Registry No.—**1a,** 65496-00-6; **1b,** 65495-92-3; **1c,** 65495-93-4; **2,** 28166-06-5; **3a,** 65495-94-5; **3b,** 65495-95-6; **3c,** 64309-10-0; 4-fluoro-3-nitroaniline, 364-76-1; 10-amino-1-decanol, 23160-46-5; 3-amino-1-propanol, 156-87-6; 6-amino-1-hexanol, 4048-33-3; tetra-*O*-acetyl-α-D-glucopyranosyl bromide, 572-09-8.

References and Notes

(1) (a) For a general review of the use of photoaffinity labels, see J. R. Knowles, *Acc. Chem. Res.*, **5**, 156 (1972); (b) G. W. J. Fleet, R. R. Porter, and J. R. Knowles, *Nature (London)*, **224**, 511 (1969).
(2) M. B. Perry and L. L. W. Heung, *Can. J. Biochem.*, **50**, 510 (1971), have prepared some other types of glucose derivatives with photolabile groups.
(3) W. Pigman and N. Richtmeyer, *J. Am. Chem. Soc.*, **64**, 369 (1962).
(4) We are deeply indebted to Doreen Lynch for developing this procedure. Only sketchy experimental details are given in ref 1b, and we have found that if conditions are not carefully controlled the major product is 4-hydroxy-3-nitrophenyl azide.
(5) Aryl azides are heat and light sensitive. It is advisable to cover flasks, etc., with aluminum foil during laboratory operations and to store products in refrigerators.
(6) Use of 1 equiv of amino alcohol and a tertiary amine, e.g., triethylamine, led to reduced yields.
(7) Obtained from Sigma Chemical Co., St. Louis, Mo. This material was used directly without purification.
(8) R. Willstätter and A. Pfannenstiel, *Ber.*, **37**, 4744 (1904).
(9) HLPC analysis of this product on a 2 ft × 1/8 in. Corasil column at 150 psi showed one major (>99%) product using benzene as eluent.
(10) The configurations of **1a–c** are assigned by analogy with numerous examples of glycosides prepared by silver salt catalyzed reactions of **4**. See ref 3 and G. Wulff, G. Rohle, and W. Krüger, *Ber.*, **105**, 1097 (1972).

Rearrangements of Acyloxyfurans and Thiophenes

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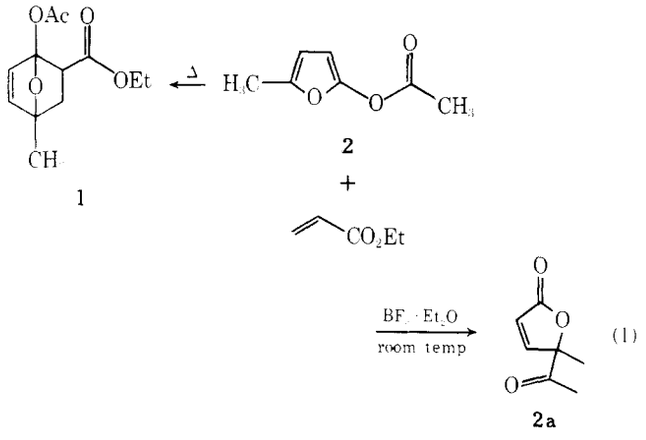
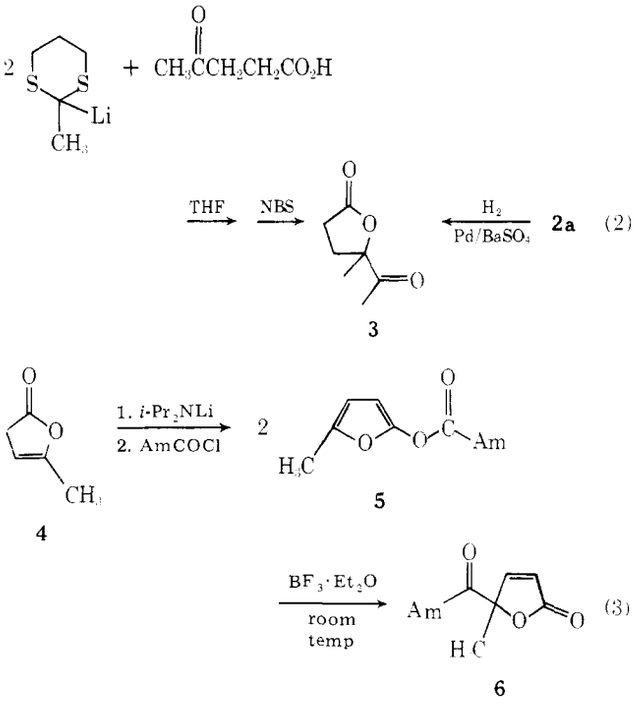
As part of a program for the synthesis of medium-ring compounds, the preparation of the bicyclic ester **1** became necessary. This could be accomplished in moderate yield by the Diels–Alder reaction shown in eq 1. Attempts to improve

