

tion is 95% complete (Figure 1C), and show a rapid decline only at the last stages of the reaction.¹¹

The bands for the intermediate in the C-H and C-D region (2905 and 2145 cm^{-1} , respectively) lie somewhat below the corresponding maxima in the spectra for gaseous 1,2-dideuterioethane (2980 and 2190 cm^{-1} , respectively). Accordingly, the intermediate appears to be an adsorbed paraffinic species different from the product ethane; in that sense, it would be consistent to ascribe the bands due to the intermediate to the reactive $\text{CH}_2\text{DCH}_2\text{-S}$ species. For such a species, however, we expect additional bands in the C-H stretching region and the deformation region;¹² the former region is somewhat obscured by the bands due to reactants and products, but we hope a detailed study of the deformation region (now in progress) will provide a firmer basis for the above tentative assignment.

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(11) The "residual" bands, included in the background, are slowly removed by treatment in deuterium. We believe these bands correspond to a species structurally similar to the intermediate but bound on sites that are less reactive catalytically.

(12) See, for example, the spectra of $\text{CH}_2\text{DCH}_2\text{-Br}$ reported by B. Bak, D. Christensen, J. Møller, and S. Detoni, *Acta Chem. Scand.*, **12**, 2021 (1958).

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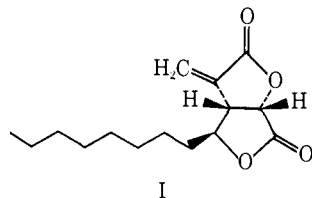
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Total Synthesis of *dl*-Avenaciolide

Sir:

We report the total synthesis of the racemic form of the naturally occurring fungicide, avenaciolide (I), a unique, bislactonic compound first isolated by Brookes, Tidd, and Turner¹ from cultures of *Aspergillus avenaceus* H. Smith.



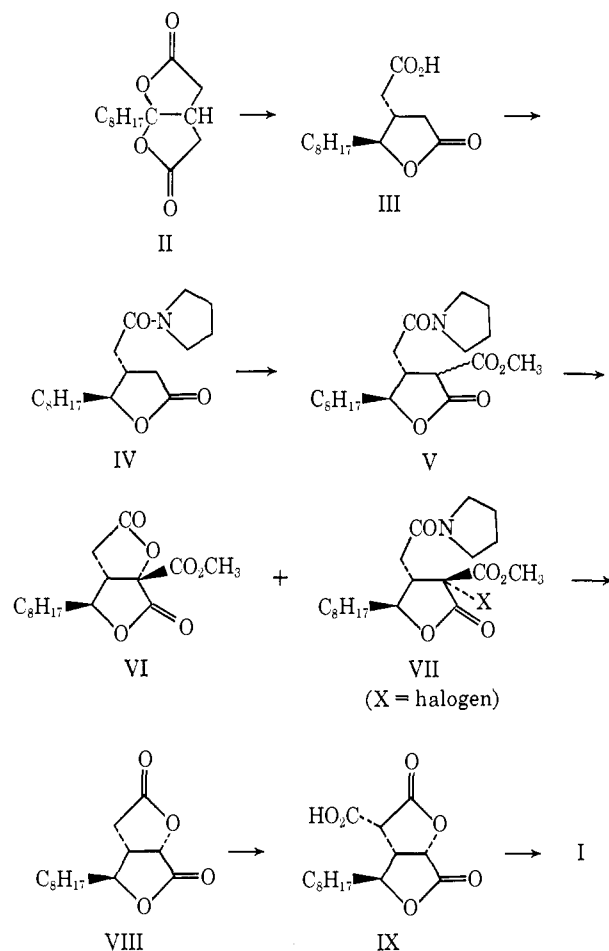
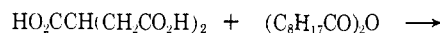
The synthesis was accomplished by the route given in Scheme I and takes advantage of new methods recently reported² by our laboratories for the efficient introduction of carboxyl and methylene groups adjacent to a butyrolactone carbonyl.

