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NUCLEAR-SUBSTITUTED 1-PHENYL-1-METHYL-1-SILACYCLOBUTANE DERIVATIVES

N. V. Ushakov and V. M. Vdovin

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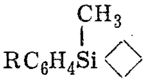
Much research has been devoted recently to a study of the effect of various types of substituents on the reactivity of the endocyclic Si−C bond of 1-silacylcobutanes in thermal [1] and anionic polymerization [1, 2] reactions, decomposition under electron impact [3, 4], and reaction with metal salts [5, 6], and also to a study of the effect of substituents on the properties of heterochain polysiltrimethylenes derived from 1-silacyclobutanes [1].

In the present paper we describe the synthesis of compounds of this type, which differ in the nature and position of the substituents in the aromatic nucleus, and which offer promise for studies in the above-indicated directions. The nuclear-substituted derivatives of 1-phenyl-1-methyl-1-silacyclobutane (I)-(VII) were obtained by the reaction of 1-methyl-1-chloro-1-silacylcobutane with the appropriate arylmagnesium bromides. The characteristics of the obtained compounds are given in Table 1.

TABLE 1. Properties of Nuclear-Substituted 1-Phenyl-1-methyl-1-silacyclobutanes RC_6H_4Si



Compound	R	Yield of analytically pure product in %	bp °C (p, torr)	n_D^{20}	d_4^{20}	MR *		Molecular weight		R_f †
						found	calculated	found	calculated	
(I)	p-CH_3	70–80	73,5–74 (3,8–4,0)	1,5308	0,9381	58,13	57,73	175,0	176,3	0,89±0,02
(II)	m-CH_3	75–85	67,5–68 (3,0)	1,5301	0,9443	57,75	57,73	176,0	176,3	0,82±0,02
(III)	p-Br	40–50	74–76 (0,05)	1,5658	1,2896	60,99	60,78	233,0	241,2	0,80±0,03
(IV)	m-Br	40–45	65–80 (0,05)	1,5628	1,2913	60,91	60,78	238,0	241,2	0,78±0,03
(V)	p-Cl	75–80	78 (1,0)	1,5482	1,0741	58,19	57,94	192,0	196,7	0,83±0,02
(VI)	p-$N(CH_3)_2$	70–80	105,5 (0,015)	–	–	–	–	201,0	205,3	0,73±0,01
(VII)	m-CF_3	65–70	62,5–63 (3,0)	1,4789	1,1284	57,85	57,82	227,0	230,3	0,94±0,02

*The MR were calculated taking into account the exaltations [7].

†The R_f were found for neutral Al_2O_3 (II activity) uner Stahl standard conditions [8]. The solvents were: n-hexane for compounds (I)-(V), a benzene–heptane mixture (1 : 2 by volume) for (VI), and a benzene–hexane mixture (1:3 by volume) for (VII).

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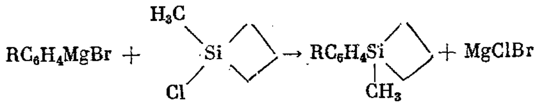

In synthesizing these compounds care should be taken when preparing the organomagnesium compounds so as to reduce the amount of products formed by coupling of the radicals, which products offer the greatest hindrance to isolating the desired products in the pure state. All of the compounds (except crystalline (VI) [9]) are colorless liquids at room temperature, which polymerize when heated. The IR spectra of these compounds contain bands at 930, 1125, and 1185 cm^{-1}, which are characteristic for the silacyclobutane ring.

EXPERIMENTAL

General Procedure. To a solution of the Grignard reagent from 1.0 mole of the aryl bromide and 1.2 g-atoms of Mg in 1100 ml of ether [in THF for (VI)] was added in 40 min a solution of 0.85 mole of 1-chloro-1-methyl-1-silacyclobutane in an equal volume of ether, after which the mixture was heated for 5 h, cooled, and decomposed first with water and then with NH_4Cl solution [(VI) was decomposed only with water, with subsequent adjustment of the pH to 8.0-8.5]. The organic layer was separated, while the aqueous layer was extracted with ether (2 × 100 ml). The combined ether extracts were washed until neutral, dried, filtered, and the solvent was removed. The residue was vacuum distilled and then chromatographed on an Al_2O_3 column. After removal of the solvent the product was redistilled in vacuo.

CONCLUSIONS

The synthesis of some nuclear-substituted derivatives of 1-phenyl-1-methyl-1-silacyclobutane by the reaction of 1-methyl-1-chloro-1-silacyclobutane with the appropriate arylmagnesium bromides was described.

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