Table IV. Efficiency of Desiccants in the Drying[a] of Acetone[b]

desiccant	residual solvent water content, ppm 6 h	24 h	72 h	other conditions
B_2O_3				18[c,d]
				47[c,e]
				107[f]
3A molecular sieves	115	152	322[g]	322[h]
$CuSO_4$ (anhydrous)	1920	972	579	1700[h]
4A molecular sieves	331	887	1720	
$CaSO_4$	1590	1600		
BaO	1910	1870[i]		
P_2O_5	*j*			1970[f]
K_2CO_3	2057	2250		

[a] Static drying modes unless specified otherwise. [b] Desiccant loading 5% w/v; initial water content 2710 ppm (0.271% w/w), unless specified otherwise. [c] Initial water content 2890 ppm (0.289% w/w). [d] Stirred, distilled, and sequentially dried, 24 h. [e] Stirred for 24 h and distilled. [f] Dried for 24 h and then distilled. [g] Contamination (2%) by mesityl oxide. [h] Fractionated sample. [i] Contamination (12%) by mesityl oxide. [j] Brown-black solutions.

Experimental Section

Desiccants. Details of the source, activation, and handling of most of the desiccants have already been described.[1] Reagent grade cupric sulfate was activated by heating at 320 °C for 15 h before use. Barium and calcium oxides were of reagent grade, and a fresh batch was used directly without activation.

Solvents. DMF, Me_2SO, and HMPT were commercial synthetic grades of 99% purity (Merck). Acetone was of analytical grade (M&B). All solvents were rigorously purified by standard methods.[8]

HMPT and Me_2SO were treated by standing over barium oxide overnight, followed by filtration, distillation from calcium hydride, and subsequent storage over 20% w/v 4A molecular sieves. Me_2SO had bp 74.5–75.0 °C at 12 mmHg, and HMPT had bp 89.0–89.5 °C at ~3 mmHg.

Commercial DMF was allowed to stand over 4A molecular sieves overnight and was filtered, distilled from phosphorus pentoxide (bp 55.8–56.0 °C at 20 mmHg), allowed to stand over anhydrous potassium carbonate, and subsequently stored over 4A molecular sieves.

Analytical grade acetone was allowed to stand over anhydrous potassium carbonate for one day and then over 4A molecular sieves overnight. Fractionation gave material, bp 56.2 °C, which was not stored but used immediately. Gas chromatographic analysis of this material showed it to be free of impurities.

Techniques. The procedure used for HMPT serves as an example. A stock solution of HMPT containing 2620 ppm of labeled water was prepared by the addition of 0.50 g of tritiated water, specific activity 0.5 mCi/mL, to the appropriate mass of purified rigorously dried HMPT. Aliquots of the stock solution (15.0 ± 0.1 mL) were syringed directly onto the appropriate desiccant contained in a 25 mL clear-fit round-bottom flask, which was immediately stoppered. Experiments were conducted at ambient temperatures (26–30 °C). Where specified, samples were stirred magnetically. Aliquots (1.00 ± 0.02 mL) were taken at time intervals as specified in Table I and assayed directly by liquid scintillation counting, as previously described.[1,2] Where necessary, viz., in the case of colored solutions or suspected contamination by soluble desiccant residues, samples were distilled before assay. Sequential drying[2] was accomplished by decanting *monosiccated* solvent onto a fresh charge of 5% w/v desiccant. Sampling was then effected at the time intervals given in the table footnotes.

Registry No.—HMPT, 680-31-9; DMF, 68-12-2; Me_2SO, 67-68-5; acetone, 67-64-1.

