Generation and Detection of a Relatively Persistent Carboxylic Acid Enol−2,2-Bis(2′,4′,6′-triisopropylphenyl)ethene-1,1-diol

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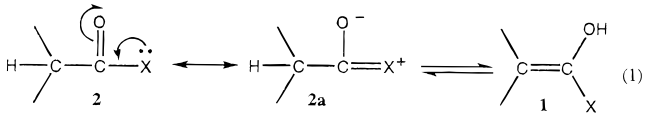
Abstract: Ditipyl ketene (tipyl = 2,4,6-triisopropylphenyl) (**20**), ditipylacetic acid (**19**), and 2,2-ditipyl bis-(trimethylsilyl) acetal **28** were prepared as potential precursors for the enol of **19**, i.e., 2,2-ditipylethene-1,1-diol (**25**). Protonation of the dianion of **19** or fluoride ion desilylation of **28** gave the radical $Tip_2C{=}C(OH)O^{\bullet}$ (**27**), and only hydration of **20** in 42:5:3 DMF-d_7:THF-d_8:H_2O or in THF-d_8:H_2O gave solutions of ≥ 98% of the enediol **25**. ^1H and ^{13}C NMR spectra of **25** and of mixtures of **25** with its *O*-mono- and dideuteriated derivatives **25-D** and **25-D_2** and linear δ(OH)[**25**] vs δ(OH) of 2,2-ditipyl-1-R-ethenols, *R* = Me, H (**30**, **31**) correlations corroborated the structure and indicated that the two OH groups are identical on the NMR time scale. A propeller arrangement for the ditipylvinyl moiety and anti arrangements for the C=C−O−H moieties where the OH groups are solvated by the dipolar aprotic solvent (e.g., DMF) are suggested for the conformation of **25**. Although solid **25** could not be isolated, it is the longest-lived 1,1-enediol prepared so far in solution. The hydration rates of di(bulky)aryl ketenes decrease with the increased bulk of the aryl groups.

Introduction

Enolization of aldehydes and ketones has been extensively studied almost from the beginning of the century, and great progress in the field was achieved in the last 15 years.[2] Even simple enols, i.e., those unsubstituted by strongly electron-withdrawing substituents were observed, and the very small equilibrium constants with their carbonyl tautomers (K_{enol}) and their acidities were measured. In contrast, enols of carboxylic acids (1,1-enediols) and their derivatives, such as esters, amides, or acyl halides (**1**) were much less extensively studied[3] and are not even mentioned in textbooks. This is due to their very low stability which is ascribed to participation of the lone pair on the heteroatom X in stabilization of the acid (or derivative) by electron donation (cf. **2a**, eq 1).[2] The anomeric interaction (OH,X) in the 1,1-enediol derivatives is much lower and may even be destabilizing.[4] Consequently, in contrast to the large number of enols which exist as stable species,[2] no long-lived, or thermodynamically stable enols of carboxylic acid derivatives are known except for the amide enol $(NC)_2C{=}C(OH)NH_2$.[5]



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The reduced stabilities are also reflected by calculations which show that the equilibrium constants K_{enol} for the carboxylic acid (**2**, X = OH)/1,1-enediol (**1**, X = OH) are much lower than those for the corresponding carbonyl/enol pairs. Recent estimations by Guthrie[4] give pK_{enol} (= −log K_{enol}) of 21.2[4a] and 19.4[4b] for the $CH_3COOH/H_2C{=}C(OH)_2$ pair. MO calculations give 20.5,[2] 26,[6] 18.8,[7] and 20.4[8] and deuterium exchange data give 19.3.[4a,9] An earlier comparison with the acetaldehyde/vinyl alcohol pair (where pK_{enol} = 6.23)[10] gave $\Delta E(H_2C{=}C(OH)_2$-$CH_3COOH) - \Delta E$ ($H_2C{=}CHOH{-}CH_3CHO$) = 10 kcal mol^{-1}.[2] Lower K_{enol} values were calculated for 1-cyclopropanecarboxylic acid (pK_{enol} = 28.3) and 3-cyclopropenecarboxylic acid (pK_{enol} = 30.2).[7]

