The largest shift/error ratio was 3.82 for y of C-29, 3.77 for z of C-31, 0.56 for other heavy atoms, and 1.80 for H atoms at this point. Final coordinates, temperature factors, and bond geometry tables are found in the Supplementary Material. All calculations were done with the Enraf-Nonius SDP package on a PDP 11/23 plus computer.

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Registry No. **1**, 83747-03-9; **10a**, 84-11-7; **10b**, 3383-21-9; **10c**, 524-42-5; **10d**, 2435-54-3; **10e**, 2435-53-2; **11a**, 97732-96-2; **11b**, 97732-97-3; **11c**, 97732-98-4; **11d**, 97732-99-5; **11e**, 97733-00-1; **12a**, 97733-01-2; **12b**, 97733-02-3; **13**, 97733-03-4.

Supplementary Material Available: Tables of positional and thermal parameters of **11a**, bond distances and angles, and observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

(21) An additional signal is presumably due to the hindered rotation of one *tert*-butyl group; similar phenomena have been observed for the tricyclic systems described in ref 1.

Oxonium Ion Electrophiles: Synthesis of the Hypotensive Oudenone

Hans Aaron Bates* and James Farina

Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11794-3400

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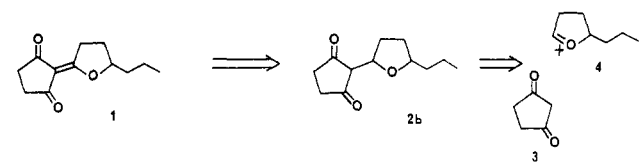
The hypotensive oudenone (**1**) has been synthesized through the intermediacy of oxonium ion **4**. Acid-catalyzed C-alkylation of 1,3-cyclopentanedione (**3**) with 5-propyltetrahydro-2-furanol (**6b**) afforded dihydrooudenone **2b**. In contrast, alkylation of **3** with 2-chloro-5-propyltetrahydrofuran (**7b**) was unsuccessful. Unsaturation was introduced into **2b** by treatment with *N*-(phenylthio)succinimide to produce **10** followed by oxidation to the corresponding sulfoxide and elimination of phenylsulfenic acid, which produced oudenone (**1**).

The hypotensive oudenone (**1**) was isolated[1] from the culture filtrate of the mushroom *Oudemansiella radicata* during an extensive examination[2] of microbial metabolites for enzyme inhibiting activity. The structure and synthesis of oudenone were reported soon thereafter.[3] The hypotensive effect of oudenone, which has been demonstrated in spontaneously hypertensive rats,[4] is caused by epinephrine biosynthesis blockade due to inhibition of tyrosine hydroxylase.[1,5] Oudenone was synthesized from 2-acetyl-1,3-cyclopentanedione in conjunction with structure elucidation,[3,6,7] and one subsequent synthesis has been reported.[8]

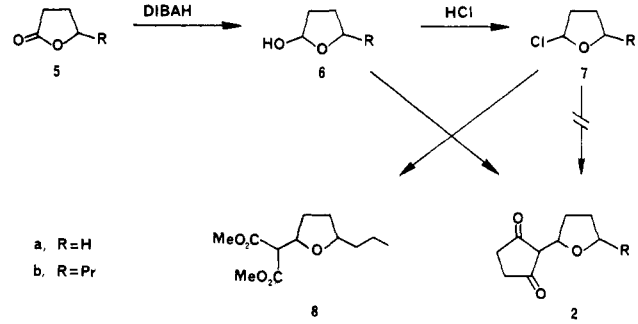
We envisioned that oudenone (**1**) might be synthesized from 1,3-cyclopentanedione (**3**) by C-alkylation with oxonium ion **4** or an equivalent species to afford **2b**, followed by introduction of unsaturation, as depicted in Scheme I. Our previous experience with α-halo ethers[9] and oxonium ions[10] suggested that this approach would be straightforward.

Scheme I



Results and Discussion

Tetrahydro-2-furanol (**6a**), which was utilized in model studies, has previously been prepared in various ways, the most popular of which is reduction of the corresponding lactone (**5a**) with DIBAH.[11] We found that **6a** was prepared more efficiently by acid-catalyzed hydration of 2,3-dihydrofuran.[12]



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Lactone **5b** was readily prepared by Knoevanagel condensation between pentanal and malonic acid to afford 2-heptenoic acid which cyclized to **5b** upon treatment with H_2SO_4.[13] Reduction of lactone **5b** with DIBAH afforded an epimeric mixture of cis and trans lactols (**6b**) in good yield. Treatment of lactol **6b** with HCl gas at −30 °C in the presence of anhydrous calcium chloride generated 2-chloro-5-propyltetrahydrofuran (**7b**).

