Total Synthesis of (±)-*cis*- and (±)-*trans*-Trikentrin A; Diels-Alder Reactions of Heteroaromatic Azadienes

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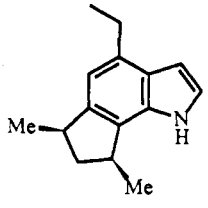
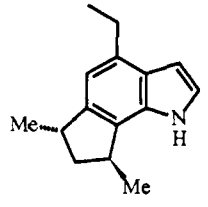
Abstract: A five-step total synthesis of *cis*- and *trans*-trikentrin A is detailed and is based on the implementation of two sequential heteroaromatic azadiene Diels-Alder reactions constituting a general approach to the preparation of substituted indoles.

Examination of the constituents of the marine sponge *Trikentrion flabelliforme* has led to the isolation and identification of *cis*- and *trans*-trikentrin A (**1** and **2**),[1] highly substituted indoles representative of a new class of alkaloids possessing antimicrobial activity. Herein, we detail the five-step total syntheses[2-4] of **1** and **2** based on the use of two sequential heteroaromatic azadiene Diels-Alder reactions[5-9] constituting a new and convergent strategy for the synthesis of substituted indoles. By design, the approach takes advantage of the unusually mild conditions disclosed for implementation of an intramolecular allene 1,2-diazine Diels-Alder reaction (100-140 °C)[10] and the observation that 6-methanesulfonyl-1,2-diazines (e.g., **3**) suffer subsequent oxidation to indoles under the reaction conditions by virtue of elimination of methanesulfinic acid, Scheme I.[10] With direct access to the requisite allene 1,2-diazines **3** from the products of the inverse electron demand Diels-Alder reactions of 3,6-bis(methylthio)-1,2,4,5-tetrazine (**5**), this 1,2,4,5-tetrazine → allene 1,2-diazine → indole Diels-Alder strategy constitutes a general approach to indole synthesis complementary to that disclosed for the preparation of indolines (alkyne 1,2-diazine → indoline).[11]



1

cis-Trikentrin A

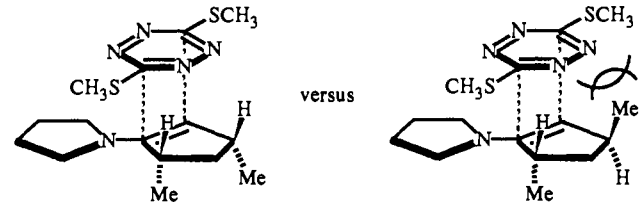


2

trans-Trikentrin A

Treatment of 3,6-bis(methylthio)-1,2,4,5-tetrazine (**5**)[10,12] with the pyrrolidine enamine of 2,4-dimethylcyclopentanone (**6**)[13] at 0-25 °C (1 h, C_6H_6) was accompanied by the evolution of nitrogen and cleanly provided the 4,5-dihydro-1,2-diazine **7** as a single diastereomer, Scheme II. Subsequent acid-catalyzed elimination of pyrrolidine (1:1 HOAc/C_6H_6, 25 °C, 10 h) provided pure 1,2-diazine **8** exclusively possessing the *cis*-dimethyl stereochemistry, and the preparative generation of **8** (85%) was conveniently carried out in one step without the intermediate isolation or purification of **7**. The clean and unanticipated generation of *cis*-**8** may be attributed to the kinetically preferred Diels-Alder participation of *cis*- versus *trans*-**6** and its reaction through a less sterically encumbered [4 + 2] cycloaddition transition state, Chart I. Oxidation of **8** to the symmetrical bis-sulfone **9** followed by selective displacement of a single sulfone by 1-aminohexa-2,3-diene (**17**)[14] provided **11** and set the stage for implementation of the intramolecular allene 1,2-diazine Diels-Alder reaction. The nucleophilic substitution reaction proved sluggish at room temperature (10%, 60 h, 25 °C, CH_2Cl_2), suffered from base-catalyzed epimerization of **11** to **12** at elevated temperatures (86%, 5:4 **11**:**12**, 70 °C, 22 h, DMF), and was most effectively conducted under pressure-promoted reaction conditions (25 °C, 6 or 13 kbar).[15]

Chart I



(1) Capon, R. J.; MacLeod, J. K.; Scammells, P. J. *Tetrahedron* **1986**, *42*, 6545.

(2) MacLeod, J. K.; Monahan, L. C. *Tetrahedron Lett.* **1988**, *29*, 391; *Aust. J. Chem.* **1990**, *43*, 329.

(3) Yasukouchi, T.; Kanematsu, K. *Tetrahedron Lett.* **1989**, *30*, 6559.

(4) Muratake, H.; Natsume, M. *Tetrahedron Lett.* **1989**, *30*, 5771. Muratake, H.; Watanabe, M.; Goto, K.; Natsume, M. *Tetrahedron* **1990**, *46*, 4179.

(5) Boger, D. L. *Bull. Soc. Chim. Belg.* **1990**, *99*, 599.

(6) Boger, D. L.; Patel, M. *Progress in Heterocyclic Chemistry*; Suschitzky, H., Scriven, E. F. V., Eds.; Pergamon Press: London, 1989; Vol. 1, pp 30-64.

(7) Boger, D. L. *Chem. Rev.* **1986**, *86*, 781.

(8) Boger, D. L. *Tetrahedron* **1983**, *39*, 2869.

(9) Boger, D. L.; Weinreb, S. M. *Hetero Diels-Alder Methodology in Organic Synthesis*; Academic Press: San Diego, CA, 1987.

(10) Boger, D. L.; Sakya, S. M. *J. Org. Chem.* **1988**, *53*, 1415.

(11) Boger, D. L.; Coleman, R. S. *J. Org. Chem.* **1984**, *49*, 2240. Boger, D. L.; Coleman, R. S. *J. Am. Chem. Soc.* **1987**, *109*, 2717.

(12) (a) Strube, R. E. *Organic Synthesis*; Wiley: New York, 1963; Collect. Vol. IV, p 967. (b) Sandström, J. *Acta Chem. Scand.* **1961**, *15*, 1575.