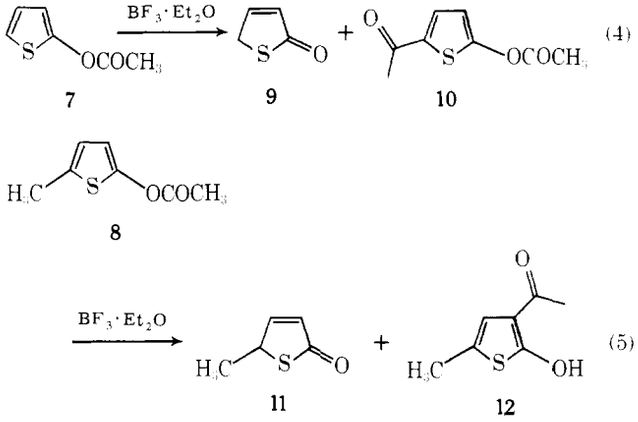


the yield by the use of Lewis acids such as boron trifluoride etherate provided the unexpected lactone **2a** in good yield. The structure of this novel rearrangement product was proven by hydrogenation[1] to butyrolactone **3** and independent synthesis of **3** by the reaction of levulinic acid with 2 equiv of 2-methyldithiane,[2] followed by oxidative removal of the dithiane moiety using NBS[3] (eq 2). Although the presence of diverse functionality should make this type of compound a versatile synthon, a literature search indicated that the preparation of this class of ketolactones had not been previously reported. Therefore, we sought to probe the extent of this rearrangement with other esters. Compound **5** was readily synthesized by quenching the lithium enolate[4] of angelicalactone **4** with

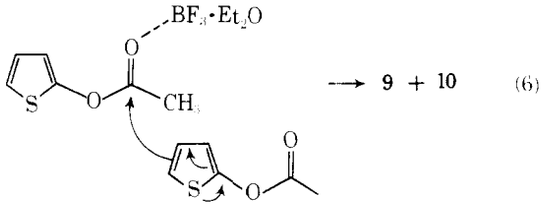


hexanoyl chloride (eq 3). Reaction of **5** with boron trifluoride etherate afforded ketolactone **6** in 40% isolated yield. A possible mechanism for this intriguing rearrangement would be one analogous to the Lewis acid catalyzed Fries rearrangement.[5]

The reactions of thiophene analogues **7** and **8**[6] produced the mixtures shown in eq 4 and 5.



Compounds **9** and **10** could arise from intermolecular attack as illustrated in eq 6.



A similar scheme can account for the formation of compounds **11** and **12** from thiophene **8**.

Experimental Section

NMR spectra were obtained with a Varian (A60) NMR spectrometer. The chemical shifts are reported in δ, using tetramethylsilane as reference. All melting points were taken upon a Fisher-Johns block and are uncorrected. Elemental analyses were determined by Galbraith Laboratories, Knoxville, Tenn. Organic solutions were dried over sodium sulfate.

General Procedure for the Synthesis of 2 and 5. A solution of

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10 mmol of angelicalactone in 5 mL of tetrahydrofuran (THF) was added over 5 min to a solution of 11 mmol of lithium diisopropylamide in 10 mL of THF at −78 °C. The solution was stirred at −78 °C for 15 min. The appropriate acid chloride (20 mmol) was added rapidly and the resulting suspension was stirred an additional 5 min. The reaction was worked up by the addition of ether and water. The aqueous layer was extracted twice with ether. The organic layer was dried, filtered, and concentrated. Column chromatography (1:10 ether/pentane) on silica gel afforded the acyloxyfurans as oils.

