Aliphatic Friedel–Crafts Acylation of Vinyl Silanes

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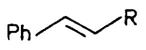
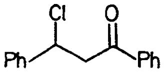
Summary Some vinyltrimethylsilanes give high yields of substitution products in aliphatic Friedel–Crafts acylation and the reaction is site-selective, acylation taking place at the carbon atom carrying the trimethylsilyl group.

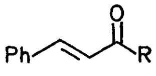
The aliphatic Friedel–Crafts reaction is not as often used as its aromatic counterpart, partly because it does not always result in simple substitution. Thus styrene (**1**) with PhCOCl and $AlCl_3$ gives the addition product (**3**) in only 23% yield. Similarly, styrene (**1**) with $PhCH_2COCl$ and $AlCl_3$ gives the product (**6**) (56%) resulting from intramolecular attack (by the intermediate carbonium ion) on the benzene ring of the phenylacetyl group. We report that a suitably placed trimethylsilyl group encourages the formation of simple substitution products.



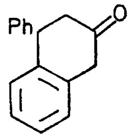
(1) R = H
(2) R = SiMe$_3$



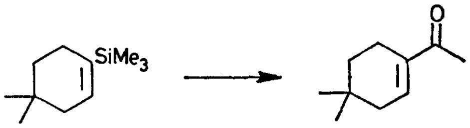
(3)



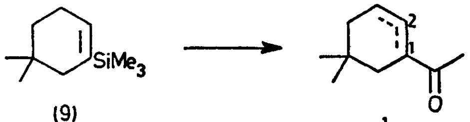
(4) R = Ph
(5) R = CH$_2$Ph



(6)

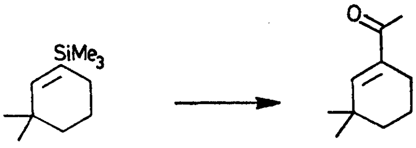


(7) (8)

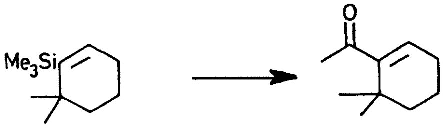


(9)

(10) Δ^1
(11) Δ^2



(12) (13)



(14) (15)

trans-β-Trimethylsilylstyrene (**2**), readily available from phenylacetylene[1] or from benzaldehyde,[2] reacts with PhCOCl and AlCl$_3$ to give a mixture of the addition (**3**) and substitution (**4**) products in roughly equal amounts (total yield 76%). By a suitable choice of work-up procedures, each of these products can be converted into the other, so that either can be made to be the sole product in high yield. With PhCH$_2$COCl and AlCl$_3$, the effect is even more dramatic, the sole product is that of simple substitution (**5**) and the yield (86%) is again improved.

In all these reactions, the site of attack on the styrene is determined by the presence of the phenyl ring. However, a relatively symmetrical olefin, *e.g.* 4,4-dimethylcyclohexene, can be expected to give mixtures of products resulting from electrophilic attack on either carbon atom of the double bond. A suitably placed SiMe$_3$ group can solve this problem. The vinylsilane (**7**), readily available from the corresponding vinyl chloride, gives the simple substitution product (**8**) (77%) when it is treated with MeCOCl and AlCl$_3$. Another vinyl silane (**9**) gives a mixture of the simple (**10**) and the deconjugated (**11**) substitution products (10 and 50%, respectively). In neither case is there any crossover product; in other words, product resulting from attack at the other end of the double bond. Site selectivity is also shown by the vinylsilanes (**12**) and (**14**), which give the simple substitution products, (**13**) (49%) and (**15**) (11%), respectively. In the latter case, the major product was the result of diacylation, in which the second acylation step probably took place on a deconjugated product analogous to (**11**). Again, no crossover products were detected.

The SiMe$_3$ group produces its effect partly by the readiness with which it is cleaved from a carbon atom next to a carbonium ion centre,[3] and partly by the stabilisation it supplies to such a carbonium ion.[4] The effect has been used to control site-selectivity in some aromatic electrophilic substitutions,[5] and also to achieve stereospecific proto- and halogeno- desilylation of vinylsilanes.[6] The epoxidation of vinylsilanes, and the site-selective hydrolysis of the epoxides to ketones,[7] is a related process. Plainly, the aliphatic Friedel–Crafts reaction has more scope in synthesis when control of the kind we observed can easily be exerted.

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