Table I. Calculated[a] Total Energies (hartrees) and Relative Energies[b] (kcal/mol) for the Transition Structures of the H_2O Addition to the Vicinal Position and the H^+ Abstraction Reactions of Cyclobutenylium (2H$^+$) and Cyclohexadienylium (3H$^+$) Ions

ion	rctn	SCF/6-31G	SCF/6-31G*	MP2/6-31G	MP2/6-31G*[c]
2H$^+$	H_2O addn	−229.973 75 (0.0)	−230.060 94 (0.0)	−230.437 13 (0.0)	(0.0)
	H^+ abstn	−229.883 67 (56.5)	−229.966 04 (40.7)	−230.354 80 (51.7)	(35.9)
3H$^+$	H_2O addn	−306.905 35 (0.0)	−307.008 21 (0.0)	−307.548 11 (0.0)	(0.0)
	H^+ abstn	−306.912 53 (−4.5)	−307.008 22 (0.0)	−307.567 42 (−12.1)	(−7.6)

[a] At the MNDO-optimized geometries. [b] In parentheses. [c] Estimated by assuming additivity of the d-polarization functions and electron correlation effects.

results comparable with those from good ab initio calculations.[7] Transition structures were located by the usual reaction coordinate method, refined by minimizing the norm of the gradient,[8] and characterized by calculating and diagonalizing the Cartesian force constant matrix.[8]

Since it is well-known that MNDO grossly overestimates the energy of the transition structures involved in hydrogen abstraction processes,[9] to obtain more reliable energies, we performed single-point ab initio calculations[10] with the large split-valence 6-31G basis set[12] (denoted SCF/6-31G), with the split-valence plud d-polarization 6-31G* basis set[13] (denoted SCF/6-31G*), and with incorporation of valence-electron correlation using second-order Moller–Plesset perturbation theory[14] with the 6-31G basis set (denoted MP2/6-31G). The best relative energies (denoted MP2/6-31G*) were estimated by assuming additivity of the d-polarization functions and correlation energy effects.[15]

Results and Discussion

The total and relative energies, calculated at the various levels of theory, of the four aforementioned transition structures are collected in Table I. It is readily seen that at the present highest level of theory, namely, from the estimated MP2/6-31G* relative energies, the transition structure for the H^+ abstraction from **2H**$^+$ is found to lie 35.9 kcal/mol above the transition structure for the H_2O addition to this ion. In sharp contrast, the transition structure for the H^+ abstraction from **3H**$^+$ lies 7.6 kcal/mol below the transition structure for the H_2O addition. Inclusion of the zero-point vibrational energy corrections (calculated from the MNDO harmonic vibrational frequencies) leads to a potential energy difference between the transition structures for H^+ abstraction and H_2O addition of 33.1 kcal/mol, in the case of **2H**$^+$, and −11.3 kcal/mol, in the case of **3H**$^+$. From these potential energy differences and the differences between the absolute entropies of the transition structures (computed by standard methods using the MNDO harmonic frequencies and the principal moments of inertia), the activated-complex theory predicts a rate constant ratio for H^+ abstraction vs H_2O addition of 2.123×10^{-24} and 1.212×10^{9} for the ions **2H**$^+$ and **3H**$^+$, respectively, at 25 °C. Thus, in contrast to the normal (nonaromatic) chemical behavior predicted for cyclobutadiene, benzene is predicted to show an aromatic chemical behavior (tendency to "revert to type") when it reacts with hydroxonium ion (H_3O^+). The latter is essentially due to the higher potential energy barrier involved in the H_2O addition to the intermediate ion **3H**$^+$, formed in the first step of the reaction, as compared to its deprotonation by H_2O. This conclusion clearly illustrates the kinetic basis of the benzene *aromaticity*.

Finally, it should be noted that the reliability of the present quantitative results rests on the assumption that the structure of the transition states at the MP2/6-31G* level of theory will be very similar in geometry to those obtained by MNDO. Admittedly, the MP2/6-31G* calculated energies of the transition structures located at this level of theory may differ somewhat from those calculated for the MNDO-optimized ones. Nevertheless, it seems unlikely that the former energies may reverse the relative energy ordering found for the above transition states using the latter approach.

