crystalline material, mp 56-57 °C (lit.[5d] mp 58 °C): $R_f$ 0.27 (chloroform-methanol-NH$_4$OH, 85:15:1); IR (CHCl$_3$) 3200, 2990, 2940, 2860, 2810, 2760, 2680, 1470, 1445, 1400, 1350, 1330, 1290, 1270, 1255, 1215, 1185, 1150, 1130, 1105, 1085, 1065, 1050, 1005, 935, 885, 865, 850 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 5.40 (br s, 1 H), 4.16 (dd, 1 H, $J$ = 10.1, 4.3 Hz), 3.69 (d, 1 H, $J$ = 10.1 Hz), 2.82 (m, 2 H), 1.2-2.3 (m, 14 H); high-resolution MS calcd for C$_{10}$H$_{19}$NO (M$^+$) *m/e* 169.1467, found *m/e* 169.1463.

**Acknowledgment.** This investigation was supported by a grant from the National Science Foundation.

**Registry No.** (±)-**1**, 23365-39-1; (±)-**2**, 23365-52-8; (±)-**3**, 10248-30-3; (±)-**4**, 486-72-6; **5**, 87101-68-6; (5*E*)-**6**, 114652-03-8; (5*Z*)-**6**, 114652-04-9; **7**, 114651-97-7; **8**, 114651-98-8; (5*E*)-**9**, 114651-99-9; (5*Z*)-**9**, 114652-00-5; (5*E*)-**10**, 114652-01-6; (5*Z*)-**10**, 114652-02-7; (±)-**11**, 114652-05-0; (*E*)-**12**, 87101-71-1; (*Z*)-**12**, 87101-72-2; (*E*)-**13**, 87101-73-3; (*Z*)-**13**, 87101-74-4; **14**, 114652-06-1; (±)-**17**, 114652-07-2; (±)-**19**, 114652-08-3; (±)-**20**, 114652-09-4; (±)-**21**, 85864-16-0; (C$_6$H$_5$)$_3$P$^+$(CH$_2$)$_4$CO$_2$H Br$^-$, 17814-85-6.

---

# Pseudoesters and Derivatives. 29.[1a] Regioselective Reactions of the 5-(Ethylthio)furan-2(5*H*)-one Anion with Electrophiles

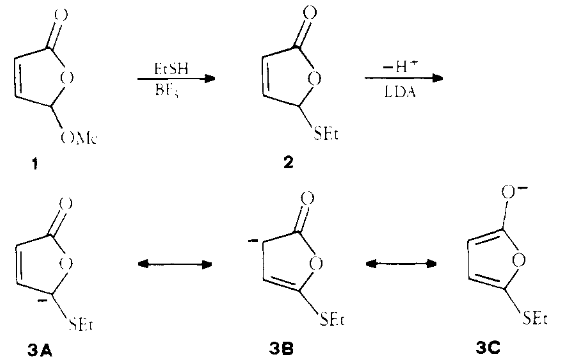
Francisco Fariña*[1b] and M. Dolores Parellada[1c]

*Instituto de Química Orgánica General C.S.I.C., Juan de la Cierva, 3, 28006 Madrid, Spain, and Departamento de Química C-1, Facultad de Ciencias, Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain*

*Received December 17, 1987*

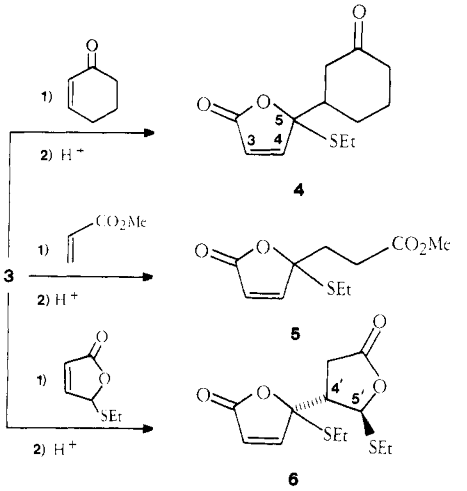
5-(Ethylthio)furan-2(5*H*)-one (**2**) was readily converted to the anion **3** by deprotonation with lithium diisopropylamide, and the reactions of **3** with a variety of electrophilic reagents were examined. The anion **3** reacted with Michael acceptors to afford exclusively the C-5-substituted adducts **4**, **5**, and **6**, while the reaction with equimolar amounts of propionaldehyde gave only the C-3-substituted adduct **9**. Anion **3** by treatment with 2.2 molar equiv of propionaldehyde afforded the 3,5-disubstituted furanone **10**. When the anion **3** was reacted with acetyl chloride or ethyl chloroformate, the electrophilic attack occurred at the carbonyl oxygen atom and the sole product was the 2,5-disubstituted furan **12** or **13**, respectively.

