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Electrochemical Reduction of Furan Derivatives Derived from Biomass

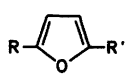
TORBEN LUND and HENNING LUND

Department of Organic Chemistry, University of Aarhus, 8000 Aarhus C, Denmark

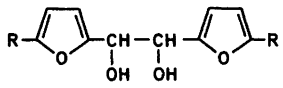
5-Hydroxymethyl-2-furancarboxaldehyde and 5-chloromethyl-2-furancarboxaldehyde have been reduced electrochemically at −0.2 V (SCE) to 5-methyl-2-furancarboxaldehyde in a two-phase system, the aqueous phase being 6 M hydrochloric acid containing 1 M sodium iodide and the organic phase dichloromethane or dichloromethane (75 %) diethyl ether (25 %). Further reduction (−0.6 to −0.8 V) gave a mixture of 2,5-hexanedione, 1,2-bis(5-methyl-2-furyl)ethene, and bis(5-methyl-2-furyl)methane, together with polymerization products. 2-Furanmethanol could be reduced to 2-methylfuran and 5,5-bis(5-methyl-2-furyl)-2-pentanone. Reaction schemes have been proposed for the formation of these compounds.

A number of carbohydrates may be transformed into furan derivatives; 2-furancarboxaldehyde (*1*) has for many years been produced from pentosanes, and 5-hydroxymethyl-2-furancarboxaldehyde (*2*) may be obtained from hexoses under acidic conditions, most easily from fructose; both *1* and *2* are thus readily available chemicals.

In the first paper in this series[1] it was shown that indirect electrolysis of activated alcohols in an acidic medium containing iodide produced hydrocarbons in good yield. This method has now been used for the reduction of *1* and *2* and some other furan derivatives in order to explore the possibilities of indirect electrochemical reduction of hexoses and pentoses under such conditions. The following furan derivatives were investigated.



1 R=H R′=CHO
2 R=CH_2OH R′=CHO
3 R=CH_2Cl R′=CHO
4 R=CH_3 R′=CHO
5 R=CH_3 R′=CH_2OH
6 R=CH_3 R′=CH_3
7 R=H R′=CH_2OH
8 R=H R′=CH_3



9 R=CH_3
10 R=H

RESULTS

Furans are generally sensitive to acids and polymerize rapidly, so it seemed doubtful that much of such substrates would survive the conditions used in the indirect electrochemical reduction of activated alcohols, 6 M acid at 30–60 °C. Two ways were tried to overcome this difficulty, 1) a slow addition of the substrate during the electrolysis in order to diminish the

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time the vulnerable material was in contact with acid and to keep the concentration of the furan low, and 2) to use an aqueous/organic two-phase system in which the furan would preferentially be in the organic phase.

Although the first alternative was an improvement in comparison with the usual bulk electrolysis it was not satisfactory, especially when the product still contained a furan ring. The use of a two-phase electrolysis, however, diminished the polymerization so fair yields of products could be obtained. Furan derivatives deactivated by an aldehyde group toward electrophilic substitution are rather stable under these conditions.

Most of the reductions were therefore made in a medium with an aqueous phase consisting of 2–6 N hydrochloric acid containing 1 M sodium iodide and an organic phase of dichloromethane (Standard medium A) or 75 % dichloromethane and 25 % diethyl ether (Standard medium B); the two phases in standard medium B had approximately the same density with the organic phase being slightly denser than the aqueous acid, so an efficient mixing of the two phases was easy during the electrolysis.

Although the partition ratios for most of the furans between dichloromethane and 6 N hydrochloric acid are from 10:1 to about 100:1 quite respectable current densities could be used; thus a current density of about 5 A dm^{-2} was obtained during the reduction of *3* controlled at −0.2 V (SCE).

Reduction of *3* in standard medium B at −0.2 V (SCE) gave *4* in good yield; further reduction of *4* in the same medium at −0.7 V yielded hexane-2,5-dione (*11*), 1,2-bis(5-methyl-2-furyl)ethene (*12*) and some bis(5-methyl-2-furyl)methane (*13*);[2] the amount of coloured, polymeric material was about 50 %.

