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Chemoselective Reduction of 3-Arylmethylidenetetrahydrofuran-2,4-diones with Triethylsilane and Sodium Cyanotrihydridoborate in Acid Media

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Abstract—3-Arylmethylidenetetrahydrofuran-2,4-diones were smoothly reduced to the corresponding 3-benzyl derivatives in 50–98% yield with triethylsilane in trifluoroacetic acid or with sodium cyanotrihydridoborate in the system tetrahydrofuran–2 N hydrochloric acid. The reduction of 3-(3-arylprop-2-en-1-ylidene)-tetrahydrofuran-2,4-diones with sodium cyanotrihydridoborate gave 3-cinnamyltetrahydrofuran-2,4-diones as the only products.

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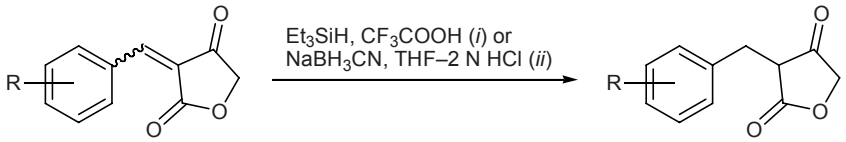
We previously described a simple and convenient procedure for selective transformation of carbo- and heterocyclic β,β′-tricarbonyl compounds into the corresponding cyclic α-alkyl-β-dicarbonyl derivatives by the action of triethylsilane in trifluoroacetic acid [1] or of cyanotrihydridoborate in THF–2 N hydrochloric acid [2]. In the present work we examined the applicability of the same reducing systems for selective reduction of the cross-conjugated double bond in 3-(arylmethylidene)- and 3-(3-arylprop-2-en-1-ylidene)tetrahydrofuran-2,4-diones.

While performing studies in the field of synthesis of biologically active heteroprostanoids on the basis of tetronic acid (tetrahydrofuran-2,4-dione), we have encountered with the necessity of developing a convenient procedure for building up 3,7-interphenylene α-prostanoid chain. For this purpose, we selected 3-(arylmethylidene)tetrahydrofuran-2,4-diones **I** [3] as appropriate intermediate products. These compounds are readily obtained as mixtures of *E* and *Z* isomers by Knoevenagel condensation of tetrahydrofuran-2,4-diones with aromatic aldehydes catalyzed by both protic [4] and Lewis acids [5]. Unlike most reactive carbocyclic and other heterocyclic analogs formed as intermediates in multi-component reactions involving β-dicarbonyl compounds and aromatic aldehydes [6], 3-(arylmethylidene)tetrahydrofuran-2,4-diones are stable compounds. They found application in the synthesis of HIV protease inhibitors which are promising for the treatment of AIDS and related diseases [5].

Construction of 3,7-interphenylene α-prostanoid chain implies chemoselective reduction of the cross-conjugated *E*,*Z*-double bond in 3-(arylmethylidene)-tetrahydrofuran-2,4-diones. Using 3-(alkoxybenzylidene)- [3] and 3-(arylmethylidene)tetrahydrofuran-2,4-diones **Ia**–**Ih** as examples, we found that these compounds can be successfully reduced both with triethylsilane in trifluoroacetic acid (method *a*) [1] and with

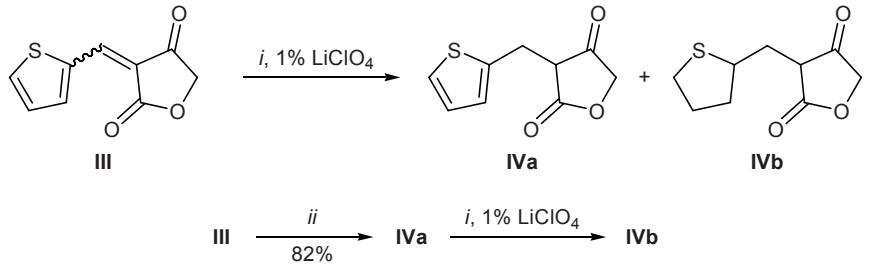
Scheme 1.



