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.

(12) Ireland, R. E.; Norbeck, D. W. *J. Org. Chem.* **1985**, *50*, 2198.

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

(1) Lomas, J. S. *J. Org. Chem.* **1985**, *50*, 4291.
(2) Lomas, J. S.; Dubois, J.-E. *Tetrahedron Lett.* **1983**, *24*, 1161.

0022-3263/87/1952-2627$01.50/0

Table I. Relative Yields from the Thermolysis of $R^1R^2R^3COH$ (R^2 = *t*-Bu) at 200 °C[a]

	R^3 = 1-HA		R^3 = [322]		R^3 = [331]	
R^1	*a*%	$\Delta\Delta G^{\ddagger}$	*a*%	$\Delta\Delta G^{\ddagger}$	*a*%	$\Delta\Delta G^{\ddagger}$
Nor[b]	18.0 ± 0.3	1.43	42.8 ± 0.4	0.27	33.5 ± 0.2	0.64
Oc[c]	29.8 ± 0.4	0.81	54.6 ± 0.2	−0.17	30.9 ± 0.3	0.76
t-Bu	16.8 ± 0.9	0.85	37.1 ± 0.5	−0.15	15.7 ± 0.2	0.86

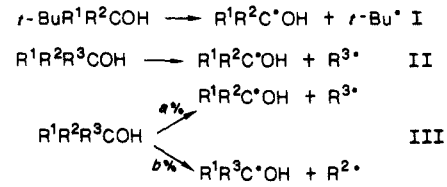
[a] Reaction III, Scheme I. *a*% is listed; *b*% = 100 − *a*%; $\Delta\Delta G^{\ddagger}$ (kcal mol^{-1}) = $-RT \log_e (a/b)$, where *b* is statistically corrected when R^1 = *t*-Bu. [b] 1-Norbornyl. [c] 1-Bicyclo[2.2.2]octyl; in toluene, all others in mesitylene.

Table II. Strain Energies (kcal mol^{-1}) of Secondary Alcohols and Alkanes[a]

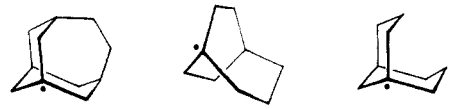
	SE(R^1R^3CHOH)				$\Delta\Delta$strain(R^3), kcal mol^{-1}						
R^3	R^1 = Nor	R^1 = Oc	R^1 = *t*-Bu	SE(R^3H)	R^1 = Nor	R^1 = Oc	R^1 = *t*-Bu	mean	solv[b]	MM2[c]	MM2[d]
1-HA	46.59	46.67	32.97	20.58	1.49	1.42	1.24	1.4	1.6	0.8	−0.8
[322]	44.97	44.66	30.90	18.31	1.00	0.72	0.46	0.7	1.8	−1.2	−2.7
[331]	39.27	38.71	25.16	12.32	1.66	1.68	1.70	1.7	1.4	0.3	−1.4
SE(R^1R^2CHOH)	25.92	25.46	11.98								

[a] $\Delta\Delta$strain from eq 9, estimated from solvolysis correlation and predicted by Allinger and Beckhaus force fields (R^2 = *t*-Bu). [b] Reference 1. [c] Reference 3; our calculations. [d] Reference 4.

Scheme I



([331]) radicals, **1**–**3**, respectively, all of which, according to the Beckhaus force field,[4] should have negative values, i.e. the radical less strained than the alkane.



1 2 3

Appropriate carboxylic acids[5] were converted to alkyl *tert*-butyl ketones by CuCl-catalyzed condensation of the acid chlorides with *t*-BuMgCl in ether.[6] Barbier reaction[7] of 1-bromobicyclo[2.2.2]octane or 1-bromonorbornane with the ketones or *t*-BuLi addition gave the required tertiary alcohols. Thermolysis at 200 °C in degassed mesitylene or toluene gave mixtures of ketones and secondary alcohols which were analyzed by GLC as described previously.[1] Results are given in Table I and were interpreted as follows.

