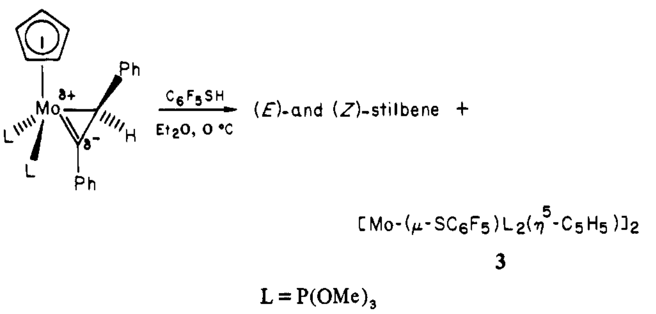
Scheme II



collapse to the 18-electron cyclic alkylidene three-electron η^2-bonding mode.

An important question remaining is the polarity of the molybdenum carbon double bond present in these molecules. The complex **1** in diethyl ether reacted instantaneously at 0 °C with the weak acid C_6F_5SH to give a mixture of *cis*- and *trans*-stilbene and the dinuclear complex **3**[7] (Scheme II). This shows that the alkylidene carbon carries a partial negative charge as found by Schrock and his co-workers[8] for a number of tantalumalkylidene complexes.

Transition-metal-vinyl complexes have been implicated in a number of organometallic reactions, and the establishment of a pathway from coordinatively *unsaturated* σ-vinyl complexes to an unusual[9] strained cyclic alkylidene complex has a number of important implications.

Acknowledgment. We thank the S.R.C. for support.

Supplementary Material Available: Atomic positional and thermal parameters for complex **1** (6 pages). Ordering information is given on any current masthead page.

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[7] Satisfactory elemental analyses and IR and NMR spectra have been observed for this complex.

[8] Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98–104.

[9] Recently (Davidson, J. L.; Shiratian, M.; Muir, Lj. M.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1979**, 30–32) it has been reported that [WC(O)C(CF$_3$)=C(CF$_3$)SMe(CO)$_2$(η^5-C_5H_5)] rearranges to [WC(CF$_3$)=C(CF$_3$)C(O)SMe(CO)$_2$(η^5-C_5H_5)] via a species [WC(CF$_3$)C(CF$_3$).C(O)SMe(CO)$_2$(η^5-C_5H_5)], which is structurally related to complexes **1** and **2**. However, these molecules carry strongly electron-withdrawing groups, and the rearrangement has been interpreted in terms of a 1,3 shift of a mercapto group. A more relevant comparison can be drawn with the interconversion of the η^1-ketenyl complex [W[C(CO)R](CO)(PMe$_3$)$_2$(η^5-C_5H_5)], formed from reaction of the carbyne [W≡CR(CO)$_2$(η^5-C_5H_5)] with PMe$_3$, into a η^2-ketenyl system [W{O⋯C⋯C⋯R}(CO)(PMe$_3$)(η^5-C_5H_5)] (Vedelhoven, W.; Eberl, K.; Kreissl, F. R. *Chem. Ber.* **1979**, *112*, 3376–3389). It could be argued that, whereas Kreissl's complex is a metalacyclopropenone, the complexes **1** and **2** are metallacyclopropenes.

Linking of Four Acetylene Molecules at a Dimolybdenum Center and the Protonation of the Resulting Metallacyclononatetraene To Form a Cation Containing a Bridging MoHC System

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Received July 30, 1980

The reaction of acetylenes with transition-metal complexes has commanded the attention of organometallic chemists for a number of years. One of the principal reasons for this continued interest in the remarkable observation by Reppe and his co-workers that certain nickel complexes catalyze the conversion of acetylene into cyclooctatetraene.[1] Recently,[2,3] there have been indications that this catalytic reaction might require two adjacent metal centers. While exploring the chemistry of the cationic complex bis(but-2-yne)carbonyl(η^5-cyclopentadienyl)molybdenum tetrafluoroborate,[4,5] we have observed an unusual cyclotetramerization reaction of coordinated but-2-yne.

