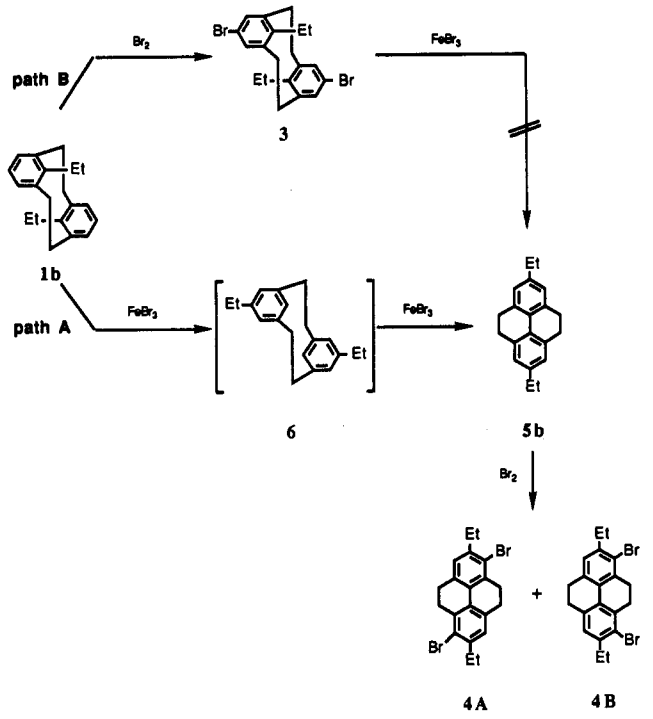
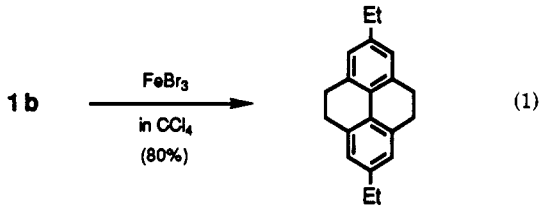
Scheme III



In fact, when 8,16-diethyl[2.2]MCP (**1b**) was treated with $FeBr_3$ in a carbon tetrachloride solution at room temperature for 3 h, the expected product, 2,7-diethyl-4,5,9,10-tetrahydropyrene (**5b**) was obtained in 80% yield (eq 1).



(1)

However, attempted isomerization of **1b** with other Lewis acids, such as $TiCl_4$ or $FeCl_3$, performed under the same reaction conditions failed. The starting compound **1b** was recovered in quantitative yield. Furthermore, reaction of 5,13-dibromo-8,16-diethyl[2.2]MCP (**3**) with $FeBr_3$ resulted only in recovery of the starting compound.

These results strongly suggest that the reaction pathway for bromination of **1b** with bromine in the presence of Fe powder proceeds via path **A** as shown in Scheme III.

It was also found that when 8,16-dimethyl[2.2]MCP (**1a**) was treated with $FeBr_3$ under the same conditions as the diethyl derivative (**1b**), the starting compound was recovered in almost quantitative yield.

It is concluded that the above isomerization reaction is strongly affected by the bulkiness of the substituents in the 8,16-positions which increase the strain in the molecule. The preparation of 2,7-diethyl-4,5,9,10-tetrahydropyrene (**5b**) from **1b** appears to be a useful route to 2,7-dialkyl-4,5,9,10-tetrahydropyrenes, and studies of the scope and limitations of the route are in progress.

Experimental Section

All melting and boiling points are uncorrected. NMR spectra were recorded at 270 MHz. Mass spectra were obtained at 75 eV using a direct inlet system.

Preparation of 5,13-Dibromo-8,16-diethyl[2.2]metacyclophane (3). A solution of 153.2 mg (0.58 mmol) of **1b**[10] in 50 mL of CCl_4 was stirred at rt as a solution of 0.56 g (3.48 mmol) of Br_2 in 10 mL of CCl_4 was added. After 5 min, the reaction mixture was poured into a large amount of ice-water. The organic layer was extracted with CH_2Cl_2. The CH_2Cl_2 solution was dried over Na_2SO_4 and evaporated in vacuo to leave a residue, which was recrystallized from hexane to afford 200 mg (82%) of **3**: colorless prisms (hexane); mp 292–293 °C; IR (KBr) 3040, 2940, 1550, 1440, 1420, 1390, 1360, 1320, 1180, 1040, 955, 860, 820, 750 cm^{-1}; NMR ($CDCl_3$) δ 0.36 (6 H, t, J = 7 Hz), 1.14 (4 H, q, J = 7 Hz), 2.56–3.04 (8 H, m), 7.16 (4 H, s); MS (m/e) 420, 422, 424 (M^+). Anal. Calcd for $C_{20}H_{22}Br_2$: C, 56.90; H, 5.25. Found: C, 56.71; H, 5.22.

