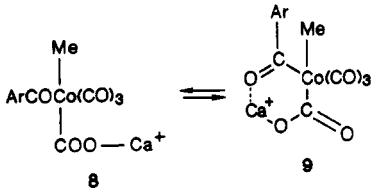

8 9

in the case of more polar 15:1 DMF–H_2O the contribution of the open-chain form 8 would be important. Of these two intermediates, we would like to consider that **9** is the key leading to the formation of **4**.[6] In the open-chain form **8**, the process of reductive elimination providing **2** contributes predominantly in the presence of only small amounts of dissolved calcium hydroxide.

Experimental Section

General Procedures. ^1H NMR spectra were obtained with a JMN-PS-100 spectrometer in $CDCl_3$. GC–MS data were obtained with a Hitachi-RMU-6M. GC analysis was carried out on a Shimazu-GC-4C gas chromatograph.

Carbonylation of Aryl Halides 1. The carbonylation of **1** (1 or 5 mmol) was carried out with 0.3 mmol of $Co_2(CO)_8$ in the presence of methyl iodide (10 or 25 mmol) and calcium hydroxide (25 or 40 mmol) in an appropriate solvent–water mixture (40 mL) at room temperature for 20 h under carbon monoxide (1 atm). Analysis of the products was performed by GC and GC–MS after addition of an appropriate internal standard. The acidic products were treated with *N,O*-bis(trimethylsilyl)acetamide in acetonitrile or diazomethane in ether before the analysis. The methyl esters of **3–6** were also isolated by column chromatography on silica gel by using ethyl acetate–hexane as eluant. The methyl esters of **3–5** were identified by comparison with those of authentic samples. The methyl ester of **6b** was a solid: mp 152–154 °C (from ethanol); MS, *m/e* 262 (M^+); ^1H NMR δ 2.32 (s, 3 H), 3.76 (s, 3 H), 3.84 (s, 3 H), 6.52 (s, 1 H), 7.12–7.44 (m, 4 H). Anal. Calcd for $C_{14}H_{14}O_5$: C, 64.12; H, 5.38. Found: C, 64.04; H, 5.35. The methyl ester of **6c** was an oil; MS, *m/e* 248 (M^+); ^1H NMR δ 3.76 (s, 3 H), 3.84 (s, 3 H), 6.56 (s, 1 H), 7.20–7.62 (m, 5 H). The methyl ester of **6d** was an oil: MS, *m/e* 282 and 284 (M^+); ^1H NMR δ 3.76 (s, 1 H), 3.82 (s, 3 H), 6.52 (s, 1 H), 7.20–7.62 (m, 4 H). The yield of **6b–d** was, however, determiened by ^1H NMR analysis of the crude products on the basis of the peak intensity of the vinylic proton [**6b**, δ 6.68 (s, 1 H). **6c**, δ 6.68 (s, 1 H). **6d** δ 6.66 (s, 1 H)] because considerable amounts of byproducts were formed by treatment with diazomethane.

(5) Arylgrycolic acid **5** might be produced by the reaction of **4** with an anionic intermediate $[MeCo(CO)_3COOH]^-$ generated in situ.[4b,7]

(6) This is partly supported by the fact that in the reaction of **1a** under phase-transfer conditions using sodium hydroxide, **2a** is obtained predominantly.[4] In this case the corresponding chelated form **9** (R = Na) is improbable.

(7) Flancalanci, A.; Gardano, A.; Abis, L.; Foa, M. *J. Organomet. Chem.* **1983**, *251*, C5.

A Simple Preparation of a 2-Lithiopropenal Equivalent

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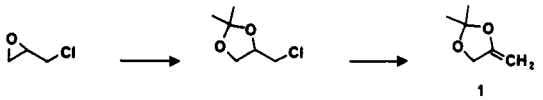
A number of acrolein enolate and acrylate ester enolate equivalents have been developed in recent years.[1] The need for efficient syntheses of α-methylene-γ-butyrolactones provided the impetus for the development of these reagents. All of the acrolein enolate equivalents which have been described to date require the unmasking of the carbonyl group subsequent to the nucleophilic addition step. A more direct approach would be to use the enolate of acrolein itself. Although several studies have described the preparation of 1,2-propadien-1-ol as a transient intermediate,[2] the corresponding alkoxide salt has remained unknown. In connection with our study of alkoxyallenes,[3] we required an efficient synthesis of a 2-lithiopropenal eqivalent (**2**). We report a convenient method for generating this anion.