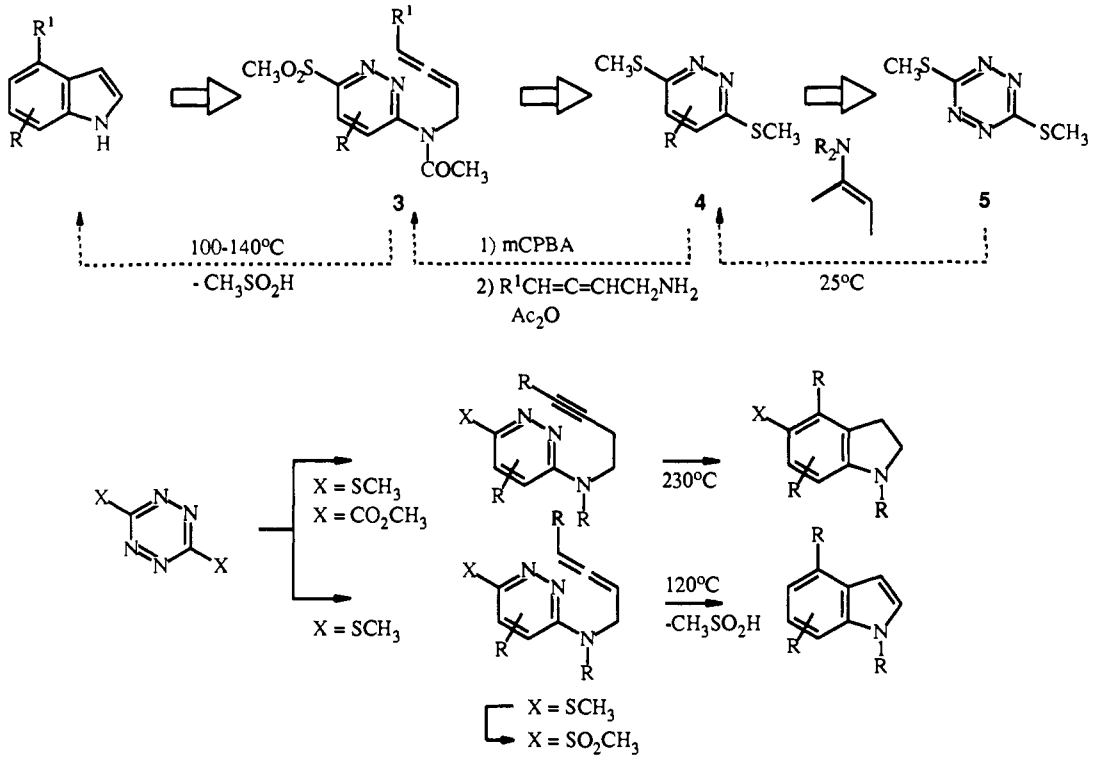
(13) The enamine **6** was prepared by treating 2,4-dimethylcyclopentanone with 2.0 equiv of pyrrolidine in benzene at reflux with continuous removal of water (Dean-Stark trap) for 11 h followed by vacuum distillation (bp 54 °C, 0.6 Torr) to give **6** (cis/trans = 3:1) in 93% yield as a colorless liquid: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 4.09 and 3.94 (1 H, two brs, C*H*=C, 1:3, trans/cis), 3.05 (4 H, m, CH_2NCH_2), 2.90 (1 H, m, C*H*CH$_3$), 2.70 (1 H, m, C*H*CH$_3$), 1.81 (4 H, m, CH_2CH_2NCH$_2$CH_2), 1.73 and 1.51 (2 H, m, CHCH_2CH), 1.19 and 0.99 (3 H, two d, CHCH_3, 1:3, trans/cis), 1.04 and 1.09 (3 H, two d, CHCH_3; 1:3, trans/cis); IR (neat) ν_{max} 3052, 2952, 2864, 2826, 1744, 1658, 1626, 1454, 1386, 1364, 1328, 1312, 1290, 1266, 1174, 1160, 760 cm^{-1}.

(14) 2,3-Hexadienylamine **17** was prepared according to the general procedure of Casara, P. *Tetrahedron Lett.* **1984**, *25*, 1891. Treatment of *N*-[(*tert*-butyloxy)carbonyl)]-3-aminopropyne (Metcalf, B.; Casara, P. *Tetrahedron Lett.* **1975**, 3337; Metcalf, B.; Biy, P.; Danzin, C.; Jung, M.; Casara, P.; Vevert, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 2551) with propionaldehyde (1.6 equiv), diisopropylamine (1.2 equiv), and CuBr (0.3 equiv) in dioxane at reflux for 12 h provided *N*-Boc-**17** (22%) as a pale yellow liquid: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.32 (1 H, m, C*H*=C=CH), 5.21 (1 H, m, CH=C=C*H*), 4.61 (1 H, brs, NH), 3.70 (2 H, brm, NHCH_2), 2.03 (2 H, m, CH_2CH$_3$), 1.45 (9 H, s, C(CH_3)$_3$), 1.01 (3 H, t, J = 7.4 Hz, CH$_2$CH_3); IR (neat) ν_{max} 3350, 2972, 2934, 2874, 1966, 1700, 1518, 1456, 1392, 1366, 1350, 1326, 1310, 1250, 1174, 1054, 872, 778 cm^{-1}. Deprotection of *N*-Boc-**17** with trifluoroacetic acid (5 equiv) in methylene chloride at 25 °C for 5 h followed by removal of the solvent and excess trifluoroacetic acid in vacuo afforded **17**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.54 (3 H, brs, NH_3), 5.49 (1 H, m, C*H*=C=CH), 5.29 (1 H, m, CH=C=C*H*), 3.59 (2 H, brm, CH_2NH$_3$), 2.05 (2 H, m, CH_2CH$_3$), 1.00 (3 H, t, J = 7.4 Hz, CH$_2$CH_3).

(15) Colter, A. K. *J. Org. Chem.* **1971**, *36*, 1898. Delombaert, S.; Ghosez, L. *Tetrahedron Lett.* **1984**, *25*, 3475.

0002-7863/91/1513-4230$02.50/0

Scheme I



Thus, treatment of **9** with **17** at room temperature at 13 kbar provided **11** in excellent yield (74%) with only minor competitive epimerization (5–15% **12**). Attempts to promote the direct intramolecular [4 + 2] cycloaddition reaction of **11** to provide **1** proved unsuccessful and provided 1,2-diazine products lacking the allene side chain. Presumably **11** suffers competitive [3.3]-sigmatropic rearrangement[10] precluding the intramolecular Diels–Alder reaction. Consistent with past observations, acylation of the free amine with acetic anhydride followed by mild thermolysis of **13** provided *N*-acetyl-*cis*-trikentrin A (diglyme, 160 °C, 23 h, 75%). This general[10] but unusual transformation presumably proceeds through an initial intramolecular allene 1,2-diazine Diels–Alder reaction, retro Diels–Alder reaction with loss of nitrogen, thermal isomerization to pyrrole **18**, and subsequent thermal elimination of methanesulfinic acid[15] to provide indole **15** (75%) directly, Scheme III. Notably, the initial intramolecular allene 1,2-diazine Diels–Alder reaction proceeds under mild reaction conditions (90–160 °C) and benefits from the enhanced dienophile reactivity of an allene as well as its entropic acceleration of the intramolecular [4 + 2] cycloaddition reaction.[16] The comparable alkene (190 °C)[17] and alkyne (220–230 °C)[10,11] 1,2-diazines undergo intramolecular [4 + 2] cycloaddition only under more vigorous reaction conditions. The preparative generation of **15** was most conveniently carried out from **11** directly by conducting the N-acylation reaction under conditions which further permit observation of the subsequent [4 + 2] cycloaddition reaction. Thus, treatment of **11** with acetic anhydride (neat, 0.3 equiv NaOAc) at 160 °C (12 h, 53%) provided **15** directly. Deacylation of **15** provided (±)-*cis*-trikentrin A identical in all comparable respects with authentic material.[18]

