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G.A. Tolstikov on his 75th anniversary

Nucleophilic Addition to Acetylenes in Superbasic Catalytic Systems: XV.* Vinylation of 2-Hydroxymethylfuran

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Abstract—2-Hydroxymethylfuran reacted with acetylene in superbasic catalytic systems MOH–DMSO (M = Na, K) under mild temperature conditions (75–85°C, 1–2 h), yielding 80% of 2-vinyloxymethylfuran. The product, as well as acetaldehyde acetals derived therefrom, turned out to be promising as modifiers for electrolyte in lithium–sulfur rechargeable batteries.

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Furan derivatives are widespread in nature [2, 3]. Many synthetic drugs, including antibiotics, cytostatics, tuberculostatics, bactericides, etc. [4–10], were obtained on the basis of furan derivatives. Some compounds of the furan series are used as sorbents for trapping industrial discharges and as components of glass fiber binding compositions [11]. In the recent years, furan derivatives have been successfully used for the development of new effective materials for lithium rechargeable batteries, e.g., as polymerizable electrolyte additives that produce a protective coating on the electrode surface [12–16].

In this respect, a promising subject for study may be 2-vinyloxymethylfuran provided that it is accessible. 2-Vinyloxymethylfuran is a highly reactive compound possessing two active polymerizable fragments (the side-chain double bond and furan ring) and is a base building block (furan ring carrier) for the synthesis of new furan derivatives. It can be converted into various acetals, thioacetals, acylals (via electrophilic addition of alcohols, diols, polyols, and acids at the vinyloxy group) [17], heterocyclic compounds (Diels–Alder reactions) [18], polymers [19, 20], etc. However, the known method for the preparation of 2-vinyloxymethylfuran from 2-hydroxymethylfuran and acetylene [21, 22] is unpractical and inefficient. Vinylation of

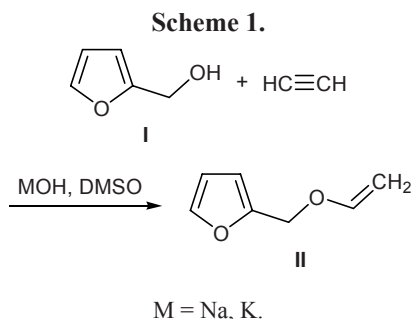
2-hydroxymethylfuran was carried out under high pressure (initial acetylene pressure 16 atm at room temperature) at 125–160°C in the presence of KOH. The reaction was accompanied by strong tarring which complicated the isolation and purification of the target vinyl ether, and the yield was 45–68% [21, 22]. 2-Hydroxymethylfuran failed to react with acetylene at a temperature below 125°C [22].

The use of superbasic catalytic systems like alkali metal hydroxide–polar aprotic solvent (such as DMSO or HMPA) in the acetylene chemistry radically extended the scope of the classical Favorskii vinylation reaction, so that many previously unknown or difficultly accessible vinyl ethers were obtained [23–25]. For example, we succeeded in effecting for the first time vinylation of allyl alcohol (a structural analog of 2-hydroxymethylfuran) in the system MOH–DMSO (M = Na, K) [26]; formerly [27], this reaction was believed to be impossible because of side processes involving prototropic shift of the double bond and [3,3]-sigmatropic rearrangement [26].

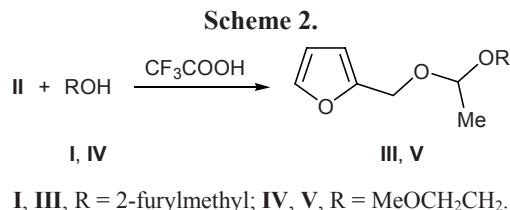
The goal of the present work was to develop efficient procedures for the direct vinylation of 2-hydroxymethylfuran with acetylene with a view to synthesize 2-vinyloxymethylfuran and acetals derived therefrom and test the products as electrolyte additives for lithium–sulfur rechargeable batteries.

* For communication XIV, see [1].

For the synthesis of 2-vinyloxymethylfuran we selected NaOH–DMSO and KOH–DMSO as superbasic catalytic systems. We anticipated that the reaction in these systems will occur under mild conditions in a selective and safe fashion. In fact, 2-hydroxymethylfuran (**I**) reacted with acetylene in MOH–DMSO (high-pressure reactor, initial acetylene pressure 10–12 atm at room temperature, 50 mol % of MOH) under relatively mild temperature conditions (75–85°C, 1–2 h) to give 80% of 2-vinyloxymethylfuran (**II**) (Scheme 1). Our attempts to increase the yield of vinyl ether **II** by raising the concentration of alkali metal hydroxide, temperature (by 10°C), or reaction time (to 3–4 h) were unsuccessful. Moreover, the yield of ether **II** decreased to 65–70% as a result of increased tarring.