In a previous paper,[2] we reported the formation of 5-(ethylthio)furan-2(5*H*)-one (**2**) by treatment of 5-methoxyfuran-2(5*H*)-one (**1**) with ethanethiol in the presence of a Lewis acid such as boron trifluoride etherate as a catalyst.



We have now found that the furanone **2** is readily converted to its anion **3** by removal of the acidic proton at the 5-position by means of a suitable base such as lithium diisopropylamide (LDA). The anion is a resonance hybrid that can act as a tridentate anion through the canonical forms **3A**, **3B**, and **3C**. According to the predictions of the HSAB principle,[3] the reactive sites of the anion will probably exhibit a different hard-soft character. Thus regioselective reactions occur at either the 3- or 5-position (**3A** or **3B**) as well as at the negatively charged oxygen (**3C**), depending upon the nature of the electrophile used.

**Scheme I**



Earlier studies on the reactions of unsaturated $\delta$-lactones with alkyl halides showed that these preferentially take place at the $\alpha$-position,[4] while Michael acceptors react exclusively at the $\gamma$-position.[5] More recent studies[6] have also indicated that reactions between lithium enolates of furanones and aldehydes afforded a mixture of the $\alpha$- and $\gamma$-adducts, in which the former predominate.

The present paper describes a study of the reactivity of the 5-(ethylthio)furan-2(5*H*)-one anion (**3**) toward several electrophilic species such as Michael acceptors, carbonyl compounds, alkyl halides, and acyl halides. The reactions usually proceed in good yields and with high regioselec-

---

(1) (a) Part 28: Fariña, F.; Jiménez, M. D.; Ortega, R.; Tito, A. *Heterocycles* **1988**, *27*, 173. (b) C.S.I.C. (c) Universidad Autónoma de Madrid.

(2) Fariña, F.; Martín, M. R.; Parellada, M. D. *J. Chem. Res. (S)* **1984**, 250; *J. Chem. Res. (M)* **1984**, 2213.

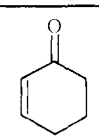
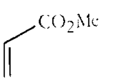
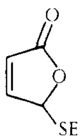
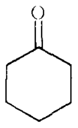
(3) (a) Ho, T. L. *Chem. Rev.* **1975**, *75*, 1. (b) Pearson, R. G. *Hard and Soft Acids and Bases*; Dowden Hutchinson and Ross: Stroudsburg, PA, 1973.

(4) Cederlund, B.; Jesperson, A.; Hörnfeldt, A. B. *Acta. Chem. Scand.* **1971**, *25*, 3656.

(5) Kraus, G. A.; Roth, B. *Tetrahedron Lett.* **1977**, 3129.

(6) Brown, D. W.; Campbell, M. M.; Taylor, A. P.; Zhang, X. *Tetrahedron Lett.* **1987**, *28*, 985.