Deliberate epimerization of **9** (30% Et_3N in THF, 65 °C, 60 h) provided **10** possessing the *trans*-dimethyl stereochemical relationship. Following the sequence employed in the synthesis of *cis*-trikentrin A, treatment of **10** with **17** under pressure-promoted reaction conditions (13 kbar, 25 °C, 48 h, 66%) followed by N-acylation of **12** under conditions that further permit the observation of the intramolecular allene 1,2-diazine [4 + 2] cycloaddition cascade provided *N*-acetyl-*trans*-trikentrin A (**16**, 50%), Scheme II. Deacylation of **16** provided (±)-*trans*-trikentrin A identical in all comparable respect with authentic material.[18]

Experimental Section[19]

(5*R,7*S**)-6,7-Dihydro-1,4-bis(methylthio)-5,7-dimethyl-5*H*-cyclopenta[*d*]pyridazine (8).** A solution of 3,6-bis(methylthio)-1,2,4,5-tetrazine[12] (**5**, 5.63 g, 32.3 mmol) in benzene (25 mL) at 0 °C was treated with the pyrrolidine enamine of 2,4-dimethylcyclopentanone (**6**,[13] 11.28 g, 2.1 equiv), and the resulting solution was allowed to warm to room temperature and stirred for 1 h. Glacial acetic acid (25 mL) was added, and the resulting reaction mixture was stirred for 10 h at room temperature before the solvent was removed in vacuo. Chromatography (SiO_2, 27 × 5 cm, 5% EtOAc–hexane) followed by recrystallization (absolute EtOH) afforded 6.59 g (7.77 g theoretical yield, 85%) of **8** as a white crystalline solid: mp 101–103 °C (EtOH): ^1H NMR ($CDCl_3$, 200 MHz) δ 3.20 (2 H, ddq, *J* = 9.5, 2, 7.2 Hz, C*H*CH_2C*H*), 2.72 (6 H, s, SCH_3), 2.55 (1 H, dt, *J* = 13.5 Hz, 9.5 Hz, CHCH*H*CH), 1.58 (1 H, dt, *J* = 13.5, 2.0 Hz, CHC*H*HCH), 1.37 (6 H, d, *J* = 7.2 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 156.9 (s, C, aromatic), 144.2 (s, C, aromatic), 39.9 (t, C-6), 38.1 (d, C-5 and C-7), 20.6 (q, C*H*CH_3), 12.8 (q, SCH_3); IR (KBr) ν_{max} 2960, 2928, 2868, 1562, 1446, 1406, 1374, 1322, 1286, 1236, 1182, 1064, 1052, 976, 926, 834, 808, 720 cm^{-1}; EIMS,

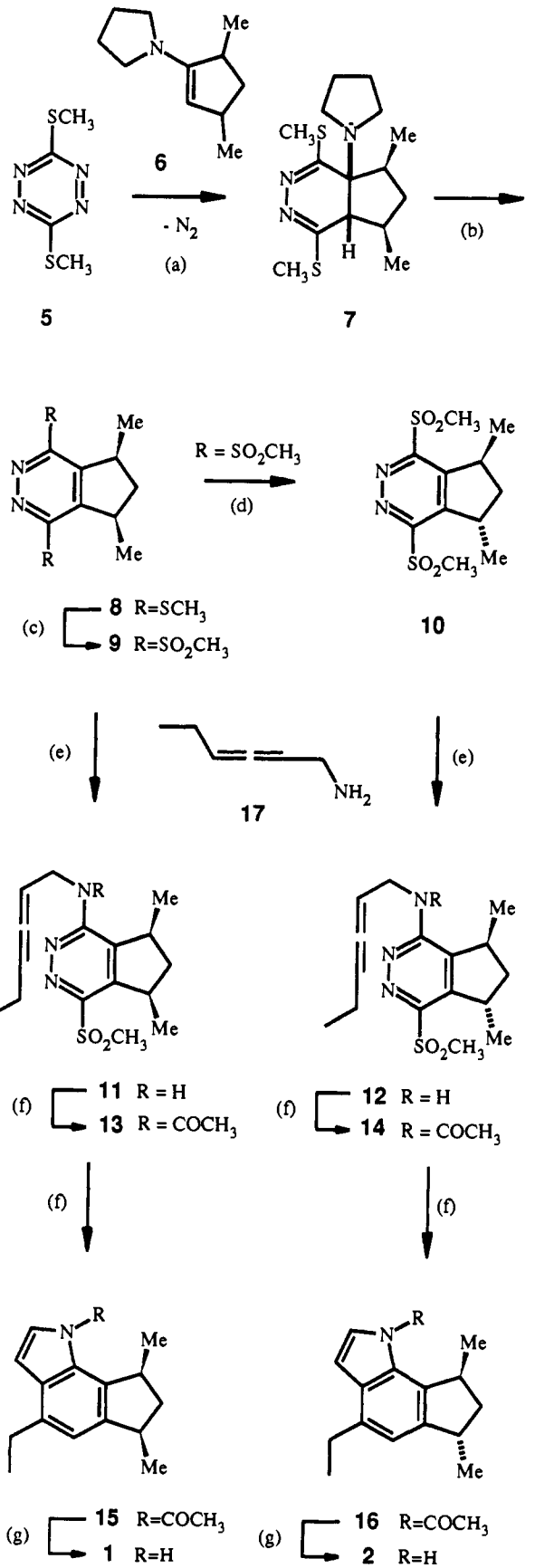
(16) Yamada, H.; Hayakawa, K.; Yasukouchi, T.; Kanematsu, K. *Tetrahedron Lett.* **1986**, *27*, 1837.

(17) Jojima, T.; Takeshiba, H.; Konotsune, T. *Chem. Pharm. Bull.* **1972**, *20*, 2191. Jojima, T.; Takeshiba, H.; Kinoto, T. *Chem. Pharm. Bull.* **1976**, *24*, 1581, 1588; **1980**, *28*, 198.

(18) The ^1H NMR and ^{13}C NMR of **1** and **2** proved identical with that of the authentic natural products. Inspection of the ^1H NMR spectrum of authentic **2** revealed that the ^1H NMR C3-H chemical shift initially reported at δ 6.12[1] is located at δ 6.59 as detailed herein.

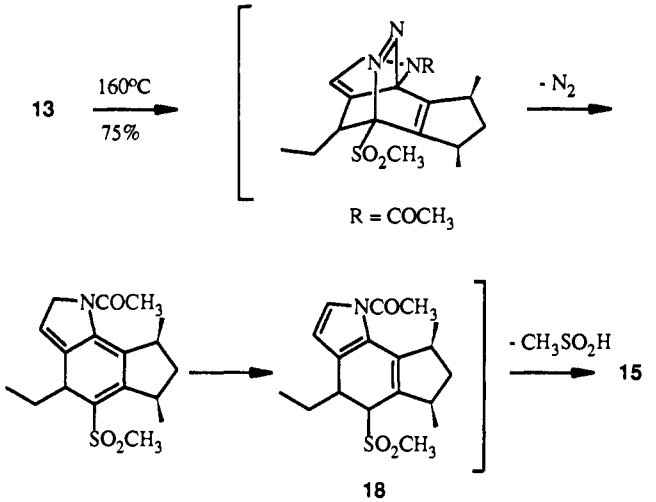
(19) ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini-200 or VXR-500S spectrometer, and chemical shifts are reported in parts per million (ppm) relative to internal tetramethylsilane (δ 0.00). Infrared spectra (IR) were recorded on a Perkin-Elmer 1800 FTIR spectrometer as KBr pellets (solids) and thin films (liquids). Melting points (mp) were determined on a Thomas Hoover capillary melting point apparatus and are uncorrected. Electron impact mass spectra (EIMS) and chemical ionization mass spectra (CIMS) were recorded on a Finnegan 4000 spectrometer. High-resolution mass spectra (HRMS) were recorded on a Kratos MS-50 spectrometer. Chromatography (flash chromatography)[20] was performed on 230–400 mesh silica gel. Benzene (C_6H_6) was distilled from calcium hydride. Tetetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Methylene chloride (CH_2Cl_2) was distilled from phosphorus pentoxide. All extraction and chromatographic solvents [methylene chloride (CH_2Cl_2), ethyl acetate (EtOAc), and hexane] were distilled prior to use. All other solvents and reagents were used as received from commercial sources. All reactions requiring anhydrous or inert reaction conditions were performed under an atmosphere of nitrogen or argon.

