A Useful Procedure for the Preparation of (*E,E*)-2,4-Dienoates: Lithium Hydroxide-Promoted Dienylation by 4-Phosphonocrotonate

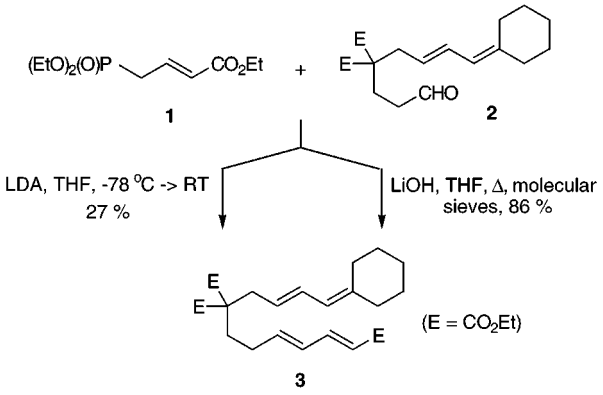
James M. Takacs,* Mohamad R. Jaber, Francis Clement, and Carol Walters

Department of Chemistry, University of Nebraska−Lincoln, Lincoln, Nebraska 68588-0304

Received May 4, 1998

Bonadies, Scettri, and co-workers[1] recently reported a useful procedure for the preparation of α,*β*-unsaturated esters in which they employ lithium hydroxide and 4A molecular sieves to promote Horner−Wadsworth−Emmons olefination of aldehydes and ketones by phosphonoacetates.[2−4] In conjunction with another project,[5] we required a number of (*E,E*)-α,*β*,*γ*,*δ*-unsaturated esters.

The base-promoted Horner−Wadsworth−Emmons olefination of aldehydes and ketones with trialkyl 4-phosphonocrotonates[6,7] has found frequent use for the preparation of 2,4-dienoates, and a variety of bases, including NaH,[7−10] LDA,[11−13] and LiHMDS,[14−16] have been commonly employed. However, for some of the dienoates we needed, these conditions proved to be unsatisfactory. For example, treatment of triethyl 4-phosphonocrotonate (**1**) with LDA (THF, −78 °C) followed by the addition of aldehyde **2** and warming to ambient temperature afforded the expected dienoate **3** in only poor yield (27%), and in addition, the product was contaminated with significant amounts of *Z* isomers. We reasoned that the low yield likely resulted from competing retro-Michael addition under these conditions. In the search to remedy this problem, we examined a number of alternative conditions and found that the Bonadies−Scettri conditions work exceptionally well with 4-phosphonocrotonates. Refluxing the mixture of **1**, **2**, $LiOH\cdot H_2O$, and 4A molecular sieves in THF afforded (*E,E*)-**3** in 86% yield and high isomeric purity at the newly formed double bonds (>95% by ^1H NMR).



We applied these conditions to the dienylations of a number of aldehydes and ketones on scales ranging from about 0.5 to 20 mmol to assess the potential scope and limitations of the method. The results are summarized in Table 1. Simple aldehydes such as benzaldehyde (entry 1) and isovaleraldehyde (entry 2) react in high yield (89% and 98%, respectively) and with good stereoselectivity (>90% one isomer as judged by ^1H NMR). Entries 3 and 4 further demonstrate that aldehydes bearing relatively stable functionality also react smoothly. The reported yields in these latter two cases are lower (74% and 72%, respectively) but reflect the overall yield for two steps, Swern oxidation followed by dienylation of the crude aldehyde. Similarly, the 72% and 64% yields listed for entries 5 and 6 are overall yields for two- and three-step sequences, respectively. It is noteworthy that we see no elimination or desilylation products derived from the chiral *β*-hydroxyaldehydes used in these latter two examples, nor do we see any evidence for epimerization of the α chiral center in the crude high field ^1H NMR spectrum.

