prepared $Na(PEG)_2BH_2$ (12 mmol) and the temperature raised to 80 °C. During the time of reaction (4 h), the formation of a viscous solid was observed, which made the stirring difficult. Tetrahydrofuran (10 mL) was therefore added in order to make the mixture homogeneous, and after cooling to room temperature, water and 1 N HCl solution to acidic pH were sequentially added and the solvent was removed under reduced pressure. Extractions and usual workup furnished a residue (0.77 g), which was purified by flash chromatography as above. Phenylethanol **11** was obtained (0.244 g, 2 mmol, 45%) along with diol **10** (0.101 g, 0.66 mmol, 15%). Also a mixture of starting malonate **9** (0.125 g, 0.53 mmol, 12%), phenylacetate $C_6H_5CH_2COOC_2H_5$ (0.088 g, 0.53 mmol, 12%), and transesterification product(s) (0.182 g, 0.31 mmol assuming as average molecular weight 590, 7% yield) were obtained.

Transesterification of Malonate 9 with Tetraethylene Glycol (TEG) (12b). In a round-bottom flask equipped with magnetic stirrer and reflux condenser, a mixture of malonate **9** (0.937 g, 3.95 mmol) and tetraethylene glycol (TEG) (3.85 g, 19.8 mmol) was kept at 180 °C for 0.5 h. After cooling, brine was added (40 mL, pH 5), and products were recovered by extractions with diethyl ether (6 × 20 mL) (0.750 g). Flash chromatography (dichloromethane–acetone, 8:2) gave starting material **9** (0.216 g, 0.914 mmol, 23%) and **12b** (0.36 g, 0.937 mmol, 24%): MS, m/z 384 (M^+); IR ν_{max} 1750, 1730 cm^{-1}; ^1H NMR δ 1.2 (t, 3 H), 3.0 (br, 1 H exchangeable with ^2H_2O), 3.40–3.75 (14 H), 3.90–4.35 (m, 4 H), 4.58 (s, 1 H), 7.30 (complex, 5 H).

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Directed Hydroxylation of Aromatics

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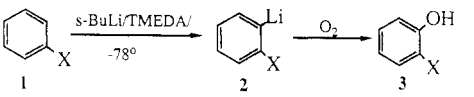
Although there are a number of mechanistically diverse methods which result in the hydroxylation of an aromatic ring,[1] it is often difficult to effect the transformation in a direct and regiospecific fashion. A potentially versatile class of procedures, the oxidation of aryl organometallics, is well-known;[2] however, examples of directed hydroxylation by application of this strategy are few.[3]

Studies on the chemical synthesis of phenolic natural products led us to investigate the oxygenation of aryllithium species which had been prepared by functional group-directed metalation (**1**[4,5] → **2** → **3**,[5] Scheme I). The one-pot lithiation/oxygenation sequence described here (*sec*-BuLi, TMEDA; then O_2) affords moderate yields of regiospecifically monohydroxylated products. Our experiments are summarized in Table I.

Entries 1–3 show the preparation of the predicted aryllithium[6] and its conversion to the corresponding phenol. Likewise, entries 4 and 5 show the expected phenolic products and illustrate the dominance of the tertiary amide group in determining the position of lithiation[7] and subsequent hydroxylation. Entries 1, 2, and

Scheme I



Scheme II

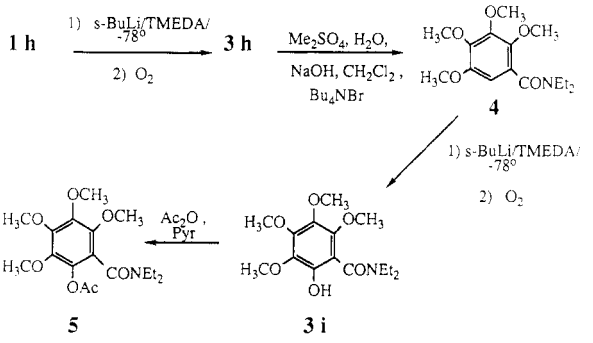
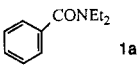
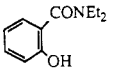
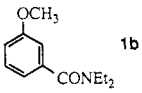
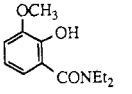
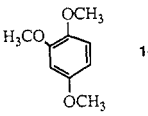
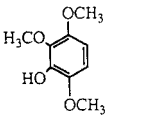
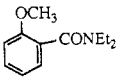
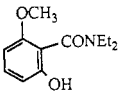
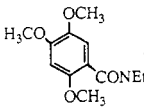
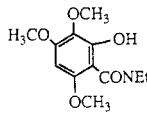
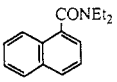
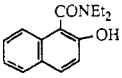
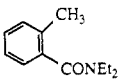
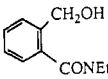
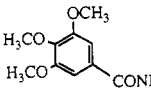
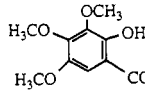