Scheme II



[a] (a) C_6H_6, 0–25 °C, 1 h; (b) C_6H_6–HOAc (1:1), 25 °C, 10 h, 85% of **8** from **5**; (c) mCPBA, CH_2Cl_2, −20 °C, 23 h, 98%; (d) Et_3N/THF (1:3), 65 °C, 60 h, 40% **10**, 55%, **9**; (e) CH_2Cl_2, 13 kbar, 25 °C, 2–4 days, 66–74%; (f) Ac_2O, NaOAc (0.3 equiv), 160 °C, 11–12 h, 50–53% **15**/**16** from **11**/**12**; (g) LiOH (2 equiv), H_2O–CH_3OH–THF (1:1:3), 25 °C, 1 h, 92–95%.

Scheme III



m/e (rel intensity) 240 (M^+, base), 225 (43), 207 (65), 191 (5), 182 (18), 147 (8), 91 (7), 77 (7); CIMS (2-methylpropane), *m/e* (rel intensity) 241 (M + H^+, base); EIHRMS, *m/e* 240.0753 ($C_{11}H_{16}N_2S_2$ requires 240.0755). Anal. Calcd for $C_{11}H_{16}N_2S_2$: C, 54.96; H, 6.71; N, 11.65; S, 26.67. Found: C, 55.16; H, 6.69; N, 11.57; S, 26.72.

The intermediate 4,5-dihydro-1,2-diazine **7** was obtained cleanly from reaction mixtures (**5** + **6**, 1 h, 25 °C) without the subsequent acetic acid treatment. Following removal of the solvent in vacuo, chromatography (SiO_2, 5% EtOAc–hexane) followed by recrystallization (absolute EtOH) afforded **7** (72%, unoptimized) as white crystalline solid: mp 133–135 °C (EtOH); ^1H NMR ($CDCl_3$, 200 MHz) δ 2.70 (2 H, m, CH_2N), 2.59 (1 H, dq, *J* = 7.0, 7.0 Hz, NCC*H*CH_3), 2.48 (3 H, s, SCH_3), 2.47 (3 H, s, SCH_3), 2.38 (2 H, m, NCH_2), 2.29 (1 H, d, *J* = 9.1 Hz, C*H*$CHCH_3$), 2.24 (1 H, m, CHC*H*HCH), 1.88 (1 H, m, CHC*H*CH_3), 1.63 (4 H, m, $CH_2CH_2NCH_2CH_2$), 1.26 (3 H, d, *J* = 7.0 Hz, CHC*H*$_3$), 1.10 (1 H, dd, *J* = 13.5, 3.7 Hz, CHCH*H*CH), 1.08 (3 H, d, *J* = 7.0 Hz, CHC*H*$_3$); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 166.8 (s, *C*=N), 161.9 (s, *C*=N), 66.6 (s, *C*NCH_2), 52.8 (d, *C*$HCHCH_3$), 48.2 (t, *C*H_2NCH_2), 41.3 (d, *C*HCH_3), 38.6 (t, $CHCH_2$*C*H), 37.5 (d, *C*HCH_3), 23.0 (t, *C*$H_2CH_2NCH_2CH_2$), 22.8 (q, $CHCH_3$), 17.7 (q, $CHCH_3$), 12.9 (q, SCH_3), 12.7 (q, SCH_3); IR (KBr) ν_{max} 2958, 2870, 2832, 1544, 1492, 1458, 1374, 1308, 1152, 1110, 1058 cm^{-1}; CIMS (2-methylpropane), *m/e* (rel intensity) 312 (M + H^+, base). Anal. Calcd for $C_{15}H_{25}N_3S_2$: C, 57.84; H, 8.09; N, 13.49; S, 20.58. Found: C, 58.16; H, 8.43; N, 13.59; S, 20.60.

Conversion of pure **7** to **8** was accomplished by stirring a solution of **7** in 1:1 benzene/glacial acetic acid at room temperature for 10 h followed by recrystallization (absolute EtOH).

(5*R,7*S**)-6,7-Dihydro-1,4-bis(methylsulfonyl)-5,7-dimethyl-5*H*-cyclopenta[*d*]pyridazine (9).** A solution of **8** (3.60 g, 15.0 mmol) in methylene chloride (65 mL) at −20 °C was treated with *m*-chloroperbenzoic acid (*m*-CPBA, 13.1 g, 4 equiv of 80–85%), and the reaction mixture was stirred for 23 h (−20 °C). The reaction mixture was warmed to room temperature, diluted with methylene chloride (40 mL), and washed with 5% aqueous $NaHCO_3$ (200 mL). The aqueous phase was extracted with methylene chloride (100 mL × 4). The combined organic layer was washed with saturated aqueous NaCl (100 mL) and dried (Na_2SO_4), and the solvent was removed in vacuo. The residue was recrystallized from EtOAc–hexane to give 4.48 g (4.56 g theoretical, 98%) of **9** as a white crystalline solid: mp 194–196 °C (EtOAc–hexane); ^1H NMR ($CDCl_3$, 200 MHz) δ 4.00 (2 H, ddq, *J* = 9.3, 1.3, 7.4 Hz, C*H*CH_2C*H*), 3.54 (6 H, s, SO_2CH_3), 2.68 (1 H, dt, *J* = 13.5, 9.3 Hz, CHC*H*HCH), 1.79 (1 H, dt, *J* = 13.5, 1.3 Hz, CHCH*H*CH), 1.58 (6 H, d, *J* = 7.4 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 161.9 (s, C,

(20) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(21) Isolation of intermediate **13** (**11**, Ac_2O, 1.7 equiv of DMAP, 90 °C, 96 h, 48% **13** + 25% **15**), and its subsequent conversion to **15** (diglyme, 160 °C, 23 h, 75%) was accomplished in preliminary studies. In these studies, it was established that the intramolecular Diels–Alder reaction of **13** is observed at temperatures as low as 90 °C competitive with the rate of N-acylation. For **13**: ^1H NMR ($CDCl_3$, 200 MHz), δ 5.35 (1 H, brm, C*H*=C=CH), 5.25 (1 H, brm, CH=C=C*H*), 4.53 (2 H, brm, NCH_2CH), 3.90 (1 H, m, $CHCH_2$C*H*), 3.47 (3 H, s, SO_2CH_3), 3.40 (1 H, m, C*H*CH_2CH), 2.70 (1 H, ddd, *J* = 13.5, 9.4, 9.4 Hz, CHC*H*HCH), 2.20 (3 H, brs, $COCH_3$), 1.88 (2 H, brm, C*H*$_2CH_3$), 1.60 (1 H, brm, CHCH*H*CH), 1.53 (3 H, d, *J* = 7.0 Hz, CHC*H*$_3$), 1.26 (3 H, two d, *J* = 9.2 Hz, CHC*H*$_3$), 0.94 and 0.80 (3 H, two t, *J* = 7.0 Hz, CH_2CH_3).

