30 mmol) was added slowly with a syringe. After 4 h of stirring at room temperature, the mixture was poured into pentane (100 mL), filtered, the solvent evaporated, and the residue treated again with pentane (50 mL). After the precipitate had settled and the solution was decanted, the solvent was evaporated to give **2** which was purified by fractional distillation: 2.05 g (80% yield); bp 84–85 °C (0.15 mmHg); ^{1}H NMR δ 0.35 (s, 18 H, $SiCH_3$), 3.13 (s, 3 H, NCH_3), 4.70 (s, 2 H, CH=); MS, *m/e* (relative intensity) 257 (30), 242 (8), 184 (9), 145 (100), 113 (10). Anal. Calcd for $C_{11}H_{23}NO_2Si_2$: C, 51.32; H, 8.94. Found: C, 51.78; H, 8.90.

Reaction of 1 and 2 with 2 Equiv of Electrophile and $SnCl_4$. General Procedure. 3,4-Bis(hydroxydimethylmethyl)tetrahydrothiophene-2,5-dione (9a). To a solution of **1** (200 mg, 0.8 mmol) and **7a** (90 mg, 1.6 mmol) in dry CH_2Cl_2 (2 mL) at −78 °C was added $SnCl_4$ (402 mg, 1.6 mmol) dropwise with a syringe. The mixture was allowed to warm to room temperature, then poured into 20 mL of Et_2O, and washed twice with 10 mL of a NH_4Cl saturated solution. The ethereal layer was separated, dried on $MgSO_4$, and analyzed by GC/MS, showing a mixture of 3% of **3**, 46% of **8a**, and 51% of **9a**. The solvent was evaporated and the crude residue eluted on a silica gel column with cyclohexane:acetone (2:1) from which **3** and **8a** were isolated. **8a**: 66 mg (41% yield); mp 105 °C; MS, *m/e* (relative intensity) 183 (9), 152 (60), 139 (27), 113 (23), 82 (100). Further elution with methanol led to **9a** as a dense yellowish oil. **9a**: 79 mg (42% yield); ^{1}H NMR ($CDCl_3$) δ 1.21 (s, 6 H, CH_3), 1.28 (s, 6 H, CH_3), 2.62 (s, 1 H, CH), 2.70 (s, 1 H, CH), 3.6 (broad, 2 H, OH); IR (neat) 3450, 2990, 1710, 1495, 1090 cm^{-1}; MS, *m/e* (relative intensity) 230 (9), 196 (15), 116 (25), 59 (100). Anal. Calcd for $C_{10}H_{16}O_4S$: C, 51.70; H, 6.94. Found: C, 51.35; H, 6.96.

3,4-Bis(hydroxy-*n*-propylmethyl)tetrahydrothiophene-2,5-dione (9b). GC/MS analyses of the reaction mixture showed 48% of **8b** and 52% of **9b**. Column chromatography on silica gel with cyclohexane:acetone (2:1) gave **8b**: 72 mg (40% yield); mp 189–190 °C; MS, *m/e* (relative intensity) 276 (1), 186 (20), 168 (4), 152 (20), 82 (100). Further elution with ethanol led to **9b** as a yellowish oil. **9b**: 98 mg (47% yield); IR (neat) 3300, 2980, 1705, 1105 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.2 (m, 6 H, CH_3), 1.5 (m, 8 H, CH_2), 2.8 (m, 2 H, CHC=O), 3.4 (m, 2 H, CHO), 4.0 (broad, 2 H, OH); MS, *m/e* (relative intensity) 258 (8), 224 (11), 116 (53), 59 (100). Anal. Calcd for $C_{12}H_{20}O_4S$: C, 55.36; H, 7.74. Found: C, 55.01; H, 7.70.

3,4-Bis(hydroxyphenylmethyl)tetrahydrothiophene-2,5-dione (9c). GC/MS analyses of the reaction mixture showed 56% of **8c** and 44% of **9c**. Column chromatography with cyclohexane:acetone (3:1) gave **8c**: 120 mg (51% yield); mp 183–184 °C; MS, *m/e* (relative intensity) 292 (3), 217 (4), 140 (25), 82 (100). Further elution with acetone led to **9c**: 91 mg (35% yield); mp 142–143 °C; IR (KBr) 3510, 3080, 3060, 2930, 1700, 1610, 1090, 745, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.30 (d, 2 H, J = 1.8 Hz, CHC=O), 5.03 (d, 2 H, J = 1.8 Hz, CHO), 5.8 (broad, 2 H, OH), 7.1 (m, 10 H, Ar H); MS, *m/e* (relative intensity) 310 (2), 296 (40), 145 (100), 77 (46). Anal. Calcd for $C_{18}H_{16}O_4S$: C, 65.84; H, 4.91. Found: C, 65.41; H, 4.91.

