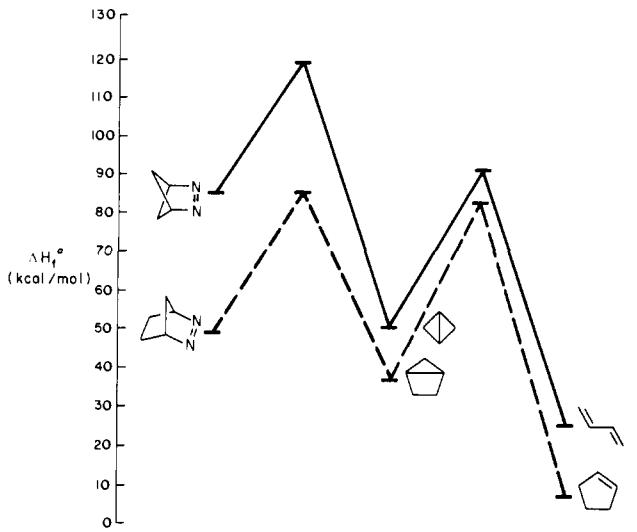

Figure 2. Energetics of the thermal decompositions of **1** and **2**.

magnitude of the kinetic isotope effect (KIE). These would then produce [2-^{2}H]- and [1-^{2}H]-butadiene, respectively. Diazoalkene **7** would be labeled equally in the allylic and vinylic CH_2 groups (ignoring the secondary KIE), and thus this route would produce a 1:1 mixture of [1-^{2}H]- and [2-^{2}H]-butadiene. However, it has been shown that [2-^{2}H]-bicyclobutane (**3-D**) produces only [1-^{2}H]-butadiene on thermolysis.[4] We find that gas-phase pyrolysis of **2-D** also produces only [1-^{2}H]-butadiene, consistent only with the "hot molecule" mechanism.

The reason that symmetrical diazene **2** shows such a large "hot molecule" effect can be seen in Figure 2, which compares the energetics of decomposition of **2** and **1**, the latter being considered a "typical" pyrazoline. Accurate activation parameters are available for all processes.[14] The heat of formation is known for each compound[15] except **2**, for which the value determined by molecular mechanics is used.[16] An error as large as 5 kcal/mol in this value would not affect the current analysis. In both cases a hydrocarbon is produced that could rearrange to another product if sufficient energy were available. The difference between **1** and **2** is that the transition state for the decomposition of **2** lies well above that for the hydrocarbon rearrangment. This is entirely a consequence of the high strain energy of **2**, which substantially raises $\Delta H_f°$ of **2** and its decomposition transition state. Even if a significant amount of excess energy is carried off by the N_2, there still could be enough energy to overcome the bicyclobutane rearrangement barrier. Thus, our results do not necessarily contradict the Bauer/Bergman analysis,[11,12] since the excess energy from **5** and **6** is much less than that from **2**. However, our results do require that a very substantial amount of the excess energy in the decomposition of **2** be localized in the hydrocarbon fragment, perhaps in the form of biradical **4**. This could indicate that the vibrational coupling in the symmetrical transition state is more effective than previously postulated[12] or the transition state for the decomposition of **2** is unsymmetrical.

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(14) See ref 1b, 5, and: Willcott, M. R.; Cargill, R. L.; Sears, A. B. *Prog. Phys. Org. Chem.* **1972**, *9*, 25-98.

(15) See ref 1b and: Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press, New York, 1970. Turner, R. B.; Goebel, P.; Mallon, B. J.; Doering, W. von E.; Coburn, J. F., Jr.; Pomerantz, M. *J. Am. Chem. Soc.* **1968**, *90*, 4315-22.

