

Figure 2. Oscillating light absorption at 450 nm (a), oscillating photoluminescence emission at 610 nm (b), and oscillating chemiluminescence emission at 610 nm (c) in the  $Ru(bpy)_3^{2+}$ -catalyzed BZ reaction. Experimental conditions are as in Figure 1.

3) of  $Ru(bpy)_3^{2+}$  can be obtained. Actually, when both reactions 2 and 3 are thermodynamically allowed, reaction 3 predominates for kinetic reasons,<sup>24</sup> and since the quantum yield of  $*Ru(bpy)_3^{2+}$ emission is high,<sup>24</sup> luminescence can be easily observed. Rubinstein and Bard<sup>25</sup> have recently shown that chemiluminescence can be obtained when organic acids are oxidized by  $Ru(bpy)_3^{3+}$  or in the presence of  $Ru(bpy)_3^{2+}$ . The reaction mechanism involves reduction of  $Ru(bpy)_3^{3+}$  by strongly reducing radicals generated in the one-electron oxidation of the organic acid. We have observed that chemiluminescence is also obtained on mixing aqueous solutions of  $Ru(bpy)_3^{3+}$  and malonic acid in 1 M H<sub>2</sub>SO<sub>4</sub>. Since the  $Ru(bpy)_3^{3+}$  concentration oscillates<sup>8,15</sup> in the BZ reaction and since a large concentration of malonic acid is also present, we thought that the oscillating reaction has to be accompanied by an oscillating chemiluminescence emission. When an aqueous solution containing 0.25 M malonic acid, 0.06 M KBrO<sub>3</sub>, 1 M  $H_2SO_4$ , and  $1.0 \times 10^{-4}$  M Ru(bpy)<sub>3</sub><sup>2+</sup> was examined for chemiluminescence in a fluorimeter, an oscillating signal was indeed recorded, although the light emission was too weak to be observed by eye.

Subsequent systematic investigations showed that (i) the chemiluminescence spectrum is identical (except for oscillations) with the photoluminescence spectrum of  $\text{Ru}(\text{bpy})_3^{2+}$  (Figure 1), (ii) the intensity and period of the oscillating chemiluminescence depend on the reactant concentrations and decrease with time, and (iii) the oscillating chemiluminescence has the same period but is out of phase compared with the oscillating light absorption at 450 nm (where the extinction coefficient of  $\text{Ru}(\text{bpy})_3^{2+}$  is much higher than that of  $\text{Ru}(\text{bpy})_3^{3+}$ ) and with the oscillating photoluminescence emission (which is due to  $\text{Ru}(\text{bpy})_3^{2+}$  absorption) (Figure 2).

The shapes of the oscillating curves shown in Figure 2 merit some comments. The shape of the light absorption oscillation (Figure 2a) shows that the interconversion of  $Ru(bpy)_3^{2+}$  and  $Ru(bpy)_3^{3+}$  is due to a smooth reaction. By contrast, the pho-

toluminescence oscillation (Figure 2b) shows a shoulder and then a sharp peak before decreasing. These features cannot be due to concomitant variations in the Ru(bpy)<sub>3</sub><sup>2+</sup> concentration because in such a case they should also appear in the light absorption oscillation curve of Figure 2a. In the same way, we can note that the chemiluminescence curve (Figure 2c) exhibits an oscillatory behavior that does not exactly reflect the changes in the Ru-(bpy)<sub>3</sub><sup>3+</sup> concentrations shown by Figure 2a. We believe that the peculiar features of the photoluminescence and chemiluminescence curves are due to the oscillating formation of radical species which may act as quenchers for \*Ru(bpy)<sub>3</sub><sup>2+</sup> and as reactants for the Ru(bpy)<sub>3</sub><sup>3+</sup> chemiluminescent reaction. A more thorough investigation of this system might reveal new details of the mechanism of the BZ reaction.

Other experiments on this artificial "firefly" system are in progress in our laboratory.

