Supplementary Material Available: Tables of atomic positional parameters, bond lengths, and bond angles for 1 (3 pages). Ordering information is given on any current masthead page.

On the Synthesis of 4-Alkoxy-2(5*H*)-furanones

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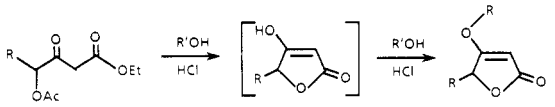
Enol ethers of β-tetronic acid represent useful synthons for the synthesis of natural products derived from β-tetronic acid (4-hydroxy-2(5*H*)-furanone, **1**).[2] As a continuation of our interest in the chemistry of **1**[3a–c] we became interested in finding a simple and convenient method for the preparation of alkyl ethers of **1**.

There exists a sizeable literature on the synthesis of these compounds. Virtually all of such reports, however, are restricted to methyl and ethyl ethers of **1** formed by using a number of different alkylating agents.[4–10]

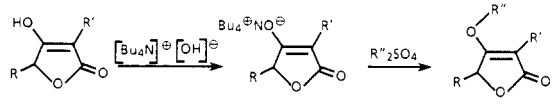
Recently, a novel route to these compounds was introduced by Gelin,[11] reporting that the desired compounds could be obtained by lactonization of γ-acetoxy-β-keto esters in the presence of 1% hydrochloric acid in methanol or ethanol (eq 1).



(1)

The benzyl ether was obtained more conveniently by refluxing **1** in benzene in the presence of benzyl alcohol and a catalytic amount of *p*-toluenesulfonic acid.[11] Boll and co-workers questioned these results.[12] They reported difficulties in repeating the procedures of the French group.[11] They also doubted the structural assignments and stated that isomeric 2-alkoxy-4(5*H*)-furanones could have been formed as well under the cited reaction condition.

Boll et al.[12] showed that 4-methoxy- and 4-ethoxy-2(5*H*)-furanones could be obtained reproducibly by stirring tetrabutylammonium tetronate with dimethyl or diethyl sulfate for 1 or 10 h, respectively (eq 2). For the preparation of 4-*O*-methyl-**1**, a second method was given. It could be obtained by alkylating **1** directly with trimethyloxonium tetrafluoroborate.



(2)

(1) On leave from Faculty of Science, Alexandria University, Egypt.
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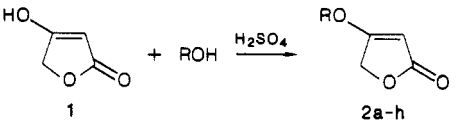
Table I. 4-Alkoxy-2(5*H*)-furanones 2 from 1



1 2a-h

no.	R	yield,[a] %
2a	methyl	44
2b	ethyl	56
2c	*n*-propyl	56
2d	1-methyleth-1-yl	65
2e	*n*-hexyl	55
2f	2,2-dimethylprop-1-yl	22
2g	cyclopentyl	40
2h	benzyl	11

[a] Yields which are not optimized are based on the molar amount of tetronic acid charged to the reaction.

Immediately after the appearance of this paper,[12] Gelin and Pollet reconfirmed the results of their initial publication.[13] By a slightly changed procedure, they reported the syntheses of 4-*O*-methyl-**1** and 4-*O*-ethyl-**1** by refluxing a solution of **1** with acetyl chloride in excess methanol or ethanol, respectively. For the preparation of *O*-benzyl-**1** a different method, namely, heating benzyl alcohol with **1** in the presence of *p*-toluenesulfonic acid, was reported. Moreover, in this paper no procedures involving 2°, 3°, or alicyclic alcohols were given. An attempt by us to use the modified Fischer Method (as these authors call it) for the preparation of a long-chain alkyl ether of **1** was unsatisfactory.