Thus we have made vinyl ether **II** accessible and opened new possibilities for further studying its properties, e.g., the reactivity toward electrophilic reagents. Uvarova [22] briefly reported on the addition of alcohol **I** at the double bond of ether **II** in the presence of HCl (reaction time ~24 h) to obtain 2-[[1-(2-furylmethoxy)ethoxy]methyl]furan (**III**) in 80% yield; the product was characterized only by physical constants and elemental analysis. We modified the reaction conditions via replacement of HCl by trifluoroacetic acid which is known as mild specific catalyst for the synthesis of acetals from vinyl ethers and hydroxy compounds [28–30]. As a result, we succeeded in shortening the reaction time to 1 h and obtaining acetal **III** in almost quantitative yield. Following a similar procedure, by reaction of 2-methoxyethanol (**IV**) with vinyl ether **II** we synthesized in quantitative yield a mixed acetal, 2-[[1-(2-methoxyethoxy)ethoxy]methyl]furan (**V**) (Scheme 2). The reactions were accompanied by appreciable heat evolution (the mixture warmed up to 50–70°C) and were almost complete when the mixtures cooled down to room temperature. The IR spectra of the reaction mixtures contained no absorption bands typical of vinyloxy (3030, 1650–1617, 1320, 1200, 960, 817 cm⁻¹) and hydroxy groups (3450 cm⁻¹). In

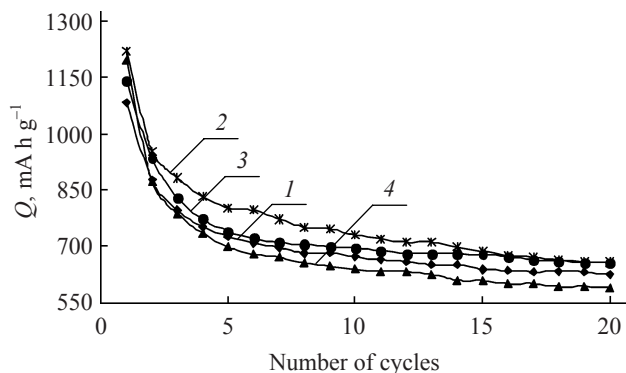


the ¹H NMR spectra we observed only one quartet at δ 4.8 ppm from the OCHO proton and only one doublet at δ 1.3 ppm from the methyl protons (CH₃CH). These data indicated that acetals **III** and **V** were the only products and that they were formed in quantitative yield.

Distillation of the products (even after neutralization with a tertiary amine or sodium carbonate) was accompanied by slight tarring, while 2-[[1-(2-methoxyethoxy)ethoxy]methyl]furan (**V**) underwent disproportionation. It is advisable to store compounds **III** and **V** in the cold, for they gradually turn dark even at room temperature.

Molecules **II**, **III**, and **V** contain ether and acetal fragments that are capable of specifically solvating lithium cation (like crown ethers). This feature may be utilized in chemical current sources to enhance their efficiency. We examined the effect of vinyl ether **II** and acetals **III** and **V** on the electrochemical properties and cycling efficiency of sulfur and lithium electrodes in lithium batteries. Compounds **II**, **III**, and **V** were added in an amount of 1 wt % to standard electrolyte. The cycling efficiency of lithium–sulfur cells was studied in the galvanostatic mode using standard and modified electrolytes. The results are shown in figure. It is seen that addition of ether **II** or acetal **III** increases the discharge capacity by 13 and 5% in the first cycle and by 4 and 5% in the 20th cycle, respectively (see figure, curves 2 and 3). Modification of electrolyte with mixed acetal **V** (curve 4) increases the discharge capacity by 10% only in the first cycle, while the discharge capacity in all subsequent cycles is lower by 0.5–5.5% than the reference value.

Presumably, charge–discharge cycling of a battery filled with an electrolyte modified with compound **II** or **III** leads to formation on the lithium electrode surface of a firm passivating film possessing a good conductivity with respect to lithium ions, and that film persists for a long time. The passivating film formed from compound **V** has poor lithium ion transport parameters. Increase of the discharge capacity in the first cycle by 13, 5, and 10% upon modification of electrolyte with compounds **II**, **III**, and **V**, respectively,



Variation of the discharge capacity Q of sulfur cathode in lithium cells with standard electrolyte (I) with no additive and containing 1% of (2) 2-vinyloxymethylfuran (II), (3) 2-[[1-(2-furylmethoxy)ethoxy]methyl]furan (III), and (4), 2-[[1-(2-methoxyethoxy)ethoxy]methyl]furan (V).

unambiguously indicates that these compounds are capable of partially dissolving lithium sulfides arising from cathodic polarization and leading to loss of active cathode sulfur.