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(5) The reaction of sodium hydride with Me_2SO has been reported to sometimes give rise to violent explosions; inter alia, see L. Brandsma, "Preparative Acetylenic Chemistry", Elsevier, Amsterdam, 1971, p 24. However, in our hands, the same reaction has been carried out a number of times using stringently dried solvent with no untoward effects. While the cause of these accidents remains undetermined, it is noteworthy that the equilibrium water content of Me_2SO is 10%, and it thus seems not unlikely that the origin of these mishaps may lie in the use of insufficiently dried solvents.
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(11) See Experimental Section.
(12) C. A. Young and R. R. Dewald, *J. Chem. Soc., Chem. Commun.*, 188 (1977).
(13) See S. S. Pizey, "Synthetic Reagents", Vol. 1, Ellis Horwood Ltd., Chichester, 1974. This author reports that the use of calcium hydride and other basic desiccants in the drying of DMF could produce significant amounts of dimethylamine. However, the presence of this amine would give rise to inflated *apparent* water contents, and the values observed here, both for statically dried and distilled samples, suggest that this side reaction is of minor importance for these desiccants.
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3,4-Dimethyl-*cis*-bicyclo[3.3.0]-3-octene-2,8-dione: A Potentially Useful Pentalenolactone Synthon

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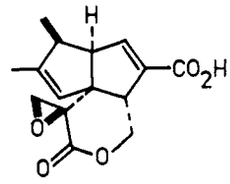
Received March 13, 1978

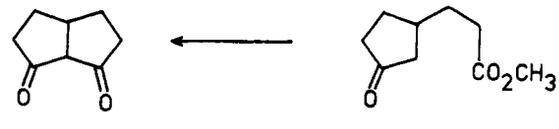
Pentalenolactone (1) is an acidic lipophylic antibiotic isolated from the fermentation broth of *Streptomyces* UC 5319



1

which exhibits inhibitory activity against nucleic acid synthesis in bacterial cells.[1,2] Both the novel structural nature of pentalenolactone together with its biological activity prompted us to consider possible routes to the synthesis of this molecule.

Inspection of the literature revealed a number of potential pentalene synthons,[3] the most interesting of which was the pentalenedione **2** reported first by Stetter[4] and more recently



2 **3**

by Eaton.[5] The salient feature of both the Stetter and Eaton routes was the base-induced internal Claisen condensation of the ester **3**, which in Eaton's hands gave an excellent yield of the dione **2**. These data inspired us to consider the possi-

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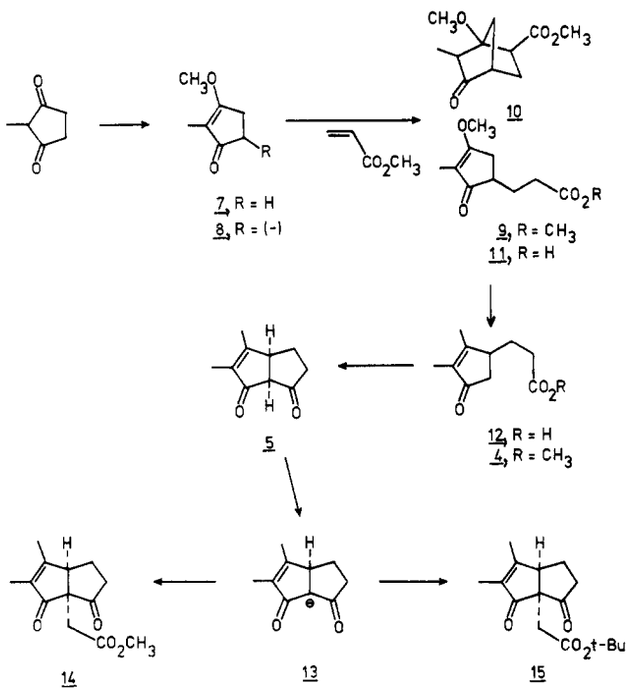
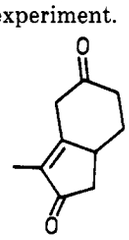


bility of carrying out a base-promoted cyclization of the cyclopentenone ester **4** in the hope that it would lead to the pentalenedione **5**. No analogous intramolecular Claisen cyclization examples were found that suggested base treatment of **4** would lead to formation of a new cyclopentanone ring (compound **5**) in preference to formation of a new cyclohexanone ring (compound **6**), and therefore we set out to resolve this question by experiment.



