Organosilicon Fragrances

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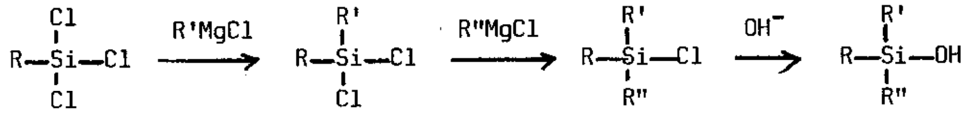
Novel and interesting investigations in the field of the chemistry of odor have been recently described by Wrobel and Wannagat.[1-5] In their search for new fragrances and for a better understanding of the relationship between the molecular structure and the olfactory properties of compounds, the authors turned their attention to silicon. The principal approach was to introduce the silicon atom into the osmophoric center of odoriferous materials. A number of compounds have been prepared and evaluated. This article briefly summarizes the synthesis and olfactory characteristics obtained.

Silicon Analogues of Tertiary Alcohols

For the preparation of tertiary dialkyl aromatic silanols, the Grignard route was the synthetic pathway of choice (see figure 1). The yields of individual synthetic steps ranged between 24% and 89%.

Silyl linalool was prepared in the manner shown in figure 2. The yields of individual steps ranged from 44-63%.[2]

A somewhat different approach was taken for the preparation of silyl derivatives of α-terpineol, α-terpinene, and carromenthane. The synthetic pathway to obtain the silyl-α-terpineol can serve



where R = CH_3, R' = CH_3, C_2H_5, CH = CH_2,

R" = $C_6H_5CH_2$, $C_6H_5Cl_2CH_2$.

Figure 1

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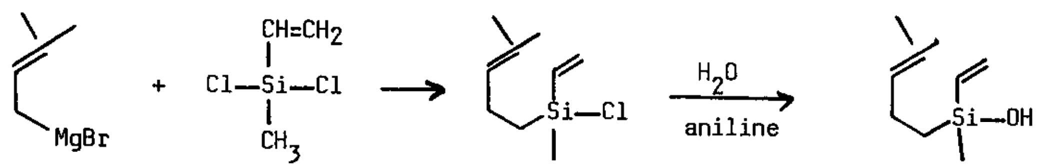


Figure 2

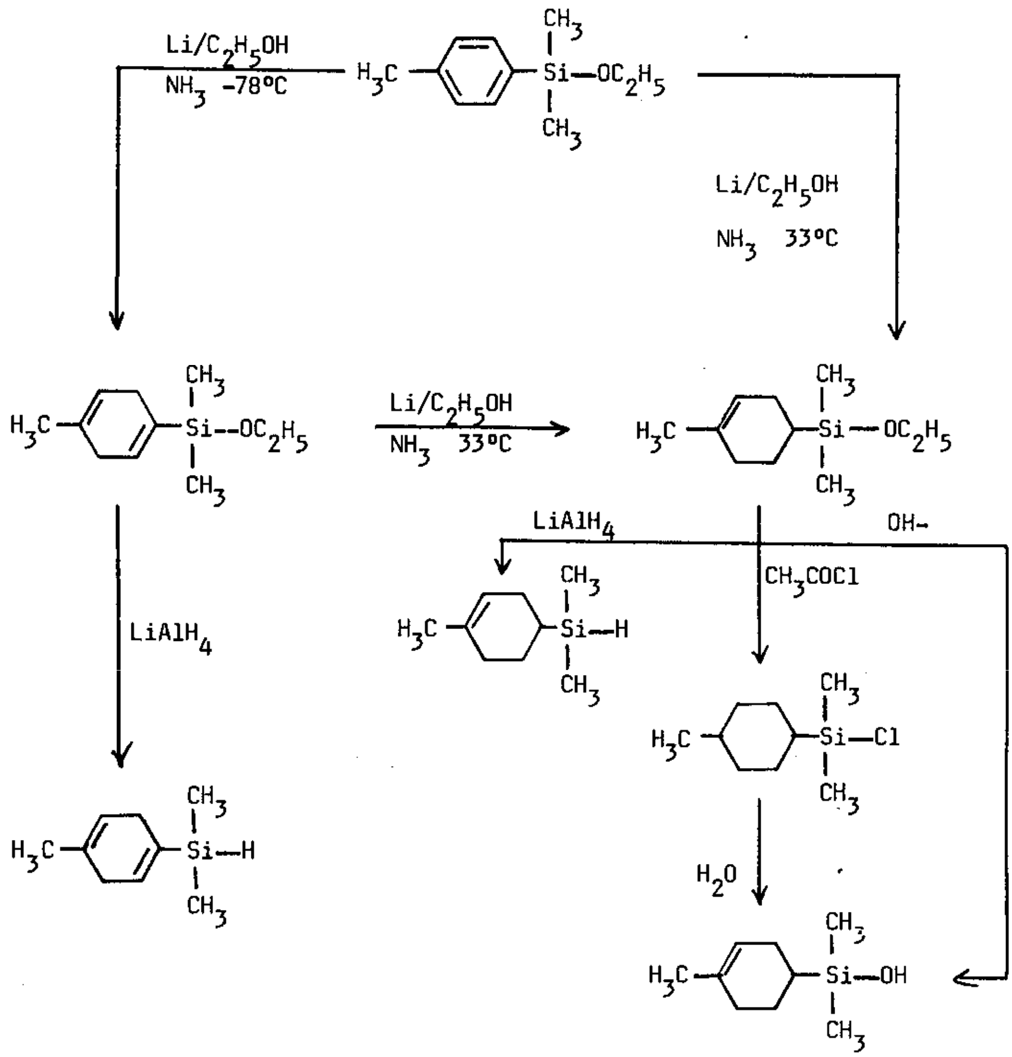
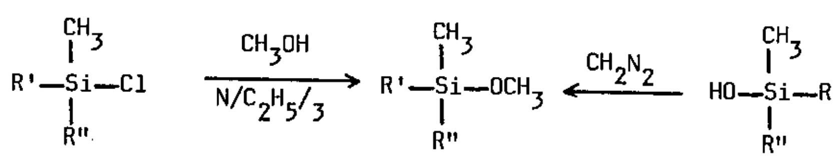