In reaction III (Scheme I), where two radicals are formed from the same tertiary alcohol, we have for $R^{3\bullet}$ eq 3 and for $R^{2\bullet}$

$$\Delta\text{strain}_{\text{calcd},R^2} = \text{SE}(R^1R^2R^3\text{COH}) - \text{SE}(R^1R^3\text{CHOH}) - \text{SE}(R^2\text{H}) \quad (4)$$

Subtracting eq 4 from 3 gives

$$\Delta\text{strain}_{\text{calcd},R^3} - \Delta\text{strain}_{\text{calcd},R^2} = \text{SE}(R^1R^3\text{CHOH}) + \text{SE}(R^2\text{H}) - \text{SE}(R^1R^2\text{CHOH}) - \text{SE}(R^3\text{H}) \quad (5)$$

If the product ratio, statistically corrected if necessary, at *T* (K) is *a*/*b*, then

$$\Delta G^{\ddagger}(R^3) - \Delta G^{\ddagger}(R^2) = \Delta\Delta G^{\ddagger} = -RT \log_e (a/b) \quad (6)$$

Combining eq 1′ with 6 gives

$$\Delta\text{strain}_{\text{expt},R^3} - \Delta\text{strain}_{\text{expt},R^2} = -\Delta\Delta G^{\ddagger}/1.02 \quad (7)$$

Consequently, by subtraction of eq 7 from 5

$$\Delta\Delta\text{strain}(R^3) - \Delta\Delta\text{strain}(R^2) = \text{SE}(R^1R^3\text{CHOH}) + \text{SE}(R^2\text{H}) - \text{SE}(R^1R^2\text{CHOH}) - \text{SE}(R^3\text{H}) + \Delta\Delta G^{\ddagger}/1.02 \quad (8)$$

which, when R^2 is *t*-Bu, simplifies to

$$\Delta\Delta\text{strain}(R^3) = \text{SE}(R^1R^3\text{CHOH}) - \text{SE}(R^1R^2\text{CHOH}) - \text{SE}(R^3\text{H}) + \Delta\Delta G^{\ddagger}/1.02 \quad (9)$$

Since the sum of the first three terms is generally not greater than about 1 kcal mol^{-1} and since neither *a* nor *b* must be too small for accurate determination, this approach is limited to $\Delta\Delta$strain differences less than about 2.5 kcal mol^{-1}, as is the case here.[8]

Strain energies (MM2 force field), derived values of $\Delta\Delta$strain and estimated (from solvolysis rates) or calculated values are listed in Table II. Consistent values close to 1.7, 1.4, and 0.7 kcal mol^{-1} are obtained for **3**, **1**, and **2**, respectively. The two adamantane-like radicals have $\Delta\Delta$strain values only a little below that of adamantane itself, whereas the more flexible radical, **2**, is only slightly more strained than the corresponding alkane. The former values are in good agreement with the estimates from the solvolysis correlation,[1] both being somewhat higher than the values calculated from the radical force fields.[3,4] The value for **2**, while smaller than the solvolysis estimate (1.8 kcal mol^{-1}), remains substantially greater than that cal-

(3) Allinger, N. L.; Yuh, Y. *QCPE* **1980**, *12*, 395 (parameters for alkyl radicals are listed in the 1982 version available from Molecular Design Ltd.). Imam, M. R.; Allinger, N. L. *J. Mol. Struct.* **1985**, *126*, 345. It should be noted that the increments for converting steric energies to heats of formation and strain energies are not the same in the 1982 program and the 1985 paper. Heats of formation calculated from the latter will be higher (Me, 0.2; primary, 1.3; secondary, 1.6; tertiary, 0.6 kcal mol^{-1}) and the strain energies of primary and secondary radicals 0.3 kcal mol^{-1} higher than those given by MMP2/1982.

(4) Peyman, A.; Hickl, E.; Beckhaus, H.-D. *Chem. Ber.*, in press. The ΔBDE data (equivalent to $\Delta\Delta$strain) quoted in ref 1 were based on a trial force field (Beckhaus, H.-D., personal communication) which has been abandoned in favor of a version which gives even lower values for the systems studied in this work.

(5) 1-HA: Langhals, H.; Rüchardt, C. *Chem. Ber.* **1974**, *107*, 1245. [322]: Golzke, V.; Langhals, H.; Rüchardt, C. *Synthesis* **1977**, 675. [331]: Colvin, E. W.; Parker, W. *J. Chem. Soc.* **1965**, 5764. Landa, S.; Podrouzkova, B.; Eyem, J. *Collect. Czech. Chem. Commun.* **1970**, *35*, 2515.

(6) Dubois, J.-E.; Boussu, M. *Tetrahedron* **1973**, *29*, 3943.

(7) Lomas, J. S. *Nouv. J. Chim.* **1984**, *8*, 365.

