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The Cationic Oligomerization of 2-Methylfuran and the Characteristics of the Oligomers

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The treatment of 2-methylfuran with phosphoric acid yields the 2,4,4-tris(5′-methyl-2′-furyl)-1-pentanol (**1**) as a tetrameric product. This product gives its acetate (**2**) on acetylation with acetic anhydride, and forms a equimolar adduct (**3**) after treatment with maleic anhydride. The structural formula of **1** is supported by the IR, UV, NMR, and mass spectral data and by the other experimental facts. The other oligomers are separated as a product (**4**) which contains tetra-, penta-, hexa-, and heptamer. The structure of these oligomers discussed, and some possible reaction mechanisms for oligomerization are suggested.

Furan and alkylfurans are polymerized to resins by the action of acidic catalysts. The structures of these polymeric substances have been the subject of a number of investigations.[1-7] However, the structures of these substances have still not been completely elucidated.

A tetramer of 2-methylfuran formed by the catalytic action of BF_3 was noted by Dunlop and Peters in 1953.[8] As the structure of this tetramer they suggested a large ring compound linked with four 5-methyl-2,5-furylene units.

In a previous paper[9] we reported the formation of 2-methylfuran tetramer by the catalytic action of phosphoric acid. We also suggested another structure for this product.

In the further investigation reported here we will present the most reliable structure of this product and will point out the presence of the other 2-methylfuran oligomers, *i.e.*, penta-, hexa-, and heptamer, in the reaction mixture. We believe that the investigation of these oligomers will provide valuable information for clarifying the structure of the 2-methylfuran polymer and the other polymeric compounds of furan and alkylfurans.

Results and Discussion

Tetramer of 2-Methylfuran and Its Related Compounds. The treatment of 2-methylfuran with phosphoric acid under reflux results in the formation of 2,4,4-tris(5′-methyl-2′-furyl)-1-pentanol **1** in a good yield. The product can be separated as a slightly colored viscous liquid by fractional distillation. Product **1** gives its acetate (**2**) after treatment with acetic anhydride in pyridine. A maleic anhydride adduct of **1** can be separated as a colorless crystalline product. Elementary analyses data indicate that this product (**3**) is an equimolar adduct of **1** and maleic anhydride.

The structural formula of **1** is based on its spectral data, elementary analyses, and other experimental facts. The elementary analysis data of **1**, **2**, and **3** correspond to their calculated values. Moreover the mass numbers of their molecular ions also correspond to their calculated molecular weights. These facts indicate that (**1**) is a tetramer of 2-methylfuran.

Several IR characteristic bands (3100, 1610, 1560, and 775 cm^{-1}) suggest the presence of a furan nucleus which reacts with a dienophile (*e.g.*, maleic anhydride).

The treatment of **1** with alkaline hydrogen peroxide results in an aqueous solution of an oxidation product mixture. This mixture contains 5-methyl-2-furoic acid as an oxidation product. This indicates the presence of 5-methyl-2-furyl groups in the structure.

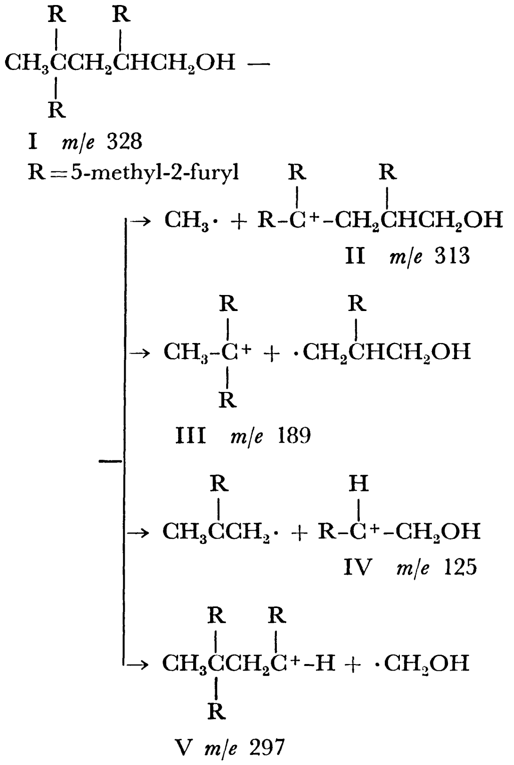
The UV absorption maximum of **1** in hexane appears at 222 nm. This absorption maximum is similar to the π-π transition absorption maximum of alkylfurans (at 215 nm for 2-methylfuran and at 218 nm for 2,5-dimethylfuran in hexane). This indicates that the π electron system of the furan nucleus does not conjugate with any other π electron system in the structure of **1**.