1-Methyl-3,4-bis(hydroxydimethylmethyl)succinimide (10a). Preparative TLC of the crude with ethanol:chloroform (4:1) gave pure **10a** as a brown wax: 122 mg (64% yield); IR (CCl_4) 3480, 2990, 1700, 1480, 1120 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.20 (s, 6 H, CH_3), 1.28 (s, 6 H, CH_3), 2.61 (s, 1 H, CHC=O), 2.68 (s, 1 H, CHC=O), 3.02 (s, 3 H, NCH_3), 4.6 (broad, 2 H, OH); MS, *m/e* (relative intensity) 227 (6), 210 (4), 196 (26), 113 (100). Anal. Calcd for $C_{11}H_{19}NO_4$: C, 57.62; H, 8.35. Found: C, 57.12; H, 8.35.

1-Methyl-3,4-bis(hydroxy-*n*-propylmethyl)succinimide (10b). Column chromatography of the crude with cyclohexane:acetone (2:1) gave **10b** as a yellow oil: 125 mg (61% yield); IR (neat) 3460, 2980, 1700, 1110 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.1 (m, 6 H, CH_3), 1.4–1.8 (broad, 8 H, CH_2), 2.8 (m, 2 H, CHC=O), 3.00 (s, 3 H, NCH_3), 3.5 (m, 2 H, CHO), 3.9 (broad, 2 H, OH); MS, *m/e* (relative intensity) 239 (9), 224 (8), 185 (26), 113 (100). Anal. Calcd for $C_{13}H_{23}NO_4$: C, 60.67; H, 9.01. Found: C, 60.47; H, 9.06.

1-Methyl-3,4-bis(hydroxyphenylmethyl)succinimide (10c). Column chromatography of the crude with cyclohexane:acetone (1:1) gave **10c**: 192 mg (72% yield); mp 62–63 °C; IR (KBr) 3480, 3085, 3040, 2920, 1700, 1605, 1140 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.02 (s, 3 H, NCH_3), 3.20 (d, 2 H, J = 1.9 Hz, CHC=O), 4.65 (d, 2 H, J = 1.9 Hz, CHO), 5.2 (broad, 2 H, OH), 7.3 (m, 10 H, Ar H); MS, *m/e* (relative intensity) 325 (1), 307 (5), 252 (10), 113 (100), 77 (55). Anal. Calcd for $C_{19}H_{19}NO_4$: C, 70.13; H, 5.88. Found: C, 70.29; H, 5.80.

1-Methyl-3-(hydroxydimethylmethyl)succinimide (11). **11** was prepared following the same general procedure of **10a–c**, simply adding dropwise, with a syringe, a solution of **7a** (46 mg, 0.8 mmol) and $SnCl_4$ (201 mg, 0.8 mmol) in CH_2Cl_2 (1 mL) to **2** (205 mg, 0.8 mmol) in CH_2Cl_2 (2 mL) at −78 °C. GC/MS analyses of the crude product showed 91% of **11** and 9% of **10a**. **11** was isolated by column chromatography with cyclohexane:acetone (2:1) as a yellow oil. **11**: 112 mg (82% yield); IR (neat) 3480, 2990, 1710, 1490, 1090 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.25 (s, 6 H, CH_3), 2.3 (m, 2 H, CH_2C=O), 2.8 (m, 1 H, CHC=O), 3.00 (s, 3 H, NCH_3), 3.4 (s, 1 H, OH); MS, *m/e* (relative intensity) 156 (21), 153 (17), 113 (100), 59 (54). Anal. Calcd for $C_8H_{13}NO_3$: C, 56.18; H, 7.65. Found: C, 56.05; H, 7.60.

