J. Am. Chem. Soc. **1985**, *107*, 3669-3676

Stable Simple Enols. 11.[1] Equilibrium Constants for the 1-Alkyl-2,2-dimesitylethenol/1-Alkyl-2,2-dimesitylethanone Systems in Hexane. The Predominance of Steric Effects on K_{enol} Values

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Received December 3, 1984

Abstract: The enol/ketone pairs of 1-alkyl-2,2-dimesitylethenols $Mes_2C{=}C(OH)R$ (**2–5**)/1-alkyl-2,2-dimesitylethanones Mes_2CHCOR (**7–10**), R = Me, Et, *i*-Pr, and *t*-Bu, were synthesized, and their spectral properties were determined. CF_3COOH-catalyzed enol/ketone equilibration in hexane at 353.6 K was followed from both sides and gave similar and accurate equilibrium constants K_{enol} = [enol]/[ketone]. The K_{enol} values for R (20 (H), 0.62 (Me), 0.31 (Et), 0.28 (*i*-Pr), 0.059 (*t*-Bu)) decrease with the bulk of R. Linear $\Delta G°$ vs. E_s and $\Delta G°$ vs. $\Delta G_c^{\ddagger}$ (free energy of activation for enantiomerization via a two ring flip process) of the enol are linear. Consequently, steric effects predominate the equilibria. The role of polar effects was discussed, and the results were compared with those for simple aliphatic uncrowded enols. The reaction of dimesitylketene with *t*-BuBr or *i*-PrBr and Li in ether gave 2,2-dimesitylvinyl dimesitylacetate.

In spite of extensive work on the kinetics and equilibria of keto–enol tautomerism (eq 1) in the past few decades,[2] *accurate* data on the equilibrium constants (K_{enol}) of eq 2 for simple enols were relatively scarce until recently. This is because the equi-

$$R^3R^2CH{-}C({=}O){-}R^1 \overset{K_{\text{enol}}}{\rightleftharpoons} R^3R^2C{=}C(OH)R^1 \qquad (1)$$

$$K_{\text{enol}} = [\text{enol form}]/[\text{keto form}] \qquad (2)$$

librium is so shifted toward the keto form that the enol concentration at equilibrium is too low to be detected directly even by sensitive spectroscopic methods. Consequently, indirect methods which either involve assumptions that have to be verified or are extremely sensitive to small amounts of impurities are used for estimating K_{enol} values.[3-6] Recent progress in the preparation of simple enols[7] enabled the study of some of their properties before their isomerization and measurement of their ketonization rate. Combination of the latter with the enolization rate of the ketone gives accurate K_{enol} values, but at present only a few accurate values were obtained by this method.[7e,g,h]

K_{enol} values for simple open-chain aldehydes and ketones, cyclic ketones, and acetophenones have been studied. Only in the latter two series is the structural variation sufficient to enable estimation of the nature of substituent effects. Values obtained by different methods frequently differ by large factors. For example, ab initio calculations of $\Delta E = E(\text{enol}) - E(\text{ketone})$ for MeCHO gave values between 10.4 and 19.5 kcal mol^{-1},[3a,b,d,e] which, however, were suggested to be overestimated by 6.6 kcal mol^{-1}.[3d] The calculations show that for RCHO, a change from R = Me to Et,[3a] and for MeCOR, a change from R = Me to Et to Pr, reduces ΔE;[3d] i.e., K_{enol} increases for larger alkyl groups.

Most of the methods used in solution are modifications of Meyer's halogenation method.[5a] The ketone is rapidly titrated by halogen which is assumed to react extremely fast with the enol, and the excess halogen is back-titrated before the equilibrium is reestablished.[5] Hence, the method is sensitive to extremely small impurities which also react rapidly with the halogen, and severe discrepancies were found between values determined by different groups.

Another method estimates K_{enol} by assuming that the ketonization rate constant is equal to the hydrolysis rate constant of the methyl enol ether.[6] This assumption is shown to be incorrect by applying LFER for substituent effects and by measuring the two rates for $CH_2{=}CHOR$, R = H and Me.[2,7d]

A relatively accurate method is that of Toullec and Dubois[5i] who halogenated ketones at sufficiently low halogen concentrations when addition is part of the rate-determining step and encounter-controlled. This method gave K_{enol} values for acetophenones which increased on increasing the electron withdrawal by meta or para substituents.[5i] However, the values were significantly smaller than those based on the kinetic estimation method.

The effects of aliphatic substituents directly attached to the enol double bond on K_{enol} are not clear. All the methods agree that for aldehydes (RCHO), K_{enol} increases on increased branching of R, i.e., *i*-Pr > Et > Me.[3,4b,6,7d,g] For dialkyl ketones (RCOR), the order of K_{enol} values determined by Toullec and Dubois is Me < Et > *i*-Pr,[5i] while a thermochemical approach gives Me > Et.[4b] There is no other systematic study for these species. Consequently, the effect of even a single series of alkyl substituents, especially on C_α, on K_{enol} is unknown.

Moreover, most of the K_{enol} values are in polar solvents, mainly in water, so that comparison with the gas-phase data is not straightforward. We know of no study of K_{enol} values in aprotic nonpolar media.

We decided to obtain accurate K_{enol} values for a series of enols where R^2 and R^3 are constant in an aprotic medium in order to evaluate the contribution of the various effects of the alkyl groups

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(3) Calculations: (a) Hehre, W. J.; Lathan, W. A. *J. Chem. Soc., Chem. Commun.* **1972**, 771. (b) Bouma, W. J.; Poppinger, D.; Radom, L. *J. Am. Chem. Soc.* **1977**, *99*, 6443. (c) Bouma, W. J.; Radom, L. *Aust. J. Chem.* **1978**, *31*, 1167, 1649. (d) Noack, W. E. *Theor. Chim. Acta* **1979**, *53*, 101. (e) Bouma, W. J.; Radom, L.; Rodwell, W. R. *Theor. Chim. Acta* **1980**, *56*, 149. (f) Franking, G.; Heinrich, N.; Schmidt, J.; Schwarz, H. *Z. Naturforsch., B; Anorg. Chem., Org. Chem.* **1982**, *37B*, 1597.

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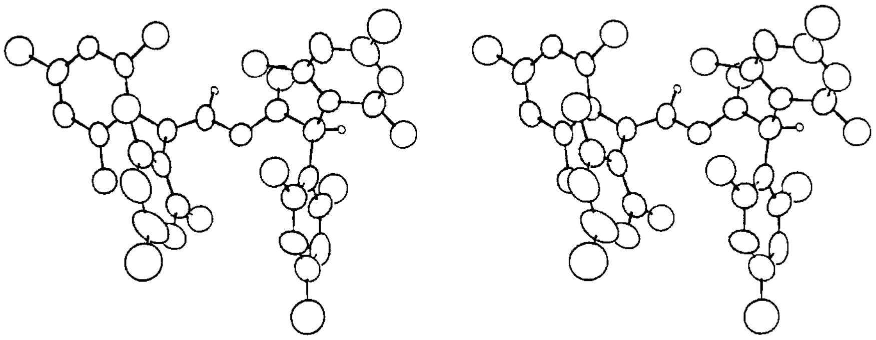
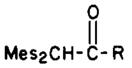


Figure 1. Stereoscopic view of compound **14**.