6

The synthesis of compound **4** has its origin in a body of data, mostly unpublished, which centers around the aprotic and low temperature conjugate addition reaction of several different enolate species with electron deficient olefins.[6] Within the context of the preparation of **4**, it occurred to us that the vinylogous ester **7** might serve as a starting point since Stork and Danheiser have shown that kinetic deprotonation of vinylogous esters derived from six-membered ring β-diketones takes place at the α'-carbon atom and not at the γ-carbon atom.[7] Several reactions of these enolate systems with electrophiles, excepting electron deficient olefins, have been observed.[7] On the assumption that **7** would form the enolate **8**, we were interested in examining the possible conjugate addition of this anion to methyl acrylate. Lee has reported that kinetic enolates derived from cyclohexenones react with acrylate esters to afford bicyclo[2.2.1]heptanone derivatives with no trace of the monocyclic Michael adducts observed.[8] We felt, however, that it might be possible to control the reaction of enolate **8** with methyl acrylate by judicious regulation of temperature and so obtain formation of the monocyclic adduct **9** in preference to the bicyclic adduct **10**. Indeed, this artifice has proven experimentally tenable using the following reaction sequence.

Treatment of 2-methylcyclopentane-1,3-dione[9] with methanol, trimethyl orthoformate, and a small amount of sulfuric acid gave the crystalline vinylogous methyl ester **7**. Kinetic deprotonation of **7** at −78 °C with 1 equiv of lithium diisopropylamide gave the enolate **8**,[10] which was then reacted with methyl acrylate to give in excellent yield a mixture of the adducts **9** and **10** in a ratio of 82:18, respectively. The question of how to deal with this mixture of adducts was answered when the esters were submitted to base hydrolysis using potassium hydroxide in water/methanol, first at 0 °C and then at room temperature. Isolation of the acidic fraction from this reaction gave a single crystalline acid identified as **11**.[11]

The conversion of **11** into the cyclopentenone ester **4** was initiated by reaction with methyllithium at −78 °C for 14 h. This reaction gave a 92% yield of a mixture of materials consisting of compounds **11** and **12** in a 1:4 ratio, respectively.[12] Methylation of this mixture with diazomethane followed by chromatography results in clean separation of the esters **4** and **9**. The overall yield for the conversion of **11** into **4** is 70% based on recovered and reused ester **9**.

Intramolecular Claisen condensation of **4** using the conditions described by Eaton (sodium methoxide in ether at room temperature) failed to give any reaction.[5] However, when benzene was substituted for ether as the solvent, rapid cyclization of **4** (10 min) occurred, providing that the reaction was carried out in a distillation apparatus at 120 °C (pot temperature) to ensure the removal of methanol. Inverse quenching of the reaction mixture with potassium dihydrogen phosphate[13] followed by standard workup gave a yellow solid which consisted of the diketone **5** together with several minor components. Sublimation of this material gave pure white crystals of **5** in 70% yield. In agreement with Eaton's findings,[5] the diketone showed little tendency to exist in the enolized form, a phenomenon that gives rise to relatively simple IR and NMR spectra for the compound. Interestingly, no evidence for the presence of the diketone **6** could be detected under a variety of cyclization conditions.[14]

Of potential importance to our intended synthesis of pentalenolactone was the viability of carbon alkylation of the β-diketone enolate derived from **5**. A sodium enolate of **5** must be the initial reaction product arising from cyclization of **4**. The same type of enolate must also result from the cyclization of **3** into **2**.[5] No reactions stemming from pentalene diketone enolates of this type have been reported, however. Although we have not attempted to alkylate the sodium enolate of **5** as it is formed from **4**, we have successfully alkylated its potassium enolate (**13**), which on reaction with either methyl iodoacetate or *tert*-butyl iodoacetate affords the corresponding ester diketones **14** and **15** in excellent yields.