In brief, Fittig condensation³ of tricarballylic acid with *n*-nonanoic anhydride at 185° afforded II in 49% yield, mp 86–87° (*Anal.* Calcd for $\text{C}_{14}\text{H}_{22}\text{O}_4$: C, 66.11; H, 8.72. Found: C, 66.06; H, 8.69). Treatment of the bislactone II with sodium borohydride in

(1) D. Brookes, B. K. Tidd, and W. B. Turner, *J. Chem. Soc.*, 5385 (1963).

(2) J. Martin, P. C. Watts, and F. Johnson, submitted for publication.

(3) R. Fittig, *Ann. Chem.*, **314**, 1 (1901).



aqueous potassium hydroxide solution led, after acidification, to pure *trans*-tetrahydro-2-(*n*-octyl)-5-oxo-3-furanacetic acid (III) in 91% yield; mp 55–56° (*Anal.* Calcd for $\text{C}_{14}\text{H}_{24}\text{O}_4$: C, 65.60; H, 9.44. Found: C, 65.47; H, 9.38). This acid lactone then was converted in 81% yield to the amide IV, mp 51–52° (*Anal.* Calcd for $\text{C}_{18}\text{H}_{31}\text{NO}_3$: C, 69.86; H, 10.10; N, 4.53. Found: C, 69.91; H, 10.15; N, 4.49), by successive treatment with thionyl chloride and pyrrolidine. The preparation of V from IV could be accomplished in one of two ways: either IV was carboxylated in 85% yield to a single carboxylic acid, mp 92–95° (*Anal.* Calcd for $\text{C}_{19}\text{H}_{31}\text{NO}_5$: C, 64.56; H, 8.84; N, 3.96. Found: C, 64.12; H, 8.90; N, 4.25), using methyl methoxymagnesium carbonate,^{2,4} followed by treatment with diazomethane, or, directly, by carbomethoxylation with sodium hydride and dimethyl carbonate in the presence of a trace of methanol. Both procedures afforded V as a viscous oil (82% yield) which by nmr analysis appears to be a single substance (*Anal.* Calcd for $\text{C}_{20}\text{H}_{33}\text{NO}_5$: C, 65.37; H, 9.05; N, 3.81. Found: C, 65.52; H, 9.15; N, 4.15). The lactonic amide V reacted rapidly with halogens in the presence of a weak base (Br_2 or I_2 in HOAc-NaOAc) to give mixtures of VI and VII, but a particularly convenient method for effecting this transformation involved shaking an ether solution of V briefly with sodium hypochlorite solution

(4) H. L. Finkbeiner and M. Stiles, *J. Am. Chem. Soc.*, **85**, 616 (1963).

(Clorox). Although it proved possible to separate VI, mp 78.5–79.5° (*Anal.* Calcd for $C_{18}H_{24}O_6$: C, 61.52; H, 7.75. Found: C, 61.23; H, 7.54), by chromatography we found it more expedient simply to take the crude mixture of VI and VII ($X = Cl$) and reflux it for 48 hr in aqueous dioxane containing hydrobromic acid. The neutral fraction, a viscous oil, isolated in 57% yield, proved to be VIII which analyzed well for $C_{14}H_{22}O_4$ (*Anal.* Found: C, 65.99; H, 8.70). Carboxylation of VIII was carried out by once again using Stiles' reagent^{2,4} and led to IX, mp 78–80° (*Anal.* Calcd for $C_{15}H_{22}O_6$: C, 60.39; H, 7.43. Found: C, 60.57; H, 7.59), in 75% yield. Methylenation of IX was accomplished² directly by brief treatment with a solution of formalin in acetic acid containing diethylamine and sodium acetate (room temperature for 1 min followed by 5 min on the steam bath). Chromatography of the product yielded almost pure *dl*-avenaciolide (I, 66% yield), mp 54–57°. One recrystallization from ether–petroleum ether (bp 30–60°) afforded the pure material, mp 55–56° (*Anal.* Calcd for $C_{15}H_{22}O_4$: C, 67.64; H, 8.33. Found: 67.69; H, 8.26).