Preparation of 1,6-Dibromo-2,7-diethyl- (4A) and 1,8-Dibromo-2,7-diethyl-4,5,9,10-dihydropyrene (4B). A solution of 153.2 mg (0.58 mmol) of **1b** in 50 mL of CCl_4 was stirred at rt as a solution of 0.56 g (3.48 mmol) of Br_2 in 10 mL of CCl_4 was added. After 2 h, the reaction mixture was poured into a large amount of ice-water. The organic layer was extracted with CH_2Cl_2. The CH_2Cl_2 solution was dried over Na_2SO_4 and evaporated in vacuo to leave a residue, which was chromatographed on silica gel, using a hexane as an eluent to afford 195 mg (80%) of a mixture of **4A** and **4B**, and the ratio of **4A** and **4B** was determined to be 60:40 by its NMR spectrum. This mixture was recrystallized from methanol to give small amounts of **4A** or **4B** as colorless prisms: mp 157–160 °C; IR (KBr) 3040, 2930, 1550, 1360, 1230, 1150, 900, 850 cm^{-1}; NMR ($CDCl_3$) δ 1.14 (6 H, t, J = 7.5 Hz), 2.68–2.92 (8 H, m), 2.85 (4 H, q, J = 7.5 Hz), 7.27 (2 H, s); MS (m/e) 418, 420, 422 (M^+). Anal. Calcd for $C_{20}H_{20}Br_2$: C, 56.93; H, 4.50. Found: C, 57.17; H, 4.80.

Preparation of 2,7-Diethyl-4,5,9,10-tetrahydropyrene (5b). A mixture of 96.9 mg (0.4 mmol) of **1b** in 50 mL of CCl_4 was stirred at rt as 1.18 g (4 mmol) of $FeBr_3$ was added. After 3 h, the reaction mixture was poured into a large amount of ice-water. The organic layer was extracted with CH_2Cl_2. The CH_2Cl_2 solution was dried over Na_2SO_4 and evaporated in vacuo, and the residue was chromatographed on silica gel with hexane as an eluent. Recrystallization from methanol gave 84 mg (80%) of 2,7-diethyl-4,5,9,10-tetrahydropyrene (**5b**): colorless prisms (methanol); mp 96–97 °C; IR (KBr) 3040, 2940, 1530, 1350, 1225, 1110, 910, 840 cm^{-1}; NMR ($CDCl_3$) δ 1.20 (6 H, t, J = 7.5 Hz), 2.68 (4 H, q, J = 7.5 Hz), 2.82 (8 H, s), 7.00 (4 H, s); MS (m/e) 262 (M^+). Anal. Calcd for $C_{20}H_{20}$: C, 91.55; H, 8.45. Found: C, 91.40, H, 8.30.

Reaction of 1b with $TiCl_4$ and $FeCl_3$. To a mixture of 96.9 mg (0.4 mmol) of **1b** in 50 mL of CCl_4 was added 4 mmol of $TiCl_4$ or $FeCl_3$ with stirring at rt. After 12 h, the reaction mixture was treated as described above to give starting material **1b** in quantitative yield.

Registry No. **1b**, 76447-47-7; **3**, 137363-46-3; **4A**, 137363-45-2; **4B**, 137363-47-4; **5b**, 76447-48-8.

(10) Yamato, T.; Arimura, T.; Tashiro, M. *J. Chem. Soc., Perkin Trans 2* **1987**, 1.