Ia–Ih **IIa–IIh**

R = H (**a**), 2-HO (**b**), 2-MeO (**c**), 2-HO-5-MeO (**d**), 3-MeO-4-HO (**e**), 3,4-$(MeO)_2$ (**f**), 4-F (**g**), 4-O_2N (**h**).

Scheme 2.



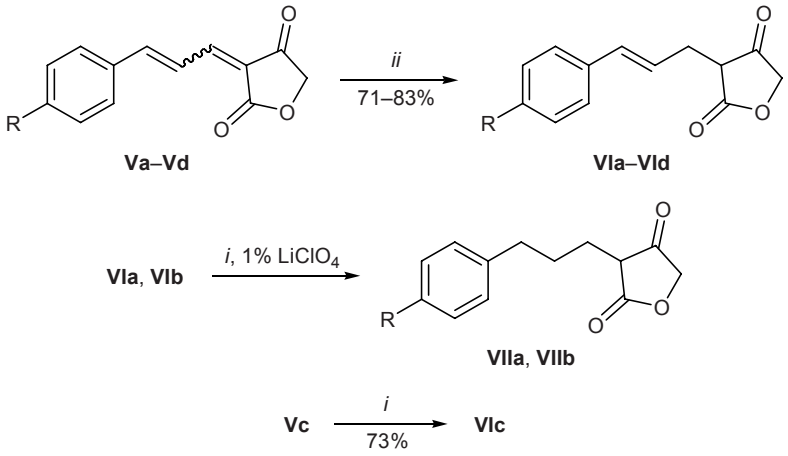
sodium cyanotrihydridoborate in a mixture of tetrahydrofuran with 2 N hydrochloric acid (method *b*) [2]. The yields of the corresponding 3-benzyltetrahydrofuran-2,4-diones **IIa**–**IIh** were 50–98% (Scheme 1). The nature and position of substituents in the aromatic ring of initial tetronic acids **Ia**–**Ih** did not affect the results of reduction, and procedure *a* did not require Lewis acid as catalyst.

The reduction of 3-(2-thienylmethylidene)tetrahydrofuran-2,4-dione (**III**) according to procedure *b* gave 3-(2-thienylmethyl)tetrahydrofuran-2,4-dione (**IVa**) as the only product, whereas the reduction of the same substrate with triethylsilane in trifluoroacetic acid (method *a*, 24 h) was accompanied by formation of a small amount of 3-(tetrahydrothiophen-2-ylmethyl)-tetrahydrofuran-2,4-dione (**IVb**) (Scheme 2). Compound **IVb** was isolated in 37–40% yield by reduction of tetronic acid **III** or **IVa** according to procedure *a* in the presence of 1% of $LiClO_4$ as catalyst (reaction time 6 days).

In contrast to 3-arylmethylidene derivatives **Ia**–**Ih**, the reduction of 3-(3-arylprop-2-en-1-ylidene)tetrahydrofuran-2,4-diones **Va**, **Vb**, and **Vd** having two conjugated double bonds in the side chain with triethylsilane in trifluoroacetic acid resulted in the formation of complex mixtures of products which we failed to identify. An exception was *p*-nitrocinnamylidene derivative **Vc** which was reduced under analogous conditions to (*E*)-3-[3-(4-nitrophenyl)prop-2-en-1-yl]-tetrahydrofuran-2,4-dione (**VIc**) in 73% yield. By contrast, the reaction of compounds **Va**–**Vd** with sodium cyanotrihydridoborate in THF–aqueous HCl gave 3-cinnamyltetrahydrofuran-2,4-diones **VIa**–**VId** as the only products (Scheme 3), regardless of hydrochloric acid concentration (2 → 12 N). These results considerably differed from those obtained in the reaction of 3-cinnamoyltetronic acids with $NaBH_3CN$ in 2 N hydrochloric acid [2, 3], where exhaustive reduction of enone system occurred with formation of 3-(3-arylpropyl)tetrahydrofuran-2,4-diones in high yield.