aromatic), 152.0 (s, C, aromatic). 40.9 (q, SO_2CH_3), 40.4 (t, C-6), 38.0 (d, C-5 and C-7), 23.4 (q, $CHCH_3$); IR (KBr) ν_{max} 3024, 2974, 2932, 2876, 1510, 1466, 1308, 1284, 1186, 1130, 1108, 1072, 956, 804, 760 cm^{-1}; EIMS, *m/e* (relative intensity) 304 (M^+, 20), 289 (8), 156 (10), 145 (base), 131 (17), 118 (23), 104 (13), 91 (16), 79 (91), 77 (26), 65 (33), 63 (27); CIMS (2-methylpropane), *m/e* (rel intensity) 305 (M + H^+, base); EIHRMS, *m/e* 304.0546 ($C_{11}H_{16}N_2O_4S_2$ requires 304.0552). Anal. Calcd for $C_{11}H_{16}N_2O_4S_2$: C, 43.41; H, 5.30; N, 9.20; S, 21.07. Found: C, 43.72; H, 5.50; N, 9.15; S, 20.84.

(5*R,7*R**)-6,7-Dihydro-1,4-bis(methylsulfonyl)-5,7-dimethyl-5*H*-cyclopenta[*d*]pyridazine (10).** A solution of **9** (204 mg, 0.67 mmol) in Et_3N/THF (1:3, 6.4 mL) was warmed at reflux under nitrogen for 60 h. The solvent was removed from the reaction mixture under reduced pressure. Chromatography (SiO, 18 × 1.8 cm, 0–30% EtOAc–hexane) afforded recovered **9** (55%) and 82 mg (40%) of **10** as a white crystalline solid: mp 165–167 °C (EtOAc–hexane); ^1H NMR ($CDCl_3$, 200 MHz) δ 4.01 (2 H, tq, *J* = 6.9, 7.0 Hz, C*H*CH_2C*H*), 3.54 (6 H, s, SO_2CH_3), 2.15 (2 H, t, *J* = 6.9 Hz, CHC*H*$_2$CH), 1.44 (6 H, d, *J* = 7.0 Hz, CHC*H*$_3$); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 161.2 (e, C, aromatic), 151.8 (e, C, aromatic), 42.1 (e, CH*C*H_2CH), 41.1 (o, SO_2CH_3), 37.8 (o, *C*HCH$_3$), 21.2 (o, CH*C*H$_3$); IR (KBr) ν_{max} 3038, 3016, 2972, 2936, 2880, 1508, 1466, 1380, 1311, 1198, 1182, 1162, 1148, 1132, 1108, 1094, 1078, 1040, 952, 824, 800, 766 cm^{-1}; EIMS, *m/e* (rel intensity) 304 (M^+, 17), 289 (8), 145 (base), 131 (11), 118 (18), 104 (8), 91 (11), 81 (63), 79 (60), 77 (19), 65 (14), 63 (17); CIMS (2-methylpropane), *m/e* (rel intensity) 305 (M + H^+, base); EIHRMS, *m/e* 304.0562 ($C_{11}H_{16}N_2O_4S_2$ requires 304.0552). Anal. Calcd for $C_{11}H_{16}N_2O_4S_2$: C, 43.41; H, 5.30; N, 9.20; S, 21.07. Found: C, 43.79; H, 5.62; N, 8.96; S, 20.80.

(5*R,7*S**)-*N*-2,3-Hexadienyl-6,7-dihydro-4-(methylsulfonyl)-5,7-dimethyl-5*H*-cyclopenta[*d*]pyridazin-1-amine (11).** A solution of the trifluoroacetic acid salt of 2,3-hexadienylamine (**17**, 0.67 g, 6.2 equiv, 3.18 mmol) and **9** (155 mg, 0.51 mmol) in methylene chloride (3 mL) was placed in a Teflon tube sealed with a brass clamp at one end and treated with anhydrous potassium carbonate (0.44 g, 3.18 mmol, 6.2 equiv). After the evolution of carbon dioxide stopped, the mixture was sealed with a brass clamp. The reaction vessel was placed in a pressure reactor (13 kbar) at 25 °C for 96 h. After depressurization, the reaction mixture was treated with H_2O (10 mL) and extracted with methylene chloride (10 mL × 4), and the combined organic phase was concentrated under reduced pressure. Chromatography (SiO_2, 20 × 2.0 cm, 0–20% EtOAc–hexane) afforded 122 mg (164 mg theoretical, 74%) of **11**, 27 mg (164 mg theoretical, 16%) of **12** as pale yellow oils, and 13 mg (9%) of recovered starting material **9**. For **11**: ^1H NMR ($CDCl_3$, 200 MHz) δ 5.47 (2 H, m, C*H*=C=C*H*), 4.76 (1 H, brt, *J* = 4.5 Hz, NH), 4.25 (2 H, m, NHCH_2CH), 3.79 (1 H, ddq, *J* = 9.4, 1.6, 7.2 Hz, CHCH$_2$C*H*), 3.42 (3 H, s, SO_2CH_3), 3.09 (1 H, ddq, *J* = 9.4, 1.6, 7.2 Hz, C*H*CH$_2$CH), 2.62 (1 H, ddd, *J* = 13.5, 9.4, 9.4 Hz, CHC*H*HCH), 2.03 (2 H, m, CH$_3$CH_2), 1.62 (1 H, ddd, *J* = 13.4, 1.6, 1.6 Hz, CHCH*H*CH), 1.50 (3 H, d, *J* = 7.2 Hz, CHCH_3), 1.35 (3H, d, *J* = 7.2 Hz, CHCH_3), 1.00 (3 H, t, *J* = 7.4 Hz, CH_3CH$_2$); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 203.0 and 202.9 (s, CH=*C*=CH), 157.7 (s, C, aromatic), 153.1 (s, C, aromatic), 146.3 (s, C, aromatic), 134.7 (s, C, aromatic), 97.5 and 97.4 (d, *C*HCCH), 89.7 (d, CHC*C*H), 41.0 (q, SO_2CH_3), 40.5 (t, NH*C*H$_2$), 39.7 and 39.6 (t, CH*C*H$_2$CH), 38.6 (d, *C*HCH$_3$), 36.1 (d, *C*HCH$_3$), 23.5 (q, CH*C*H$_3$), 21.9 (t, *C*H$_2$CH$_3$), 19.84 and 19.76 (q, CH*C*H$_3$), 13.4 and 13.3 (q, CH$_2$*C*H$_3$); IR (neat) ν_{max} 3316, 2966, 2934, 2872, 1966, 1674, 1586, 1496, 1458, 1404, 1382, 1310, 1224, 1166, 1122, 1070, 1036, 952, 874, 796, 760 cm^{-1}; EIMS, *m/e* (rel intensity) 321 (M^+, 17), 306 (base), 292 (23), 254 (13), 242 (62), 226 (21), 212 (11), 198 (10), 147 (10), 96 (16), 91 (11), 86 (36), 84 (56), 79 (48), 77 (25), 65 (23), 53 (41); CIMS (2-methylpropane), *m/e* (rel intensity) 322 (M + H^+, base); EIHRMS, *m/e* 321.1508 ($C_{16}H_{23}N_3O_2S$ requires 321.1511). Anal. Calcd for $C_{16}H_{23}N_3O_2S$: C, 59.79; H, 7.21; N, 13.07; S, 9.97. Found: C, 59.96; H, 7.55; N, 13.15; S, 9.77.