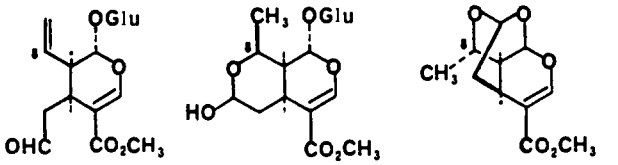
(16) Kao, J.; Huang, T.-N. *J. Am. Chem. Soc.* **1979**, *101*, 5546-57.

Total Synthesis of (-)-Sarracenin by Photoannelation[1]

S. W. Baldwin* and M. T. Crimmins

Paul M. Gross Chemical Laboratory
Duke University, Durham, North Carolina 27706
Received December 1, 1981

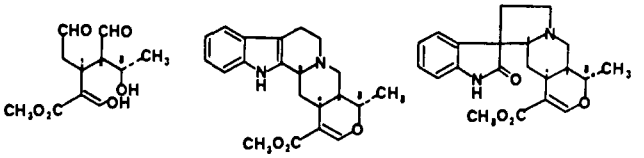
The secoiridoids such as secologanin (**1**) and moronoside (**2**) comprise a sizable subclass of the large group of natural products known as the iridoids.[2] These compounds are of interest primarily because of the demonstrated involvement of some of their members in the biosynthesis of several classes of alkaloids. In addition, some possess significant biological activity of their own.[3] The secoiridoids usually occur as glucosides although there are exceptions, a recent one being sarracenin (**3**), the total synthesis of which is the subject of this report.



1 **2** **3**

The isolation and single-crystal X-ray determination of sarracenin was reported in 1976 by Miles.[4] Sarracenin appears to be the same as the material derived from the emulsin (or acid) hydrolysis of morronoside (**2**) as previously reported by Souzu and Mitsuhashi,[5] although the discrepancy in the published specific rotations of the two samples (-68.8 vs. -35.6°) is bothersome.

Miles (among others) has made the observation that a suitably unraveled sarracenin, e.g., **4** (or **2**) is stereochemically disposed to be a convenient biosynthetic source of the nontryptophan 10-carbon portion of indole alkaloids such as ajmalicine (**5**) and mitraphylline (**6**) and perhaps others. The combination of bio-



4 **5** **6**

logical activity, biosynthetic interest, and unique molecular architecture make sarracenin an attractive target for synthesis, and in 1978 Whitesell and co-workers reported its preparation in 15 steps from 1,5-cyclooctadiene.[6] Described here is a seven-step total synthesis of racemic sarracenin as well as a synthesis of (-)-sarracenin which verifies that the absolute configuration of the natural material is as depicted.[7]

Logical retrosynthetic analysis suggests the following simple scheme for the synthesis of sarracenin involving first the photochemical addition of methyl diformylacetate (**9**) to a suitable alkene acetal, followed by dehydrative cyclization of the resultant bis hemiacetal to afford the natural product. Although this photochemical approach to other iridoids related to loganin has been previously employed by Büchi[8] and Uskokovic and Par-

(1) (a) Paper 8 in the series of photochemical annelations. Part 7: Baldwin, S. W.; Wilkinson, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 3634. (b) Supported by the National Institutes of Health (GM 26266). (c) Presented in part at the 180th National Meeting of the American Chemical Society, Las Vegas, NV, Aug 25, 1980; Abstract No. ORGN 41.

(2) Inoye, H.; Ueda, S.; Takeda, Y. *Heterocycles* **1976**, *4*, 527.

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(5) Souzu, I.; Mitsuhashi, H. *Tetrahedron Lett.* **1969**, 2725.

(6) Whitesell, J. K.; Matthews, R. S.; Helbling, A. M. *J. Org. Chem.* **1978**, *43*, 784.