In accord with our previous results,[9] 2-chloro-5-propyltetrahydrofuran (**7b**) rapidly alkylated dimethyl sodiomalonate to afford a mixture of *cis* and *trans*-dimethyl 2-(5-propyltetrahydrofuran-2-yl)malonate (**8**). In contrast, **7b** did not react with the sodium salt of 1,3-cyclopentanedione (**3**) to give the desired alkylation product **2b**. This unwelcome lack of reactivity might have been anticipated from the reported failure of 2-chlorotetrahydrofuran (**7a**) to react with 1,3-cyclopentanedione, which was attributed to the insolubility of 1,3-cyclopentanedione and decomposition of 2-chlorotetrahydrofuran.[14] Alternatively, competitive *O*-alkylation may have interfered with the desired C-alkylation.[15,16] Various alternatives[17] including the use of crown ethers,[18] and thallium salts[15] were not expected to improve this reaction.

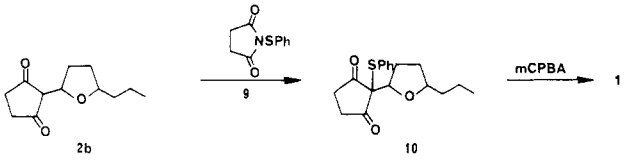
Acid-catalyzed C-alkylation of 1,3-cyclopentanedione (**3**) was next explored. After some experimentation we found that tetrahydro-2-furanol (**6a**) reacted with 1,3-cyclopentanedione at 20 °C in the presence of 200 mol % trifluoroacetic acid to afford **2a**. The desired dihydrooudenone (**2b**) as a mixture of cis and trans isomers was obtained from **6b** in analogous fashion. Compounds **2a** and **2b** slowly decompose to unidentified materials when stored at ambient temperature.

Precedent for acid-catalyzed alkylation of 1,3-cyclopentanediones includes the Torgov reaction with phenylallyl alcohols[19] and aldol condensation with aldehydes.[20] Acid-catalyzed alkylation of other 1,3-dicarbonyl compounds by tertiary and secondary alcohols has also been reported.[21] A probable mechanism for the formation of **2** involves generation of oxonium ion **4** which C-alkylates the predominant enol form of 1,3-cyclopentanedione.[14]

We now set out to introduce the double bond via phenylselenenylation, followed by oxidation.[22-24] Although 2-methyl-1,3-cyclopentanedione reacted with phenylselenenyl chloride as reported,[23] the analogous reaction of **2b** gave none of the desired product, but only a complex mixture of unidentified products.

Phenylsulfenylation has recently been advocated as preferable to phenylselenenylation for synthesis of 2-alkylidene-1,3-cyclopentanediones.[24] Preparation of the required *N*-(phenylthio)succinimide (**9**) proved unexpectedly difficult. Reaction between *N*-bromosuccinimide and thioanisole according to a literature procedure[25] afforded only a mixture of succinimide and diphenyl disulfide. This mixture could be separated chromatographically and identified; however, its ^1H NMR and melting point deceptively corresponded to that reported for *N*-(phenylthio)succinimide (**9**). Most importantly, this mixture did not undergo known reactions of *N*-(phenylthio)succinimide. In contrast, *N*-(phenylthio)succinimide (**9**) was successfully prepared from phenylmercaptan and *N*-chlorosuccinimide.[26] The ^{13}C NMR spectrum of **9** differed from that of the mixture of succinimide and diphenyl disulfide. Authentic **9** successfully phenylsulfenylated dibenzoylmethane, 1,3-cyclopentanedione, and 2-methyl-1,3-cyclopentanedione, as previously described.[24,27]

Reaction of **2b** with *N*-(phenylthio)succinimide (**9**) in the presence of triethylamine gave phenylthio dione **10**



which was oxidized to the corresponding phenyl sulfoxide with *m*-chloroperbenzoic acid. Elimination[24,28] of phenylsulfenic acid at 65 °C provided oudenone (**1**). Column chromatography to remove various sulfur-containing byproducts which arose from decomposition of phenylsulfenic acid,[29] afforded pure oudenone, the spectral and physical properties of which were consistent with the literature.[3]