The starting material for **2** was 2,2-dimethyl-4-methylene-1,3-dioxolane (**1**) which was prepared from epichlorohydrin and acetone according to known procedures[4] (eq 1). Dioxolane **1** was stable to storage at −10



(1)

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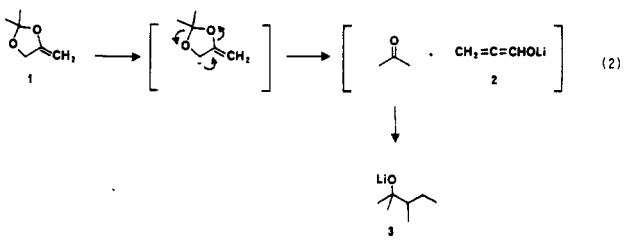
°C for several weeks.[5] Treatment of **1** with ca. 2 equiv of *sec*-butyllithium in tetrahydrofuran at −78 °C for 20–30 min produced a solution of anion **2** (eq 2).[6] Allylic de-



(2)

protonation was followed by fragmentation to **2** and acetone. The addition of the second equivalent of *sec*-butyllithium to acetone took place more rapidly than either proton transfer from acetone to **2** or nucleophilic addition of **2** to acetone. The stable solution of **2** which was obtained in this manner was suitable for addition to electrophiles.

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(2) (a) Bock H.; Mohmand, S.; Hirabayashi, T.; Semkow, A. *Chem. Ber.* **1982**, *115*, 1339. (b) Hakiki, A.; Ripoll, J.-L.; Thuillier, A. *Tetrahedron Lett.* **1984**, 3459. (c) Capon, B.; Siddhanta, A. K.; Zucco, C. *J. Org. Chem.* **1985**, *50*, 3580.

(3) Tius, M. A.; Ousset, J.-B., unpublished results.

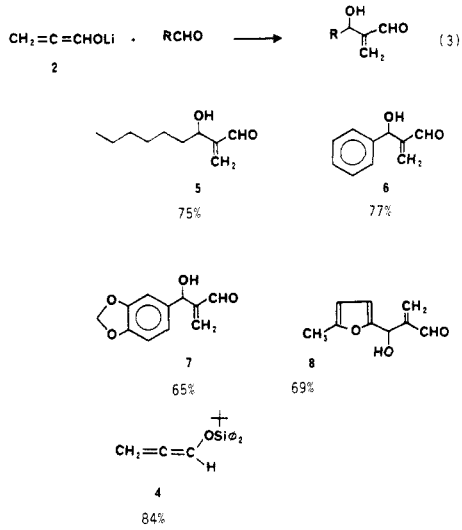
(4) Scharf, H.-D.; Wolters, E. *Chem. Ber.* **1978**, *111*, 639. See also: Mattay, J.; Thünker, W.; Scharf, H.-D. *Liebigs Ann. Chem.* **1981**, 1105. **1**: ^1H NMR (300 MHz, $CDCl_3$) δ 4.47 (dd, J = 1.2, 1.1 Hz, 2 H), 4.24 (dd, J = 2.3, 1.1 Hz, 1 H), 3.81 (dd, J = 2.3, 1.2 Hz, 1 H), 1.43 (s, 6 H).

(5) Dioxolane **1** was stored neat over anhydrous K_2CO_3.

(6) (a) Evans, D. A.; Andrews, G. C.; Buckwalter, B. *J. Am. Chem. Soc.* **1974**, *96*, 5560. (b) Still, W. C.; Macdonald, T. L. *J. Am. Chem. Soc.* **1974**, *96*, 5561. (c) Still, W. C. *Tetrahedron Lett.* **1976**, 2115. (d) Still W. C.; Macdonald, T. L. *J. Org. Chem.* **1976**, *41*, 3620. (e) Evans, D. A.; Baillargeon, D. J.; Nelson, J. V. *J. Am. Chem. Soc.* **1978**, *100*, 2242.

