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Formal [1,3] Rearrangement of 2-Furylmethyl and 2-Thienylmethyl Vinyl Ethers[#]

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Abstract: Benzyl and naphthylmethyl vinyl ethers are inert in LPDE medium, whereas heteroaromatic methyl vinyl ethers, viz., 2-furyl and 2-thienylmethyl vinyl ethers undergo formal $\{1,3\}$ rearrangement in LPDE medium.

Lithium perchlorate in diethyl ether (LPDE) has attracted considerable attention in recent years as a powerful medium to bring about a number of organic reactions¹. In particular, the facile transformation of allyl vinyl ethers to products of a formal 1,3-sigmatropic rearrangement in this medium reported first by Grieco *et al*² has turned out to be a useful complimentary to thermal [3,3]-Claisen rearrangement. Our long standing interest in claisen rearrangement as well as our recent findings³ on the mechanism of this [1,3] rearrangement brought about by LPDE prompted us to investigate the behavior of other potential systems like benzyl vinyl ethers, furfuryl vinyl ethers and thienytmethyl vinyl ethers in LPDE.

While benzyl vinyl ethers do not undergo the thermal Claisen rearrangement⁴ that readily compared to the isomeric aryl allyl ethers, furyl vinyl ether is reported to yield a mixture of products upon thermolysis⁵. In contrast to this, 3.5-dimethoxyfurfuryl isoprenyl ether undergoes the Claisen rearrangement furnishing the products of [3,3]-sigmatropic shift⁶. These reports as well as the recent disclosure of Walsh *et al*⁷ on the oxy-Cope rearrangement of the substrates involving 2,3-double bond of the benzofuran prompted us to report our findings on the behavior of the heteroarylmethyl vinyl ethers in LPDE. In this communication, we describe a facile [1,3] rearrangement of a few 2-furylmethyl vinyl ethers and 2-thienylmethyl vinyl ethers in LPDE. When benzyl vinyl ether 1 and 1-naphthylmethylvinyl ether 2 were treated with LPDE at room temperature even after twenty days there was no reaction (Scheme 1).

[#] Dedicated to Prof. T.R.Govindachari, Advisor, Centre for Agrochemical Research, SPIC Science Foundation, Madras on the occasion of his 80th birthday.



Scheme 1

However, when 2-furylmethyl vinyl ethers 3-7 and 2-thienylmethyl vinyl ethers 8 and 9 were exposed to LPDE, they were smoothly transformed to the respective formal [1,3] rearrangement products 3a-9a in modest yield (Scheme 2 and Table 1).

Scheme 2



Table 1

Entry	Vinyt ether	Product (†)	Yield (%)
1	CH2-0 <u>3</u>		60
2		СH ₂ - СНО <u>4а</u>	50 ⁸⁹
3		СН ₂ -СНО <u>5а</u>	60 [®]
4			65 ⁹
5		CH ₂ CH ₂ CHO	60 ⁸⁹
6	2 (s, CH ₂ -0) <u>8</u>		50
7		CH ₂ -CHO <u>9a</u>	70 ¹⁰

All reactions are conducted with 0.2 vinyl ether in 3M LPDE at ambient temperature for 6h.

(Contaminated with 20-25% of unknown aldehydic products.

✤ All aldehydic products showed satisfactory high resolution mass spectral values.

The high propensity to undergo this formal [1,3] rearrangement exhibited by the 2-furylmethyl and 2thienylmethyl vinyl ethers is in sharp contrast to the inertness exhibited by the benzyl vinyl ethers under similar conditions, which parallels the reactivity of heteroarylmethyl halides and benzyl halides in solvolytic reactions, the relative reactivity being heteroarylmethyl halide > allyl halide > benzyl halide.⁸ To our knowledge, this is the first report of a formal [1,3] rearrangement of heteroarylmethyl vinyl ethers in LPDE. This provides a simple and mild route for the synthesis of γ -heteroaryl propanals. We are currently extending this study to 3-heteroarylmethylvinyl ethers.

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- 9. Data for the compound <u>6a</u>: ¹H-NMR (400 MHz/CDCl₃) δ : 9.66 (t, J=1.46 Hz, 1H), 7.35 (m, 1H), .2 (m, 3H), 7.05 (m, 2H), 6.25 (dd, J=1.46, 2.93 Hz, 1H), 5.94 (d, J=3.42 Hz, 1H), 3.6 (m, 1H), 3.1 (dd, J=6.83, 13.18 Hz, 1H), 2.89 (dd, J=7.79, 13.67 Hz, 1H), 2.7 (ddd, J=1.5, 8.8, 17.4 Hz, 1H), 2.6 (ddd, J=1.5, 4.6, 17.4 Hz, 1H). ¹³C-NMR (100.5MHz, CDCl₃) δ : 201.14 (d), 155.99 (s), 141.36 (s), 138.70 (d), 129.11 (d), 128.37
- (d), 126.49 (d), 110.12 (d), 105.87 (d), 46.38 (t), 40.08 (t), 35.21 (d).
 Data for compound <u>9a</u>: ¹H-NMR (400 MHz / CDCl₃) δ: 9.72 (t, J=1.46 Hz, 1H), 7.23 (m, 2H), 7.18 (dd, J=0.98, 5.85 Hz, 1H), 7 (m, 2H), 6.9 (dd, J=3.4, 5.8 Hz, 1H), 6.8 (d, J=3.42 Hz, 1H), 4.84 (t, J=7.32 Hz, 1H), 3.2 (ddd, J=1.95, 7.81, 15.62 Hz, 1H), 3.12 (ddd, J=1.46, 7.32, 15.62 Hz, 1H).
 ¹³C-NMR (100.5MHz, CDCl₃) δ : 199.89 (d), 162.35 (s), 160.50 (s), 147.12 (s), 138.74 (s), 129.09 (d), 129.07 (d), 126.80 (d), 124.37 (d), 124.33 (d), 115.73 (d), 115.51 (d), 50.73 (t), 39.72(d).

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