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THE SYNTHESIS OF OLEFINS FROM β-KETOSILANES

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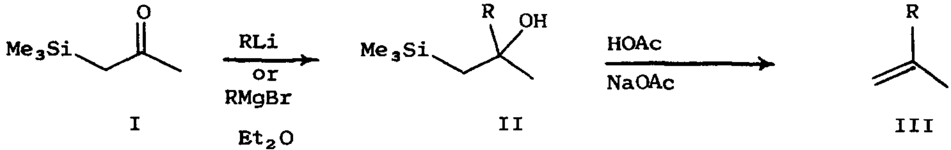
Like acyloxysilanes,[1] β-ketosilanes can react with a nucleophile in two ways. We have found that the reaction of a β-ketosilane with alkoxide gives a product resulting from displacement at the silicon atom, while the reactions with Grignard reagents and with organolithium compounds give only products resulting from addition to the carbonyl group.[2] Since the β-hydroxyalkylsilanes formed in the latter reactions can be converted into olefins,[3] the process serves as a potential synthetic route to these compounds.

Although some aspects of the chemistry of β-ketosilanes (and the isomeric enol silyl ethers) have been actively investigated during recent years,[4] their reactions with nucleophilic reagents have not received much attention. Their facile hydrolysis and alcoholysis to ketones[5] presumably proceeds via displacement at silicon (although reversible addition of water to the carbonyl group could also be occurring), and reduction ($LiAlH_4$) has been reported to occur predominantly at the carbonyl.[6] Their reactions with metal alkoxides and with organometallic reagents have not been reported.[7]

We find that trimethylsilylacetone[5] (I) reacts with sodium n-butoxide (Et_2O, 30 min, room temperature) predominantly at the silicon atom, giving n-butoxytrimethylsilane[1,8] in 77% yield.[9] The reactions with Grignard reagents and organolithium compounds take the opposite course, as shown. Products formed by displacement at the silicon atom could not be detected.

The reaction of I with excess n-butyllithium (Et_2O, 1.5 hr at 0°), followed by aqueous workup, yielded the tertiary alcohol IIa,[10] b.p. 71-73° (4 mm), in 80% yield (isolated). The other possible product, n-butyltrimethylsilane,[1,8] was not present (0.1% would have been detectable). The alcohol IIa was also prepared from the reaction of I with butylmagnesium bromide.



a (R = Bu)
b (R = C_5H_{11})
c (R = Ph)

The homologous alcohol IIb,[10] b.p. 54° (0.5 mm) was available in 84% yield[9] from the reaction of I with excess n-pentylmagnesium bromide. An identical sample of IIb was prepared independently by the reaction of trimethylsilylmethylmagnesium chloride with 2-heptanone. Similarly, alcohol IIc[10,11] (b.p. 81-83° (0.7 mm)) was prepared by the reaction of I with either phenyllithium or phenylmagnesium bromide.

When IIb was dissolved in glacial acetic acid saturated with sodium acetate and heated at 50° for one-half hour, facile β-elimination occurred to give 2-methyl-1-heptene (IIIb) in 90% yield,[9] uncontaminated by the isomeric 2-methyl-2-heptene.[12] Elimination of the benzylic alcohol IIc to give α-methylstyrene[8] (IIIc) was even more rapid, occurring within minutes after dissolving in acetic acid at room temperature.

We are continuing to actively investigate the chemistry of β-ketosilanes, as well as their preparation, with a view toward developing further synthetic applications.[2,13]

REFERENCES

1. See P. F. Hudrlik and R. Feasley, preceding communication.

2. A third reaction - enolization - is also possible. In preliminary experiments, we have found that trimethylsilylacetone (I) is enolized by lithium di-isopropylamide (THF, -78°). When treated with methyl iodide (THF-DMSO, warmed to room temperature), a 2:1 mixture of 1-trimethylsilyl-2-butanone and 3-trimethylsilyl-2-butanone is formed (satisfactory IR, NMR, and mass spectra were obtained).

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7. The reactions of the corresponding silyl esters ($R_3SiCH_2CO_2R'$) with $LiAlH_4$ and with Grignard reagents has been shown to occur at carbonyl. See Yu. I. Baukov, G. S. Burlachenko, and I. F. Lutsenko, J. Gen. Chem. USSR, 35, 1178 (1965); I. F. Lutsenko, Yu. I. Baukov, G. S. Burlachenko, and B. N. Khasapov, J. Organometal. Chem., 5, 20 (1966).

8. An authentic sample was available for comparison.

9. Yield determined by VPC using an internal standard.

10. Satisfactory IR, NMR, and mass spectra were obtained. The peak at highest m/e in the mass spectra corresponded to loss of water from the parent ion.

11. Alcohol IIc was the only product formed in these reactions; phenyltrimethylsilane[8] was not detectable. Purification was difficult since distillation resulted in partial dehydration.

12. A mixture of the isomeric olefins was prepared by the dehydration ($POCl_3$-pyridine) of 2-methyl-2-heptanol.

13. We thank Research Corporation and The Research Council of Rutgers University for financial support.