R^1. Enols substituted by two β-crowded aryl groups were prepared a long time ago by Fuson[8] and are known to be stable.[9] We recently measured several equilibrium constants for several di- and triaryl ethenols[10] and found that the K_{enol} values can be measured conveniently and accurately. We therefore prepared the 1-alkyl-2,2-dimesitylethenols **2–5** and their isomeric ketones **7–10** and measured K_{enol} of eq 1 for each pair from both sides. The K_{enol} value for the pair of 1-hydrogen derivatives **1** and **6** was previously measured.[10c]

Results

Synthesis. Enol **1** was previously prepared by reduction of dimesitylketene **11** with $LiAlH_4$,[11] and the corresponding aldehyde **6** was obtained by oxidation of the corresponding alcohol.[10c] Enol

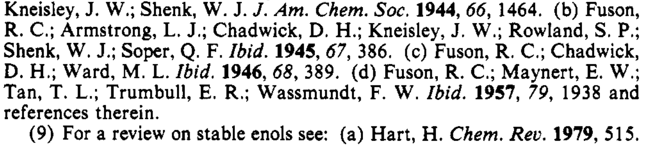


$Mes_2CH\text{-}C(=O)\text{-}R$

$Mes_2C{=}C(OH)R$	$Mes_2CH\text{-}C(=O)\text{-}R$
1: R = H	**6**: R = H
2: R = Me	**7**: R = Me
3: R = Et	**8**: R = Et
4: R = *i*-Pr	**9**: R = *i*-Pr
5: R = *t*-Bu	**10**: R = *t*-Bu

2 was obtained in 70% yield as the exclusive product according to Fuson's method by addition of methylmagnesium bromide to **11**.[8b] However, in attempts to prepare enols **3–5** by a similar method, the only reaction was the reduction of **11** to **1**, presumably by transfer of the β-hydrogen of the Grignard reagent (eq 3). Similar reductions (e.g., with *t*-BuMgBr) were reported by Fuson et al.[8a]

Chastrette and Amouroux who encountered a similar problem in Grignard addition to hindered ketones showed that addition of $LiClO_4$ to the reaction mixture increased the ratio of the adduct to the reduction product.[12] By using a similar approach, the addition of ethylmagnesium bromide to **11** gave a 1:1 ratio of **1** to **3** (eq 4).



$$RCH_2C(-)(-)\text{-}MgX + \underset{\mathbf{11}}{Mes_2C{=}C{=}O} \longrightarrow RCH{=}C\langle + Mes_2C{=}C\langle^{H}_{OMgX} \xrightarrow{H_2O} \underset{\mathbf{1}}{Mes_2C{=}CHOH} \quad (3)$$

However, addition of $LiClO_4$ did not affect the addition of isopropyl- and *tert*-butylmagnesium bromides to **11**, since only **1** was obtained. When the reaction of isopropylmagnesium bromide was conducted in refluxing THF containing $LiClO_4$,[13] isopropyl dimesitylacetate $Mes_2CHCOO\text{-}i\text{-}Pr$ (**12**) was obtained. Reaction of *tert*-butyl bromide under the same conditions resulted only in the formation of dimesitylacetic acid.

$$Mes_2C{=}C{=}O + EtMgBr \xrightarrow{LiClO_4/\text{ether}} \underset{\mathbf{1},\ 50\%}{Mes_2C{=}CHOH} + \underset{\mathbf{3},\ 50\%}{Mes_2C{=}C(OH)Et} \quad (4)$$

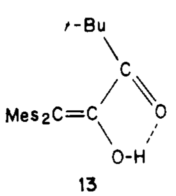
Since reaction of **11** with anhydrous *tert*-butyl alcohol resulted in the isolation of only dimesitylacetic acid,[13] it is possible that a *tert*-butyl ester was initially formed and then converted (thermally or hydrolytically) to the acid.

The enols **4** and **5** were finally obtained by addition of the lithium reagents in ether to **11** at −18 and −40 °C, respectively, without interference from formation of **1** (eq 5).

$$\underset{11}{Mes_2C{=}C{=}O} + RLi \xrightarrow{\text{ether}} \xrightarrow{H_2O} Mes_2C{=}C(OH)R \quad (5)$$

$$\begin{array}{ll} R = i\text{-Pr} & 4,\ 43\% \\ R = t\text{-Bu} & 5,\ 55\% \end{array}$$

When the reaction with *t*-BuLi was repeated at −78 °C in petroleum ether, an additional product was formed. Its IR spectrum showed OH and C=O stretchings at 3300 and 1680 cm^{-1}, respectively, and its ^1H NMR showed one *tert*-butyl group and two mesityl groups and an OH which disappeared in D_2O. The high-resolution (EI) mass spectra showed a molecular peak at m/z 364.2402 consistent with the formula $C_{25}H_{32}O_2$ and cleavage patterns that showed the presence of the Mes_2CH^+ moiety (m/z 251), $MesCO^+$ (m/z 147), and $t\text{-}Bu^+$ (m/z 57; base peak). Chemical ionization mass spectrometry showed the highest peak at m/z 365 (MH^+). Structure **13** is consistent with these data and with the ^{13}C spectrum, as well as with the fact that structurally related enols are known.[14] However, a consistent elementary analysis with this structure was not obtained, and attempts to obtain crystals for X-ray crystallography to solve this problem had failed.



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In attempts to obtain **4** and **5** by a Barbier-type reaction, metallic lithium was added to a mixture of **11** and isopropyl bromide or *tert*-butyl bromide, respectively, in ether at −18 °C. In both cases, an identical unsaturated ester was obtained in

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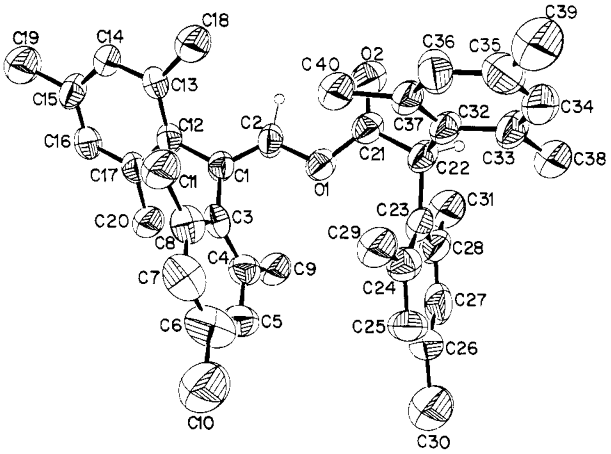
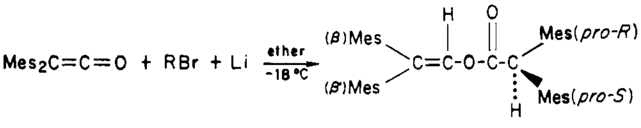
Table I. Important Bond Lengths and Angles for **14**[a,b]



bond	length, Å	angle	deg	angle	deg
O(1)-C(2)	1.408 (6)	C(2)-O(1)-C(21)	116.5 (6)	O(2)-C(21)-C(22)	123.4 (7)
O(1)-C(21)	1.351 (8)	C(2)-C(1)-C(3)	121.4 (7)	C(21)-C(22)-C(23)	113.9 (6)
C(1)-C(2)	1.339 (9)	C(2)-C(1)-C(12)	117.1 (7)	C(21)-C(22)-C(32)	113.3 (6)
C(1)-C(3)	1.486 (9)	C(3)-C(1)-C(12)	121.5 (6)	C(22)-C(23)-C(24)	124.3 (6)
C(1)-C(12)	1.503 (7)	O(1)-C(2)-C(1)	117.1 (6)	C(22)-C(23)-C(28)	117.0 (6)
O(2)-C(21)	1.197 (8)	C(1)-C(3)-C(4)	121.8 (5)	C(22)-C(32)-C(33)	115.4 (6)
C(21)-C(22)	1.517 (7)	C(1)-C(3)-C(9)	120.3 (7)	C(22)-C(32)-C(37)	126.1 (7)
C(22)-C(23)	1.549 (9)	O(1)-C(21)-O(2)	123.6 (8)		
C(22)-C(32)	1.54 (1)	O(1)-C(21)-C(22)	113.0 (6)		

[a] The compound crystallized in the monoclinic $P2_1/c$ space group. The dimensions of the unit cell which contained four molecules are a = 15.137 Å, b = 15.079 Å, c = 15.750 Å, β = 110.02°. The R value is 0.094. [b] C-C bond lengths in the mesityl rings are mostly 1.36–1.40 Å. Exceptions are C(35)-C(36) (1.35 Å), C(3)-C(8) and C(32)-C(33) (1.43 Å), and C(12)-C(13) (1.41 Å). C-Me bond lengths are 1.49–1.52 Å. All the angles within the aromatic ring or of two aromatic carbons and a methyl group are 117.4–123.1°, except for the C(25)-C(24)-C(29) angle which is 115.9 (7)°.

