# 64. The Pyrolysis of Fur-2-ylmethyl Vinyl Ethers

## by Alan F. Thomas

Research Laboratories, *Firmenich & Cie*, 1211 Geneva 8

*Summary.* The pyrolysis of fur-2-ylmethyl vinyl ether and its next highest homologue, the propenyl ether, is described. Products from two reaction mechanisms are observed, namely a 3-substituted 2-methylfuran from an electrocyclic mechanism, and 1,2-di-(fur-2-yl)-ethane and furylpropanal from a biradical mechanism.

In the course of investigations that led to the synthesis of dendrolasin [1] [2], the fact that the diene ether **1** of fur-2-ylmethanol could be induced to rearrange thermally quite easily was contrasted with the stability of its vinyl ether (**2**) [3]. In this paper, results from the pyrolysis of fur-2-ylmethyl vinyl ether (**2**) are described.

**Results.** – As reported by *Watanabe & Conlon* [3], fur-2-ylmethyl vinyl ether (**2**) can be made in 30–35% yield by mercuric acetate-catalyzed ether exchange from fur-2-ylmethanol and ethyl vinyl ether. All attempts to raise the yield by varying the conditions were unsuccessful. Preliminary experiments with the ether pyrolyzed in the injection chamber of a gas chromatograph showed that it was little changed below 350°, but that at 370–400°, a number of products was formed. A typical chromatogram with the injector temperature at 400° showed about 25% starting material (**2**), together with the following major products: 2-(2-methylfur-3-yl-ethanal (**3**) (25%), 3-(fur-2-yl-propanal (**4**) (35%), and some fur-2-ylmethanol, together with about 5% of 1,2-di-(fur-2-yl)-ethane (**5**). Traces of unidentified products were also observed.
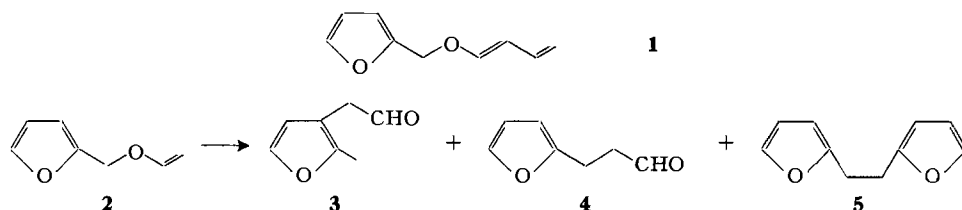


When this experiment was repeated on a larger scale by pyrolysis of the ether **2** in benzene solution over glass helices in a current of nitrogen, it was found that the rate of addition of the solution to the column and the flow of nitrogen through the column were critical. If the pyrolysis time was too long, the only components isolated were the known furylpropanal (**4**) [4] and 1,2-di-(fur-2-yl)-ethane (**5**). Factors favouring the production of the rearranged aldehyde **3** were greater dilution of the benzene solution, and rapid throughput. Under the most favourable conditions (column temperature 370°, with fairly rapid addition of a 10% solution in benzene of the vinyl ether), the following yields were attained: compound **3**, 37%; compound **4**, 21%; fur-2-ylmethanol, 3.5%; 1,2-di-(fur-2-yl)-ethane (**5**), 9%; recovered starting material, 27%. In

order to purify the compounds, only preparative gas chromatography could be used, since both the aldehydes **3** and **4** were polymerized by distillation.

No crystalline derivatives of aldehyde **3** were isolated, but on reduction with lithium aluminium hydride in ether, the corresponding alcohol was obtained.

The *cis*- and *trans*-propenyl ethers (**6a** and **6b**) of fur-2-ylmethanol were also prepared. They were separated by preparative gas chromatography, and pyrolyzed in the injector system of a gas chromatograph at 370°. Four peaks were observed, in addition to starting material, and these were ascribed the structures of 2-(2-methyl-fur-3-yl-propanal (**7**) (7%), 2-methyl-3-(fur-2-yl)-propanal (**8**) (45%), fur-2-ylmethanol (36%) and 1,2-di-(fur-2-yl)-ethane (**5**) (10%). No difference in the behaviour of the two isomeric ethers was observed. The structural attributions of the compounds **7** and **8** are primarily on spectral grounds (see experimental section) and gas chromatographic retention data, since insufficient material was available for extensive studies.
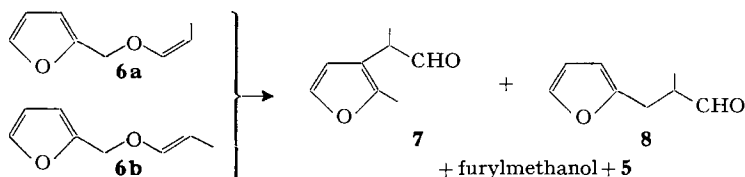


