δ 7.59 (dd, J = 16.5, 11 Hz, 1 H), 7.10–7.53 (m, 9 H), 6.94 (b d, J = 10.05 Hz, 1 H), 6.81 (b d, J = 16.5 Hz, 1 H), 6.54 (ddd, J = 16.5, 10.5, 1 Hz, 1 H), 5.70 (b d, J = 16.5 Hz, 1 H), 5.17 (d, J = 10.5 Hz, 1 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 140.68 (d) 137.09 (d), 136.95 (s), 136.80 (d), 136.44 (s), 132.15 (s), 128.83 (d), 128.63 (d), 128.25 (d), 127.46 (d), 126.91 (d), 126.21 (d), 125.39 (d), 117.48 (t) ppm.

(1*E*,3*E*)-1-Phenyl-4-(phenylthio)-1,3,5-hexatriene (7k) was prepared on a 0.50-mmol scale from *trans*-cinnamaldehyde in 83% yield. The triene was found to be unstable and polymerized on standing at room temperature and was not fully characterized: R_f 0.25 (1% ether/petroleum ether); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.18–7.46 (m, 11 H), 6.99 (dd, J = 16.5, 10.5 Hz, 1 H), 6.58–6.98 (m, 2 H), 7.75 (d, J = 16.5 Hz, 1 H), 5.33 (dt, J = 10.5, 1.5 Hz, 1 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 136.87 (s), 136.48 (d), 135.50 (s), 135.16 (d), 132.72 (s), 130.53 (d), 129.70 (d), 128.90 (d), 128.65 (d), 128.09 (d), 126.67 (d), 126.34 (d), 123.30 (d), 118.99 (t) ppm.

Reaction of Aldehyde (8) with Allylborane (4). Preparation of (*E*)-5-Acetoxy-8-azido-3-(phenylthio)-1,3-octadiene (9). To the allene **3** (260 mg of 94% pure material, 3.9 mmol, neat) was added 9-BBN (7.8 mL of 0.5 M solution in THF, 3.9 mmol). After stirring at 35 °C for 2 h, the mixture was cooled to 25 °C, and a solution of 2-acetoxy-5-azidopentanal (**8**)[22] (650 mg, 3.5 mmol) in THF (1 mL) was added slowly. After 2 h, 4 N sodium hydroxide (10 drops) was added, and stirring was continued for another 2 h. A small aliquot (ca. 0.2 mL) was removed, and the solvent was evaporated. ^{1}H NMR spectroscopy showed only the *E* isomer of **9** to the limits of detection of our 300-MHz instrument. The reaction mixture was then diluted with pentane (8 mL) and washed with brine (3 × 3 mL). The organic layer was dried (Na_2SO_4) and concentrated in vacuo, and the residue was purified by flash chromatography (30:1 hexane/ethyl acetate) to give 1.04 g (93%) of **9**, which was found to be a >97:<3 ratio of *E* and *Z* isomers: R_f 0.54 (5/1 hexane/ethyl acetate); IR (neat) 2096 (s), 1738 (s), 1624 (w), 1582 (s), 1479 (m), 1439 (m), 1370 (s), 1235 (br) 1023 (m), 925 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.40–7.16 (m, 5 H), 6.79 (dd, J = 16.9, 10.6 Hz, 1 H), 5.76 (dd, J = 16.9, 1.2 Hz, 1 H), 5.71–5.68 (m, 2 H), 5.35 (dd, J = 10.6, 1.2 Hz, 1 H), 3.29 (t, J = 6.7 Hz, 2 H), 2.05 (s, 3 H), 1.82–1.53 (m, 4 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.07 (s), 136.50 (s), 134.33 (s), 133.24 (d), 130.56 (d), 130.23 (d), 129.02 (d), 126.84 (d), 120.63 (t), 69.76 (d), 51.03 (t), 31.79 (t), 24.57 (t), 21.04 (q) ppm; MS *m/e* (rel intensity) 289 (0.3), 230 (18), 191 (5), 178 (12), 120 (30), 109 (11), 91 (15), 77 (14), 43 (100); HRMS (CI) calcd for $C_{16}H_{20}NO_2S$ ($MH^+ - N_2$) 290.1215, found 290.1218.