The pinacol *9* (mixture of (±) and meso) could be obtained in 85 % yield by direct electrolytic reduction of *4* at −1.6 V in 0.1 M aqueous sodium hydroxide. Indirect reduction of *9* in the standard medium B gave *12* in 12 % yield together with rearranged products and polymeric material. Similarly, 1,2-diphenyl-1,2-dihydroxyethane gave a mixture of stilbene and 2,2-diphenylacetaldehyde on reduction in 60 % aqueous acetic acid containing sodium iodide and 2 N hydrochloric acid.

5-Methylfuranmethanol (*5*) produced *13* in 50–60 % yield on treatment under stirring with N hydrochloric acid and dichloromethane at ambient temperature. Indirect electrochemical reduction of *5* in the standard medium gave *11* and *13* in the ratio 3:2 besides polymeric material.

Treatment of 2,5-dimethylfuran (*6*) in the standard medium at 35 °C for 2 h gave *11* in quantitative yield. Interesting enough, although *13* is structurally analogous to *6*, it is stable under similar conditions for at least 20 h.

It was attempted to demonstrate that *5* was an intermediate in the reduction of *4* to *11* and *13* by reducing *4* in the absence of iodide; in 2 N hydrochloric acid the reduction proceeded more slowly than in the presence of iodide, and *9*, *11*, *12*, and *13*, but no *5* was found as products. During a reduction of *4* in 0.1 N hydrochloric acid, however, *5* was detected by GLC in 2.5 % yield.

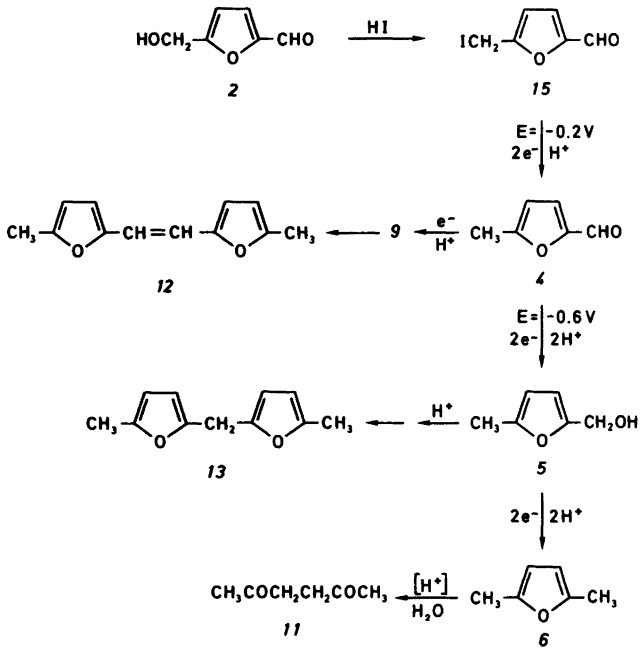
Reduction of *7* in the standard medium gave, besides the expected *8* (45 %) 5,5-bis(5-methyl-2-furyl)-pentanone-2 (*14*) (10 %).

DISCUSSION

Electrolysis using a two-phase solvent system is a useful technique[3–7] when stability or solubility of substrate and/or products are unfavourable for a one-phase electrolysis; in some

cases emulsions and phase-transfer reagents have been used.[4–7] The technique may be successful even if the partition coefficient between organic and aqueous phase is rather unfavourable (~100). The mass transport from the organic phase through the aqueous phase to the electrode is sufficient rapid when the stirring is efficient; under such conditions indirect electrolysis is favourable.

The main products from the indirect electrochemical reduction of 5-hydroxymethylfurancarboxaldehyde *2* under standard conditions are hexane-2,5-dione (acetonylacetone, *11*), 1,2-bis(5-methyl-2-furyl)ethene (*12*), and bis(5-methyl-2-furyl)methane (*13*). These compounds are suggested to be formed according to Schemes 1–3.