The alkylation procedure of Boll[12] employs tetrabutylammonium tetronate and a dialkyl sulfate as an alkylating agent. Thus, since only dimethyl and diethyl sulfates are readily available, this method is not a general one. The procedure for obtaining 4-alkoxy-2(5*H*)-furanones introduced by Gelin depends on ethyl 4-acetoxy-3-keto esters as starting materials; these compounds again are not readily available. Lastly, the most simple preparation for 4-methoxy-2(5*H*)-furanones, namely, the reaction of **1** with diazomethane, due to the unavailability of higher diazoalkanes as convenient starting materials, is of very limited use for the synthesis of analogues of the 4-methyl ether of **1**.

Due to the above-cited ambiguities, the restrictions, and the cumbersome nature of these and the older methods, we concluded an improved synthesis method was needed. We decided to develop a simple way to prepare the desired 4-*O*-alkyl-**1** compounds that would be versatile enough to synthesize a wide range of different 4-alkoxy derivatives of **1**, not only just its methyl or ethyl ethers.

Results and Discussion

We found that **1** reacts with alcohols in concentrated H_2SO_4 medium in different ways depending on the nature of the alcohol. Thus, 1° or 2° alcohols reacted smoothly with **1** to give the desired 4-alkoxy-2(5*H*)-furanones **2a–h** in yields up to 65% (isolated but not optimized) (Table I). In the case of 3° alcohols, **3a–c**, the reaction products were the isomeric C-alkylated 3-alkyl-4-hydroxy-2(5*H*)-furanones **4a–c**, and not the O-alkylated **1**.

From an analysis of the reaction mixtures by TLC, GC-MS, and ^1H NMR spectroscopy, it became evident that a competing reaction, namely, polymerization of these alcohols by the action of concentrated H_2SO_4, took place.[14–18] The ratio of the rate of polymerization to the

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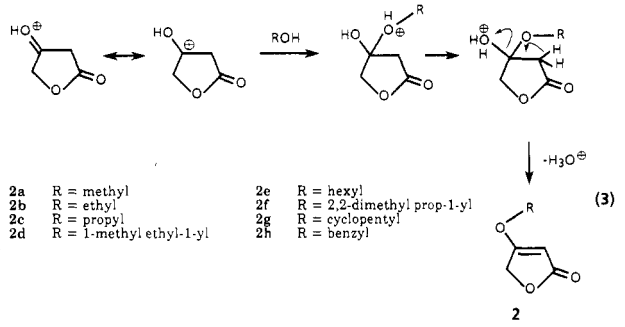
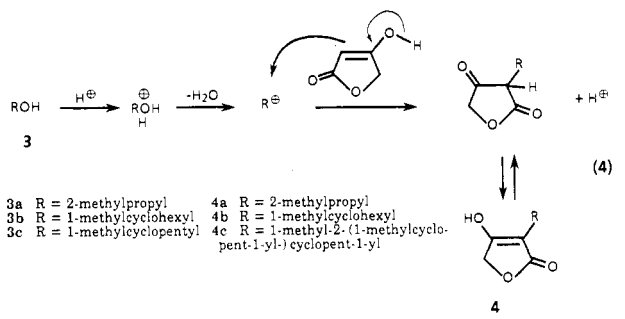
rate of alkylation apparently is dependent on the nature of the alcohol, thus the ratio of polymerization product to alkylation in the case of benzyl alcohol is very high, in favor of polymerization product and responsible for the low yield of **2h**.[14] A plausible explanation of the formation of type-**2** compounds in case of 1° and 2° alcohols is to assume that it proceeds under acidic conditions by the attack of the alcohol oxygen atom of C-4 of **1**. This is followed by proton transfer and elimination of water to give type-**2** compounds (eq 3). When a 3° alcohol (**3a–c**) is employed in this

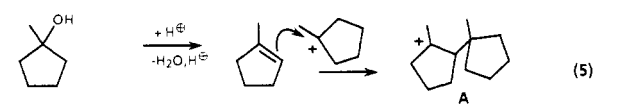


reaction, the more stable 3° carbocation is formed and is attacked by the enolic form of **1** to afford type-**4** compounds (eq 4). While alcohols **3a** and **3b** react with **1** in



their initial carbocationic forms, **3c** dehydrates and reacts first with its initially formed carbocation to make a dimeric carbocation which subsequently is attacked by **1** to form **4c**.