(7) Biosynthetic considerations require that the absolute configuration of (-)-sarracenin be as depicted in **3**, with C-8 of the *S* configuration. This was assured by the laboratory conversion of natural morronside (**2**, *S* configuration) to sarracenin.[5]

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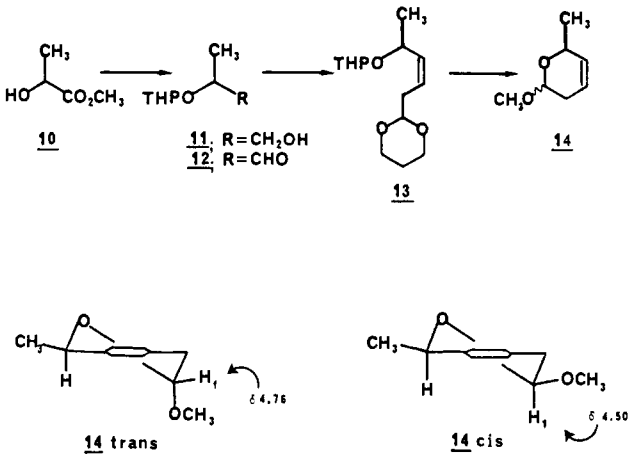
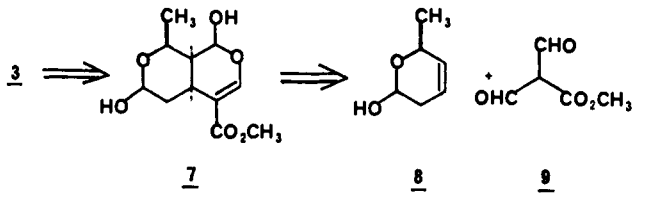
Scheme I



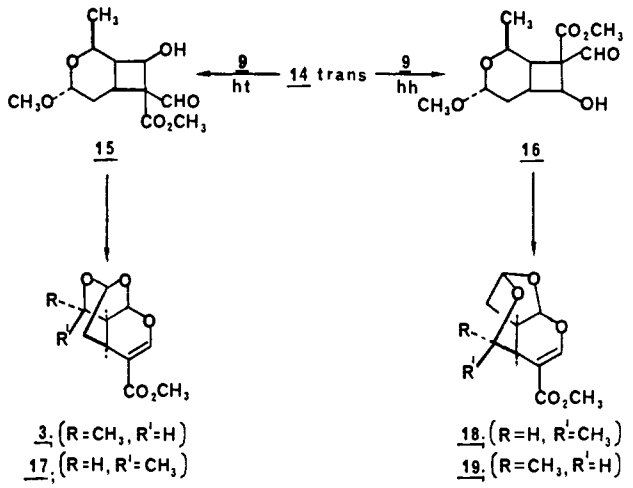
tridge,[9,10] our continuing interest in photochemical routes to natural products, as well as our previous utilization of **9** as a photochemical addend,[11] make this approach compelling.



A convenient synthesis of a suitable alkene acetal (**8**) was accomplished as outlined in Scheme I. (±)-Methyl lactate (**10**) was converted to its tetrahydropyranyl ether (DHP/PPTS/CH_2Cl_2),[12] which was successively reduced to the primary alcohol **11** with lithium aluminum hydride and reoxidized with oxalyl chloride activated Me_2SO[13] to give THP aldehyde **12** in 88% yield for the three steps.[14,15] Exposure of **12** to the protected propionaldehyde phosphorane described by Stowell[16] produced alkene **13** as a mixure of THP diastereoisomers and of >90% *Z* stereochemical purity. Acidic methanolysis (CH_3OH/PPTs) of **13** cleaved the THP and acetal protecting groups with concomitant formation of a 1:1 equilibrium mixture of methyl acetals **14**. It was expected on the basis of the anomeric effect[17] that the preferred conformation of *trans*-**14** would have a pseudoaxial methoxyl, giving a pseudoequatorial orientation the C_5 methyl group. The preferred conformation of *cis*-**14** was expected to place both pyran substituents in pseudoequatorial positions. Separation of the acetal isomers **14** was accomplished by careful chromatography on silica gel. The less polar and more polar isomers were assigned cis and trans stereochemistry, respectively, on the basis of the ^1H NMR absorptions of H_1. In particular H_1 in *cis*-**14** occurs as a doublet at δ 4.76 (J = 4.7 Hz) and in *trans*-**14** at δ 4.50 (J = 5.5 Hz), trends which are in accord with expectations for equatorial vs. axial protons in cyclohexane systems.[18] In addition these values are consistent with those reported for a series of related dihydropyran acetals.[17]