Thus we have synthesized in high yield and characterized for the first time by spectral data (IR and NMR) 2-vinyloxymethylfuran (II) and acetals III and V derived therefrom as promising building blocks for organic synthesis and efficient electrolyte additives for lithium–sulfur rechargeable batteries.

EXPERIMENTAL

The IR spectra were recorded from samples prepared as thin films (neat) on a Bruker JFS-25 spectrometer in the range from 400 to 4000 cm^{-1} . The ^1H and ^{13}C NMR spectra were measured at room temperature on a Bruker DPX-400 spectrometer at 400.13 and 100.62 MHz, respectively, using CDCl_3 as solvent and HMDS as internal reference. The mass spectrum was obtained on a Shimadzu GCMS-QP5050A instrument (SPB-5 capillary column, 60 $\text{m} \times 0.25$ mm, film thickness 0.25 μm ; injector temperature 150°C; carrier gas helium, flow rate 0.7 ml/min, split ratio 1:15; oven temperature programming from 60 to 150°C at a rate of 5 deg/min; quadrupole mass analyzer; electron impact, 70 eV; ion source temperature 150°C; a.m.u. range 34–400).

Test vial cells with an aluminum cathode coated with carbon and a composition consisting of elemental sulfur, charcoal, and poly(ethylene oxide) (65:30:5 by weight) and a lithium anode were used in electrochemical experiments. Porous polypropylene was used as separator, and a 2 M solution of $(\text{CF}_3\text{SO}_2)_2\text{NLi}$ in

1,2-dimethoxyethane–1,3-dioxolane (1:1), as electrolyte. Charge–discharge cycling was performed on a setup for testing chemical current sources in the voltage range from 1.25 to 3.0 V; polarizing current density 0.25 mA/cm^2 .

2-Vinyloxymethylfuran (II). A 1-l rotating high-pressure reactor was charged with 9.81 g (100 mmol) of 2-hydroxymethylfuran I, 2.0 g (50 mmol) of sodium hydroxide, and 100 ml of DMSO, acetylene was supplied to a pressure of 12 atm, and the mixture was stirred for 2 h at 75–85°C. When the reaction was complete, the mixture was diluted with an equal volume of water and extracted with diethyl ether (6 \times 30 ml). The extracts were combined, washed with water, and dried over Na_2CO_3 , and the solvent was distilled off on a rotary evaporator. Vacuum distillation of the residue gave 9.94 g (80%) of vinyl ether II, bp 39°C (8 mm), $n_D^{20} = 1.4739$; published data [22]: bp 63°C (20 mm), $n_D^{20} = 1.4745$. IR spectrum, ν , cm^{-1} : 600 m, 742 s, 817 s, 885 w, 922 s, 946 m, 961 m, 979 m ($\text{CH}_2=$, $\text{C}=\text{C}$), 997 m, 1017 m, 1054 s, 1079 m, 1152 s, 1192 v.s., 1227 m, 1268 w, 1285 w (COC , $\text{C}=\text{C}$), 1320 s ($\text{C}=\text{C}$), 1360 m, 1369 m, 1391 w, 1455 w (CH_2), 1503 m ($\text{C}=\text{C}$), 1617 s, 1638 s, 1648 sh ($\text{CH}_2=\text{CHO}$), 2872 m, 2927 m, 2977 w (CH_2), 3030 v.w, 3050 v.w, 3118 w, 3150 w ($=\text{C}-\text{H}$). ^1H NMR spectrum, δ , ppm: 4.11 d.d (1H, *cis*- $\text{CH}=\text{}$, $^3J = 6.7$, $^2J = 2.0$ Hz), 4.35 d.d (1H, *trans*- $\text{CH}=\text{}$, $^3J = 14.4$, $^2J = 2.0$ Hz), 4.71 s (2H, CH_2O), 6.39 m (2H, 3-H, 4-H), 6.52 d.d (1H, $=\text{CHO}$, $^3J = 14.4$, 6.7 Hz), 7.44 d (1H, 5-H, $J = 0.8$ Hz). ^{13}C NMR spectrum, δ_C , ppm: 151.45 ($\text{OCH}=\text{}$), 150.61 (C^2), 143.30 (C^5), 110.71 (C^3), 110.02 (C^4), 87.88 ($\text{CH}_2=\text{}$), 62.59 (OCH_2). Mass spectrum, m/z (I_{rel} , %): 124 (3) $[\text{M}]^+$, 95 (2) $[\text{M} - \text{HCO}]^+$, 81 (100) $[\text{M} - \text{C}_2\text{H}_3\text{O}]^+$, 53 (7) $[\text{C}_4\text{H}_5]^+$. Found, %: C 67.70; H 6.57. $\text{C}_7\text{H}_8\text{O}_2$. Calculated, %: C 67.73; H 6.50.

