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SELECTIVE REDUCTION OF α,β-UNSATURATED TERPENE CARBONYL COMPOUNDS USING HYDROSILANE-RHODIUM(I) COMPLEX COMBINATIONS

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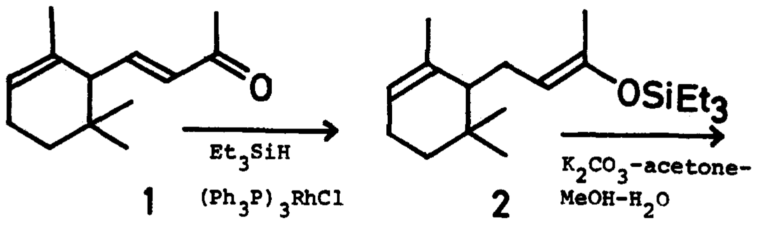
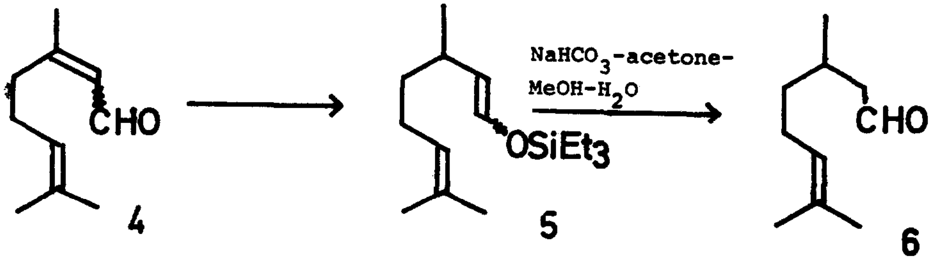
The reduction of α,β-unsaturated carbonyl compounds has been effected chemically by dissolving alkali metals in liquid ammonia[1] and amalgamated zinc hydrochloric acid[2]. However, these reactions often cause undesired side reactions, because of the required strongly basic or acidic conditions. Sodium borohydride also has been employed in certain cases, but lacks general utility[3]. The homogeneous transition metal complex catalysed reduction of unsaturated compounds, most of which proved to involve metal hydride complex, is the subject of current interest[4]. However, there have so far been few attempts to gain selectivity for homogeneous reduction of α,β-unsaturated carbonyl compounds[5,6]. We wish to report in this paper a new selective reduction of α,β-unsaturated carbonyl compounds by means of hydrosilane-rhodium(I) complex combinations under mild conditions[7,8].

The α,β-unsaturated carbonyl compounds involving an isolated double bond in the same molecule were chosen for the substrates. A selective hydrogenation of the double bond conjugated to carbonyl group in such compounds by metal catalysed hydrogenation has not always afforded sufficient results because of a lack of consistent selectivity[9]. However, this hydrogenation can be easily achieved by the use of rhodium(I) complex catalysed hydrosilation without any isomerization of the remaining double bond.