The position of the side-chain double bond in reduction products **VIa**–**VId** was unambiguously determined by analysis of their ^{13}C NMR spectra which displayed a signal at δ_C 25.2–25.9 ppm from the exocyclic methylene carbon atom, as well as by comparing chemical shifts of protons in the allyl fragment of regioisomeric enol derivatives of **VIa**–**VId** [3].

Scheme 3.



V, **VI**, R = H (**a**), F (**b**), O_2N (**c**), Cl (**d**); **VII**, R = H (**a**), F (**b**).

The side-chain double bond in 3-cinnamyl derivatives **VIa** and **VIb** can be reduced by the action of triethylsilane in trifluoroacetic acid; however, this reaction is much more difficult as compared to the reduction of the cross-conjugated double bond in 3-(arylmethylidene)tetrahydrofuran-2,4-diones under analogous conditions, and the presence of lithium perchlorate as catalyst is necessary. The yields of reduction products **VIIa** and **VIIb** in 48 h were 79 and 37%, respectively. The double bond in nitro-substituted compound **VIc** was not reduced under the same conditions, presumably due to deactivating effect of the nitro group which is a strong electron acceptor. On the other hand, no such effect on the conjugated double bond was observed for 2-(4-nitrophenyl)acryloyl analogs [2] and 3-(4-nitrobenzylidene)tetrahydrofuran-2,4-dione (**Ih**). The double bond in these compounds was reduced with equal efficiencies using both reducing systems.

Thus the reduction of readily accessible 3-(arylmethylidene)tetrahydrofuran-2,4-diones with triethylsilane in trifluoroacetic acid or with sodium cyanotrihydridoborate in THF–2 N hydrochloric acid provides a convenient route to the corresponding 3-benzyl derivatives with various substitution patterns in the benzene ring. The system $NaBH_3CN$/THF–2 N HCl ensures selective reduction of the 1,3-diene fragment in 3-(3-arylprop-2-en-1-ylidene)tetrahydrofuran-2,4-diones to 3-cinnamyl derivatives in high yield. The use of the same system for the reduction of 3-cinnamoyl- and 3-(3-arylprop-2-en-1-ylidene)tetrahydrofuran-2,4-diones makes it possible to obtain 3-substituted tetronic acids with different degrees of saturation of the hydrocarbon chain.

EXPERIMENTAL

The melting points were determined on a Boetius melting point apparatus. The IR spectra were recorded in KBr on a UR-20 instrument. The ^1H and ^{13}C NMR spectra were measured on a Bruker Avance-500 spectrometer at 500 and 125.7 MHz, respectively, using tetramethylsilane as internal reference.

Initial 3-arylmethylidene- (**Ia**–**Ih**, **III**) and 3-(3-arylprop-2-en-1-ylidene)tetrahydrofuran-2,4-diones (**Va**–**Vd**) were synthesized according to the procedures described in [4, 5]. 3-(3-Phenylprop-2-en-1-yl)tetrahydrofuran-2,4-dione (**VIa**) and 3-(3-phenylpropyl)-tetrahydrofuran-2,4-dione (**VIIa**) were reported previously [3].

Reduction of 3-arylmethylidene- and 3-(3-arylprop-2-en-1-ylidene)tetrahydrofuran-2,4-diones Ia–Ih, III, and Va–Vd (*general procedure***).** *a*. Triethylsilane, 0.40 ml (2.5 mmol), was added in portions under stirring to a solution of 1 mmol of the corresponding 3-substituted tetronic acid in 5 ml of trifluoroacetic acid. In the reduction of 3-(3-arylprop-2-en-1-yl) derivatives, trifluoroacetic acid contained 1% of $LiClO_4$. The mixture was stirred at room temperature until the reaction was complate (TLC) and evaporated under reduced pressure, the residue was cooled and washed with several portions of cold hexane, and the crystalline product was washed with water, dried in air, and purified by recrystallization.

b. 3-Substituted tetronic acid **Ia**–**Ih**, **III**, or **Va**–**Vd**, 1 mmol, was dissolved in 6 ml of THF, and 5 ml of 2 N hydrochloric acid was added under stirring. In some cases, partial precipitation of the initial compound occurred. Sodium cyanotrihydridoborate, 0.16 g (2.5 mmol), was added in portions to the resulting solution or suspension, and separated initial compound gradually dissolved. The mixture was stirred for 12 h at room temperature, tetrahydrofuran was removed under reduced pressure, the remaining aqueous phase was cooled, and the crystalline product was filtered off, washed with cold water, dried in air, and purified by recrystallization.