40–44% yield. It was identified as 2,2-dimesitylvinyl dimesitylacetate (**14**) (eq 6) by its UV and IR spectra (λ_{max} = 261 nm (log ϵ = 4.19), ν_{max} = 1730 cm^{-1}) and by its ^{1}H and ^{13}C NMR. Its 70-eV mass spectra showed the highest peak at m/z 280 (corresponding to **1**), and since a dimer of **1** was prepared by Fuson[15] and by Bailey and co-workers[16] by oxidation of **1** and was identified by the latter as 2,2-dimesityl-2-((2,2-dimesitylvinyl)-oxy)ethanal,[16] an unequivocal structural determination was obtained by X-ray crystallography.



$$\mathrm{Mes_2C{=}C{=}O + RBr + Li \xrightarrow[-18\,^\circ C]{ether} ({\beta})Mes({\beta'})Mes\,C{=}C(H){-}O{-}C(=O){-}CH\,Mes(\mathit{pro\text{-}R})\,Mes(\mathit{pro\text{-}S})} \qquad (6)$$

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Important bond lengths and angles of **14** together with the numbering scheme are given in Table I. A stereoscopic view is given in Figure 1. Other crystallographic data are given in the supplementary Tables S1–S4. It can be seen that in the solid state, the conformation is a propeller conformation where all the four rings are twisted in the same direction. The torsional angles are defined by the C(ortho)-C(ipso)-C(sp^2)-C(sp^2) planes for the rings attached to the double bond and by the C(ortho)-C(ipso)-C(sp^3)-H planes for the other two rings. They are 58° for the β-mesitylvinyl and 61° for the β'-mesitylvinyl groups, whereas the torsional angles of the *pro-R* and the *pro-S* rings are 36° and 33°, respectively. The twist angle of the double bond is 11°, and the plane of the carbonyl group deviates from that of the double bond by 25°.

In a preliminary experiment to determine the source of the hydrogens of **14**, the reaction mixture was neutralized at the end of the reaction with D$_2$O/DCl. The ^{1}H NMR spectrum of the product was identical with that of **14** from neutralization with HCl/H$_2$O, indicating the absence of deuterium incorporation.

Table II. UV Spectra in Hexane

enol	λ_{max}, nm (log ϵ)	ketone	λ_{max}, nm (log ϵ)
1[a]	210 (4.52), 252 (4.23)	**6**[b]	220 (4.28), 267 (3.08)
2	207 (4.52), 256 (4.23)	**7**	207 (4.54), 264 (2.83)
3	207 (4.52), 256 (4.17)	**8**	205 (4.55), 264 (3.76)
4	206 (4.53), 256 (4.11)	**9**	209 (4.58), 262 (3.54)
5	201 (4.74), 257 (4.04)	**10**	207 (4.61), 262 (3.91)

[a] Rodebush and Feldman [Rodebush, W. H.; Feldman, I. *J. Am. Chem. Soc.* **1946**, *68*, 896] reported λ_{max} (hexane) 253 nm (4.23). [b] Data from ref 10c.

The ketones **7–10** were prepared by a CF$_3$COOH-catalyzed ketonization of the enols in hexane (eq 7).

$$\underset{\mathbf{2\text{–}5}}{\mathrm{Mes_2C{=}C(OH)R}} \xrightarrow[\text{hexane, reflux}]{\mathrm{CF_3COOH}} \underset{\mathbf{7\text{–}10}}{\mathrm{Mes_2CHCOR}} \qquad (7)$$

Separation of the ketone/enol mixtures formed was aided by the fact that the ketone always precipitated first on crystallization from ethanol.

Structure Determination and Spectral Properties. Since stable simple enols are still uncommon,[9] an unequivocal structural determination was desired in spite of the availability of the isomeric ketones and the equilibrium studies. Hence, the structures of **1–3** and **5** were determined by X-ray crystallography. Whereas the details will be given elsewhere,[17] it is sufficient to mention that the conformation of all the enols is that of a two-bladed propeller.

The UV spectra of **1–10** are of interest, both for evaluating the auxochromic effect of the OH group and for deciding whether the difference in the UV spectra of the ketones and enols enables the determination of K_{enol} values at low concentrations. The data are given in Table II. Both λ_{max} (252–257 nm) and log ϵ (4.04–4.23) values for the enols are only slightly sensitive to the nature of R. The lowest log ϵ is for **5**, the enol with the bulkier

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(17) Nugiel, D. A.; Biali, S. E.; Rappoport, Z.; Kaftory, M., unpublished results.

Table III. ^{13}C NMR Data for $Mes_2C{=}C(OH)R$ in $CDCl_3$ at 223 K[a]

assignment	enol 1	2	3	4	5
β- and β′-*o-Me*	20.95, 20.84 20.69, 20.54	20.77	20.86	20.86	28.74
β- and β′-*p-Me*	21.41, 22.69	20.92	20.86	21.38	28.74
C_β	112.77	109.51	108.07	106.68	107.47
Mes–*C*–H	129.42, 129.54	129.04	128.39	128.26	128.01
Mes–*C*–H	130.39, 130.75	129.85	129.12	129.17	129.80
Mes–ipso-*C*	134.23	132.32	130.25	130.20	132.82
Mes–ipso-*C*	135.69	135.30	131.67	131.69	135.23
Mes–*C*–Me	136.80, 137.08	135.49	134.86	134.73	135.55
Mes–*C*–Me	137.55	136.61	135.40	135.23	136.33
Mes–*C*–Me	137.95	138.42	136.50	136.37	138.80
Mes–*C*–Me	138.27	139.01	138.44	138.42	139.61
C_α	143.89	148.91	153.17	155.69	156.19
R		17.29	12.11[b] 24.35[c]	17.86[b] 29.53[d]	28.74[b] 37.46[e]

[a] TMS as an internal standard. [b] *Me* signal. [c] CH_2 signal. [d] *C*H signal. [e] *C*–Me_3 signal.

R, and this reflects the highest extent of deconjugation of the Mes and the C=C chromophores, as was indeed observed in the solid state.[17] Comparison with log ε for the higher λ_{max} of diphenylethylene (248 nm (4.15))[18] does now show the expected strong auxochromic effect of the OH group. However, the latter effect is superimposed on a decrease in ε due to the higher torsional angles of the β-aryl rings in **1–5**,[17] compared with diphenylethylene,[19] making difficult the evaluation of the effect of the OH group alone on the spectrum.

The long-wavelength maxima λ_{max} of the ketones decrease slightly, and the trend in ε is to increase with the increased bulk of R. Most of the log ε values are much higher than expected (2.83–3.91) for a nonconjugated carbonyl group, even when the contribution of the Mes_2CH moiety to log ε is subtracted from the observed values. A tentative explanation with no independent evidence is a charge-transfer interaction between the RCO and the Mes_2C moieties.

The ^{1}H NMR spectra at room temperature are consistent with the suggested structure. Since a dynamic NMR probes in the enols which takes place at a lower temperature[20] will be discussed in great detail elsewhere,[21] we will present the ^{1}H NMR spectra of **2–5** there in order to avoid duplication.

The decoupled ^{13}C NMR spectra of the enols **2–5** at 223 K show broad signals due to the presence of a dynamic process. Since 223 K is above the coalescence temperature of all the signals, a different signal for each carbon was not observed. The coalescence temperature for **1** is higher, and separate signals for each carbon were observed (Table III). An unequivocal assignment of each signal was not obtained due to extensive overlap of signals in the coupled spectra. The assignment was therefore based on analogy with the ^{13}C spectrum of trimesitylethenol (**15**).[22] The chemical

$$\underset{\textbf{15}}{Mes_2C{=}C(OH)Mes} \qquad \underset{\textbf{16}}{R^1R^2C{=}CHOH}$$

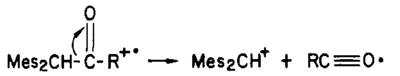
shifts of C_α and C_β are interesting since the only previous values are those for the vinyl alcohols **16**, $R^1 = R^2 = H$ or Me[7d,i] (e.g., for **16**, $R^1 = R^2 = H$; C_α 149 Hz, C_β 94.4 Hz)[7d] and for **15** (C_α 148.77 Hz; C_β 114.55 Hz).[22] In **2–5**, C_α is shifted upfield and C_β is shifted downfield compared with the values for **15**. The shifts of C_α and C_β increase with the bulk of R, except for $\delta(C_\alpha)$ for **4** and **5** where the order is reversed. This is the opposite trend for that found for **16** with the increased bulk at cis position to the OH.[7i] The disubstituted enol **1** differs from the other enols since C_α is lower than for **15** and the effect on C_β is larger than for the other enols. The dependence of $\delta(C_\alpha)$ and $\delta(C_\beta)$ on the bulk of R is ascribed to the contribution of structure **17b** in which

$$\underset{\textbf{17a}}{Mes_2C{=}C(OH)R} \leftrightarrow \underset{\textbf{17b}}{Mes_2\bar{C}{-}C({=}O^{+}H)R}$$

C_β is negatively charged, while C_α is attached to a positively charged atom, and hence the signals of C_α and C_β are shifted to a higher and a lower field, respectively. The elongation of the C_α–C_β bond reduces the interaction between the alkyl and the β-aryl group, and the contribution of **17b** should become more significant for the bulkier R's.