1-Methyl-3-(hydroxy-*n*-propylmethyl)-4-(hydroxydimethylmethyl)succinimide (12). To a solution of **2** (200 mg, 0.8 mmol) in CH_2Cl_2 (2 mL) was added a mixture of **7a** (44 mg, 0.8 mmol) and $SnCl_4$ (201 mg, 0.8 mmol) in CH_2Cl_2 (0.5 mL) dropwise at −78 °C. After 1 h at this temperature, a mixture of **7b** (66 mg, 0.8 mmol) and $SnCl_4$ (201 mg, 0.8 mmol) in CH_2Cl_2 (0.5 mL) was added dropwise. After 8 h at −78 °C the mixture was warmed at room temperature, treated with 15 mL of Et_2O, and washed twice with 10 mL of a saturated solution of NH_4Cl. The ethereal layer was separed and dried on $MgSO_4$; GC/MS analyses of the crude showed the presence of 5% of **11**, 8% of **10b**, and 87% of **12** which was isolated by preparative TLC with CCl_4:ethanol (4:1) as a brown dense oil. **12**: 136 mg (73% yield); IR (CCl_4) 3470, 2980, 1700, 1110, 1085 cm^{-1}; ^{1}H NMR δ 1.0 (m, 3 H, CH_3), 1.24 (s, 3 H, CH_3CO), 1.26 (s, 3 H, CH_3CO), 1.2–1.6 (broad, 4 H, CH_2), 2.8 (m, 2 H, CHCO), 3.00 (s, 3 H, NCH_3), 3.9 (broad, 2 H, OH); MS, *m/e* (relative intensity) 210 (6), 192 (2), 182 (10), 113 (100), 59 (16), 43 (20). Anal. Calcd for $C_{12}H_{21}NO_4$: C, 59.24; H, 5.38. Found: C, 59.01; H, 5.34.

2-Methyl-3,4-dicarboxy-2,4-octadiene (13). **12** (100 mg, 0.4 mmol) was added to a 10% solution of NaOH (5 mL) and the mixture boiled until all the oil was dissolved; 8 mL of AcOH and 5 mL of Ac_2O were added, and the solution was maintained under stirring for 2 h at room temperature. The mixture was extracted twice with 10 mL of Et_2O and then washed with three portions of water (10 mL). The ethereal layer was separated, dried on $MgSO_4$ and, after evaporation of the solvent and high vacuum treatment for 3 h, **13** was obtained as a waxy material solidifying on standing. **13**: 63 mg (75% yield); IR (KBr) 3460, 2980, 1725, 1650, 1470 cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 0.9 (m, 3 H, CH_3), 1.3–1.7 (broad, 10 H, CH_2 and CH_3C=), 6.85 (t, 1 H, J = 6 Hz, CH=), 8.3 (broad, 2 H, OH); MS, *m/e* (relative intensity) 212 (3), 179 (9), 142 (100). Anal. Calcd for $C_{11}H_{10}O_4$: C, 62.26; H, 7.54. Found: C, 62.46; H, 7.50.

Registry No. **1**, 91210-72-9; **2**, 91210-73-0; **3**, 3194-60-3; **4**, 1121-07-9; **5**, 543-20-4; **7a**, 67-64-1; **7b**, 123-72-8; **7c**, 100-52-7; **8a**, 91210-74-1; **8b**, 91210-75-2; **8c**, 91278-68-1; **9a**, 91210-76-3; **9b**, 91210-77-4; **9c**, 91210-78-5; **10a**, 91210-79-6; **10b**, 91210-80-9; **10c**, 91210-81-0; **11**, 91210-82-1; **12**, 91210-83-2; **13**, 91228-88-5; $(Me_3Si)_2S$, 3385-94-2; Me_3SiCl, 75-77-4; $SnCl_4$, 7646-78-8.

A Convenient Method for Hydrazone Hydrolysis

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Protection of the carbon–oxygen double bonds in aldehydes and ketones as carbon–nitrogen double bonds has become a valuable strategy in organic synthesis.[1] The carbon–nitrogen double-bonded derivatives, compared with

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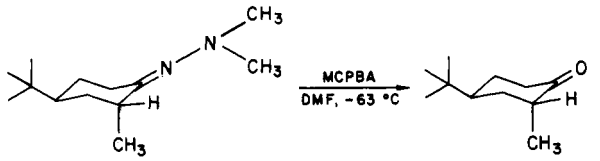
their parent carbonyl compounds, exhibit marked differences in reactivity due largely to the lower acidity of protons on the α-carbons and their greater tolerance to self-condensation. Stereospecific generation of α-lithio imines,[2] oxime ethers,[3] and hydrazones[4] and their subsequent reaction with electrophiles have produced, in good yields and with high regio- and stereoselectivity, alkylated carbonyl compounds which are otherwise difficult to obtain in pure form. Corey's hydrazone alkylation[4,5] is one such example.