**Registry No.** Ru(bpy)<sub>3</sub><sup>2+</sup>, 15158-62-0; BrO<sub>3</sub><sup>-</sup>, 15541-45-4; malonic acid, 141-82-2.

## **Chiral Total Synthesis of Compactin**

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Compactin<sup>1a</sup> (from *Penicillium brevicompactum*) [or ML-236B<sup>1b</sup> (from *P. citrinum*), **1a**], monacolin K<sup>2a</sup> (or mevinolin,<sup>2b</sup> **1b**), and dihydro compounds **2a** and **2b**,<sup>3</sup> which are potent inhibitors of 3-hydroxy-3-methylglutaryl coenzyme A (HMG-CoA) reductase, have attracted considerable interest because of their high hypocholesterolemic activity.<sup>4</sup> This important family of polyketide-derived compounds possesses a highly functionalized hexahydronaphthalene (or *trans*-octalin) skeleton substituted with a  $\beta$ -hydroxy  $\delta$ -lactone moiety.

In this communication, we report an enantioselective and convergent synthesis of 1a,<sup>5</sup> which is also adaptable to the synthesis of the other related compounds 1b, 2a, and 2b. Our synthetic strategy outlined in Scheme I encompasses several interesting synthetic facets. (1) The intramolecular Diels-Alder reaction of 4 via exo orientation was considered to be a viable approach for the construction of the *trans*-octalone system 3, since deca-1,7,9-trien-3-one cyclized exclusively to *trans*-octalone.<sup>6</sup> (2) The concomitant asymmetric induction of four asymmetric centers, C8, C9, C14, and C17 in 3, might be realized in this [4 + 2]

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<sup>(2) (</sup>a) Endo, A. J. Antibiot. 1979, 32, 852. (b) Alberts, A. W.; Chen, J.; Kuron, G.; Hunt, V.; Huff, J.; Hoffman, C.; Rothrock, J.; Lopez, M.; Joshua, H.; Harris, E.; Patchett, A.; Monaghan, R.; Currie, S.; Stapley, S.; A.-Schönberg, G.; Hensens, O.; Hirshfield, J.; Hoogsteen, K.; Liesch, J.; Springer, J. Proc. Natl. Acad. Sci. U.S.A. 1980, 77, 3957.
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Scheme I



reaction, because the asymmetric center at C13 was expected to control the approach of the dienophile from a single diastereomeric face by steric and stereoelectronic interactions.<sup>7</sup> (3) Wadsworth-Emmons coupling of the optically active segments A (5) and B(6) was envisioned for the expeditious preparation of the requisite (E,E,E)-trienone 4. (4) Development of an asymmetric synthesis of 6, a masked  $\beta$ -hydroxy  $\delta$ -lactone, should be valuable for the preparation of polyketide-derived natural products.

Preliminary studies on the intramolecular Diels-Alder reaction of racemic  $7^9$  led to *trans*-octalone 8 with the desired relative stereochemistry.<sup>10</sup> Thus, S configuration at C13 in 7 (4) is

(7) Although the preference of one diastereomeric transition state over the other in endo (or exo) intramolecular Diels-Alder reactions has been ac-counted for only in terms of steric interaction,<sup>8a</sup> stereoelectronic control due to favorable orbital overlap<sup>8b</sup> between an allylic substituent bond and an incipient bond should play a signification role: in the present case, the transition states in which the allylic C13-O bond is nearly perpendicular to the diene plane may be greatly stabilized. Thus, we postulated that the two exo transition states i, leading to desired 3, and ii, leading to the undesired isomer, are preferred by stereoelectronic interaction and that i is more favored because of the absence of an unfavorable steric interaction between 13-H and 15-H in ii.



