high E stereoselectivity (by TLC and NMR) of the reductive elimination was not unexpected: a recent study of the Julia olefin synthesis[12] has shown that the olefin stereochemistry is independent of the stereochemistry of the acyloxy sulfone[13] precursor and sensitive to proximate alkyl branching.[14] It is noteworthy that isolated sulfones are cleaved only very slowly under the conditions for reductive elimination of β-benzoyloxy sulfones.

Alkylation of **11** by geranyl chloride followed by (iodomethyl)trimethylsilane gave the β-silyl sulfone **13**. Attempts to separate **13** from unreacted **12** on silica gel led to decomposition; of the several products, moenocinol benzyl ether and the diene **14** were identified.[15] However, treatment of the mixture (ca. 1:1) of **12** and **13** with n-$Bu_4NF{\cdot}3H_2O$ in refluxing THF cleanly converted **13** to moenocinol benzyl ether which was then easily separated from **12** by chromatography. Finally, reductive debenzylation gave moenocinol (**1**), having IR and NMR spectra identical with those of natural **1** obtained by degradation of prasinomycin.[16]

Registry No. **1**, 19953-93-6; **2**, 3238-98-0; **3**, 73199-51-6; **4**, 73199-52-7; **5**, 73199-53-8; **6**, 55802-98-7; **7**, 73199-54-9; **8**, 73199-55-0; **9**, 73199-56-1; **10**, isomer 1, 73199-57-2; **10**, isomer 2, 73199-58-3; **11**, 73199-59-4; **12**, 73199-60-7; **13**, 73199-61-8; **14**, 73199-62-9; geranyl chloride, 5389-87-7; isobutyric acid lithium dianion, 57344-34-0.

(11) IR (film) 1320, 1305, 1150 ($ArSO_2$) cm^{-1}; NMR ($CDCl_3$) δ 7.8–7.98 and 7.5–7.7 (m, 2 H and 3 H, $ArHSO_2$), 7.3 (s, 5 H, ArH), 5.4 (t with further fine splitting, J = 7 Hz, $=CHCH_2$), 5.15–5.30 (m, 2 H, CH=CH), 4.50 (s, 2 H, CH_2O), 4.00 (2 H, d, J = 7 Hz, $=CHCH_2$), 3.03 (t, 2 H, J = 7 Hz, $ArSO_2CH_2$), 2.07 (app d, 4 H, $=CCH_2CH_2C=$), 1.73 (d, 3 H, J = 1 Hz, $CH_3C=$), 0.91 (s, 6 H). Homogeneity was established by TLC and NMR. No evidence for the presence of the cis isomer could be adduced.

(12) M. Julia and J.-M. Paris, *Tetrahedron Lett.*, 4833 (1973).

(13) P. J. Kocienski, B. Lythgoe, and S. Ruston, *J. Chem. Soc., Perkin Trans. 1*, 829 (1978).

(14) P. J. Kocienski, B. Lythgoe, and I. Waterhouse, *J. Chem. Soc., Perkin Trans. 1*, in press.

(15) Moenocinol benzyl ether does not isomerize to **14** on chromatography. It is likely that the confluence of carbonium ion stabilizing features (the sulfone group occupies a position which is tertiary, homoallylic, and β to silicon) is responsible for the observed lability of **13**.

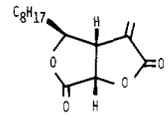
(16) We thank Dr. William A. Slusarchyk, Squibb Institute for Medical Research, for spectra of natural **1**.

Philip J. Kocienski
Department of Organic Chemistry
The University
Leeds LS2 9JT, England
Received November 6, 1979

Efficient Synthesis of a Bislactone Skeleton Leading to *dl*-Avenaciolide

Summary: Treatment of 2-halodecanal and potassium ethyl malonate under phase-transfer catalysis condition gave ethyl tetrahydro-4-(ethoxycarbonyl)-2-octyl-5-oxo-3-furanacetate in one step. This compound was successfully converted into dihydro-4-octylfuro[3,4-*b*]furan-2,6-(3*H*,4*H*)-dione, which is an important key intermediate for the synthesis of *dl*-avenaciolide.