Asymmetric Diels–Alder Reactions of Carboxylic Ester Dienophiles Promoted by Chiral Lewis Acids

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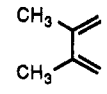
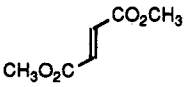
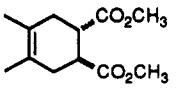
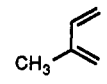
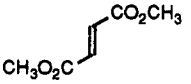
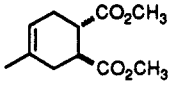
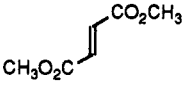
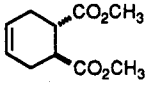
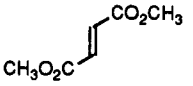
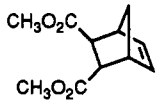
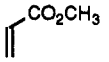
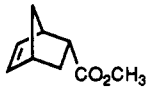
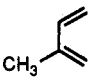
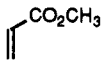
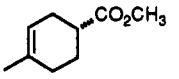
The Diels–Alder reaction has proven to be a powerful stratagem in organic synthesis.[1] An area which has received considerable interest in recent years is the control of absolute stereochemistry.[2] One successful method

(1) For a review of Diels–Alder reactions see: (a) Desmoni, G.; Tacconi, G.; Pollini, G. P. *Natural Product Synthesis Through Pericyclic Reactions*; ACS Monograph 180; American Chemical Society: Washington, DC, 1984; Chapter 5. (b) Hamer, J. *1,4-Cycloaddition Reactions*; Academic: New York, 1967.

0022-3263/92/1957-0396$03.00/0

Table I. Diels–Alder Reactions Promoted by Chiral Lewis Acid 1

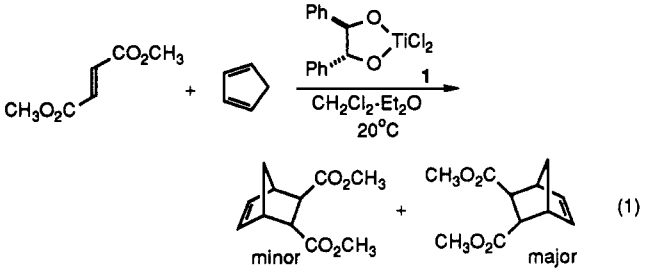
entry	diene	dienophile	major product	isolated yield, %	ee,[a] %
1				79	92
2				79	88
3				78	60
4				86	80
5				84[b]	66
6				88[c]	26[d]
7				68	16[d]
8				85[e]	36[f]
9				91	37[g]

[a] Enantiomeric excess of the cycloadducts from the dimethyl fumarate was determined by splitting of the methoxy peaks on 360-MHz ^{1}H NMR using chiral shift reagent Eu(hfc)$_3$ (Aldrich). [b] Toluene was used as the reaction solvent. [c] Hexanes–toluene (6:4) was used as the reaction solvent. [d] The reaction was conducted at −45 °C. [e] Only endo isomer was detected by ^{1}H NMR. [f] Enantiomeric excess was determined by a Weinreb's amidation of the Diels–Alder adduct with (*S*)-α-methylbenzylamine.[14] [g] The enantiomeric excess was determined by carrying the cycloadduct to α-terpineol.[9]

developed thus far utilizes chiral auxiliaries which are incorporated into the substrate and subsequently must be removed from the product by some chemical means. In this case, the stereochemical outcome is dictated by the absolute stereocenter on the substrate (substrate control). An alternate method, which has not yet been as thoroughly explored, involves placement of the stereocenter on the reagent (reagent control).[3,4] An example of this is the use of chiral Lewis acids to catalyze the cycloaddition and simultaneously induce asymmetry into the product. The works of Narasaka,[4b] Chapuis,[4c] and Corey[4d] which involve highly reactive oxazolidinone dienophiles were successful.[5] However, the less reactive carboxylic ester dienophiles, to date, have shown low enantioselectivity under these reagent-controlled conditions.[4a,i] The purpose of this article is to describe our studies directed toward the development of such a chiral Lewis acid which induces asymmetric Diels–Alder reactions with ester dienophiles.

