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Preliminary communication

CONVERSION OF SOME ALKENYLTRIMETHYLSILANES INTO SILYL ENOL ETHERS

ROBERT F. CUNICO
Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115 (U.S.A.)

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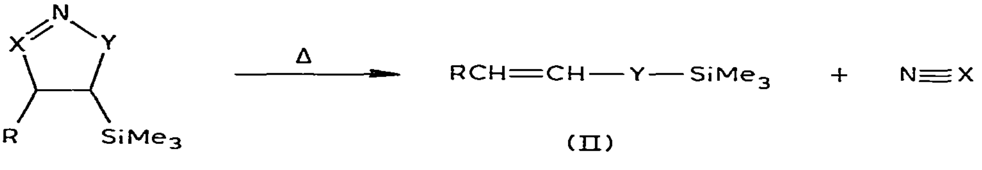
Summary

The cycloaddition products (5-trimethylsilylisoxazolines) between alkenyltrimethylsilanes and acetonitrile oxide undergo thermolytic rearrangement-cycloreversion to afford silyl enol ethers of retained stereochemistry vs. the starting alkenylsilanes.

We have reported earlier on a novel mode of reaction established for pyrazolines ($X = N$, $Y = CH_2$, $R = CO_2Me$) in which thermolysis effects migration of the trimethylsilyl group accompanied by loss of nitrogen to afford homologuised species II ($Y = CH_2$, $R = CO_2Me$) [1]. A characteristic of this "silatropic cycloreversion" is the stereospecificity by which it occurs, *trans*-I affording *E*-II and *cis*-I, *Z*-II. More recently, a communication has appeared which postulates behior within the triazoline I ($X = N$, $Y = NSiMe_3$, R = H or Ph) to explain the observed formation of II ($Y = NSiMe_3$, R = H or Ph) when alkenylsilanes are treated with trimethylsilyl azide [2]. We present results here which suggest an even wider applicability of this type of mechanism in affording results which may be of considerable synthetic utility.



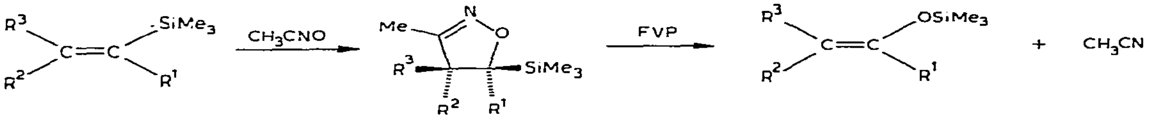
(I)

Thus (see Scheme 1), cycloaddition of vinyltrimethylsilane (III) with acetonitrile oxide afforded the isoxazoline (VI) (80%, b.p. 64°C/3 mmHg; NMR (CCl_4): δ 0.09 s, 9H; δ 1.96, t, *J* 1 Hz, 3H; δ 2.51—2.94, m, 2H; δ 3.81, d of d,

J 11 Hz, 16 Hz, 1H) regiospecifically as shown. Subsequent flash vacuum pyrolysis (FVP) at 550°C and 0.5 mmHg afforded a product mixture which GLC and spectral data indicated consisted of only acetonitrile and the silyl enol ether IX in quantitative mass recovery. A GLC determination (internal standard method) confirmed a high yield (95%) of IX.

In order to probe the stereochemistry of the overall transformation, the *E/Z* isomer pair IV and V were independently prepared [3] and subjected to the reaction sequence. NMR analysis of the cycloaddition products indicated that only VII (25%, b.p. 53°C/0.6 mmHg; NMR (CCl_4): δ −0.05, s, 9H; δ 0.93, s, 3H; δ 1.00, d, J 7 Hz, 3H; δ 1.74, d, J 1 Hz, 3H; δ 2.98, q, J 7 Hz, 1H) was obtained from IV (100% *E*-isomer), while the sample of V (85/15 *Z/E*) afforded in 50% yield a 92/8 mixture of VIII/VII* (VIII b.p. 50°C/0.4 mmHg; NMR (CCl_4): δ 0.02, s, 9H; δ 1.03, d, J 7 Hz, 3H; δ 1.07, s, 3H; δ 1.79, s, 3H; δ 2.74, q, J 7 Hz, 1H). FVP of VII then gave X [4], while VIII afforded XI [4]. In both instances, NMR assay was employed to determine that the yields of silyl enol ethers were near quantitative (± 5%). Each silyl ether appeared to be free of the other, although some X would be expected in the sample of XI obtained. However, analytical conditions were not found which would have detected a small amount (ca. 5%) of cross-contamination.

SCHEME 1



(III, $R^1 = R^2 = R^3 = H$;
IV, $R^1 = R^2 = Me; R^3 = H$;
V, $R^1 = R^3 = Me; R^2 = H$)

(VI, $R^1 = R^2 = R^3 = H$;
VII, $R^1 = R^2 = Me; R^3 = H$;
VIII, $R^1 = R^3 = Me; R^2 = H$)

(IX, $R^1 = R^2 = R^3 = H$;
X, $R^1 = R^2 = Me; R^3 = H$;
XI, $R^1 = R^3 = Me; R^2 = H$)

It can be seen that at least formally, the conversion of VI, VII and VIII into, respectively, IX, X and XI may be understood within the context of the "silatropic cycloreversion" process described above. Overall, these highly stereospecific reactions afford a method whereby alkenyltrimethylsilanes can be transformed into silyl enol ethers of retained configuration. The latter are, in general, species of high synthetic utility [5], and the control of stereochemistry exhibited by the present system could provide these in high isomeric purity for use in further stereochemical studies. Of particular current interest, for example, is the diastereoselection exhibited by *E*- and *Z*-enolates (XII) in the aldol condensation [6]. These are obtainable stereospecifically from *E*- and *Z*-silyl enol ethers [4, 6b], but no general method yet exists for the synthesis of each of the latter in high isomeric purity [7]. We are now investigating the present chemistry with this end in mind.

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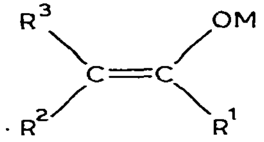
*Small amounts (10—15% by weight) of the self-addition product of acetonitrile oxide (3,4-dimethylfuroxane) were also present in distilled samples of VII and VIII.



(XII, M = Li or BR_2)

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