Reaction of Aldehyde (8) with Allyltitanium Reagent (1). The procedure by Yamamoto[4b] was followed exactly. To a solution of 1-(phenylthio)-1-(trimethylsilyl)-2-propene (223 mg, 1.0 mmol) in THF (2.5 mL) was added *n*-butyllithium (0.45 mL of 2.24 M solution in hexanes, 1.0 mmol) at 0 °C. After being stirred for 1 h, the solution was cooled to −78 °C, and titanium isopropoxide (0.30 mL, 280 mg, 1.0 mmol) was added. After 10 min, the mixture was warmed to 0 °C, stirred for 1 h to complete the formation of reagent **1**, and recooled to −78 °C. The aldehyde **8**[22] (158 mg, 0.85 mmol) in THF (0.5 mL) was then added, and the solution was stirred for 10 min at −78 °C, 1 h at 0 °C, and 1 h at room temperature. The mixture was poured into 2 N HCl and extracted with ether. The organic layer was dried (Na_2SO_4) and concentrated. Flash chromatography of the residue (gradient elution from 1:50 to 1:5 ethyl acetate/hexane) gave 79 mg (29%) of **9** (R_f 0.54 in 1:5 ethyl acetate/hexane), 52 mg (22%) of **10** (R_f 0.26 in 1:5 ethyl acetate/hexane), and 68 mg (22%) of **11** (R_f 0.12 in 1:5 ethyl acetate/hexane). Diene **9** proved to be an inseparable 95:5 *E*:*Z* mixture by ^{1}H NMR spectroscopy.

For **10**: NMR of the purified product showed an 85:15 ratio of *E*:*Z* isomers. Data for *E* isomer: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.38–7.26 (m, 5 H), 6.67 (dd, J = 16.8, 10.7 Hz, 1 H), 5.80 (d, J = 8.8 Hz, 1 H), 5.74 (dd, J = 16.8, 1.1 Hz, 1 H), 5.32 (dd, J = 10.6, 1.1 Hz, 1 H), 4.70–4.61 (m, 1 H), 3.31 (t, J = 6.2 Hz, 2 H), 1.76–1.54 (m, 5 H) ppm; MS *m/e* (rel intensity) 247 (8), 228 (9), 190 (16), 160 (37), 147 (25), 110 (56), 91 (57), 77 (63), 71 (77), 65 (45), 53 (100), 43 (72); HRMS (EI) calcd for $C_{14}H_{17}NOS$ ($M^+ - N_2$) 247.1031, found 247.1030.

For **11** (NMR showed a mixture of several stereoisomers, which were not separated): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.35–7.10 (m, 5 H), 6.68 (t, J = 6.7 Hz, 1 H), 3.73–3.58 (m, 1 H), 3.57–3.38 (m, 1 H), 3.29 (t, J = 7.7 Hz, 2 H), 2.64 (m, 2 H), 1.90–1.38 (m, 4 H) ppm; MS *m/e* (rel intensity) 365 (4), 222 (6), 167 (19), 151 (9), 149 (10), 109 (5), 91 (7), 73 (100), 43 (17); HRMS (EI) calcd for $C_{17}H_{27}N_3O_2SSi$ (M^+) 365.1593, found 365.1580.

Acknowledgment. We thank the National Institutes of Health (Grant GM-35572), the Dreyfus Foundation (Award for Newly Appointed Faculty in Chemistry, 1984–89), and Eli Lilly & Company (Lilly Grantee 1988–9) for financial support of this research. We also thank S. Degan and J. Schkeryantz for experimental assistance.