General procedure for electrophilic addition of alcohols to 2-vinyloxymethylfuran (II). Trifluoroacetic acid, 0.5 to 1 wt %, was added to a mixture of 3.7 g (30 mmol) of vinyl ether II and 30 mmol of alcohol I or IV. The mixture warmed up by 30–50°C. It was allowed to cool down to room temperature, stirred for 0.5–1 h, and neutralized with NaHCO_3 or Bu_3N (0.1 g).

2-[[1-(2-Furylmethoxy)ethoxy]methyl]furan (III). Colorless liquid which turned dark on storage, bp 112–113°C (2 mm), $n_D^{20} = 1.4910$. IR spectrum, ν , cm^{-1} : 600 m, 735 s, 810 m, 913 m, 969 m ($\text{C}=\text{C}$), 1010 s, 1090 s, 1133 s, 1150 s, 1220 m, 1270 m,

1280 m (COC, C=C), 1338 m, 1372 m, 1394 m, 1446 m (CH₂, Me), 1503 m (C=C), 2871 m, 2935 m, 2992 m (CH₂, Me), 3116 m, 3145 m (=C-H). ¹H NMR spectrum, δ, ppm: 1.33 d (3H, Me, ³J = 5.2 Hz), 4.48 d and 4.54 d (2H each, CH₂O, ²J = 12.8 Hz), 4.88 q (1H, OCHO, ³J = 5.2 Hz), 6.29 m (4H, 3-H, 4-H), 7.36 d (2H, 5-H, J = 0.8 Hz). Found, %: C 64.73; H 6.30. C₁₂H₁₄O₄. Calculated, %: C 64.85; H 6.35.

2-[[1-(2-Methoxyethoxy)ethoxy]methyl]furan (V). Colorless liquid which turned dark on storage, bp 82–84°C (2 mm), n_D^{20} = 1.4582. IR spectrum, ν, cm⁻¹: 601 m, 750 s, 815 m, 853 m, 885 m, 920 s, 949 m, 971 m, 991 m (C=C), 1015 s, 1067 s, 1100 s, 1124 s, 1150 s, 1200 m, 1225 m, 1244 m, 1282 w (COC, C=C), 1340 m, 1369 m, 1387 m, 1454 m (CH₂, Me), 1504 m (C=C), 2827 m (OMe), 2879 s, 2930 s, 2987 s (CH₂, Me), 3118 w, 3148 w (C=C). ¹H NMR spectrum, δ, ppm: 1.30 d (3H, Me, ³J = 5.2 Hz), 3.33 s (3H, OMe), 3.49 t (2H, OCH₂, ³J = 4.8 Hz), 3.54–3.59 m and 3.64–3.70 m (1H each, OCH₂), 4.46 d and 4.51 d (1H each, CH₂O, ²J = 12.8 Hz), 4.81 q (1H, OCHO, ³J = 5.2 Hz), 6.27 m (2H, 3-H, 4-H), 7.35 d (1H, 5-H, J = 0.8 Hz). Found, %: C 60.06; H 8.11. C₁₀H₁₆O₄. Calculated, %: C 59.98; H 8.05.