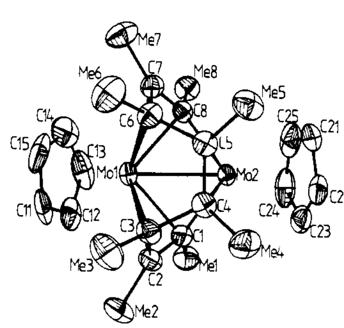

Figure 1. Drawing[19] of **2** showing 50% probabiity ellipsoids; all methyl and cyclopentadienyl hydrogens are omitted for clarity. Only the major (77.3%) orientation of the disordered cyclopentadienyl ring attached to Mo(1) is shown. Bond lengths: Mo(1)–C(1) = 2.237 (2), Mo(1)–C(2) = 2.346 (3), Mo(1)–C(3) = 2.313 (3), Mo(2)–C(4) = 2.234 (3), Mo(2)–C(5) = 2.231 (2), Mo(1)–C(6) = 2.317 (2), Mo(1)–C(7) = 2.348 (2), Mo(1)–C(8) = 2.234 (2), C(1)–C(2) = 1.412 (4), C(2)–C(3) = 1.427 (3), C(3)–C(4) = 1.507 (3), C(4)–C(5) = 1.439 (3), C(5)–C(6) = 1.509 (3), C(6)–C(7) = 1.434 (4), C(7)–C(8) = 1.412 (4) Å.

In refluxing acetonitrile the complex [Mo(CO)(MeC$_2$Me)$_2$(η^5-C_5H_5)]BF$_4$ loses one molecule of carbon monoxide to form [Mo(NCMe)(MeC$_2$Me)$_2$(η^5-C_5H_5)]BF$_4$ (**1**).[6,7] Electrochemical observations[8] showed that this cation readily and irreversibly accepted *one* electron. In seeking to find suitable chemical reagents capable of providing one electron, the reaction of **1** with sodium dicarbonylcyclopentadienyliron in tetrahydrofuran at room temperature was examined. A rapid reaction occurred affording [Fe$_2$(CO)$_4$(η^5-C_5H_5)$_2$] together with a purple crystalline dimolybdenum complex **2**. [^{1}H NMR (C_6D_6) τ 4.91 (s, 5 H, C_5H_5), 6.20 (s, 5 H, C_5H_5), 7.60 (s, 6 H, Me), 7.75 (s, 6 H, Me), 8.00 (s, 6 H, Me), 9.01 (s, 6 H, Me); ^{13}C (C_6D_6, ^{1}H decoupled) δ 174.3, 119.6, 97.4 (C_5H$_5$), 91.3 (C_5H$_5$), 71.0, 69.0, 33.0 (Me), 25.2 (Me), 22.0 (Me), 18.4 (Me)]. Elemental analyses and mass spectroscopy indicated that **2** had the molecular formula [Mo$_2$(MeC$_2$Me)$_4$(η^5-C_5H_5)$_2$] in agreement with the NMR data. In order to define the structure a single-crystal X-ray diffraction study was undertaken.

Crystal Data for 2. $C_{26}H_{34}Mo_2$, $M = 537.9$, triclinic, space group $P\bar{1}$, $a = 8.449$ (1), $b = 10.114$ (2), $c = 14.872$ (3) Å; $\alpha = 86.66$ (2), $\beta = 80.88$ (1), $\gamma = 63.78$ (1)°; $U = 1125.6$ (4) Å^3; $Z = 2$; $D_c = 1.587$ g cm^{-3}; $F(000) = 2548$; μ(Mo Kα) = 11.0 cm^{-1}. Current $R = 0.0201$ ($R = 0.0199$)[9] for 4635 absorption-corrected, observed [$I > 3\sigma(I)$] intensities (Syntex P2$_1$ diffractometer) with $3° < 2\theta < 60°$ and weight $w = 1/\sigma^2(F_o)$. As shown in Figure 1, the molecule contains an octamethyl-substituted molybdenacyclononatetraene bonded to a second molybdenum atom. The C_8 chain begins and ends with σ bonds to Mo(2); atoms C(1),

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[1] Reppe, W; Schlichting, O; Klager, K; Toepel, T. *Liebigs Ann. Chem.* **1948**, *560*, 1–92.

[2] Wilke, G. *Pure Appl. Chem.* **1978**, *50*, 677–690.

[3] Knox, S. A. R; Stansfield, R. F. D; Stone, F. G. A; Winter, M. J; Woodward P. *J. Chem. Soc., Chem. Commun.* **1978**, 221–223.

[4] Bottrill, M; Green, M. *J. Chem. Soc., Dalton Trans.* **1977**, 2365–2371.

[5] Bottrill, M; Green, M. *J. Am. Chem. Soc.* **1977**, *99*, 5795–5796.

[6] Allen, S. R; Baker, P. K; Barnes, S. G; Green, M; Trollope, L; Muir, Lj. M; Muir, K. W. *J. Chem. Soc., Dalton Trans.*, in press.