The NMR spectrum of **1** reveals six heteroaromatic protons at τ 4.2—4.4. These protons correspond to the ring protons of three 5′-methyl-2′-furyl groups.[10]

Therefore the signals which appear as two singlets at τ 7.80 (6H) and 7.82 (3H) must correspond to the protons of three methyl groups attached to the 5′-position of the furan nucleus. The other signals correspond to the following functional groups; the methyl group attached to tertiary aliphatic carbon (τ 8.56, 3H), the hydroxyl group (τ 8.42, 1H; this signal disappears after treatment with D_2O), the methylene group attached to the hydroxyl group (τ 6.72, 2H; this signal is shifted to τ 6.10 in the spectrum of the acetate **2**), the methine group attached to the hydroxymethyl group (τ 7.30, 1H, quintet; this signal is shifted to τ 7.80 in the spectrum of **2**), and another methylene group between tertiary aliphatic carbon and the methine group (τ 7.72, 2H; this signal overlaps with the broad singlet at τ 7.80).

The mass spectrum of **1** indicates a possible fragmentation mechanism, as is shown in the following schemes. Most heterocyclic-system fragmentation occurs by means of β-fission. The fission process is initiated by the loss of one of the non-bonded electrons of the heteroatom, which induces the "*onium ion*". Therefore, it is possible to form four fragment ions (II—V) on the β-fission process from the molecular ion (I), as is shown in Scheme I. The fragment ion III is a tertiary carbonium ion which is stabilized by two furan nuclei. Therefore, it appears as a predominant peak at *m*/*e* 189. This fragment ion is also possibly forms by the successive fragmentation of V

Scheme I.



$$\mathrm{CH_3\overset{R}{\underset{R}{C}}CH_2\overset{R}{C}HCH_2OH} \quad \text{I } m/e\ 328$$

R = 5-methyl-2-furyl

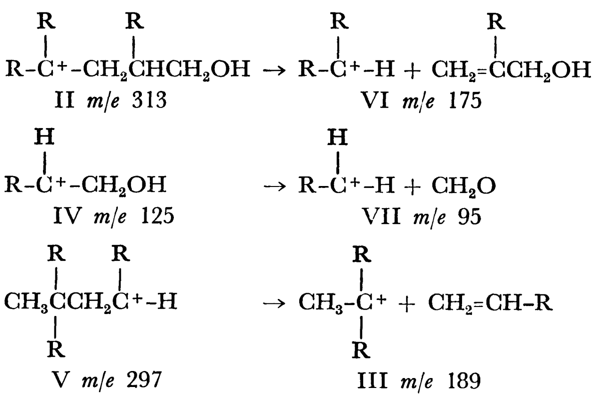
$$\rightarrow \mathrm{CH_3\cdot + R\text{-}\overset{R}{C}{}^+\text{-}CH_2\overset{R}{C}HCH_2OH} \quad \text{II } m/e\ 313$$

$$\rightarrow \mathrm{CH_3\text{-}\overset{R}{\underset{R}{C}}{}^+ + \cdot CH_2\overset{R}{C}HCH_2OH} \quad \text{III } m/e\ 189$$

$$\rightarrow \mathrm{CH_3\overset{R}{C}CH_2\cdot + R\text{-}\overset{H}{C}{}^+\text{-}CH_2OH} \quad \text{IV } m/e\ 125$$

$$\rightarrow \mathrm{CH_3\overset{R}{\underset{R}{C}}CH_2\overset{R}{C}{}^+\text{-}H + \cdot CH_2OH} \quad \text{V } m/e\ 297$$

Scheme II.