The nmr and infrared spectra of the synthetic product were identical in every respect with those of natural *l*-avenaciolide. Spectral data also fully support the structures assigned to the other new compounds mentioned in this report.

A full paper dealing with the broader aspects of this synthesis and of our attempts to utilize the carboxyl group of III to functionalize the methylene group of the lactone ring will be published at a later date.

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Mass Spectrometric Evidence for the Existence of 1,2-Dioxetanedione (Carbon Dioxide Dimer) A Chemiluminescent Intermediate

Sir:

The compound 1,2-dioxetanedione (C_2O_4) has been suggested by Rauhut, *et al.*,¹ as a volatile compound capable of exciting a fluorescer and as being an intermediate in the oxidation of oxalate esters by hydrogen peroxide.

In private discussion with Dr. Rauhut we learned that he had been unsuccessful in identifying the compound using various methods including conventional mass spectrometry. This and other evidence¹ indicated that the compound, if it existed, must be unstable; however, some volatile compound was capable

(1) M. M. Rauhut, *Accounts Chem. Res.*, **2**, 80 (1969), and references cited therein.

of passing through a gas phase to excite a fluorescer.¹ A mass spectrometer with a direct inlet system was available,² and it was hoped that the intermediate could be seen by directly introducing the gaseous products of a hydrogen peroxide–oxalate ester reaction to the spectrometer.

A sample tube of $\frac{3}{8}$ in. heavy wall Pyrex was connected through a stainless steel needle valve to the inlet of a Bendix Model 12 mass spectrometer. The electron energy was 70 eV. In the sample tube were placed 0.1 cc of a saturated ($\sim 1 M$) solution of H_2O_2 (98%) in Octoil (di-2-ethylhexyl phthalate) and 0.3 cc of a saturated ($\sim 0.08 M$) solution of bis(2,4,5-trichloro-6-carbobutoxyphenyl) oxalate in Octoil. To this was added 0.01 g of sodium salicylate as a catalyst.

The sample was given a preliminary, but short, evacuation and isolated for 15–60 min behind the needle valve. The needle valve was then opened slightly to the mass spectrometer. Large peaks were observed at 17, 18, 28, 32, 34, and 44 amu by means of an oscilloscope trace. Other smaller peaks attributable to the solvent were also evident. The spectrum was scanned with the analog output and recorded. Because of the fleeting nature of the spectrum (1–5 min) only a portion of the spectrum was recorded at a time. Peaks at 88 (C_2O_4) and 60 amu (CO_3) were observed. Their intensities were about equal ($\pm 20\%$) and initially at least one order of magnitude greater than background. The intensities of these peaks dropped (along with the intensity of the peak at 44 amu) and eventually reached background level. The spectrum could be repeated by reisolating the sample for a period of time and then reopening the valve to the mass spectrometer. The intensity of the peak at 44 amu was from 10 to 1000 times that of the peak at 88 amu. The longer periods of isolation were associated with the larger ratios, as would be expected from the proposed decomposition of 1,2-dioxetanedione to carbon dioxide.¹

There may have been peaks at 40 (C_2O) and 56 amu (C_2O_2), but there was strong background in these regions and the results are uncertain. There was no indication of a peak at 72 (C_2O_3) or at 76 amu (CO_4). There were no peaks between 88 and 150 amu which could be attributed to anything but background. The mass spectrometer was replaced by a tube containing a paper strip impregnated with 9,10-bis(phenylethynyl)anthracene in dimethyl phthalate. The gases evolving from the sample were passed over the paper strip and slight luminescence was seen. In addition luminescence (due to the sodium salicylate catalyst) was seen in the reaction mixture. This effect is more pronounced if dimethyl phthalate is used as the reacting medium but this material was too volatile for the mass spectrometer study.

Acknowledgment. We wish to thank Dr. M. M. Rauhut for evoking our interest in this problem.

(2) H. F. Cordes and S. R. Smith, *J. Phys. Chem.*, **72**, 2189 (1968).

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