

REACTION OF TRIMETHYLCHLOROSILANE WITH EPOXYKETONES IN THE PRESENCE OF MAGNESIUM

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Abstract

Mixture of the trimethylchlorosilane, magnesium and hexamethylphosphoric-triamid, HMPT, react with epoxyketones to produce tetrasilyciated compounds, which are the results of the addition of two trimethylsilyl (TMS) groups to the carbonyl function and two TMS groups to the epoxide cycle. After elimination of $(\text{Me}_3\text{Si})_2\text{O}$ silyciated enoxsilanes are obtained which under acidic conditions gives β - silyciated ketones.

Introduction

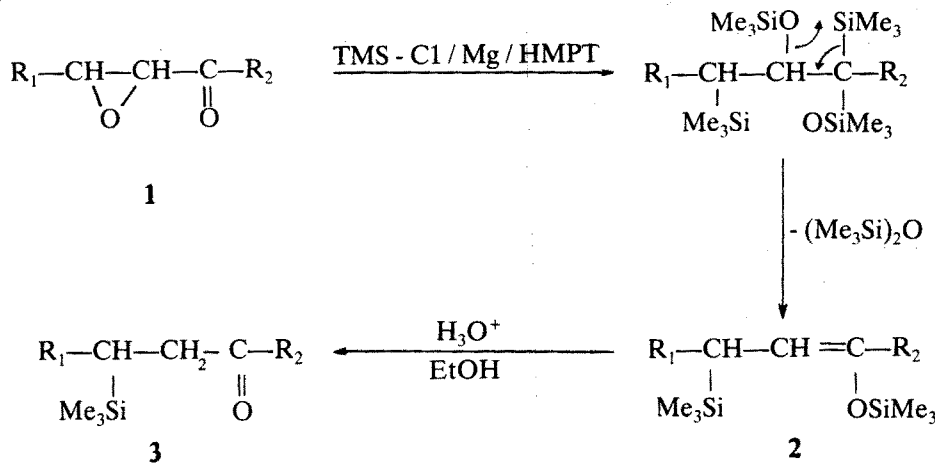
In the previous works we have shown that TMS - Cl reacts with different α, β - unsaturated aldehydes and ketones in the presence of, magnesium to give derivatives with two TMS groups at the 1, 4 positions [1-5], which after hydrolysis, leads to β - silyciated aldehydes or ketones.

According to certain similarities of epoxides with those of double bonds, we decided to investigate the possibility of synthesizing β - silyciated ketones from epoxy ketones, which are readily available. Comparing these results with those of cyano - epoxides [8] and

α, β - unsaturated ketones [4], once again, showed the possibility of synthesizing the corresponding organosilyciated compounds, and led us to an alternative method for preparing β - silyciated ketones.

Results

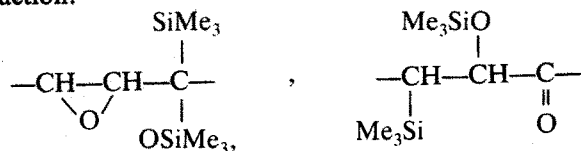
Addition of 1 (1a - 1f) to the mixture of TMS - Cl / Mg / HMPT gave 3 (3a - 3f), according to the following reactions:



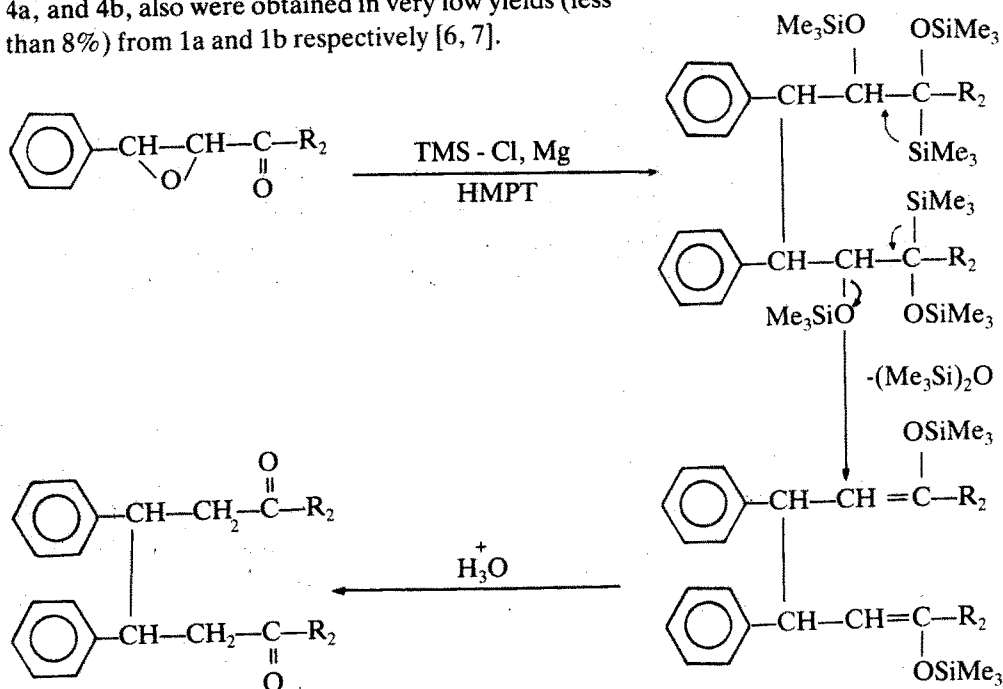
- a $\text{R}_1 = \text{R}_2 = \text{ph}$
- b $\text{R}_1 = \text{ph}, \text{R}_2 = \text{CH}_3$
- c $\text{R}_1 = \text{C}_6\text{H}_4\text{O}, \text{R}_2 = \text{ph}$
- d $\text{R}_1 = \text{C}_6\text{H}_4\text{S}, \text{R}_2 = \text{ph}$
- e $\text{R}_1 = n\text{-C}_4\text{H}_9, \text{R}_2 = \text{ph}$
- f $\text{R}_1 = \text{CH}_3, \text{R}_2 = \text{ph}$

Key words: silylation, Epoxyketones

β -silylated enoxysilanes, 2a - 2f, were obtained in good yields, which can easily produce the corresponding ketones 3a to 3f in acidic media. In these reactions two types of silylation are possible. We are not able to predict the priority of them in the course of the reaction.



In addition to the above silylation reactions compounds 4a, and 4b, also were obtained in very low yields (less than 8%) from 1a and 1b respectively [6, 7].



The results confirm that the opening of an epoxy ring is due to the C-O bond cleavage, and formation of anion radical. The mechanism of these reactions were proposed before and will not be discussed here [1, 9].

Experimental Section

The silylation conditions were similar to those

reported earlier [1, 2]. Compounds 3a - 3f and the intermediate enoxysilanes, 2, were identified by spectroscopic methods, or by comparison with their authentic samples. The yields, melting points, and their IR C = O frequencies of the products are given in Table I.

Conclusion

Silylating reactions of epoxyketones led to the formation of carbon silicone bond, and a new method for preparation of β -silylated ketones.

Acknowledgement

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Table 1

Compound	m.p. / b.p.	C = O, cm	% yield
3 a	88 C	1690	57
3 b	95-105 C/1 mmHg	1692	54-60
3 c	130-140 C/0.4 mmHg	1685	50-55
3 d	150-160 C/0.2 mmHg	1690	56
3 e	112-118 C/0.5 mmHg	1682	80
3 f	100-108 C/1 mmHg	1682	60-65

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