Acknowledgment. The calculations were carried out by using the IBM 3083 and IBM 4341 computers at the Centre d'Informàtica de la Universitat de Barcelona.

Registry No. **2H**$^+$, 12316-90-4; **3H**$^+$, 26812-57-7.

Supplementary Material Available: Cartesian coordinates of the MNDO-optimized transition structures for the H_2O addition and the proton loss reactions of **2H**$^+$ and **3H**$^+$ (3 pages). Ordering information is given on any current masthead page.

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Tandem [2,3]-Sigmatropic Rearrangement of Sulfonium Ylides and Bromine Allylic Rearrangement on a 4-Methoxy-2-pyrone Derivative

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Sulfur ylides are being used increasingly in synthetic chemistry by means of their [2,3]-sigmatropic rearrangements. Ando and co-workers[1] have throughly investigated the formation and rearrangement of these ylides which

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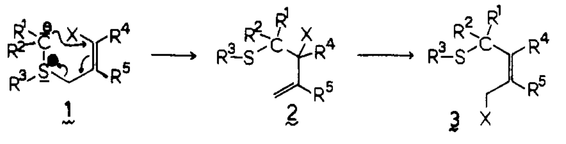
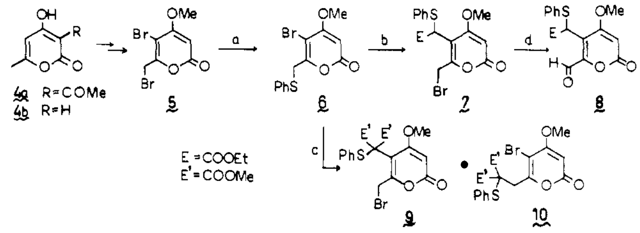
Scheme I



Scheme II^a



^{a}(a) PhSNa/MeOH/25 °C; (b) Rh$_2$(OAc)$_4$/ethyl diazoacetate/toluene/55 °C; (c) Rh$_2$(OAc)$_4$/dimethyl diazomalonate/toluene/70 °C; (d) (i) pyridine/25 °C, (ii) 4-(dimethylamino)nitrosobenzene, (iii) aqueous HCl/benzene.

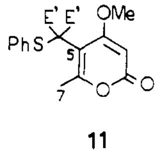
have been extensively used in the last years.[2] Some significant products, i.e., betweenanenes,[3] sarkomycin,[4] and khellin derivatives,[5] have been synthesized through the Sommelet–Hauser [2,3]-sigmatropic rearrangement of sulfur ylides.

The general rearrangement is depicted in Scheme I (**1** → **2**). If tautomer **3** is more stable than tautomer **2**, conversion of **2** into **3** can occur either directly under the [2,3]-sigmatropic rearrangement experimental conditions or in a subsequent step as we have already shown.[6] However, at the best of our knowledge no X groups different from hydrogen have been used in the transformations **1** → **3**. Such an overall process would imply a novel and important modification of allylic systems.

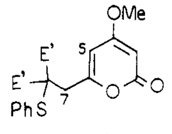
Triacetic acid lactone, **4b**, is one of the most simple polyketides[7] and is also easily obtained from the industrially available dehydroacetic acid, **4a**.[8] Both **4a** and **4b** are important building blocks and efforts have been made to alkylate them at C-3[9] and at C-5.[6,10] Also, the lengthening of the chain at C-6 has been accomplished by means of polyanion chemistry[11] and Wittig reactions.[12]

We have transformed **5**[13] into the known thioether **6**[14] using sodium thiophenolate in methanol as indicated in Scheme II. Treatment of **6** with ethyl diazoacetate under rhodium acetate catalysis afforded **7** in 37% yield, 39% of starting material being recovered. The structural assignment was unambiguous since the ^{1}H NMR spectrum exhibits no absorptions either at δ 5.80–5.90 (H-5 region) or at 1.8–2.0 (CH$_3$-C-6 region). Instead, an AB system appeared at δ 3.7–4.05 due to the diastereotopic bromomethylene protons. This one-pot transformation is the overall result of a tandem [2,3]-sigmatropic rearrangement of a sulfonium ylide followed by a [1,3] bromine allylic rearrangement. In addition, Kröhnke oxidation[15] of **7** gave the aldehyde **8** in 83% yield.