In spite of their very low thermodynamic stability, 1,1-enediols and their anions were suggested as "unobserved" intermediates in the decarboxylation of 2-phenyl-1,1-cyclohexane dicarboxylic acid[11a] and in the reductive debromination of 1-bromo-2-phenylcyclohexanecarboxylic acid.[11b] 1,1-Enediol derivatives were suggested as intermediates in the bromination of acyl chlorides.[12] Ester and amide "enols" (**1**, X = OR and NRR′) were suggested as intermediates in the addition of alcohols to ketenes,[13] the acid-catalyzed hydration of ketenimines,[14] and the electrophilic substitution of malonamide.[15] Other suggested intermediates are an anhydride enol (**1**, X = OCOR) in the electrophilic addition to Ac_2O[16] and acyl halide

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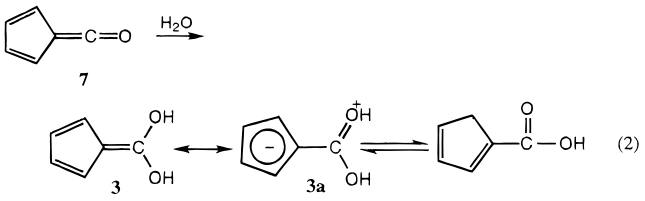
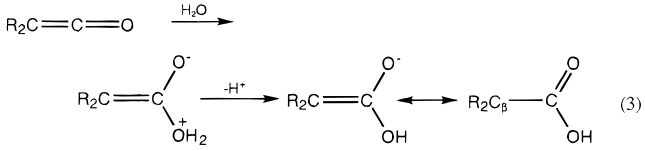
enols (**1**, X = halogen) in the addition of H-Hal to ketenes.[17] None of these intermediates was isolated or even observed, except for a recent brief report of the observation of amide enols.[14b]

Several enediols were observed since 1987. Following an early work of Kobayashi et al.[18] the groups of Wirz[19,20] and Kresge[20,21] generated the enediol of cyclopentadiene-1-carboxylic acid (**3**, pK_{enol} = 6.7)[19a] and indene-1-carboxylic acid (**4**, pK_{enol} = 7.26),[21a] PhC(OH)=C(OH)$_2$ (**5**, pK_{enol} = 15.4),[20a] and PhC(CN)=C(OH)$_2$ (**6**, pK_{enol} = 7.22)[20b] which are electronically stabilized at C_β. These were generated mostly by flash photolysis of diazoketones which by a Wolff rearrangement[22] led to short-lived ketenes which were then hydrated. Although ketene hydration to carboxylic acids was extensively investigated mechanistically, the intermediates were never observed until Urwyler and Wirz[19a] generated 6-fulvenone **7** in water and identified its hydration product as the enediol **3** which then tautomerized rapidly to the carboxylic acid (eq 2). By using fast kinetics techniques, pH-rate profiles, spectrophotometric titrations, and thermodynamic cycles involving the enolate, the carboxylate, and the enediolate anions, p*K*a's of the enediols and K_{enol} values were calculated.[19−21] The pK_{enol} values demonstrate that substituents stabilize the 1,1-enediols by up to >14 orders of magnitude compared with the value of 21 estimated for CH$_2$=C(OH)$_2$.[4a] Those for **3** and **6** are in the range for simple stable enols such as acetaldehyde (6.23)[10] or acetone (8.33)[10] in water at 25 °C. Kresge stated that "These substances have also been called 'ketene hydrates'. Their chemistry, however, is quite different from other carbonyl, e.g., aldehyde and ketone, hydrates and more like that of the enol isomers of aldehydes and ketones. We consequently prefer the term 'carboxylic acid enols'".[21a] For evaluating this statement, *direct* structural evidence on the structure of these species, which is at present lacking, is necessary.



(2)

The substituent effects are both kinetic and thermodynamic. In order to observe the 1,1-enediols, their generation by ketenes hydration ought to be much faster than their destruction by tautomerization. This can be achieved either by accelerating the hydration reaction or by decreasing the ketonization rate. For simple enols conjugation of the enolic moiety to aromatic rings reduces the ketonization rate.[23] Ketene hydration proceeds through an in-plane nucleophilic attack of water on the carbonyl carbon, initially generating a zwitterion and afterwards a carbanion whose charges are resonatively delocalized on C_β[2,17d,24] (eq 3). Consequently, electron withdrawing C_β substituents will stabilize the transition state of the hydration and accelerate the reaction.



