of route II has not been reported. Since the cyclization which occurs during the reverse anhydropenicillin rearrangement represents chemical precedent for this pathway, it seems desirable to subject route II to more direct tests. Appropriate experiments are in progress.

Acknowledgment. We thank Bristol Laboratories for generous financial support.

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Received July 28, 1969

Evidence for Intermediates during Hydrogenation over Zinc Oxide

Sir:

Hydrogenation of ethylene over solid catalysts appears to be a two-step surface process[1,2]

$$\underset{}{C_2H_4\cdot S + H\cdot S} \rightleftarrows \underset{\text{I}}{CH_3CH_2\cdot S}$$

$$CH_3CH_2\cdot S + H\cdot S \longrightarrow C_2H_6(\text{gas})$$

The infrared spectrum of hydrogen-treated, adsorbed ethylene on nickel suggests the presence of a C_2H_5–S species, but this species appears too stable in hydrogen to be the reactive intermediate, I.[3,4] Thus, to date, direct physical evidence (as opposed to mechanistic inference) for I is lacking. We report in this letter infrared observations during the hydrogenation of ethylene over zinc oxide that provide physical evidence for I. Zinc oxide gives simpler results than metals insofar as the formation of I appears to be irreversible;[5] hence the reaction with deuterium would lead to formation of a single species CH_2DCH_2–S rather than the multiplicity of species ($C_2H_{5-x}D_x$–S) expected for nickel.

When ethylene is circulated over zinc oxide, prominent bands due to adsorbed ethylene (readily reversible) appear in the C–H region at 3060 and 2980 cm^{-1}.[6] If gaseous deuterium is then admixed with the ethylene (D_2:C_2H_4 = 116:12 mm) reaction commences, and the band at 2980 cm^{-1} broadens and decreases as new bands appear at 2905 and 2145 cm^{-1} along with bands ascribable to adsorbed deuterium.[7,8] If the ethylene is trapped out but deuterium circulation is continued, the new bands decrease initially at a rapid rate and then more slowly. The initial rate of removal of this species is comparable to the rate of the catalytic reaction.[9]

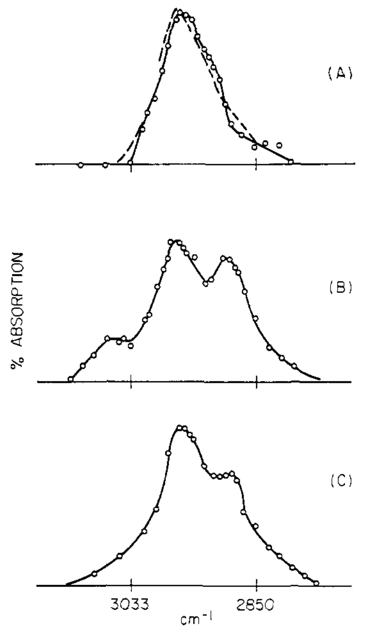

Figure 1. Spectra during reaction in the C–H region (spectral slit width 18 cm^{-1}): (A) 100% conversion (the dotted line is the spectrum of gaseous CH_2DCH_2D with the transmission scaled so that the peak intensities coincide); (B) 60% conversion; (C) 95% conversion.

Subsequent evacuation through a liquid nitrogen trap for 30 min reveals a residual band at 2145 cm^{-1} (and 2905 cm^{-1}) but, even when the catalyst is reexposed to the trapped out ethylene and dideuterioethane, this band has only one-third the intensity it had under reaction conditions. Resumption of the reaction by admission of a charge of deuterium brings about immediate restoration of the band intensities.

Figure 1 shows the difference spectra in the C–H region during reaction in a circulating system.[10] Spectra were computed by using as background the spectra of zinc oxide after reaction was complete and hydrocarbons had been trapped out for 4 min. Use of this "background," which includes a residual peak at 2905 cm^{-1}, results in a difference spectrum for 100% conversion (Figure 1A) essentially identical with the spectrum of gaseous 1,2 dideuterioethane under comparable conditions with the per cent transmission scaled to give the same peak intensity (dashed line). Under reaction conditions (Figure 1B) three peaks are seen. The 3060-cm^{-1} peak is ascribable to adsorbed ethylene and shows a gradual decline as the run proceeds; the center peak contains contributions from adsorbed ethylene (2980 cm^{-1}) and the product ethane (2980 cm^{-1}), and changes relatively little as the run proceeds. The species giving rise to bands at 2905 cm^{-1} (and 2145 cm^{-1}) is an intermediate; it appears at the onset of the reaction, stays roughly constant until the reaction is about 70% complete, and then starts a slow decline. These bands, however, are still apparent even when the reac-

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[1] G. C. Bond, "Catalysis by Metals," Academic Press, New York, N. Y., 1962, pp 229–279.