(8) An approximation to eq 8 has been shown to give results for R^2 = Ad and R^3 = Oc closely similar to those obtained by the conventional kinetic procedure.[1]

culated. It appears therefore from this and previous work[1] that both the force fields which have been proposed for alkyl radicals generally underestimate their strain energies, perhaps by even more than our results suggest. Kruppa and Beauchamp have recently proposed for 1-adamantyl, on the basis of PES studies,[9] a value of 3.7 kcal mol^{-1}, as compared to our value of 2.4 kcal mol^{-1} and calculated values of 2.5 and 0.9 kcal mol^{-1} according to the Allinger[3] and Beckhaus[4] force fields, respectively. Bridgehead radicals are apparently more rigid than current force fields, which include a soft out-of-plane bending energy parameter, would imply.

(9) Kruppa, G. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 2162.

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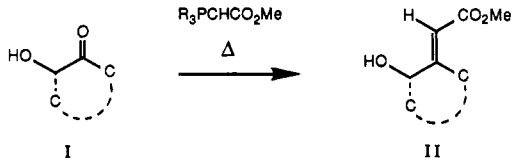
The Stereoselective Synthesis of Acyclic and Exocyclic Trisubstituted Olefins via a Hydroxyl-Directed Wittig Reaction

Summary: Both acyclic and cyclic α-hydroxy ketones undergo an accelerated Wittig reaction with stabilized phosphonium ylides to give *E*-trisubstituted olefins in moderate to good chemical yield.

Sir: The stereocontrolled assembly of tri- and tetrasubstituted olefins—particularly exocyclic ones—is a general problem that continues to attract attention.[1] One impetus for this activity is the incorporation of such moieties in the structures of a variety of interesting natural (and unnatural) products.[2] However there remains a need to develop methodology that is both general and tolerant of sensitive functionality and/or chiral centers which may also be present in such target molecules.

We now wish to report on our observation that both acyclic and exocyclic α-hydroxy ketones such as I undergo an accelerated Wittig reaction with stabilized phosphonium ylides to give the (*E*)-alkenes II selectively in moderate to good chemical yield.[3,4] This simple procedure offers a distinct advantage over related ketone olefination reactions in terms of both mildness and flexibility. A previously unrecognized directing effect of the neighboring hydroxyl group is proposed to account for the enhanced rate and *E* selectivity.[5]



I II

As may be seen from our tabulated results, this reaction has been successfully applied to 3-hydroxy-2-butanone (**1a**), 3-hydroxy-3-methyl-2-butanone (**3a**), 1-hydroxy-2-butanone (**5a**), 2-hydroxycyclohexanone (**12a**), and the highly functionalized pyranone **14a** to give moderate to good yields of the corresponding *E* olefins **2a**, **4a**, **6a**, **13a**, and **15** (entries 1, 2, 7, 10, 18 and 21 Table I).[6,7] In none of these cases was any appreciable amount of the isomeric *Z* olefin (or related material) isolated. It should be noted that compounds **3a** and **5a** reacted much more slowly with Ph_3PCHCO_2Me than the other substrates and required either higher temperatures or the use of a more reactive ylide, n-Bu_3PCHCO_2Me, which was conveniently generated in situ from n-$Bu_3P^+CH_2CO_2Me$ Br^- and Et_3N.[8] The latter procedure proved to be the method of choice for these hindered substrates (compare entries 5–10). On the other hand, Wittig olefination of 1-hydroxy-3-methyl-2-butanone (**7a**) was extremely sluggish and produced product **8a** in only 10% yield under even the best conditions (entries 11–15). In this case a competitive tautomerization occurred and the resulting aldehyde **10** then reacted with ylide to give the disubstituted olefin **11**.[9] The

(1) Recent efforts in this area include: Negishi, E.; Zhang, Y.; Cederbaum, F. E.; Webb, M. B. *J. Org. Chem.* **1986**, *51*, 4082. Corey, E. J.; Siebel, W. L. *Tetrahedron Lett.* **1986**, 905, 909. Shibasaki, M.; Sodeoka, M. *Ibid.* **1985**, 3491. Koreeda, M.; Patel, P. D.; Brown, L. *J. Org. Chem.* **1985**, *50*, 5910. Larson, G. L.; Prieto, J. A.; Hernandez, A. *Tetrahedron Lett.* **1981**, 1575. Srekumar, C.; Darst, K. P.; Still, W. C. *J. Org. Chem.* **1980**, *45*, 4262.