Results and Discussion

A survey of various C_2-symmetrical diol ligands employing boron, tin, and titanium Lewis acids led us to choose a titanium Lewis acid of type 1 (eq 1) in which



(1)

optically active hydrobenzoin was used as the ligand.[6] The optically pure hydrobenzoin was readily synthesized following Sharpless' osmylation procedure.[7]

The results of the Diels–Alder reactions as exemplified by eq 1 are summarized in Table I. The chiral Lewis acid 1 was generated by converting (*R*,*R*)-hydrobenzoin to the dilithiodialkoxide species upon reaction with 2 equiv of *n*-butyllithium in ether. The mixture was then diluted

(2) (a) Paquette, L. A. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1984; Chapter 7. (b) Wurziger, H. *Kontakte (Darmstadt)* **1984**, 3. (c) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1984**, 876. (d) Evans, D. A.; Chapman, K. T.; Bisaha, J. *J. Am. Chem. Soc.* **1988**, *110*, 1238. (d) Helmchen, G.; Karge, R.; Weetman, J. In *Modern Synthetic Methods*; Scheffold, R., Ed.; Springer Verlag; Berlin, 1986; Vol. 4, p 261. (e) Reed, L. A., III; Davis, J.; Choy, W.; Masamune, S. *J. Org. Chem.* **1983**, *48*, 4441 and references cited therein. (f) Roush, W. R.; Gillis, H. R.; Ko, A. I. *J. Am. Chem. Soc.* **1982**, *104*, 2269 and references cited therein.

(3) (a) Narasaka, K. *Synthesis* **1991**, 1. (b) Tomioka, K. *Synthesis* **1990**, 542.

(4) (a) Rebiere, F.; Riant, O.; Kagan, G. B.; *Tetrahedron Asymmetry* **1990**, *1*, 199. (b) Narasaka, K.; Iwasawa, N.; Inoue, M.; Yamada, T.; Nakashima, M.; Sugimori, J. *J. Am. Chem. Soc.* **1989**, *111*, 5340. (c) Chapuis, C.; Jurczak, J. *Helv. Chim. Acta* **1987**, *70*, 436. (d) Corey, E. J.; Imwinkelried, R.; Pikul, S.; Xiang, Y. B. *J. Am. Chem. Soc.* **1989**, *111*, 5493. (e) Hayashi, Y.; Narasaka, K. *Chem. Lett.* **1989**, 793. (f) Kelly, T. R.; Whiting, A.; Chandrakumar, N. S. *J. Am. Chem. Soc.* **1986**, *108*, 3510. (g) Bednarski, M.; Maring, B.; Danishefsky, S. *Tetrahedron Lett.* **1983**, *24*, 3451. (h) Marvoka, K.; Sakurai, M.; Fujiwara, J.; Yamamoto, H. *Tetrahedron Lett.* **1986**, *27*, 4895. (i) Hashimoto, S.-H.; Komeshima, N.; Koga, K. *J. Chem. Soc. Chem. Commun.* **1979**, 437. (j) Furuta, K.; Shimizu, S.; Miwa, Y.; Yamamoto, H. *J. Org. Chem.* **1989**, *54*, 1483. (k) Kaufamann, K.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 545. (l) Corey, E. J.; Imai, N.; Zhang, H.-Y. *J. Am. Chem. Soc.* **1991**, *113*, 728.

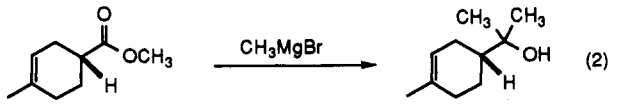
(5) For comparison of the reactivity of oxazolidinone and carboxylate ester in Diels–Alder reaction see reference 2d.

(6) For review of other C_2-symmetrical ligand see: (a) Whitesell, J. K. *Chem. Rev.* **1989**, *89*, 1581. (b) Alexakis, A.; Mangeney, P. *Tetrahedron Asymmetry* **1990**, *1*, 477.

(7) Jacobsen, E. N.; Marko, I.; Mungall, W. S.; Schroder, G.; Sharpless, K. B. *J. Am. Chem. Soc.* **1988**, *110*, 1968.

with dichloromethane, and titanium tetrachloride was added at which time lithium chloride precipitated.[8] The dienophile followed by the diene were then added. The reactions were generally carried out for 2–12 h as monitored by capillary GC. The reactions involving methyl acrylate were allowed to go as long as 48 h. The hydrobenzoin is readily recovered in near quantitative amounts (>98%) with slight decomposition being observed. Dimethyl fumarate reacts with cyclopentadiene with a high degree of enantioselectivity (entry 4) as well as with less reactive acyclic dienes (entries 1 and 2). In the case of acyclic dienes, alkyl substituents in the 2- and 3-position enhance the enantioselectivity (compare entries 1–3). Reactions employing methyl acrylate as the dienophile also give good yields but lower enantioselectivities (entries 8 and 9).[9]