$$\underset{\text{II } m/e\ 313}{\mathrm{R\text{-}\overset{R}{C}{}^+\text{-}CH_2\overset{R}{C}HCH_2OH}} \rightarrow \underset{\text{VI } m/e\ 175}{\mathrm{R\text{-}\overset{R}{C}{}^+\text{-}H + CH_2{=}\overset{R}{C}CH_2OH}}$$

$$\underset{\text{IV } m/e\ 125}{\mathrm{R\text{-}\overset{H}{C}{}^+\text{-}CH_2OH}} \rightarrow \underset{\text{VII } m/e\ 95}{\mathrm{R\text{-}\overset{H}{C}{}^+\text{-}H + CH_2O}}$$

$$\underset{\text{V } m/e\ 297}{\mathrm{CH_3\overset{R}{\underset{R}{C}}CH_2\overset{R}{C}{}^+\text{-}H}} \rightarrow \underset{\text{III } m/e\ 189}{\mathrm{CH_3\text{-}\overset{R}{\underset{R}{C}}{}^+ + CH_2{=}CH\text{-}R}}$$

(Scheme II). The other fragment ions (II and IV) may be changed to minor fragment ions (VI and VII) with the elimination of neutral molecules (Scheme II). The mass spectrum of **1** indicates the presence of these ions (III, IV, VI and VII). The peak at *m/e* 43 may be due to CH_3CO^+, which is generally found in the mass spectra of 5-methyl-2-substituted furan compounds.

The facts presented above support the idea that the 2-methylfuran tetramer (**1**) definitely corresponds to 2,4,4-tris(5′-methyl-2′-furyl)-1-pentanol. This structure present a clue to elucidating the reaction mechanism of oligomerization.

Meisel and others reported the trimer of thiophene in 1950.[11] They indicated the structure of this compound and presented a reaction mechanism. This investigation will suggest a possible reaction mechanism to form **1** from 2-methylfuran; it is shown in Fig. 1,

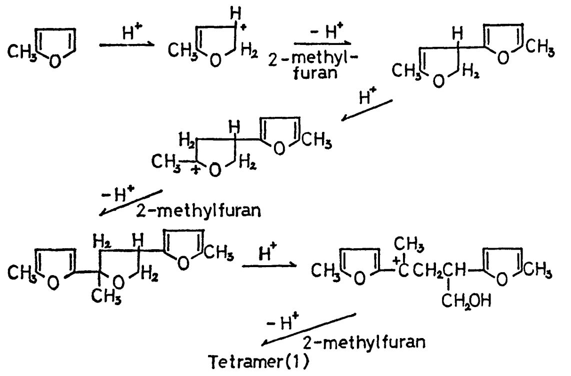


Fig. 1. A possible reaction mechanism for tetramerization.

The Other 2-Methylfuran Oligomers. The other 2-methylfuran oligomers can be separated as product **4** by the molecular distillation of the residue remaining after the removal of **1**. This product **4** is a slightly colored waxy substance. The elementary analysis data indicate that **4** correspond to the oligomer. The mass spectrum of **4** reveals the presence of a number of oligomers, *i.e.*, tetra-, penta-, hexa-, and heptamer.

Product **4** resembles **1** very closely in IR, UV, and NMR spectral patterns. These facts indicate a considerable structural resemblance between them. However, one of the appreciable differences between **1** and **4** is the ratio of the heteroaromatic proton signal intensities to the total one; **1** has a value of 6H/24H, but **4** has a value of 6H/30H. In addition, **4** has a strong IR characteristic band at 1700 cm^{-1}. This indicates the presence of a carbonyl group in the structure of **4**. These facts suggest that the pentamer is formed from **1** or another tetrameric precursor, accompanied by the ring cleavage of the furan nucleus. Some possible reaction routes illustrating this idea are shown in Fig. 2.

The structure of the tetrameric precursor is not necessarily the same as **1**. It is possible that the tetramer contained in **4** is another precursor for oligomerization. The tetramer contained in **4** could not be separated in this work. Therefore, we can not elucidate the structural difference between **1** and the tetramer in **4**. This problem is an interesting subject for investigation in the future.

