A New Synthesis of Cyclopentenones: Dihydrojasmone

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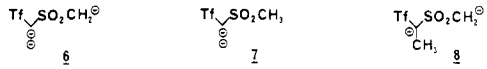
A new general olefin synthesis, via alkylation of an α-trifyl sulfone and subsequent Ramberg–Bäcklund elimination of triflinate and SO_2, is here applied to the synthesis of cyclopentenones, including dihydrojasmone and methylenomycin B.

In a recent report[1] we described a general synthesis of olefins via the Ramberg–Bäcklund reaction,[2] utilizing the mesyltriflone reagent **1**. This method has now been successfully applied to the synthesis of several natural products. In this paper we describe the synthesis of some cyclopentenones, including dihydrojasmone (**5a**) and 2,3-dimethylcyclopentenone (**5b**), from which methylenomycin B has recently been made.[3] 2-Hydroxy-3-methyl-2-cyclopentenone is the flavoring ingredient of maple syrup[4] and has also been found in roasted coffee.[5] It has been synthesized[6] from 3-methyl-2-cyclopentenone (**5c**). In recent years, much work has been devoted[6,7] to preparation of ketones of the type **5**, and our present method, outlined in Scheme I, represents a novel and useful alternative.

The α,α,α′-trianion **6** (which results from the reaction of **1** with 3 equiv of *n*-butyllithium in THF at −50 °C[1]) was allowed to react with excess methyl iodide to give **2b** in 95% yield. The dihydrojasmone precursor, **2a**, however, is most efficiently made by first methylation of the α,α-dianion **7** (which results from reaction of **1** with 2 equiv

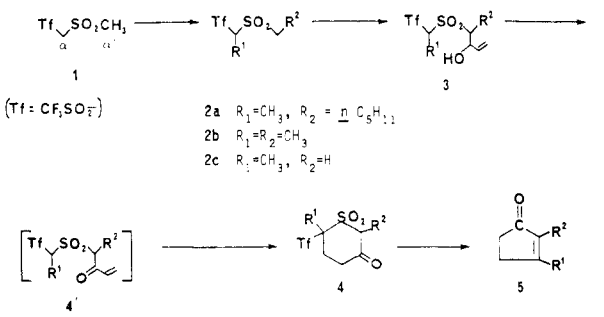


of *n*-butyllithium in THF at −78 °C), followed by generation of the new α,α′-dianion **8** (with another equivalent of *n*-butyllithium in THF at −78 °C), and finally alkylation with 1-iodopentane. An acid workup of this "one-pot reaction" gives a 70% yield of dialkylated product **2a**.

Formation of the α,α′-dianion of sulfones **2** with 2 equiv of *n*-butyllithium in THF at −78 °C followed by slow addition of acrolein leads to allylic alcohols **3**. This crude product was treated with either activated manganese dioxide or Jones reagent to give cyclic keto sulfones **4** via oxidation and spontaneous cyclization. TLC of the reaction medium as the reaction proceeded showed no indication of a stable enone intermediate **4′**. The oxidation/cyclization is apparently very facile under neutral as well as acidic conditions.

The final step to generate **5** from **4** via the Ramberg–Bäcklund reaction was accomplished in quantitative yield

Scheme I



by treatment of **4** with excess potassium carbonate in THF at reflux for 3–5 h. Compounds **5** were identified by comparison of their IR, ^1H NMR, and MS with those recently described.[8] The yields of the various steps have not been optimized. Further development and applications of this method are in progress and will be reported later.