(5*R,7*R**)-*N*-2,3-Hexadienyl-6,7-dihydro-4-(methylsulfonyl)-5,7-dimethyl-5*H*-cyclopenta[*d*]pyridazin-1-amine (12).** A solution of the trifluoroacetic acid salt of 2,3-hexadienylamine (**17**, 0.38 g, 1.8 mmol, 9.0 equiv) and **10** (60.5 mg, 0.20 mmol) in methylene chloride (1 mL) was placed in a Teflon tube sealed with a brass clamp at one end and treated with anhydrous potassium carbonate (0.35 g, 2.5 mmol, 12.5 equiv). After the evolution of carbon dioxide stopped, the mixture was sealed with a brass clamp. The reaction vessel was placed in a pressure reactor (13 kbar) at 25 °C for 48 h. After depressurization, the reaction mixture was treated with H_2O (10 mL) and extracted with methylene chloride (10 mL × 4), and the combined organic phase was concentrated under reduced pressure. Chromatography (SiO_2, 16 × 1.3 cm, 0–20% EtOAc–hexane) afforded 42.5 mg (64 mg theoretical, 66%) of **12**. For **12**: ^1H NMR ($CDCl_3$, 200 MHz) δ 5.47 (2 H, m, C*H*=C=C*H*), 4.87 (1 H, brs, NH), 4.24 (2 H, m, NHCH_2CH), 3.83 (1 H, dq, *J* = 3.7, 7.1 Hz, C*H*CH$_2$CH), 3.42 (3 H, s, SO_2CH_3), 3.30 (1 H, dq, *J* = 3.7, 7.0 Hz, CHCH$_2$C*H*), 2.04 (4 H, m, CH$_3$CH_2, CHCH_2CH), 1.35 (3 H, d, *J* = 7.1 Hz, CH_3CH), 1.29 (3 H, two d, *J* = 7.0 Hz, CH_3CH), 1.00 (3 H, two t, *J* = 7.5 Hz, CH_3CH$_2$); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 202.8 (s, CH=*C*=CH), 158.1 and 158.0 (s, C, aromatic), 153.2 (s, C, aromatic), 146.7 (s, C, aromatic), 133.9 (s, C, aromatic), 97.7 and 97.6 (d, *C*H=C=CH), 89.8 and 89.7 (d, CH=C=*C*H), 42.2 (t, NH*C*H$_2$), 41.0 (q, SO_2CH_3), 39.74 and 39.69 (t, CH*C*H$_2$CH), 37.6 (d, *C*HCH$_2$CH), 35.5 (d, CHCH$_2$*C*H), 21.93 and 21.87 (t, *C*H$_2$CH$_3$), 21.2 (q, CH*C*H$_3$), 18.25 and 18.16 (q, CH*C*H$_3$), 13.4 and 13.2 (q, CH$_2$*C*H$_3$); IR (neat) ν_{max} 3388, 2964, 2932, 2872, 1964, 1576, 1490, 1458, 1406, 1378, 1306, 1166, 1126, 1080, 954, 874, 794, 760 cm^{-1}; EIMS, *m/e* (rel intensity) 321 (M^+, 13), 306 (base), 292 (23), 254 (15), 242 (57), 226 (28), 212 (13), 198 (12), 147 (10), 96 (11), 91 (11), 86 (25), 84 (42), 79 (26), 77 (20), 65 (15), 53 (22); CIMS (2-methylpropane), *m/e* (rel intensity) 322 (M + H^+, base); EIHRMS, *m/e* 321.1508 ($C_{16}H_{23}N_3O_2S$ requires 321.1511).

***N*-Acetyl-*cis*-trikentrin A (15).** A solution of **11** (363 mg, 1.13 mmol) and anhydrous sodium acetate (30 mg, 0.3 equiv) in acetic anhydride (3.5 mL) was stirred vigorously at 160 °C for 12 h.[21] The cooled reaction mixture was poured into 20 mL of water, extracted with methylene chloride (10 mL × 5), dried (Na_2SO_4), and concentrated under reduced pressure. Chromatography (SiO_2, 17 × 1.6 cm, 0–5% EtOAc–hexane) afforded 152 mg (288 mg theoretical, 53%) of pure **15** as a pale yellow oil: ^1H NMR ($CDCl_3$, 200 MHz) δ 7.34 (1 H, d, *J* = 3.9 Hz, NC*H*CH), 6.99 (1 H, s, Ar*H*), 6.69 (1 H, d, *J* = 3.9 Hz, NCHC*H*), 3.95 (1 H, m, C*H*CH$_3$), 3.29 (1 H, m, C*H*CH$_3$), 2.86 (2 H, q, *J* = 7.4 Hz, CH_2CH$_3$), 2.67 (1 H, ddd, *J* = 12.8, 8.7, 8.7 Hz, CHC*H*HCH), 2.64 (3 H, s, COCH$_3$), 1.35 (3 H, d, *J* = 7.0 Hz, CHCH_3), 1.31 (3 H, t, *J* = 7.5 Hz, CH$_2$CH_3), 1.28 (1 H, ddd, *J* = 12.8, 6.8, 6.8 Hz, CHCH*H*CH), 1.11 (3 H, d, *J* = 6.8 Hz, CHCH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 168.1 (s, *C*=O), 147.5 (s, C, aromatic), 135.2 (s, C, aromatic), 133.4 (s, C, aromatic), 132.4 (s, C, aromatic), 129.7 (s, C, aromatic), 125.3 (d, C-2), 119.0 (d, C-5), 108.0 (d, C-3), 42.2 (t, C-7), 39.7 (d, *C*HCH$_3$), 39.2 (d, *C*HCH$_3$), 26.0 (t, *C*H$_2$CH$_3$), 24.2 (q, CO*C*H$_3$), 23.7 (q, CH*C*H$_3$), 22.5 (q, CH*C*H$_3$), 15.2 (q, CH$_2$*C*H$_3$); IR (neat) ν_{max} 2960, 2930, 2868, 1718, 1542, 1476, 1456, 1394, 1364, 1324, 1258, 1234, 1190, 910, 730 cm^{-1}; EIMS, *m/e* (rel intensity) 255 (M^+, 54), 240 (36), 213 (28), 198 (base), 182 (7), 168 (19), 154 (7); CIMS (2-methylpropane), *m/e* (rel intensity) 256 (M + H^+, base); EIHRMS, *m/e* 255.1628 ($C_{17}H_{21}NO$ requires 255.1623). Anal. Calcd for $C_{17}H_{21}NO$: C, 79.96; H, 8.29; N, 5.49. Found: C, 80.22; H, 8.56; N, 5.19.