[2] R. L. Burwell, Jr., A. B. Littlewood, M. Cardew, G. Pass, and C. T. H. Stoddard, *J. Amer. Chem. Soc.*, **82**, 6272 (1960).

[3] R. P. Eischens and W. A. Pliskin, *Advan. Catal.*, **10**, 1 (1958).

[4] L. H. Little, "Infrared Spectra of Adsorbed Species," Academic Press, New York, N. Y., 1966, pp 100–137.

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[6] Band positions were determined at higher resolution than that for Figure 1 and are accurate to about 10 cm^{-1}.

[7] R. P. Eischens, W. A. Pliskin, and M. J. D. Low, *J. Catal.*, **1**, 180 (1962).

[8] A. L. Dent and R. J. Kokes, *J. Phys. Chem.*, **73**, 3772, 3781 (1969).

[9] In this estimate we assume that the species responsible for the new bands is present in amounts comparable to the initially adsorbed ethylene. This assumption is supported by the relative intensity of the 2905-cm^{-1} band compared with the initial intensity of the 2980-cm^{-1} band.

[10] These spectra were run on a Perkin-Elmer Model 112c spectrometer with the expanded scale procedure similar to that described in ref 3, p 50. The per cent absorption of the strongest peak is about 10%.

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 CH_2DCH_2–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.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

[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 CH_2DCH_2–Br reported by B. Bak, D. Christensen, J. Møller, and S. Detoni, *Acta Chem. Scand.*, **12**, 2021 (1958).

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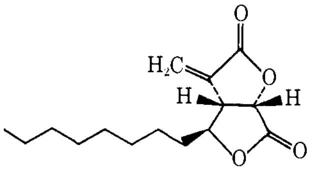
Total Synthesis of *dl*-Avenaciolide

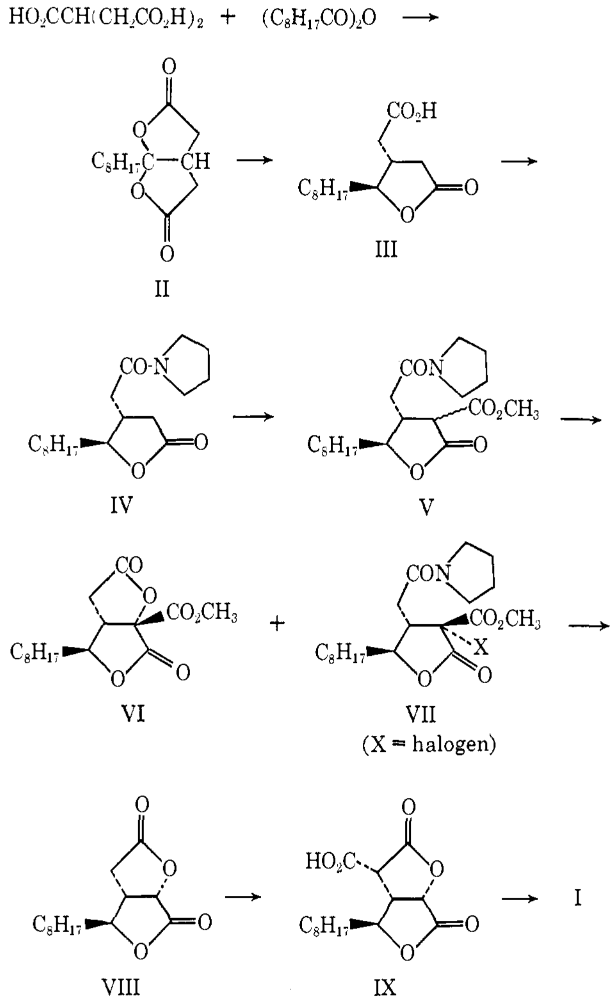
Sir:

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 Turner[1] from cultures of *Aspergillus avenaceus* H. Smith.



I

The synthesis was accomplished by the route given in Scheme I and takes advantage of new methods recently reported[2] by our laboratories for the efficient introduction of carboxyl and methylene groups adjacent to a butyrolactone carbonyl.



In brief, Fittig condensation[3] of tricarballylic acid with *n*-nonanoic anhydride at 185° afforded II in 49% yield, mp 86–87° (*Anal.* Calcd for $C_{14}H_{22}O_4$: C, 66.11; H, 8.72. Found: C, 66.06; H, 8.69). Treatment of the bislactone II with sodium borohydride in 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 $C_{14}H_{24}O_4$: 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 $C_{18}H_{31}NO_3$: 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 $C_{19}H_{31}NO_5$: 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 $C_{20}H_{33}NO_5$: 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

[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).

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