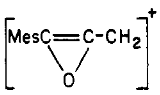
When the temperature was raised to 296 K, the signals of **2** in $CDCl_3$ were shifted to a lower field. The Δδ values were +0.33 ppm for C_α and +0.49 for C_β. In Me_2SO-d_6 the Δδ values were −1.34 ppm for C_β and +0.23 ppm for C_α.

The base peak in the electron impact mass spectra of the enols is the molecular peak, and for the ketones it is *m/z* 251 (Mes_2CH^+). This fits the lower heat of formation of the enol radical ion in the gas phase[10a] and the possibility of a direct α-cleavage in the ketones (eq 8) to give the stable Mes_2CH^+ ion.

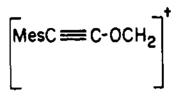


$$Mes_2CH{-}\overset{O}{\overset{\|}{C}}{-}R^{+\bullet} \longrightarrow Mes_2CH^{+} + RC{\equiv}O^{\bullet} \qquad (8)$$

In the mass spectra of **2** (and with lower intensity for **3**), a peak of relatively high abundance appears at *m/z* 173. Speculations suggest the alternative structures **18** and **19** but further studies are required for a more definite assignment.



18



19

Equilibration Studies. The keto ⇌ enol equilibration was studied in hexane at 353.6 K. This was the optimal temperature for obtaining the equilibrium values in reasonable times without severe interference from side reactions. In equilibrations in daylight, small new spots were detected on a TLC plate and new signals appeared in the NMR spectra. Consequently, the reaction was studied in the dark in the presence of a catalytic amount of CF_3COOH (eq 9) in order to accelerate the establishment of the equilibria. K_{enol} remained unchanged when the catalyst con-

$$Mes_2CHCOR \xrightleftharpoons{K_{enol},\ CF_3COOH,\ hexane} Mes_2C{=}C(OH)R \qquad (9)$$

centration was increased 5-fold in the reaction of **2**. The NMR spectra of each ketone/enol pair is different with significant overlap of the Mes signals, but the most convenient probe was the integration of the two separate signals of the methyl groups of R. K_{enol} values were calculated from these ratios. In each case, the equilibrations were studied by starting from either the ketone or the enol. The compositions were determined at different times until similar time-independent compositions were obtained from both sides. The K_{enol} values, their errors (judged by repeated integrations of different points at equilibrium), their average values for reactions from both sides, and the derived $\Delta G°$ values are given in Table IV.

Ketones **7–9** can enolize in two directions, but the isomeric enols $Mes_2CHC(OH){=}CR^1R^2$ (R^1, R^2 = H or Me) were never detected by NMR.

Discussion

In addition to the synthesis of few additional simple enols the important features of our results concern the K_{enol} values. These include their magnitude, accuracy and steric and electronic effects on them, comparison of aliphatic and aromatic substituted enols

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[19] The calculated torsional angles in diphenylethylene are 30° and 30°: Stegemeyer, H.; Rapp, W. *Ber. Bunsenges. Phys. Chem.* **1971**, *75*, 1165.

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[21] Nugiel, D. A.; Biali, S. E.; Rappoport, Z., unpublished results.

[22] Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1984**, *106*, 477.

Table IV. K_{enol} Values for 1-Alkyl-2,2-dimesityl Systems in Hexane at 353.6 K[a]

R	equilib	K_{enol} from enol side	K_{enol} from keto side	K_{enol} av	% enol at equilib	$\Delta G°$, kcal mol^{-1}
H[i]	**1** ⇌ **6**	20.5 ± 0.5	19.3 ± 0.5	20 ± 1	95 ± 2	−2.1 ± 0.1
Me	**2** ⇌ **7**	0.65 ± 0.02[b,c]	0.62 ± 0.01[b,c]	0.64 ± 0.02	39 ± 1	0.32 ± 0.01
Et	**3** ⇌ **8**	0.30 ± 0.02[b,c]	0.31 ± 0.01[b,c]	0.31 ± 0.02	24 ± 1.5	0.83 ± 0.05
i-Pr	**4** ⇌ **9**	0.28 ± 0.005[c,d]	0.27 ± 0.005[c,e]	0.28 ± 0.02	22 ± 8	0.90 ± 0.05
t-Bu	**5** ⇌ **10**	0.0057 ± 0.0005[f,g]	0.0061 ± 0.0005[f,h]	0.0059 ± 0.0005	0.6 ± 0.06	3.63 ± 0.24

[a] Substrate = 8.5 mM; catalyst 0.25%, CF_3COOH (0.4 mM). [b] Points were taken after 14, 18, 24, 36, and 48 h. [c] Equilibrium mixture was present after 14 h. [d] Points were taken after 10, 20, 32, and 44 h. [e] Points were taken after 6, 18, 24, and 36 h. [f] Points were taken after 2, 4, 6, 18, and 32 h. [g] Equilibrium was achieved after 6 h. [h] Points were taken after 3, 6, 18, and 35 h. [i] Data from ref 10c.

and analogy of the trends for crowded and uncrowded enols, the possibility of obtaining K_{enol} values by extrapolation, and the fact that the values were measured in aprotic media.

Accuracy of the K_{enol} Values. A most satisfactory aspect of our results is the accuracy of our values. This is not at all obvious since literature K_{enol} values for the same substrate often differ by more than an order of magnitude,[2] so that discussion of quantitative and qualitative trends is frequently unwarranted. The reason is that the very low enol concentrations are determined by indirect methods which are subject to large errors.[2] Moreover, determination of K_{enol} values involves assumptions (e.g., that halogen addition to the enol is encounter-controlled) which have to be validated for each new system, and the encounter-controlled rate constant is taken from other sources.[5i,j]

In contrast, our values which are based on actual observation of the two species at equilibrium are much more accurate. Since the same value was obtained by approaching the equilibrium from both sides, errors due to a very slow equilibration are excluded. Consequently, we believe that our values are the best obtained so far for any series of enol/ketone pairs.

However, our ^{1}H NMR detection method gives relatively accurate values only within the relatively narrow range of [enol]/[ketone] ratios of 100–0.1. Our value for the **5**/**10** system is already out of this range, and the error is larger than for the other pairs. Other detection methods will be needed if the present series is to be extended to bulkier R's.

Magnitude of the K_{enol} Values. Contribution from the Solvent Effect. Our K_{enol} values are distinguished by their high magnitude. They are similar or even higher than the K_{enol} values for acetylacetone or ethyl acetoacetate[23] and higher by orders of magnitude than those of aliphatic or aromatic uncrowded enols. For example, log K_{enol} values in water for acetophenone, acetaldehyde, and acetone are −7.90,[7b] −6.55,[7e] and −8.22,[7g] respectively, while log K_{enol} values for the β,β-dimesityl analogues $Mes_2C{=}C(OH)Ph$, **1**, and **2** are 0.0,[24] 1.3,[10c] and −0.9, respectively, in hexane. These differences of 8 orders of magnitude include substituent, solvent, and temperature effects. The solvent effect should be important since enols are stabilized much more than ketones by hydrogen bonding to the solvent,[24,25] and the values above for the uncrowded enols are in water while our values are in hexane.

A rough estimation of the solvent effect on K_{enol} values is obtained from the only study of solvent effect on K_{enol} for the aryl-substituted acenaphthenol–acenaphthenone series,[25] a system structurally similar to ours. K_{enol} changes from 2.6 in Me_2SO to ≤ 0.006 in hexane, i.e., 4 kcal mol^{-1}, were attributed to the hydrogen-bonding effect.[25] We predict that our K_{enol} values will be 10^2–10^3 higher in water than in hexane; i.e., K_{enol} values for the β,β-dimesityl-substituted enols are $\geq 10^{10}$ times higher than for simple aliphatic enols.

These large differences raise three related questions. First, why are the mesityl-substituted enols so stable compared with the aliphatic enols? Is this only an enol stabilization effect or is it coupled with destabilization of the ketones? Second, are the effects of the mesityl and the alkyl groups steric or electronic? Third, are the high values for our enols useful for studying properties of simpler enols or are the effects in the two families different?

