Chemistry

Corresponding Member of the Academy of Sciences of the USSR R. Kh. FREIDLINA, E. Ts. CHUKOVSKAYA

1963

SovietRxiv

Abstract

Full Text

Chemistry

Corresponding Member of the Academy of Sciences of the USSR R. Kh. FREIDLINA, E. Ts. CHUKOVSKAYA

TELOMERIZATION OF ALLYL COMPOUNDS WITH SILICON HYDRIDES IN THE PRESENCE OF DICYCLOHEXYL PEROXYDICARBONATE

In the present work we have studied the reactions of methyldichlorosilane with allyl acetate, allyl chloride, and decene in the presence of dicyclohexyl peroxydicarbonate.* The use of peroxydicarbonates as initiators of reactions of silicon hydrides with unsaturated compounds has not been described in the literature; however, it could be expected that $C_6H_{11}OCOO$ radicals, formed during the decomposition of p.o.d.c., would be capable of initiating such reactions. The kinetics of the decomposition of p.o.d.c. in various solvents has been studied in detail in the works of G. A. Razuvaev, L. M. Terman, and co-workers ([1,2]). They described the addition of isopropyl alcohol to maleic acid under the action of p.o.d.c., with the formation of terebic acid ([3]).

Previously we described the thermal telomerization of ethylene with various silicon hydrides at 300° ([4,18]) and at 200° in the presence of $TiCl_4$ ([5]). Silicon hydrides react with unsaturated compounds at 120—140° in the presence of iron and nickel carbonyls ([6,7]). According to the literature, platinum catalysts ([8,9]) and acyl and alkyl peroxides ([10]) are widely used for initiating such reactions. However, the use of all the listed methods of initiating the reaction under consideration is associated with limitations: at 300°, unsaturated compounds with functional substituents cannot be used, and α-olefins partially polymerize; these difficulties are not eliminated (in the presence of $TiCl_4$) by lowering the temperature to 200°. In the case of using metal carbonyls, telomerization does not take place, and only the adduct of a silicon hydride with an unsaturated compound is formed, as well as unsaturated organosilicon compounds. Reactions in the presence of platinum or H_2PtCl_6 also in many cases proceed toward the formation of the adduct of a silicon hydride with an unsaturated compound, without an admixture of telomers ([4,9,11,17]). Attempts to use a number of alkyl and acyl peroxides to initiate the reactions under discussion in steel autoclaves gave negative results, which is explained by inhibition by the walls ([4,9,12]).

In connection with all the foregoing, it seemed of interest to use p.o.d.c. as an initiator of the reaction of silicon hydrides with unsaturated compounds, assuming that carrying out the reaction under mild conditions, at 55—60°, would

make it possible to eliminate the difficulties listed.

Indeed, it was found that reactions between allyl compounds and methyldichlorosilane can be successfully carried out at 55—60°, with formation of a mixture of telomers according to the equation

$$CH_3SiCl_2H + nCH_2 = CHCH_2R \rightarrow CH_3SiCl_2(CH_2CHCH_2R)_{nH},$$

where $R = C_7H_{15}$; Cl; $OCOCH_3$. In the case $R = Cl$, telomers with $n = 1$—3 were isolated individually (conversion of allyl chloride 50—70%), and in the case $R = OCOCH_3$, telomers with $n = 1, 2$ (conversion of allyl acetate about 70%). The properties of the compounds obtained are summarized in Table 2.

* Hereinafter abbreviated as p.o.d.c.

It should be noted that replacing methyldichlorosilane by triethylsilane or methyldiethoxysilane lowers the conversion of allyl acetate in the reaction under consideration to 12-18%. This is consistent with literature data ([13]) on the low activity of such silicon hydrides in peroxide-initiated radical reactions.

In all the reactions studied by us that were carried out under conditions usually favoring formation of the adduct, i.e., with an excess of silicon hydride, telomers with $n > 1$ were formed in high yields. Table 1 gives a comparison of the yields of the products of the reaction of allyl acetate with silicon hydrides as a function of the ratio of the starting reagents and the initiators used.

Table 1

Molar ratio $\frac{RSiCl_2H}{CH_2=CHCH_2OAc}$	R	Catalyst	Temp., °C	Yield of $n = 1$, % of total products	Yield of telomers with $n > 1$, % of total products	Reference
2 : 1	CH_3	p.o.d.c.	55-60	39	61	see experiment “1” in the experimental part ([9])
1.1 : 1	CH_3	0.06% Pt/C	95	100	–	
2 : 1	C_6H_5	tert-butyl perbenzoate	86	74	26	([14])

As is seen from the data of Table 1, in the presence of Pt/C only the adduct is formed, whereas in the presence of tert-butyl perbenzoate, in addition to the adduct, a viscous unidentified residue is obtained, amounting to 26% of the sum of products. In the presence of p.o.d.c., at the same ratio of the starting reagents, the yield of telomers with $n > 1$ was 61%.