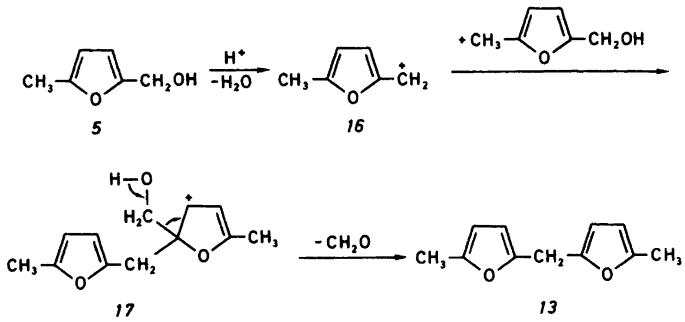


Scheme 1.

The reduction of *2* to *4* follows the reduction path for activated carbinols described previously.[1] The further reduction of *4* at a more negative potential is suggested to give a mixture of *5* and *9*, although none of them are detected as products during reductions under standard conditions. Under less acidic conditions in the absence of iodide *5* and *9* have been detected albeit in rather low yields. *5* is an activated alcohol and is rapidly reduced to *6* under standard conditions; in acid solution *6* is quantitatively hydrolyzed to *11*. *5* is unstable under acidic conditions and a significant part of the polymeric material is believed to be formed from *5*.

The intermediacy of *5* is also made plausible by the formation of *13*. This compound is suggested to be formed as described in Scheme 2. It has previously[2] been prepared by condensation of *8* with formaldehyde.

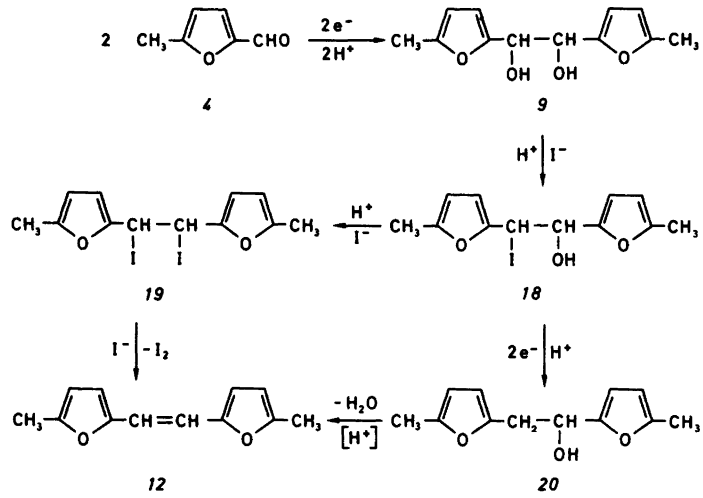
The carbocation *16* is assumed to attack the furan ring at C-2 forming the carbocation *17*. A loss of the hydroxyl proton followed by an electron shift results in an internal redox reaction with formation of formaldehyde and *13*. A somewhat analogous reaction has been



Scheme 2.

observed in an electrophilic substitution reaction in which a π-electron rich alcohol, 4-methoxybenzyl alcohol (anisyl alcohol), on treatment with bromine formed formaldehyde and 4-bromoanisole.[8]

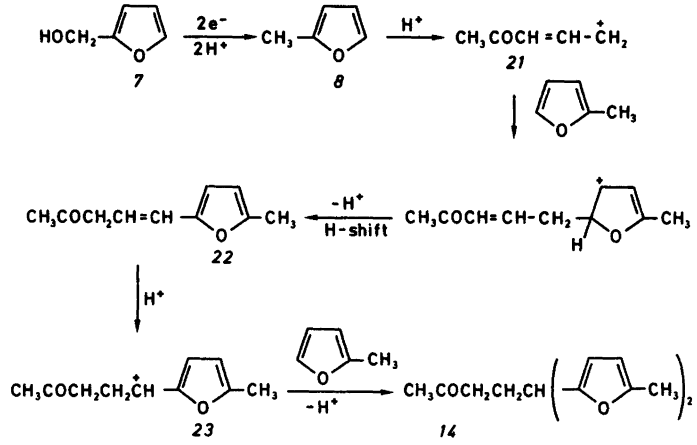
In Scheme 3 two reaction paths are proposed for the formation of *12*; after reaction of *9* with hydrogen iodide to the *vic* iodoalcohol *18* the further reaction might be a reduction to



Scheme 3.