0022-3263/87/1952-2625$01.50/0

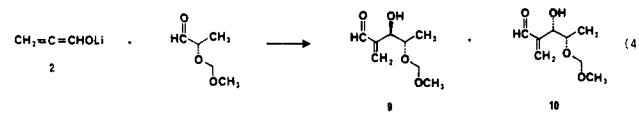
The best results were obtained from the reaction of **2** with aliphatic and aromatic aldehydes (eq 3). The yields for these additions varied from 65% to 77%. The addition of **2** to ketones, however, took place in low yield, perhaps due to competing proton transfer either to **2** or to the lithium alkoxide **3**. *p*-Methylacetophenone and 4-*tert*-butylcyclohexanone both furnished less than 10% of the anticipated addition product. The addition of **2** to benzyl bromide and phenethyl bromide was unsuccessful. The presence of HMPA or TMEDA did not improve the reaction.



The rate of addition of anion **2** to acetone and ketones in general appears to be far slower than for addition to aldehydes. To demonstrate this more convincingly, the stoichiometry of *sec*-butyllithium and **1** was varied. A solution of anion **2** was prepared in THF at −78 °C from 1.2 mmol of *sec*-butyllithium and 1.2 mmol of dioxolane **1**. Anion formation was presumed to be complete after 20–30 min. The solution of anion **2** was treated with a THF solution of 1 mmol of heptanal or 1 mmol of benzaldehyde. Aqueous workup furnished adducts **5** or **6** in 73% or 75% yield, respectively. This result indicates that the nucleophilic addition of **2** to ketones is very slow at −78 °C. Furthermore, the addition of **2** to benzophenone, a nonenolizable ketone, did not take place, even upon gradual warming of the reaction mixture to 0 °C. Unreacted benzophenone was recovered in 98% yield.

Anion **2** was converted to silyl ether **4** in 84% yield by treatment with *tert*-butyldiphenylchlorosilane. This reaction makes a variety of allenyl silyl ethers[7] readily available. It should be possible from trimethylsilyl or triethylsilyl allenyl ethers to obtain solutions of **2** which are free of alkoxide **3**.

Since the addition reactions of **2** were most successful with aldehydes, it was desirable to learn whether any diastereofacial preference for the addition of **2** to an α-alkoxy aldehyde would be observed.[8] Accordingly, the reaction of **2** with 2-(methoxymethoxy)propanal[9] was examined (eq 4). The diastereoselectivity was modest, and a 3:1 ratio of threo **9** and erythro **10** isomers was observed. The identity of the addition products was established by comparison of the ^{1}H NMR spectra with the reported spectra for the corresponding methyl esters.[10]



In conclusion, an efficient and convenient synthesis of a 2-lithiopropenal equivalent from 2,2-dimethyl-4-methylene-1,3-dioxolane has been described. This anion added efficiently to aldehydes (65–77%) and was trapped on oxygen with *tert*-butyldiphenylchlorosilane (84%). Anion **2** will be useful for the preparation of furanones, furans, butenolides, 2-substituted acrolein derivatives, and allene ethers.

Experimental Section

All reactions were performed in flame-dried glass apparatus equipped with rubber septa under a static nitrogen or argon atmosphere. *sec*-Butyllithium was titrated according to the procedure of Watson and Eastham.[11] Thin-layer chromatography was performed on EM Reagents precoated Silica Gel 60 F-254 analytical plates (0.25 mm). Flash chromatography was performed on Brinkmann silica gel (0.040–0.063 mm) using mixtures of ethyl acetate and hexane.

Proton nuclear magnetic resonance spectra were recorded at 300 MHz on a Nicolet NT-300 spectrometer (Oxford magnet) or on a Varian XL-100 spectrometer. Infrared spectra were recorded on a Beckman IR-10 or on a Nicolet 5MX FT spectrometer. Electron impact mass spectra were recorded on a Varian MAT-311 spectrometer. Analyses were performed by Canadian Microanalytical Service, Ltd., Vancouver, B.C.

Addition of 2 to Aldehydes. General Procedure. A solution of 2,2-dimethyl-4-methylene-1,3-dioxolane (1.2 equiv, 1.2 mmol) in 8 mL of THF was treated at −78 °C with *sec*-butyllithium (2.2 equiv, 2.2 mmol). Anion formation was presumed to be complete after 20–30 min.