REFERENCES

- Oparina, L.A., Khil'ko, M.Ya., Chernysheva, N.A., Shaikhudinova, S.I., Parshina, L.N., Preiss, T., Henkelmann, J., and Trofimov, B.A., *Russ. J. Org. Chem.*, 2005, vol. 41, p. 656.
- Semenov, A.A., *Ocherk khimii prirodnykh compoundi* (A Survey on the Chemistry of Natural Compounds), Novosibirsk: Nauka, 2000.
- Tolstikov, G.A., Tolstikova, T.G., Shul'ts, E.E., Sorokina, I.V., Chernov, S.V., and Kharitonova, Yu.V., *Biologicheskii aktivnye vysshie furanoterpenoidy i ikh proizvodnye* (Biologically Active Higher Furanoterpenoids), Kartsev, V.G., Moscow: IBS Press, 2003, vol. 1, p. 104.
- Uspekhi khimii furana* (Advances in the Furan Chemistry), Lukevits, E.Ya., Riga: Zinatne, 1978, p. 302.
- Foroumadi, A., Soltani, F., and Mirzaei, M., *Pharmazie*, 2003, vol. 58, p. 347.
- Bakkestuen, A.K., Gundersen, L.-L., Langli, G., Liu, F., and Nolsoe, J.M., *Bioorg. Med. Chem. Lett.*, 2000, vol. 10, p. 1207.
- Gundersen, L.-L., Nissen-Meyer, J., and Spisberg, B., *J. Med. Chem.*, 2002, vol. 45, p. 1383.
- Brændvang, M. and Gundersen, L.-L., *Bioorg. Med. Chem.*, 2005, vol. 13, p. 6360.
- Bakkestuen, A.K., Gundersen, L.-L., and Utenova, B.T., *J. Med. Chem.*, 2005, vol. 48, p. 2710.
- Mashkovskii, M.D., *Lekarstvennye sredstva* (Drugs), Moscow: Novaya Volna, 2006, p. 1206.
- Golino, C.M., Kielmeyer, W.H., Rude, C.A., Taylor, T.J., and Thiessen, L.K., US Patent no. 5589536, 1996; *Chem. Abstr.*, 1996, vol. 125, no. 121584.
- Matsuda, Y., Ishikawa, M., Yoshitake, S., and Morita, M., *J. Power Sources*, 1995, vol. 54, p. 301.
- Aurbach, D., Zaban, A., Gofer, Y., Abramson, O., and Ben-Zion, M., *J. Electrochem. Soc.*, 1995, vol. 142, p. 687.
- Mao, H., US Patent no. 5879834, 1997; *Chem. Abstr.*, 1997, vol. 126, no. 240724.
- Mao, H. and Wainwright, D.S., US Patent no. 6074776, 1998; *Chem. Abstr.*, 1998, vol. 130, no. 15816.
- Amine, K., Liu, J., Vissers, D.R., and Lu, W., US Patent Publ. no. 20060147809, 2006; *Chem. Abstr.*, 2006, vol. 145, no. 127575.
- Mikhaleva, A.I. and Gusarova, N.K., *Atsetilen: reaktsii i proizvodnye* (Acetylene: Reactions and Derivatives), Irkutsk: Ottisk, 2006, p. 297.
- Ichihara, A. and Oikawa, H., *Curr. Org. Chem.*, 1998, vol. 2, p. 365.
- Vorob'eva, A.I., Onina, S.A., Musina, I.D., Kolesov, S.V., Muslukhov, R.R., Parshina, L.N., Oparina, L.A., Trofimov, B.A., and Monakov, Yu.B., *Vysokomol. Soedin. B*, 2004, vol. 46, p. 364.
- Vorob'eva, A.I., Sagitova, D.R., Sadykova, G.R., Parshina, L.N., Trofimov, B.A., and Monakov, Yu.B., *Vysokomol. Soedin. B*, 2007, vol. 49, p. 571.
- Rychkova, A.G. and Keller, R.E., *Zh. Obshch. Khim.*, 1961, vol. 31, p. 1849.
- Uvarova, N.I., *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim.*, 1962, no. 1, p. 78.
- Trofimov, B.A., *Russ. J. Org. Chem.*, 1995, vol. 31, p. 1233.
- Trofimov, B.A., *Curr. Org. Chem.*, 2002, vol. 6, p. 1121.
- Trofimov, B.A., *Sovremennye problemy organicheskoi khimii* (Current Problems in Organic Chemistry), Potekhin, A.A., Kostikov, R.R., and Bred, M.S., Eds., St.-Petersburg: VVM, 2004, vol. 14, p. 131.
- Trofimov, B.A., Oparina, L.A., Lavrov, V.I., and Parshina, L.N., *Zh. Org. Khim.*, 1990, vol. 26, p. 725.
- Reppe, J.W., *Neue Entwicklungen auf dem Gebiete der Chemie des Acetylens und Kohlenoxyds*, Berlin: Springer, 1949, p. 7.
- Nedolya, N.A. and Trofimov, B.A., *Zh. Org. Khim.*, 1985, vol. 21, p. 271.
- Gorelova, O.V., Oparina, L.A., Parshina, L.N., Gusarova, N.K., and Trofimov, B.A., *Russ. J. Org. Chem.*, 2001, vol. 31, p. 1683.
- Vysotskaya, O.V., Oparina, L.A., Parshina, L.N., Gusarova, N.K., and Trofimov, B.A., *Russ. J. Org. Chem.*, 2002, vol. 38, p. 1082.