The configuration around the newly formed stereocenter was determined by correlating cycloadduct **2** from entry 9 to α-terpineol (eq 2). Treatment of enantioenriched



(2)

2 α-terpineol

product **2** with excess methylmagnesium bromide afforded enantioenriched synthetic α-terpineol ($[\alpha]^{23}_D$ = +37.3, *c* = 1.5, CH_3CH_2OH) corresponding to the *R* enantiomer.[10] The stereochemistry of the product was reaffirmed by saponifying the cycloadduct from entry 2, Table I. The crude diacid displayed a rotation ($[\alpha]^{25}_D$ = +21.3 *c* = 0.75, CH_3OH) corresponding to the *S,S* enantiomer.[11] The *S,S* diacid and (*R*)-terpineol are initially derived from the preferential attack of the diene on the *si* face of methyl acrylate and the *si,si* face of dimethyl fumarate.[12]

It has been shown that solvents can have an influence on enantioselection; this proved equally true in our system.[4b] Reactions of cyclopentadiene and dimethyl fumarate in various solvent systems show that the highest enantioselectivities were obtained in a 4:1 dichloromethane–ether mixture (entries 4–6). This reaction system also displays a dramatic temperature dependance. Optimal enantioselection was obtained at 0 °C and room temperature (80% ee in each case). Upon addition of $TiCl_4$ to a solution of the dilithioalkoxide at 0 °C a white precipitate of LiCl is formed. Presumably the chiral catalytic species is formed very slowly at −78 °C, because no precipitate is noted after 1 h and the reaction proceeds in 91% yield with no enantioselection. Forming the chiral Lewis acid at 0 °C and then cooling the reaction mixture to −78 °C gives a rate of reaction too slow to be of any significance. Cooling the reaction mixture to −45 °C after the catalyst formation results in a modest yield of 68% and a low enantioselectivity of 16%. It was also found that relative to the dienophile 1–1.5 equiv of Lewis acid were necessary for a high degree of enantioselection. Reaction of cyclopentadiene and dimethyl fumarate in the presence of 0.25 equiv of Lewis acid resulted in a yield of 90% with 16% ee. It has been demonstrated that 4-Å molecular sieves can enhance the enantioselection in the Diels–Alder reaction when using only catalytic amounts of Lewis acid.[4b] The opposite proved true in our case. Reactions run in the presence of 4-Å molecular sieves gave a 76% yield with a diminished enantioselectivity of 6%.

In conclusion, we have shown that high enantioselectivities are possible with the chiral Lewis acid promoted Diels–Alder reaction of carboxylic esters.[13] (*R,R*)-Hydrobenzoin, a simple and readily available compound, was effective as the chiral ligand when titanium was used as the Lewis acid.

Experimental Section

General. CH_2Cl_2 and toluene were distilled from calcium hydride. Ether was distilled from sodium–benzophenone ketyl. TLC and column chromatography were done with E. Merck silica gel. All reactions were run under a nitrogen atmosphere and concentrations were performed under reduced pressure with a rotary evaporator. The purity of all compounds was judged to be >99% by VPC and ^1H NMR determinations.

General Procedures for Chiral Lewis Acid Formation. To a suspension of hydrobenzoin (0.225 g, 1.05 mmol) in 2 mL of Et_2O at 0 °C was added *n*-BuLi (0.84 mL of 2.5 M in hexanes, 2.1 mmol). The resulting slurry was dissolved in 8 mL of CH_2Cl_2, and $TiCl_4$ (1.05 mL of 1.0 M solution in CH_2Cl_2, 1.05 mmol) was added at which time LiCl precipitated. The mixture was used as such.

General Procedure for the Diels–Alder Reaction. The reaction of dimethyl fumarate and cyclopentadiene is typical. To a mixture of Lewis acid, as prepared above, was added dimethyl fumarate (0.1 g, 0.7 mmol) followed by cyclopentadiene (0.29 mL, 3.5 mmol). The mixture was stirred at room temperature for 2 h and was quenched with 5 mL of 1 N HCl. The aqueous phase was extracted (3 × 10 mL of CH_2Cl_2). The combined organic phases were dried ($MgSO_4$) and concentrated. Flash chromatography of the crude yellow oil (SiO_2, 16:1 hexanes–EtOAc) yielded 0.13 g of enantioenriched Diels–Alder products as a colorless oil.

