

THE SYNTHESIS OF OLEFINS AND KETONES FROM CARBONYL COMPOUNDS  
AND CARBANIONS ALPHA TO SILICON

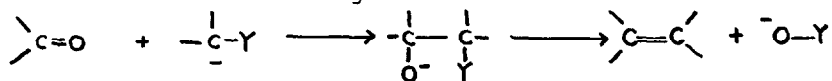
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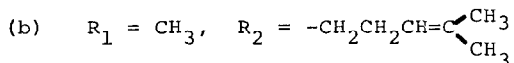
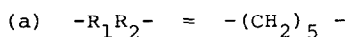
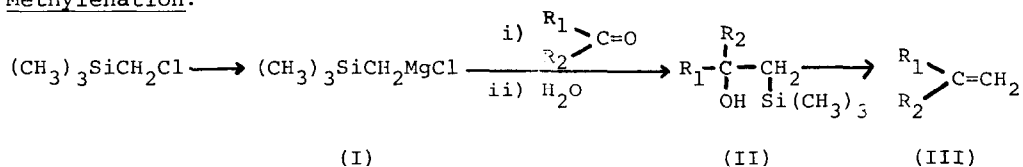
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We wish to report our studies in the synthesis of olefins from carbonyl compounds and carbanion alpha to silicon according to the following sequence of operations ( $Y = \text{SiR}_3$ ):<sup>1</sup>



Together, these reactions constitute a synthetic method complementing the Wittig reaction<sup>2</sup> ( $Y = \text{PR}_3^+$ ) and Corey's olefin synthesis with sulfinamide<sup>3</sup> ( $Y = \text{SONR}_2$ ).

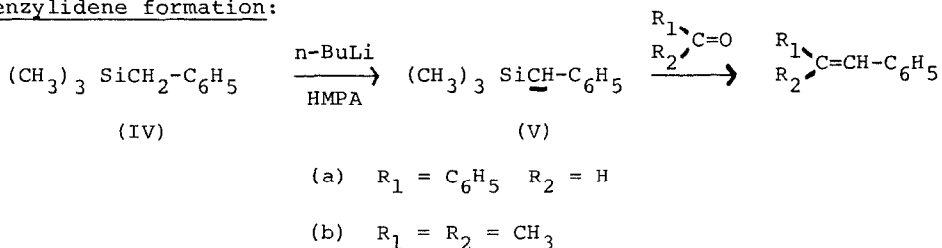
Methylenation:



The trimethylsilylmethyl magnesium chloride was prepared in ether by a reported procedure.<sup>4</sup> The appropriate carbonyl compound in ether was added and the reaction was refluxed for 4-6 hours. On working up, the  $\beta$ -silylcarbinol could be obtained in good yield. The corresponding sodium salt, prepared from the alcohol and sodium hydride, decomposed on reflux in

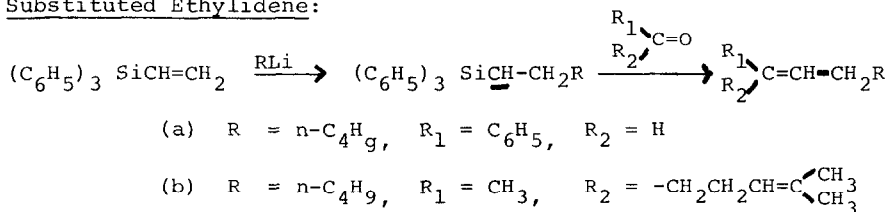
tetrahydrofuran to the olefin. In this manner, methylene cyclohexane (from cyclohexanone) and 2,6-dimethyl-1,5-heptadiene (from 2-methyl-2-heptene-6-one) could be obtained in better than 50% overall yield (isolated). The olefins are not contaminated with other double bond isomers. This method of methylenation appears to be operationally simpler and cleaner than the Wittig reaction.

Benzylidene formation:



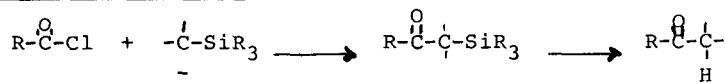
The trimethylsilybenzyl carbanion (V) was prepared from trimethylbenzylsilane and butyllithium in hexamethylphosphoramide<sup>5</sup> (HMPA). The resultant red solution (the existence of the carbanion was demonstrated by quenching the mixture with  $\text{D}_2\text{O}$  and IV was recovered and found to be > 85% deuterated at the benzyl group) was reacted with the appropriate carbonyl compounds. The mixture, after overnight stirring at room temperature, gave on working up the olefin directly in better than 50% yield. We have obtained stilbene from benzaldehyde (cis-trans ratio approximately 1:1 by nmr and also by isolation) and trans-1,2-diphenylpropene from acetophenone.

Substituted Ethylidene:



The addition of organolithium compound to vinyl silane is well known.<sup>6</sup> Carbanion of structure VI, was generated by the reaction of equal moles of organolithium compound and triphenylvinylsilane in ether<sup>7</sup>. To the solution, the appropriate carbonyl compound was added. The mixture, on working up, gave the corresponding olefin in good yield. We have prepared 1-phenyl-1-hexene (from butyllithium and benzaldehyde) and 2,6-dimethyl-2,6-dodecadiene (from butyllithium and 2-methyl-2-heptene-6-one) by this method. In both cases, VPC showed them to be 1:1 mixture of cis- and trans- isomers. This method may be useful for the synthesis of trisubstituted olefins having structure similar to some insect Juvenile Hormones.<sup>8</sup>

Ketones from Acid chlorides:



The facile conversion of  $\beta$ -silylketone to ketone is well known<sup>9</sup>. Its synthetic potential appears not to have been explored. We found that the reaction of I with acid chlorides affords, after hydrolysis with dilute hydrochloric acid, methyl ketones in reasonable yields (50-70%). For example, benzoyl chloride, 3-cyclopentyl-propanoylchloride and decanoylchloride gave acetophenone, 4-cyclopentyl-2-butanone and 2-undecanone respectively. Similarly, trimethylsilylbenzyl carbanion (V) reacted with benzoyl chloride to give  $\alpha$ -phenylacetophenone.

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References

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