***N*-Acetyl-*trans*-trikentrin A (16).** A solution of **12** (204 mg, 0.63 mmol) and anhydrous sodium acetate (18 mg, 0.3 equiv) in acetic anhydride (3 mL) was stirred vigorously at 160 °C for 11 h. The cooled reaction mixture was poured into 10 mL of water, extracted with methylene chloride (10 mL × 4), dried (Na_2SO_4), and concentrated under reduced pressure. Chromatography (SiO_2, 18 × 2.0 cm, 0–5% EtOAc–hexane) afforded 81 mg (162 mg theoretical, 50%) of pure **16** as a white solid: mp 73–75 °C (hexane); ^1H NMR ($CDCl_3$, 200 MHz) δ 7.35 (1 H, d, *J* = 3.9 Hz, NCH), 7.00 (1 H, s, ArH), 6.70 (1 H, d, *J* = 3.9 Hz, NCHC*H*), 4.18 (1 H, m, C*H*CH$_3$), 3.38 (1 H, m, C*H*CH$_3$), 2.87 (2 H, q, *J* = 7.7 Hz, CH_2CH$_3$), 2.65 (3 H, s, COCH$_3$), 1.95 (2 H, m, CHCH_2CH), 1.34 (3 H, d, *J* = 7.0 Hz, CHCH_3), 1.31 (3 H, t, *J* = 7.6 Hz, CH$_2$CH_3), 1.09 (3 H, d, *J* = 7.0 Hz, CHCH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 167.8 (s, *C*=O), 147.0 (s, C, aromatic), 135.2 (s, C, aromatic), 133.9 (s, C, aromatic), 132.1 (s, C, aromatic), 129.7 (s, C, aromatic), 125.4 (d, C-2), 118.9 (d, C-5), 108.0 (d, C-3), 43.1 (t, C-7), 39.7 (d, *C*HCH$_3$), 37.6 (d, *C*HCH$_3$), 26.1 (t, *C*H$_2$CH$_3$), 24.8 (q, CO*C*H$_3$), 21.7 (q, CH*C*H$_3$), 20.6 (q, CH*C*H$_3$), 15.2 (q, CH$_2$*C*H$_3$); IR (KBr) ν_{max} 2956, 2852, 1712, 1548, 1474, 1396, 1364, 1334, 1320, 1248, 1232, 1194, 1036, 952, 908, 872, 716, 696 cm^{-1}; EIMS, *m/e* (rel intensity) 255 (M^+, 40), 240 (28), 213 (31), 198 (base), 179 (24), 167 (22), 154 (12), 141 (15), 115 (5); CIMS (2-methylpropane), *m/e* (rel intensity) 256 (M + H^+, base); EIHRMS, *m/e* 255.1626 ($C_{17}H_{21}NO$ requires 255.1623). Anal. Calcd for $C_{17}H_{21}NO$: C, 79.96; H, 8.29; N, 5.49. Found: C, 80.36; H, 8.58; N, 5.50.

***cis*-Trikentrin A (1).** A solution of **15** (60 mg, 0.24 mmol) and LiOH·H_2O (21 mg, 0.50 mmol, 2.0 equiv) in THF–H_2O–CH_3OH (3:1:1) (2 mL) was allowed to stir at 25 °C for 1 h. The reaction mixture was treated with 10 mL of saturated NH_4Cl and was extracted with methylene chloride (5 mL × 5). The organic layer was dried (Na_2SO_4) and concentrated in vacuo. Chromatography (SiO_2, 17 × 1.4 cm, 0–5% EtOAc–hexane) afforded 48 mg (50.4 mg theoretical, 95%) of **1** as a colorless oil which darkens on standing: ^1H NMR ($CDCl_3$, 500 MHz) δ 8.08 (1 H, brs), 7.15 (1 H, dd, *J* = 2.4, 3.1 Hz), 6.84 (1 H, s), 6.59 (1 H, dd, *J* = 2.0, 3.3 Hz), 3.44 (1 H, ddq, *J* = 8.8, 7.5, 7.5 Hz), 3.22 (1 H, ddq, *J* = 8.8, 7.5, 7.5 Hz), 2.94 (1 H, dq, *J* = 15.0, 7.5 Hz), 2.93 (1 H, dq, *J* = 15.0, 7.5 Hz), 2.60 (1 H, ddd, *J* = 12.3, 7.5, 7.5 Hz), 1.50 (3 H, d, *J* = 6.8 Hz), 1.37 (3 H, d, *J* = 7.0 Hz), 1.36 (3 H, t, *J* = 7.5 Hz), 1.32 (1 H, ddd, *J* = 12.3, 8.8, 8.8 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 143.4, 135.4, 132.8, 127.3, 126.7, 123.2, 114.3, 101.6, 44.8, 39.0, 37.3,

26.6, 21.1, 20.8, 15.1; IR (neat) ν_{max} 3428, 2958, 2868, 1620, 1500, 1456, 1402, 1360, 1126, 1064, 862, 786, 726 cm^{-1}; EIMS, *m/e* (rel intensity) 213 (M^+, 57), 198 (base), 184 (10), 169 (19), 154 (7), 90 (5), 77 (3); CIMS (2-methylpropane), *m/e* (rel intensity) 214 (M + H^+, base); EIHRMS, *m/e* 213.1514 ($C_{15}H_{19}N$ requires 213.1518).

***trans*-Trikentrin A (2).** A solution of **16** (75 mg, 0.29 mmol) and $LiOH\cdot H_2O$ (26 mg, 0.62 mmol, 2.1 equiv) in $THF-H_2O-CH_3OH$ (3:1:1) (2 mL) was allowed to stir at 25 °C for 1 h. The reaction mixture was treated with 10 mL of saturated NH_4Cl and was extracted with methylene chloride (5 mL × 5). The organic layer was dried (Na_2SO_4) and concentrated in vacuo. Chromatography (SiO_2, 17 × 1.4 cm, 0-5% EtOAc-hexane) afforded 58 mg (63 mg theoretical, 92%) of 2 as a white crystalline solid: ^1H NMR ($CDCl_3$, 500 MHz) δ 8.01 (1 H, brs), 7.16 (1 H, dd, *J* = 3.1, 2.4 Hz), 6.83 (1 H, s), 6.59 (1 H, dd, *J* = 3.3, 2.0 Hz),[18] 3.52 (1 H, ddq, *J* = 7.3, 3.7, 7.3 Hz), 3.41 (1 H, ddq, *J* = 7.1, 7.1, 7.1 Hz), 2.93 (2 H, q, *J* = 7.7 Hz), 2.04 (1 H, ddd, *J* = 12.3, 7.5, 3.9 Hz), 1.96 (1 H, ddd, *J* = 12.4, 7.3, 7.3 Hz), 1.36 (3 H, t, *J* = 7.5 Hz), 1.33 (3 H, d, *J* = 7.1 Hz), 1.30 (3 H, d, *J* = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 142.9, 135.5, 132.5, 127.6, 126.5, 123.2, 114.4, 101.8, 43.9, 38.0, 36.1, 26.6, 20.9, 20.1, 15.0; IR (KBr) ν_{max} 3394, 2952, 2920, 2864, 1624, 1498, 1448, 1404, 1374, 1318, 1126, 1104, 1058, 896, 866, 786, 732 cm^{-1}; EIMS, *m/e* (rel intensity) 213 (M^+, 49), 198 (base), 184 (11), 169 (23), 154 (10), 90 (5), 77 (4); CIMS (2-methylpropane), *m/e* (rel intensity) 214 (M + H^+, base); EIHRMS, *m/e* 213.1523 ($C_{15}H_{19}N$ requires 213.1518.