**Table I. Reactions of Anion 3 with Electrophilic Reagents**

| entry | electrophile (equiv) | base$^a$ | products | ratio$^b$ | yield,$^c$ % |
|---|---|---|---|---|---|
| 1 |  (1.1) | LDA | **4**$^d$ | | 75 |
| 2 | (1.1) | $K_2CO_3$ | **4** + **6** | 2:1 | 50 (**4**), 35 (**6**) |
| 3 |  (1.1) | LDA | **5** + **6** | 3:1 | 55 (**5**), 25 (**6**) |
| 4 | (1.1) | $K_2CO_3$ | **5** + **6** | 1.6:1 | 45 (**5**), 40 (**6**) |
| 5 |  (1.1) | LDA | **6a** + **6b** | 5:1 | 70 |
| 6 | (1.1) | $K_2CO_3$ | **6a** + **6b** | 5:1 | 70 |
| 7 | EtCHO (1.1) | LDA | **9** | | 70 |
| 8 | EtCHO (2.2) | LDA | **10**$^d$ | | 85 |
| 9 |  (1.1) | LDA | **11** + **6** | 1:1 | 55$^e$ |
| 10 | MeCOCl (1.1) | LDA | **12** | | 60 |
| 11 | EtOCOCl (1.1) | LDA | **13** | | 60 |

$^a$Under the conditions described in the Experimental Section. $^b$By NMR. $^c$Isolated yields; nonoptimized. $^d$Mixture of two diastereomers. $^e$Combined yield.

tivity, which appears to be controlled by the nature of the electrophile.

## Results and Discussion

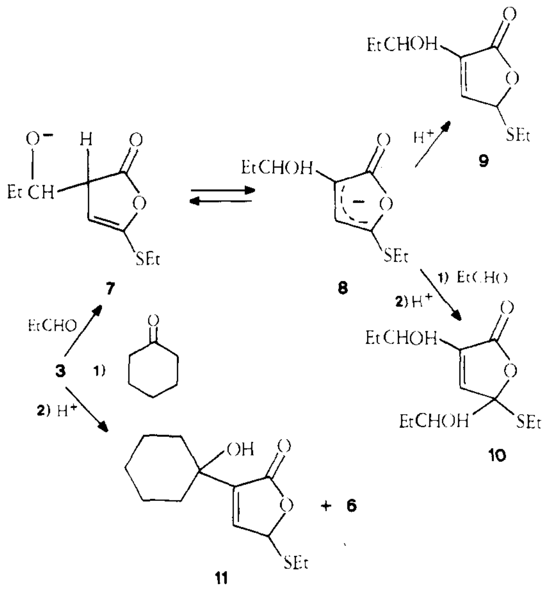
**Reactions with Michael Acceptors.** Reactions of the (ethylthio)furanone anion **3**, generated with LDA at −78 °C in tetrahydrofuran, with different Michael acceptors such as cyclohexenone, methyl acrylate, or the starting (ethylthio)furanone **2** exclusively occur at the 5-position, no reaction being observed at the other positions (Scheme I).

Assignment of structures to the 5-substituted furanones **4**, **5**, and **6** was made on the basis of the $^1$H NMR spectra (Table II). These spectra lacked resonances corresponding to the H-5 acetal-type proton, but contained signals assignable to the H-3 and H-4 olefinic protons, the chemical shifts and coupling constants of which are similar to those of the starting furanone **2**. The $^{13}$C NMR spectra (Table III) confirmed the 5-substitution by the presence of C-5 quaternary carbons at $\delta$ 94.5–97.5.

The results obtained in these reactions are summarized in Table I (entries 1, 3, and 5). The reaction of (ethylthio)furanone **2** with itself (entry 5) afforded the expected Michael adduct **6** in 70% yield as a 5:1 mixture of diastereomers **6a** and **6b**, which could be separated by column chromatography. Both **6a** and **6b** displayed relatively small coupling constants of 4–5 Hz between H-4′ and H-5′ compatible with a trans orientation of these two protons, as would be expected by assuming that attack of anion **3** only occurs from the less hindered face of the furanone.[7] Therefore, **6a** and **6b** must be C-5 epimers, although no further attempts were made to assign the configuration of the individual isomers.

In the reaction of the anion **3** with methyl acrylate (entry 3) the expected Michael adduct **5** was accompanied by minor amounts of the self-condensation product **6**, due to the competitive reaction with the furanone **2**, which acts as an effective Michael acceptor.

**Scheme II**



The regioselectivity observed in these reactions is compatible with the predictions of the HSAB principle. Thus the C-5 site of anion **3** behaves as a soft center and prefers to attack the $\beta$-carbon of the enone, which is a much softer electrophile than the carbonyl carbon.