3-Benzyltetrahydrofuran-2,4-dione (IIa). Yield 81 (*a*), 84% (*b*); mp 167–169°C. IR spectrum, ν, cm^{-1}: 1395, 1415, 1450, 1550, 1580–1680 br, 1710. ^1H NMR spectrum (CF_3CO_2D), δ, ppm: 3.67 s (2H, PhC**H**$_2$), 4.84 s (2H, 5-H), 7.26–7.32 m (3H, H_{arom}), 7.33–7.39 m (2H, H_{arom}). ^{13}C NMR spectrum (CF_3CO_2D), δ_C, ppm: 28.85 (CH_2), 70.81 (C^5), 103.36 (C_{quat}), 129.43 (CH_{arom}), 130.08 (2C, CH_{arom}), 131.19 (2C, CH_{arom}), 138.04 (C_{quat}), 178.80 (C=O), 184.19 (C=O). Found, %: C 69.74; H 5.38. $C_{11}H_{10}O_3$. Calculated, %: C 69.46; H 5.30.

3-(2-Hydroxybenzyl)tetrahydrofuran-2,4-dione (IIb). Yield 50 (*a*), 55% (*b*); mp 138–140°C. IR spectrum, ν, cm^{-1}: 1465, 1595, 1630 sh, 1645 br, 1710. ^1H NMR spectrum (CF_3CO_2D), δ, ppm: 3.62 s (2H, C_6H_4C**H**$_2$), 4.77 s (2H, 5-H), 6.96 d (1H, H_{arom}, ^3J = 8.5 Hz), 6.99 t (1H, H_{arom}, ^3J = 7.5 Hz), 7.19 br.t (1H, H_{arom}, ^3J = 7.0 Hz), 7.27 br.d (1H, H_{arom}, ^3J = 6.0 Hz). ^{13}C NMR spectrum (CF_3CO_2D), δ_C, ppm: 23.04 (CH_2), 70.85 (C^5), 103.95 (C_{quat}), 118.11 (CH_{arom}), 125.13 (CH_{arom}), 126.81 (C_{quat}), 130.82 (CH_{arom}), 132.78 (CH_{arom}), 153.24 (C_{quat}), 179.61 (C=O), 184.33 (C=O). Found, %: C 63.99; H 5.08. $C_{11}H_{10}O_4$. Calculated, %: C 64.07; H 4.89.

3-(2-Methoxybenzyl)tetrahydrofuran-2,4-dione (IIc). Yield 53 (*a*), 90% (*b*); mp 150–153°C. IR spectrum, ν, cm^{-1}: 1500, 1605 br, 1665 br, 1725. ^1H NMR spectrum (CF_3CO_2D), δ, ppm: 3.60 s (2H, $C_6H_4C\mathbf{H}_2$), 4.10 s (3H, OCH_3), 4.75 s (2H, 5-H), 7.04 t (1H, H_{arom}, ^3J = 7.5 Hz), 7.10 d (1H, H_{arom}, ^3J = 8.5 Hz), 7.28–7.33 m (2H, H_{arom}). ^{13}C NMR spectrum (CF_3CO_2D), δ_C, ppm: 23.06 (CH_2), 58.11 (OCH_3), 70.58 (C^5), 103.75 (C_{quat}), 114.50 (CH_{arom}), 125.30 (CH_{arom}), 128.30 (C_{quat}), 130.90 (CH_{arom}), 132.64 (CH_{arom}), 157.49 (C_{quat}), 180.11 (C=O), 183.99 (C=O). Found, %: C 65.34; H 5.42. $C_{12}H_{12}O_4$. Calculated, %: C 65.45; H 5.49.