Table I

entry	starting material		reaction product		yield, %
1		1a		3a	37
2		1b		3b	51
3		1c		3c	34
4		1d		3d	46
5		1e		3e	52
6		1f		3f	34
7		1g		3g	49
8		1h		3h	48

(1) (a) For a short discussion of the problem and some key references, see: Dolson, M. G.; Swenton, J. S. *J. Am. Chem. Soc.* **1981**, *103*, 2361. (b) For a review, see: Wedemeyer, K.-F. *Methoden der Organischen Chemie. Phenole*; Muller, E., Ed.; Georg Thieme Verlag: Stuttgart, 1976; Vol. VI/1C.

(2) (a) Garst, J. F.; Smith, C. D.; Ferrar, A. C. *J. Am. Chem. Soc.* **1972**, *94*, 7707. (b) Sosnovsky, G.; Brown, J. H. *Chem. Rev.* **1966**, *66*, 529.

(3) (a) Gilman, H.; Swiss, J.; Cheney, L. C. *J. Am. Chem. Soc.* **1940**, *62*, 1963. (b) Air oxygenation of arylcopper species prepared from aryllithium reagents has been reported: Lambert, G. J.; Duffey, R. P.; Dalzell, H. C.; Razdan, R. K. *J. Org. Chem.* **1982**, *47*, 3350. (c) A procedure involving lithiation–boration–oxidation was used for the conversion of **1a** to **3a** by: Beak, P.; Brown, R. A. *J. Org. Chem.* **1982**, *47*, 34. (d) The Beak procedure[3c] was applied for the ortho hydroxylation of *N,N*-dimethyl-3,4-(methylenedioxy)benzamide: Iwao, M.; Reed, J. N.; Snieckus, V. *J. Am. Chem. Soc.* **1982**, *104*, 5531.

(4) Amides **1** were prepared from the corresponding acids by the method of: McCabe, E. T.; Barthel, W. F.; Gertler, S. I.; Hall, S. A. *J. Org. Chem.* **1954**, *19*, 493.

(5) All new compounds were characterized by infrared and NMR spectroscopy and by high-resolution mass spectroscopy (satisfactory M^+).

(6) Gschwend, H. W.; Rodriguez, H. R. *Org. React. (N. Y.)* **1979**, *26*, 1–360.

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4 lead to products previously obtained by ortho lithiation of *O*-aryl carbamates[8] and demonstrate the complementarity of these two approaches. Entry 5 is of some interest for the synthesis of highly oxygenated flavones[9] (see also entry 8 and the synthesis of **3i**).

Hydroxylation of lithiated 1-naphthamide **1f** occurs at C-2 as expected from previous lithiation investigations.[10] This directed hydroxylation is viewed by us as a model for the preparation of the 2-hydroxy-1-naphthalenecarboxylic acid portion of neocarcinostatin.[11]

Hydroxylation of lithiated *o*-toluamide **1g** leads to the benzyl alcohol **3g**, oxygenated at the position of preferential lithiation.[12] Phthalides may be derived from *o*-(hydroxymethyl)benzamides.[3c,13]

Hydroxylation of 3,4,5-trimethoxybenzamide **1h** (entry 8) provides facile entry to the tetraoxygenated benzoyl system.[9] Attempts to dihydroxylate benzamide **1h** by treatment with 4 equiv *sec*-butyllithium and extended exposure to oxygen resulted only in the recovery of the monohydroxylated product. This is consistent with the observations of Snieckus et al. which suggested that ortho dilithiation of a mono benzamide could be achieved by double halogen–metal exchange but not by deprotonation.[14]

The preparation of a pentaoxygenated benzamide **3i**[15] was accomplished by stepwise functionalization of benzamide **1h** (Scheme II). Thus, methylation of the monohydroxylated **3h** gave the tetramethoxy benzamide **4**. Then hydroxylation via the standard procedure (see below) gave the pentaoxygenated system **3i**, characterized as its acetate **5**.