The above Michael additions have also been carried out with the anion **3** being generated by potassium carbonate in a solid–liquid two-phase system in the presence of a phase-transfer catalyst.[8] The results (Table I, entries 2, 4, and 6) were similar to those obtained by using LDA as a base, although the adducts **4** and **5** were obtained in lower yields. Thus, in the reaction with cyclohexenone, the adduct **4** was accompanied by the self-condensation product **6**, which appears as a byproduct, whereas in the reaction with methyl acrylate the proportion of **6** was increased significantly with respect to adduct **5**.

**Reactions with Carbonyl Compounds.** When the anion **3** was treated with equimolar quantities of propionaldehyde (see Table I, entry 7) followed by protonation of the anionic intermediate **8**, the 3-substituted furanone **9** was obtained in a regiospecific manner and in good yield (Scheme II).

Regiochemical assignment of **9** was made on the basis of the $^1$H and $^{13}$C NMR spectra. Thus, its $^1$H NMR spectrum exhibited a signal at $\delta$ 7.16 corresponding to a single olefinic proton coupled ($J$ = 1.5 Hz) with the H-5 acetal-type proton. This substitution pattern was further supported by the $^{13}$C NMR spectrum, which showed the C-3 as a quaternary carbon at $\delta$ 137.9, while C-4 and C-5 appeared as tertiary carbons at $\delta$ 145.4 and 84.3, respectively.

The regioselectivity of the reaction may be rationalized in terms of the hard nature of the carbonyl group, which favors the initial attack to a center such as the C-3 site of the anion **3**, which is harder than the C-5.

When the reaction of the anion **3** was effected with 2.2 molar equiv of aldehyde, the sole product obtained was **10**, which originated from the reaction with two propionaldehyde molecules at the 3- and 5-positions of the furanone (Scheme II). The reaction presumably involves the initial formation of the 3-substituted anion **7**. Subsequent isomerization of the anion **7** to the carbanionic interme-

---

[7] Fariña, F.; Martín, M. V.; Sánchez, F.; Maestro, M. C.; Martín, M. R. *Heterocycles* **1983**, *20*, 1761.

[8] González, J.; Sánchez, F.; Torres, T. *Synthesis* **1983**, 911.

**Table II. $^1$H NMR Data of 3- and 5-Substituted 5-(Ethylthio)furan-2(5*H*)-ones**

| compd | H-3 | H-4 | H-5 | $J_{3,4}$ | $J_{4,5}$ | other |
|---|---|---|---|---|---|---|
| **2** | 6.21 | 7.41 | 6.11 | 5.6 | 1.7 | 2.70 (q, 2 H), 1.34 (t, 3 H) |
| **4** | 6.18 | 7.32 | | 5.4 | | 2.78–1.94 (m, 7 H), 2.35 (q, 2 H), 1.80–1.50 (m, 2 H), 1.20 (t, 3 H) |
| **5** | 6.14 | 7.30 | | 5.5 | | 3.68 (s, 3 H), 2.89–1.91 (m, 6 H), 1.20 (t, 3 H) |
| **6a** | 6.25 | 7.37 | | 5.5 | | 5.33 (d, 1 H), 2.95–2.66 (m, 5 H), 2.41 (q, 2 H), 1.30 (t, 3 H), 1.22 (t, 3 H) |
| **6b** | 6.25 | 7.37 | | 5.5 | | 5.75 (d, 1 H), 2.87–2.48 (m, 5 H), 2.32 (q, 2 H), 1.28 (t, 3 H), 1.16 (t, 3 H) |
| **9** | | 7.16 | 6.05 | | 1.5 | 4.47 (dddd, 1 H), 2.72 (q, 2 H), 1.92–1.60 (m, 2 H), 1.33 (t, 3 H), 0.99 (t, 3 H) |
| **10** | | 7.14 | | | | 4.45 (ddd, 1 H), 3.77 (ddd, 1 H), 2.45 (m, 3 H), 1.95–1.70 (m, 4 H), 1.45–1.35 (m, 1 H), 1.22 (t, 3 H), 1.06 (t, 3 H), 1.00 (t, 3 H) |