Sir: Considerable attention[1-4] has been focussed on avenaciolide (**1**), a unique antifungal bislactone, which was first isolated from *Aspergillus avenaceaus* by Turner.[1]

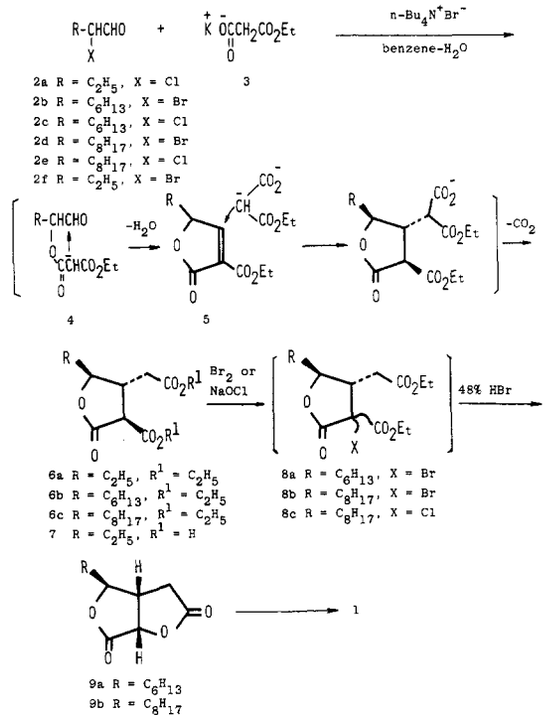


1

trans-Tetrahydro-2-octyl-5-oxo-3-furanacetic acid derivatives, known key intermediates for the synthesis of *dl*-**1**, have been independently prepared via several steps by Johnson[3a] and by Schlessinger.[3b] We now report a one-step synthesis of ethyl *trans,trans*-tetrahydro-2-alkyl-4-(ethoxycarbonyl)-5-oxo-3-furanacetate (**6**) by the reaction of α-halo aldehyde and potassium ethyl malonate (**3**) in a two-phase system consisting of water and benzene in the presence of tetra-*n*-butylammonium bromide (TBAB). Furanone **6c** was conveniently converted into bislactone **9b**, precursor of *dl*-**1**.[3a]

A mixture (1:2) of 2-bromodecanal (**2d**) and **3** was stirred vigorously in a benzene–H_2O (55:45) system containing 0.05 equiv of TBAB for 40 h under reflux. Workup in the usual manner gave **6c**[5] in 66% yield. The yield of **6c** was de-

Scheme I



(1) Isolation: (a) D. Brookes, B. K. Tidd, and W. B. Turner, *J. Chem. Soc.*, 5385 (1963); (b) J. J. Ellis, F. H. Stodola, R. F. Vesonder, and C. A. Glass, *Nature (London)*, **203**, 1382 (1964).

(2) Structure assignment: D. Brookes, S. Sternhell, B. K. Tidd, and W. B. Turner, *Aust. J. Chem.*, **18**, 373 (1967).

(3) Syntheses of *dl*-avenaciolide: (a) W. L. Parker and F. Johnson, *J. Am. Chem. Soc.*, **91**, 2708 (1969); W. L. Parker and F. Johnson, *J. Org. Chem.*, **38**, 2489 (1973); (b) J. L. Herrmann, M. H. Berger, and R. H. Schlessinger, *J. Am. Chem. Soc.*, **95**, 7923 (1973); J. L. Herrmann, M. H. Berger, and R. H. Schlessinger, *ibid.*, **101**, 1544 (1979); (c) H. Takei, Y. Fukuda, H. Mizutani, K. Sugaya, and T. Taguchi, Abstracts, 36th Symposium on Synthetic Organic Chemistry, Tokyo, June 1975, p 39. (d) E. Fujita, Y. Nagao, and K. Kaneko, Abstracts III, 26th meeting of the International Union of Pure and Applied Chemistry, Sept 1977, Tokyo, Japan, p 1019.

(4) Syntheses of optically active avenaciolide: (a) R. C. Anderson and B. Fraser-Reid, *J. Am. Chem. Soc.*, **97**, 3870 (1975); (b) M. Niwa, M. Iguchi, and S. Yamamura, *Tetrahedron Lett.*, 3661 (1975).

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creased to 38%, when the chloroaldehyde **2e** was used in place of **2d**. Furanones **6a** (31% yield from **2a** and 58% yield from **2f**) and **6b** (68% yield from **2b** and 44% yield from **2c**) were obtained in a similar manner. The furanone **6** is thought to be converted via the Michael addition of **3** to possible intermediate **5**. The hydrolysis of **6a** in 2 N aqueous NaOH gave the dicarboxylic acid **7**[6] in 76% yield (Scheme I).