The planned irradiation of **14** with methyl diformylacetate (**9**)[19] followed by intramolecular bis-acetal formation can in principle afford four different products of consequence as a result of head–tail (ht) and head–head (hh) regiochemical orientations, each with the further possibility of addition cis and trans to the eventual C-8 methyl group. A preponderence of the desired ht regiochemistry was anticipated on the basis of previous work[8,11] with unsymmetrical alkenes, and it was expected that the pseudoaxial methoxyl group in *trans*-**14** would direct the photoaddition from the side cis to the methyl group, the overall orientation required for sarracenin (ht, cis). In the event, irradiation of a hexane/methylene chloride solution of **9** and *trans*-**14** followed by filtration of the crude product though a short silica gel column afforded a 20% yield of photoproducts, which without further characterization was cyclized under acidic conditions (TsOH/CH_2Cl_2/1 h) to give a 75% yield of tricyclic bis acetals.

A combination of analytical gas chromatography and ^1H NMR analysis revealed the presence of four closely related compounds in the approximate ratio of 12:4.2:2.8:1. Trituration of this mixture with pentane led to the essentially quantitative separation of the major isomer, mp 106–107.5 °C, which proved to be identical in all respects (IR, ^1H NMR, ^{13}C NMR) with comparison spectra of racemic sarracenin (**3**) (mp, 107–108 °C)[6] and also identical with comparison spectra (^1H NMR, ^{13}C NMR) of natural (−)-sarracenin.[20] Further fractional crystallization afforded the next most prevelant isomer which proved by direct spectral comparison (IR, ^1H NMR, ^{13}C NMR) to be 8-epi-sarracenin (**17**), formed by a ht, trans addition of **9** to *trans*-**14**.[20] The net result



of this study is the seven-step formation of crystalline sarracenin in 7% overall yield from methyl lactate. The low material yield[21] is in part compensated for by the shortness of the synthetic sequence and by the ease in obtaining pure sarracenin. The identity of the two remaining minor products has not yet been established although it is likely that they are bis aceals **18** and **19**, the two possible products resulting from cis and trans hh photoaddition. It is interesting to note that when *cis*-**14** is utilized in the pho-

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(15) Elemental composition data for compounds **11**, **12**, and **13** were within acceptable limits (±0.3%). Compound **14** was sufficiently labile to preclude C, H analysis, although all synthetic intermediates gave spectral data in complete accord with the assigned structures.

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(18) Bhacca, N. S.; Williams, D. S. "Application of NMR Spectroscopy in Organic Chemistry"; Holden-Day, Inc.: San Francisco, CA, 1969; pp 47–49.

(19) A summary of the several routes to **9** can be found in: Nakane, M.; Gollman, H.; Hutchinson, C. R.; Knutson, P. L. *J. Org. Chem.* **1980**, *45*, 2536.

(20) We are indebted to Professor D. H. Miles for comparison spectra of natural (−)-sarracenin and to Professor J. K. Whitesell for comparison spectra of (±)-sarracenin and (±)-8-*epi*-sarracenin.