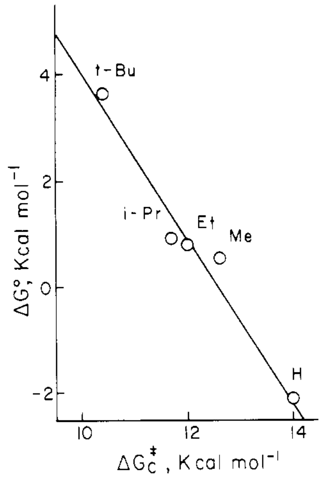

Figure 2. Plot of $\Delta G°$ values for the $Mes_2CHCOR \rightleftharpoons Mes_2C{=}C(OH)R$ equilibration vs. Taft's E_s values.

Substituent Effects on K_{enol} in 1-Alkyl-2,2-dimesityl Systems. The K_{enol} value decreases by 3300-fold ($\Delta\Delta G° = 5.7$ kcal mol^{-1}) from the 1-H (**1**/**6**) to the 1-*t*-Bu (**5**/**10**) system. The change in the five systems is sufficiently large to enable separation of steric and polar effects, provided that one of them is dominant. A plot of $\Delta G°$ vs. Taft's steric parameter E_s[26] shows good linearity (Figure 2) with a slope of −2.0 and a correlation coefficient $r = 0.991$. Similar plots of $\Delta G°$ vs. Charton's steric parameters ν[27] or vs. Dubois' modified E_s' values[28] are also linear with $r = 0.989$. In contrast, a plot of $\Delta G°$ vs. Taft's σ^* values[29] in nonlinear with $r = 0.922$ for the best line. From both the linearity with E_s values and the appreciable slope, and since the differences in the polar effects of the alkyl groups are either small (as judged by the σ^* values)[29] or nonexistent,[30] we conclude that the main effect of the substituent R on the change in K_{enol} values is steric. The polar effects are either small or constant along the series.

Preliminary results for the $Mes_2C{=}C(OH)C_6H_4X$/$Mes_2CHCOC_6H_4X$ (X = meta or para substituent) where the steric effect is constant gave Hammett's ρ value > 1.[24] Consequently, if the difference in the σ^* values is real, the electronic effect is expected to reduce K_{enol} in our system with the increase in the bulk of R; i.e. the electronic and steric effects operate in the same direction.

The decrease in K_{enol} on increasing the bulk of the α substituent contrasts previous observations on K_{enol} values in triaryl-substituted systems. Fuson's generalizations[8b] give the impression that a more bulkier substituent makes the enol isolable; i.e., increased bulk results in a higher K_{enol}. This was quantitatively corroborated for

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(24) Nadler, E. B. N.; Rappoport, Z., unpublished results.

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(26) Taft, R. W., Jr. *J. Am. Chem. Soc.* **1953**, *75*, 4538.

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(29) Taft, R. W., Jr. *J. Am. Chem. Soc.* **1952**, *74*, 2729.

(30) Earlier references were summarized by: Shorter, J. In "Advances in Linear Free Energy Relationships"; Chapman, N. L., Shorter, J., Eds.; Plenum Press: London and New York, 1972; Chapter 2. For summary of recent references but opposite view see: Hanson, P. *J. Chem. Soc., Perkin Trans. 2* **1984**, 101.

the 1-aryl-2,2-dimesityl systems **19**/**20** where K_{enol} (eq 10) in-

$$\underset{\mathbf{19}}{\mathrm{Mes_2CHC({=}O)Ar}} \overset{K_{\mathrm{enol}}}{\rightleftharpoons} \underset{\mathbf{20}}{\mathrm{Mes_2C{=}C(OH)Ar}} \qquad (10)$$

creases with the increased bulk of the α-aryl group.[10b,c,31] Clearly, the combined steric and polar effects for aliphatic and aromatic substituents on K_{enol} values is opposite: bulk increases K_{enol} for bulky aromatic and decreases it for bulky aliphatic substituents.

Another interesting difference is that for simple aliphatic enols RCHO, all the methods show that branching at the β-position increases K_{enol}.[3,4b,6] A more appropriate comparison is with enols of ketones, and for RCOR, R = Me, Et, and *i*-Pr, the most reliable log K_{enol} values in water from one source are −8.46, −7.68, and −8.05.[5i] If these values are "corrected" for the increase of K_{enol} by the β-alkyl group, by using the data for RCHO, then α-alkyl substituents reduce K_{enol} values, as found in our system. Moreover, for substituted acetophenones, the ρ value for K_{enol} in water[5i] is close to ours.[24] Consequently, the effects of α-alkyl groups seem similar in the simple aliphatic and in the crowded β,β-dimesityl-substituted systems. Indeed, the quantitative change in K_{enol} from R = H to Me to Ph in our system in hexane is only slightly smaller than for the $H_2C{=}C(OH)R$ system in water. *The important conclusion at present is that our accurate data in hexane could be used for generalizing the substituent effects on the stabilities of less crowded and aliphatic enols in water.* We generalize that an α-alkyl substituent in a keto–enol system will decrease K_{enol} by its steric effect.

For understanding the magnitude and the trend of the K_{enol} values, two effects are important: (i) The double bond of the enols is shorter than the single C(1)–C(2) sp^3–sp^2 bond in the ketones (since the steric compression energy will be larger for the bulkier aliphatic substituents, the relative percentage of the ketones with the bulkier R's will increase, as was observed) and (ii) the polar effect of alkyl groups should be mainly hyperconjugative and more important when the double bond is more polar, i.e., in the ketones.

For example, the calculated stabilizing energies (HF-4-31G) of CH_3 with C═C (in propene) and with C═O (in acetaldehyde) are 3.9 and 10.4 kcal mol^{-1},[32] respectively. The respective experimental values (5.3 and 9.7 kcal mol^{-1})[33] are in the same order. C–C hyperconjugative stabilization is more important than C–H hyperconjugative stabilization in carbenium ions,[34] and if this also applies for the polar carbonyl group, we expect again that the bulkier R will stabilize the ketone better. Consequently, both steric and hyperconjugative effects can account for the observed trend, but the linearity of $\Delta G°$ with E_s is consistent with predominance of the former. Otherwise the differential hyperconjugative stabilizations (C═O vs. C═C) of the alkyl group should also be linear with E_s, but the hyperconjugative effect should increase approximately linearly with the number of β-C–C bonds, while the increase in E_s values is "telescopic" with regard to the number of such bonds. More information on this point could be gained if reliable K_{enol} values for systems MesC(R)═C(OH)Mes would be available.[35]

We postpone the answer to the question why the K_{enol} values are so high until more K_{enol} values will be available. The presence of the bulky β-mesityl groups is obviously responsible for the high values, but the multiplicity of effects (steric, hyperconjugative, polar, hydrogen bonding) requires the study of additional systems for delineating the contribution of each effect. Steric effects alone cannot serve as the explanation since the highest K_{enol} obtained so far is for the trimesityl system (**19**/**20**, Ar = Mes),[10c] whereas the bulky aliphatic tri-*tert*-butyl system exists only as the ethanone which is both thermodynamically and kinetically more stable.[36] In hexane, the replacement of the bulky α-mesityl group of the **19**/**20** system, Ar = Mes, by the bulky *t*-Bu group of **5**/**10** results in a 13 000-fold decrease in K_{enol}. Apparently, the change β-Mes → β-*t*-Bu also leads to a lower K_{enol}.

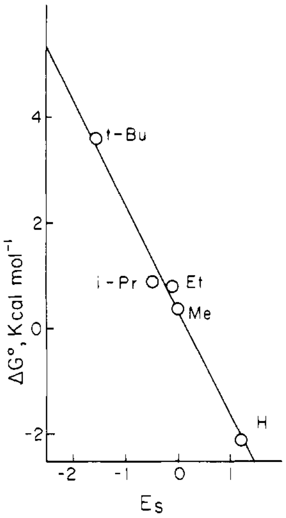

Figure 3. Plot of $\Delta G°$ values for the $\mathrm{Mes_2CHCOR} \rightleftharpoons \mathrm{Mes_2C{=}C(OH)R}$ equilibration vs. $\Delta G_c^{\ddagger}$ for the two ring flip enantiomerization of $\mathrm{Mes_2C{=}C(OH)R}$.