The structure of **4c**, as a 3-[1-methyl-2-(1-methylcyclopent-1-yl)cyclopent-1-yl]-4-hydroxy-2(5*H*)-furanone was determined by elemental analysis and a detailed ^{1}H NMR and MS analysis. The latter showed the molecular ion peak at *m/e* (relative intensity) 264.1722 (M^+, $(C_{16}H_{24}O_3)^+$, 5.5) and the base peak at *m/e* 164.1529 $(C_{12}H_{20})^+$. The carbocation A involved in this reaction could be easily formed by the attack of 1-methylcyclopentene (formed in situ) on the 1-methylcyclopentenium ion in the medium (eq 5).



The proposed mechanism is based on the structure of the reaction products and also on the fact that no rearrangements of the carbon skeleton were observed when 1° or 2° alcohols were used. A rearrangement would be indicative for an intermediate carbocation formation. Thus, *n*-propyl or neopentyl alcohol gave rise to formation of only the unrearranged alkoxy ether; no ^{1}H NMR evidence for *O*-(1-methyleth-1-yl)-**1** or *O*-(2-methylbut-2-yl)-**1** was detected. However, when a 3° alcohol was employed, the rather stable carbocation was formed and reacted with the enolic tautomer of **1** to give the 3-*O*-alkyl-**1** compounds.

Experimental Section

IR spectra were obtained on a Perkin-Elmer Model 599 spectrometer and were calibrated against the 1601 cm^{-1} band of polystyrene. ^{1}H NMR spectra were recorded on an IBM NR-80 spectrometer. Chemical shifts are reported on the δ scale in parts per million downfield from internal tetramethylsilane (Me_4Si) and apparent coupling constants (*J*) are given in hertz (Hz). A Hewlett-Packard 5995 gas chromatograph/mass spectrometer was used to record MS data at 70 eV. Melting points were determined on a Mel-Temp melting point apparatus and are uncorrected. Analytical TLC was performed by using the ascending technique with EM silica gel 60 F_{254} precoated on plastic sheets. Column chromatography was done with EM silica gel 60 (0.040 = 0.063 mm). Microanalyses were performed by M-H-W Laboratories, Phoenix, AZ.

Preparation of 4-Alkoxy-2(5*H*)-furanone 2. General Method. To a solution of 5 mmol of tetronic acid (**1**) in 1.5 mL of the appropriate alcohol was added dropwise 1 mL of concentrated sulfuric acid. After being stirred for 2 h at room temperature, the reaction mixture was diluted with 10 mL water and extracted three times with 10 mL ether. The combined ether layers were dried over anhydrous $MgSO_4$. The solvent was distilled off and the product was isolated by column chromatography using ether as an eluent.

4-Methoxy-2(5*H*)-furanone (2a): from **1** and methanol, yield 44%; mp 66 °C (lit.[11] mp 63 °C); ^{1}H NMR ($CDCl_3$) δ 3.91 (s, 3 H, CH_3), 4.63 (d, 2 H, OCH_2, $J_{3,5}$ = 1 Hz), 5.11 (t, 1 H, =CH, $J_{3,5} \simeq$ 1 Hz); IR (KBr) 3110, 1780, 1740, 1630 cm^{-1}.

4-Ethoxy-2(5*H*)-furanone (2b): from **1** and ethanol, yield 56%; faint yellow liquid; ^{1}H NMR ($CDCl_3$) δ 1.45 (t, 3 H, CH_3, J = 7 Hz), 4.15 (q, 2 H, CH_2, J = 7 Hz), 4.68 d, 2 H, OCH_2, $J_{3,5} \simeq$ 1 Hz), 5.12 (t, 1 H, =CH, $J_{3,5} \simeq$ 1 Hz); IR (neat) 3110, 2980, 1775, 1740, 1620 cm^{-1}. Anal. Calcd for $C_6H_8O_3$: C, 56.24; H, 6.29. Found: C, 55.98; H, 6.30.