Ketones also react under the conditions described above, but their dienylation is relatively slow. Using 2 equiv each of $LiOH\cdot H_2O$ and 4-phosphonocrotonate increases the reaction rate, and under these conditions, the cyclohexanones shown in entries 7 and 8 afford dienylation products in high yield (99% and 94% after 12 h at reflux, respectively). In each case, the dienoates are obtained with high stereoselectivity, and despite the presence of excess LiOH, no evidence of competing ester hydrolysis was observed. The dienylation of cyclohexanone has been reported in the literature, and the comparison to those results again highlights the advantage of this method over earlier procedures. Robinson and co-workers reported that the reaction of cyclohexanone with triethyl 4-phosphonocrotonate using NaH as the base (THF−HMPA, 25 °C) afforded the dienoate in only 32% yield.[9]

In conclusion, we have successfully adapted a procedure, recently reported by Bonadies, Scettri, and coworkers[1] for the LiOH-promoted Horner−Wadsworth−Emmons reactions of aldehydes and ketones with phosphonoacetates, to the corresponding dienylations using trialkyl 4-phosphonocrotonates. These conditions

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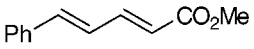
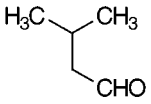
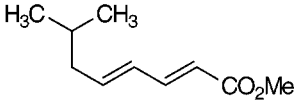
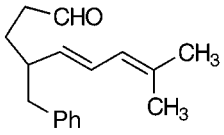
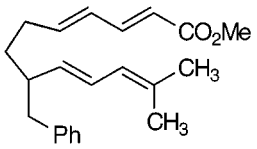
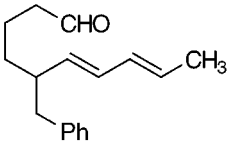
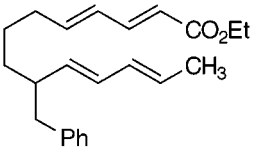
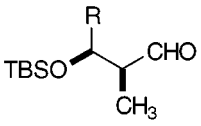
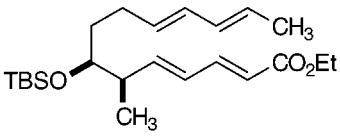
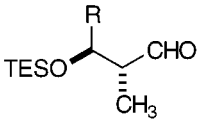
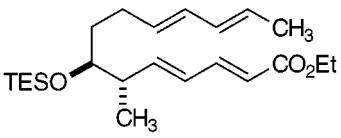
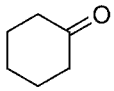
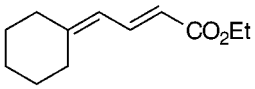
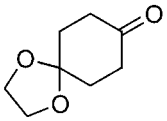
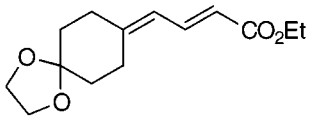
S0022-3263(98)00841-X CCC: $15.00
Published on Web 08/28/1998

Table 1. Horner–Wadsworth–Emmons Dienylation of Some Aldehydes and Ketones Promoted by LiOH and Molecular Sieves[a]

entry	substrate	dienoate	% yield (# steps)[b]
1	PhCHO		89
2			98
3			74 (2)[c]
4			72 (2)[c]
5[d]			72 (3)[e]
6[d]			64 (2)[f]
7			99[g]
8			94[g]

[a] Unless noted otherwise, all reactions employ 1.1 equiv of trialkyl 4-phosphonocrotonate, 1.1 equiv of $LiOH \cdot H_2O$, and 1.5 g of activated 4A molecular sieves per mmol of aldehyde or ketone heated at reflux for approximately 12 h (reactions times were not optimized). [b] The yields given for entries 3–6 reflect the overall yield for two- or three-step reaction sequences without purification of the intermediates. [c] Overall yield for Swern oxidation of the corresponding alcohol followed by dienylation of the crude aldehyde. [d] R = $CH_2CH_2CH{=}CH{-}CH{=}CHCH_3$. [e] Overall yield for mono-deprotection of the di(*tert*)butyldimethylsilyl ether, followed by Swern oxidation of the corresponding alcohol, and dienylation of the crude aldehyde. [f] Overall yield for half-reduction of the corresponding Weinreb amide followed by dienylation of the crude aldehyde. [g] 2.2 equiv of the phosphonocrotonate and 2.2 equiv of $LiOH \cdot H_2O$ were employed.

effect reaction in high yield with good stereoselectivity and are found to be particularly useful in the case of base-labile aldehydes and with ketones.