Further work with the diketone **5** pursuant to the total synthesis of pentalenolactone is in progress.

Experimental Section

General Section. Nuclear magnetic resonance (NMR) spectra were recorded at 100 MHz on a Jeolco Model JNM-MH-100 high-resolution spectrometer. Samples were examined in deuteriochloroform containing 1% by volume of tetramethylsilane. Infrared spectra were recorded on a Perkin-Elmer Model 467 grating spectrophotometer. Samples were analyzed in spectrograde chloroform solutions of 0.1 mm thickness. Mass spectra were obtained on a Dupont Model 21-940 B mass spectrometer.

Chromatography was performed as follows. The silica, #7731 gel G type 60 for TLC, was placed in a sintered glass funnel packed dry. Solvent was flushed through the silica gel under water aspirator vacuum, and the silica was repressed to avoid channeling between the glass and the silica. The compound was deposited with a minimal amount of solvent and then eluted with solvent using the water aspirator as a vacuum source.

Preparation of the Vinylogous Ester 7. To a solution of 2-methylcyclopentane-1,3-dione (20.0 g, 0.1786 M), trimethyl orthoformate (117 mL), and methanol (350 mL) was added concentrated sulfuric acid (9.9 mL). The resulting mixture was refluxed for 2 h, whereupon the majority of the methanol was removed under vacuum. Saturated $NaHCO_3$ was added until the mixture was pH 8. Extraction with $CHCl_3$ followed by filtration of the extracts through $MgSO_4$ and

evaporation to dryness resulted in a yellow solid which on sublimation at 70 °C (10^{-3} mm) gave white crystals of **7** (21.3 g, 95%): mp 59.5–60 °C; R_f (silica) (5% CH_3OH in $CHCl_3$) 0.56, (ether) 0.26; IR ν_{max} 1690 (w, C=O), 1630 (s, C=C—OCH_3) cm^{-1}; NMR δ 1.6 (s, 3 H), 2.2 (m, 2 H), 2.65 (m, 2 H), 4.00 (s, 3 H); MS *m/e* 126 (100), 111 (25), 96 (62), 95 (32), 83 (45).

Preparation of the Acid 11. To a 1 M THF solution of lithium diisopropylamide [84.5 mmol; prepared from 11.83 mL of diisopropylamine and 34.9 mL of *n*-butyllithium (2.42 M)] was added **7** (10.642 g, 84.5 mmol, 1 M in THF) at such a rate as to keep the internal temperature of the reaction below −67 °C. After addition was complete, the mixture was stirred for 20 min, whereupon methyl acrylate (84.5 mmol, neat) was added sufficiently slowly to keep the internal temperature of the reaction below −65 °C. The resulting mixture was stirred for 2 h at −78 °C and then quenched at −78 °C with 18 mL of 6 N HCl followed by 10 mL of water. Extraction with ether (3 × 100 mL) and drying the combined extracts first over $NaSO_4$ and then by filtration through $MgSO_4$ followed by evaporation gave 16.85 g of an oil (94% crude yield) consisting of a 82:18 mixture (NMR analysis) of the esters **9** and **10**, respectively.

A portion of this mixture (7.626 g, 36 mmol) dissolved in methanol (36 mL) was treated with 2.37 g of 85% KOH in water (36 mL) at 0 °C. The resulting mixture was stirred at 0 °C for 30 min and then at room temperature for 2 h, followed by extraction with ether (100 mL). Acidification of the aqueous phase to pH 3 with 6 N HCl, extraction with CH_2Cl_2, and drying first over Na_2SO_4 and then by filtration through $MgSO_4$ followed by evaporation of the solvent gave 6.6 g of **11** (mp 105–110 °C; 92.5% yield). Two recrystallizations from ether/$CHCl_3$ gave **11**: mp 119–120 °C; IR ν_{max} 1735–1690 (broad, CO_2H and C=O), 1630 (s, C=C—OCH_3) cm^{-1}; NMR δ 1.6 (s, 3 H), 1.6–3.0 (m, 7 H), 3.95 (s, 3 H); MS *m/e* 198 (34), 153 (12), 139 (68), 126 (100).