**Discussion.** – The fact that the aldehyde (**4**) is obtained, is in accord with the existence of a radical pair of type **9**, similar to that already proposed for the high temperature rearrangement of fur-3-ylmethyl dienyl ethers [2], and for the high temperature rearrangement of diene ethers of cyclohexenols [5]. Formation of 1,2-di-(fur-2-yl)-ethane (**5**) indicates that the radical pair can dissociate completely to a furfuryl radical, two of which combine. This conclusion is supported by the fact that dilution of the solution causes the yield of difurylethane to fall. Formation of the fur-3-yl aldehyde **3** is presumably by way of an electrocyclic process.

Judging by the limited data available for the methyl substituted vinyl ethers **6**, since the proportion of aldehyde **8** to aldehyde **7** increases markedly as compared with the proportion for the lower homologue, it seems that the electrocyclic reaction is still less favoured in this case.
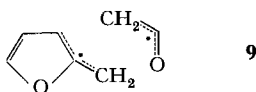


This pyrolysis represents a further means for preparing 3-substituted furans from 2-substituted furans, although the difficulties of carrying out the reaction reproducibly, and of purification of the products restricts its use.

**Experimental.** – Infrared spectra were measured with a *Perkin-Elmer* Type 125 spectrophotometer. Nuclear magnetic resonance spectra were obtained with a *Varian* type A-60 instrument[1]). Mass spectra were measured on the *Atlas* CH4 mass spectrometer, using an inlet temperature of about 150° and electrons of 70 eV energy. Gas chromatography was carried out on a *Carlo Erba* Fractovap Type P (preparative) or a *Carlo Erba* Type GT (analytical and semi-preparative), or a *Firmenich* type 59 T[2]).

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[1])  Measured in ppm with tetramethylsilane (internal) as 0.00 ppm.
[2])  Built by *E. Palluy, Firmenich & Cie.*

*Fur-2-ylmethyl vinyl ether* (**2**) was prepared [3] from fur-2-ylmethanol (20 g), ethyl vinyl ether (80 g), and mercuric acetate (3 g). After 6 h reflux, the mixture was distilled, rapidly at first, then more carefully, when the product was obtained at bp 42°/10 Torr.

*Fur-2-ylmethyl cis- and trans-1-propenyl ethers* (**6a and 6b**) were obtained in a similar manner; the mixture of ethers distilled at bp 54°/12 Torr.

$$C_8H_{10}O_2 \quad \text{Calc. C 69.54 \quad H 7.30\% \quad\quad Found C 69.34 \quad H 7.34\%}$$

The two ethers were separated by preparative gas chromatography, and then had the following properties: (a) substance with shorter retention time on a Carbowax column, NMR. spectrum: 1.50 ($d$ of $d$, $J = 6.5$ and 1.5 Hz, 3 H, $CH_3$–CH=CH–), 4.38 ($d$ of $q$, $J = 6.5$ and 6.0 Hz, 1H, $CH_3$–$CH$=CH–, *cis*; the *trans*-coupling constant is much larger), 4.54 ($s$, 2H, furan-$CH_2$O–), 5.86 ($d$ of $q$, $J = 6.0$ and 1.5 Hz, 1H, $CH_3$–CH=$CH$–), 6.17 (2H, furan $\beta$-$H$), 7.20 (1H, furan $\alpha$-$H$). (b) Substance with longer retention time on Carbowax column, NMR. spectrum: 1.48 ($d$ of $d$, $J = 6.5$ and 1.5 Hz, 3H, $CH_3$–CH=CH–), 4.67 ($d$ of $q$, $J = 6.5$ and 12.5 Hz, 1H, $CH_3$–$CH$=CH– *trans*, because of the high coupling constant), 4.43 ($s$, 2H, furan-$CH_2$O–), 6.07 ($d$ of $q$, $J = 12.5$ and 1.5, 1H, $CH_3$–CH=$CH$– *trans*), 6.14 (2H, furan $\beta$-$H$), 7.19 (1H, furan $\alpha$-$H$). The mass spectra of the two compounds were identical, $m/e$ (% of most intense fragment): 81 (100), 53 (26), 27 (13), 39 (3), 138 ($M^+$, 2.5).