The furanone **6c** was treated with an equivalent amount of Br_2 in CCl_4 to give the 4-bromofuranone **8b**[7] which was used without isolation for the next step. Heating **8b** in a mixture (1:3.5:10) of 48% HBr–H_2O–dioxane for 30 h under reflux gave the desired bislactone **9b** in 55% yield[8] from **6c**. The bislactone **9a** was obtained in 53% yield in a similar manner. Compound **9b** was successfully converted into *dl*-avenaciolide[9] by Johnson's procedure.[3a]

The present reaction provides an excellently simplified route for the construction of the bislactone skeleton of **9**.

Registry No. (±)**1**, 26057-70-5; (±)**2a**, 73368-19-1; (±)**2b**, 73368-20-4; (±)**2c**, 73368-21-5; (±)**2d**, 73368-22-6; (±)**2e**, 73368-23-7; (±)**2f**, 58031-09-7; **3**, 6148-64-7; (±)**6a**, 73368-24-8; (±)**6b**, 73368-25-9; (±)**6c**, 73368-26-0; (±)**7**, 73368-27-1; **8a**, 73368-28-2; **8b**, 73368-29-3; **8c**, 73368-30-6; (±)**9a**, 73368-31-7; (±)**9b**, 39949-88-7.

Supplementary Material Available: Experimental section describing the preparation details and spectral data (IR, ^1H NMR, and ^{13}C NMR) of **6a–c**, **7**, **9a**, and **9b** (4 pages). Ordering information is given on any current masthead page.

(5) IR 1787 and 1740 cm^{-1}; ^1H NMR (CCl_4) δ 0.89 (m, 3 H), 1.1–2.0 (m, 20 H), 2.35–3.14 (m, 3 H), 3.40 (d, 1 H, J = 9 Hz), 4.08 (q, 2 H, J = 7 Hz), 4.20 (q, 2 H, J = 7 Hz), 3.90–4.40 (m, 1 H). The relative stereochemistry of the C-2 alkyl group and the C-3 acetic acid chain is confirmed to be trans by eventual transformation of **6c** to **1**. That of the acetic acid chain and the C-4 ester group is also assigned as trans on the basis of the reaction mechanism and ^1H NMR coupling constant of 4-H (9 Hz): A. Takeda, T. Sakai, S. Shinohara, and S. Tsuboi, *Bull. Chem. Soc. Jpn.*, **50**, 1133 (1977). All compounds exhibited acceptable elemental analyses. The yields are for isolated products.

(6) In the ^1H NMR spectrum of **7**, irradiation at δ 1.70 (CH_2 of ethyl group) converted the multiplet (2-H) at δ 4.17 into a sharp signal. This fact indicates that the ethyl group of **7** is bonded at the C-2 position.

(7) The formation of **8b** was confirmed by the ^1H NMR.

(8) The analogous cyclization of chlorofuranone **8c** (NaOCl) gave **9b** in 40% yield.

(9) The IR and ^1H NMR spectra of **1** were identical with those reported by Turner[1a] and Johnson.[3a] ^{13}C NMR (25 MHz, $CDCl_3$) δ 14.1 (q), 22.6 (t), 24.8 (t), 29.1 (t), 29.2 (t), 31.7 (t), 35.9 (t), 43.9 (d), 74.2 (d), 85.2 (d), 126.0 (t), 134.3 (s), 167.3 (s), 169.7 (s).

Takashi Sakai, Hiroshi Horikawa, Akira Takeda*

Department of Synthetic Chemistry
School of Engineering, Okayama University
Tsushima, Okayama 700, Japan

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Triazoline Photochemistry. Pyrrole Formation by Retro-Diels-Alder Synthesis

Summary: Irradiation of triazoline **3**, prepared by intramolecular azide–olefin cycloaddition, in methanol solution gives pyrrole methyl ester **4**.

Sir: The photoconversion of triazolines to aziridines has been studied in some detail.[1] Stereochemical evidence suggests that nitrogen elimination proceeds in homolytic fashion to give a short-lived 1,3-diradical, from which ring closure occurs to give the aziridine. We wish to describe the new triazoline photoreaction **3** → **4**, for which a mechanism involving the ketene intermediate **7** is postulated.