1,2-bis(5-methyl-2-furyl)ethanol *20* which on acid catalyzed loss of water formed *12*, or *18* could form the *vic* diiodo compound *19*, which would react with iodide with formation of iodine and *12*. No evidence has been obtained for either way, although the former seems most likely.

The ratio of 11:13 was higher (5–10:1) during the reduction of *2*, *3*, or *4* in the standard medium than during the reduction of *5* (3:2). This is in accordance with the lower concentration of *5* during the reduction of *2–4* compared to that during the reduction of *5*, and that the formation of *13* is second order in *5*.



Scheme 4.

The products from the reduction of 2-furanmethanol *7* include 5,5-bis(5-methyl-2-furyl)-2-pentanone (*14*); this compound has previously been obtained[9] by treatment of *8* with strong sulfuric acid at 60 °C. The formation of *14* is proposed to follow Scheme 4.

Protonation of *8* forms the allylic carbocation *21*, which attacks *8* in an electrophilic substitution reaction to *22*. Protonation of *22* to *23* followed by another electrophilic attack on *8* produces *14*.

The investigation has shown that it is possible to transform carbohydrate derivatives to low molecular compounds containing less oxygen using indirect electrolysis in acidic solution containing iodide, albeit in only modest to fair yields. Possibly better yields may be obtained using another cell design which would allow shorter reaction times and thus less polymerization of reactive intermediates.

EXPERIMENTAL

Materials. 5-Hydroxymethyl-2-furancarboxaldehyde (*2*) was prepared from fructose in DMF using Dowex 50X8 (50–100 mesh) as acid catalyst.[10] 5-Chloromethyl-2-furancarboxaldehyde was prepared from fructose.[11]

Apparatus. An ordinary H-cell with a Nafion® cation-exchange membrane was used either with a mercury pool or an amalgamated copper plate as cathode and a carbon anode; reference electrode was SCE. A 100 V/10 A potentiostat from Tage Juul, Copenhagen, was used.

The yields were determined by GLC using a Hewlett-Packard 5790 gaschromatograph with a FFAP-column using anisole as internal standard; injection temperature 100 °C, 90 °C for 10 min to 200 °C with 6 °C min^{-1}.

For the ^1H NMR spectra was used a 80 MHz Varian CFT-20 spectrometer and for ^{13}C NMR spectra a 100 MHz Varian XL-100 spectrometer. For highly complex NMR-spectra a 300 MHz Varian XL-300 spectrometer was used.

Reduction of 3. 5-Chloromethyl-2-furancarboxaldehyde (*3*) (2.0 g) was reduced at −0.2 V at a mercury pool cathode using a two-phase catholyte consisting of an aqueous phase (125 ml, 1 M NaI, 6 M HCl) and an organic phase (100 ml, dichloromethane (75 %) and diethyl ether (25 %)), T=20 °C. After completion of the reduction the phases were separated, the aqueous phase extracted with dichloromethane (100–200 ml), and the organic solvent

evaporated partly leaving about 10 ml, which was analyzed by GLC using anisole as internal standard. Yield of *4* 76 %. The stability of *4* in a 1:1 mixture of dichloromethane and 6 M hydrochloric acid was ascertained by following the concentration of *4* in such a mixture for 20 h; other 5-substituted furan aldehydes showed a similar stability.