Although yields in these preliminary studies are only fair,[16] they are, even at this stage, useable. Furthermore, the method complements others as it may be used to convert readily available starting materials to compounds with substitution patterns which are otherwise difficult to engineer.

The conversion of **1e** to **3e** provides a typical experimental procedure. Methods of purification and characterization are given for other hydroxylation products (**3**) and for **4**.

Experimental Section

General Procedures. Proton nuclear magnetic resonance spectra were taken on a Varian EM-360 spectrometer and on a Bruker 250 spectrometer. Chemical shifts are reported relative to tetramethylsilane in parts per million. Infared spectra were taken on a Perkin-Elmer 681 spectrophotometer, and absorptions are reported in cm^{-1}. High-resolution mass spectra were taken on a Kratos mass spectrometer at 70 eV. Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Packing material for flash chromatography was Merck silica gel 60. Chromatotron separations were performed with commercial silica gel plates. THF was distilled from Na/benzophenone ketyl; TMEDA was distilled from Na.

***N*,*N*-Diethyl-2-hydroxy-3,4,6-trimethoxybenzamide (3e).** To a solution of trimethoxybenzamide **1e** (200 mg, 0.750 mmol) and freshly distilled TMEDA (0.23 mL, 1.5 mmol) in 10 mL of anhydrous THF cooled to −78 °C was added *sec*-BuLi (1.1 mL of 1.4 M solution in cyclohexane, 1.5 mmol). The solution was stirred at −78 °C for 1 h under N_2; during this time it became yellow in color. Next, O_2 was bubbled through the rapidly stirring solution; the reaction mixture became light yellow in appearance. The reaction mixture was allowed to come to room temperature and exposure to O_2 gas was continued for 6 h. Quenching with dilute HCl was followed by addition of EtOAc. The aqueous and organic phases were separated, and the aqueous solution was extracted with EtOAc (2×). The combined organic solution was extracted with 5% NaOH. After acidification of the basic solution, the aqueous solution was extracted with EtOAc (3×). The combined organic solution was washed with brine, dried with Na_2SO_4, and concentrated to yield a white solid. Recrystallization from EtOAc/hexane afforded a white crystalline solid: 110 mg (52%); mp 142–143 °C; NMR (60 MHz, $CDCl_3/Me_4Si$) 1.20 (t, J = 7 Hz, 6 H), 3.40 (q, J = 7 H, 4 H), 3.76 (s, 3 H), 3.90 (s, 3 H), 3.94 (s, 3 H), 6.10 (s, 1 H); IR ($CHCl_3$) 3510, 1620, 1510, 1120 cm^{-1}; M^+ ($C_{14}H_{21}O_5N$) calcd 283.1419, found 283.1409.

***N*,*N*-Diethyl-2-hydroxybenzamide (3a).** A 100-mg sample of amide **1a** (0.565 mmol) gave a crude product, which was subjected to flash chromatography (eluent EtOAc/hexane = 1/3); 40 mg (37%) of a colorless oil was recovered. Reduced pressure distillation [150 °C (0.5 mm)] afforded a white crystalline solid, mp 100–101 °C (lit.[8] mp 101 °C).

***N*,*N*-Diethyl-2-hydroxy-3-methoxybenzamide (3b).** The crude product obtained from 100 mg (0.483 mmol) of amide **1b** was purified on a Chromatotron (eluent EtOAc) to afford 55 mg (51%) of an oily solid. Reduced pressure distillation [130 °C (0.5 mm)] gave white crystals, mp 85–87 °C (lit.[8] mp 82–83 °C).

2,3,6-Trimethoxyphenol (3c). Lithiation of 244 mg (1.45 mmol) of 1,2,4-trimethoxybenzene[17] was followed by quenching with O_2 and the usual workup. The product was purified by elution from a Chromatotron (EtOAc/hexane = 1/4), affording 90 mg (34%) of a colorless oil. This was distilled at 135–140 °C (0.9 mm). (Note: this phenol becomes yellow on standing). NMR (60 MHz, $CDCl_3/Me_4Si$) 3.80 (s, 6 H), 3.85 (s, 3 H), 5.60 (br, 1 H, exchangeable in D_2O), 6.32 (d of AB q, J = 9 Hz, 1 H), 6.58 (d of AB q, J = 9 Hz, 1 H); IR ($CHCl_3$) 3550, 1590, 1500, 1070 cm^{-1}; M^+ ($C_9H_{12}O_4$) calcd 184.0735, found 184.0748.