The telomerization of allyl chloride by silicon hydrides has not been described in the literature. In the presence of tert-butyl peroxide in glass, allyl chloride does not react with phenyldichlorosilane ([14]), whereas in the presence of platinum catalysts only the adduct and by-products are formed ([11,15]).

In the presence of p.o.d.c., telomerization of allyl chloride with methyldichlorosilane proceeds with high conversion; moreover, even at the molar ratio $CH_3SiCl_2H : CH_2{=}CHCH_2Cl = 3 : 1$, the content of telomers with $n > 1$ is 56%, calculated on the sum of reaction products. With a threefold excess of allyl chloride, products with $n > 3$ constitute 72% of the telomer mixture. To study the effect of the nature of the initiator and the reaction temperature on the distribution of the yields of individual telomers, we propose in the future to carry out a kinetic study.

Thus, the results obtained show that the use of p.o.d.c. makes it possible to lower the reaction temperature, to involve α-olefins and unsaturated compounds containing functional substituents in the reaction, and on this basis to develop the synthesis of silicon compounds with polyfunctional radicals.

Experimental Part

1. Reaction of allyl acetate with methyldichlorosilane. In a three-necked flask equipped with a stirrer, reflux condenser, and thermometer, 115 g (1 mole) of CH_3SiCl_2H, 53 g (0.53 mole) of $CH_2{=}CHCH_2OCOCH_3$, and 5 g of p.o.d.c. were heated at 55-60° for 6 hours. After removal of the starting substances, a telomer with $n = 1$ was obtained, 25.4 g (23% of theory, calculated on $CH_2{=}CHCH_2OCOCH_3$; 39% of the sum of products), and a telomer with $n = 2$, 5-acetoxy-2-(acetoxymethyl)-pentylmethyldichlorosilane, 35.5 g (22% of theory, 54% of the sum of products). The residue of telomers with $n > 2$ was 4.5 g (7% of the sum of products). Here and in the following experiments the yields are given

for fractions boiling within a range of 3-5°. A small portion of such a fraction was redistilled and used for analysis and determination of constants (Table 2).

2. Reaction of methyldichlorosilane with allyl chloride.
a) In a steel ampoule autoclave,* placed in a water bath, 57 g (0.5 mole) of CH_3SiCl_2H, 13 g (0.17 mole) of $CH_2{=}CHCH_2Cl$, and 1.3 g of DCPD were heated at 60° for 6 hours. After distillation of the starting substances, a telomer with $n = 1$ was obtained, 7.8 g (24% of theory, 44% of the total products); a telomer with $n = 2$, 5-Cl, 2-chloromethylpentyldichlorosilane, 4.2 g (9.2% of theory, 24% of the total products); a telomer with $n = 3$, 7-Cl, 2,4-bis(chloromethyl)-

pentylmethyldichlorosilane, 3.2 g (5.5% of theory, 18% of the total products); the residue of telomers with $n > 3$ amounted to 2.4 g (14% of the total products). Titration found Cl% in the residue: 17, 20, 15, 29. Average molecular weight, ~ 440.

b) Carrying out the reaction under the same conditions, but with charges of CH_3SiCl_2H 23 g (0.2 mole), $CH_2{=}CHCH_2Cl$ 46 g (0.6 mole), and DCPD 3 g led to the formation of telomers with $n = 1$-3, 8.5 g (28% of the total products); the residue of telomers with $n > 3$, 22 g (72% of the total products).

* Experiments in steel reactors are poorly reproducible. This same reaction was carried out in glass (see experiment 2 "c").

Table 2

Formula	b.p., °C	n_D^{20}	d_4^{20}	MR, found	MR, calc.	Si, %, found	Si, %, calc.	Cl, %, found	Cl, %, calc.
$CH_3SiCl_2CH_2CH_2CH_2CH_2Cl$*	94 at 40 mm	1.4610	1.2046	–	–	10.33	–	36.94; 37.25; 36.88	37.01
$CH_3SiCl_2CH(CH_3)CH_2CH_2Cl$	69–70 at 1 mm	1.4700	1.1950	–	–	10.10	10.48	26.78	26.45
$CH_3SiCl_2(CH_2CH_2CH_2CH_2CH_2Cl)_2$	108 at 0.25 mm	1.4840	1.2378	79.65	80.28	8.64; 8.63	8.15	20.18; 20.16	20.57
$CH_3SiCl_2CH_2CH_2CH_2CH_2CH_2CH_2Cl$ · CH_2Cl**	79–80 at 1 mm	1.4535	1.1618	49.34	48.87	13.08; 12.61	13.05	33.27; 33.16	32.96
$CH_3SiCl_2CH_2CH_2CH_2OCH_2CH_2Cl$	115–118 at 0.08 mm	1.4623	1.1656	74.39	73.61	9.02; 8.55	8.90	23.16; 22.23	22.55
CH_3SiCl_2H	90 at 1 mm	1.4188***	0.9620	70.91	71.18****	10.76; 10.80	10.99	27.61; 26.74	27.77

* b.p. 181-183°, n_D^{20} 1.4610 (16), n_D^{20} 1.4580 (1), d_4^{20} 1.2045 (1).
** b.p. 84.2 at 6.5 mm (17), n_D^{20} 1.4534 (9), d_4^{20} 1.151 (9).
*** b.p. 111-114 at 30 mm, n_D^{20} 1.4490, d_4^{20} 0.9600 (18).
**** The calculation is based on data of group refractions: CH_3SiCl_2H, calculated from the refraction of the Si–H bond (9) and equal to 27.64.