A solution of aldehyde (1 equiv, 1 mmol) in 2 mL of THF was added via cannula to the rapidly stirring solution of **2** at −78 °C. After ca. 15 min the reaction was quenched by the addition of 5 mL of water. After warming to room temperature the reaction mixture was partitioned between ether and water. The ethereal layer was washed with water and brine and was dried over $MgSO_4$. Concentration followed by flash chromatography produced the reaction products in 65–84% yield (oils).

5: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.56 (s, 1 H), 6.47 (s, 1 H), 6.08 (s, 1 H), 4.48 (dd, J = 7.5, 5.0 Hz, 1 H), 2.7 (br s, 1 H), 1.7–0.86 (m, 13 H); IR (neat) 3400, 2900, 1690, 1450 cm^{-1}; mass spectrum, m/e 170 (M^+), 169 ($M^+ - 1$), 155 ($M^+ - CH_3$), 141 (M^+ −CHO) 99, 85, 55, 43, 29, calcd for $C_{10}H_{18}O_2$ 170.1307, found 170.1261.

6: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.58 (s, 1 H), 7.38–7.25 (m, 5 H), 6.44 (s, 1 H), 6.16 (s, 1 H), 5.62 (d, J = 4 Hz, 1 H), 2.8 (d, J = 4 Hz, 1 H); IR (neat) 3400, 2850, 1680, 1480, 1440 cm^{-1}; mass spectrum, m/e 162 (M^+), 161 ($M^+ - 1$), 144 ($M^+ - H_2O$), 133 (M^+ − CHO), 115 (M^+ −CHO − H_2O), 107, 77, calcd for $C_{10}H_{10}O_2$ 162.0681, found 162.0690.

7: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.58 (s, 1 H), 6.82–6.73 (m, 3 H), 6.46 (s, 1 H), 6.14 (s, 1 H), 5.93 (s, 2 H), 5.50 (br s, 1 H), 2.84 (br s, 1 H); IR (neat) 3400, 2850, 1670, 1480, 1440, 1240 cm^{-1}; mass spectrum, m/e 206 (M^+), 205 ($M^+ - 1$), 188 ($M^+ - H_2O$), 177 (M^+ − CHO), 159 (M^+ − CHO − H_2O), 121, calcd for $C_{11}H_{10}O_4$ 206.0579, found 206.0586.

8: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.61 (s, 1 H), 6.59 (s, 1 H), 6.24 (s, 1 H), 6.10 (d, J = 3 Hz, 1 H), 5.90 (d, J = 3 Hz, 1 H), 5.58 (d, J = 5 Hz, 1 H), 2.88 (d, J = 5 Hz, 1 H), 2.27 (s, 3 H); IR (neat)

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(9) 2-(Methoxymethoxy)propanal was prepared in three steps from (*S*)-(−)-ethyl lactate: (i) $ClCH_2OCH_3$, diisopropylethylamine, dichloromethane; (ii) lithium aluminum hydride, ether, −78 °C; (iii) oxalyl chloride, Me_2SO, triethylamine, tetrahydrofuran, −78 °C. Amato, J. S.; Karady, S.; Sletzinger, M.; Weinstock, L. M. *Synthesis* **1979**, 970.

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3400, 2900, 1675, 1550, 1440 cm^{-1}; mass spectrum, m/e 166 (M^+), 165 ($M^+ - 1$), 148 ($M^+ - H_2O$), 137 ($M^+ - CHO$), 119 ($M^+ - CHO - H_2O$), 105, 82, 43, 28, calcd for $C_9H_{10}O_3$ 166.0630, found 166.0640.

4: ^1H NMR (300 MHz, $CDCl_3$) δ 7.7-7.6 (m, 4 H), 7.4-7.3 (m, 6 H), 6.6 (t, J = 6 Hz, 1 H), 5.1 (d, J = 6 Hz, 2 H), 1.07 (s, 9 H); IR (neat) 2900, 1950, 1460, 1440, 1200, 1100 cm^{-1}; mass spectrum, m/e 294 (M^+), 295 ($M^+ + 1$), 279 ($M^+ - CH_3$), 255 ($M^+ - C_3H_3$), 237 ($M^+ - C_4H_9$), 217 ($M^+ - C_6H_5$), calcd for $C_{19}H_{22}SiO$ 294.1440, found 294.1429.