Registry No. **2**, 6212-77-7; **3**, 123289-30-5; **4**, 123307-77-7; **6a**, 123289-31-6; **6b**, 123289-32-7; **6c**, 110027-07-1; **6d**, 83877-78-5; **6e**, 123289-33-8; **6f**, 110027-08-2; **6g**, 123289-34-9; **6h**, 123289-35-0; **6i**, 123289-36-1; **6j**, 108782-20-3; **6k**, 123289-37-2; **7a**, 123289-38-3; **7b**, 123289-39-4; **7c**, 110027-09-3; **7d**, 83877-76-3; **7e**, 123289-40-7; **7f**, 110027-10-6; **7g**, 123289-41-8; **7h**, 123289-42-9; **7i**, 123289-43-0; **7j**, 108782-19-0; **7k**, 123289-44-1; **8**, 123289-45-2; (*E*)-**9**, 123289-46-3; (*Z*)-**9**, 123289-47-4; **10**, 123289-48-5; **11**, 123289-49-6; 9BBN, 280-64-8; hexanal, 66-25-1; nonanal, 124-19-6; isobutyraldehyde, 78-84-2; cyclohexanecarboxaldehyde, 2043-61-0; benzaldehyde, 100-52-7; phenylacetaldehyde, 122-78-1; 5-bromopentanal, 1191-30-6; 4-bromobutanal, 38694-47-2; 5-azidopentanal, 114642-97-6; tetrahydropyran, 142-68-7; bromoaldehyde, 7726-11-6; 4-azidobutanal, 99545-47-8; *trans*-cinnamaldehyde, 14371-10-9; 1-(phenylthio)-1-(trimethylsilyl)-2-propene, 78905-13-2.

Supplementary Material Available: ^{1}H and ^{13}C NMR spectra for all new compounds which do not have elemental analyses (43 pages). Ordering information is given on any current masthead page.

The Reaction of Sodium *N*-Methylbenzohydroxamate with Sanger's Reagent and the Unusual Mass Spectrum of the Product

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Current interest in the chemistry of *N*-methylbenzohydroxamic acids (NMBHAH) includes examples of alkylation with methyl groups on both the carbonyl O[1] or thiocarbonyl[2] and on the hydroxamate O.[3] The exact nature of the reaction conditions, whether the acid is present as the acid or its salt, determines the position of alkylation. Our interest in these species as potential single electron transfer nucleophiles (SET) in nucleophilic aromatic substitution[4] and α-nucleophiles[5,6] prompts us to report in this paper the reactivity of the sodium salt of *p*-ClNMBHAH with 2,4-dinitrofluorobenzene (Sanger's reagent). The chemical behavior of this system is previously not reported, and it is not clear from elementary considerations where an activated aromatic system should attach.

The Na *p*-ClNMBHA was prepared by addition of an equivalent amount of NaOMe in MeOH to freshly pre-

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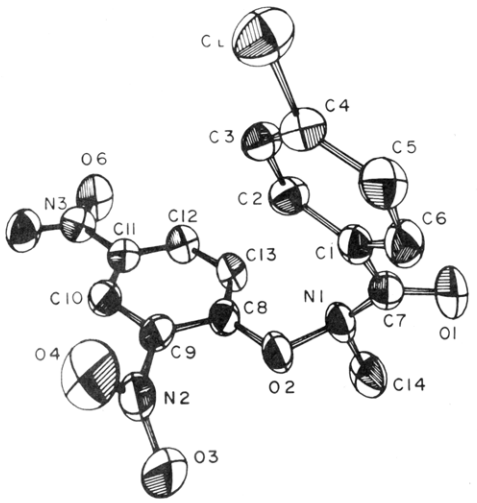
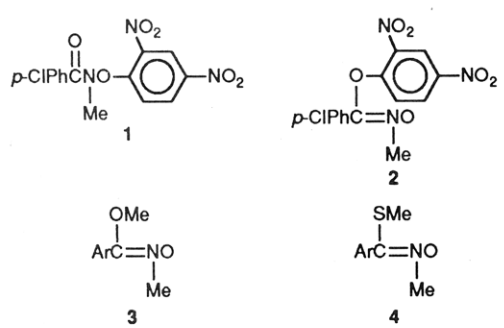


Figure 1. ORTEP diagram of the product of Sanger's reagent and *p*-ClNMBHA Na salt.

pared *p*-ClNMBHAH.[7] To this solution was then added 1 equiv of Sanger's reagent to give an exothermic reaction and formation of a colorless precipitate immediately. After standing for 48 h the precipitate was filtered, giving a solid which melted at 143–5 °C. Subsequent reactions showed that the extended reaction time was unnecessary. Satisfactory microanalysis (±0.5) for a 1:1 product was obtained. The product was characterized by GCMS, IR, NMR analyses, and its structure was finally proven by X-ray single-crystal analysis as follows.