3-(2-Hydroxy-5-methoxybenzyl)tetrahydrofuran-2,4-dione (IId). Yield 67 (*a*), 86% (*b*); mp 162–164°C. IR spectrum, ν, cm^{-1}: 1430, 1440, 1470, 1510, 1610 sh, 1645 sh, 1660, 1720. ^1H NMR spectrum (pyridine-d_5), δ, ppm: 3.65 s (3H, OCH_3), 4.03 s (2H, $C_6H_3C\mathbf{H}_2$), 4.77 s (2H, 5-H), 6.81 d.d (1H, 4′-H, ^3J = 8.5, ^4J = 2.0 Hz), 7.09 d (1H, 3′-H, ^3J = 8.5 Hz), 7.28 br.s (1H, 6′-H). ^{13}C NMR spectrum (pyridine-d_5), δ_C, ppm: 22.92 (CH_2), 55.57 (OCH_3), 67.95 (C^5), 98.49 (C_{quat}), 112.38 (CH_{arom}), 116.16 (CH_{arom}), 116.65 (CH_{arom}), 128.25 (C_{quat}), 150.28 (C_{quat}), 153.56 (C_{quat}), 176.56 (C=O), 177.07 (C=O). Found, %: C 60.81; H 5.15. $C_{12}H_{12}O_5$. Calculated, %: C 61.01; H 5.12.

3-(4-Hydroxy-3-methoxybenzyl)tetrahydrofuran-2,4-dione (IIe). Yield 78 (*a*), 90% (*b*); mp 134–136°C. IR spectrum, ν, cm^{-1}: 1415, 1435 sh, 1520, 1610 br, 1665 br, 1720. ^1H NMR spectrum, δ, ppm: in CF_3CO_2D: 3.62 s (2H, $C_6H_3C\mathbf{H}_2$), 3.96 s (3H, OCH_3), 4.86 s (2H, 5-H), 6.82 d (1H, H_{arom}, ^3J = 7.5 Hz), 6.90–7.00 m (2H, H_{arom}); in D_2O [$Me_3Si(CD_2)_2CO_2Na$]: 3.41 s (2H, $C_6H_3C\mathbf{H}_2$), 3.84 s (3H, OCH_3), 4.73 s (2H, 5-H), 6.79 d (1H, 5′-H, ^3J = 8.0 Hz), 6.83 d.d (1H, 6′-H, ^3J = 8.0, ^4J = 1.0 Hz), 6.91 br.s (1H, 2′-H). ^{13}C NMR spectrum, δ_C, ppm: in CF_3CO_2D: 28.07 (CH_2), 57.93 (OCH_3), 70.74 (C^5), 103.46 (C_{quat}), 114.64 (CH_{arom}), 117.25 (CH_{arom}), 123.30 (CH_{arom}), 132.95 (C_{quat}), 144.53 (C_{quat}), 149.09 (C_{quat}), 178.76 (C=O), 183.97 (C=O); in D_2O [$Me_3Si(CD_2)_2CO_2Na$]: 28.72 (CH_2), 58.85 (OCH_3), 70.93 (C^5), 102.53 (C_{quat}), 115.39 (CH_{arom}), 118.47 (CH_{arom}), 123.59 (CH_{arom}), 134.73 (C_{quat}), 146.15 (C_{quat}), 150.35 (C_{quat}), 179.44 (C=O), 182.37 (C=O). Found, %: C 60.96; H 5.06. $C_{12}H_{12}O_5$. Calculated, %: C 61.01; H 5.12.