[7] The formation of the corresponding hexafluorophosphate salt was described (Watson, P. L; Bergman, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 2698–2703) during the preparation of this manuscript.

[8] Allen, S. R; Green, M; Norman, N. C., unpublished observations.

[9] The X-ray structures of **2** and **3** were solved by conventional heavy-atom Patterson and difference Fourier techniques and the nonhydrogen framework readily established for both. All hydrogen atoms in **2** except those on the disordered cyclopentadienyl group attached to Mo(1) were located and subsequently constrained to idealized geometries with C–H = 0.96 Å. In **3** all methyl and cyclopentadienyl hydrogens were likewise located and refined.

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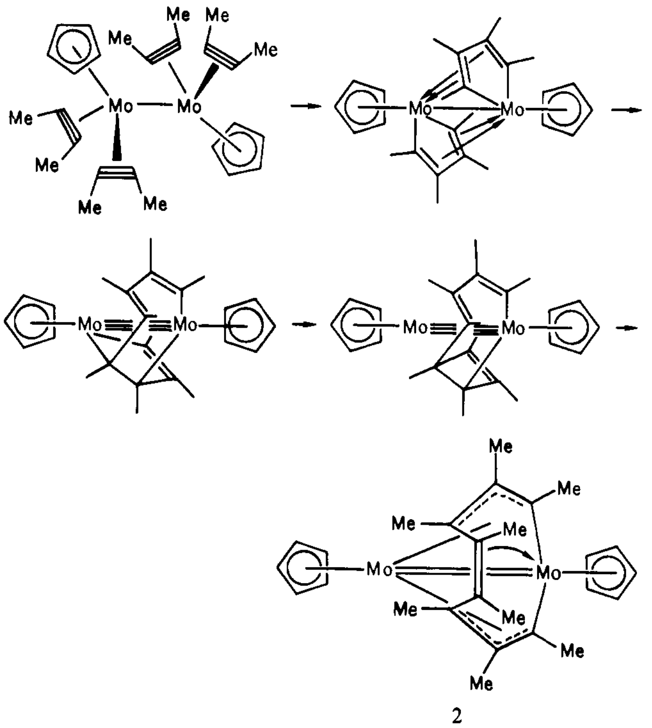
Scheme I[a]



[a] Methyl groups omitted for clarity.

C(2), C(3) and C(6), C(7), C(8) coordinate to Mo(1) via an η^3-allylic interaction, while C(4) and C(5) bond as an η^2-olefinic fragment to Mo(2). The Mo–Mo distance [2.595 (1) Å] reflects[10] double bond character.

Previously it has been reported[3] that in *refluxing octane* the complex $[Mo_2(\mu_2\text{-}\eta^2\text{-}HC_2H)(CO)_4(\eta^5\text{-}C_5H_5)_2]$ reacts with the electronegatively substituted acetylene $C_2(CO_2Me)_2$ to form a dinuclear complex $[Mo_2[(MeO_2CC_2CO_2Me)(HC_2H)(MeO_2CC_2CO_2Me)_2](\eta^5\text{-}C_5H_5)_2]$ isostructural with **2**. It was suggested,[3] although not proven, that the immediate precursor of the nine-membered ring was a "flyover" complex, in which three linked acetylenes bridged two molybdenum atoms. We believe that such a reaction path is unlikely to be followed in the formation of **2**.

It is suggested that the first step in the reaction sequence involves dimerization of a paramagnetic species formed by a one-electron addition to the cation **1**, leading to a dimolybdenum system (Scheme I) in which each molybdenum carries two coordinated but-2-yne molecules. The problem is then how to transfer all four but-2-yne molecules to one molybdenum center. One way this could be achieved is illustrated in Scheme I and involves the initial formation of two molybdenacyclopentadiene systems disposed on opposite sides of the molecule, thus allowing coordination with the adjacent molybdenum center. In such a system a molybdenum carbon σ bond and a coordinated olefin of an adjacent molybdenacyclopentadiene have the correct orientation to allow an "insertion" reaction to occur. This would be followed by reductive elimination and a ring-opening reaction to form a molybdenacyclononatetraene. We have observed that the reaction leading to complex **2** can be extended to a variety of acetylenes, and it is thought that a study of the regioselectivity of these systems will provide support for this reaction path.