Dimethyl (4*S*,5*S*)-1,2-dimethylcyclohexene-4,5-dicarboxylate: IR (neat) 1740 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 1.56 (s, 6 H), 2.05–2.23 (m, 4 H), 2.74–2.78 (m, 2 H), 3.63 (s, 6 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 175.2, 123.7, 51.6, 41.8, 34.0, 18.4. Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.62; H, 8.01.

Dimethyl (4*S*,5*S*)-1-methylcyclohexene-4,5-dicarboxylate: IR (neat) 1740 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 1.64 (s, 3 H), 2.06–2.38 (m, 4 H), 2.75 (dt, 1 H, *J* = 5.3, 10.8 Hz), 2.85 (dt, 1 H, *J* = 5.2, 10.8 Hz), 3.65 (s, 3 H), 3.66 (s, 3 H), 5.33 (br s, 1 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 175.3, 175.2, 132.1, 118.9, 51.7, 41.6, 41.0, 32.4, 27.96, 22.88. Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.61. Found: C, 61.98; H, 7.52.

Dimethyl (4*S*,5*S*)-cyclohexene-4,5-dicarboxylate: IR (neat) 1726 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 2.12–2.19 (m, 2 H), 2.36–2.43 (m, 2 H), 2.81–2.85 (m, 2 H), 3.67 (s, 6 H), 5.66 (d, 2 H, *J* = 2.3 Hz); ^{13}C NMR (90 MHz, $CDCl_3$) δ 175.2, 124.8, 51.8, 41.1, 27.8. Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.34; H, 7.20.

Dimethyl (2*S*,3*S*)-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate: IR (neat) 1737 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$)

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δ 1.46 (dd, 1 H, J = 1.5 Hz, 8.9 Hz), 1.62 (d, 1 H, J = 8.9 Hz), 2.69 (dd, 1 H, J = 1.3, 4.1 Hz), 3.13 (br s, 1 H), 3.27 (br s, 1 H), 3.38 (t, 1 H, J = 4.0 Hz), 3.65 (s, 3 H), 3.72 (s, 3 H), 6.07 (dd, 1 H, J = 2.7, 5.5 Hz), 6.29 (dd, 1 H, J = 3.2, 5.3 Hz); ^{13}C NMR (90 MHz, $CDCl_3$) δ 174.7, 173.5, 137.4, 135.0, 52.0, 51.7, 47.7, 47.7, 47.5, 47.5, 47.2, 47.0, 46.9, 45.5, 45.5. Anal. Calcd for $C_{11}H_{14}O_4$: C, 62.84; H, 6.71. Found: C, 62.93; H, 6.75.

Methyl (4*R*)-1-methylcyclohexene-4-carboxylate: IR (neat) 1741 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.59–1.76 (m, 1 H), 1.65 (s, 3 H), 1.98–2.02 (m, 3 H), 2.21–2.23 (m, 2 H), 2.45–2.53 (m, 1 H), 3.68 (s, 3 H), 5.38 (br s, 1 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 176.5, 133.7, 119.2, 51.6, 39.1, 29.3, 27.7, 25.5, 23.5. Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.00; H, 9.17.

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Registry No. 1, 137435-03-1; 2, 137492-77-4; (*R*,*R*)-hydrobenzoin, 52340-78-0; dimethyl fumarate, 624-49-7; methyl acrylate, 96-33-3; 2,3-dimethyl-1,3-butadiene, 513-81-5; 2-methyl-1,3-butadiene, 78-79-5; 1,3-butadiene, 106-99-0; cyclopentadiene, 542-92-7; dimethyl (4*S*,5*S*)-1,2-dimethylcyclohexene-4,5-dicarboxylate, 137492-78-5; dimethyl (4*S*,5*S*)-1-methylcyclohexene-4,5-dicarboxylate, 137492-79-6; dimethyl (4*S*,5*S*)-cyclohexene-4,5-dicarboxylate, 137492-80-9; dimethyl (2*S*,3*S*)-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate, 135357-64-1; methyl (2*R*)-bicyclo[2.2.1]-hept-5-ene-2-carboxylate, 72203-34-0; (+)-α-terpineol, 7785-53-7.