3-(3,4-Dimethoxybenzyl)tetrahydrofuran-2,4-dione (IIf). Yield 52 (*a*), 60% (*b*); mp 148–150°C. IR spectrum, ν, cm^{-1}: 1520, 1665 br, 1720. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.47 s (2H, $C_6H_3C\mathbf{H}_2$), 3.83 s (6H, OCH_3), 4.59 s (2H, 5-H), 6.76 d (1H, 5′-H, ^3J = 8.0 Hz), 6.81 d.d (1H, 6′-H, ^3J = 8.0, ^4J = 2.0 Hz), 6.83 d (1H, 2′-H, ^4J = 2.0 Hz), 10.35 br.s (1H, OH, enol). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 26.83 (CH_2), 55.84 (OCH_3), 55.91 (OCH_3), 67.80 (C^5), 100.99 (C_{quat}), 111.27 (CH_{arom}), 111.97 (CH_{arom}), 120.34 (CH_{arom}), 131.05 (C_{quat}), 147.63 (C_{quat}), 148.89 (C_{quat}), 174.50 (C=O), 178.25 (C=O). Found, %: C 62.72; H 5.57. $C_{13}H_{14}O_5$. Calculated, %: C 62.39; H 5.64.

3-(4-Fluorobenzyl)tetrahydrofuran-2,4-dione (IIg). Yield 87 (*a*), 95% (*b*); mp 174–176°C. IR spectrum, ν, cm^{-1}: 1520, 1605 br, 1645 br.sh, 1710 sh. ^1H NMR spectrum (pyridine-d_5), δ, ppm: 3.74 s (2H, $C_6H_4C\mathbf{H}_2$), 4.76 s (2H, 5-H), 7.05 t (2H, 3′-H, 5′-H, $^3J_{HH} \approx {}^3J_{HF}$ = 9.0 Hz), 7.47 d.d (2H, 2′-H, 6′-H, $^3J_{HH}$ = 9.0, $^4J_{HF}$ = 6.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: in pyridine-d_5: 27.24 (CH_2), 67.75 (C^5), 98.76 (C_{quat}), 115.20 and 115.37 ($C^{3'}$, $C^{5'}$), 130.46 and 130.52 ($C^{2'}$, $C^{6'}$), 136.78 (C_{quat}), 160.76 and 162.69 ($C^{4'}$), 176.17 (C=O); in CD_3CO_2D: 27.64 (CH_2), 70.73 (C^5), 103.58 (C_{quat}), 117.43 and 117.61 ($C^{3'}$, $C^{5'}$), 131.50 and 131.57 ($C^{2'}$, $C^{6'}$), 134.28 (C_{quat}), 163.37 and 165.31 (C–F), 178.76 (C=O), 183.98 (C=O). Found, %: C 63.82; H 4.29. $C_{11}H_9FO_3$. Calculated, %: C 63.46; H 4.36.

3-(4-Nitrobenzyl)tetrahydrofuran-2,4-dione (IIh). Yield 98 (*a*), 73% (*b*); mp 224–226°C (decomp.). IR spectrum, ν, cm^{-1}: 1515, 1600, 1620–1660 br, 1720. ^1H NMR spectrum (pyridine-d_5), δ, ppm: 3.82 s (2H, $C_6H_4C\mathbf{H}_2$), 4.84 s (2H, 5-H), 7.57 d (2H, H_{arom}, ^3J = 8.5 Hz), 8.11 d (2H, H_{arom}, ^3J = 8.5 Hz). ^{13}C NMR spectrum (pyridine-d_5), δ_C, ppm: 27.98 (CH_2), 67.97 (C^5), 97.36 (C_{quat}), 123.79 (2C, CH_{arom}), 129.73 (2C, CH_{arom}), 146.70 (C_{quat}), 148.79 (C_{quat}), 176.08 (C=O), 177.10 (C=O). Found, %: C 56.10; H 3.82. $C_{11}H_9NO_5$. Calculated, %: C 56.17; H 3.86.