2-Acetoxy-5-methylfuran (2): colorless oil, 40% yield; IR (film) 1785, 1620, 1570, 1175 cm^{-1}; NMR ($CDCl_3$) δ 2.25 (d, J = 1 Hz, 3 H), 2.29 (s, 3 H), 5.82 (d, J = 3 Hz, 1 H), 6.02 (d of t, J = 3 Hz, 1 Hz, 1 H).

2-Hexanoyloxy-5-methylfuran (5): colorless oil, 40% yield; IR (film) 2964, 2940, 2880, 1780 cm^{-1}; NMR ($CDCl_3$) δ 0.7–1.9 (m, 9 H), 2.25 (d, 3 H), 5.75 (d, 1 H), 5.94 (d of t, 1 H).

General Procedure for the Boron Trifluoride Etherate Promoted Rearrangements. To a solution of 1.75 mmol of heterocyclic ester in 4 mL of benzene at 0 °C was added 1.75 mmol of distilled boron trifluoride etherate. The solution was allowed to warm slowly to room temperature and stirred until TLC indicated that reactant had been consumed (4–20 h). The solution was then diluted with ether, washed with sodium bicarbonate and brine, dried, and concentrated. The crude product was filtered through silica gel to afford pure product.

5-Acetyl-5-methyldihydro-2(5*H*)-furanone (2a): 65% yield; bp 65 °C (2 mm); IR (film) 1780, 1725, 1600 cm^{-1}; NMR ($CDCl_3$) δ 1.61 (s, 3 H), 2.20 (s, 3 H), 6.20 (d, J = 6 Hz, 1 H), 7.45 (d, J = 6 Hz, 1 H).

Anal. Calcd for $C_7H_8O_3$: C, 59.99; H, 5.75. Found: C, 59.88; H, 5.80.

5-Hexanoyl-5-methyldihydro-2(5*H*)-furanone (6): 40% yield; bp 77 °C (2 mm); IR (film) 2960, 2935, 2870, 1780, 1725, 1600 cm^{-1}; NMR ($CDCl_3$) δ 0.7–1.7 (m, 9 H), 1.64 (s, 3 H), 2.6 (m, 2 H), 6.23 (d, J = 6 Hz, 1 H), 7.5 (d, J = 6 Hz, 1 H).

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 65.70; H, 8.20.

5-Acetylthiophen-2-ol Acetate (10): 45% yield; mp 103–105 °C; IR (mull) 1775, 1660 cm^{-1}; NMR ($CDCl_3$) δ 2.38 (s, 3 H), 2.55 (s, 3 H), 6.84 (d, J = 4 Hz, 1 H), 7.62 (d, J = 4 Hz, 1 H).

Anal. Calcd for $C_8H_8O_3S$: C, 52.16; H, 4.38. Found: C, 52.19; H, 4.41.

3-Acetyl-5-methylthiophen-2-ol (12): 40% yield, oil; IR (film) 1735, 1630 cm^{-1}; NMR ($CDCl_3$) δ 2.26 (s, 6 H), 6.26 (br s, 1 H); high-resolution mass spectrum, m/e 156.02327 ($C_7H_8O_2S$ requires 156.02451).

4-Hydroxy-4-methyl-5-oxohexanoic Acid γ-Lactone (3). (A) Platinum oxide (10 mol %) and **2a** were stirred at 23 °C in ethanol (0.5 M) under a balloon of hydrogen until TLC indicated that the reaction was complete. The mixture was filtered through Celite and concentrated in vacuo to yield **3:** 97% yield, colorless oil; IR (film) 1790, 1725 cm^{-1}; NMR ($CDCl_3$) δ 1.55 (s, 3 H), 2.32 (s, 3 H), 2.6 (m, 4 H).

(B) An acetone solution of the protected ketolactone (0.86 mmol) was added to a rapidly stirred solution of *N*-bromosuccinimide (5 mmol, 0.3 M in aqueous acetone) at 0 °C. The solution was stirred 15 min at 0 °C, then 5 min at 25 °C. It was then poured into a mixture of hexane/chloroform and saturated sodium bicarbonate. The organic layer was separated, dried, and concentrated. Chromatography on silica gel using 1:4 ether/pentane afforded 0.11 g (90%) of a colorless oil which was identical in all respects (TLC, IR, NMR) with the material prepared in A.