Bromination of cyclohexenone **1a**[2] with *N*-bromosuccinimide–azobis(isobutyronitrile) in CCl_4 gives **1b**, which undergoes tetraethylammonium acetate promoted elimination of HBr to give azido dienone **2** in 80% overall isolated yield (Scheme I).[2] Triazoline **3** (mp 164–165 °C) is obtained from **2** in refluxing benzene solution by azide–olefin intramolecular cycloaddition.[3] The structure of **3** is formulated on the basis of elemental analysis (Anal. Calcd for $C_{19}H_{22}N_4O_3$: C, 64.39; H, 6.26; N, 15.81. Found: C, 64.40; H, 6.28; N, 15.76.)[4] and spectral data: ^1H NMR ($CDCl_3$) δ 3.73 (3 H, s, urethane methyl), 5.28 (1 H, s with weak allylic coupling, H_a), 6.40 (1 H, d with weak allylic coupling, H_b, J_{bc} = 10 Hz), 3.17 (1 H, sharp d, H_c, J_{bc} = 10 Hz); IR ($CHCl_3$) 1660, 1725 cm^{-1}; electron impact spectrum, m/e 354. Stereochemical assignment in **3** is tentatively made by way of chemically based supposition (vide infra).

Brief Pyrex-filtered irradiation of **3** in methanol solution gives pyrrole carboxylic ester **4** in essentially quantitative yield (oil, isolated by silica gel chromatography in 75% yield): ^1H NMR ($CDCl_3$) δ 3.67 (3 H, s, methyl), 3.72 (3 H, s, methyl), 3.5–3.9 (1 H, m, H_d), 6.45 (1 H, m, H_a), 5.83 (1 H, m, H_b), 6.62 (1 H, m, H_c); chemical ionization spectrum, m/e 359. On the other hand, irradiation of **3** in benzene solution gives the cyclobutane-1,3-dione dimer of ketene **7** of undetermined stereochemistry (Scheme II). This assignment is based primarily on chemical ionization mass spectral analysis (m/e 653), on ^1H and ^{13}C NMR data, and on the presence of infrared absorption at 1810 cm^{-1}. Furthermore, the dimeric substance is converted to **4** on treatment with sodium methoxide in methanol at room temperature.

We believe a reasonable mechanism for these phototransformations involves homolytic extrusion of molecular nitrogen from **3** to give diradical **5**, from which recombination gives the bridged intermediate **6**. Tricycle **6** is formally an intramolecular pyrrole–ketene Diels–Alder adduct,[5] and retro-Diels–Alder reaction of **6** (thermal or photochemical?)[6] would lead to the pyrrole ketene **7**; reaction of **7** with methanol gives the methyl ester **4**, while in the nonnucleophilic solvent benzene, ketene dimerization results in formation of the cyclobutane-1,3-dione.

(1) P. Scheiner in "Selective Organic Transformations", Vol. 1, B. S. Thyagarajan, Ed., Wiley-Interscience, New York, 1970, pp 327–62.

(2) The preparation of **1a** begins with the enaminone of 1,3-cyclohexanedione and benzylaniline, which was sequentially alkylated with ethyl iodide (lithium diisopropylamide in THF/HMPA) and 1-bromo-3-chloropropane (LDA in THF/HMPA). Debenzylation (H_2, 5% Pd/c) was followed by treatment with *n*-butyllithium and methyl chloroformate to give **1a**. For recent developments in synthetic methodology of vinylogous amides, see F. J. Vinick and H. W. Gschwend, *Tetrahedron Lett.*, 315 (1978), and references cited therein. Spectral data for **2** include the following: ^1H NMR δ ($CDCl_3$) 7.55–7.08 (5 H, m), 6.78 (1 H, dd, J = 10, 2 Hz), 6.21 (1 H, d, J = 10 Hz), 5.69 (1 H, d, J = 2 Hz), 3.76 (3 H, s), 3.35–3.02 (2 H, m), 2.30–1.05 (6 H, m), 0.72 (3 H, t, J = 6.5 Hz); IR (neat) 2080, 1725, 1640 cm^{-1}.

(3) A. Padwa, *Angew. Chem., Int. Ed. Engl.*, **15**, 123 (1976).

(4) Microanalysis was carried out by Spang Microanalytical Laboratory, Eagle Harbor, MI.

(5) A. G. Schultz and M. Shen, *Tetrahedron Lett.*, 2969 (1979), and references cited therein.

(6) J. L. Ripoll, A. Rouessac, and F. Rouessac, *Tetrahedron*, **34**, 19 (1978).

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