**Table III. $^{13}$C NMR Data of 3- and 5-Substituted 5-(Ethylthio)furan-2(5*H*)-ones**

| compd | C-2 | C-3 | C-4 | C-5 | other |
|---|---|---|---|---|---|
| **2** | 171.5 | 122.1 | 153.3 | 85.4 | 24.2, 14.7 |
| **4** | 170.7 | 120.8 | 156.1 | 97.5 | 209.0, 45.5, 42.7, 40.9, 26.3, 24.2, 22.1, 14.2 |
| **5** | 170.8 | 120.8 | 156.9 | 94.7 | 172.8, 51.9, 30.4, 28.5, 22.6, 14.4 |
| **6a** | 173.3 | 121.5 | 155.0 | 94.45 | 169.8, 83.6, 48.1, 30.5, 26.2, 22.7, 14.6, 14.15 |
| **6b** | 173.5 | 122.1 | 154.5 | 95.2 | 169.7, 83.9, 48.1, 30.4, 26.2, 22.7, 14.6, 14.1 |
| **9** | 171.4 | 137.9 | 145.4 | 84.3 | 68.4, 28.4, 24.95, 15.0, 9.5 |
| **10** | 171.1 | 139.0 | 147.5 | 97.3 | 75.6, 67.6, 28.9, 25.7, 22.4, 14.5, 10.9, 9.6 |

diate **8** enables the reaction with a second aldehyde molecule to afford the 3,5-disubstituted furanone **10**, which is obtained in 85% yield as a mixture of diastereomers (Table I, entry 8).

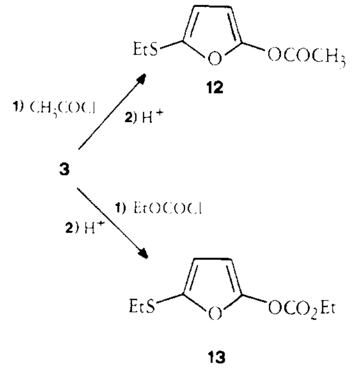
The reaction of the anion **3** with cycloalkanones such as cyclohexanone was also investigated. The $^1$H NMR spectrum of the crude product showed signals assignable to the Michael adduct **11** and to the self-condensation product **6** in a ca. 1:1 ratio (Table I, entry 9), although compound **11** proved difficult to purify by chromatography. This result is in accord with the known fact that the carbonyl group in ketones is less rapidly attacked by nucleophiles than that of aldehydes.

**Reaction with Alkyl and Acyl Halides.** Attempts of alkylation of anion **3** with soft alkyl halides such as methyl iodide or allyl bromide did not produce the expected alkylated derivative. Instead the only compound obtained corresponded to the self-condensation product **6**, thus indicating that, under the conditions used, the competitive Michael addition with another molecule of **2** is the most favored reaction.

When the reaction of the anion **3** was effected with hard electrophiles such as acetyl chloride or ethyl chloroformate (see Table I, entries 10 and 11), it exclusively took place through the hard carbonyl oxygen atom to afford the 2,5-disubstituted furans **12** and **13** (Scheme III). The observed behavior of the anion **3** toward hard electrophiles is not unprecedented, various ((trimethylsilyl)oxy)furans having been obtained recently by silylation of unsaturated lactones.[6,9] Furthermore, 2(3*H*)-furanones are known to react with acylating agents to afford (acyloxy)furans.[10]

Structural assignments of compounds **12** and **13** were based upon characteristic spectroscopic properties, mainly the $^1$H and $^{13}$C NMR data. The $^1$H NMR spectra of these compounds displayed two signals assignable to olefinic protons with a pattern very similar to that observed for the H-3 and H-4 protons in a furan ring. Moreover, the $^{13}$C NMR spectrum of compound **12** showed a signal at $\delta$ 166.4 that corresponds to an ester carbonyl carbon which does not coincide with the lactone carbonyl carbon of the starting furanone ($\delta$ 171.5). Furthermore, in the $^{13}$C NMR spectrum of compound **13**, the lactone carbonyl carbon was also absent and showed a signal at $\delta$ 152.1 assignable to a carbonyl carbon of type OCOOEt. These data corroborated the proposed structures.