*Pyrolysis of fur-2-ylmethyl vinyl ether* (**2**). Pyrolysis experiments on a gas chromatograph were made on the *Firmenich* type 59 T instrument with the injection chamber at 370–400°, and the column at 200°. The yields have been discussed in the theoretical section. Larger-scale experiments employed a glass tube filled with glass helices, 25 mm i.d., heated at 370° along 33 cm. The substance to be pyrolyzed was dissolved in benzene (10% solution) and was added at about 10 ml/min, while a current of dry nitrogen was flowing at 150 ml/min. For analysis, the products were purified by gas-liquid partition chromatography, when they were recovered in the following order:

1. Recovered fur-2-ylmethyl vinyl ether.

2. *2-[2-Methylfur-3-yl)-ethanal* (**3**), IR. spectrum (cm$^{-1}$) 2720, 1720 (CHO); NMR. spectrum: 2.12 ($s$, 3H, furyl-$CH_3$), 3.23 ($d$, $J = 1.5$ Hz, 2H, furyl–$CH_2$–CHO), 6.07 ($d$, $J = 1.5$ Hz, furan $\beta$-$H$), 7.08 ($d$, $J = 1.5$ Hz, 1H, furan $\alpha$-$H$), 9.50 ($t$, $J = 1.5$ Hz, 1H, –$CH_2$–$CHO$); mass spectrum: 95 (100), 43 (82), 124 ($M^+$, 30).

$$C_7H_8O_2 \quad \text{Calc. C 67.73 \quad H 6.50\% \quad\quad Found C 67.25 \quad H 6.58\%}$$

3. *3-(Fur-3-yl)-propanal* (**4**). NMR. spectrum: 2.5–2.9 ($m$, 4H, –$CH_2$–$CH_2$–), 5.90 ($d$, $J = 3$ Hz, 1H, furan $\beta$-$H$), 6.15 ($m$, 1H, furan $\beta$-$H$) 7.17 (1H, furan $\alpha$-$H$), 9.75 ($t$, $J = 0.9$ Hz, 1H, –$CHO$); mass spectrum: 81 (100), 68 (74), 95 (68), 124 ($M^+$, 64), 53 (54), 39 (38), 27 (30), 41 (29), 43 (27).

$$C_7H_8O_2 \quad \text{Calc. C 67.73 \quad H 6.50\% \quad\quad Found C 67.63 \quad H 6.77\%}$$

4. *Fur-2-ylmethanol*, and

5. *1,2-Di-(fur-2-yl)-ethane*, both identical with authentic samples.

*2-(2-Methylfur-3-yl)-ethanol*. The fur-3-yl-ethanal (**3**, 100 mg), prepared as described above, and purified by preparative gas chromatography, was reduced with lithium aluminium hydride in ether. After decomposing the excess reagent with a few drops of water, filtration and concentration gave an almost pure product that was purified by gas chromatography for analysis. NMR. spectrum: 2.13 ($s$, 3H, furyl-$CH_3$), 2.42 ($t$, $J = 6$ Hz, –$CH_2$–$CH_2$O–), 3.51 (broad $t$, $J = 6$ Hz, 2H, –$CH_2$–$CH_2$–O), 6.03 ($d$, $J = 1.8$ Hz, 1H, furan $\beta$-$H$), 7.02 ($d$, $J = 1.8$ Hz, 1H, furan $\alpha$-$H$). Mass spectrum: 95 (100), 43 (44), 126 ($M^+$, 26).

$$C_7H_{10}O_2 \quad \text{Calc. C 66.64 \quad H 7.99\% \quad\quad Found C 66.35 \quad H 7.81\%}$$