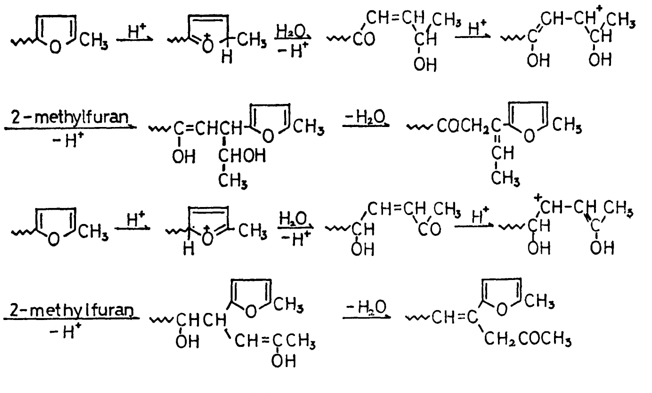


Fig. 2. Some possible propagation mechanisms for oligomerization.

Experimental

The elementary analyses were performed by the microanalytical division in the Department of Applied Chemistry of Osaka University. The infrared spectra were obtained with JASCO IR-G infracord as a neat liquid. The ultraviolet spectra were obtained with a Hitachi model 124 spectrometer. The mass spectra were obtained with a Hitachi RMU-6E spectrometer at 70 eV. The nuclear magnetic resonance spectra at 100 MHz were obtained with a Nippon Denshi JNM-P-100 instrument. The molecular distillation was carried out in a micro pot still in order to separate the oligomeric product.

The 2-methylfuran was prepared by the Wolff-Kishner reduction of 2-furaldehyde and was purified by fractional distillation; bp 62.8 °C (750 mmHg).

Oligomerization Reaction of 2-Methylfuran with Phosphoric Acid. One hundred and fifty grams of 2-methylfuran were stirred vigorously under reflux; then 8 g of phosphoric acid were added, drop by drop over a 10-minute period. The dark brown reaction mixture was stirred for an additional 30 min; then the reaction mixture was poured into a potassium carbonate solution and extracted with ether. The extract was dried over anhydrous magnesium sulfate, the ether and unchanged 2-methylfuran were removed by fractional distillation, and then it was concentrated under vacuum at room temperature. About 110 g of a brown viscous liquid was obtained as a residue.

*2,4,4-Tris(5′-methyl)-2′-furyl-1-pentanol (**1**).* The residual liquid was distilled, giving 57 g (38%) of **1** as a slightly colored viscous liquid; bp 200 °C (3 mmHg); n_D^{20} 1.5290. This product gave a satisfactory elementary analysis for **1**.

Found: C, 73.05; H, 7.35%. Calcd for $C_{20}H_{24}O_4$: C, 73.17; H, 7.31%.

UV max (hexane) 222 nm (ε 25100); IR (liquid film) 3400 (OH), 3100, 1608, 1555, and 775 cm^{-1} (a series of characteristic bands due to 2,5-disubstituted furan nuclei); NMR (CCl_4) τ 4.2—4.4 (m, 6H, β,β′-ring protons of furan nuclei), 6.68 (d, 2H, J=7 Hz, $C\underline{H}_2OH$), 7.30 (quintet, 1H, J=7 Hz, $CH_2\overset{|}{C}\underline{H}CH_2OH$), 7.72 (d, 2H, $-\overset{|}{\underset{|}{C}}C\underline{H}_2\overset{|}{C}H-$, overlapped with a broad singlet at τ 7.80), 7.80 (s, 6H, $C\underline{H}_3$ of 5-methyl-2-furyl groups), 7.82 (s, 3H, $C\underline{H}_3$ of another 5-methyl-2-furyl group), 8.42 (s, 1H, $CH_2O\underline{H}$, washed out with D_2O) and 8.56 (s, 3H, $CH_3\overset{|}{\underset{|}{C}}CH_2$); mass spectrum (70 eV) *m*/*e* (rel. intensity) 328 (9), 190 (16), 189 (100), 175 (10), 125 (5), 122 (5), 95 (7), 43 (12).

*Oxidation of the Tetramer (**1**) with Alkaline Hydrogen Peroxide.* One gram of **1** was added to a mixture of 1.2 g of potassium hydroxide and 40 ml of hydrogen peroxide (30% aqueous solution) with vigorous stirring, after which the mixture was left to stand four weeks. Then the mixture was treated with manganese (IV) oxide to decompose the excess hydrogen peroxide and filtered. The firtrate was neutralized with phosphoric acid and extracted with ether. According to thin-layer chromatographic separation (5 cm × 10 cm Wakogel UA Plate and Polyamide UA Plate; solvent: benzene: acetic acid, 40 : 1), 5-methyl-2-furoic acid was found in the extract as an oxidation product. An authentic sample of 5-methyl-2-furoic acid was prepared from 5-methyl-2-furaldehyde.