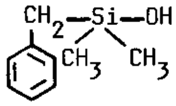
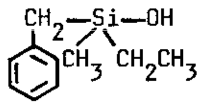
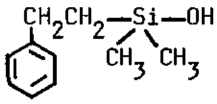
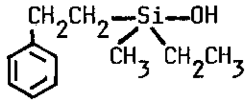
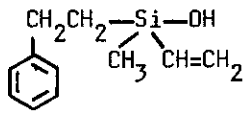
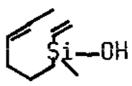
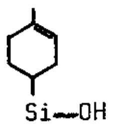
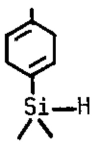
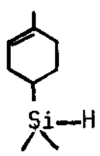
Figure 3



where R' = CH_3, C_2H_5, CH = CH_2 and R" = $C_6H_5CH_2$, $C_6H_5CH_2CH_2$

Figure 4

Table I

Compound	Fragrance
	Very similar to benzyldimethyl carbinol. Floral bouquet with strong scent of lily-of-the-valley and hyacinth.
	Similar to benzyl-ethyl-carbinol but with more accented hyacinth note
	Similar to β-phenyldimethylcarbinol; the hyacinth note more perceptible but that of the lily-of-the-valley less
	Similar to the corresponding carbinol and to the compound above, hyacinth note more accented and that of the lily-of-the-valley less, also, a slight "wooden" note
	Similar to the corresponding carbinol; lily-of-the-valley note more accented, more "green" scent, and somewhat less sweet
	Similar to linalool but less sweet with a clear hyacinth note
	An intense floral scent, somewhere between the fragrance of α-terpineol and linalool (lilac/lily-of-the-valley)
	Herbo-turpentinic fragrance similar to terpinolene
	Similar to limonene

as the example of this preparative route (see figure 3).

The chemical structures of prepared silanols were unequivocally verified by elemental analysis and IR and H-NMR spectra. The purity of the compounds was determined chromatographically.

All of the silanols were colorless liquids and could be distilled under reduced pressure without any trace of decomposition. Their boiling points were very similar to those of corresponding carbinols.

The olfactory characteristics of the synthesized silanols are described in Table I.

Clearly there is a high degree of fragrance similarity between the silanols and their carbinol counterparts. This similarity in olfactory characteristics is, in fact, in accordance with the Beets odor theory.[6] In the case of benzyldimethylcarbinol and its silanol analogue, one third of a