Experimental Section

General. All solvents were distilled under nitrogen before use. THF was distilled from Na/benzophenone. Optical rotations were recorded at ambient temperature. ^1H NMR and ^{13}C spectra were recorded in $CDCl_3$ unless noted otherwise. For ^{13}C spectra, the number of attached protons was determined using the DEPT pulse sequence and indicated in parentheses (s = no attached protons, d = CH, t = CH_2, and q = CH_3). Combustion analyses were performed by M-H-W Analytical Labs, and high-resolution mass spectral determinations were performed by the Midwest Center for Mass Spectrometry.

General Procedure for the Horner−Wadsworth−Emmons Dienylation Using LiOH·H_2O. A suspension of the aldehyde (1 equiv), triethyl 4-phosphonocrotonate or methyl diethyl-4-phosphonocrotonate (1.1 equiv), LiOH·H_2O (1.1 equiv), and activated 4A molecular sieves (beads, 4−8 mesh, 1.5 g/mmol of aldehyde) in THF (overall 0.1−0.2 M in aldehyde) and under a nitrogen atmosphere was heated at reflux for ca. 12 h (reaction times not optimized). The crude reaction mixture was filtered through a short plug of silica gel, eluting with ether. The mixture was concentrated on a Rotovap, and the residue was purified by flash column chromatography on silica. The reactions of ketones were carried out identically with the exception that 2.2 equiv of both the 4-phosphonocrotonate and LiOH·H_2O were used.

Preparation of Dienoate 3. Aldehyde **1** (152.3 mg, 0.57 mmol), triethyl 4-phosphonocrotonate (190.0 mg, 0.63 mmol), LiOH·H_2O (20.1 mg, 0.63 mmol), and sieves (610 mg) afforded dienoate **3** (167.0 mg, 86%) after flash chromatography (9:1 hexane/EtOAc): TLC analysis (9:1 hexane/EtOAc) R_f = 0.21; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (1 H, dd, J = 10.5, 4.8 Hz), 6.32 (1 H, dd, J = 10.9, 3.6 Hz), 6.10 (1 H, dd, J = 10.9, 4.4 Hz), 6.01 (1 H, dd, J = 6.4, 6.8 Hz), 5.73 (1 H, d, J = 15.3 Hz), 5.64 (1 H, d, J = 10.9 Hz), 5.29 (1 H, dt, J = 14.9, 7.6 Hz), 4.20−4.00 (6 H, m), 2.62 (2 H, d, J = 7.7 Hz), 2.20−1.90 (6 H, m), 1.50−1.40 (8 H, m), 1.15−1.05 (9 H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8 (s), 166.8 (s), 144.3 (d), 142.6 (s), 142.4 (d), 130.0 (d), 128.7 (d), 124.0 (d), 121.3 (d), 119.7 (d), 61.0 (t), 60.9 (t), 59.9 (t), 57.3 (s), 37.0 (t), 36.2 (t), 31.2 (t), 29.0 (t), 28.3 (t), 27.6 (t), 27.5 (t), 26.6 (t), 14.1 (q), 13.9 (q). HRMS−FAB m/z: calcd for $C_{26}H_{38}O_6$ + Li^+ 453.2828, found 453.2821.

Methyl (2*E*,4*E*)-5-Phenyl-2,4-pentadienoate.[17] Benzaldehyde (204.2 mg, 1.92 mmol), methyl diethyl-4-phosphonocrotonate (500.0 mg, 2.12 mmol), LiOH·H_2O (88.8 mg, 2.12 mmol), and sieves (3 g) afforded the title compound (321.4 mg, 89%) after flash chromatography (9:1 hexane/EtOAc): TLC analysis (85:15 hexane/EtOAc) R_f = 0.43; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52−7.45 (3 H, m); 7.38−7.30 (3 H, m); 6.92−6.85 (2 H, m); 6.02 (1 H, d, J = 15.3 Hz), 3.78 (3 H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.3 (s), 144.6 (d), 140.3 (d), 135.8 (s), 128.8 (d), 128.6 (d), 127.0 (d), 126.0 (d), 120.7 (d), 51.3 (q).