(21) The low efficiency of the photocycloaddition step is probably a consequence of energy wasting cis/trans isomerization of the excited state of **9** as has been seen for other β-dicarbonyl compounds when irradiated in the presence of alkenes substituted with basic heteroatoms; unpublished results.

tochemical step rather than *trans*-**14**, the ratio of the ht products **3** and **17** decreases from 2.9:1 to 1.7:1, while a 1:1 mixture of the two alkenes affords a product ratio of 2.2:1.[22]

In a sequence of related experiments, L-(+)-ethyl lactate (*S* configuration) has been converted to optically active (-)-sarracenin, mp 124-125 °C (lit.[4] 127-128 °C). The apparently low optical yield of this sequence ($[\alpha])^{23}_D$ - 20.9°) is puzzling in light of the close correlation between the melting points of the synthetic and natural material but may be partially due to trace contaminants and concentration differences. However, the previously mentioned discrepancy concerning the specific rotation of the natural material makes a valid comparison difficult. This point, as well as an alternative synthesis of optically active dihydropyrans such as **14**, is under current investigation.

(22) The ratios of the four products derived from pure *trans*-**14** pure *cis*-**14**, and as 1:1 mixture of the two was 12:4.2:2.8:1, 6.6:3.9:1.7:1, and 9.2:4.2:2.3:1, respectively.

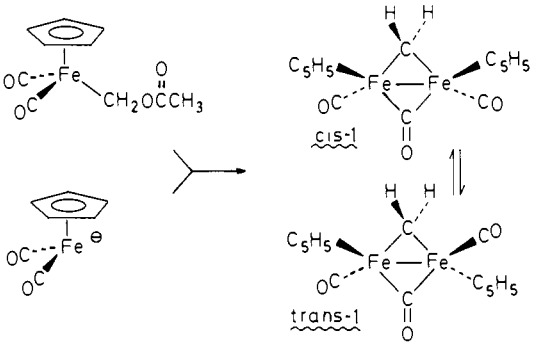
Synthesis and Interconversions of Dinuclear Iron Complexes with μ-CH_3, μ-CH_2, and μ-CH Ligands

Charles P. Casey,* Paul J. Fagan,† and William H. Miles

Department of Chemistry, University of Wisconsin Madison, Wisconsin 53706

Received September 28, 1981

The increasing interest in the synthesis and chemistry of bimetallic bridged methylene complexes[1-7] stems from the demonstrated or proposed involvement of these and related species in carbon monoxide reduction chemistry,[2] olefin metathesis reactions,[3] alkyne polymerizations,[3] and methylene transfer reactions.[4] In this communication, we report the synthesis of the new iron complex[5,6] $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)$ (**1**)($Cp{=}\eta^5\text{-}C_5H_5$) and the facile conversion of **1** to the cationic bridging methyl and bridging methylidyne complexes $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_3)]^+$ (**2**) and $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH)]^+$ (**3**).[7] The reactions of compounds **1**, **2**, and **3** provide an additional example of the stepwise interconversion of μ-CH_3, μ-CH_2, and μ-CH ligands; only two other somewhat related examples of these interconversions are known.[1d,11,8]



Slow addition of a THF solution of $K[CpFe(CO)_2]$ to a refluxing THF solution of $CpFe(CO)_2CH_2O_2CCH_3$[10] produced a 1:2.1 mixture of $[CpFe(CO)_2]_2$ (**4**) and the bridging methylene complex **1** (50% crude yield, 3.4:1 mixture of *cis*-**1**:*trans*-**1**). The separation of **1** from **4** proved difficult but was accomplished by slow column chromatography (alumina:warm hexane) using a specialized apparatus (see supplementary material). Slow chromatography takes advantage of the fact that *cis*-**1** and *trans*-**1** equilibrate more rapidly than they are eluted and that *trans*-**1** elutes substantially faster than either *cis*-**1** or **4** which elute at very similar rates.[11] The yield of analytically pure **1** was greater

† NSF Postdoctoral Fellow, 1981-1982.

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(5) For other iron complexes with the μ-CH_2 ligand, see: (a) Sumner, C. E.; Jr.; Riley, P. E.; Davis, R. E.; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 1752-1754 ($Fe_2(CO)_8(\mu\text{-}CH_2)$). (b) Herrmann, W. A.; Bauer, C. *J. Organomet. Chem.*, **1981**, *204*, C21-C24 ($Fe_2(C_5H_5)_2(NO)_2(\mu\text{-}CH_2)$).