*Pyrolysis of fur-2-ylmethyl propenyl ether*. This was carried out in the gas chromatograph as described above for the furylmethyl vinyl ether pyrolysis. The gas chromatography trace was very similar to that obtained with the lower ether, except that the retention times of the first two peaks were slightly longer, and the yields were different (see theoretical section). The first two products from the column were identified as (a) *2-[2-methyl-fur-3-propanal* (**7**), mass spectrum 43 (100), 57 (80), 109 (50), 58 and 71 (42), 81 (36), 138 ($M^+$, 4,5); and (b) *2-methyl-3-(fur-2-yl)-propanal* (**8**), NMR. spectrum: 1.07 ($d$, $J = 6$ Hz, 3H, $CH_3$–CH<), 2.3–3.1 ($m$, 3H, furyl-$CH_2$–CH<), 5.84 ($d$, $J = 3$ Hz, 1H, furan $\beta$-$H$), 6.16 ($m$, 1H, furan $\beta$-$H$), 7.20 (1H, furan $\alpha$-$H$), 9.53 (1H, –$CHO$).

LITERATURE

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[5] *A. F. Thomas* & *G. Ohloff*, unpublished work.

# 65. Die nucleofuge Aktivität von Substituenten am Brückenkopf von Bicyclo[2.2.2]octan und Chinuclidin

## Das $k_{OTs}/k_{Br}$-Verhältnis als mechanistisches Kriterium

Fragmentierungsreaktionen, 24. Mitteilung

### von C. A. Grob, K. Kostka und F. Kuhnen

Institut für Organische Chemie der Universität Basel

(2. III. 70)

*Summary.* The rate ratios $k_{OTs}/k_{Br}$ of the bridgehead tosylate and bromide of bicyclo[2.2.2]-octane and quinuclidine, respectively, have been determined in 80 vol.-% ethanol. The high ratio for the bicyclo[2.2.2]octane derivatives ($3,3 \cdot 10^3$ at 25°) indicates a highly ionic transition state. Since nucleophilic assistance to ionisation by solvent is precluded in this system a ratio of $10^3$ or greater is typical for the «limiting» $S_N1$ mechanism. Lower $k_{OTs}/k_{Br}$ ratios therefore reflect increasing nucleophilic participation in the transition state of substitution and elimination reactions.

The high $k_{OTs}/k_{Br}$ ratio for 4-substituted quinuclidines, namely $1,6 \cdot 10^3$ at 25°, indicates the absence of anchimeric nitrogen participation in the transition state of this synchronous fragmentation. The rates of the 4-haloquinuclidines follow the normal order of nucleofugal activity for halides in solvolysis reactions.

Nach einem Vorschlag von *DePuy* & *Bishop* [1] kann das Verhältnis der RG.[1])-Konstanten eines *p*-Toluolsulfonates (Tosylates) und des entsprechenden Bromides ($k_{OTs}/k_{Br}$) in gewissen Fällen als Mass der Lösung der betreffenden Bindungen im Übergangszustand betrachtet werden. Systematische Untersuchungen von *Hoffmann* [2] haben die Gültigkeit dieses Kriteriums für das Ausmass der Ladungstrennung im Übergangszustand zahlreicher Substitutions- und Eliminations-Reaktionen bestätigt.

Je nach Substrat und Mechanismus kann das $k_{OTs}/k_{Br}$-Verhältnis zwischen einem Bruchteil von Eins und ca. $10^3$ variieren. Ein grosser Zahlenwert zeigt einen hohen Grad von Ladungstrennung im Übergangszustand an und *vice versa*. Typische $S_N2$- und $E2$-Reaktionen ergaben Werte um Eins oder kleiner als Eins, $S_N1$- und $E1$-Reaktionen grössere Werte bis zu ca. $10^3$. Infolge der extrem hohen RG. von tertiären Tosylaten bei solvolytischen Reaktionen[2]) musste zur Bestimmung des $k_{OTs}/k_{Br}$-Verhältnisses von *t*-Butyl-Derivaten die Elimination in Acetonitril herangezogen werden. Für diese vermutlich über das Carbonium-Ion verlaufende Reaktion wurde bei 0° ein Verhältnis von ca. 5000 geschätzt [2].

In einer anschliessenden Untersuchung von solvolytischen Reaktionen bestätigte *Hoffmann* die obige Beziehung zwischen Polarität des Übergangszustandes und

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[1]) RG. = Reaktionsgeschwindigkeit.
[2]) Tertiäre Tosylate sind in der Regel nicht isolierbar [3].