and subsequently, attack of methoxide ion opposite the methylthio ligand is preferred by a factor of 10. It is possible that the neutral esters are undergoing a direct displacement not involving a pentacoordinate species of ground-state geometry and thus the mode of attack may also be governed by the relative abilities of the various ligands to be displaced. This provides a working hypothesis to explain the differing modes for attack by nucleophiles on the two systems **1** and **2**.

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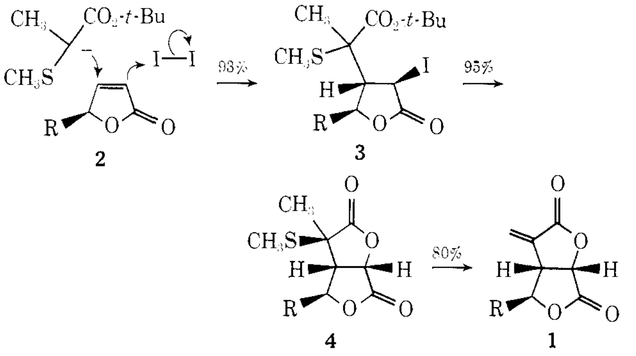
An Efficient Total Synthesis of *dl*-Avenaciolide

Sir:

Herein we describe a stereospecific total synthesis of *dl*-avenaciolide (**1**), a novel fungicidal bislactone isolated from *Aspergillus avenaceus* G. Smith.[1] Salient features of this construction include: (a) substitution of both the β and α positions of a Michael receptor using a conjugate addition–halogenation sequence,[2] (b) transformation of an α-methyl-α-thiomethylbutyrolactone into its corresponding α-methylene analog,[3] and (c) realization of the synthetic objective **1** in 70% overall yield starting from lactone **2**.[4]



R = *n*-octyl

To a solution of *tert*-butyl α-lithio-α-thiomethylpropionate[5] (1 equiv, 1 *M* in THF) was added (20 min) at $-78°$ lactone **2** (1 equiv, 1 *M* in THF). After stirring for 2 hr at $-78°$, iodine (1.2 equiv, 1 *M* in THF) was added to the reaction mixture (30 min additional stirring at $-78°$). Standard acid–base work-up (0–5°) afforded the iodo lactone **3** (oil)[6] as the sole reaction product (93%).[7] Conversion of **3** into the bislactone **4** was carried out in two stages: first, reaction of **3** (1 equiv, 1 *M* in benzene) with *p*-toluenesulfonic acid monohydrate (10% by weight) at reflux for 3 hr, and second, stirring this mixture with solid sodium bicarbonate at room temperature for 30 min. Filtration and evaporation of this benzene solution gave **4** (oil)[6] in 95% yield.[7] Introduction of the α-methylene moiety was accomplished by oxidation of **4** (1 equiv, 0.5 *M* in CH_2Cl_2) with *m*-chloroperbenzoic acid (1 equiv) to its corresponding sulfoxide (CH_3S to CH_3SO) followed by treatment of the sulfoxide (1 equiv) with succinic anhydride (3 equiv) for 30 min at 140°.[8] Treatment of this mixture with 10% hydrochloric acid followed by extraction with sodium bicarbonate and one crystallization from ether–petroleum ether gave pure *dl*-avenaciolide (**1**, mp 55–56°) in 80% yield.[9]

It is worthy of note that pure avenaciolide can be obtained from the lactone **2** without purification of any synthetic intermediates. The methods described in the foregoing are being used in the construction of other naturally occurring lactone systems.

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(1) The isolation of avenaciolide was first reported by D. Brookes, B. K. Tidd, and W. B. Turner, *J. Chem. Soc., Chem. Commun.*, 5385 (1973). A total synthesis of avenaciolide, conceptually quite different from that described here, has been reported by W. L. Parker and F. Johnson, *J. Org. Chem.*, **38**, 2489 (1973).

(2) We have found this reaction quite general with respect to addend and receptor combinations.

(3) This reaction sequence is also quite general and constitutes a useful means of preparing structurally complex unsaturated acids and esters as well as lactones.

(4) A preparation of 2 (oil) has been described by A. Nobuhara, *Agr. Biol. Chem.*, **34**, 1745 (1970). We have prepared 2 (mp 36–38.5°) in 75% overall yield starting from nonylaldehyde by the scheme shown below (R = *n*-octyl).

$$\mathrm{RCHO} + \mathrm{LiC{\equiv}CO_2Et} \longrightarrow \mathrm{RCHOHC{\equiv}CCO_2Et} \longrightarrow \mathrm{RCHOHC{\equiv}CCO_2H} \longrightarrow \mathbf{2}$$

(5) For a description of the preparation and handling of lithium enolates of simple ester systems, see R. J. Cregge, J. L. Herrmann, C. S. Lee, J. E. Richman, and R. H. Schlessinger, *Tetrahedron Lett.*, 2425 (1973).

(6) All compounds exhibited satisfactory spectral and physical properties. The stereochemistry of intermediates 3 and 4 follows from their 100-MHz nmr spectra.

(7) The yields reported are for isolated products.

(8) Similar sulfoxide to olefin transformations have been recently reported by B. M. Trost and T. N. Salzmann, *J. Amer. Chem. Soc.*, in press. We thank Professor Trost for communicating an account of this work to us prior to its publication.

(9) The authors would like to thank Drs. J. J. Ellis, F. H. Stodola, and F. Johnson for samples of *l*-avenaciolide.

Dimers of α,β,β-Trifluorostyrene

Sir:

Fluorinated olefins often cycloadd to other olefins in biradical fashion.[1] Some are known to cyclodimerize in a head-to-head manner, presumably *via* the most stable biradical.[2] The correspondingly facile dimerization of α,β,β-trifluorostyrene (TFS) has been reported,[3] but the product has been thought to be a 50:50 mixture of **3** and **4** on ^{19}F nmr evidence.[4]

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(1) References include: (a) D. D. Coffman, P. L. Barrick, R. D. Cramer, and M. S. Raasch, *J. Amer. Chem. Soc.*, **71**, 490 (1949), and references cited therein; (b) P. D. Bartlett, L. K. Montgomery, and B. Seidel, *ibid.*, **86**, 616 (1964); (c) P. D. Bartlett, *Science*, **159**, 833 (1968), and references cited therein; (d) J. D. Roberts and C. M. Sharts, *Org. React.*, **12**, 1 (1962).

(2) A. L. Henne and R. P. Ruh, *J. Amer. Chem. Soc.*, **69**, 279 (1947).

(3) M. Prober, *ibid.*, **75**, 968 (1953).

(4) M. P. Votinov, V. A. Kosobutskii, and A. F. Dokukina, *Vysokomol. Soedin., Ser. A*, 10, 1137 (1968); *Polym. Sci. USSR*, 10, 1318 (1968).