and other transition metal complexes, supported platinum catalysts, and Speier's catalyst modified by additives. Freshly distilled allyl glycidyl ether (Table 2) and that with admixture **VIII** (Table 3) were used. In presence of the bisdicarbollyl complex $Pt(C_2B_9H_{11})_2$ **IX**, dimethylglyoximate complex $Pt(DMG)_2$ **X**, and dimethyl sulfoxide complex *cis*- $Pt(DMSO)_2Cl_2$ **XI**, the reaction proceeded smoothly and involved no temperature jump characteristic of hydrosilylation in presence of Speier's catalyst. The reaction time was 4–7 h, and the yield varied within the range 43–50%. In presence of other metal complexes, such as nickel dimethylglyoximate Ni(DMG)_2 (**XII**) and bisdicarbollyl complexes of cobalt, $Co(C_2B_9H_{11})_2^{-}K$ (**XIII**), iron $Fe(C_2B_9H_{11})_2^{-}K$ (**XIV**), and nickel Ni($C_2B_9H_{11})_2$ (**XV**), the reaction almost failed (Table 4).

The supported catalysts were prepared by treating silica gel surface with bis[chloro(dimethylamino)carbenium] hexachloroplatinate (catalyst **XVI**), by modifying porous glass with (diallylaminopropyl)triethoxy-silane or trichloro(2-cyanoethyl)silane with subsequent treating with Speier's catalyst (silica gel–supported platinum catalysts **XVII and XVIII**), as well as by modifying silica gel with triethoxy(vinyl)silane (catalyst **XIX**). The supported catalysts were used 3–4 times; therewith, their activity gradually decreased. The yields of compound I varied from 30 to 75%. The highest yield was achieved on catalyst **XIX** (see Table 4).

Speier's catalyst was modified immediately before use by mixing with an additive and heating the resulting mixture at 50–60°C for 5–10 min. Propylene, dimethylglyoxime, DMSO, phthalonitrile, potassium 7,8-dicarba-nido-undecaborate, potassium oxalate, triethoxy(vinyl)silane, and vinylsilatrane were used as additives. With freshly distilled allyl glycidyl ether,

Run no.	Catalyst	Reaction mixture temperature during addition, °C	Time, h	Yield of product I, %
1	SC ^a	70–85	1.0	72.4
	SC	70–85	2.0	74.0
	SC	70–90	0.5	61.4
	SC	70–90	1.5	78.9
2	SC with triethoxy(vinyl)silane	80–95	0.5	72.3
	SC with triethoxy(vinyl)silane	80–95	1.5	78.0
3	SC with acetone	80–95	0.5	73.2
	SC with acetone	80–95	1.5	77.8
4	SC with DMG ^b	80-120	0.5	75.6
5	SC with allyl metacrylate	130–150	5.0	60.0 ^c
6	Pt(DMG) ₂	80–95	0.5	73.0
7	$Pty(DMSO)_2$	80–95	1.0	58.4
8	Pt(acac) ₂	65–105	3.0	66.9
				1

Table 3. Hydrosilylation of freshly distilled (98.1%) allyl glycidyl ether with triethoxysilane (procedure b)

^a (SC) Speier's catalyst. ^b (DMG) Dimetylglyoxime. ^c Procedure *a* (see Experimental).

	11010 01
no. Temperature, °C Time,	h product I, %
1 IX 130–140 4	43.0
2 X 7	50.0
3 XII	1–2
4 XIII 10	0
5 XIV	0
6 XV	0
7 XVI 115–125 2.5	41.0
150–160 10	49.0
8^{a}_{b} XVII 120 0.5	57.0
8 0 6.0	58.2
	59.0
8 ^u 7	40.0
9^{a}_{b} XVIII 4.0	39.1
9 ⁶	32.7
9 ^c 4.5	31.6
10^{a}_{b} XIX 0.5	75.0
10° 1.0	62.9
10°_{4} 2.5	57.2
10^{d} 6.0	60.8
10 ^e 3.0	48.4
11 SC 120–130 2.0	56.0
12 SC + DCUB ¹ 130–140 $0.5-1$	65.0
13 SC + $C_3H_6^{g}$ 120–130 2.0	66.5
14 SC + DMG 120–130 1.0	61.1
15 SC + DMSO 120–130 7.0	72.0
16 SC + phthalonitrile $120-130$ 1.0	60.0
17 SC + $K_2C_2O_4$ 140 3.0	71.1
$18 \qquad SC + triethoxy(vinyl)silane \qquad 70 \qquad 1.0$	66.0
19 SC + vinylsilatrane 105–115 1.5	59.8
3.0	61.4
$20 \qquad SC + acetone \qquad 70 \qquad 1.0$	63.0
21 SC + Pr_2S^n 90–123 1.5	55.1
22 SC + $(Et_2O + BF_3)$ 100 1.0	0
130–160 0.5	63.5
23 SC + DMSO 120 1.0	66.4

Table 4. Hydrosilylation of allyl glycidyl ether (main substance 97.3%, acrylate **VIII** 0.17%) with triethoxysilane (procedure a)

^{a-e} Successive syntheses on the same catalyst sample. ^f (DCUB) Potassium 7,8-dicarba-*nido*-undecaborate. ^g Prepared according to [20]. ^h Procedure c (see Experimental).

the acetone, triethoxy(vinyl)silane, and dimethylglyoxime additives scarcely affected hydrosilylation (see Table 3): The reactions proceeded with heat release, and the yields of the final product were the same as in the presence of Speier's catalyst alone. At the same time, the use of additives in hydrosilylation of allyl glycidyl ether containing acrylate **VIII** improves the yield (see Table 4). This especially relates to such additives as potassium 7,8-dicarba-*nido*-undecaborate, dimethylglyoxime, phthalonitrile, and potassium oxalate. The use of additives in the last case allowed us to decrease the catalyst concentration from 10^{-4} to 10^{-5} M and the reaction temperature, $0-120^{\circ}$ C. In the absence of additives, the reaction failed even at $120-130^{\circ}$ C.