Experimental Section

General Procedures. Routine ^1H NMR spectra were recorded at 80 MHz on a Varian HFT-80 spectrometer; higher resolution ^1H NMR spectra were recorded at 300 MHz on a Varian NT-300NB spectrometer; ^{13}C NMR were recorded on a Varian CFT-20 spectrometer. Unless other otherwise noted, ^1H NMR spectra were obtained in $CDCl_3$ solution with an internal Me_4Si reference. IR spectra were recorded on a Unicam SP 1000 spectrophotometer. Low-resolution mass spectra were recorded on a HP 5984A spectrometer, and high-resolution mass spectra were obtained on a Kratos MS-30 spectrometer. Gas chromatography was performed on a 6 ft × $^1/_8$ in. 10% SE-30 column in an HP 5830A chromatograph with flame ionization detection. Reactions were generally run under nitrogen and stirred magnetically. After extraction, organic phases were generally washed with saturated NaCl and dried over anhydrous $MgSO_4$. Solutions were evaporated in vacuo on a rotary evaporator.

Dihydro-5-propyl-2(3*H*)-furanone (5b). Pentanal (25.8 g, 300 mmol), malonic acid (31.2 g, 300 mmol, 100 mol %), and Et_3N (45.3 g, 447 mmol, 150 mol %) were refluxed under nitrogen for 1 h.[13] The mixture was cooled, acidified with 1 M HCl (350 mL)

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to pH 0.7, and extracted 5 times with ether. The combined organic phase was washed with brine, dried over $MgSO_4$, filtered and evaporated. The residue was treated with 85% H_2SO_4 (32 g) at 85 °C for 1 h, neutralized to pH 7 with 20% Na_2CO_3 (300 mL), and extracted 5 times with ether. The combined organic phase was washed wiith brine and dried, and the solvent was evaporated to give crude **5b** (29.04 g, 76%) which was purified by Kugelrohr distillation (135–155 °C, 35 mm) to afford a yellow oil (20.79 g, 54% yield): GC (180 °C) 3.52 min, 89% pure; ^1H NMR ($CDCl_3$) δ 0.95 (3 H, t, CH_3), 1.55 (6 H, m, $OCCH_2CH_2CH_3$, CH_2CH_2CHO), 2.40 (2 H, d, $CH_2C{=}O$), 4.46 (1 H, t, CHO); ^{13}C NMR ($CDCl_3$) δ 13.19, 18.17, 27.62, 28.44, 37.26, 80.42, 176.87; IR consistent with published spectrum.[30]

Tetrahydro-2-furanol (6a). 2,3-Dihydrofuran (5.00 g, 71.4 mmol) was added to 1 M aqueous sulfuric acid (50 mL). The mildly exothermic reaction was stirred for 20 min and then extracted 6 times with ethyl acetate. The organic phase was washed with saturated sodium carbonate (10 mL) and dried over sodium sulfate. Evaporation of the solvent in vacuo afforded crude product (4.97 g) which was purified by kugelrohr distillation (95–125 °C (60 torr)) to provide tetrahydro-2-furanol (3.76 g, 60%), slightly contaminated with ethyl acetate. Conventional distillation of the crude product afforded pure tetrahydro-2-furanol in lower yield (28%), bp 84–85 °C (40 torr) [lit.[11] bp 88–89 °C (35 torr)]. As has previously been reported,[11] NMR shows that tetrahydro-2-furanol exists in equilibrium with 15% 4-hydroxybutanal. Immediately after distillation, very little 4-hydroxybutanal was present. Partial decomposition occurred after 1 week at −10 °C. Mass, IR, and ^1H NMR spectra were in agreement with previously reported spectra.[11]