Preparation of Ester 4. Methyllithium (89 mL, 1.7 M) was added dropwise to a solution of the acid **11** (12 g, 60.6 mmol; mp 105–110 °C; 0.5 M in THF) at −78 °C (internal temperature not exceeding −68 °C). The resulting dark orange solution was stirred for 12 h, quenched by pouring into 60 mL of 3 N HCl at 0 °C, and extracted with CH_2Cl_2 (2 × 100 mL), and the organic extracts were then evaporated to dryness. The resulting oil was dissolved in saturated Na_2CO_3 (40 mL) containing water (20 mL), and the aqueous solution was extracted with ether (100 mL). The aqueous phase was acidified with 6 N HCl (40 mL) and then extracted with CH_2Cl_2 (2 × 200 mL). The organic extract was dried first over Na_2SO_4 and second by filtration through $MgSO_4$ and then evaporated to an oil (10.55 g, 96% crude mass balance) consisting of the acids **12** and **11** in a ratio of 3:1 (NMR analysis), respectively.

This mixture of acids dissolved in CH_2Cl_2 was methylated with diazomethane (prepared in ether) at 0 °C, and the resulting mixture of the esters **4** and **9** was chromatographed on silica (100 g) by elution with 1:1 hexane/ether and then ether. From this chromatography there was obtained pure **4** (oil, 5.982 g) and pure **9** (oil, 2.89 g), which is a 77% overall yield of **4** from **11** based on recovered and reused ester **9**: R_f (silica) (ether) 0.63; IR ν_{max} 1735 (s, CO_2CH_3), 1695 (s, C=O), 1645 (m, C=C) cm^{-1}; NMR δ 1.65 (s, 3 H), 2.20 (s, 3 H), 1.9–2.85 (m, 7 H); MS *m/e* 196 (30), 165 (9), 123 (100).

Preparation of the Pentalenedione 5. Sodium methoxide (1.08 mL of a 1 M solution in methanol) was added to benzene (12 mL), and the resulting mixture was distilled until the head temperature reached 80 °C. Ester **4** (0.212 g, 1.08 mmol) in a small amount of benzene was then added, and the resulting mixture was distilled (80 °C head temperature, 120 °C pot temperature) for 5 min. The mixture was rapidly cooled to 0 °C, poured into a saturated solution of potassium dihydrogen phosphate, stirred for 3 min, extracted with CH_2Cl_2 (3 × 10 mL), dried over Na_2SO_4 followed by filtration through $MgSO_4$, and then evaporated to a yellow waxy solid which on sublimation at 70 °C (10^{-6} mm) gave a white solid (0.115 g, 70%): mp 83–84 °C; R_f (silica) (1:1 ether/$CHCl_3$) 0.48, (ether) 0.39; IR ν_{max} 1760 (s, C=O), 1700 (m, C=O), 1650 (w, C=C) cm^{-1}; NMR δ 1.65 (s, 3 H), 2.15 (s, 3 H), 2.28 (m, 4 H). 2.50 (d, 1 H), 3.20 (m, 1 H); MS *m/e* 164 (100), 136 (15), 135 (9), 122 (24), 121 (26), 108 (65). Anal. C, 73.16; H, 7.33.