Experimental Section

General. Proton magnetic resonance spectra were recorded on a Varian EM-390 spectrometer; chemical shifts are expressed in parts per million downfield from tetramethylsilane as internal standard. Infrared spectra were recorded on a Perkin-Elmer 137 spectrometer and the data are presented in microns. Mass spectra were determined on a Hewlett-Packard Model 5985 spectrometer. Melting points (uncorrected) were determined on a Mel-Temp apparatus in open capillary tubes. Tetrahydrofuran (THF) was distilled from sodium–benzophenone ketyl. Manganese dioxide (MnO_2) was obtained from Aldrich and used directly. *n*-Butyllithium was titrated periodically with 2,5-dimethoxybenzyl alcohol as indicator. Trifyl fluoride was a gift from 3M Co. Other commercially supplied chemicals were distilled when appropriate and stored under nitrogen in the freezer. The silica gel used for chromatography was Kieselgel 60 (0.040–0.063 mm/230–400 mesh ASTM). Thin-layer chromatography was performed on 0.25-mm silica gel, glass-backed plates with the designation GHLF (Analtech). Reactions were carried out under an atmosphere of dry nitrogen in flame-dried glassware. Transfer of moisture-sensitive liquids was performed by hypodermic syringe or cannula through rubber septa. Elemental analyses were carried out by Galbraith Laboratories, Knoxville, TN.

Mesyltriflone (1). Ethylmagnesium bromide (127.5 mL, 0.255 mol, 2 M in THF) was added dropwise over 30 min to a mechanically stirred solution of dimethyl sulfone (20 g, 0.212 mol) in 400 mL of dry THF contained in a nitrogen-flushed, flame-dried, 1-L three-neck flask, equipped with a dry ice–acetone condenser. After the addition, stirring was continued at room temperature under nitrogen for 1 h, during which time the initial gummy precipitate that formed became a suspended powder. Triflyl fluoride (CF_3SO_2F; 3M Co.) was then bubbled directly into the stirred solution, until all of the solid had dissolved. The

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solution was allowed to stir overnight. HCl (75 mL, 3 N) was then cautiously added, with stirring. The resulting two-phase mixture was transferred to a separatory funnel and separated. The aqueous phase was extracted with another 100 mL of ether. The combined organics were washed with brine and dried over magnesium sulfate, and the solvent was removed in vacuo. The crude product was recrystallized from water and then dried over phosphorus pentoxide, in vacuo, yielding 13 g (54%): mp 115–116 °C; ^{1}H NMR (acetone-d_6) δ 3.40 (s, 3 H), 5.75 (s, 2 H).

Anal. Calcd for $C_3H_5S_2O_4F_3$: C, 15.93; H, 2.23; S, 28.35; F, 25.20. Found: C, 15.93; H, 2.11; S, 28.53; F, 24.68.

α-Methyl-α'-pentylmesyltriflone (2a). *n*-Butyllithium (5.1 mL, 8.70 mmol, 1.7 M in hexane) was added dropwise to a stirred THF solution of 0.984 g (4.35 mmol) of mesyltriflone (1) under nitrogen at −78 °C. The bath was allowed to warm to −50 °C, 0.27 mL (4.35 mmol) of methyl iodide was added, and the mixture was warmed further to 0 °C. The solution was recooled to −78 °C and then 2.55 mL (4.35 mmol) of *n*-butyllithium (1.7 M in hexane) was added dropwise. The resulting mixture was warmed to −50 °C, stirred for 10 min, and then recooled to −78 °C. Pentyl iodide (0.63 mL, 4.79 mmol) was introduced dropwise and the bath was allowed to slowly warm to room temperature over 1 h. HCl (8 mL, 3 N) was added and the resulting mixture was transferred to a separatory funnel with 200 mL of ether. The aqueous phase was removed and extracted with 20 mL of ether. The combined organics were washed with saturated sodium bisulfite solution, dried over magnesium sulfate, and evaporated in vacuo to afford 1.27 g of crude product as an amber oil. This was purified by chromatography on silica gel using petroleum ether/methylene chloride (60:40). Combining the appropriate fractions and evaporation of solvent afforded 0.94 g (70%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.9 (brt, 3 H), 1.2–1.65 (m, 6 H), 1.95 (d, J = 8 Hz, 3 H), 1.7–2.1 (m, 2 H), 3.3–3.55 (m, 2 H), 4.55 (q, J = 8 Hz, 1 H); IR (CH_2Cl_2) λ_{max} 3.25, 7.29, 7.5, 8.3, 8.75, 9.0 μm.