3-(2-Thienylmethyl)tetrahydrofuran-2,4-dione (IVa). Yield 82% (*b*), mp 137–139°C. IR spectrum, ν, cm^{-1}: 1400, 1415 sh, 1450, 1545 sh, 1600, 1605–1680 br, 1710 sh. ^1H NMR spectrum (CD_3CO_2D), δ, ppm: 3.71 s (2H, $C_4H_3SC\mathbf{H}_2$), 4.70 s (2H, 5-H), 6.85–6.87 m (2H, thiophene), 7.11 br.d (1H, thiophene, ^3J = 5.0 Hz). ^{13}C NMR spectrum (CD_3CO_2D), δ_C, ppm: 21.84 (CH_2), 68.48 (C^5), 101.14 (C_{quat}), 124.56 (CH, thiophene), 125.91 (CH, thiophene), 127.71 (CH, thiophene), 142.43 (C_{quat}), 175.61 (C=O), 178.40 (C=O). Found, %: C 55.20; H 4.01. $C_9H_8O_3S$. Calculated, %: C 55.09; H 4.11.

3-(Tetrahydrothiophen-2-ylmethyl)tetrahydrofuran-2,4-dione (IVb). Yield 37–40% (*a*, 6 days), mp 94–95°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 1400 br, 1440, 1555 sh, 1605 br, 1635 br.sh,

1715. ^{1}H NMR spectrum (CD_3CO_2D), δ, ppm: 1.67 sext (1H, thiophene, J = 6.5 Hz), 1.87–1.95 m (1H, thiophene), 1.99 sext (1H, thiophene, J = 6.0 Hz), 2.07 sext (1H, thiophene, J = 6.0 Hz), 2.46 d (2H, $C_4H_7SC\mathbf{H}_2$, J = 7.5 Hz), 2.76–2.81 m (1H, thiophene), 2.86–2.91 m (1H, thiophene), 3.62 quint (1H, CHS, J = 7.0 Hz), 4.68 s (2H, 5-H). ^{13}C NMR spectrum (CD_3CO_2D), δ_C, ppm: 29.70 (CH_2), 30.81 (CH_2), 32.93 (CH_2), 37.28 (CH_2), 48.11 (CH), 68.42 (C^5), 100.71 (C_{quat}), 176.01 (C=O), 179.02 (C=O). Found, %: C 53.52; H 6.15. $C_9H_{12}O_3S$. Calculated, %: C 53.98; H 6.04.

3-[(*E*)-3-(4-Fluorophenyl)prop-2-en-1-yl]tetrahydrofuran-2,4-dione (VIb). Yield 80% (*b*), mp 156–158°C. IR spectrum, ν, cm^{-1}: 1450, 1550 sh, 1580–1665 br, 1715. ^{1}H NMR spectrum (pyridine-d_5), δ, ppm: 3.35 d (2H, 3-CH_2, ^3J = 6.0 Hz), 4.80 s (2H, 5-H), 6.46 d.t (1H, $CH_2C\mathbf{H}$=CH, ^3J = 16.0, 6.0 Hz), 6.57 d (1H, CH_2CH=C**H**, $^3J_{trans}$ = 16.0 Hz), 7.06 t (2H, 3′-H, 5′-H, $^3J_{HH} \approx {}^3J_{HF}$ = 8.5 Hz), 7.32 d.d (2H, 2′-H, 6′-H, $^3J_{HH}$ = 8.5, $^4J_{HF}$ = 5.5 Hz). ^{13}C NMR spectrum (pyridine-d_5), δ_C, ppm: 25.64 (CH_2), 67.71 (C^5), 97.67 (C_{quat}), 115.54 and 115.71 ($C^{3'}$, $C^{5'}$), 127.62 (CH=), 128.12 and 128.18 ($C^{2'}$, $C^{6'}$), 129.44 (CH=), 134.47 (C_{quat}), 161.29 and 163.23 (C–F), 175.58 (C=O), 176.03 (C=O). Found, %: C 66.41; H 4.68. $C_{13}H_{11}FO_3$. Calculated, %: C 66.66; H 4.73.