Treatment of **6** with dimethyl diazomalonate under rhodium acetate catalysis led to **9** and **10** in 32% and 9% yield, respectively. The structural assignment of compounds **9** and **10** was based on the chemical shifts of C-5 and C-7 (the carbon atom directly bound to C-6). Thus, for **9** the absorptions appear at δ 111.7 and 25.7, values that are comparable to the C-5 absorption (δ 109.9) in compound **11**[6b] and to the C-7 absorption (δ 26.1) in 6-(bromomethyl)-2*H*-pyran-2-one derivatives.[13] For compound **10** C-5 resonates at δ 98.8 comparable to δ 97–99 in 5-bromo-2*H*-pyran-2-one derivatives[13] and C-7 at δ 38.1 value comparable to 38.5 for compound **12**[6b]



11



12

Compound **9** results again from a tandem [2,3]-[1,3] double rearrangement whereas **10** arises from the Stevens [1,2] rearrangement. The competition between [2,3] and [1,2] rearrangements using dimethoxycarbonylcarbene was already described in the chemistry of these pyrones.[6b]

Conversions of **6** into **7** and **9** are the first reported examples of the unprecedented tandem [2,3]-sigmatropic rearrangement of sulfonium ylides and allylic rearrangement of a bromine atom. The pyrone **8** exhibits a carbon chain at C-5 and an aldehyde function at C-6 which make it an interesting candidate for further elaboration of different substituents at both positions.

Experimental Section

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker WP80SY spectrometer. Infrared spectra were recorded on a Perkin-Elmer 1310 spectrometer. Mass spectra were obtained on a Hewlett-Packard 5985B GC-MS system.

5-Bromo-4-methoxy-6-[(phenylthio)methy]-2*H*-pyran-2-one (6). A solution of sodium thiophenolate (from sodium (1.58 g, 67.7 mmol) and thiophenol (7.49 g, 68.1 mmol)) in methanol (172 mL) was added during 1 h at room temperature, under argon atmosphere and magnetic stirring, onto a solution of the lactone **5**[13] (10.0 g, 33.6 mmol) in methanol (312 mL). The solution was kept overnight at −18 °C and the formed precipitate was filtered off and washed with cold water affording 8.35 g of lactone **6**. The filtrate was evaporated to dryness and was partitioned between methylene chloride and water. The organic layer was dried with sodium sulfate and evaporated. The residue (3.76 g) was chromatographed under pressure through a silica gel column (230–400 mesh). Using hexane/ethyl acetate (75:25) as eluent an additional

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crop of **6** (1.69 g) was obtained. The total yield of pyrone **6** was 91% and the spectroscopic data of the product were identical with those reported:[14] mp 109–111 °C [lit.[14] mp 109.5–110.5 °C].