**Scheme III**



## Conclusion

We believe that the reactions outlined in this paper provide a simple and rather mild method for the regioselective formation of new bonds, in particular carbon–carbon bonds at the 3- and 5-positions of the 2(5*H*)-furanones. This approach has a wide potential utility in the synthesis of important substituted lactones.

## Experimental Section

Melting points were obtained in a Büchi apparatus in open capillary tubes and are uncorrected. IR spectra were recorded on a Nicolet FT-5DX spectrometer under the conditions specified for each compound and are given in cm$^{-1}$. $^1$H NMR (200 MHz) and $^{13}$C NMR spectra were recorded on a Bruker WP-200-SY instrument. Chemical shifts are reported in ppm ($\delta$) downfield from internal Me$_4$Si for CDCl$_3$ solutions. Mass spectra were recorded in a Hewlett-Packard 5985 spectrometer at 70 eV. Microanalyses were performed with a Perkin-Elmer Model 240 analyzer. Thin-layer chromatography was performed on Merck PR-254 silica gel with the eluting solvents indicated. Column chromatography was performed with Merck 60 (70–230 mesh) F$_{254}$ silica gel washed with a 0.1 M solution of KH$_2$PO$_4$.

**General Procedures. Method A.** A solution of lithium diisopropylamide (1.38 mmol) was prepared by addition at −78 °C, under a dry nitrogen atmosphere, of 0.92 mL (1.38 mmol) of a 1.5 M solution of *n*-butyllithium to a solution of 139 mg (1.38 mmol) of diisopropylamine in 4 mL of tetrahydrofuran. A solution of 200 mg (1.38 mmol) of 5-(ethylthio)furan-2(5*H*)-one (**2**) in 3 mL of dry tetrahydrofuran was added, and the mixture was further stirred for 15 min at −78 °C. A solution of the electrophile (1.45 mmol) in 3 mL of THF was then added. After being stirred for 1 h at −78 °C, the reaction mixture was allowed to warm to room temperature. The solution was poured into saturated aqueous ammonium chloride and extracted with ethyl acetate. The combined extracts were dried (MgSO$_4$), filtered, and concentrated under reduced pressure. The crude isolated products were subjected to simple column chromatography on silica gel.

**Method B.** To a mixture of **2** (300 mg, 2.08 mmol) and the corresponding $\alpha,\beta$-unsaturated compound (2.5 mmol) in aceto-

---

(9) (a) Pelter, A.; Al-Bayati, R.; Lewis, W. *Tetrahedron Lett.* **1982**, *23*, 353. (b) Pelter, A.; Al-Bayati, R.; Pardasani, P. *Tetrahedron Lett.* **1986**, *27*, 749.

(10) Kraus, G. A.; Roth, B. *J. Org. Chem.* **1978**, *43*, 2072.

nitrile (8 mL) were added finely powdered anhydrous potassium carbonate (1.12 g, 8 mmol) and tetrabutylammonium hydrogen sulfate (34 mg, 0.10 mmol). The mixture was stirred for 4 h at room temperature. The inorganic salts were filtered by suction and washed with acetonitrile (15 mL). The pure products were obtained by simple column chromatography on silica gel.

**5-(Ethylthio)-5-(3′-oxocyclohexyl)furan-2(5*H*)-one (4).** The crude product obtained following the general procedure (method A), using 2-cyclohexen-1-one as electrophile, was chromatographed on silica gel (9:1 toluene–ethyl acetate): yield 75%; colorless oil; IR (neat) 1780, 1765, 1710, 1600; $^1$H and $^{13}$C NMR data are given in Tables II and III, respectively; MS *m/z* (relative intensity) 240 (0.7, $M^{\bullet+}$), 180 (87.6), 179 (63.2), 144 (15.1), 133 (76.5), 115 (100). Anal. Calcd for $C_{12}H_{16}O_3S$: C, 60.00; H, 6.66; S, 13.33. Found: C, 60.21; H, 6.93; S, 13.15.