4-Propoxy-2(5*H*)-furanone (2c): from **1** and 1-propanol, yield 56%; bright yellow liquid, ^{1}H NMR ($CDCl_3$) δ 1.1 (t, 3 H, CH_3, J = 6 Hz), 1.77 (m, 2 H, CH_2), 4.0 (t, 2 H, CH_2O, J = 6 Hz), 4.63 (d, 2 H, OCH_2, $J_{3,5}$ = 1 Hz), 5.06 (t, 1 H, =CH, $J_{3,5}$ = 1 Hz); IR (neat) 3120, 2960, 1760, 1620 cm^{-1}; MS, *m/e* (relative intensity) 142 (M^+, 27), 43 ($C_3H_7^+$, 100). Anal. Calcd for $C_7H_{10}O_3$: C, 59.14; H, 7.09. Found: C, 58.96; H, 7.30.

4-(1-Methyleth-1-oxy)-2(5*H*)-furanone (2d): from **1** and 2-propanol, yield 65%; mp 43 °C; ^{1}H NMR ($CDCl_3$) δ 1.40 (d, 6 H, 2 CH_3, J = 4.8 Hz), 4.46 (m, 1 H, CH), 4.60 (d, 2 H, CH_2O, $J_{3,5} \simeq$ 1 Hz), 5.04 (t, 1 H, =CH, $J_{3,5} \simeq$ 1 Hz); IR (KBr) 3120, 2990, 1760, 1620 cm^{-1}. Anal. Calcd for $C_7H_{10}O_3$: C, 59.14; H, 7.09. Found: C, 58.91; H, 7.31.

4-Hexoxy-2(5*H*)-furanone (2e): from **1** and 1-hexanol, yield 55%; faint yellow liquid; ^{1}H NMR ($CDCl_3$) δ 0.7–2.0 (m, 11 H, aliphatic H); 4.02 (t, 2 H, CH_2, J = 6 Hz), 4.61 (d, 2 H, CH_2O, $J_{3,5} \simeq$ 1 Hz), 5.06 (t, 1 H, =CH, $J_{3,5} \simeq$ 1 Hz); IR (neat) 3110, 2930, 1775, 1745, 1620 cm^{-1}. Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 64.96; H, 8.87.

4-(2,2-Dimethylprop-1-oxy)-2(5*H*)-furanone (2f): from **1** and 2,2-dimethylpropanol, yield 22%; mp 72 °C (*n*-hexane); ^{1}H NMR ($CDCl_3$) δ 1.0 (s, 9 H, 3 CH_3), 3.65 (s, 2 H, CH_2), 4.65 (d, 2 H, CH_2O, $J_{3,5} \simeq$ 1 Hz), 5.03 (t, 1 H, =CH, $J \simeq$ 1 Hz); IR (KBr) 2950, 1770, 1730, 1610 cm^{-1}. Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.41; H, 8.32.

4-Cyclopentoxy-2(5*H*)-furanone (2g): from **1** and cyclopentanol, yield 40%; mp 83 °C (ether/petroleum ether); ^{1}H NMR ($CDCl_3$) δ 1.5–2.1 (m, 8 H, $(CH_2)_4$), 4.60 (d, 2 H, CH_2O, $J \simeq$ 1 Hz), 4.71 (m, 1 H, OCH), 5.05 (t, 1 H =CH, J = 1 Hz); IR (KBr) 3110, 2980, 1750, 1610 cm^{-1}. Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.13; H, 7.39.

4-(Benzyloxy)-2(5*H*)-furanone (2h): from **1** and benzyl alcohol, yield 11%; mp 111 °C (lit.[10] mp 104 °C); ^{1}H NMR ($CDCl_3$) δ 4.66 (d, 2 H, CH_2O, $J_{3,5} \simeq$ 1 Hz), 5.07 (s, 2 H, OCH_2 Ar); 5.18

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(t, 1 H, =CH, $J \simeq 1$ Hz), 7.39 (s, 5 H, Ar H); IR (KBr) 3110, 2950, 1780, 1740, 1620 cm^{-1}. Anal. Calcd for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30. Found: C, 69.61; H, 5.53.