6-(Bromomethyl)-5-[(ethoxycarbonyl)(phenylthio)-methyl]-4-methoxy-2*H*-pyran-2-one (7). A solution of ethyl diazoacetate (4.183 g, 36.7 mmol) in toluene (5 mL) was added dropwise during 3 h over a magnetically stirred mixture of the bromo lactone **6** (4.00 g, 12.2 mmol), a catalytic amount of rhodium(II) acetate, and toluene (45 mL) kept at 55 °C. Quantitative evolution of nitrogen was observed. The final mixture was washed with 2 N HCl and with aqueous sodium chloride. The organic layer was dried with sodium sulfate and evaporated. The residue was chromatographed through silica gel (230–400 mesh) with mixtures of hexane/ethyl acetate. A total of 1.545 g (4.7 mmol) of the starting material **6** was recovered, eluting with 80% hexane. Finally 1.854 g (37%) of **7** was eluted with 75% hexane: mp 154–156 °C; IR ($CHCl_3$) 1725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20 (t, 3 H, J = 7 Hz), 3.80 (s, 3 H), 3.70, 3.85, 3.90, 4.05 (AB system, 2 H, J = 11 Hz), 4.20 (q, 2 H, J = 7 Hz), 4.90 (s, 1 H), 5.55 (s, 1 H), 7.20–7.55 (m, 5 H); ^{13}C NMR ($CDCl_3 + CD_3OD$) δ 13.2, 23.5, 47.5, 56.1, 62.1, 89.6, 111.3, 128.6, 128.7, 132.2, 134.2, 156.6, 162.4, 168.2; MS, m/z (relative intensity) 414 (7), 412 (M^+, 7), 305 (64), 303 (44), 277 (23), 275 (26), 259 (21), 247 (32), 245 (25), 239 (49), 233 (29), 225 (43), 179 (37), 169 (20), 167 (23), 151 (20), 125 (54), 124 (20), 123 (43), 111 (24), 110 (29), 109 (100), 95 (27), 83 (21), 77 (25), 69 (68), 66 (32), 65 (40), 59 (42), 53 (23), 51 (27), 43 (40). Anal. Calcd for $C_{17}H_{17}BrO_5S$: C, 49.40; H, 4.15; Br, 19.33; S, 7.76. Found: C, 49.46; H, 3.82; Br, 19.27; S, 7.78.

5-[(Ethoxycarbonyl)(phenylthio)methyl]-6-formyl-4-methoxy-2*H*-pyran-2-one (8). A solution of pyrone **7** (800 mg, 1.94 mmol) in anhydrous pyridine (16 mL) was stirred for 6 h at room temperature. Ether (140 mL) was added and a white precipitate of the corresponding pyridinium bromide (940 mg, 99%) was formed. It was very hygroscopic and was used without further purification. 4-Nitroso-*N*,*N*-dimetylaniline (280 mg, 1.87 mmol) and a suspension of potassium carbonate (1.402 g, 10.3 mmol) in water (4 mL) were added at room temperature in the indicated order to a stirred solution of the above pyridinium salt (840 mg, 1.71 mmol) in ethanol (8 mL). The mixture was stirred at room temperature for 30 min and at 0 °C for 1 h. The formed precipitate (819 mg) was the unstable nitrone *N*-[[5-[(ethoxycarbonyl)(phenylthio)methyl]-4-methoxy-2-oxo-2*H*-pyran-6-yl]-methylene]-4-(dimethylamino)aniline *N*-oxide (99%). A mixture of this nitrone (745 mg, 1.55 mmol), benzene (31 mL) and 2N HCl (53 mL) was strongly stirred at room temperature for 21 h. The organic layer was washed with aqueous sodium chloride, dried with sodium sulfate and evaporated. The residue was chromatographed through a silica gel column (230–400 mesh) using hexane:ethyl acetate (1:1) to afford the aldehyde **8** (457 mg, 85%): mp 103-105 °C; IR (KBr) 2930, 2850, 1720, 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20 (t, 3 H, J = 7 Hz), 3.85 (s, 3 H), 4.20 (q, 2 H, J = 7 Hz), 5.75 (s, 1 H), 6.00 (s, 1 H), 7.3 (m, 5 H), 9.30 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.0, 45.5, 56.7, 62.3, 94.6, 117.5, 129.1, 132.5, 134.9, 148.6, 160.4, 167.5, 168.1, 184.5; MS m/z 348 (M^+, 10), 319 (5), 302 (16), 239 (17), 167 (39), 139 (23), 109 (100), 69 (34), 65 (28). Anal. Calcd for $C_{17}H_{16}O_6S$: C, 58.61; H, 4.63; S, 9.20. Found: C, 58.13; H, 4.79; S, 9.24.