The crude mixture obtained following the general procedure (method B) contained **4** and **6** in a 2:1 ratio. After chromatography (9:1 toluene–ethyl acetate), **4** was obtained in 50% yield.

**5-(Ethylthio)-5-[2′-(methoxycarbonyl)ethyl]furan-2(5*H*)-one (5).** The crude reaction mixture obtained following the general procedure (method A), using methyl acrylate as electrophile, contained compounds **5** and **6** in a 3:1 ratio; the crude product was chromatographed on silica gel (20:1 dichloromethane–acetonitrile). The first fraction afforded **6**. Further elution gave **5** in 55% yield as a colorless oil: IR (neat) 1793, 1770, 1737, 1597, 1170; the NMR data are given in Tables II and III; MS *m/z* (relative intensity) 230 (0.8, $M^{\bullet+}$), 169 (36.8), 137 (20.5), 109 (100), 59 (20.4). Anal. Calcd for $C_{10}H_{14}O_4S$: C, 52.17; H, 6.09; S, 13.91. Found: C, 52.30; H, 6.35; S, 13.75.

The crude mixture obtained following the general procedure (method B) contained **5** and **6** in a 1.6:1 ratio. After chromatography (9:1 toluene–ethyl acetate), compound **5** was obtained in 45% yield.

**5-(Ethylthio)-5-[5′-(ethylthio)-2′-oxotetrahydrofuran-4′-yl]furan-2(5*H*)-one (6a + 6b).** The crude mixture obtained following the general procedure (method A or B), using a second molecule of furanone **2** as electrophile, contained the adduct **6** (70%) as a mixture of diastereomers **6a** and **6b** in a 5:1 ratio. The diastereomers were separated by column chromatography (8:2 toluene–ethyl acetate). The major isomer **6a** was eluted first and isolated as a colorless oil: IR (neat) 1795, 1780, 1600; $^1$H and $^{13}$C NMR data are given in Tables II and III, respectively; MS *m/z* (relative intensity) 288 (4.2, $M^{\bullet+}$), 226 (3.3), 165 (26.7), 137 (40.3), 109 (100). Anal. Calcd for $C_{12}H_{16}O_4S_2$: C, 50.00; H, 5.55; S, 22.20. Found: C, 50.20; H, 5.80; S, 22.10.

The second compound eluted corresponded to the minor isomer **6b** and after crystallization was isolated as a solid: mp 108–109 °C (from carbon tetrachloride); IR (Nujol) 1793, 1782, 1608; the NMR data are given in Tables II and III; MS *m/z* (relative intensity) 288 (7.3, $M^{\bullet+}$), 226 (3.6), 165 (26.0), 137 (36.0), 109 (100). Anal. Calcd for $C_{12}H_{16}O_4S_2$: C, 50.00; H, 5.55; S, 22.20. Found: C, 50.27; H, 5.33; S, 21.96.

**5-(Ethylthio)-3-(1′-hydroxypropyl)furan-2(5*H*)-one (9).** The crude mixture obtained from equimolar amounts of (ethylthio)furanone **2** and propionaldehyde following the general procedure (method A) was purified by chromatography on silica gel (9:1 toluene–ethyl acetate): yield 70%; colorless oil; IR (neat) 3440, 1760; $^1$H and $^{13}$C NMR data are given in Tables II and III, respectively; MS *m/z* (relative intensity) 202 (28.8, $M^{\bullet+}$), 173 (100), 155 (21.7), 144 (36.0), 113 (43.0). Anal. Calcd for $C_9H_{14}O_3S$: C, 53.46; H, 6.93; S, 15.84. Found: C, 53.70; H, 6.94; S, 15.76.

**3,5-Bis(1′-hydroxypropyl)-5-(ethylthio)furan-2(5*H*)-one (10).** The crude mixture obtained from the (ethylthio)furanone **2** and 2.2 equiv of propionaldehyde following the general procedure (method A) was purified by chromatography on silica gel (8:2 toluene–ethyl acetate) to afford **10** as a colorless oil in 85% yield: IR (neat) 3500–3200, 1770, 1740; $^1$H and $^{13}$C NMR data are given in Tables II and III, respectively; MS *m/z* (relative intensity) 260 (0.4, $M^{\bullet+}$), 202 (16.0), 184 (99.7), 155 (94.7), 141 (47.7), 95 (97.8), 57 (100.0).