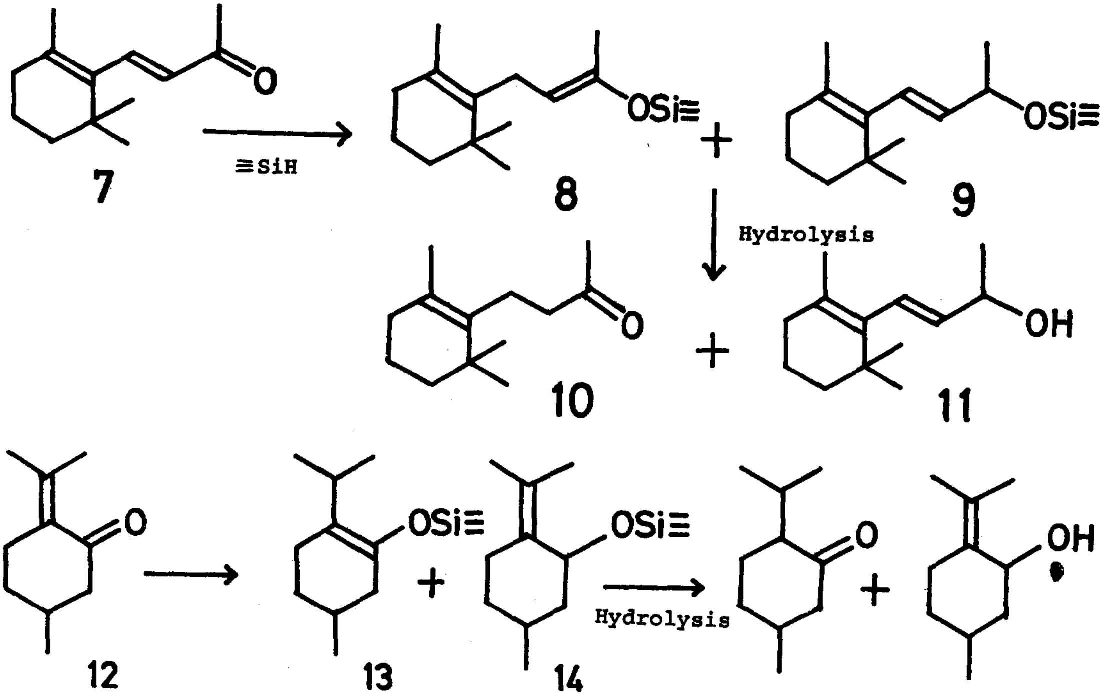
α-Ionone(1) was treated with slight excess of triethylsilane in the presence of a catalytic amount of $(Ph_3P)_3RhCl$ (0.5 Mol %) under nitrogen at 50° for 2 hr., then α-ionone(1) was completely consumed. The resulting silylenolether 2 (bp. 119°/0.4 mm) was hydrolysed by K_2CO_3-acetone-MeOH-H_2O solution and dihydroionone (3) was obtained in 96 % yield (based on 1)[10]. The nmr spectra of silylenolether 2 and dihydroionone 3 demonstrated that no isomerization of the remaining double bond had occurred during the reaction. In a similar manner, citral(4) was hydrogenated to citronellal(6) in 97 % yield via silylenolether 5 (bp. 76°/0.3 mm). Citral has thus been hydrogenated in complete selectivity for the first time. It should be noted that the catalytic hydrogenation using the homogeneous catalyst cannot be used to prepare citronellal because of the extensive decarbonylation[11], while the hydrosilation can be achieved without any deactivation by such a side reaction.



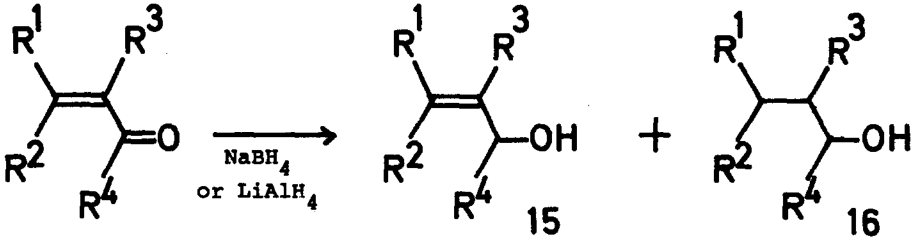


On the other hand, in the case of β-ionone(7) which is one of the conjugated dienones, the formation of dihydro-β-ionone(10) and an alcohol(11) was observed. The ratio of the ketone 10 to the alcohol 11 was found to be greatly affected by the hydrosilane employed. For example, the ratio of the ketone 10 versus the alcohol 11 was 91/9 with phenyldimethylsilane; 10/11 = 44/56 with triethylsilane;

0/100 with diethylsilane and diphenylsilane. Thus, the selective hydrogenation of β-ionone(7) was achieved by phenyldimethylsilane-rhodium(I) complex combination in high selectivity, and the complete selective reduction of the carbonyl of β-ionone(7) was performed by hydrosilane-rhodium(I) complex combiantions. A similar trend was also observed in the case of the hydrosilation of pulegone(12). The ratio of the silylenolether 13 versus silylether 14 was found to be as follows: 13/14 = 75/25 with phenyldimethylsilane; 50/50 with triethylsilane and tri-n-propylsilane; 0/100 with diethylsilane and diphenylsilane.



Sodium borohydride reduction of conjugated carbonyl compounds was reported to result in the formation of almost equal amounts of the alcohol 15 and 16[12], often accompanied by an isomerization of the double bond[13]. Lithium aluminumhydride reduction of these compounds gave the alcohol 16 predominantly, but the conversion of the reaction was rather low[13]. Thus, the present results demonstrated that the dihydrosilane-rhodium(I) complex combination in the reduction of β-ionone(7) and pulegone(12) displayed an exceedingly higher selectivity than that of metal hydrides such as lithium aluminum hydride and sodium borohydride.



Consequently, the hydrosilane-rhodium(I) complex combination may open a novel device for the selective hydrogenation or the reduction of α,β-unsaturated aldehydes and ketones in special of terpenes.

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