5-[Bis(methoxycarbonyl)(phenylthio)methyl]-6-(bromomethyl)-4-methoxy-2*H*-pyran-2-one (9) and 6-[2,2-Bis-(methoxycarbonyl)-2-(phenylthio)ethyl]-5-bromo-4-methoxy-2*H*-pyran-2-one (10). A solution of dimethyl diazomalonate (316 mg, 2.0 mmol) in toluene (2 mL) was added during 2 h over a stirred mixture of pyrone **6** (327 mg, 1.0 mmol), a catalytic amount of rhodium(II) acetate, and toluene (8 mL) kept at 70 °C under an argon atmosphere. Quantitative nitrogen evolution was observed. The mixture was washed with 2 N HCl and with aqueous sodium chloride. The organic layer was dried with sodium sulfate and evaporated. The residue was chromatographed through a silica gel column (230–400 mesh) with hexane/ethyl acetate mixtures. The following products were eluted: 6-[2,2-bis(methoxycarbonyl)-2-(phenylthio)ethyl]-5-bromo-4-methoxy-2*H*-pyran-2-one (**10**) with 70% hexane (40 mg, 9%): mp 143–145 °C; IR ($CHCl_3$) 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.40 (s, 2 H), 3.85 (s, 6 H), 3.95 (s, 3 H), 5.50 (s, 1 H), 7.25–7.60 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 38.1, 53.4, 56.9, 62.7, 88.9, 98.8, 128.9, 130.1, 137.0, 157.3, 160.9, 166.3, 167.7; MS, m/z (relative intensity) 458 (1), 456 (M^+, 1), 377 (100), 317 (32), 315 (43), 267 (57), 207 (26), 205 (33), 203 (26), 179 (44), 177 (23), 149 (61), 147 (52), 109 (44), 91 (23), 83 (27), 69 (42), 65 (28), 59 (49), 53 (39). Anal. Calcd for $C_{18}H_{17}BrO_7S$: C, 47.28; H, 3.75; Br, 17.47; S, 7.01. Found: C, 47.41; H, 3.55; Br, 17.34; S, 6.83. Pyrone **9** eluted with 60% hexane: mp 125–126 °C; IR ($CHCl_3$) 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.55 (s, 3 H), 3.85 (apparent s, 8 H), 5.40 (s, 1 H), 7.25–7.40 (m, 3 H), 7.50–7.70 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 25.7, 54.2, 56.4, 65.9, 89.8, 111.7, 128.6, 129.5, 130.3, 138.0, 158.0, 160.9, 166.6, 167.8; MS, m/z (relative intensity) 458 (0.2),456 (M^+, 0.2), 235 (37), 233 (32), 218 (29), 167 (21), 109 (100), 77 (26), 69 (68), 65 (35), 59 (66), 53 (23), 45 (22). Anal. Calcd for $C_{18}H_{17}BrO_7S$: C, 47.28; H, 3.75; Br, 17.47; S, 7.01. Found: C, 47.45; H, 3.72; Br, 17.19; S, 7.05.

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Registry No. **5**, 105525-73-3; **6**, 93338-98-8; **7**, 116054-34-3; **8**, 116054-35-4; **8** (pyridinium bromide), 116054-36-5; **9**, 116054-37-6; **10**, 116054-38-7; *N*-[[5-[(ethoxycarbonyl)(phenylthio)-methyl]-4-methoxy-2-oxo-2*H*-pyran-6-yl]methylene]-4-(dimethylamino)aniline *N*-oxide, 116054-39-8; dimethyl diazomalonate, 6773-29-1.

Carboxamidation of Organolithium and Organomagnesium Reagents by a Two-Step One-Flask Reaction. Promotion by Magnesium Alkoxides

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An organometallic route to aldehydes that has found some synthetic application is based on the reaction of an organolithium[1] or Grignard[2] reagent with dimethylformamide (eq 1). Reaction 1 involves the formation of a

$$RLi + Me_2NCHO \rightarrow \underset{\mathbf{1}}{RCH(OLi)NMe_2} \xrightarrow{H^+} \underset{\mathbf{2}}{[RCH(OH)NMe_2]} \xrightarrow{H^+} RCHO \quad (1)$$

hemiaminal derivative, **1**, which undergoes facile hydrolysis and results in the corresponding aldehyde. Indeed, hemiaminals **2**, with a few exceptions,[3] are not stable enough to be isolated, and this is perhaps the reason that the synthetic potential of this interesting class of organic compounds has not been fully exploited. The α-(dialkylamino)alkoxide group, however, has been shown to direct orthometalation in aromatic systems as well as functioning as a protected aldehyde or ketone.[4] The

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