The mass spectrum was that of *N*-methyl *p*-chlorobenzamide (NMCBA), although the retention time was not that of authentic *N*-methyl *p*-chlorobenzamide (6.303 min on a capillary cross-linked methyl silicon gum column), nor was the IR (FTIR Nicolet 5DXB spectrometer) the same as NMCBA. The IR of the product had no ν_{NH} and had $\nu_{C=O}$ at 1671 (contrast $\nu_{C=O}$ for NMCBA at 1630 cm^{-1}). The IR of the carbonyl region (1700–1600 cm^{-1}) of the product was remarkably similar to that of *O*-phenylbenzohydroxamic acid, independently synthesized by benzoylation of *O*-phenylhydroxylamine.[8] This spectroscopy favors the structure **1** as opposed to **2** but does not rule out **2** entirely.

The NMR was characterized by an aromatic region δ (9–6.5 ppm) showing the presence of the 3-proton 2,4-dinitrobenzene, and an A2,B2, *p*-chlorobenzoyl portion. The NCH_3 signal was at 3.62 ppm. If a single isomer (the *Z*) were formed, this signal could not distinguish between **1** and **2**. Reference 1 gives the N-Me signal at 3.51 for **3** and Coates,[2] for the similarly alkylated (methylthio)nitrone, **4**, has this signal also at 3.51 ppm.



(7) Literature preparation. See: Brink, C. P.; Fish, L. L.; Crumbliss, A. L. *J. Org. Chem.* **1985**, *50*, 2277; **1980**, *45*, 4670; **1982**, *47*, 1171.
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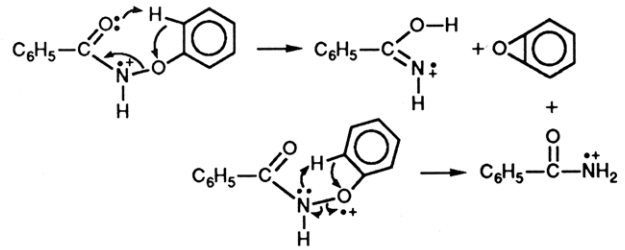
Scheme I. Possible Routes for Extrusion of Phenylene Oxide Moieties from O-Phenylated Hydroxamic Acids



The structural ambiguity was finally removed by X-ray single-crystal analysis of the structure; the ORTEP drawing is shown in Figure 1. As can be seen, the structure is indeed **1**.

Having proven the structure of the product, one can now comment on the fact that the MS of this compound consists of only the NMCBA spectrum. When the MS of the model compound *O*-phenylbenzohydroxamic acid was determined, it too showed only the spectrum of benzamide. Thus both O-phenylated species suffer loss of the *O*-phenyl group in the form of the extrusion of the elements of the corresponding phenylene oxide as a neutral leaving group. This is not a usual route to fragmentation in that it must involve a two bond cleavage.

A possible mechanism appears in Scheme I.

Experimental Section

NMR spectra were recorded on a Varian EM 360 or a Varian XL200 instrument in $CDCl_3$ unless specifically noted. Infrared were recorded on a Beckman Acculab-4 for routine characterization, but the IR study of model compounds was done on a Nicolet 5DXB FTIR spectrometer. GC–mass spectroscopy was done on a Hewlett-Packard 5890GC with a 5970 mass selective detector equipped with a 7646 computer workstation. Microanalytical results were obtained from Desert Analytics, Tucson, AZ.

Preparations of Materials. The *p*-Chloro-*N*-methylbenzohydroxamic acid was prepared by a literature method as noted.

O-Phenylbenzohydroxamic acid was prepared by benzoylation of *O*-phenylhydroxylamine, made by the method of Bumgardner and Lilly,[8] as follows: 1.00 g (6.88 mmol) of the hydrochloride salt of *O*-phenylhydroxylamine was stirred with 10.0 mL of saturated sodium bicarbonate solution while the mixture was cooled in an ice–water bath. To the resulting solution was added, via syringe, an equivalent amount of benzoyl chloride. An immediate precipitate occurred, which was filtered to give 1.39 g (95%) of a white material, recrystallized from ethyl acetate–petroleum ether, mp 137–139 °C (Meltemp).