Preparation of 3-Alkyl-4-hydroxy-2(5*H*)-furanone (4). General Method. To a well-stirred equimolar amount of 1 and alcohol 3 was added 1 mL of concentrated H_2SO_4. The mixture was allowed to stir at 35–40 °C for 3 h and then diluted with water and extracted with ether. The organic layer was dried over anhydrous $MgSO_4$. The solvent was removed by distillation and the product was isolated by column chromatography using ether as an eluent.

3-(1,1-Dimethyleth-1-yl)-4-hydroxy-2(5*H*)-furanone (4a): from 1 and 2-methyl-2-propanol, yield 80%; mp 186 °C; ^1H NMR (Me_2SO-d_6) δ 1.16 (s, 9 H, 3 CH_3), 4.43 (s, 2 H, OCH_2), 11.3 (br s, 1 H, OH); IR (KBr) 1700 cm^{-1}; MS, *m/e* (relative intensity) 156 (M^+, 4), 101 ($M^+ - R + 1$, 100). Anal. Calcd for $C_8H_{12}O_3$: C, 61.53; H, 7.75. Found: C, 61.59; H, 7.81.

3-(1-Methylcyclohex-1-yl)-4-hydroxy-2(5*H*)-furanone (4b): from 1 and 1-methylcyclohexanol, yield 25.5%; mp 190–191 °C; ^1H NMR (Me_2SO-d_6) δ 0.9–1.8 (m, 13 H, aliphatic H), 4.5 (s, 2 H, OCH_2), 11.4 (br s, 1 H, OH); IR (KBr) 2920, 1692 cm^{-1}; MS, *m/e* (relative intensity) 196 (M^+, 1), 101 ($M^+ - R + 1$, 100), 96 (31), 95 (12). Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.80; H, 8.16.

3-[1-Methyl-2-(1-methylcyclopent-1-yl)cyclopent-1-yl]-4-hydroxy-2(5*H*)-furanone (4c): from 1 and 1-methylcyclopentanol, yield 17% based on the alcohol charged to the reaction); mp 199 °C, ^1H NMR (Me_2SO-d_6) δ 0.6–2.3 (m, 22 H, aliphatic H), 4.47 (s, 2 H, OCH_2), 11.34 (br s, 1 H, OH); IR (KBr) 2920, 1705 cm^{-1}; MS, *m/e* (relative intensity) 264 (M^+, 8.5), 164 (100). Anal. Calcd for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15. Found: C, 72.53; H, 9.08.

Improved Synthesis of *N*-Benzyl-5-ethyl-1,2,3,4-tetrahydropyridine

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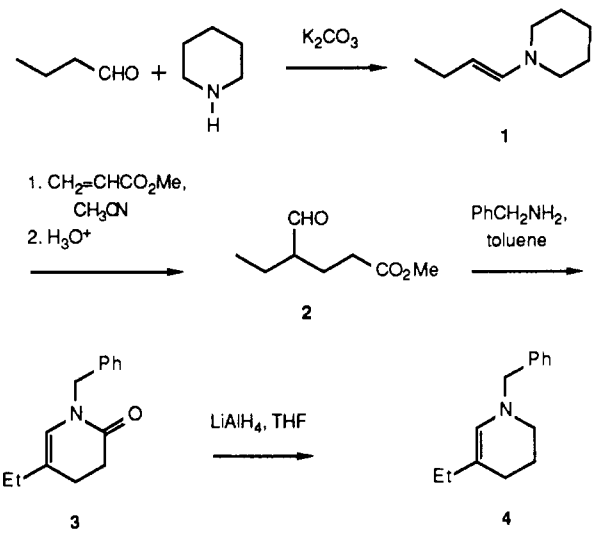
The title compound (4) is a useful synthon for the elaboration of indole alkaloids.[1] To date, the most convenient synthesis of 4 appears to be that of Ziegler and coworkers.[1b,c] In this synthesis, 4 is prepared from butanal in a seven-step route that proceeds in 31% overall yield. In this paper, we report an improved synthesis which delivers enamine 4 in only four steps in an overall yield of 80%.