The role of additives evidently consists in that they form platinum complexes which do not react with acrylate **VIII**. Previously [14] we used the example of hydrosilylation of allyl phenyl ether with triethoxysilane to show that Speier's catalyst modified with triethoxy(vinyl)silane slows down isomerization. In our case, too, additives probably act by the same mechanism.

EXPERIMENTAL

Gas chromatography was carried out on a Tsvet-500 chromatograph with a thermal conductivity detector, using 3000x3-mm metallic column packed with 5% of SE-300 on Chromaton N-AW-DMCS; injector and detector temperatures 300°C. The oven temperature was programmed from 60 to 290°C at a rate of 16°C/min with 1- and 3-min isotherms at the initial and final temperatures, respectively. Carrier gas helium, flow rate 40 ml min⁻¹.

Identification of admixtures in the reaction product was carried out by adding reference substances and by mass spectrometry. The mass spectra were obtained on a Hewlett–Packard HP-5971 A GC–MS system, ionizing voltage 70 V. Gas chromatography was carried out on a 25000 × 0.32-mm quartz capillary column, stationary phase DB-5, film thickness 25 μ m. The oven temperature was programmed from 50 to 280°C at a rate 7°C/min. Carrier gas helium, flow rate 0.8 ml min⁻¹.

Platinum bisdicarbollyl complex was prepared according to [15] and iron and nickel bisdicarbollyl complexes, according to the Hawthorn method [16]. Platinum and nickel dimethylglyoximates were obtaimed by treating NiCl₂· $6H_2O$ and K₂PtCl₄ with dimethylglyoxime [17, 18]. The carbenium salt was prepared according to [19].

Synthesis of supported catalysts. a. Modification of porous glass with functionalyzed organosilicon compounds. Porous glass containing 96% of SiO₂ and 4% of B₂O₃ was used, pore diameter 40–50 Å. specific surface 100–50 m²g⁻¹, porosity 30%. Before treatment it was dried for 2.5 h at 200–250°C; adsorbed water content was controlled by IR spectroscopy.

b. Catalyst XVII. Porous glass, 30 g, was treated with a solution of 32.5 g of (diallylaminopropyl)triethoxysilane in 150 ml of toluene and refluxed for 26 h. The glass was filtered, washed with benzene $(3 \times 20 \text{ ml})$, and extracted in a Soxhlet apparatus for 7 h with hexane. After that it was filtered, washed with ether $(2 \times 10 \text{ ml})$, and dried in a vacuum (1 mm Hg) for 2 h at 50°C. The modified porous glass was treated with a solition of 2.34 g of H₂PtCl₆·6H₂O in 30 ml of 2-propanol and kept for 1.5 months at room temperature. The glass was filtered off, washed with water $(3 \times 30 \text{ ml})$, ethanol $(3 \times 30 \text{ ml})$, and ether $(2 \times 30 \text{ ml})$ and dried first in air and then in a vacuum (1 mm Hg) at 20°C for 6 h. A reddish-brown catalyst with a platinum content of 0.06% was obtained.

Catalysts **XVIII** and **XIX** were obtained analogously. Catalyst **XVI** was prepared according to [20].

Hydrosilylation of allyl glycidyl ether in the presence of Speier's catalyst. All the reactions were carried out under nitrogen.

a. A 0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ in 2-propanol, 0.02 ml, was mixed with 1.5–3 ml of a mixture of 5.9 ml of allyl glycidyl ether and 9.2 ml of triethoxysilane and the mixture was heated to 60– 110°C. After 0.5–6 min, vigorous heat evolution took place, and the reaction mixture warmed up to 120– 160°C. When the temperature began to decrease, the rest reagent mixture was added dropwise at 110– 130°C, and the resulting mixture was heated at 120– 130°C until complete reaction (GLC monitoring).

b. The reagent and catalysts amount were the same as in the above procedure. A mixture of the catalyst and allyl glycidyl ether was heated to $60-70^{\circ}$ C, and triethoxysilane was added at a rate providing maintaining a preset temperature (90–100°C). After the addition was complete, the resulting mixture was heated for 1–3 h at 90–145°C until complete reaction.

c. The reaction was carried out by adding allyl glycidyl ether to a mixture of triethoxysilane and the catalyst. The reagent amounts were the same as in the above procedures.

Hydrosilylation in presence of a modified Speier's catalyst and complex compounds was carried out analogously. The amounts of additives were 0.02–0.05 ml (g) per 0.02 ml of Speier's catalyst. The catalyst concentration was 1.3×10^{-4} – 7.6×10^{-4} M.

Hydrosilylation of allyl glycidyl ether in presence of supported catalysts. A mixture of 1.5 g of a catalyst, 1.2 ml of allyl glycidyl ether, and 1.95 ml of triethoxysilane was heated at $110-120^{\circ}$ C until complete reaction. The liquid was decanted, and the catalyst was washed with hexane (2×3 ml). A new portion of the reagents was added to the catalyst, and the procedure was repeated.

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