Anal. Calcd for $C_{13}H_{11}NO_2$: C, 73.56; H, 5.20; N, 6.57. Found: C, 73.13; H, 5.20; N, 6.36. IR ν 3160 (NH) 1660, 1580, 760, 700 cm^{-1}; ^1H NMR, two sets of two multiplets centered at 8.10, and 7.45 ppm (acetone-d_6); ^{13}C NMR δ 115.4, 119.5, 122.6, 127.6, 128.7, 129.5, 132.3, 160.0, 180.5 ppm (proton decoupled vs TMS). The mass spectrum is described in the text.

Reaction of Sodium *p*-Chloro-*N*-methylbenzohydroxamate (*p*-ClNMBH) with Sanger's Reagent. A 516-mg (2.49-mmol) sample of sodium *p*-ClNMBH was dissolved in 10.0 mL of dry methanol, in a flask protected by a $CaCl_2$ tube. To this solution, at room temperature, was added (through a rubber septum) 0.32 mL of Sanger's reagent (Aldrich, 97%). A white precipitate formed immediately. After 48 h (subsequent experiments showed the delay was unnecessary) the precipitate was filtered, giving 650 mg (75%) of a white solid, mp 143–145 °C.

Anal. Calcd for $C_{14}H_{10}N_3O_6Cl$: C, 47.81; H, 2.87; N, 11.95, Cl, 10.08. Found: C, 47.34; H, 2.62; N, 11.54; Cl, 9.85. IR ν 1671 ($\nu_{C=O}$), 1597, 1548, 790, 750 cm^{-1}; ^1H NMR $A_2'B_2'$ centered at 7.48 (4 H), ABX, at δ 8.87 and 8.52–8.46 (3 H), 3.55 (3 H); MS discussed in the text.

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thank the Orscheln foundation of Moberly Missouri for the purchase of the Hewlett-Packard 5890 GCMS with a computer work station.

Registry No. 1, 123381-63-5; Na-*p*-ClNMBHA, 123381-62-4; Sanger's reagent, 70-34-8; *O*-phenylhydroxylamine hydrochloride, 6092-80-4; *O*-phenylbenzohydroxamic acid, 4380-77-2.

Supplementary Material Available: Tables of positional and thermal parameters, hydrogen atom positions, and anisotropic thermal parameters (3 pages). Ordering information is given on any current masthead page.

Synthesis of Chiral 2,6-Dithiabicyclo[3.1.1]heptane. The Dithia Parent Analogue of the TXA_2 Nucleus[1]

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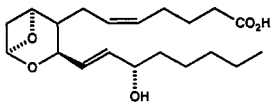
Thromboxane A_2 (TXA_2), a potent blood platelet aggregating component of the arachidonic acid cascade, is thought to play a central role in many pulmonary–cardiovascular disorders.[2] Until recently,[3] the chemical

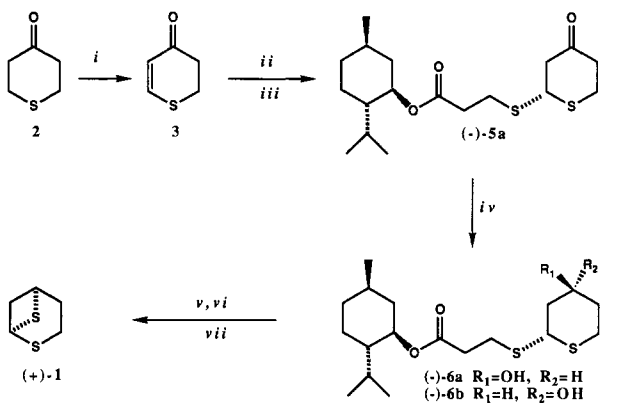


TXA_2

1

structure of this labile natural product remained uncertain, and in order to further the understanding of its biochemical and chemical properties, efforts have been made to synthesize more stable analogues or derivatives.[4] Although computer calculations have been carried out on the parent and on sulfur-substituted model analogues of the bicyclic oxetane ring system,[5] the synthesis of these unadorned heterocyclic compounds has not been described. Since ring substitution on heterocycles greatly adds stability toward ring opening and polymerization,[6] the synthesis of TXA_2[3] itself and, as well as, other ring-substituted heteroatom analogues have been published.[4] Since the bicyclic ring moiety is reported to be a prerequisite for the biochemical activity in TXA_2,[3] we felt it useful to try to prepare, by Ohuchida et al.[4a] methodology, the (less strained by 10.5 kcal/mol; MMX[7] calculation) parent nucleus 1 to see if

Scheme I[a]



[a] (i) NCS/pyridine/CH_2Cl_2/0 °C; (ii) (–)-4/*i*-$PrNEt_2$/DMF; (iii) hexanes/–10 °C; (iv) LS-Selectride/THF/–78 °C; (v) chromat (silica); (vi) MsCl/Et_3N/CH_2Cl_2/0 °C; (vii) $(Me_3Si)_2NLi$/THF/reflux 2 h.

any of the reported properties of the more fully elaborated sulfurated derivative of TXA_2[4] are retained in this simple system.