**5-(Ethylthio)-3-(1′-hydroxycyclohexyl)furan-2(5*H*)-one (11).** The crude reaction mixture obtained following the general procedure (method A), using cyclohexanone as electrophile, contained compounds **11** and **6** in a ca. 1:1 ratio; combined isolated yield 55%. Attempts to purify the crude mixture by chromatography (9:1 toluene–ethyl acetate) failed to afford compound **11** in a pure form. A sample contaminated with minor amounts of **6** gave the following $^1$H NMR data assigned to **11**: $^1$H NMR 7.08 (d, 1 H, $J = 1.6$ Hz), 6.00 (d, 1 H, $J = 1.6$ Hz), 2.72 (q, 2 H, $J = 7.3$ Hz), 1.85–1.55 (m, 10 H), 1.30 (t, 3 H, $J = 7.3$ Hz); MS (obtained in a GC–MS system) *m/z* (relative intensity) 242 (1.5, $M^{\bullet+}$), 224 (100), 195 (32.1), 163 (84.3), 135 (60.1).

**2-Acetoxy-5-(ethylthio)furan (12).** The crude product obtained from (ethylthio)furanone **2** and acetyl chloride following the general procedure (method A) was purified by chromatography on silica gel (toluene as eluent). Compound **12** was isolated as a colorless oil in 60% yield: IR (neat) 1793, 1606; $^1$H NMR 6.51 (d, 1 H, $J = 3.2$ Hz), 5.87 (d, 1 H, $J = 3.2$ Hz), 2.72 (q, 2 H, $J = 7.3$ Hz), 2.29 (s, 3 H), 1.25 (t, 3 H, $J = 7.3$ Hz); $^{13}$C NMR 166.4, 152.3, 138.5, 119.7, 94.5, 30.5, 20.5, 15.0; MS *m/z* (relative intensity) 186 (11.9, $M^{\bullet+}$), 144 (100), 115 (87.8), 87 (23.1). Anal. Calcd for $C_8H_{10}O_3S$: C, 51.61; H, 5.37; S, 17.20. Found: C, 51.85; H, 5.60; S, 17.05.

**2-((Ethoxycarbonyl)oxy)-5-(ethylthio)furan (13).** The crude product obtained from (ethylthio)furanone **2** and ethyl chloroformate following the general procedure (method A) was purified by chromatography on silica gel (toluene as eluent). Compound **13** was isolated as a colorless oil in 60% yield: IR (neat) 1780, 1610; $^1$H NMR 6.51 (d, 1 H, $J = 3.2$), 5.86 (d, 1 H, $J = 3.2$ Hz), 4.33 (q, 2 H, $J = 7.1$ Hz), 2.73 (q, 2 H, $J = 7.4$ Hz), 1.38 (t, 3 H, $J = 7.1$ Hz), 1.25 (t, 3 H, $J = 7.4$ Hz); $^{13}$C NMR 152.1, 151.1, 139.1, 119.6, 94.25, 65.9, 30.4, 15.0, 14.0; MS *m/z* (relative intensity) 216 (0.9, $M^{\bullet+}$), 144 (22.4), 115 (100), 87 (43.8).

**Acknowledgment.** Financial support from the Secretaría de Estado de Universidades e Investigación is gratefully acknowledged.

**Registry No.** **2**, 94014-37-6; **4**, 114583-59-4; **5**, 114583-60-7; **6** (C-5 epimer 1), 114583-61-8; **6** (C-5 epimer 2), 114583-62-9; **9**, 114583-63-0; **10**, 114583-64-1; **11**, 114583-65-2; **12**, 114583-66-3; **13**, 114583-67-4; $H_2C{=}CHCO_2Me$, 96-33-3; EtCHO, 123-38-6; MeCOCl, 75-36-5; EtOCOCl, 541-41-3; 2-cyclohexen-1-one, 930-68-7; cyclohexanone, 108-94-1.