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(9) (a) All new compounds exhibited satisfactory IR and <sup>1</sup>H NMR spectral properties as well as analytical  $(\pm 0.3\%)$  or exact mass data. (b) The specific rotations,  $[a]_D$ , (concentration) in CHCl<sub>3</sub> of representative intermediates are as follows: **3**, +37.4° (0.4); **4**, -1.4° (2.3); **5**, -1.2° (1.5); **6**, -2.5° (1.1); **10**, -13.4° (1.0); **11**, -37.5° (1.2); **12**, +3.1° (1.9); **14**, -22.1° (1.1); **15**, +7.8° (1.0); **16**, -16.0° (1.1); **17** +27.4° (2.0); **18**, +50.5° (1.3); **19**, +57.6° (0.6); **20**, +130.4° (0.9); **21**, +130.8° (0.5°) **20**, +120.4° (0.8); **21**, +120.8° (0.6)

(10) These studies including the C13-substituent and Lewis acid effects on stereoselectivity will be discussed in a separate publication.



required for obtaining the desired absolute stereochemistry in the optically active series.



The synthesis of segment A (5) in its optically active form started from readily available 4(S)- $\gamma$ -lactone  $9^{11}$  (Scheme II). Lactone opening (LiOMe, MeOH) and silvlation (t-BuMe<sub>2</sub>SiCl) gave a chromatographically easily separable 1:1 mixture of recovered 9 and silvl ether 10 in 94% overall yield. Recovered 9 was recycled to produce 10. Hydrogenolysis  $(H_2/Pd, EtOH)$  of 10 followed by Collins oxidation yielded the aldehyde 11 (79%). Stereoselective preparation of (E,E)-diene 12 was accomplished by addition of *trans*-crotyl phenyl sulfone anion<sup>12</sup> (-78 °C, 3 min) followed by quenching with  $Ac_2O$  and subsequent reductive elimination of sulfone acetate<sup>13</sup> [3% Na(Hg), -24 °C] in 75% overall yield.<sup>14</sup> Condensation of **12** with the lithium anion of dimethyl methylphosphonate produced segment A (5), 85% yield.14

The synthesis of segment B (6) was designed to utilize the inexpensive and convenient asymmetric reduction of  $\beta$ -keto acid derivatives with baker's yeast.<sup>15</sup> After considerable preliminary experiments 13<sup>16</sup> was chosen as a starting material because it carried the functionality capable of further elaboration to 6

(12) It is essential to use trans-crotyl phenyl sulfone of high isomeric purity for stereoselective formation of 12. The sulfone of 96% E was prepared from commercial trans-2-buten-1-ol ( $E \ge 96\%$ ) in two steps (36% yield): (i) 1.15 equiv of Ph<sub>3</sub>P, 1.0 equiv of NBS, CH<sub>2</sub>Cl<sub>2</sub>, 0 °C, 30 min; (ii) 0.5 equiv of NaSO<sub>2</sub>Ph-2H<sub>2</sub>O, MeOH, 25 °C, 42 h.

(13) Kocienski, P. J.; Lythgoe, B.; Ruston, S. J. Chem. Soc., Perkin Trans. 1 1978, 829.

(14) 360-MHz <sup>1</sup>H NMR spectra of 12 and 5 revealed the presence of 4%

(14) 506-M12 H Mirk Spectra of 12 and 51 evaluation for the presence of 4% of 14-E,16-Z and 6% of 14-Z,16-E isomers.
(15) (a) Lemieux, R. U.; Giguere, J. Can. J. Chem. 1951, 29, 678. (b) Deol, B. S.; Ridley, D. D.; Simpson, G. W. Aust. J. Chem. 1976, 29, 2459.
Fráter, G. Helv. Chim. Acta 1979, 62, 2829.
(16) Prepared from 5-hexen-2-one [CO(OEt)<sub>2</sub>, NaH; 76%; bp 115–116 °C (20 mmHg)] cf.: Soloway, S. B.; LaForge, F. B. J. Am. Chem. Soc. 1947, 60, 2677

69. 2677.