Titration found in the residue Cl%: 8.22, 7.99. Average molecular weight ~880.

c) Carrying out the reaction in a three-necked flask analogously to experiment 1 in a solution of benzene or chlorobenzene, with charges of CH_3SiCl_2H 115 g (1 mole), CH_2=$CHCH_2Cl$ 50 g (0.66 mole), DCHP 5 g, solvent 60-90 ml over 8 hours, led to the formation of telomers with n = 1–3.23 g (57% of the sum of products). The residue of telomers with $n > 3$, 17 g (43% of the sum of products), by titration was found to contain Cl%: 11.23, 11.54. Average molecular weight ~600. Constants and analyses of the substances obtained, see Table 2.

3. **Reaction of methyldichlorosilane with decene-1.** The reaction was carried out analogously to experiment 1. As a result of 7-hour heating of 14 g (0.1 mole) of decene-1, 17.2 g (0.15 mole) of CH_3SiCl_2H, and 1.4 g of DCHP, a telomer with n = 1, 5 g (19.6% of theory, 67% of the sum of products), and a residue of telomers with $n > 1$, 2.5 g (33% of the sum of products), were obtained. By titration, Cl% was found in the residue: 12.13; 12.42. The average molecular weight of the residue was ~640. Conversion of decene-1 was about 40%.

As a result of the investigation carried out, it was found that dicyclohexyl peroxydicarbonate initiates the reactions of silicon hydrides with unsaturated compounds at 55-60° with high conversion, and the telomerization of allyl chloride with methyldichlorosilane has been studied (telomers with n = 1–3 were isolated individually), as well as of allyl acetate (telomers with $n = 1, 2$ were isolated individually).

Received
5 III 1963

CITED LITERATURE

1. L. M. Terman, Candidate dissertation, Gorky, 1961.

2. G. A. Razuvaev, L. M. Terman, ZhOKh, **30**, 2387 (1960); Collection of scientific works of the Institute of Physico-Organic Chemistry, Academy of Sciences of the BSSR, 1960, p. 51.

3. L. M. Terman, G. A. Razuvaev, G. G. Petukhov, DAN, **136**, 1349 (1960).

4. R. Kh. Freidlina, Izv. AN SSSR, OKhN, **1957**, 1333.

5. R. Kh. Freidlina, E. Ts. Chukovskaya, Tsao-I, A. N. Nesmeyanov, DAN, **137**, 885 (1961).

6. R. Kh. Freidlina, E. Ts. Chukovskaya, Tsao-I, A. N. Nesmeyanov, DAN, **132**, 374 (1960).

7. R. Kh. Freidlina, E. Ts. Chukovskaya, Izv. AN SSSR, OKhN, **1963**, 761.

8. G. H. Wagner, C. O. Strother, Brit. pat. No. 670,617 (1952); Chem. Abstr., **46**, 8894 (1952).

9. J. L. Speier, J. A. Webster, G. H. Barnes, J. Am. Chem. Soc., **79**, 974 (1957).

10. J. L. Speier, J. A. Webster, J. Org. Chem., **21**, 1044 (1956).

11. V. A. Ponomarenko, B. A. Sokolov et al., DAN, **106**, 76 (1956).

12. E. T. McBee, C. W. Roberts, G. W. R. Puerckhauer, J. Am. Chem. Soc., **79**, 2329 (1957).

13. E. W. Pietrutza, L. N. Sommer, F. C. Whitmore, J. Am. Chem. Soc., **70**, 484 (1948). D. Seyferth, S. C. Rochow, J. Org. Chem., **20**, 250 (1955).

14. J. L. Speier, R. Zimmerman, J. Webster, J. Am. Chem. Soc., **78**, 2278 (1956).

15. J. W. Ryan, G. K. Menzie, J. L. Speier, J. Am. Chem. Soc., **82**, 3601 (1960).

16. K. Shine, Chem. Abstr., **55**, 15341 (1961).

17. L. Goodman, R. M. Silverstein, A. Benitz, J. Am. Chem. Soc., **79**, 3073 (1957).

18. A. N. Nesmeyanov, R. Kh. Freidlina, E. Ts. Chukovskaya, DAN, **112**, 271 (1957).

19. J. A. Vogel, W. T. Gresswell, J. Leicester, J. Phys. Chem., **58**, 174 (1956).

Note: Figure translations are in progress. See original paper for figures.