5-Propyltetrahydrofuran-2-ol (6b). Lactone **5b** (500 mg, 3.84 mmol) in 5 mL of toluene was cooled to −20 °C external temperature under N_2, and DIBAH (5.6 mL, 1.5 M in toluene, 8.4 mmol, 219 mol %) was added by syringe over 5 min.[31] After 30 min at 0 °C (external temperature), a solution of 2 M 2-propanol in toluene (15.3 mL) followed by H_2O (1.9 mL) was added. After 20 min, $MgSO_4$ (1.9 g) and Celite (1.9 g) were added, and after 20 min, the mixture was filtered, the solid was washed 3 times with ether, and the solvent was evaporated to give *cis*- and *trans*-**6b** (450 mg, 89% yield): GC (200 °C) 1.27 min; mass spectrum, *m/e* 130 (1, M+), 87 (100), 69 (49), 57 (59), 55 (51), 43 (42), 41 (45); ^1H NMR ($CDCl_3$) δ 0.95 (3 H, br t, CH_3), 1.40 (6 H, m, $OCCH_2CH_2CH_3$, CH_2CH_2CHO), 1.90 (2 H, m, CH_2CO), 3.60 (1 H, m, OCH), 3.80 (1 H, s, OH), 5.40 (1 H, br t, $HC(OH)O$); ^{13}C NMR ($CDCl_3$) δ 13.72, 18.84, 19.06, 28.84, 29.06, 33.01, 33.81, 37.42, 39.26, 76.94, 80.20, 97.51, 97.64.

2-Chloro-5-propyltetrahydrofuran (7b). Hydrogen chloride gas was slowly bubbled into 5-propyltetrahydrofuran-2-ol (**6b**) (300 mg, 2.31 mmol) and $CaCl_2$ (800 mg) in 3 mL of methylene chloride at −30 °C (external) for 10 min. More methylene chloride (1 mL) was added and the solution was dried over calcium chloride (400 mg) and then filtered. Evaporation of the solvent at 25 °C gave **7b** (240 mg, 70% yield): mass spectrum, *m/e* 113 (100 M − Cl), 95 (52), 69 (10), 58 (10), 55 (10); ^1H NMR ($CDCl_3$) δ 0.90 (3 H, br t, CH_3), 1.45 (6 H, m), 2.35 (2 H, m, CH_2CHCl), 4.5 (1 H, m, $OCHPr$), 6.30 (1 H, br t, HCCl). This very reactive material can be stored at −10 °C for a day or two with no decomposition.

Dimethyl (5-Propyltetrahydrofuran-2-yl)malonate (8). Dimethyl malonate (132 mg, 1.00 mmol, 100 mol %) was added dropwise to a suspension of NaH (55 mg of 50% dispersion in mineral oil rinsed with hexane, 1.15 mmol, 115 mol %) in dimethoxyethane (1 mL, distilled from $LiAlH_4$) at 0 °C.[9] After 5 min, 2-chloro-5-propyltetrahydrofuran (**7b**) (148 mg, 1.00 mmol) in 1,2-dimethoxyethane was added over 5 min by syringe. After 35 min, water (0.25 mL) was added, the organic layer was decanted, and the aqueous layer was extracted twice with ether (3 mL). The evaporation of the solvent from the combined organic phases and kugelrohr distillation (95–115 °C, 0.6 mm) provided a 2:1 mixture of *trans* and *cis*-8 (125 mg, 51% yield): GC (180 °C); ^1H NMR ($CDCl_3$) δ 0.95 (3 H, t, CH_3), 1.4 (6 H, m), 1.75–2.25 (2 H, m), 3.45 and 3.50 (1 H, two d, J = 12 Hz; $CH(CO_2Me)_2$), 3.71 (3 H, s, OCH_3), 3.75 (3 *H*, s, OCH_3), 3.95 (1 H, m, HCO), 4.50 (1 H, m, HCO).

2-(Tetrahydrofuran-2-yl)-1,3-cyclopentanedione (2a). Reaction between 1,3-cyclopentanedione (98 mg, 1.00 mmol, 100 mol %) and tetrahydrofuran-2-ol (**6a**) (88 mg, 1.00 mmol) as described for the synthesis of **2b** afforded crude **2a** (100 mg, 60% yield) which was purified by chromatography to give **2a** (57 mg, 34% yield), mp 115–116 °C: ^1H NMR ($CDCl_3$) δ 1.9 (4 H, m), 2.45 (4 H, m, $O{=}CCH_2$), 3.87 (2 H, m, CH_2O), 4.70 (1 H, t, OCH); ^{13}C NMR ($CDCl_3$) δ 25.60, 29 (br), 31.65, 68.30, 77.58, 116.76, C=O not observed.