<sup>(11)</sup> The benzyloxymethylated 9 ( $[\alpha]^{24}_{D}$  +18.0° (c 1.6, CHCl<sub>3</sub>)) was prepared from 4(S)-(hydroxymethyl)butyrolactone [Taniguchi, M.; Koga, K.; Yamada, S. *Tetrahedron* 1974, 30, 3574] by the standard method (PhCH<sub>2</sub>OCH<sub>2</sub>Cl, *i*-Pr<sub>2</sub>NEt, CH<sub>2</sub>Cl<sub>2</sub>).

(Scheme III). Saponification (KOH, EtOH, H<sub>2</sub>O), reduction (baker's yeast, D-glucose, H<sub>2</sub>O, 25 °C, 2 days), and methylation (CH<sub>2</sub>N<sub>2</sub>) produced chiral  $\beta$ -hydroxy ester 14, 35% yield, in >99% ee as determined by <sup>1</sup>H NMR chiral shift studies [360 MHz, Eu(tfc)<sub>3</sub>]. The absolute configuration was tentatively assigned by analogy to the reduction of 3-oxohexanoate<sup>15a</sup> and confirmed by eventual conversion to natural product 1a (vide infra). This ester 14, after conversion to its THP ether, was reduced with DIBAL-H to afford the aldehyde 15 in 85% yield. Transformation of 15 to a chromatographically readily separable 1:1 mixture of  $16^{17}$  and its 3-R isomer was performed in a straightforward manner in five steps (48% overall): (i) aldol condensation (EtOAc, LDA, -78 °C), (ii) deprotection of THP ether (PPTS, EtOH), (iii) acetonide formation (2,2-dimethoxypropane, p-TsOH), (iv) reduction (LiAlH<sub>4</sub>), and (v) protection (PhCH<sub>2</sub>Br, NaH, DMF). Finally, careful ozonolysis of 16 (MeOH,  $-78 \text{ °C} \rightarrow \text{Me}_2\text{S}$ ) completed the preparation of segment B (6) in 88% yield.

The coupling of 5 and 6 in THF (1.3 equiv of NaH, 1.0 equiv of 6, 0 °C, 5 min  $\rightarrow$  25 °C, 10 min) smoothly produced the (E,E,E)-trienone 4, 86% yield. Cyclization of 4 in refluxing chlorobenzene ( $N_2$ , 82 h) proceeded more slowly than 7 to give the desired *trans*-octalone 3(28%) and two cis isomers (45% and 9%).<sup>18</sup> The stereochemistry on the octalone ring of 3, which embodies five correct asymmetric centers out of six in the carbon framework of 1a, was evident from its <sup>1</sup>H NMR spectrum.<sup>18</sup> K-Selectride reduction (2 equiv in THF, 25 °C) of 3 introduced selectively the requisite axial alcohol 17 (87%).<sup>19</sup> Esterification



with 2(S)-methylbutyric anhydride (DMAP, pyridine, 25 °C, 20 h) yielded **18** (70%),<sup>19,20</sup> which was debenzylated (Li/NH<sub>3</sub>, -78 °C. , 10 min; 73%) and oxidized [Collins, PDC(DMF), and  $CH_2N_2$ ] to the methyl ester 19 (65%). Exposure of 19 to 47% aqueous HF-CH<sub>3</sub>CN (1:10) at 25 °C for 1 h resulted in desilylation, deprotection of the acetonide, and subsequent lactonization to afford 20, mp 178-180 °C, 70% yield. The final operation remaining for the completion of the synthesis, regioselective dehydration of the C13 axial OH in 20, was initiated by selective protection of the lactonic OH as the tert-butyldimethylsilyl ether 21 (65%). Dehydration under the mild condition (SOCl<sub>2</sub>, pyridine;  $0 \,^{\circ}C$ , 15 min  $\rightarrow$  25  $^{\circ}C$ , 15 min) followed by removal of the silvl protecting group [47% aqueous HF-CH<sub>3</sub>CN (1:10), 25 °C, 30 min] completed the synthesis of 1a (51% from 21), which was identical (mp, 360-MHz NMR, IR, UV, MS,  $[\alpha]_D$ , TLC) with natural ML-236B (compactin).