Preparation of the Esters 14 and 15. To a solution of potassium hexamethyldisilizane (1.2 mmol, 1 M in THF) was added at −78 °C diketone **5** (200 mg, 1.2 mmol, 1 M in THF), and the resulting mixture was then stirred for 35 min before methyl iodoacetate (0.12 mL, 1.2 mmol) was added. The reaction was stirred at −78 °C for 20 min and then warmed to 0 °C and stirred for an additional 20 min. Saturated ammonium chloride (1 mL) was added to quench the reaction, which was then extracted with ether (3 × 2 mL). The organic extract was washed with 10% $NaHSO_3$ (1 mL), dried by filtration through $MgSO_4$, and evaporated to give essentially pure **14** as an oil (285 mg, ca. 99%). Preparation of the ester **15** from **5** and *tert*-butyl iodoacetate was carried out in the manner just described for **14**. Physical data for the esters **14** and **15** are as follows.

Compound **14**: R_f (silica) (ether) 0.74; IR ν_{max} 1755 (s, C=O), 1730 (m, CO_2CH_3), 1700 (m, C=O), 1650 (w, C=C) cm^{-1}; NMR δ 1.65 (s, 3 H), 2.15 (s, 3 H), 2.30 (m, 4 H), 2.90 (AB q, J_{AB} = 18 Hz, $\Delta\nu_{AB}$ = 70.2, 2 H), 3.25 (m, 1 H), 3.60 (s, 3 H); MS *m/e* 236 (98), 205 (43), 194 (78), 177 (20), 176 (26), 163 (60), 135 (100).

Compound **15**: R_f (silica) (ether) 0.86; IR ν_{max} 1755 (s, C=O), 1730 (m, CO_2-*t*-Bu), 1700 (m, C=O), 1650 (w, C=C) cm^{-1}; NMR δ 1.4 (s, 9 H), 1.65 (s, 3 H), 2.15 (s, 3 H), 2.20 (m, 4 H), 2.83 (AB q, J_{AB} = 16 Hz, $\Delta\nu_{AB}$ = 62, 2 H), 3.25 (m, 1 H); MS *m/e* 278 (0), 222 (100), 206 (76), 180 (80), 135 (32), 122 (64).

Acknowledgment This research was supported by P.H.S. Grant CA-21496-01. Support from the Hoffmann-La Roche Foundation is gratefully acknowledged.

Registry No.—**4**, 67226-55-5; **5**, 67226-56-6; **7**, 3883-56-5; **9**, 67226-57-7; **10**, 67226-58-8; **11**, 67226-59-9; **12**, 67226-60-2; **14**, 67226-61-3; **15**, 67226-62-4; 2-methylcyclopentane-1,3-dione,765-69-5; methyl acrylate, 96-33-3; methyl iodoacetate, 5199-50-8; *tert*-butyl iodoacetate, 49827-15-8.

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(9) We thank Dr. Pius A. Wehrli of the Hoffmann-La Roche Co. for a generous sample of this material as well as an excellent experimental description for the preparation of it.
(10) The regiointegrity of this enolate was determined by quenching with DCl. This enolate undergoes alkylation reactions in excellent yield, and thus it parallels the behavior already found for the six-membered ring cases (ref 7).
(11) We have found that base treatment for 30 min at 0 °C brings about the retro-Michael reaction of **10** to the ester **9** and that hydrolysis of **9** occurs only at room temperature or above.
(12) Longer reaction times lead to products derived from the carboxylic acid portion of **11**.
(13) This excellent quenching procedure is described in ref 5.
(14) Other bases attempted for the cyclization of **4** into **5** include lithium and potassium methoxide, potassium *tert*-butoxide, lithium and potassium hexamethyldisilizane, and lithium diisopropylamide. The amide bases did not give cyclization products, and all of the alkoxide bases gave lower yields of **5** relative to sodium methoxide.

Cis to Trans Interconversion of Cyclic α-Hydroxy Epoxides

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Received March 13, 1978

During the course of pondering synthetic strategies directed toward the synthesis of the sesquiterpene eriolangin (**1**),[1] it occurred to us that the synthon **2** possessed a number of functional and stereochemical features potentially amenable to an expeditious resolution of this interesting problem. Mo-

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