The synthesis of enamine 4 is summarized in Scheme I. The piperidine enamine of butanal (1) is prepared in 81% yield by the reaction of the aldehyde with 2.4 equiv of piperidine in the presence of anhydrous potassium carbonate.[2] Aldehyde ester 2 is obtained in 65% yield by the Michael addition of enamine 1 to methyl acrylate in acetonitrile.[2b] Nitrogen is introduced by condensation of 2 with benzylamine to provide unsaturated lactam 3. This reaction proceeds cleanly by distilling and draining off the toluene–water and toluene–methanol azeotropes; unsaturated lactam 3 is obtained in a 96% yield. Reduction of 3 with 5 equiv of lithium aluminum hydride in tetrahydrofuran at room temperature for 24 h affords enamine 4 in 89% yield after distillation. Each of the reactions in this sequence proceeds sufficiently cleanly that the four-step sequence can be carried out without purification of intermediates. When the crude intermediates are carried on in this manner, endocyclic enamine 4 is obtained in 80% overall yield.

Scheme I



Experimental Section

1-(*N*-Piperidinyl)-1-butene (1). Piperidine (25.0 g, 29.0 mL, 0.294 mol) and anhydrous K_2CO_3 (6.00 g, 0.0434 mol) were added to a 100-mL round-bottomed flask equipped with a magnetic stirring bar. The mixture was placed under nitrogen and cooled to 0 °C with an ice bath. Butanal (9.00 g, 11.0 mL, 0.125 mol) was added over a 1-h period with a syringe pump. The reaction mixture was stirred for an additional 2 h at 0 °C. The solids were filtered and washed with ether. The solvent was removed with a rotary evaporator, and the resulting crude product was purified by distillation under reduced pressure to give 14.0 g (81%) of 1 as a colorless liquid: bp 35–36 °C (1.0 Torr) [lit.[2a] bp 70–71 °C (10 Torr)]; IR (film) 1665 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.96 (t, 3, J = 7.4), 1.55 (m, 6), 1.98 (ddq, 2, J = 7.4, 6.8, 1.0), 2.73 (t, 4, J = 5.3), 4.42 (dt, 1, J = 13.9, 6.8), 5.83 (d, 1, J = 13.9); ^{13}C NMR ($CDCl_3$) δ 15.81, 23.69, 24.34, 25.43, 50.08, 103.24, 139.51. Anal. Calcd for $C_9H_{17}N$: C, 77.63; H, 12.31; N, 10.06. Found: C, 77.38; H, 12.52; N, 10.01.

Methyl 4-Formylhexanoate (2). A 250-mL round-bottomed flask equipped with a magnetic stirring bar was charged with a solution of 7.00 g (50.0 mmol) of enamine 1 in 35 mL of dry acetonitrile. The solution was cooled below 5 °C with an ice–salt bath. A solution of methyl acrylate (5.66 mL, 5.41 g, 63.0 mmol, 1.25 equiv) in acetonitrile (15.0 mL) was added with stirring to the reaction mixture over a 0.5-h period with a syringe pump. The reaction mixture was allowed to warm to room temperature and stirred for 8 h. A reflux condenser was attached, and the solution was heated at reflux for 36 h. Acetic acid (3.0 mL) and distilled water (20.0 mL) were added, and the resulting solution was heated at reflux for 8 h. The mixture was allowed to cool to room temperature, the aqueous phase was saturated with NaCl, and the solution was extracted with ether. The organic extract was washed with 5% HCl, 5% $NaHCO_3$, and saturated aqueous NaCl. The ether layer was dried over $MgSO_4$, filtered, and reduced in volume with a rotary evaporator to give 5.80 g of crude product. The material was purified by distillation under reduced pressure to give 5.14 g (65%) of 2 as a colorless liquid, bp 42–48 °C (0.22–0.12 Torr) [lit.[2b] bp 95–98 °C (10 Torr)]; IR (film) 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.95 (t, 3, J = 7.5), 1.49–1.86 (m, 3), 1.96 (m, 1), 2.32 (m, 3), 3.67 (s, 3), 9.60 (d, 1, J = 2.4); ^{13}C NMR ($CDCl_3$)

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