6-Methyl-2-*n*-pentyl-6-[(trifluormethyl)sulfonyl]tetrahydrothiopyran-3-one 1,1-Dioxide (4a). *n*-Butyllithium (3.3 mL, 5.54 mmol, 1.7 M in hexane) was added dropwise with stirring to 0.818 g (2.64 mmol) of substituted mesyltriflone **2a** in 40 mL of dry THF at −78 °C under nitrogen. The bath was allowed to warm to −50 °C and stirred at that temperature for 20 min. The mixture was recooled to −78 °C and 0.53 mL (7.91 mmol) of acrolein was added dropwise. The bath was allowed to warm to 0 °C, 10 mL of saturated ammonium chloride solution was added, and the mixture was transferred to a separatory funnel with 200 mL of ether. The aqueous phase was removed and extracted with an additional 50 mL of ether. The combined organic phase was dried over magnesium sulfate, and the solvent was removed in vacuo. The crude residue was stirred in 40 mL of acetone, cooled to 0–5 °C, and treated with 1 mL of chromic acid solution (2.67 M chromium trioxide) in one portion. Stirring was continued at 0–5 °C for 1 h, with periodic addition of more chromic acid solution as required to oxidize all of the intermediate allyl alcohol (monitored by TLC, methylene chloride). The solution was finally diluted with 50 mL of water and extracted with three 50-mL portions of methylene chloride. The combined organic phase was washed with 25 mL of water and dried over magnesium sulfate, and the solvent was removed in vacuo. The crude product was purified by passing down a short column of silica with methylene chloride. The appropriate fractions were combined, and the solvent was evaporated to give 0.4 g (42%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.9 (brt, 3 H), 1.2–1.8 (m, 6 H), 2.0 (s, 3 H), 1.9–2.5 (m, 3 H), 2.6–3.3 (m, 3 H), 4.75 (dd, J_1 = 8 Hz, J_2 = 5 Hz); IR (CH_2Cl_2) 3.3, 5.74, 7.35, 8.35, 9.15 μm; MS, m/e 365 (M+).

Anal. Calcd for $C_{12}H_{19}S_2O_5F_3$: C, 39.55; H, 5.26; S, 17.60; F, 15.64. Found: C, 39.15; H, 5.78; S, 17.71; F, 15.65.

Dihydrojasmone (5a). Keto sulfone **4a** (0.219 g, 0.601 mmol) and 0.17 g (1.201 mmol) of finely ground anhydrous potassium carbonate were combined in 5 mL of dry THF and heated to reflux under nitrogen for 3 h. The solvent was then evaporated in vacuo to dryness and the resulting residue was extracted into ether and filtered through Celite. Evaporation of the filtrate gave 0.10 g (100%) of a clear liquid which was homogeneous on TLC (methylene chloride). Spectral samples were obtained by passing down a silica plug with methylene chloride as eluent: ^{1}H NMR ($CDCl_3$) δ 0.85 (br t, 3 H), 1.0–1.6 (m, 6 H), 2.05 (s, 3 H), 1.9–2.6 (m, 6 H); IR (CH_2Cl_2) 3.29, 5.90, 6.06, 7.27, 9.43 μm; MS, m/e 166 (M^+) (lit. ref 8).