Reduction of 4. 5-Methyl-2-furancarboxaldehyde (*4*) (2.0 g) was reduced at a mercury pool or amalgamated copper plate as above at −0.6 to −0.8 V; extraction and determination of yields as above; 2,5-hexanedione (acetonylacetone, *11*) 10−20 %, 1,2-bis(5-methyl-2-furyl)-ethene (*12*) 35−5 %, and bis(5-methyl-2-furyl)methane (*13*) 2−4 %. The higher the yield of *11* the lower the yield of *12* and *vice versa*. Low temperatures, less negative potentials, or addition of a surfactant as cetylpyridinium bromide favoured the formation of *12* (35 % yield), whereas lower potentials, dichloromethane as organic phase, and an amalgamated copper electrode promoted a higher yield of *11*. *11*, *12*, and *13* was, however, always accompanied with about 50 % polymeric material of undefined structure. *12*, ^{1}H NMR ($CDCl_3$): δ 2.31 (d, 0.95 Hz, 6 H), 6.00 (2 quartets, 3.2 Hz, 0.95 Hz, 2 H), 6.18 (d, 3.2 Hz, 2 H), 6.69 (s, 2 H). ^{13}C NMR ($CDCl_3$): δ 13.69, 107,81, 109.36, 113.83, 151.78, 151.88. MS (*m/e*, %): 189(15), 188(100), 173(16), 145(51), 43(26). *13*, ^{1}H NMR ($CDCl_3$): δ 2.34(s,6H), 3.92 (s, 2 H), 5.89 (m, 4 H). ^{13}C NMR ($CDCl_3$): 13.2, 27.2, 105.8, 106.6, 149.7, 150.6. MS (*m/e*, %): 190(10), 177(11), 176(100), 175(28), 161(29), 133(19), 105(22), 95(30), 43(46).

Reduction of 4. *4* (11.1 g) in 30 % aqueous alcohol (0.1 M sodium hydroxide, 0.5 M sodium chloride) was reduced at −1.6 V at 35−40 °C. After completion of the reduction the catholyte was extracted with diethyl ether, which was washed with water, dried over molecular sieves A4 and evaporated leaving 9.4 g of a mixture of approximately equal amounts of the meso- and (±)-pinacols, 1,2-bis(5-methyl-2-furyl)-1,2-dihydroxyethane *9*, (yield 85 %). ^{1}H NMR ($CDCl_3$): δ 2.25 (s, 6 H), 4.84 (s, 2 H), 5.85 (m, 2 H), 6.04 (d, 2 H); the other isomer: δ 2.25 (s, 6 H), 4.84 (s, 2 H), 5.85 (m, 2 H), 6.14 (d, 2 H); the signal at 2.25 from the two isomers can be seen as two singlets. ^{13}C NMR ($CDCl_3$): 13.4, 69.62, 69.85, 106.1, 109.1, 151, 152. MS (m/e, %): 222(6), 204(23), 188(11), 175(100), 111(24), 109(34), 105(25), 53(18), 41(22).

Reduction of 5. 5-Methyl-2-furanmethanol (*5*) (2.0 g) was reduced analogous to *3*, yielding *11* (16 %) and *13* (11 %) together with polymeric products. *5* is not stable under the reaction conditions.

Reduction of 9. 1,2-Bis(5-methylfuryl)-1,2-dihydroxyethane (*9*, mixture of meso and (±)) was reduced at −0.2 V analogous to *3*. Besides products from polymerization (>60 %) and pinacol rearrangement (5 %) *12* was isolated in 12 % yield.

Reduction of 7. 2-Furanmethanol (*7*) (3 g) was reduced in 6 N hydrochloric acid and 1 M sodium iodide with diethyl ether as organic phase. The ether was evaporated leaving 1.36 g of a crude product consisting of 45 % 2-methylfuran and 10 % 5,5-bis(5-methyl-2-furyl)-2-pentanone (*14*). *14*, ^{1}H NMR ($CDCl_3$): δ 2.11 (s, 3 H), 2.21 (m,$J_{3,4}$ 7.43Hz, $J_{4,5}$ 7.56Hz, 2 H), 2.25 (d, 1.00 Hz, 6 H), 2.44 (t, 7.43 Hz, 2 H), 3.97 (t, 7.56 Hz, 1 H), 5.87 (2q, 2.98 Hz, 1.00 Hz, 2 H), 5.95 (d, 2.98 Hz, 2 H). ^{13}C NMR ($CDCl_3$): 13.44, 26.70, 29.84, 37.90, 41.08, 105.82, 106.43, 150.78, 152.93, 208.13. MS (*m/e*, %): 246(12), 188(100), 175(81), 43(42).

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