Methyl (2*E*,4*E*)-7-Methyl-2,4-octadienoate. Isovaleraldehyde (165.7 mg, 1.92 mmol), methyl diethyl-4-phosphonocrotonate (500.0 mg, 2.12 mmol), LiOH·H_2O (88.8 mg, 2.12 mmol), and sieves (3 g) afforded the title compound (290.2 mg, 98%) after flash chromatography (4:1 hexane/EtOAc): TLC analysis (85:15 hexane/EtOAc) R_f = 0.53; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (1 H, dd, J = 10.1, 5.2 Hz), 6.15 (2 H, m), 5.95 (1 H, d, J = 15.7 Hz), 3.86 (3 H, s), 2.06 (2 H, t, J = 6.4 Hz), 1.75−1.70 (1 H, m), 0.90 (6 H, d, J = 6.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.3 (s), 144.9 (d), 143.2 (d), 129.3 (d), 118.7 (d), 51.0 (q), 42.1 (t), 28.1 (d), 22.1 (q). HRMS−EI m/z: calcd for $C_{10}H_{16}O_2$ 168.1150, found 168.1141.

Methyl (2*E*,4*E*,9*E*,11*E*)-8-Benzyl-12-methyl-2,4,9,11-tridecatetraenoate. (5*E*)-4-Benzyl-8-methyl-5,7-nonadienal (900 mg of crude aldehyde obtained from Swern oxidation of the corresponding alcohol (928.6 mg, 3.80 mmol)), triethyl 4-phosphonocrotonate (964.8 mg, 4.08 mmol), LiOH·H_2O (171.4 mg, 4.08 mmol), and sieves (6.0 g) afforded the title compound (891.9 mg, 74% overall from the alcohol) after flash chromatography (95:5 hexane/EtOAc): TLC analysis (95:5 hexane/EtOAc) R_f = 0.27; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35−7.10 (6 H, m), 6.20−6.00 (3 H, m), 5.85−5.75 (2 H, m), 5.38 (1 H, dd, J = 8.8, 6.2 Hz), 3.77 (3 H, s), 2.70−2.60 (2 H, m), 2.40−2.20 (3 H, m), 1.79 (3 H, s), 1.75 (3 H, s), 1.65−1.50 (1 H, m), 1.45−1.30 (1 H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.6 (s), 145.2 (d), 144.5 (d), 140.2 (s), 134.4 (d), 129.2 (d), 128.3 (d), 128.1 (d), 127.4 (d), 125.8 (d), 124.8 (d), 118.6 (d), 51.3 (q), 44.2 (d), 42.3 (t), 33.0 (t), 30.7 (t), 25.8 (q), 18.2 (q). HRMS−EI m/z: calcd for $C_{22}H_{28}O_2$ = 324.2089, found 324.2079.

Methyl (2*E*,4*E*,10*E*,12*E*)-9-Benzyl-2,4,10,12-tetradecatetranoate. (6*E*,8*E*)-5-Benzyl-6,8-decadienal (1.40 g of crude aldehyde obtained from Swern oxidation of the corresponding alcohol (1.450 g, 5.93 mmol)), triethyl 4-phosphonocrotonate (1.50 g, 6.35 mmol), LiOH·H_2O (266.2 mg, 6.35 mmol), and sieves (9.0 g) afforded the title compound (1.350 g, 72% overall from the alcohol) after flash chromatography (4:1 hexane/EtOAc): TLC analysis (85:15 hexane/EtOAc) R_f = 0.44; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35−7.10 (6 H, m), 6.20−5.90 (4 H, m), 5.80 (1 H, d, J = 15.3 Hz), 5.60−5.50 (1 H, m), 5.37 (1 H, dd, J = 8.9, 6.0 Hz), 3.75 (3 H, s), 2.65−2.60 (2 H, m), 2.32−2.28 (1 H, m), 2.20−2.08 (2 H, m), 1.72 (3 H, d, J = 6.4 Hz), 1.50−1.20 (4 H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.5 (s), 145.1 (d), 144.4 (d), 140.3 (s), 134.9 (d), 131.5 (d), 130.5 (d), 129.1 (d), 128.3 (d), 128.0 (d), 127.2 (d), 125.7 (d), 118.7 (d), 51.3 (q), 44.2 (d), 42.1 (t), 33.7 (t), 32.8 (t), 26.3 (t), 17.9 (q). HRMS−EI m/z: calcd for $C_{22}H_{28}O_2$ 324.2089, found 324.2085.