***N*,*N*-Diethyl-2-hydroxy-6-methoxybenzamide (3d).** The standard procedure converted 500 mg (2.40 mmol) of amide **1d** to material which was purified on a Chromatotron (eluent EtOAc/hexane = 1/1) to afford 250 mg (46%) of a white solid. Recrystallization from $CHCl_3$ gave white crystals, mp 139–140 °C (lit.[8] mp 139–140 °C).

***N*,*N*-Diethyl-2-hydroxy-1-naphthalenecarboxamide (3f).** A sample of naphthamide **1f** (800 mg, 3.52 mmol) was converted to 2-hydroxy-1-naphthamide **3f**, which was isolated by trituration with EtOAc as a white solid (291 mg, 34%). Recrystallization (EtOAc, hexane) afforded white crystals: mp 204–205 °C; NMR (60 MHz, acetone-d^6/Me_4Si) 1.14 (t, J = 7 Hz, 6 H), 2.95 (br s, exchangeable in D_2O), 3.33 (q, J = 7 Hz, 4 H), 7.00–7.76 (m, 6 H); IR ($CHCl_3$) 3180, 3025, 1600, 1510, 1285, 1195 cm^{-1}; M^+

(7) Reviews which focus on the directing effect of the tertiary amide and the use of this effect in synthesis: (a) Beak, P.; Snieckus, V. *Acc. Chem. Res.* **1982**, *15*, 306. (b) Snieckus, V. *Heterocycles* **1980**, *14*, 1649.

(8) Sibi, M. P.; Snieckus, V. *J. Org. Chem.* **1983**, *48*, 1935.

(9) Naturally occurring flavones which contain 2,3,4,5- and 2,3,4,6-tetraoxygenated benzoyl components (compare **3e**, **3h**) are known. Related compounds contain a 2,3,4,5,6-pentaoxygenated benzoyl equivalent (see **3i**). For leading references, see: Iinuma, M.; Iwashima, K.; Matsuura, S. *Chem. Pharm. Bull.* **1984**, *32*, 4935. Iinuma, M.; Tanaka, T.; Matsuura, S. *Chem. Pharm. Bull.* **1984**, *32*, 3354.

(10) (a) Watanabe, M.; Snieckus, V. *J. Am. Chem. Soc.* **1980**, *102*, 1457. (b) Jacobs, S. A.; Harvey, R. G. *Tetrahedron Lett.* **1981**, 1093.

(11) Edo, K.; Mizugaki, M.; Koide, Y.; Seto, S.; Furihata, K.; Otake, N.; Ishida, N. *Tetrahedron Lett.* **1985**, *26*, 331.

(12) (a) Ludt, R. G.; Griffiths, J. S.; McGrath, K. N.; Hauser, C. R. *J. Org. Chem.* **1973**, *38*, 1668. Vaulx, R. L.; Puterbaugh, W. H.; Hauser, C. R. *J. Org. Chem.* **1964**, *29*, 3514. (b) Beak, P.; Tse, A.; Hawkins, J.; Chen, C.-W.; Mills, S. *Tetrahedron* **1983**, *39*, 1983.

(13) de Silva, S. O.; Reed, J. N.; Snieckus, V. *Tetrahedron Lett.* **1978**, 5099.

(14) Mills, R. J.; Horvath, R. F.; Sibi, M. P.; Snieckus, V. *Tetrahedron Lett.* **1985**, *26*, 1145.

(15) (a) For earlier approaches to the pentaoxygenated benzoyl system, see: Baker, W. *J. Chem. Soc.* **1941**, 662. (b) Various biological activities have been attributed to flavonoids which contain a fully oxygenated A-ring, see: Burnham, W. S.; Sidwell, R. W.; Tolman, R. L.; Stout, M. G. *J. Med. Chem.* **1972**, *15*, 1075. (c) For more recent suggestions of potential medicinal use, see: Otsuka Pharm. Co. Ltd., Japanese Patent JP 60, 25, 923, 1985; *Chem. Abstr.* **1985**, *103*, 59301x. Okuda, J.; et al. Eur. Pat. Appl. EP 118 571, 1984; *Chem. Abstr.* **1984**, *102*, 78636f. Delalande, S. A., Belg. Pat. BE 895 464, 1983; *Chem. Abstr.* **1984**, *100*, 85390h. Yu, Y. et al. *Yao Hsueh Hsueh Pao* **1979**, 14, 447; *Chem. Abstr.* **1980**, *92*, 18834j.