3-[(*E*)-3-(4-Nitrophenyl)prop-2-en-1-yl]tetrahydrofuran-2,4-dione (VIc). Yield 73 (*a*), 83% (*b*); mp 178–181°C. IR spectrum, ν, cm^{-1}: 1400, 1445, 1525, 1595, 1655 br, 1720. ^{1}H NMR spectrum (pyridine-d_5), δ, ppm: 3.38 d (2H, 3-CH_2, ^3J = 6.0 Hz), 4.83 s (2H, 5-H), 6.62 d (1H, CH_2CH=C**H**, $^3J_{trans}$ = 16.0 Hz), 6.71 d.t (1H, $CH_2C\mathbf{H}$=CH, ^3J = 16.0, 6.0 Hz), 7.43 d (2H, H_{arom}, ^3J = 8.5 Hz), 8.15 d (2H, H_{arom}, ^3J = 8.5 Hz). ^{13}C NMR spectrum (pyridine-d_5), δ_C, ppm: 25.85 (CH_2), 67.73 (C^5), 97.09 (C_{quat}), 124.19 (2C, CH_{arom}), 127.02 (2C, CH_{arom}), 128.96 (CH=), 133.17 (CH=), 144.59 (C_{quat}), 146.83 (C_{quat}), 175.80 (2C, C=O). Found, %: C 59.74; H 4.33. $C_{13}H_{11}NO_5$. Calculated, %: C 59.77; H 4.24.

3-[(*E*)-3-(4-Chlorophenyl)prop-2-en-1-yl]tetrahydrofuran-2,4-dione (VId). Yield 71% (*b*), mp 135–137°C. IR spectrum, ν, cm^{-1}: 1490, 1550 sh, 1645 br, 1715. ^{1}H NMR spectrum (CD_3CO_2D), δ, ppm: 3.10 d (2H, 3-CH_2, ^3J = 6.5 Hz), 4.71 s (2H, 5-H), 6.26 d.t (1H, $CH_2C\mathbf{H}$=CH, ^3J = 15.5, 6.5 Hz), 6.42 d (1H, CH_2CH=C**H**, $^3J_{trans}$ = 15.5 Hz), 7.25 d (2H, H_{arom}, ^3J = 8.5 Hz), 7.31 d (2H, H_{arom}, ^3J = 8.5 Hz). ^{13}C NMR spectrum (CD_3CO_2D), δ_C, ppm: 25.17 (CH_2), 68.56 (C^5), 99.97 (C_{quat}), 127.79 (CH=), 128.45 (2C, CH_{arom}), 129.51 (2C, CH_{arom}), 130.59 (CH=), 133.41 (C_{quat}), 137.23 (C_{quat}), 175.62 (C=O), 178.84 (C=O). Found, %: C 62.38; H 4.39. $C_{13}H_{11}ClO_3$. Calculated, %: C 62.29; H 4.42.

3-[3-(4-Fluorophenyl)propyl]tetrahydrofuran-2,4-dione (VIIb). Yield 37% (*a*), mp 104–107°C. IR spectrum, ν, cm^{-1}: 1515, 1590–1670 br, 1720. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.79 quint (2H, $CH_2C\mathbf{H}_2$-CH_2, ^3J = 7.5 Hz), 2.24 t (2H, 3-CH_2, ^3J = 7.5 Hz), 2.58 t (2H, $C_6H_4C\mathbf{H}_2$, ^3J = 7.5 Hz), 4.64 s (2H, 5-H), 6.92 t (2H, 3′-H, 5′-H, $^3J_{HH} \approx {}^3J_{HF}$ = 8.5 Hz), 7.10 d.d (2H, 2′-H, 6′-H, $^3J_{HH}$ = 8.5, $^4J_{HF}$ = 6.0 Hz), 10.65 br.s (1H, OH, enol). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 20.77 (CH_2), 29.42 (CH_2), 34.71 (CH_2), 67.78 (C^5), 100.94 (C_{quat}), 114.88 and 115.05 ($C^{3'}$, $C^{5'}$), 129.64 and 129.70 ($C^{2'}$, $C^{6'}$), 137.60 (C_{quat}), 160.23 and 162.17 (C–F), 174.42 (C=O), 174.63 (C=O). Found, %: C 65.89; H 5.58. $C_{13}H_{13}FO_3$. Calculated, %: C 66.09; H 5.55.

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