Correlation of $\Delta G°$ with Rotational Barriers. The dominant role of steric effects in determining the K_{enol} values is reminiscent of their importance in determining the rotational barriers in systems **1**–**5**.[20,21] As will be reported elsewhere, $\Delta G_c^{\ddagger}$ values for the two-ring flip of the mesityl rings which leads to coalescence and propeller enantiomerization in **1**–**5** are linearly correlated with E_s values.[21] Consequently, the $\Delta G°$ and the $\Delta G_c^{\ddagger}$ values for the enols are linearly correlated (Figure 3), with a slope of −1.6 and $r = 0.987$. The important conclusion is that unaccessible $\Delta G°$'s and $\Delta G_c^{\ddagger}$'s can be obtained by using this relationship. The limitations is that low $\Delta G°$'s are associated with low $\Delta G_c^{\ddagger}$'s, and it is difficult to obtain the latter by DNMR method. If lower $\Delta G°$ values could be obtained by using a method different from NMR, low rotational barriers could be obtained from Figure 3.

Side Products. **12**, **13**, and **14** were obtained as side products during the synthesis of the enols. The source of the oxygen of **12** and **13** and the extra carbon of **13** is not clear.[37] The most plausible route for formation of **14** is reduction of **11** by the lithium reagent to the enolate of **1**, which then adds to a second molecule of **11**, followed by protonation and ketonization (eq 11).

$$\underset{\mathbf{11}}{\mathrm{Mes_2C{=}C{=}O}} \xrightarrow{t\text{-BuLi}} \mathrm{Mes_2C{=}CHO^-} \xrightarrow{\mathrm{Mes_2C{=}C{=}O}}$$

$$\mathrm{Mes_2C{=}CH{-}O{-}C({-}O^-){=}Mes_2} \xrightarrow{H^+} \rightarrow \mathbf{14} \qquad (11)$$

However, since the **14** formed by neutralization with DCl/D_2O does not contain an sp^3-D, this mechanism is incorrect.[38]

Experiment Section

General Methods. Melting points were determined with a Thomas-Hoover apparatus and are uncorrected. Infrared spectra were taken with a Perkin-Elmer 157G spectrometer and UV spectra were measured with a 2000 Bausch & Lomb Spectronic spectrophotometer. The UV data are given in Table II. Mass spectra were recorded with a MAT-311 instrument at 70 eV. The X-ray diffraction of a single crystal of **14** was measured on a PW1100 Philips four-circle computer-controlled diffractometer equipped with a five-focus Mo X-ray tube and a graphite crystal monochromator in the incident beam.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker WH-300 pulsed FT spectrometer operating at 300.133 and 75.46 MHz for ^{1}H and ^{13}C, respectively. The ^{1}H NMR samples were prepared by dissolving ca. 20

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[31] Biali, S. E.; Rappoport, Z., unpublished results.

[32] Radom, L.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 289.

[33] For collection of data, see Table VII in ref 32.

[34] Radom, L.; Poppinger, D.; Haddon, R. C. In "Carbonium Ions"; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1976; Vol. 5, Chapter 38.

[35] Synthesis of these systems is now under work in our laboratory.

[36] Tidwell, T. T. *Tetrahedron* **1978**, *34*, 1855.

[37] The possibility that $LiClO_4$ oxidizes the Grignard reagent to ROMgBr (which presumably adds to **11**) was suggested by Prof. H. Hart (personal communication).

[38] Careful integration of the methyl and methine signals of the sample quenched with DCl/D_2O showed that the incorporation of deuterium at either the sp^2 or the sp^3 position is ≤5%.

mg of the compound in 0.5 mL of solvent. The field/frequency regulations were maintained by locking to the solvent's deuterium. The free-induction decay signals were digitized and accumulated on an Aspect 200 computer (32K). The ^{13}C NMR spectra are given in Table III in δ values, using tetramethylsilane as the reference.

Solvents and Materials. Tetrahydrofuran was distilled from sodium benzophenone ketyl under nitrogen immediately before use. Ether was distilled from LiAlH$_4$, and petroleum ether (40–60 °C) was distilled from sodium. In each case, only the middle fraction was collected and stored over 4-Å molecular sieves. The deuterated NMR solvents were the best commercial samples and were used without further purification.

1,1-Dimesityl-1-propen-2-ol (2), mp 90 °C [lit.[8b] mp 97–98 °C], was prepared according to Fuson:[8b] IR (CCl$_4$) ν_{max} 3510 (OH), 1630 (C=C) cm^{-1}; mass spectrum, m/z 294 (M$^+$, 100%), 279 (M – Me, 45%), 251 (Mes$_2$CH$^+$, 29%), 173 (MesC≡COCH$_2$, 24%), 158 (MesC≡C—Me, 11%), 130 (158 – C$_2$H$_4$, 11%). Anal. Calcd for C$_{21}$H$_{26}$O: C, 86.55; H, 8.90. Found: C, 86.45; H, 9.17.

1,1-Dimesitylacetone (7), mp 140 °C [lit.[8b] mp 145–146 °,C] was prepared according to Fuson:[8b] IR (Nujol) ν_{max} 1700 (C=O), 1610 (C=C) cm^{-1}; ^{1}H NMR (CDCl$_3$, room temperature) δ 2.04 (12 H, s, 4Me), 2.25 (6 H, s, 2Me), 2.29 (3 H, s, Me), 5.32 (1 H, s, CH), 6.82 (4 H, s, Ar—H); mass spectrum, m/z 294 (M$^+$, 3%) 251 (Mes$_2$CH$^+$, 100%), 221 (Mes$_2$CH$^+$ – 2Me, 12%), 206 (Mes$_2$CH$^+$ – 3Me, 7.5%), 57 (MeCOCH$_2$, 11%), 43 (MeCO$^+$, 12%).

1,1-Dimesityl-1-buten-2-ol (3). To a Grignard reagent prepared from ethyl bromide (0.55 mL, 7.2 mmol) and magnesium chips (0.17 g, 7.2 mmol) in dry ether (15 mL), LiClO$_4$ (1.17 g, 11 mmol) was added in one portion followed by a dropwise addition of a solution of dimesitylketene (1 g, 3.6 mmol) in benzene (10 mL) during 20 min. The mixture was refluxed during the addition and kept at 80 °C for 40 h. The solution was poured over 0.1 M aqueous HCl (20 mL) and washed with 0.1 M aqueous K$_2$CO$_3$ solution (20 mL), and the organic phase was dried and evaporated. The remaining brown oil (0.9 g) was shown by NMR to be a 1:1 mixture of the enols **1** and **3**. Chromatography of the oil on dry silica column (Woelm TSC) using toluene as the eluant gave several fractions. The first fraction (0.4 g, 40%) was 1,1-dimesityl-1-buten-2-ol (**3**). Recrystallizing from EtOH gave pink plates: mp 110–112 °C; IR (CCl$_4$) ν_{max} 3520 (OH), 1630 (C=C) cm^{-1}; mass spectrum, m/z 308 (M$^+$, 100%), 293 (M – Me, 50%), 251 (Mes$_2$CH$^+$, 33%), 221 (Mes$_2$CH$^+$ – 2Me, 7%), 206 (Mes$_2$CH$^+$ – 3Me, 7%), 173 (MesC≡COCH$_2$$^+$, 9%), 159 (MesC≡CO$^+$, 10%), 145 (MesC$^+$=CH$_2$, 20%). Anal. Calcd for C$_{22}$H$_{28}$O: C, 85.66; H, 9.15. Found: C, 85.86; H, 9.27.

The second fraction was the reduced enol **1** (0.4 g, 40%) and was identified by its NMR.

1,1-Dimesityl-2-butanone (8). A solution of 1,1-dimesityl-1-buten-2-ol (**3**) (0.2 g, 0.5 mmol) in dry hexane (40 mL) containing CF$_3$COOH (0.01 mL, 0.09 mmol) was refluxed for 15 h. The solvent was evaporated, and the green oil obtained (0.2 g) was chromatographed on a silica column by using benzene as the eluant, giving 1,1-dimesityl-2-butanone (0.15 g, 75%) which was crystallized from EtOH: mp 133–135 °C; IR (Nujol) ν_{max} 1715 (C=O), 1620 (C=C) cm^{-1}; ^{1}H NMR (CDCl$_3$, room temperature) δ 1.13 (3 H, t, J = 7 Hz, Me), 2.02 (12 H, s, 4Me), 2.12 (2 H, q, J = 7 Hz, CH$_2$), 2.24 (6 H, s, 2Me), 5.35 (1 H, s, CH), 6.80 (4 H, s, Mes—H); mass spectrum, m/z 280 (Mes$_2$C=CHOH, 5%), 266 (Mes$_2$CH=CHOH – CH$_2$, 15%), 251 (Mes$_2$CH$^+$, 100%), 236 (Mes$_2$CH$^+$—Me, 17%), 119 (Mes$^+$, 13%). Anal. Calcd for C$_{22}$H$_{28}$O: C, 85.66; H, 9.15. Found: C, 85.80; H, 8.84.