Ethyl (2*E*,4*E*,10*E*,12*E*)-*anti*-7-*t*-Butyldimethylsilyloxy-6-methyl-2,4,10,12-tetradecatetraenoate. (6*E*,8*E*)-*anti*-2-Methyl-3-*tert*-butyldimethylsilyloxy-6,8-decadienal (988 mg of crude aldehyde obtained via selective mono-deprotection (HF−pyridine) of the corresponding doubly TBS-protected diol (1.400 g, 3.40 mmol) followed by Swern oxidation of the resulting crude alcohol), triethyl 4-phosphonocrotonate (1.000 g, 3.99 mmol), LiOH·H_2O (167.7 mg, 3.99 mmol), and sieves (5.0 g) afforded the title compound (941 mg, 72% overall from the protected diol) after flash chromatography (95:5 hexane/EtOAc): TLC analysis (95:5 hexane/EtOAc) R_f = 0.21; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (1 H, dd, J = 9.5, 5.5 Hz), 6.20−5.90 (4 H, m), 5.80 (1 H, d, J = 15.2 Hz), 5.62−5.50 (2 H, m), 4.20 (2 H, q, J = 7.1 Hz), 3.65−3.60 (1 H, m), 2.45−2.40 (1 H, m), 2.20−2.00 (2 H, m), 1.75 (3 H, d, J = 6.4 Hz), 1.55−1.40 (2 H, m), 1.30 (3 H, t, J = 7.1 Hz), 1.03 (3 H, d, J = 6.7 Hz), 0.90 (9 H, s), 0.03 (6 H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1 (s), 146.3 (d), 145.0 (d), 131.5 (d), 131.2 (d), 130.5 (d), 128.2 (d), 127.0 (d), 119.6 (d), 75.0 (d), 60.1 (t), 42.4 (d), 33.8 (t), 28.4 (t), 25.8 (q), 18.1 (s), 17.0 (q), 15.5 (q), 14.2 (q), −5.3 (q), −4.5 (q). HRMS−FAB m/z: calcd for $C_{23}H_{40}O_3Si$ + Li^+ 399.2906, found 399.2907.

Ethyl (2*E*,4*E*,10*E*,12*E*)-(6*S*,7*S*)-6-Methyl-7-triethylsilyloxy-2,4,10,12-tetradecatetraenoate. (6*E*,8*E*)-(2*R*,3*S*)-2-Methyl-3-triethylsilyloxy-6,8-decadienal (884 mg of crude aldehyde obtained via DIBAL-H reduction of the corresponding Weinreb amide (1.060 g, 2.98 mmol)), triethyl 4-phosphonocrotonate (895.1 mg, 3.58 mmol), LiOH·H_2O (150.0 mg, 3.58 mmol), and sieves (4.5 g) afforded the title compound (752.8 mg, 64% overall from the amide) after flash chromatography (95:5 hexane/EtOAc): TLC analysis (95:5 hexane/EtOAc) R_f = 0.23; $[\alpha]_D$ = −31.0° (*c* 1.36, EtOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30−7.20 (1 H, m), 6.20−6.10 (2 H, m), 6.05−5.95 (2 H, m), 5.80 (1 H, d, J = 15.3 Hz), 5.60−5.50 (2 H, m), 4.20 (2 H, q, J = 6.8 Hz), 3.65−3.60 (1 H, m), 2.45−2.40 (1 H, m), 2.20−2.00 (2 H, m), 1.75 (3 H, d, J = 6.1 Hz), 1.50−1.40 (2 H, m), 1.30 (3 H, t, J = 7.3 Hz), 1.12−0.90 (12 H, m), 0.65−0.55 (6 H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1 (s), 146.6 (d), 145.0 (d), 131.5 (d), 131.2 (d), 130.5 (d), 127.8 (d), 126.9 (d), 119.5 (d), 75.3 (d), 60.0 (t), 42.5 (d), 33.7 (t), 28.5 (t), 17.9 (q), 14.7 (q), 14.2 (q), 6.9 (q), 5.1 (t). HRMS−FAB m/z: calcd for $C_{23}H_{40}O_3Si$ + Li^+ 399.2906, found 399.2904.