2-(5-Propyltetrahydrofuran-2-yl)-1,3-cyclopentanedione (2b). Lactol **6b** (1.43 g, 11.0 mmol) followed by trifluoroacetic acid (2.51 g, 22.0 mmol, 200 mol %) was added to 1,3-cyclopentanedione (1.08 g, 11.0 mmol, 100 mol %) suspended in CH_2Cl_2 (15 mL). After 1.5 h at room temperature, the solvent was evaporated and saturated sodium carbonate was added to pH 10.5. The solution was extracted 3 times with CH_2Cl_2. The aqueous phase was adjusted to pH 2 with 6 M HCl and extracted 5 times with methylene chloride to provide crude **2b** (1.79 g, 78% yield). Flash chromatography (acetone/methylene chloride 1:1) gave **2b**, a mix of cis and trans isomers (981 mg, 43%) which by TLC was one spot (R_f 0.44, UV visualization, acetone–methylene chloride 1:1): GC (210 °C); mass spectrum, *m/e* 210.1249 (18, M^+, calcd 210.1256), 140 (48), 138 (55), 125 (100), 95 (27); ^1H 300-MHz NMR ($CDCl_3$) (cis–trans mix 57:43 by NMR) δ 0.93 and 0.95 (3 H, t, CH_3, 1.20–2.10 (8 H, m, $CH_2CH_2CH_3$, $OCHCH_2CH_2$), 2.55 (4 H, m, $O{=}CCH_2$), 3.90 and 4.06 (1 H, p, HCO), 4.80 (1 H, m, HCO); ^{13}C NMR ($CDCl_3$) δ 14.06, 19.49, 19.59, 26.92, 30.84, 31.45, 31.62, 32.46, 33.35, 37.81, 77.11, 77.55, 79.92, 80.25, 116.98, 185.00, 203.15.

***N*-(Phenylthio)succinimide (9)** was prepared from recrystallized *N*-chlorosuccinimide in 40% yield as previously described.[26] Recrystallization was unnecessary since the product was one spot by TLC, R_f = 0.55 (ether–EtOAc 1:1), and had the reported melting point (115°–116 °C: ^1H NMR ($CDCl_3$) δ 2.79 (4 H, s), 7.25 (3 H, m) 7.60 (2 H, m); ^{13}C NMR ($CDCl_3$) δ 28.58, 129.29, 129.79, 132.00, 176.37.

Oudenone (1). *N*-(Phenylthio)succinimide (72.8 mg, 0.350 mmol, 100 mol %) and triethylamine (42.49 mg, 0.4% mmol, 120 mol %) were added to dione **8** (73.7 mg, 0.350 mmol) dissolved in dry methylene chloride (2 mL).[24,27] After 12 h at 20 °C, the solvent was evaporated and 2 mL of water was added. The pH was adjusted to 1.4 with 1 M HCl, and the aqueous layer was extracted 4 times with methylene chloride. The methylene chloride solution was then extracted twice with saturated sodium carbonate solution and dried over anhydrous sodium sulfate to provide crude **10** (77.7 mg, 70% yield).

Crude **10** (77.7 mg, 0.243 mmol) in methylene chloride (2 mL) was treated with *m*-chloroperbenzoic acid (50.4 mg, 0.292 mmol, 120 mmol %) at 0 °C for 40 min.[28] More methylene chloride (2 mL) was added, and the solution was extracted twice with saturated sodium bicarbonate and once with brine and dried over anhydrous sodium sulfate. The solvent was evaporated, chloroform (3 mL) was added, and the mixture was heated at 65 °C for 2 h. The solvent was evaporated to afford crude oudenone contaminated with sulfur-containing compounds (72 mg). Flash chromatography (chloroform/acetone 9:1) afforded pure oudenone (1) (13.9 mg, 27% yield): TLC (chloroform–acetone 9:1): R_f 0.29; mp 74–75 °C (lit. mp 77–78 °C[3]); ^1H 300-MHz NMR ($CDCl)_3$ δ 0.98 (3 H, t, CH_3), 1.3–2.3 (6 H, m), 2.59 (4 H, s, $O{=}CCH_2$), 3.22 (1 H, ddd, J = 9.9, 9.4, 20.6 Hz, $=CCH_2$), 3.59 (1 H, ddd, J = 4.9, 10.1, 20.6 Hz, $=CCH_2$), 4.90 (1 H, p, J = 6.8 Hz, HCO); ^{13}C NMR ($CDCl_3$) δ 13.87, 18.72, 26.91, 33.79, 34.67, 35.00, 36.81, 90.53, 109.34, 184.68, 200.90, 204.28. The 80-MHz ^1H NMR spectrum was consistent with the literature spectrum.[3]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research and to the National Science Foundation for Grant CHE 811412 which enabled purchase of the 300-MHz NMR spectrometer.

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