Preparation of 9 and 10. To a solution of oxalyl chloride (1.4 equiv, 2.9 mmol, 37 mg) in 15 mL of THF at -78 °C was added 44 μL (3 equiv, 6.3 mmol) of Me_2SO in 3 mL of THF dropwise over 10 min. A solution of 250 mg (1 equiv, 2.1 mmol) of (*S*)-(+)-2-(methoxymethoxy)propan-1-ol[9] in 3 mL of THF was added via cannula over 8 min at -78 °C. The solution was stirred for 25 min at -78 °C. Triethylamine (7 equiv, 14.7 mmol, 1.5 g) was added, and the mixture was stirred for an additional 20 min at -78 °C.[12]

A solution of 285 mg (1.2 equiv, 2.5 mmol) of 2,2-dimethyl-4-methylene-1,3-dioxolane (1) in 6 mL of THF was treated at -78 °C with 2.2 equiv (4.6 mmol) of *sec*-butyllithium. After 15 min the solution of the aldehyde was transferred to the anion solution via cannula.[12] After ca. 10 min the reaction was quenched by the addition of 10 mL of water. The reaction mixture was partitioned between ether and water. The ethereal layer was washed with water and brine and was dried ($MgSO_4$). Evaporation followed by flash chromatography produced 183 mg of **9** and 61 mg of **10** (67% yield).

9: ^1H NMR (300 MHz, C_6D_6) δ 9.14 (s, 1 H), 6.36 (s, 1 H), 5.52 (s, 1 H), 4.80 (br s, 1 H; with decoupling, dd, J = 4.0, 3.2 Hz), 4.57 (AB q, J = 6.7 Hz, 2 H), 4.12 (dq, J = 6.4, 3.2 Hz, 1 H), 3.12 (s, 3 H), 3.06 (d, J = 4.0 Hz, 1 H), 0.95 (d, J = 6.4 Hz, 3 H); IR (neat) 3450, 2900, 1680, 1600, 1440, 1380 cm^{-1} ; mass spectrum, m/e 174 (M^+, very weak), 113 ($M^+ - OCH_2OCH_3$), 112 ($M^+ - HOCH_2OCH_3$), 89, 85, 55, 45, 29, 28, calcd for $C_8H_{14}O_4$ 174.1956, found 174.1959.

10: ^1H NMR (300 MHz, C_6D_6) δ 9.20 (s, 1 H), 6.13 (s, 1 H), 5.42 (s, 1 H), 4.50 (dd, J = 6.0, 4.9 Hz, 1 H), 4.34 (AB q, J = 6.8 Hz, 2 H), 3.74 (dq, J = 6.5, 4.9 Hz, 1 H), 3.00 (s, 3 H), 2.85 (d, J = 6.0 Hz, 1 H), 1.04 (d, J = 6.5 Hz, 3 H); IR (neat) 3450, 2900, 1680, 1600, 1440, 1380 cm^{-1}; mass spectrum, m/e 174 (M^+, very weak), 113 ($M^+ - OCH_2OCH_3$), 112 ($M^+ - HOCH_2OCH_3$), 89, 85, 55, 45, 29, 28, calcd for $C_8H_{14}O_4$ 174.1956, found 174.1961; peak match for m/e 113, calcd for $C_6H_9O_2$ 113.0589, found 113.0603.

Preparation of *p*-Nitrobenzoyl Esters of 6 and 7. To a solution of 3 mmol (1 equiv) of hydroxy aldehyde **6** or **7** in 20 mL of dry dichloromethane was added 2,6-lutidine (0.95 equiv), and the mixture was stirred at 25 °C for 15 min. *p*-Nitrobenzoyl chloride (0.9 equiv) was added, and the progress of the reaction was monitored by thin-layer chromatography. After 3-4 h the reaction was quenched by addition of aqueous $NaHCO_3$. The reaction mixture was partitioned between dichloromethane and water, and the organic phase was washed with water and brine and was dried over anhydrous $MgSO_4$. Evaporation of the solvent followed by flash chromatography produced **11**, the *p*-nitrobenzoyl ester of **6** in 88% yield, and **12**, the *p*-nitrobenzoyl ester of **7** in 85% yield (based on *p*-nitrobenzoyl chloride).