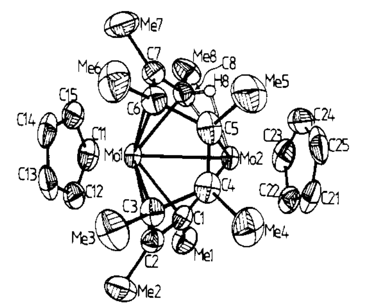


Figure 2. Drawing[19] of the cation in **3** showing 50% probability ellipsoids; all methyl and cyclopentadienyl hydrogens are omitted for clarity. The 3c–2e interaction between Mo(2), H(8), and C(8) is shown with hollow bonds. Bond lengths: Mo(1)–C(1) = 2.216 (3), Mo(1)–C(2) = 2.350 (4), Mo(1)–C(3) = 2.317 (4), Mo(2)–C(4) = 2.240 (4), Mo(2)–C(5) = 2.287 (4), Mo(1)–C(6) = 2.341 (5), Mo(1)–C(7) = 2.321 (4), Mo(1)–C(8) = 2.233 (4), C(1)–C(2) = 1.426 (5), C(2)–C(3) = 1.414 (6), C(3)–C(4) = 1.499 (5), C(4)–C(5) = 1.429 (7), C(5)–C(6) = 1.524 (6), C(6)–C(7) = 1.412 (6), C(7)–C(8) = 1.435 (7) Å.

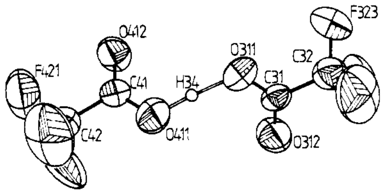
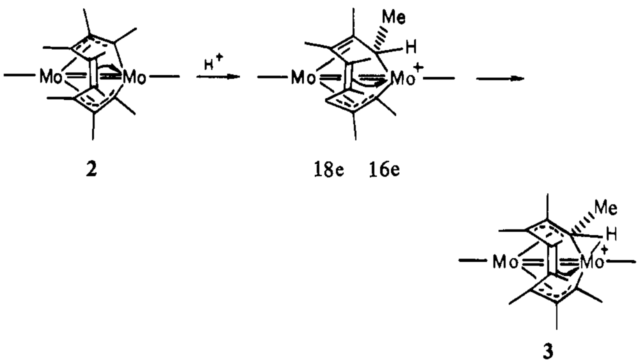


Figure 3. Drawing[19] of the anion present in **3**.

Scheme II[a]



[a] C_5H_5 ligands and methyl groups omitted for clarity.

Table I. Selected Bond Lengths (Å) and Angles (deg)

	2	3
Mo(1)–Mo(2)	2.595 (1)	2.614 (1)
Mo(2)–C(8)	2.096 (2)	2.196 (5)
Mo(2)–H(8)		1.88 (8)
C(8)–H(8)		0.89 (7)
Mo(2)–H(8)–C(8)		99 (5)
Mo(2)–C(1)	2.089 (2)	2.130 (4)
C(7)–C(8)–Me(8)	119.9 (2)	122.2 (4)

The availability of a simple synthesis of the symmetrically substituted complex **2** provided an opportunity to begin to explore the chemistry of these unusual molecules. For our initial studies the protonation reaction was chosen. Treatment of **2** with an excess of anhydrous trifluoroacetic acid at 0 °C led to a rapid reaction and the formation of the purple crystalline salt $[Mo_2(H)(MeC_2Me)_4(\eta^5\text{-}C_5H_5)_2][(CF_3CO_2)_2H]$ (**3**) [^1H NMR ($CDCl_3$) τ 4.48 (s, 5 H, C_5H_5), 5.38 (s, 5 H, C_5H_5), 7.27 (s, 3 H, Me), 7.30 (s, 3 H, Me), 7.33 (s, 3 H, Me), 7.48 (d, 3 H, Me, J_{HH} = 3 Hz), 7.87 (s, 3 H, Me), 7.96 (s, 3 H, Me), 9.03 (d, 3 H, Me, J_{HH} = 2 Hz), 9.06 (s, 3 H, Me), 19.37 (m, 1 H, MoHC)]. The ^1H NMR spectra confirmed that protonation had indeed occurred, but in order to examine more closely the nature of this reaction an X-ray study was conducted with a suitable crystal of **3**.

Crystal data for (3). $C_{30}H_{36}F_6Mo_2O_4$, M = 765.9, monoclinic, space group $P2_1/c$; a = 10.648 (2), b = 15.119 (4), c = 19.655 (6) Å; β = 105.30 (2)°; U = 3052.0 (7) Å^3; Z = 4; D_c = 1.666 g cm^{-3}; $F(000)$ = 1320; μ(Mo Kα) = 8.4 cm^{-1}. Current R = 0.0293 (R = 0.0294) for 3781 observed intensities [$I > 3\sigma(I)$] with 3° < 2θ < 55° and weight $w = 1/(\sigma^2\{F_o\} + 0.00023F^2)$.