(6) We have recently learned that **1** has been prepared by several other groups: (a) Korswagen, R.; Alt, R.; Ziegler, M. L. *Angew. Chem.*, in press. Also see unpublished work cited in ref 1t. (b) Pettit, R., private communication.

(7) A number of complexes closely related structurally to **1**, **2**, and **3** have been reported: (a) Herrmann, W. A.; Plank, J. *Z. Naturforsch. B*, **1980**, *35*, 680-688 ($Fe_2(C_5H_5)_2(CO)_2(\mu\text{-}CO)[\mu\text{-}CH(CO_2R)]$). (b) Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1980**, 441-442 ($M_2(C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH(CH_3))$ (M = Fe, Ru)). (c) Davies, D. L.; Dyke, A. F.; Knox, S. A. R.; Morris, M. J. *J. Organomet. Chem.* **1981**, *215*, C30-C32 ($Ru_2(C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)$). (d) Meyer, B. B.; Riley, P. E.; Davis, R. E. *Inorg. Chem.* **1981**, *20*, 3024-3029 ($Fe_2(C_5H_5)_2(CO)_2(\mu\text{-}CO)[\mu\text{-}CH(CH_3)]$). (e) Dyke, A. F.; Knox, S. A. R.; Naish, P. J. *J. Organomet. Chem.* **1980**, *199*, C47-C49 ($Ru_2(C_5H_5)_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(CH_3)_2]$). (f) Dawkins, G. M.; Green, M.; Orpen, A. G.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1982**, 41-43. ($\{Fe_2(C_5H_5)_2(\mu\text{-}CO)[\mu\text{-}(C_6H_5)_2PCH_2P\text{-}(C_6H_5)_2](\mu\text{-}CH_3)\}^+$). (g) Nitay, M.; Priester, W.; Rosenblum, M. *J. Am. Chem. Soc.* **1978**, *100*, 3620-3622 ($[Fe_2(C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CR)]^+$). (h) Davies, D. L.; Dyke, A. F.; Endesfelder, A.; Knox, S. A. R.; Naish, P. J.; Orpen, A. G.; Plaas, D.; Taylor, G. E. *J. Organomet. Chem.* **1980**, *198*, C43-C49 ($[Ru_2(C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CR)]^+$). (i) La Croce, S. J.; Menard, K. P.; Cutler, A. R. *Ibid.* **1980**, *190*, C79-C83 ($\{Fe_2(C_5H_5)_2(\mu\text{-}CO)[\mu\text{-}(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2](\mu\text{-}C(OCH_3))\}^+$).

(8) (a) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726-7727. (b) Calvert, R. B.; Shapley, J. R.; Schultz, A. J.; Williams, J. M.; Suib, S. L.; Stucky, G. D. *Ibid.* **1978**, *100*, 6240-6241. (c) Schultz, A. J.; Williams, J. M.; Calvert, R. B.; Shapley, J. R.; Stucky, G. D. *Inorg. Chem.* **1979**, *18*, 319-323. (d) Dimas, P. A.; Duesler, E. N.; Lawson, R. J.; Shapley, J. R. *J. Am. Chem. Soc.* **1980**, *102*, 7787-7789.

(9) Plotkin, J. S.; Shore, S. G. *Inorg. Chem.* **1981**, *20*, 284-285.

(10) Green, M. L. H.; Ishaq, M.; Whiteley, R. N. *J. Chem. Soc. A* **1967**, 1508-1515.

(11) The mixture of red *cis*-**1** and purple *trans*-**1** can be separated by thin layer chromatography (silica gel; 75:15:10 hexane-CH_2Cl_2-ether; *trans*-**1**, R_f 0.70; *cis*-**1**, R_f 0.44; **4**, R_f 0.40).

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