Application of the described methodology to the synthesis of analogues and refinement of stereoselectivity are currently under investigation.

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Registry No. 1a, 73573-88-3; 3, 82080-53-3; 4, 82080-54-4; 5, 82065-57-4; 6, 82065-58-5; 7, 82080-55-5; 8, 82065-59-6; 9, 82065-60-9; 10, 82065-61-0; 11, 82065-62-1; 12, 82065-63-2; 13, 17605-06-0; 14, 82065-64-3; 15, 82065-65-4; 16, 82065-66-5; 17, 82065-67-6; 18, 82065-68-7; 18 debenzylated derivative, 82065-69-8; 19, 82065-70-1; 20, 82065-71-2; 21, 82080-56-6; 16, 3(R) isomer, 82110-38-1; 2(S)methylbutyric anhydride, 65527-79-9; trans-crotyl phenyl sulfone, 72863-24-2; trans-2-buten-1-ol, 504-61-0; 5-hexen-2-one, 109-49-9.

Supplementary Material Available: Spectroscopic data (NMR and IR) for new compounds described in this paper (27 pages). Ordering information is given on any current masthead page.

## Novel Binuclear Platinum(III) Diphosphite Complexes

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Relatively few platinum(III) complexes have been reported to date. The best characterized are Pt-Pt-bonded binuclear species, with Pt-Pt distances in the range 2.47-2.56 Å.<sup>2</sup> In recent experiments we have found that binuclear Pt(III) complexes can be generated readily through oxidative addition to a binuclear platinum(II) tetrakis(diphosphite),  $Pt_2(pop)_4^{4-}(pop = P_2O_5H_2^{2-})$ .<sup>3</sup> The platinum(III) products of halogen and methyl iodide oxidative-addition reactions are described in this communication.

The binuclear Pt(II) species  $Pt_2(pop)_4^{4-}$  reacts rapidly with halogens (or CH<sub>3</sub>I) to give  $Pt_2(pop)_4X_2^{4-}$  (or  $Pt_2(pop)_4(CH_3)I^{4-}$ ).<sup>4</sup> The Pt-Pt distance in  $Pt_2(pop)_4Cl_2^{4-}$  (Figure 1)<sup>5</sup> is 2.695 (1) Å,

<sup>(17)</sup> The desired stereochemistry of 16 was evident from <sup>1</sup>H NMR data:  $H_{4\alpha}$  (6 1.15) appeared as doublet of triplet ( $J_{4\alpha,4\beta} = 12.7$  Hz,  $J_{4\alpha,3} = J_{4\alpha,5} = 11.5$  Hz).

<sup>(18)</sup> Characteristic <sup>1</sup>H NMR data of 3:  $J_{9,14} = J_{8,9} = 11.5$  Hz,  $J_{8,17} = 5.3$ Hz,  $J_{14,15} = 1.8$  Hz,  $J_{14,16} = 2.7$  Hz,  $J_{15,16} = 10.0$  Hz,  $J_{16,17} = 5.2$  Hz,  $J_{15,17} = 1.2$  Hz,  $J_{13,14} \simeq 2$  Hz; major cis,  $J_{9,14} = 6.2$  Hz; minor cis,  $J_{9,14} = 6.0$  Hz. (19) The narrow  $W_{1/2}$  (7 Hz) of the ester carbinol proton (10-H,  $\delta$  5.14)

of 18 supported the depicted C10 stereochemistry in 17. (20) 2(S)-Methylbutyric anhydride [bp 65.5 °C ( $\sim 1 \text{ mmHg}$ ),  $[\alpha]^{24}_{\text{D}}$ +29.2° (neat)] was prepared from 2(S)-methylbutanol (Nakarai) by the standard procedures; see ref 5a.