α,α'-Dimethylmesyltriflone (2b). Mesyltriflone (1) (0.411 g, 1.82 mmol) was dissolved in 17 mL of dry THF and then cooled under nitrogen to −78 °C. To this stirred solution was added 3.74 mL (6.0 mmol) of *n*-butyllithium (1.6 M in hexane) dropwise. The cooling bath was allowed to warm to −50 °C and the mixture was stirred at this temperature for 1.5 h, during which time the insoluble dianion **7** disappeared to give the soluble trianion **6**. The solution was then recooled to −78 °C and 0.4 mL (6.36 mmol) of methyl iodide was introduced dropwise. The cooling bath was then allowed to warm to room temperature. After the mixture was stirred for 45 min, 10 mL of 1 N hydrochloric acid was added dropwise and the mixture was transferred to a separatory funnel with 150 mL of ether. The organic phase was washed two times with 10 mL of 1 N hydrochloric acid, once with 10 mL of saturated sodium bisulfite, and once with 10 mL of brine and then dried over magnesium sulfate. The solvent was then removed in vacuo, yielding 0.44 g (95%) of a pale yellow liquid. This oil is most conveniently prepared for subsequent anion chemistry by passing down a short column of silica in methylene chloride: ^{1}H NMR ($CDCl_3$) δ 1.5 (t, J = 7 Hz, 3 H), 1.95 (d, J = 7 Hz, 3 H), 3.5 (q, J = 7 Hz, 2 H), 4.6 (q, J = 7 Hz, 1 H).

2,6-Dimethyl-6-[(trifluoromethyl)sulfonyl]tetrahydrothiopyran-3-one 1,1-Dioxide (4b). Method A (Jones Oxidation). Dimethylmesyltriflone (**2b**) (1.05 g, 4.12 mmol) was dissolved in 40 mL of dry THF and cooled under nitrogen to −78 °C. To this stirred solution was added 5.6 mL (9.50 mmol) of *n*-butyllithium (1.7 M in hexane) dropwise. The cooling bath was allowed to warm to −55 °C and stirred for 15 min. The solution was recooled to−78 °C and 0.55 mL (8.26 mmol) of acrolein was added dropwise. The bath was allowed to warm to 0 °C over 1 h. This cold (0 °C) mixture was then treated with 15 mL of saturated ammonium chloride and extracted with ether (2 × 150 mL). The combined organics were washed with brine and dried over magnesium sulfate, and the solvent was removed in vacuo. The residue was dissolved in 25 mL of acetone, and the mixture was cooled to 0 °C and then treated in one portion with 1.5 mL of Jones reagent. Stirring was continued at 0 °C as judicious amounts of reagent were added to complete the oxidation of allylic alcohol (monitored by TLC, methylene chloride). After 1 h, excess oxidant was destroyed by addition of isopropyl alcohol and the solution was diluted with water and extracted with methylene chloride. The combined methylene chloride extracts were washed several times with water, dried over magnesium sulfate, and evaporated in vacuo to give 1.16 g of crude yellow syrup, purified by passing down a short column of silica in methylene chloride. Evaporation of the appropriate fractions gave an oil which crystallized: 0.4 g (30%); mp 115–122 °C (methylene chloride-/petroleum ether).

Method B (Manganese Dioxide Oxidation). Dimethylmesyltriflone (**2b**) (0.535 g, 2.1 mmol) was dissolved in 10 mL of dry THF and cooled under nitrogen to −78 °C. To this stirred solution was added 2.6 mL (4.4 mmol) of *n*-butyllithium (1.7 M in hexane) dropwise. The cooling bath was allowed to warm to −55 °C and stirred for 15 min. The solution was recooled to −78 °C and treated dropwise with 0.18 mL (2.74 mmol) of acrolein, and the bath was allowed to warm to 0 °C over 1 h. This cold mixture was treated with 5 mL of saturated ammonium chloride and extracted with 75 mL of ether. The organic phase was washed with brine, dried over magnesium sulfate, and evaporated to give 0.61 g of crude product, purified by chromatography on silica in methylene chloride, yielding 0.5 g (77%) of the allylic alcohol as a mixture of diastereomers (TLC shows two components, R_f 0.2 and 0.4 with methylene chloride). The mixture of diastereomers was dissolved in 10 mL of methylene chloride, treated with 1.0 g of activated manganese dioxide under nitrogen, and stirred at room temperature for 18 days. Additional manganese dioxide was added during this period to drive the reaction to completion. A single product is formed: TLC showed the two-spot allylic alcohol mixture disappears to give one new, higher R_f material (R_f 0.5, methylene chloride). The mixture was then filtered through Celite and evaporated in vacuo to afford 0.45 g (90%) of crystalline product, identical in every respect with that obtained in method A above: ^{1}H NMR ($CDCl_3$) δ 1.63 (d, J = 7 Hz, 3 H), 2.0 (br s, 3 H), 2.1–3.3 (m, 4 H), 4.9 (q, J = 7 Hz, 1 H); IR (CH_2Cl_2)