4-Hydroxy-4-methyl-5-oxohexanoic Acid γ-Lactone 1,3-Propylene Dithioketal. Levulinic acid (2.5 mmol) is added dropwise to a solution of 2-lithio-2-methyldithiane (5.0 mmol) at −78 °C. The solution was allowed to warm to −10 °C, then stored in the refrigerator for 20 h. The reaction mixture was then poured into ice and extracted twice with ether/chloroform. The aqueous layer was then acidified to pH 3, extracted with chloroform, dried, and concentrated: 86% yield, colorless liquid; IR (film) 1775, 750 cm^{-1}; NMR ($CDCl_3$) δ 1.55 (s, 3 H), 1.62 (s, 3 H), 1.8–3.6 (m, 10 H).

Anal. Calcd for $C_{10}H_{16}O_2S_2$: C, 51.66; H, 6.94. Found: C, 51.73; H, 7.02.

Acknowledgment. We wish to thank the Department of Health, Education and Welfare for generous financial assistance through Grant No. 5 S05 RR07034 administered by the Iowa State University Research Foundation.

Registry No.—**2,** 65748-93-8; **2a,** 65748-94-9; **3,** 30246-17-4; **4,** 591-12-8; **5,** 65748-95-0; **6,** 65748-96-1; **7,** 36448-58-5; **8,** 65748-97-2; **10,** 65748-98-3; **12,** 65748-99-4; acetyl chloride, 75-36-5; AmCOCl, 142-61-0; 4-hydroxy-4-methyl-5-thioxohexanoic acid γ-lactone 1,3-propylene dithioketal, 65749-00-0; levulinic acid, 123-76-2; 2-lithio-2-methyldithiane, 27969-97-7.

References and Notes

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(2) D. Seebach and E. J. Corey, *J. Org. Chem.*, **40,** 231 (1975).
(3) E. J. Corey and B. Erickson, *J. Org. Chem.*, **36,** 3557 (1971).
(4) G. A. Kraus and B. Roth, *Tetrahedron Lett.*, 3129 (1977).
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An Efficient Synthesis of Enol Carbonates

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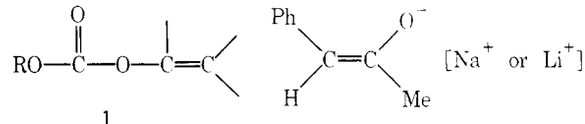
Acid of Hg^{2+} catalyzed transesterification provides ready access to most carboxylic acid enol esters. Alternatively, these useful synthetic intermediates and valuable polymer precursors can be made by a second scheme involving acylation of metal enolates with carboxylic acid anhydrides.[1] Because the required starting materials are either unstable or unknown, neither of these complementary routes can be adapted to the preparation of enol carbonates (**1**). Simple enol esters have been obtained by variations of the second scheme wherein the anhydride has been replaced by the analogous acid halide. However, competitive *C*-acylation of the ambident enolate anion has generally made such processes impractical, a point forcefully demonstrated in the extensive enolate acetylation studies of House.[1] For example, *O*-acetylation of **2** was nearly quantitative with Ac_2O in dimethoxyethane.



1 2

However, with AcCl only 24–50% of the *O*-acetyl product was found and this was contaminated by 14–22% of the *C*-acetyl isomer and unspecified amounts of the *O,C*-diacyl species (from *C*- then *O*-acylation).[2] Even less promising product mixtures were obtained in earlier investigations of the reaction of sodium enolates with ethyl chloroformate.[3]

Recent communications from this laboratory have illustrated a few of the unique advantages of enol carbonates (**1**) as synthetic intermediates.[4] These and other results have encouraged us to examine further the acylation of enolates with chloroformates in the hope of developing a broadly useful synthesis of **1**.

Two potential routes to **1** readily extrapolated from the data of House et al. were not explored. These authors reported only *O* attack from treatment of α-mercuri ketones with acetyl chloride.[1] However, the costs and dangers endemic to work with organomercurials led us to discard an approach based on this observation. They also found exclusive *O*-acylation in the reaction of potassium cyclohexanone enolate with ethyl chloroformate (39% yield).[1] Generalization of this scheme was abandoned because of the expense and technical problems inherent in the preparation and use of tritylpotassium, the base required in the best applicable synthesis of potassium enolates.

However, this final result of House did provide an important lead by suggesting that selective *O*-acylation could be accomplished by coercing a lithium enolate to mimic a potassium enolate, an effect sometimes achieved by carrying out

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