*2,4,4-Tris(5′-methyl-2′-furyl)-1-pentyl Acetate (**2**).* We dissolve 8.2 g of **1** in 50 g of pyridine and cooled in ice bath; then 36.5 g of acetic anhydride were added, and the mixture was left standing for eight days at room temperature. The reaction mixture was then treated with 1.6 liter of water and extracted with 300 ml of ether. The extract was thoroughly washed with water and distilled under reduced pressure, giving 6.4 g (70%) of **2** as a slightly colored viscous liliquid; bp 182 °C (2 mmHg); n_D^{23} 1.5135.

Found: C, 71.15; H, 7.35%. Calcd for $C_{22}H_{26}O_5$: C, 71.33; H, 7.07%.

IR (liquid film) 1725 (C=O, ester), 3100, 1608, 1555, and 775 cm^{-1} (a series of characteristic bands due to 2,5-disubstituted furan nuclei); NMR (CCl_4) τ 4.2—4.4 (m, 6H, β,β′-ring protons of furan nuclei), 6.02 (d, 2H, J=7 Hz, $C\underline{H}_2OAc$), 7.08 (quintet, 1H, J=7 Hz, $CH_2\overset{|}{C}\underline{H}CH_2OAc$), 7.72 (d, 2H, overlapped with a broad singlet at τ 7.80), 7.80 (s, 6H, $C\underline{H}_3$ of 5-methyl-2-furyl groups), 7.82 (s, 3H, $C\underline{H}_3$ of another 5-methyl-2-furyl groups), 8.10 (s, 3H, $C\underline{H}_3CO$) and 8.56 (s, 3H, $C\underline{H}_3\overset{|}{\underset{|}{C}}CH_2$); mass spectrum (70 eV) *m*/*e* (rel. intensity) 370 (2), 310 (2), 228 (4), 190 (15), 180 (100), 175 (4), 167 (2), 145 (3), 125 (4), 122 (2), 43 (13).

*Maleic Anhydride Adduct (**3**).* One gram of maleic anhydride and 1.0 g of **1** were dissolved in 10 ml of ether under reflux; then the solution was cooled to room temperature and left to stand for two weeks. A colorless, transparent, crystalline product was obtained; 0.13 g (10%); mp 151.7 °C.

This product gave a satisfactory elementary analysis for an equimolar adduct of **1** and maleic anhydride.

Found: C, 67.11; H, 6.10%. Calcd for $C_{24}H_{26}O_7$: C, 67.60; H, 6.10%.

Mass spectrum (70 eV) *m*/*e* (rel. intensity) 426 (trace), 328 (9), 190 (18), 189 (100), 175 (5), 125 (9), 98 (7), 95 (9), 54 (9), 43 (18), 28 (11), 26 (7).

This spectrum reasonably represents the superimposed spectrum of **1** and maleic anhydride (molecular weight, 98). This compound can appear from the adduct **3** as the result of the retro-Diels Alder process.

Separation of a Mixture of 2-Methylfuran Oligomers. Fifty-two grams of a hard brown brittle substance remained in the vacuum distillation flask after the removal of **1**. From 5.2 g of this substance, 2.1 g of an oligomeric product **4** was separated by molecular distillation; bp 195—200 °C (10^{-4} mmHg). The product **4** is a yellow, waxy substance and gave a satisfactory elementary analysis for the 2-methylfuran oligomers.

Found: C, 72.58; H, 7.38%. Calcd for $(C_5H_6O)_n$: C, 73.17; H, 7.31%.

UV max (methanol) 221 nm (ε 23,200); IR (thin film) 3400 (OH), 1700 (C=O), 3100, 1608, 1555, and 775 cm^{-1} (a series of characteristic bands due to 2,5-disubstituted furan nuclei); NMR (CCl_4) τ 4.1—4.4 (m, 6H, β,β′-ring protons of furan nuclei), 6.68 (d), 7.30 (quintet), 7.72, 7.80 (s), 7.82 (s), 7.85 (m), 8.60 (s) and 8.4—8.7 (m); mass spectrum (70 eV) *m*/*e* (rel. intensity) 328 (5), 410 (9), 492 (3), 574 (trace), 189 (100) and others.

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