(16) Quenching the intermediate aryllithium from amide **1h** with the MoOPH reagent resulted in a decreased yield (25%) of phenol **3h**. For the reaction of arylmagnesium bromides with MoOPH, see: Lewis, N. J.; Gabhe, S. Y.; De LaMater, M. R. *J. Org. Chem.* **1977**, *42*, 1479.

(17) Locksley, H. D.; Murray, J. G. *J. Chem. Soc. C* **1970**, 392.

($C_{15}H_{17}O_2N$) calcd 243.1259, found 243.1237. This product was identical in all respects with an authentic sample prepared from 2-hydroxy-1-naphthalenecarboxylic acid.

***N,N*-Diethyl-2-(hydroxymethyl)benzamide (3g).** A 152-mg sample (0.800 mmol) of *o*-toluamide **1g** was subjected to the standard procedure. The crude product mixture was treated with 30 mg of $NaBH_4$ in 5 mL of THF to reduce overoxidized material. Flash chromatography (EtOAc/hexane = 1/1 followed by EtOAc) then gave 80 mg (49%) of a colorless oil: NMR (60 MHz, $CDCl_3/Me_4Si$) 0.97–1.33 (m, 6 H), 3.20 (q, J = 7 Hz, 2 H), 3.53 (q, J = 7 Hz, 2 H), 3.94 (s, 1 H, exchangeable in D_2O), 4.53 (s, 2 H), 7.20–7.33 (m, 4 H); IR ($CHCl_3$) 3400, 1600, 1285, 1010 cm^{-1}; M^+ ($C_{12}H_{17}O_2N$) calcd 207.1259, found 207.1254.

***N,N*-Diethyl-2-hydroxy-3,4,5-trimethoxybenzamide (3h).** Trimethoxybenzamide **1h** (410 mg, 1.53 mmol) was treated according to the standard procedure. The crude product was purified on a Chromatotron (eluent EtOAc/hexane = 1/1) to afford 210 mg (48%) of a white solid. Reduced pressure distillation [130 °C (0.5 mm)] gave crystals: mp 87–88 °C; NMR (250 MHz, $CDCl_3/Me_4Si$) 1.24 (t, J = 7 Hz, 6 H), 3.46 (q, J = 7 Hz, 4 H), 3.77 (s, 3 H), 3.95 (s, 6 H), 6.54 (s, 1 H), 6.95 (br s, 1 H, exchangeable in D_2O); IR ($CHCl_3$) 3505, 1620, 1580, 1210, 1110 cm^{-1}; M^+ ($C_{14}H_{21}O_5N$) calcd 283.1419, found 283.1406.

***N,N*-Diethyl-2,3,4,5-tetramethoxybenzamide (4).** A two-phase system consisting of 90 mg (0.32 mmol) of benzamide **3h**, 0.20 mL (2.1 mmol) of dimethyl sulfate, 160 mg (0.500 mmol) of *n*-Bu_4NBr, and 29 mg (0.72 mmol) of NaOH in 6 mL of CH_2Cl_2 and 6 mL of water was stirred overnight. After acidification with dilute HCl the phases were separated, and the aqueous phase was extracted (3×) with EtOAc. The combined organic solution was washed with brine, dried over Na_2SO_4, and concentrated. Elution of the product from a Chromatotron with EtOAc/hexane (1/1) gave 60 mg (63%) of a colorless oil. This was distilled at 125–127 °C (0.7 mm): NMR (60 MHz, $CDCl_3/Me_4Si$) 0.96–1.35 (m, 6 H), 3.03–3.50 (m, 4 H), 3.86 (s, 6 H), 3.90 (s, 3 H), 3.97 (s, 3 H), 6.50 (s, 1 H); IR ($CHCl_3$) 3030, 1608, 1570, 1110, 1065 cm^{-1}; M^+ ($C_{15}H_{23}O_5N$) calcd 297.1576, found 297.1587.