5.71, 7.41, 7.55, 8.33, 8.77, 9.26, 9.71 μm; MS, m/e 308 (M^+).

Anal. Calcd for $C_8H_{11}S_2O_5F_3$: C, 31.17; H, 3.60; S, 20.80; F, 18.49. Found: C, 31.34; H, 3.44; S, 20.83; F, 18.16.

1,2-Dimethylcyclopentenone (5b). Cyclic keto sulfone **4b** (0.155 g, 0.503 mmol) and 0.14 g (1.01 mmol) of finely ground anhydrous potassium carbonate were combined in 6 mL of dry THF and heated to reflux under nitrogen for 5 h. The solution was cooled to room temperature, evaporated in vacuo, and extracted with ether. This was filtered through Celite, and the filtrate was evaporated in vacuo to give a pale yellow liquid, 0.058 g (100%), homogeneous on TLC: ^1H NMR ($CDCl_3$) δ 1.7 (br s, 3 H), 2.05 (s, 3 H), 2.1–2.6 (m, 4 H); IR (CH_2Cl_2) 5.92, 6.06 μm; MS, m/e 110 (M^+) (lit. ref 8).

α-Methylmesyltriflone (2c). See synthesis of **2a**. After the addition of methyl iodide and subsequent warming to 0 °C, the reaction was quenched with excess 1 N HCl. Ether extraction affords colorless crystals in 95% yield: mp 74–75 °C (methylene chloride/petroleum ether); ^1H NMR ($CDCl_3$) δ 1.95 (d, J = 7 Hz, 3 H), 3.30 (s, 3 H), 4.60 (q, J = 7 Hz, 1 H).

Anal. Calcd for $C_4H_7S_2O_4F_3$: C, 20.00; H, 2.94; S, 26.69; F, 23.73. Found: C, 20.19; H, 2.75; S, 26.93; F, 23.37.

6-Methyl-6-[(trifluoromethyl)sulfonyl]tetrahydrothiopyran-3-one 1,1-Dioxide (4c). This compound was synthesized according to method A above: 30% yield; mp 116–117 °C; ^1H NMR ($CDCl_3$) δ 2.0 (br s, 3 H), 2.25–3.28 (m, 4 H), 4.51 (AB q, J = 12 Hz, 2 H); IR (CH_2Cl_2) 5.70, 7.38, 7.47, 8.33, 8.82, 9.16, 9.35 μm.

Anal. Calcd for $C_7H_9S_2O_5F_3$: C, 28.57; H, 3.08; S, 21.79; F, 19.37. Found: C, 28.58; H, 3.06; S, 21.98; F, 19.03.

3-Methyl-2-cyclopentenone (5c). See procedure for **5b** (reaction time 7 h): yield 50%;[9] ^1H NMR ($CDCl_3$) δ 2.15 (br s, 3 H), 2.3–2.7 (m, 4 H), 5.9 (q, J = 1 Hz, 1 H); IR (neat) 3.32, 5.86, 6.15, 7.02, 7.14, 7.30, 7.60, 7.84, 8.16, 8.55, 8.85, 10.05, 11.98 μm (lit. ref 8).