1,1-Dimesityl-3-methyl-1-buten-2-ol (4). To a solution of dimesitylketene (1 g, 3.6 mmol) in dry ether (10 mL), 2-bromopropane (0.7 g, 5.7 mmol) and a freshly cut lithium wire (40 mg, 5.7 mmol) were added in an argon atmosphere. The mixture was stirred at –18 °C until all the lithium was consumed and then for additional 2 h. After the usual workup, dimesitylacetic acid (0.2 g) was recovered from the K$_2$CO$_3$ wash. The remaining oil was crystallized from ether/ethanol, giving colorless plates (0.4 g, 43%) of 1,1-dimesityl-3-methyl-1-buten-2-ol: mp 125 °C; IR (Nujol) ν_{max} 3495 (OH), 1630 (C=C) cm^{-1}; mass spectrum, m/z 322 (M$^+$, 100%), 307 (M – Me, 12%), 265 (M – 4Me, 18%), 251 (Mes$_2$CH$^+$, 38%), 237 (Mes$_2$CH$^+$ – Me, 9%), 187 (MesCH=C-*i*-Pr, 11%), 159 (MesC=C=O, 20%), 43 (C$_3$H$_7$$^+$, 12%). Anal. Calcd for C$_{23}$H$_{30}$O: C, 85.66; H, 9.38. Found: C, 85.46; H, 9.02.

1,1-Dimesityl-3-methyl-2-butanone (9). A solution of 1,1-dimesityl-3-methyl-1-buten-2-ol (0.2 g, 0.6 mmol) in dry hexane (40 mL) containing CF$_3$COOH (0.01 mL, 0.09 mmol) was refluxed overnight. The solvent was evaporated, and the residue was crystallized from EtOH, giving 1,1-dimesityl-3-methyl-2-butanone (0.14 g, 70%): mp 95 °C; IR (Nujol) ν_{max} 1705 (C=O), 1620 (C=C) cm^{-1}; ^{1}H NMR (CDCl$_3$, room temperature) δ 1.17 (6 H, d, J = 6.5 Hz, 2Me), 2.04 (12 H, s, 4Me), 2.24 (6 H, s, 2Me), 2.92 (1 H, m, J = 6.5 Hz, CH), 5.57 (1 H, s, CH), 6.80 (4 H, s, Mes—H); mass spectrum, m/z 322 (M, 24%), 251 (Mes$_2$CH$^+$, 100%), 221 (Mes$_2$CH$^+$ – 2Me, 9%), 43 (C$_3$H$_7$$^+$, 10%). Anal. Calcd for C$_{23}$H$_{30}$O: C, 85.66; H, 9.37. Found: C, 85.83; H, 9.14.

1,1-Dimesityl-3,3-dimethyl-1-buten-2-ol (5). To a solution of dimesitylketene (1 g, 3.6 mmol) in dry ether (30 mL) which was kept at –40 °C in argon atmosphere a solution of 1 M *tert*-butyllithium in pentane (Foote Mineral Co., 2.5 mL, 4.7 mmol) was added dropwise during 15 min, and the mixture was stirred for additional 3 h and worked up as described in the preparation of **2**. Dimesitylacetic acid (0.4 g) was recovered from the neutralized K$_2$CO$_3$ wash. The remaining oil was crystallized from ether/ethanol giving 1,1-dimesityl-3,3-dimethyl-1-buten-2-ol (0.4 g, 55%): mp 138 °C; IR (Nujol) 3520 (OH), 1620 (C=C) cm^{-1}; mass spectrum, m/z 336 (M$^+$, 33%), 251 (Mes$_2$CH$^+$, 100%), 132 (MesCH, 83%), 57 (C$_4$H$_9$$^+$, 37%). Anal. Calcd for C$_{24}$H$_{32}$O: C, 85.71; H, 9.52. Found: C, 85.83; H, 9.64.

When the same reaction was exactly reported at –78 °C in petroleum ether, in addition to **5** a yellow solid (0.1 g), mp 188 °C which is tentatively **13** with the following spectral properties, was obtained: IR (Nujol) ν_{max} 3300 (OH), 1680 (C=O), 1610 (C=C) cm^{-1}; ^{1}H NMR (CDCl$_3$, room temperature) δ 1.25 (9 H, s, *t*-Bu), 2.06 (6 H, br s, 2Me), 2.13 (6 H, br s, 2Me), 2.21 (3 H, s, Me), 2.25 (3 H, s, Me), 5.12 (1 H, s, OH, disappears in D$_2$O), 6.75 (2 H, s, Mes—H), 6.87 (2H, s, Mes—H); ^{13}C NMR (50.325 MHz, CDCl$_3$) δ 20.79 (*o*-Me), 21.38 (*p*-Me), 26.82 (CMe$_3$), 44.42 (*C*Me$_3$), 120.37 (C$_\beta$), 129.30 (*m*-Mes—C), 130.14 (*m*-Mes—C), 131.15 (ipso-Mes—C), 134.37 (ipso-Mes—C), 135.92 (*p*-Mes—C), 137.09 (*o*-Mes—C), 137.82 (*p*-Mes—C), 138.98 (*o*-Mes—C), 147.15 (C$_\alpha$), 203.37 (C=O) (assignment is based on analogy with the ^{13}C spectrum of **15**[22] and on the relative intensities of the peaks); EI mass spectrum, m/z (70 eV), high-resolution 364.2402 (C$_{25}$H$_{32}$O$_2$, M), 349.2168 (C$_{24}$H$_{29}$O$_2$, M – Me); mass spectrum, m/z 364 (M, 8%), 349 (M – Me, 85%), 251 (Mes$_2$CH$^+$, 25%), 147 (MesCO$^+$, 40%), 131 (MesC, 27%), 119 (Mes, 27%), 91 (C$_7$H$_7$$^+$, 28%), 57 (C$_4H_9$, 100%); CI mass spectrum, m/z (isobutane 120 °C) 365 (MH$^+$, 37%), 349 (M – Me, 10%), 309 (MH – Me$_2$C=CH$_2$, 12%), 251 (Mes$_2$CH$^+$, 29%), 217 (MesCHCO-*t*-Bu (?), 80%), 161 (MesCH$_2$CO, 20%), 147 (MesCO, 13%), 133 (MesCH$_2$, 100%). Anal. Calcd for C$_{25}$H$_{32}$O$_2$: C, 82.35; H, 8.85. Found (several times): C, 75.80; H, 8.53.

1,1-Dimesityl-3,3-dimethyl-2-butanone (10). To a solution of 1,1-dimesityl-3,3-dimethyl-1-buten-2-ol (0.2 g, 0.6 mmol) in dry hexane (40 mL), CF$_3$COOH (0.01 mL, 0.09 mmol) was added, and the mixture was refluxed overnight. The solvent was evaporated, and crystallization of the residue from EtOH gave 1,1-dimesityl-3,3-dimethyl-2-butanone (0.14 g, 70%): mp 172–174 °C; IR (Nujol) ν_{max} 1730 (C=O), 1620 (C=C) cm^{-1}; ^{1}H NMR (CDCl$_3$, room temperature) 1.19 (9 H, s, *t*-Bu), 2.11 (12 H, s, 4Me), 2.22 (6 H, s, 2Me), 5.62 (1 H, s, CH), 6.77 (4 H, s, Mes—H); mass spectrum, m/z 336 (M, 9%), 251 (Mes$_2$CH$^+$, 100%), 221 (Mes$_2$CH$^+$ – 2Me, 9%), 57 (C$_4$H$_9$$^+$, 14%). Anal. Calcd for C$_{24}$H$_{32}$O: C, 85.71; H, 9.52. Found: C, 85.72; H, 9.42.