***N,N*-Diethyl-2-hydroxy-3,4,5,6-tetramethoxybenzamide (3i).** Hydroxylamine of 36 mg (0.12 mmol) of amide **4** gave material which was purified on a Chromatotron. Elution with EtOAc/hexane (1/1) afforded 15 mg (43%) of a colorless oil: NMR (60 MHz, $CDCl_3/Me_4Si$) 1.15 (t, J = 7 Hz, 6 H), 3.02–3.47 (m, 4 H), 3.76 (s, 6 H), 3.83 (s, 3 H), 3.90 (s, 3 H); IR ($CHCl_3$) 3500, 1620, 1120, 1035 cm^{-1}.

***N,N*-Diethyl-2-acetoxy-3,4,5,6-tetramethoxybenzamide (5).** A 10-mg sample (0.030 mmol) of amide **3i** and 0.06 mL (0.6 mmol) of acetic anhydride were dissolved in 0.5 mL (0.6 mmol) of pyridine. The reaction mixture stirred at room temperature overnight. Then water was added, stirring was continued for 1 h, and the reaction mixture was extracted (3×) with EtOAc. The combined organic solution was washed with aqueous $NaHCO_3$ and with brine, dried over Na_2SO_4, and concentrated. The product, purified on a Chromatotron (eluent EtOAc/hexane = 1/1) was isolated as a colorless oil (8 mg, 75%). An analytical sample was obtained by reduced pressure distillation [150 °C (0.8 mm)]: NMR (250 MHz, $CDCl_3/Me_4Si$) 1.07 (t, J = 7 Hz, 3 H), 1.20 (t, J = 7 Hz, 3 H), 2.25 (s, 3 H), 3.09–3.25 (m, 2 H), 3.40–3.72 (m, 2 H), 3.83 (s, 3 H), 3.86 (s, 3 H), 3.91 (s, 3 H), 3.94 (s, 3 H); IR (CH_2Cl_2) 2905, 1730, 1615, 1450, 1110, 1038 cm^{-1}; M^+ ($C_{17}H_{25}O_7N$) calcd 355.1631, found 355.1619.

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Degenerate Cope Rearrangement of 4-Vinylcyclopentene

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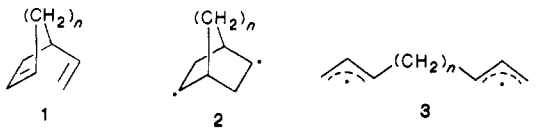
Cope rearrangements of hydrocarbons having a 1,5-hexadiene moiety take place through a variety of mechanistic paths and span an enormous range of reactivities.[2] Near one extreme, the degenerate valence isomerization shown by semibullvalene has $\Delta G^{\ddagger}$ equal to 5.5 kcal/mol at −140 °C;[3] at the other, systems like bicyclo[3.3.0]octa-2,6-diene fail to show appreciable rearrangement even under extreme thermal conditions.[4]

4-Vinylcycloalkenes (**1**) offer the prospect of correlating systematic homologous structural variations with Cope rearrangement reactivities, for the $-(CH_2)_n-$ bridge between C3 and C6 of the 1,5-hexadiene unit provides geometrical restrictions of graded severity on ground- and transition-state structures (**2**) if C1–C6 bond making is then well advanced. If, on the other hand, C3–C4 cleavage were well ahead of C1–C6 bond formation in the transition state, no ring-strain effects on transition state structures (**3**) would be seen.



1 2 3

The degenerate Cope rearrangement of 4-vinylcyclohexene and several competitive thermal rearrangements shown by this hydrocarbon have been studied in great detail,[5,6] but Cope rearrangements of other 4-vinylcycloalkenes are unreported. Thus no comparative considerations of reactivity differences for even two different members of the series have been possible.

3-Vinylcyclobutene, **1** (n = 0), reacts thermally to form *trans*-1,3,5-hexatriene so fast that, presumably, a degenerate Cope process may never be seen for it experimentally.[7] We have followed the Cope rearrangement of 4-vinylcyclopentene, the next lowest member of the homologous series of dienes **1**, one subject to substantial geometrical constraints in transition-state structure **2**.

Results

Condensation of cyclopentene-4-carbaldehyde (**4**) with (dideuteriomethylene)triphenylphosphorane in Me_2SO-d_6/THF gave 4-(ethenyl-2,2-d_2)cyclopentene. At 360 MHz, the ^1H NMR spectrum showed two 2 H multiplets at 2.10 and at 2.48 ppm for the diasteriomeric C3,5 and C3′,5′ protons, the H-C4 multiplet at 2.85 ppm, C1,2 olefinic protons as a singlet at 5.67 ppm, and the ethenyl-C1 proton

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