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[10] Klinger, R. J; Butler, W.; Curtis, M. D. *J. Am. Chem. Soc.* **1975**, *97*, 3535–3536.

The structure determination[9,11] (Figures 2 and 3) revealed that protonation had resulted in the placement of a proton between the carbon-molybdenum σ bond of **2** (Scheme II) with the principal changes in geometry occurring in the region of C(8) and Mo(2) (Figure 2, Table I), the Mo(2)-C(8) distance increasing from 2.096 (2) Å in **2** to 2.196 (5) Å in **3**. Such a shift is similar to, although slightly smaller than, those observed in M-H-M systems relative to their unprotonated analogoues,[12-14] since in these systems the bent C-H-Mo interaction, which is also reflected in the high-field ^{1}H shift of the hydrogen, is best described as three center two electron, with the (X-ray distorted) bond lengths and angles reflecting considerable Mo(2)-C(8) interaction. The effect of protonation on the remainder of the C_8 chain is slight, leaving the connectivity unchanged with only very minor modification of bond lengths and angles, reflecting the stability of this mode of coordination; bonds to Mo(2) are slightly lengthened (by ca. 0.02 Å), and the Mo-Mo bond is still within the range appropriate for a double bond at 2.614 (1) Å.

The anion was found to consist of two trifluoroacetate groups linked by a short, strong, nearly symmetrical hydrogen bond [O···O, 2.429 (5) Å] and the hydrogen located and refined without constraints [O(311)-H(34) = 1.34 (7), O(411)-H(34) = 1.10 (7) Å; O(311)-H(34)-O(411) = 175 (7)°].

In contrast with the C—H··M interactions previously observed,[15,16] the bent CHMo system present in the cation **3** closely resembles the kind of interaction which it has been postulated[17,18] leads to an α-hydrogen abstraction reaction. As is shown in Scheme II if protonation occurs at a carbon α to the molybdenum, then the cationic electron-deficient molybdenum center which is generated is ideally placed to participate in such a three-center interaction, thus providing strong support for Schrock's suggestion. Suitable neutron diffraction studies are planned to define the precise location of the bridging hydrogen.

Acknowledgment. We thank the S.R.C. for support and Dr. N. J. Connelly for help with the electrochemical observations.

Supplementary Material Available: Atomic positional and thermal parameters and bond lengths for complexes **2** and **3** (18 pages). Ordering information is given on any current masthead page.

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(11) The bridging hydrogen atom was located as the highest difference electron density peak associated with the cation **3**, bridging the C(8)-Mo(2) vector at 1.10 Å from C(8) and 1.85 Å from Mo(2); unconstrained isotropic refinement of this hydrogen gave the bond lengths and angles given in Table I.

(12) Petersen, J. L; Stewart, Jr., R. P. *Inorg. Chem.* **1980**, *19*, 186-191.

(13) Petersen, J. L; Dahl, L. F; Williams, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 6610-6620.

(14) Petersen, J. L; Williams, J. M. *Inorg. Chem.* **1978**, *17*, 1308-1312.

(15) Cotton, F. A; La Cour, J; Stanislowski, A. G. *J. Am. Chem. Soc.* **1974**, *96*, 754-760.

(16) Williams, J. M; Brown, R. K; Schultz, A. J; Stucky, G. D; Ittel, S. D. *J. Am. Chem. Soc.* **1978**, *100*, 7401-7409. Ittel, S. D; Van-Catledge, F. A; Hesson, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 6905-6911.

(17) Wood, C. D; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3210-3222.

(18) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98-104.

(19) Sheldrick, G. M. SHELXTL structure analysis system, Göttingen, Federal Republic of Germany, 1980.