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Dipivaloylketene and Its Unusual Dimerization to a Permanently Stable α-Oxoketene

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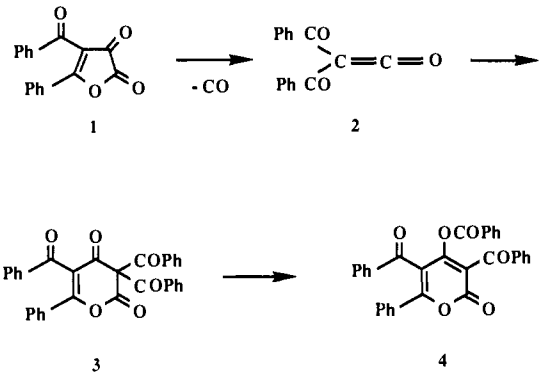
Abstract: Dipivaloylketene (**8**) is obtained by flash vacuum pyrolysis of 5-*tert*-butyl-4-pivaloyl-2,3-dihydrofuran-2,3-dione (**7**) at temperatures between 250 and 500 °C. It is stable in solution below 0 °C and dimerizes at room temperature to **10**, which involves an unusual [2+4] cycloaddition reaction between one α-oxoketene unit and the carbonyl double bond of a second molecule, thus preserving the ketene functionality. The structure of the highly hindered ketene **10** was proved by X-ray crystallography. This compound is stable for months in the open air at high humidity.

Introduction

There is considerable current interest in the chemistry of ketenes[2] because of their use as synthetic building blocks, because of mechanistic considerations,[3] and because of the discovery of a number of unusual rearrangements.[4]

α-Oxoketenes are particularly reactive and cannot normally be isolated under usual reaction conditions. Several examples have been detected by low-temperature IR spectroscopy at 77 K or in Ar matrix at ca. 12 K.[3a-b,4a-b,5] Steric hindrance makes the ketenes persistent; thus, isopropyl(isopropylcarbonyl)ketene is reported to be observable by IR spectroscopy in CCl_4 solution, at 20 °C for 2-3 days,[6] and *tert*-butyl(*tert*-butylcarbonyl)ketene to be stable under similar conditions for several months.[7] *tert*-Butyl(ethoxycarbonyl)ketene is similarly persistent.[8]

Dibenzoylketene (**2**), generated from furandione **1**, is stable at 77 K but under ordinary reaction conditions dimerizes to α-pyrone **4** in a process involving a [2+4] cycloaddition of one ketene molecule to the C=C bond of another (eq 1), followed by an acyl 1,3-shift.[4a]



(1)

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(2) *The Chemistry of Ketenes, Allenes, and Related Compounds*; Patai, S., Ed.; Wiley-Interscience: Chichester, England, 1980; Parts 1 and 2. Snider, B. B. *Chem. Rev.* **1988**, *88*, 793-811. Moore, H. W.; Decker, O. H. W. *Ibid.* **1986**, *86*, 821-830. Moore, H. W.; Gheorghiu, M. D. *Chem. Soc. Rev.* **1981**, *10*, 289.

(3) (a) Clemens, R. J.; Witzeman, J. S. *J. Am. Chem. Soc.* **1989**, *111*, 2186. (b) Witzeman, J. S. *Tetrahedron Lett.* **1990**, *31*, 1401. (c) Coleman, R. S.; Grant, E. B. *Ibid.* **1990**, *31*, 3677. Emerson, D. W.; Titus, R. L.; Gonzales, R. M. *J. Org. Chem.* **1990**, *55*, 3572. Gong, L.; Leung-Toung, R.; Tidwell, T. T. *Ibid.* **1990**, *55*, 3634. Allen, A. D.; Gong, L.; Tidwell, T. T. *J. Am. Chem. Soc.* **1990**, *112*, 6396. Wang, X.; Houk, K. N. *Ibid.* **1990**, *112*, 1754. Valenti, E.; Pericas, M. A.; Moyano, A. *J. Org. Chem.* **1990**, *55*, 3582. Gheorghiu, M. D.; Parvulescu, L.; Popescu, A. *Ibid.* **1990**, *55*, 3713.

(4) (a) Wentrup, C.; Winter, H.-W.; Gross, G.; Netsch, K.-P.; Kollenz, G.; Ott, W.; Biedermann, A. G. *Angew. Chem.* **1984**, *96*, 791; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 800. (b) Wentrup, C.; Netsch, K.-P. *Angew. Chem.* **1984**, *96*, 792; *Angew. Chem.; Int. Ed. Engl.* **1984**, *23*, 802. (c) Nguyen, M. T.; Ha, T.-K.; More O'Ferrall, R. A. *J. Org. Chem.* **1990**, *55*, 3251. (d) Ben Cheikh, A.; Chuche, J.; Manisse, N.; Pommelet, J. C.; Netsch, K.-P.; Lorencak, P.; Wentrup, C. *Ibid.* **1990**, *55*, 970-975. (e) Wentrup, C.; Lorencak, P. *J. Am. Chem. Soc.* **1988**, *110*, 1880. (f) Wentrup, C.; Blanch, R.; Briehl, H.; Gross, G. *Ibid.* **1988**, *110*, 1874. (g) Wentrup, C.; Gross, G.; Berstermann, H.-M.; Lorencak, P. *J. Org. Chem.* **1985**, *50*, 2877. (h) Ohkita, M.; Tsuji, T.; Suzuki, M.; Murakami, M.; Nishida, S. *Ibid.* **1990**, *55*, 1506. (i) Chow, K.; Nguyen, N. V.; Moore, H. W. *Ibid.* **1990**, *55*, 3876.

(5) Maier, G.; Reisenauer, H. P.; Sayrac, T. *Chem. Ber.* **1982**, *115*, 2192-2201.

(6) Nikolaev, V. A.; Frenkh, Yu.; Korobitsyna, I. K. *Zh. Org. Khim.* **1978**, *14*, 1147-1160; *J. Org. Chem. USSR (Engl. Transl.)* **1978**, *14*, 1069-1079.

(7) Nikolaev, V. A.; Frenkh, Yu.; Korobitsyna, I. K. *Zh. Org. Khim.* **1978**, *14*, 1433-1441; *J. Org. Chem. USSR (Engl. Transl.)* **1978**, *14*, 1338-1346.

(8) Newman, M. S.; Zuech, E. A. *J. Org. Chem.* **1962**, *27*, 1436.

0002-7863/91/1513-4234$02.50/0