HYDROSILYLATION OF N-ALLYLPYRROLIDINE AND N-ALLYLPIPERIDINE*

É. Ya. Lukevits, A. E. Pestunovich,
M. G. Voronkov, and T. M. Kupch

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It was found that the hydrosilylation of N-allylpyrrolidine and N-allylpiperidine by trialkylsilanes, triethoxysilane, and 3H-heptamethyltrisiloxane in the presence of $H_2PtCl_6 \cdot 6H_2O$ proceeds to form γ-adducts.

In the hydrosilylation of allylamine and its N-alkyl and N-alkylsilyl derivatives, the silyl group adds to the terminal atom of the double bond to form γ-adducts [2-6].

We have carried out the hydrosilylation of N-allylpyrrolidine (I) and N-allylpiperidine (II) with trialkylsilanes, triethoxysilane, and 3H-heptamethyltrisiloxane in the presence of a 0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol. Signals of the protons of the $SiCH(CH_3)CH_2N$ grouping are absent in the PMR

TABLE 1. Hydrosilylation of N-Allylpyrrolidine (I) and N-Allylpiperidine (II)

Starting compounds	Amounts of reagents				Order of mixing the reagents*	Heating time at 100°, h	Yield	
	I (or II), g	hydrosilane		catalyst, ml			g	%
		g	m-mole					
I, $CH_3(C_4H_9)_2SiH$	4,35	6,34	40	0,13	A	12	7,27	93
I, $(C_2H_5)_3SiH$	4,04	4,17	36	0,05	A	12	5,24	64
II, $CH_3(C_3H_7)_2SiH$	4,88	5,37	39	0,10	B	17	6,95	69,8
II, $CH_3(C_4H_9)_2SiH$	3,13	3,92	25	0,13	A	12	4,22	59,5
II, $CH_3(C_5H_{11})_2SiH$	4,51	6,95	36	0,10	B	17	8,55	76,2
II, $(C_2H_5)_3SiH$	6,00	6,00	48 †	0,05	C	0,5	9,20	80
II, $C_2H_5(C_3H_7)_2SiH$	9,20	10,68	74	0,05	A	15	14,28	72
II, $C_2H_5(C_4H_9)_2SiH$	4,26	6,03	34	0,08	B	17	3,09	26,1
II, $(C_3H_7)_3SiH$	4,26	5,54	34	0,10	B	17	4,70	48,7
II, $(C_4H_9)_3SiH$	4,26	7,05	34	0,10	B	17	4,30	38,8
II, $(C_2H_5O)_3SiH$	12,52	16,40	100	0,06	C	4	19,30	66,7
II, $CH_3[(CH_3)_3SiO]_2SiH$	2,07	3,65	16	0,02	C	2	2,67	48

*The letter A indicates the catalyst was added gradually to a mixture of the silane and alkene, B indicates the alkene was added dropwise to the heated (to 100°) mixture of silane and catalyst (0.05 ml), and the remaining amount of catalyst was then added gradually, while C indicates the mixture of silane and catalyst was added dropwise to the heated (to 100°) alkene. The course of the reaction was followed from the disappearance of the ν_{SiH} and $\nu_{C=C}$ absorption bands in the IR spectrum.

† The amount of II is indicated. A 10% excess (52 mmole) of the triethylsilane was used.

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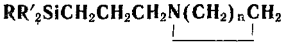
TABLE 2



$RR'_2SiCH_2CH_2CH_2N(CH_2)_nCH_2$

R	R′	*n*	Bp, °C (pressure, mm)	n_D^{20}	d_4^{20}
CH_3	C_4H_9	3	130—132 (4)	1,4635	0,8484
C_2H_5	C_2H_5	3	100—102 (2)	1,4660	0,8571
CH_3	C_3H_7	4	131 (3)	1,4660	0,8531
CH_3	C_4H_9	4	138—141 (2)	1,4670	0,8547
CH_3	C_5H_{11}	4	162—166 (1)	1,4660	0,8501
C_2H_5	C_2H_5	4	125—128 (4)	1,4700	0,8647
C_2H_5	C_3H_7	4	134 (2)	1,4680	0,8581
C_2H_5	C_4H_9	4	148—150 (3)	1,4668	0,8600
C_3H_7	C_3H_7	4	143—146 (2)	1,4700	0,8553
C_4H_9	C_4H_9	4	172—176 (3)	1,4697	0,8552
C_2H_5O	C_2H_5O	4	115—117 (2)	1,4400	0,8350
CH_3	$(CH_3)_3SiO$	4	117 (1)	1,4339	0,8922

Table 2 (continued)

MR_D		Empirical formula	Found, %			Calc., %		
found	calc.		C	H	N	C	H	N
87,56	87,36	$C_{16}H_{35}NSi$	71,3	13,4	10,2*	71,2	13,0	10,4*
73,50	73,27	$C_{13}H_{29}NSi$	68,6	13,0	12,7*	68,6	12,8	12,3*
82,95	82,89	$C_{15}H_{33}NSi$	71,0	13,0	5,5	70,5	13,0	5,4
92,06	91,99	$C_{17}H_{37}NSi$	72,2	12,9	9,5*	72,0	13,1	9,9*
101,53	101,41	$C_{19}H_{41}NSi$	73,4	12,9	4,3	73,2	13,2	4,4
78,27	77,90	$C_{14}H_{31}NSi$	69,9	13,0	11,4*	69,6	12,9	11,6*
87,32	87,40	$C_{16}H_{35}NSi$	71,0	12,6	10,1*	71,2	13,0	10,4*
95,98	96,50	$C_{18}H_{39}NSi$	72,3	13,4	4,3	72,6	13,2	4,7
92,50	92,15	$C_{17}H_{37}NSi$	71,2	13,2	4,9	72,0	13,1	4,9
106,18	105,80	$C_{20}H_{43}NSi$	73,9	13,6	4,2	73,7	13,3	4,3
80,58	80,54	$C_{14}H_{31}NO_3Si$	57,7	—	4,7	58,0	10,7	4,8
101,47	101,65	$C_{15}H_{37}NO_2Si_3$	52,2	10,8	3,9	51,8	10,7	4,0

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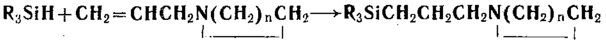
*Si.

spectra of all of the addition products. In addition, signals from the protons of the $Si-CH_2$ grouping (δ 0.53 and 0.45 ppm, respectively) are observed in the spectra of the products of the addition of triethoxysilane and 3H-heptamethyltrisiloxane to N-allylpiperidine. Consequently, these reactions also proceed with the formation of γ-adducts.



$$R_3SiH + CH_2{=}CHCH_2N(CH_2)_nCH_2 \longrightarrow R_3SiCH_2CH_2CH_2N(CH_2)_nCH_2$$

I n=3; II n=4

The structures of the products of the addition of the trialkylsilanes to N-allylpiperidine (II) are also confirmed by the agreement in their physical constants and IR absorption spectra and the constants and spectra of trialkyl(3-piperidinopropyl)silanes, which we previously obtained from trialkyl(3-chloropropyl)silane and piperidine [7].

The order of mixing the reagents (in equimolecular quantities) has a substantial effect on the reaction rate, which is greatest in the case of the addition of a mixture of the hydrosilane containing the catalyst to the heated alkene. The order of mixing the reagents did not affect the direction of hydrosilylation. The conditions used to carry out the reactions are presented in Table 1. The physical constants and results of analysis of the compounds obtained are presented in Table 2.

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