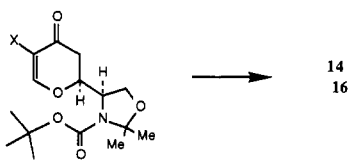
(2) Examples of both natural and unnatural products that contain exocyclic olefins of this type include the following. The bryostatins: Pettit, G. R.; Kamano, Y.; Herald, C. L.; Tozawa, M. *J. Am. Chem. Soc.* **1984**, *106*, 6768 and references therein. Zoapatonol: Levine, S. D.; Adams, R. E.; Chen, R.; Cotton, M. L.; Hirsch, A. F.; Kane, V. V.; Konajia, R. M.; Shaw, C.; Wachter, M. P.; Chin, E.; Huttermann, R.; Ostrowski, P. *Ibid.* **1979**, *101*, 3404. The carbocyclins: Bartman, W.; Beck, G. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 751.

(3) In a reaction which complements ours, (triphenylphosphorylidine)ketene reacts with α-hydroxy ketones to give butenolides though the intermediate is in fact an acylated α-hydroxy ketone: Bestmann, H. J. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 115. Nickisch, K.; Klose, W.; Bohlmann, F. *Chem. Ber.* **1980**, *113*, 2038. The reaction of stabilized ylides with unprotected α-hydroxy aldehydes is well-known: Barrett, A. G. M.; Broughton, H. B. *J. Org. Chem.* **1984**, *49*, 3673. Schoenenberger, B.; Summermatter, W.; Ganter, C. *Helv. Chim. Acta* **1982**, *65*, 2333. Olejniczak, K.; Frank, R. W. *J. Org. Chem.* **1982**, *47*, 380. See also: Bunce, R. A.; Pierce, J. D. *Tetrahedron Lett.* **1986**, 5583.

(4) It has been reported that a variety of protected α-hydroxy 2-, 3-, and 4-keto sugars react smoothly with Ph_3PCHCO_2Et in boiling CH_3CN to give a single (though not always predictable) geometric isomer in each case: Tulshian, D. B.; Tsang, R.; Fraser-Reid, B. *J. Org. Chem.* **1981**, *46*, 3764. The facility of these reactions as compared to our control experiments is understandable since additional oxygen substituents at the α- or α′-position would be expected to make the carbonyl group more electrophilic via inductive activation.

(5) The effect of nucleophilic groups such as alkoxides which are incorporated into (unstabilized) ylides has been investigated and discussed: Maryanoff, B. E.; Reitz, A. B.; Duhl-Emswiler, B. A. *J. Am. Chem. Soc.* **1985**, *107*, 217. Linderman, R. J.; Meyers, A. I. *Tetrahedron Lett.* **1983**, 3043.

(6) Compounds **1a**, **3a**, and **12a** were purchased from Aldrich Chemical Co.; **5a** and **7a** were prepared from 3-methyl-2-butanone and 2-butanone, respectively, by using a bromination/displacement sequence: Guetle, J. P.; Spassky, N.; Boucherot, D. *Bull. Soc. Chim. Fr.* **1972**, 4217. Gaudry, M.; Marquet, A. *Tetrahedron* **1970**, *26*, 5611. Catch, J. R.; Elliott, D. F.; Hey, D. H.; Jones, E. R. H. *J. Chem. Soc.* **1948**, 272. **14a** and **16** were prepared in one step from the dihydropyrones **19** and **20** via base-catalyzed conjugate addition of MeOH. Both **19** and **20** are known compounds: Garner, P.; Ramakanth, S. *J. Org. Chem.* **1986**, *51*, 2609. The silyl ethers were generally prepared by using the standard method: Corey, E. J.; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190.



19 (X = OAc)
20 (X = H)

(7) Satisfactory IR, ^1H NMR, and HRMS or combustion analyses have been obtained for these substances. The NMR samples for compounds **14–18** were heated to 60 °C to observe conformer averaged spectra.

(8) Cf.: Trippett, S.; Walker, D. M. *J. Chem. Soc.* **1961**, 1266.

(9) Base-(or acid-)catalyzed tautomerization of α-hydroxycarbonyl compounds is a well-known phenomenon in the carbohydrate field. Cf.: Speck, J. C., Jr. *Adv. Carbohydr. Chem.* **1958**, *13*, 63.

0022-3263/87/1952-2629$01.50/0