2,2-Dimesitylvinyl Dimesitylacetate (14). In an argon atmosphere, freshly cut lithium wire (40 mg, 5.7 mmol) was added to a mixture of dimesitylketene (1.0 g, 3.6 mmol) and *tert*-butyl bromide (0.69 g, 5 mmol) in dry ether (20 mL) with stirring at –18 °C and the stirring continued for 2 h after the dissolution of all the lithium. The mixture was poured into 1 N aqueous HCl solution (20 mL), washed with 0.1 M aqueous K$_2$CO$_3$ (20 mL), and separated, and the organic phase was dried and evaporated, giving a pink oil. Crystallization from ether/ethanol gave colorless crystals (0.35 g, 44%) of the ester **14**, mp 175 °C, which was identified by its X-ray diffraction and spectral properties. Dimesitylacetic acid (0.6 g) was recovered by neutralization of the K$_2$CO$_3$ solution: UV (hexane) λ_{max} 220 nm (log ϵ = 4.66), 261 (4.19); IR (Nujol) ν_{max} 1730 (C=O) 1630 (C=C) cm^{-1}; ^{1}H NMR (CDCl$_3$, room temperature) δ 1.73 (6 H, s, 2Me), 1.89 (12 H, s, 4Me), 2.24 (12 H, s, 4Me), 5.35 (1 H, s, CH), 6.59 (2 H, s, Mes—H), 6.70 (6 H, s, Mes—H), 7.31 (1 H, s, CH); ^{13}C NMR (CDCl$_3$, room temperature) δ 20.23, 20.67, 20.75, 20.87, (4Me), 51.45 (CH), 123.40 (C$_\beta$), 128.59, 129.83, 130.34, 132.16, 132.54, 133.83, 135.98, 136.10, 136.43, 137.26, 137.53 (11 C–Mes), 137.79 (C$_\alpha$), 171.38 (C=O); mass spectrum, m/z 280 (Mes$_2$C=CHOH, 17%), 279 (Mes$_2$C=CHO, 13%), 278 (Mes$_2$C=C=O, 16%), 251 (Mes$_2$CH$^+$, 100%). Anal. Calcd for C$_{40}$H$_{46}$O: C, 85.97; H, 8.30. Found: C, 86.26; H, 8.41.

When the same reaction was conducted under identical conditions except for quenching with D$_2$O/DCl instead of H$_2$O/HCl, the same relative integration of the protons was obtained; i.e., deuterium was not incorporated.

When the procedure used for the preparation of the enol **4** was repeated at 0 °C rather than at –18 °C, **14** was obtained in 40% yield and was identified by its melting point and ^{1}H NMR spectrum.

Isopropyl Dimesitylacetate (12). To a Grignard reagent prepared from isopropyl bromide (35 mL, 3.6 mmol) and Mg turnings (90 mg, 3.6 mmol) in dry THF (15 mL), LiClO$_4$ (0.58 g, 5.4 mmol) was added in one portion. After its dissolution, dimesitylketene (0.5 g, 1.8 mmol) in THF (10 mL) was added dropwise to the solution during 20 min. The

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mixture was kept overnight at 70 °C and worked up as described for **14** above. The orange oil obtained (0.45 g) was chromatographed on dry silica column (Woelm TSC) by using toluene as the eluant. Crystallization from EtOH gave 0.35 g (65%) of colorless crystals of isopropyl dimesitylacetate: mp 90 °C; UV (hexane) λ_{max} 207 nm (log ϵ = 4.56), 265 (2.89); IR (Nujol) ν_{max} 1725 (C=O), 1610 (C=C) cm^{-1}; ^1H NMR (CD_2Cl_2, room temperature) δ 1.16 (6 H, d, J = 6.3 Hz, 2Me), 1.95 (12 H, s, 4Me), 2.14 (6 H, s, 2Me), 4.98 (1 H, *m*, J = 6.3 Hz, CH), 5.18 (1 H, s, CH), 6.70 (4 H, s, Mes—H); mass spectrum, m/z 338 (M, 13%), 251 (Mes_2CH^+, 100%), 236 (Mes_2CH^+ − Me, 4%), 221 (Mes_2CH^+ − 2Me, 10%), 206 (Mes_2CH^+ − 3Me, 6%), 43 (C_3H_7, 8%). Anal. Calcd for $C_{23}H_{30}O_2$: C, 81.61; H, 8.93. Found: C, 81.97; H, 9.05.

Equilibration Studies. Approximately 20 mg of the ketone or the enol was dissolved in 25 mL of spectroscopic hexane, and the solution was divided into several pressure ampules which were wrapped in aluminum foil and were kept in an oil bath in the dark at 80.3 ± 0.1 °C. If the ampules of the enols were kept at daylight, decomposition took place as reflected by the appearance of new (non-ketonic) signals in the NMR. For example, the reaction of **5** gave signals (in $CDCl_3$) at 0.99 (s), 2.19 (s), 4.7 (AB q), 6.6 (s), and 9.54 (s) ppm.

Samples were withdrawn after a few hours, the solvent was evaporated, and the ^1H NMR spectra in $CDCl_3$ were recorded. The relative ratios of the two species were determined by integration of the methyls of the alkyl groups for each one of the keto/enol pairs. In several cases, a corroboration for this ratio was obtained from the integration of the ketonic CH and enolic OH protons, but this was impossible when traces of CF_3COOH still remained, since exchange with the OH resulted in a higher integration. Care was taken to ensure complete relaxation of the various hydrogens in order to obtain reliable integration. When two or three samples taken at different reaction times gave a similar enol/ketone composition, this was regarded as the equilibrium value. In all cases, the equilibrium compositions obtained by starting from the enol or from the ketone were identical within the accuracy of the integration.

Acknowledgment. We are indebted to Silvio Biali for discussions and for some experiments with **13** and **14**, to Prof. H. Schwarz for the mass spectra of **14**, to Dr. S. Cohen for the X-ray crystallography of compound **14**, and to Dr. L. Radom for discussions. This work was supported by a grant from the United States–Israel Binational Science Foundation (BSF), Jerusalem, Israel, to whom we are grateful.

Registry No. 1, 54288-04-9; **2**, 89959-15-9; **3**, 96040-90-3; **4**, 96040-91-4; **5**, 89959-16-0; **6**, 94203-58-4; **7**, 96040-92-5; **8**, 96040-93-6; **9**, 96040-94-7; **10**, 96040-95-8; **11**, 87871-33-8; **12**, 96040-98-1; **13**, 96040-97-0; **14**, 96040-96-9; dimesitylacetic acid, 5740-42-1; isopropyl bromide, 75-26-3; *tert*-butyl bromide, 507-19-7; ethyl bromide, 74-96-4.

Supplementary Material Available: Tables S1–S4 giving the crystallographic data for compound **14** (6 pages). Ordering information is given on any current masthead page.

Stereo- and Regioselective Palladium-Catalyzed, 1,4-Acetoxychlorination of 1,3-Dienes. 1-Acetoxy-4-chloro-2-alkenes as Versatile Synthons in Organic Transformations

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Abstract: Palladium-catalyzed oxidation of 1,3-dienes in the presence of LiCl and LiOAc produces 1-acetoxy-4-chloro-2-alkenes with high selectivity. The reaction is stereospecific and cyclic dienes give an overall cis 1,4-addition (>97–98% cis). The stereospecificity of the reaction also holds in acyclic systems as shown by the oxidation of (*E*,*E*)- and (*E*,*Z*)-2,4-hexadiene to (*R**,*R**)- and (*R**,*S**)-**10**, respectively. The mechanism of the acetoxychlorination is now well understood. It proceeds via a trans acetoxypalladation of the diene to produce an intermediate (4-acetoxy-1,2,3-η^3-allyl)palladium species, followed by an oxidation-induced nucleophilic attack at C-1 with inversion. Kinetic studies indicate that *p*-benzoquinone, which is a unique oxidant for the reaction, not only serves as an oxidant but also acts as a ligand to palladium. The chloroacetate products are useful synthons in organic transformations. Sequential substitutions of the chloro and acetoxy groups allow a *regiochemical choice*, and the fact that the allylic chloro group can be substituted with either clean retention or inversion allows a *stereochemical choice*. These principles are demonstrated in a number of cases. It is shown that the acetoxychlorination approach allows a *complete control* of the 1,4-relative stereochemistry with a unique choice of functionality at the asymmetric center.

Regio- and stereocontrolled 1,4-addition to conjugated dienes is of synthetic interest. Methods for achieving such additions include cycloaddition of singlet oxygen[1,2] and nitroso compounds[3,4] followed by reduction.[5] We recently reported a few stereo- and regioselective 1,4-additions to conjugated dienes.[6,7] These oxi-

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