A New and Efficient Total Synthesis of Streptonigrin

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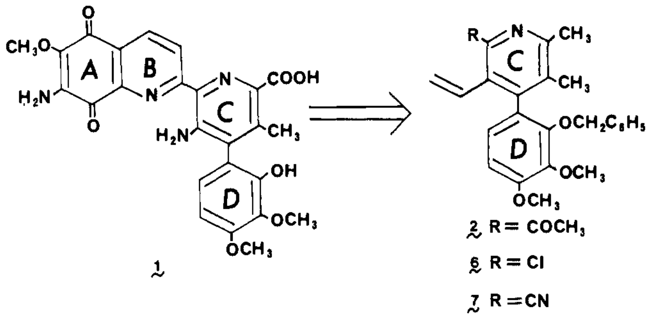
Rochester, New York 14627

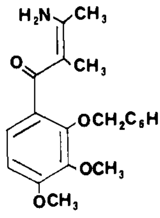
Received September 15, 1980

The antitumor antibiotic streptonigrin was shown in 1963 by Rao, Biemann, and Woodward to have the tetracyclic aminoquinone structure **1**.[1] Since that time a stream of publications have reported approaches to the synthesis of this polyfunctional molecule.[2-4] The first synthesis of its carbon framework was achieved in these laboratories in 1978,[3a] and an imaginative total synthesis of streptonigrin in 0.013% yield in over 30 steps from 2-benzyloxy-3,4-dimethoxybenzaldehyde was recently reported by Weinreb and co-workers.[5] We now describe concurrent studies in this area which have led to a short and efficient total synthesis of this intricate molecule by utilizing a more direct C-ring construction than the sequence employed by the Weinreb group.

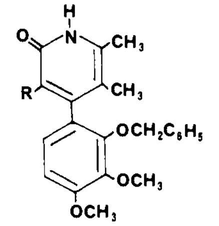
It is clear from our preliminary communication[3a] that synthesis of **1** requires early construction of the C-D arylpyridine rings containing substituents appropriate for facile conversion to those in the target antibiotic. In the Weinreb synthesis this was achieved by a nonregiospecific imino Diels-Alder reaction, aromatization, and a subsequent Sommelet-Hauser rearrangement sequence to introduce functionality at the vacant 3-position of the pyridine intermediate. Our strategy involves a regiospecific 3-acyl-2-pyridone construction, leading to the key C-D vinylpyridine **2**, since Friedländer condensation should lead to attachment of rings A and B, while the stable vinyl group should serve as convenient precursor to the C-ring amino group.



Thus, condensation of the readily available β-keto enamine **3**[6]



3



4 R = COCH₃
5 R = CHOHCH₃

with methyl acetoacetate (xylenes, reflux, -H$_2$O, 14 h) led with unusual regiospecificity[7] to the acylpyridone **4** in 97% yield:[8] mp 216-217 °C;[9a] NMR[9b] δ 1.68 (3 H, s), 2.32 (3 H, s), 2.44 (3 H,

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(1) Rao, K. V.; Biemann, K.; Woodward, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 2532.

(2) For a review, see: Hibino, S. *Heterocycles* **1977**, *6*, 1485.

(3) (a) Kende, A. S.; Naegely, P. C. *Tetrahedron Lett.* **1978**, 4775. (b) Kim, D.; Weinreb, S. M. *J. Org. Chem.* **1978**, *43*, 121. (c) *Ibid.* **1978**, *43*, 125. (d) Wittek, P. J.; Liao, T. K.; Cheng, C. C. *Ibid.* **1979**, *44*, 870. (e) Rao, K. V.; Kuo, H.-S. *J. Heterocycl. Chem.* **1979**, *16*, 1241.

(4) For fascinating recent studies on the biosynthesis of streptonigrin, see: Gould, S. J.; Darling, D. S. *Tetrahedron Lett.* **1978**, 3207. Gould, S. J.; Chang, C. C. *J. Am. Chem. Soc.* **1977**, *99*, 5496; **1978**, *100*, 1624; **1980**, *102*, 1702. Gould, S. J. Chang, C. C.; Darling, D. S.; Roberts, J. D.; Squillacote, M. *Ibid.*, **1980**, *102*, 1707.

(5) Basha, F. Z.; Hibino, S.; Kim, D.; Pye, W. E.; Wu, T.-T.; Weinreb, S. M. *J. Am. Chem. Soc.* **1980**, *102*, 3962.

(6) Liao, T. K.; Wittek, P. J.; Cheng, C. C. J. *Heterocycl. Chem.* **1976**, *13*, 1283.

(7) Breitmaier, E.; Gassenman, S.; Bayer, E. *Tetrahedron* **1970**, *26*, 5907. This reference describes the inverse regiochemistry from what we find in our system.

(8) The analogous condensation with ethyl nitroacetate failed under a variety of conditions.

(9) (a) All compounds for which a melting point is reported gave satisfactory combustion analyses. (b) All NMR spectra were recorded at 100 MHz in CDCl$_3$ unless otherwise noted.

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