An Improved Procedure of the Pechmann Condensation in the Synthesis of 8-Ethyltrimethoxy-6*H*-benzo[*d*]naphtho[1,2-*b*]-pyran-6-ones Structurally Related to the Aglycon of Gilvocarcins

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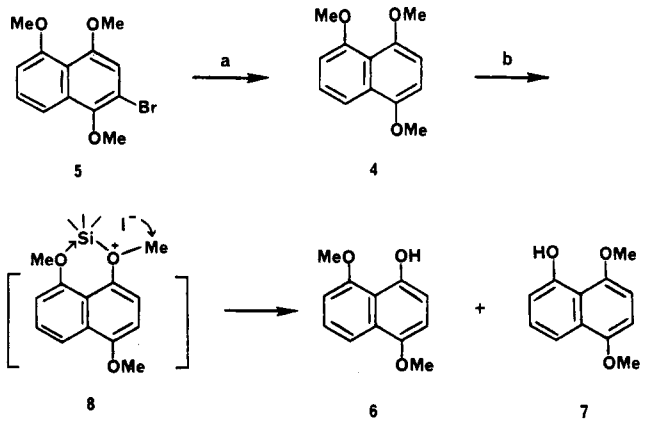
The antitumor and antibiotic activities of gilvocarcins,[2] chrysomycin,[3] and ravidomycins[4] have prompted several syntheses of defucogilvocarcins[5] and the related *C*-glycosides.[6] We have recently described the synthesis of the 12-demethoxydefucogilvocarcin ring system[7] via the Pechmann condensation[8] and subsequent regioselective oxidation with selenium dioxide. The use of the Pechmann condensation in the preparation of benzo[*d*]naphtho[1,2-*b*]pyran-6-ones from dihydroxynaphthalenes and 2-carbethoxycyclohexanones was first reported by Chebaane[8a] and subsequently by Daves[6b] and McGee.[5f] We now report a concise synthesis, utilizing an improved Pechmann condensation procedure, of trimethoxy-8-ethyl-6*H*-benzo-[*d*]naphtho[1,2-*b*]pyran-6-ones such as **1** and **2**, structurally related to the aglycon of gilvocarcins, and describe the related unexpected products formed in the condensation reaction.

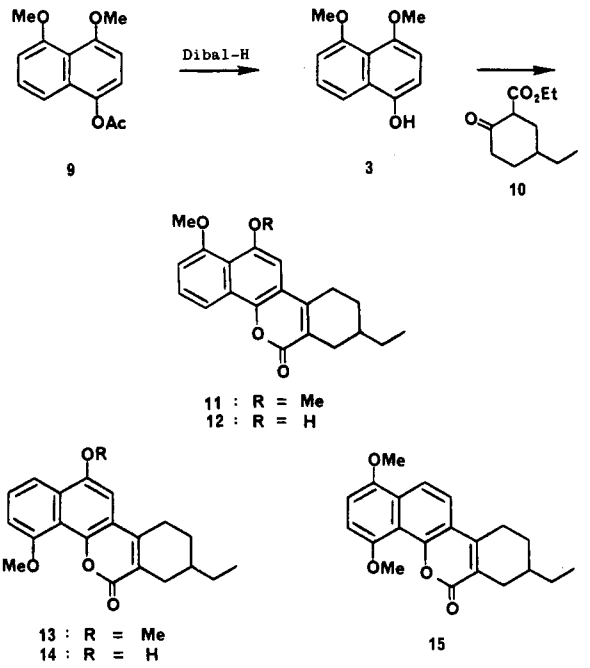
Initially, we attempted to prepare the required 4,5-dimethoxy-1-naphthol (**3**) from the monodemethylation of 1,4,5-trimethoxynaphthalene (**4**),[9] obtained from the debromination of 2-bromo-1,4,5-trimethoxynaphthalene (**5**)[5a] with 10% Pd/C in formic acid and DMF (86% yield) (Scheme I). However, monodemethylation of **4** with trimethylsilyl iodide[10] gave only the undesired isomers **6** and **7** (94% yield) in a ratio of 3:1. Spectral data and melting points of **6**[11] and **7**[12a] are identical with those reported. Presumably, the C-4 and C-5 oxygens chelated via a trimethylsilyl group as depicted in structure **8** led to

Scheme I[a]



[a] (a) 10% Pd/C, HCO_2H, DMF, 150 °C; (b) Me_3SiI, $CHCl_3$, 25 °C, 48 h.

Scheme II



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