Thus, the synthesis of (+)- or (–)-1 was accomplished in seven steps, from commercially available 4-thiapyrone 2 (Scheme I).[4a,8b] Conversion of 2 into the unsaturated derivative 3 by treatment with 1 equiv of NCS and pyridine in CH_2Cl_2 at 0 °C followed by base-catalyzed (*i*-$PrNEt_2$)[4a,8a] Michael type addition of optically pure menthol mercapto ester (–)-4[8b] ($[\alpha]^{23}_D$ –70.4° (*c* = 1.0, MeOH)), prepared from *l*-menthol esterification of 3-mercapto propionic acid, in DMF quantitatively afforded the diastereomeric mixture (–)-**5a** and (–)-**5b** with the anticipated anomeric selectivity in excess of 95% (determined by 400-MHz ^1H NMR spectroscopy).[8b]

Fractional crystallization (hexanes, –10 °C) afforded pure (–)-**5a** in 25% overall yield from 2. Reduction (LS-Selectride in THF at –78 °C) of (–)-**5a** gave no better than a 2:1 mixture of the epimeric alcohols (–)-**6a**[8b] and (–)-**6b**[8b] in 80% yield. Chromatographic separation of (–)-**6a** from (–)-**6b** on silica and mesylation of the free hydroxy group followed by treatment with $(Me_3Si)_2NLi$ in THF (at reflux for 2 h) afforded, after workup and sublimation of the resulting crude residue, (+)-2,6-dithiabicyclo[3.1.1]heptane [mp 44–45 °C, $[\alpha]^{23}_D$ +84.8° (*c* = 0.24, $CHCl_3$)] in 40% yield. Similarly, using *d*-menthol, the (–) enantiomer[8b] [mp 42–43 °C, $[\alpha]^{23}_D$ –101.5° (*c* = 2.64, $CHCl_3$)] was also obtained in 40% yield.

The chemistry of 1, as expected, is dominated by the strain in the bicyclic thietane moiety. For example, in the presence of a nucleophile such as a catalytic amount of benzyl mercaptan, the four-membered ring readily transsulfurates to the benzyl thiolated derivative 7. Loss of benzyl mercaptan then gives dihydrothiapyran, 8, which can also participate in the further addition–elimination processes that ultimately lead to the complex mixture of unsaturated thiapyran derivatives observed (^1H NMR, eq

(1) Dedicated to Prof. E. C. Taylor on the occasion of his 65th birthday.

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(7) Obtained from Serena Software, P.O. Box 3076, Bloomington, IN 47402-3076.

(8) (a) Casy, G.; Lane, S.; Taylor, R. J. K. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1397. (b) All new compounds had satisfactory combustion analyses and or high-resolution mass spectra. Optical purity is based on successive fractional crystallizations and comparison of the rotations to the enantiomers. The variance of the optical rotation between (+)-1 and (–)-1 is due to the polymerization and decomposition of the compound during recrystallization. (+)-4: R_f (20% ether/pentane) 0.50; mp 34 °C; $[\alpha]^{23}_D$ +70.8° (*c* = 1.0, EtOH); ^1H NMR ($CDCl_3$) δ 0.7–1.7 (19 H, m), 2.6–2.8 (4 H, m), 4.7 (1 H, dt, J_1 = 10.6 and J_2 = 4.4 Hz); ^{13}C NMR ($CDCl_3$) δ 170.6, 74.2, 46.6, 40.6, 38.5, 33.9, 31.0, 25.9, 23.1, 21.6, 20.4, 19.5, 16.0. (–)-4: mp 34 °C; $[\alpha]^{23}_D$ –70.3° (*c* = 1.0, EtOH).

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