During our syntheses of chiral dienes[6] to study their chiroptical properties, we were in need of a cyclohexanone in which a 2-methyl substituent is oriented in an axial position. Following Corey's procedure,[4] we obtained the *N,N*-dimethylhydrazone of *trans*-4-*tert*-butyl-2-methylcyclohexanone (1). The cleavage of 1 to obtain 2 could



1 2

be achieved by $NaIO_4$.[4] The limitations of this reagent are that it is expensive and very large reaction volumes were necessary even for a 0.1-mol scale. Since we needed the ketone 2 in preparative scales an alternate method of hydrazone cleavage was necessary. *m*-Chloroperbenzoic acid seemed to be the reagent of choice only if we could prevent epimerization of the product by *m*-chlorobenzoic acid. First we noted, by cleaving the *N,N*-dimethylhydrazone of 4-*tert*-butylcyclohexanone, that the reaction was very facile in many solvents, giving 4-*tert*-butylcyclohexanone in quantitative yields. Of various conditions employed for the target molecule 1, the one using 2 equiv of MCPBA in DMF at −63 °C was found to give ketone 2 in quantitative yield and without isomerizing the axial methyl group to the more stable equatorial position. Moreover, the reaction could be carried out in a very short time, using a relatively inexpensive reagent (MCPBA), and it was amenable to very small as well as large quantities of substrate.

An alternative method of hydrolysis of 1 is by quarternization of the hydrazone with CH_3I followed by aqueous hydrolysis.[4b,7] This procedure also yields unisomerized ketone 2 but, in our hands, the yield was quite low (≃20%).

Experimental Section

The hydrazone 1 (60.0 g, 0.285 mol) was dissolved in 1.0 L of dry DMF and the solution was cooled to −63 °C (dry ice/$CHCl_3$). *m*-Chloroperbenzoic acid (80–90%; 90.0 g, 0.57 mol) was slowly added while the solution was being stirred and the temperature maintained. After 0.5 h, *the cold solution* was poured into $NaHCO_3$ (~60 g) solution and diluted with more ice-cold water to completely dissolve the DMF. The cold mixture was immediately extracted twice with hexane. The hexane extract was washed with cold sodium bisulfite, $NaHCO_3$, and water. The solution was filtered through Na_2SO_4 and evaporated and the residue was distilled under vacuum, bp 75 °C (1.25 mm) to yield 45.5 g (95%) of *trans*-4-*tert*-butyl-2-methylcyclohexanone (2): ^1H NMR ($CDCl_3$) δ 0.90 (s, 9 H), 1.15 (d, J = 7 Hz, 3 H), 1.15–2.8 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 16.84 (q), 26.18 (t), 27.40 (q), 32.44 (s), 32.99 (t), 38.03 (t), 41.35 (d), 42.96 (d), 216.11 (s).

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Registry No. 1, 58911-80-1; 2, 3211-26-5; MCPBA, 937-14-4.

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Mercury in Organic Chemistry. 29.[1] An Improved, Stereospecific Approach to Vinylmercurials via Hydroboration–Mercuration of Alkynes

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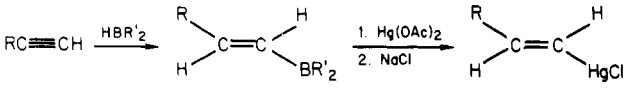
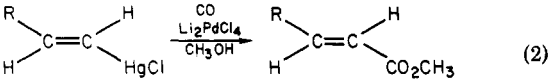
In recent years vinylmercurials have proven to be valuable intermediates in the synthesis of symmetrical[2,3] and unsymmetrical[4] 1,3-dienes, 1,4-dienes,[5] α,β-unsaturated ketones,[6] carboxylic acids and esters,[7] enol esters,[8] butenolides,[9] and (π-allyl)palladium compounds.[10,11] Some years ago we reported a convenient approach to vinylmercurials via hydroboration of alkynes with either dicyclohexylborane[12] or catecholborane[13] and subsequent transmetalation by mercuric acetate (eq 1). In that work,



(1)

alkynes of low molecular weight, usually containing eight of less carbons, were employed and the overall hydroboration–mercuration procedure was observed to be highly stereospecific. In the intervening years, carbonylation of these organomercurials (eq 2) has established that the



(2)

mercuration step is not stereospecific for alkynes of higher

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