<sup>(1) (</sup>a) California Institute of Technology; (b) Washington State University.

<sup>(2) (</sup>a)  $K_2[Pt_2(SO_4)_4(H_2O)_2]$ , Pt-Pt = 2.47 Å: Muravieskaya, G. S.; Kukina, G. A.; Orlova, V. S.; Evstefera, O. N.; Porai-Koshits, M. A. Dokl. Akad. Nauk. SSSR 1976, 226, 596-599. (b) Pt<sub>2</sub>(O<sub>2</sub>C<sub>2</sub>F<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>)<sub>4</sub>(NC<sub>6</sub>H<sub>7</sub>)<sub>2</sub>, Pt-Pt = 2.557 Å: Schagen, J. D.; Overbeck, A. R.; Schenk, H. *Inorg. Chem.* **1978**, *17*, 1938–1940. (c)  $Pt_2(C_5H_4NO)_2(NH_3)_4(NO_3)_2$ , Pt-Pt = 2.539 (1) Å: Hollis, L. S.; Lippard, S. J. J. Am. Chem. Soc. 1981, 103, 6761-6763. (d)  $Na_2[Pt_2(HPO_4)_4(H_2O)_2]$ , Pt-Pt = 2.486 (2) Å: Cotton, F. A.; Falvello, L. R.; Han, S. Inorg. Chem. 1982, 21, 1709-1710.

<sup>(3)</sup> Striking luminescence led to the discovery of the platinum anion (Sperline, R. P.; Dickson, M. K.; Roundhill, D. M. J. Chem. Soc., Chem. Commun. 1977, 62-63), and the emission intensity linearity has been used for the spectrophotometric detection of trace platinum (Dickson, M. K.; Peltee, S. K.; Roundhill, D. M. Anal. Chem. 1981, 53, 2159-2160. The compound K<sub>4</sub>[Pt<sub>2</sub>(pop)<sub>4</sub>]·2H<sub>2</sub>O has been structurally characterized (Filomena Dos Remedios Pinto, M. A. Sadler, P. J.; Neidle, S.; Sanderson, M. R.; Subbiah, A. J. Chem. Soc., Chem. Commun. 1980, 13-15).

<sup>(4)</sup>  $K_4[Pt_2(pop)_4X_2]$  (X = Cl, Br) was prepared by adding excess X<sub>2</sub> and then KX to an aqueous solution of  $K_4[Pt_2(pop)_4]\cdot 2H_2O$  at room temperature.  $[Ph_4As]_4[Pt_2(pop)_4I_2]$  was prepared by adding excess  $I_2$  to  $[Ph_4As]_4[Pt_2(pop)_4]$ in acetonitrile solution. Anal. Calcd for  $K_4[Pt_2(pop)_4L_2]$ : P. 2002 (Cl, 5.77. Found: P, 19.0; Cl, 6.17. Anal. Calcd for  $K_4[Pt_2(pop)_4C_2]$ -2H<sub>2</sub>O: P, 20.2; Cl, 5.77. Found: P, 19.0; Cl, 6.17. Anal. Calcd for  $K_4[Pt_2(pop)_4B_2]$ : P, 19.3; Br, 12.5. Found: P, 19.2; Br, 12.4. Anal. Calcd for  $[Pt_4As]_4[Pt_2(pop)_4L_2]$ : P, 9.00; I, 9.22. Found: P, 9.80; I, 9.22. Anal. Calcd. for K4[Pt<sub>2</sub>(pop)<sub>4</sub>(CH<sub>3</sub>)I]: C, 0.95; H, 0.88; I, 10.0; P, 19.6. Found: C, 1.25; H, 0.78; I, 10.5; P, 19.4. The complexes are diamagnetic 1:4 electrolytes and are very stable both in the solid state and in solution.