Ethyl (2*E*)-5-Cyclohexyl-2,4-pentadienoate.[18] Cyclohexanone (490.7 mg, 5.0 mmol), triethyl 4-phosphonocrotonate (2.75 g, 11.0 mmol), LiOH·H_2O (462.0 mg, 11.0 mmol), and sieves (7.5 g) afforded the title compound (971.3 mg, quantitative) after flash chromatography (90:10 hexane/EtOAc): TLC analysis (90:10 hexane/EtOAc) R_f = 0.40; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65−7.41 (1 H, m), 5.90 (1 H, d, J = 11.8 Hz), 5.72 (1 H, d, J = 15.8 Hz), 4.11 (2 H, q, J = 7.1 Hz), 2.41−2.06 (4 H, m), 1.52 (6 H, br s), 1.22 (3 H, t, J = 7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.4 (s), 153.8 (s), 140.0 (d), 120.3 (d), 118.6 (d), 59.7 (t), 37.5 (t), 29.6 (t), 28.3 (t), 27.7 (t), 26.3 (t), 14.1 (q). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.38; H, 9.11.

Ethyl (2*E*)-5-(4-Ethyleneketal)cyclohexyl-2,4-pentadienoate. 1,4-Cyclohexanedione *mono*-ethylene ketal (3.124 g, 20.0 mmol), triethyl 4-phosphonocrotonate (11.01 g, 44.0 mmol), LiOH·H_2O (1.85 g, 44.0 mmol), and sieves (30 g) afforded the title compound (4.740 g, 94%) after flash chromatography (65:

(17) CAS Registry Number 24196-39-2; see: Cho, C. S.; Uemura, S. *J. Organomet. Chem.* **1994**, *465*, 85−92.

(18) Huang, Y.; Shen, Y.; Zheng, J.; Zhang, S. *Synthesis* **1985**, 57−8.

35 hexane/EtOAc): TLC analysis (65:53 hexane/EtOAc) R_f = 0.35; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (1 H, dd, J = 14.9, 11.7 Hz), 5.98 (1 H, d, J = 12.1 Hz), 5.81 (1 H, d, J = 15.3 Hz), 4.19 (2 H, q, J = 7.2 Hz), 3.97 (4 H, br s), 2.56−2.53 (2 H, m), 2.39−2.36 (2 H, m), 1.75−1.71 (4 H, m), 1.28 (3 H, t, J = 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.5 (s), 150.7 (d), 140.0 (d), 121.6 (d), 119.8 (s), 108.3 (s), 64.4 (t), 60.1 (t), 35.9 (t), 35.2 (t), 34.1 (t), 26.2 (t), 14.3 (q). HRMS−EI *m*/*z*: calcd for $C_{14}H_{20}O_4$ 252.1361, found 252.1369.

Acknowledgment. Financial support of this work by the National Institutes of Health (GM34927) is gratefully acknowledged. We thank Dr. Celia Kingsbury for obtaining the results given in Table 1 entry 8, the NIH (SIG 1-S10-RR06301) for NMR instrumentation funding, and the NSF (CHE-93000831) for GC-MS instrumentation funding.

JO980841C

Additions and Corrections

Vol. 63, 1998

J. Edgar Anderson,*, Anthony I. Ijeh, Christine Storch Daniele Casarini, and Lodovico Lunazzi*. Eclipsed Conformation of the Exocyclic N−CH_2 Bond in *N*-Neopentylpiperidines and the Stereodynamic Consequences As Studied by Dynamic NMR Spectroscopy and Molecular Mechanics Calculations.

Page 3312, Table 2. In column 4, numbers **2b** and **2e** should be interchanged. The data in columns 5 and 6 are correct.

JO984086V

S0022-3263(98)04986-X
Published on Web 06/25/1998