11: mp 115-116 °C; ^1H NMR (300 MHz, C_6D_6) δ 9.26 (s, 1 H), 7.61 (d, J = 8.9 Hz, 2 H), 7.50 (d, J = 8.9 Hz, 2 H), 7.13 (m, 2 H), 7.00 (m, 3 H), 6.82 (s, 1 H), 5.14 (s, 2 H); mass spectrum, m/e 311 (M^+, weak), 207, 161, 150, 116, 104, 77, 44, calcd for $C_{17}H_{13}NO_5$ 311.0794, found 311.0797. Anal. Calcd for $C_{17}H_{13}NO_5$: C, 65.59; H, 4.21; N, 4.50. Found: C, 65.76; H, 4.26; N, 4.50.

12: mp 138-139 °C ^1H NMR (300 MHz, C_6D_6) δ 9.26 (s, 1 H), 7.64 (d, J = 8.6 Hz, 2 H), 7.54 (d, J = 8.6 Hz, 2 H), 6.86 (s, 1 H), 6.74 (s, 1 H), 6.62 (d, J = 7.8 Hz, 1 H), 6.47 (d, J = 7.9 Hz, 1 H), 5.17 (s, 2 H), 5.15 (s, 2 H); mass spectrum, m/e 357 ($M^+ + 2$), 356 ($M^+ + 1$), 355 (M^+), 205, 150, 86, 84, 44, calcd for $C_{18}H_{13}NO_7$: 355.3032. Found: 355.3036. Anal. Calcd for $C_{18}H_{13}NO_7$: C, 60.85; H, 3.69; N, 3.94. Found: C, 60.48; H, 3.79; N, 3.88.

Acknowledgment is made to the National Science Foundation (CHE-8602328) and to the Research Corporation (#9243) for their generous support.

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Communications

A Simpler Procedure for Determining Relative Radical Strain Energies by Alcohol Thermolysis and Molecular Mechanics

Summary: Relative strain energies of bridgehead alkyl radicals formed in alcohol thermolysis can be assessed by product analysis and molecular mechanics calculations.

Sir: Activation energies for the thermolysis of tertiary alcohols *t*-BuR^1R^2COH, where R^1 and R^2 are tertiary alkyl groups (reaction I, Scheme I) correlate with the strain energy (SE) change associated with the loss of the *t*-Bu group (eq 1),[1]

$$\Delta G^{\ddagger}(200\ °C) = 69.1 - 1.02\Delta\text{strain} \quad (1)$$

where

$$\Delta\text{strain} = \text{SE}(t\text{-Bu}R^1R^2\text{COH}) - \text{SE}(R^1R^2\text{CHOH}) \quad (2)$$

In the more general case (reaction II, Scheme I), we can write

$$\Delta\text{strain}_{\text{calcd},R^3} = \text{SE}(R^1R^2R^3\text{COH}) - \text{SE}(R^1R^2\text{CHOH}) - \text{SE}(R^3\text{H}) \quad (3)$$

which implies that the strain energy of the radical is the same as that of the alkane. If this were true the formation of $R^{3\bullet}$ would follow eq 1, but, in practice, for bridgehead radicals the activation energy is always higher than expected; i.e., the effective (or experimental) strain energy change is less than eq 3 suggests. It is convenient to define this $\Delta\text{strain}_{\text{expt},R^3}$ by putting the measured activation energy into eq 1:

$$\Delta\text{strain}_{\text{expt},R^3} = [69.1 - \Delta G^{\ddagger}(R^3)]/1.02 \quad (1')$$

The difference ($\Delta\Delta$strain) between $\Delta\text{strain}_{\text{calcd}}$ and $\Delta\text{strain}_{\text{expt}}$ corresponds to the strain energy of formation of $R^{3\bullet}$ from R^3H, referenced to 2-methylpropane $\rightarrow$ *t*-Bu$^\bullet$ as zero.[1,2] Values for 1-adamantyl, 1-bicyclo[2.2.2]octyl, and 1-norbornyl are 2.4, 4.0, and 7.7 kcal mol^{-1}, respectively. We wish now to report a simpler procedure for obtaining relative $\Delta\Delta$strain values by the same reaction and its application to the study of some new radicals.

In view of the disagreement between $\Delta\Delta$strain values estimated by correlating the above data with tosylate solvolysis activation energies[1] and those predicted by MM2 calculations[3,4] with force fields parametrized for radicals, it was interesting to investigate 1-homoadamantyl (1-HA), 1-bicyclo[3.2.2]nonyl ([322]) and 1-bicyclo[3.3.1]nonyl

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