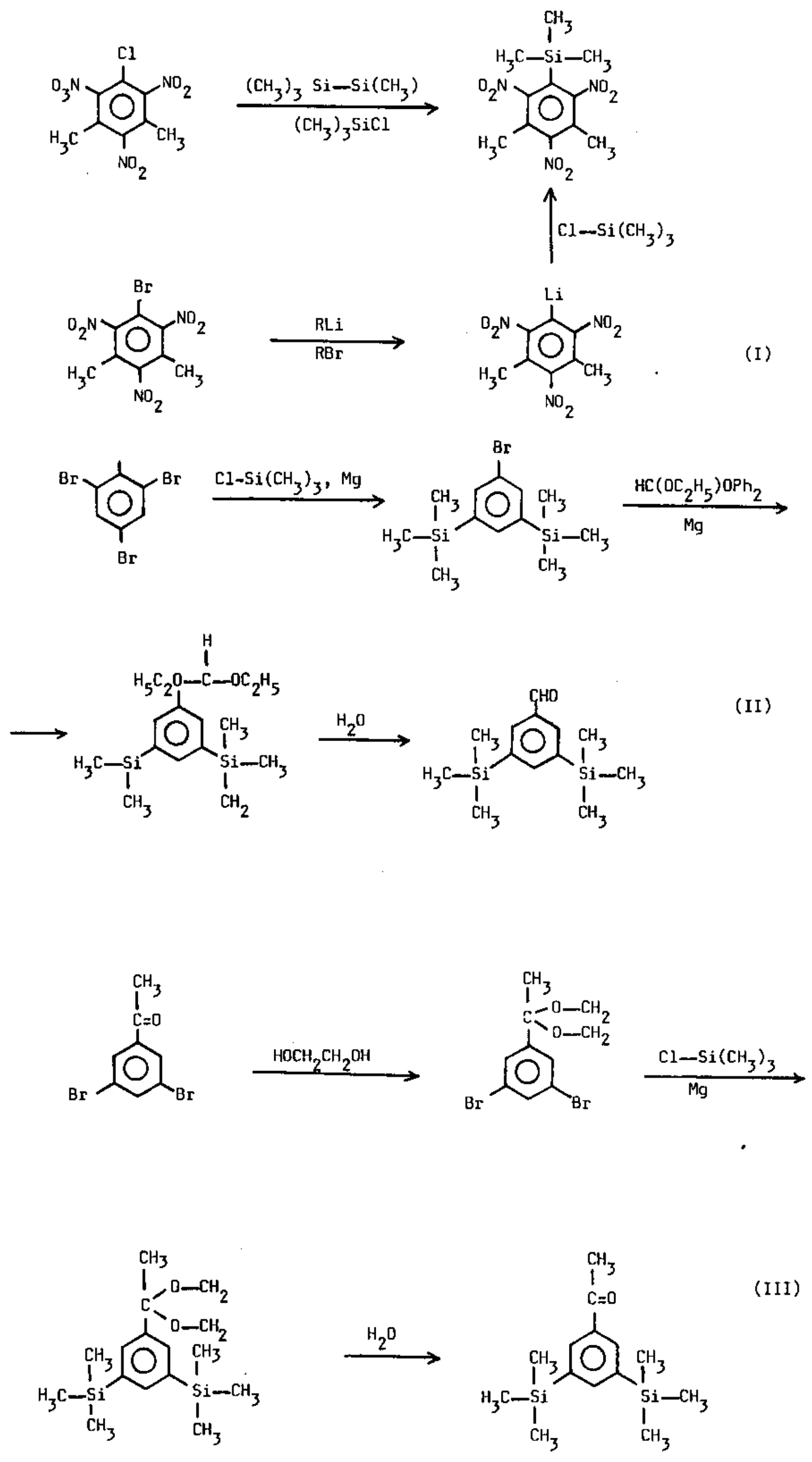


Figure 5

group of one hundred panelists could not differentiate between the two, but two thirds of the panelists judged the fragrance of the silanol more pleasant.

Methoxysilanes

Methoxysilanes were synthesized from the corresponding chlorosilanes or silanols according to the reaction scheme in figure 4.

In contrast to silanols, the methoxysilanes have been found to exhibit distinctly different scents from their carbon ether counterparts. For example, the methyl ether of benzyldimethylcarbinol has a camphoric-radishy odor while its methoxysilane analogue has a floral-honey-like scent with a mint note, more like the acetate of benzyldimethylcarbinol.

Silyl Derivatives of Musk Scents

The musk scent substances have been widely employed in studies aimed at deducing a relationship between the molecular structure of a compound and its fragrance.[6] It is thus not surprising that Wrobel and Wannagat have explored the potential of silicon derivatization in this field as well.

A variety of compounds were prepared and three of the preparative approaches adopted are shown in figure 5. All three of the materials shown here are crystalline solids stable at ambient temperatures. However, only one (I) exhibited typical musk scent. Indeed, it was judged as being more pleasant and more fragrant than the "xylene" musk itself. The other two compounds (II and III) were odorless. Wrobel and Wannagat attributed this lack of odor to the increase of the molecular volume of these compounds brought about by substitution, in each case, of a hydrogen atom by two bulky trimethylsilyl moieties. In this respect, it is worth noting that the germanium analogues of "xylene" musks were also found to be practically odorless.

These investigations by Wrobel and Wannagat may open a new and exciting direction for future studies in the field of fragrances.

Acknowledgement

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