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Registry No. 1, 93916-15-5; **2a**, 93916-04-2; **2a**·$2Li^+$, 96247-06-2; **2b**, 93915-93-6; **2b**·$2Li^+$, 96247-07-3; **2c**, 93915-89-0; **2c**·Li^+, 96247-08-4; **3a**, 96247-09-5; **3b**, 96247-10-8; **3c**, 96247-11-9; **4a**, 96247-12-0; **4a′**, 96247-13-1; **4b**, 96247-14-2; **4b′**, 96247-15-3; **4c**, 96247-16-4; **4c′**, 96247-17-5; **5a**, 1128-08-1; **5b**, 1121-05-7; **5c**, 2758-18-1; **6**, 96247-18-6; **7**, 96247-19-7; **8**, 96247-20-0; CF_3SO_2F, 335-05-7; $CH_3(CH_2)_4I$, 628-17-1; $MeSO_2Me$, 67-71-0; acrolein, 107-02-8.

(9) This low yield was partly due to the instability of **5c**.

Methylation of Polysubstituted Electron-Rich Aromatics and Their Birch Reduction

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3,4,5-Trimethoxybenzoic, 3,5-dimethoxybenzoic, and (3,5-dimethoxyphenyl)acetic acids, and their esters, react with either 1 or 2 mol of (methylthio)methyl chloride (MTM-Cl) and zinc chloride to form the 2-mono- or 2,6-bis[(methylthio)methyl] (MTM) derivatives, which yield the corresponding methyl derivatives with Raney nickel. Normal Birch reduction also removes the methylthio group and, in the benzoic acids, the aromatic ring is converted to dihydroresorcinols. In the phenylacetic acid case, only with more vigorous reduction conditions is the dihydroresorcinol formed.

In the course of other studies directed toward the synthesis of quassinoids, we had occasion to require practical syntheses of the 2,6-dimethyl-3,5-dimethoxy and -3,4,5-trimethoxy aromatic acids **1c–3c** (Chart I). The most amenable approach to these compounds seemed to be electrophilic aromatic substitution of two one-carbon synthons on an appropriate aromatic acid or ester. However, traditional methods for effecting this transformation proved futile. Strong Lewis acid conditions were known to promote demethylation of methoxy groups when conjugated to electron-withdrawing substituents (e.g., 1; R = OMe → R = OH), and formylation reactions (such as Gattermann or Gattermann–Koch) would be expected to stop at the monoacylation stage. Hydroxymethylation/chloromethylation reactions using chloromethyl methyl ether, generated in situ from formaldehyde/hydrochloric acid/methanol, were ineffective in alkylating 3,4,5-trimethoxybenzoic acid **1a** or ester **1b**.[2] Reaction of methyl gallate (3,4,5-trihydroxybenzoate) with formaldehyde/hydrochloric acid/methanol did result in substitution at the two residual aromatic positions, but the product proved to be the diarylmethane bis(lactone) **4a**, characterized as **4b** after permethylation. Compound **4** presumably arises from interception of a transiently generated quinomethane species by unreacted methyl gallate.

To surmount these problems we sought a reagent to activate the alkylation but create a poor leaving group at the benzylic position. We now report that chloromethyl methyl sulfide (MTM-Cl), catalyzed by zinc chloride in either methylene chloride or 1,2-dichloroethane, is an excellent reagent for effecting this alkylation and for generating compounds **5–8**. Chloromethyl methyl sulfide had been used in the past under strong Lewis acid conditions ($TiCl_4$)[3] for alkylating simple aromatics, and recently, Tamura and co-workers have described the use of ethyl chloromethyl thioglycolate for this same purpose.[4] We find that either predominant monoalkylation (to **5**) or bisalkylation (**6–8**) can be achieved by choice of stoichiometry or reaction times and that regioselectivity of alkylation using compounds **2a,b** or **3a,b** strongly favors reactions at the 2- and 6-positions, with virtually no substitution at the 4-position. Prolonged reaction times after

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