(3)

The thermodynamic stabilization is illustrated by the zwitterionic hybrid **3a** of **3** (eq 2) in which the electron rich dioxy function is positively charged and the five-membered ring is negatively charged, i.e., aromatic. The enediols are acidic (e.g., pK_a(**6**) = 0.99)[20b] and enolates which should ketonize much more readily than the less nucleophilic enols[25] were suggested as intermediates in the ketonization of 1,1-enediols.[21a] In all these cases the hydration and ketonization are very fast.[19−21]

Another approach to observable 1,1-enediols is based on the success in isolating both kinetically and thermodynamically stable simple enols stabilized by bulky aromatic substituents by Fuson[26] and by us.[27] O'Neill and Hegarty[28] reported the formation of the 2,2-diaryl-1,1-enediol **8** and the ester enol **9** when Ar = pentamethylphenyl and of the enediol **10**, Ar = mesityl. Enediol **8** was generated by Bu_4NF cleavage of its bis(trimethylsilyl) acetal and characterized by UV and IR spectra and the lack of ^{1}H NMR CH signal of the isomeric acid. **9** was prepared similarly from the trimethylsilyl acetal of *tert*-butyl bis(pentamethylphenyl)acetate. **8** and **9** decayed to the acid and to the ester, respectively, with $\tau_{1/2}$ of several hours in neutral solution and their air oxidation gave stable radicals.

$Ar_2C=C(OH)_2$	$(C_6Me_5)_2C=C(OH)OBu\text{-}t$	$Ar_2C=C=O$	$Ar_2CHCOOH$
8: Ar=C_6Me_5	**9**	**11**: Ar=C_6Me_5	**12**: Ar=C_6Me_5
10: Ar=Mes		**13**: Ar=Mes	
		14: Ar=Ph	

Hegarty et al.[29] hydrated bis(pentamethylphenyl)ketene **11** in MeCN−H_2O mixtures and observed a long-lived intermediate identified as enediol **8**. Dimesitylketene **13** hydrates 3−4 times faster than **11**, but three orders of magnitude slower than diphenylketene **14**, demonstrating that bulky substituents increase the kinetic stability of ketenes. The kinetic data are for the decay rates of the ketenes, thus avoiding the question of the stabilities of the 1,1-enediols.

The bulkier are the two β-aryl substituents, the more stable is the enol.[27] Hence, the best candidate for a stable 1,1-enediol is 2,2-bis(2′,4′,6′-tri-*tert*-butylphenyl)ethene-1,1-diol, but we

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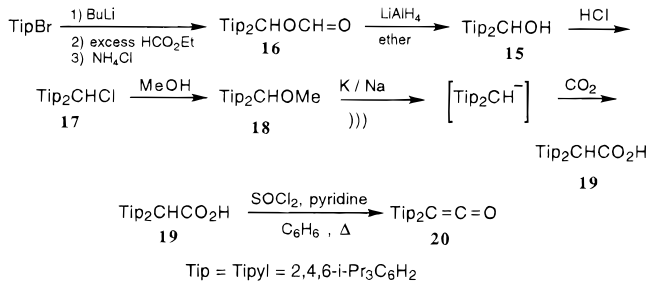
Scheme 1



failed in our attempt to prepare a precursor for it. Smaller aryl groups are therefore required. 2-Aryl-1-acenaphthyl enol is more stable when Ar = 2,4,6-triisopropylphenyl(tipyl) than when Ar = mesityl (Mes),[30] and tipyl confers higher kinetic stability than mesityl to 1,2-diaryl-1,2-ethenediols.[31] The keto/enol equilibrium constants K_{enol} are higher for tipyl- than for mesityl-substituted enols,[32,33] and the effect of the buttressing in a pentamethylphenyl group compared with Mes on K_{enol} value is small.[34] Consequently, we assumed that two β-tipyl groups would confer a higher stability to the 1,1-enediol moiety than that hitherto achieved for the Mes and C_6Me_5 analogs. This prediction was corroborated and the observation and study of the corresponding 1,1-enediol is the subject of the present paper.

Results and Discussion

Synthesis of Ditipylacetic Acid and Ditipylketene. The relatively simple synthetic routes to the less crowded dimesityl and bis(pentamethylphenyl) acetic acids[29] failed to give ditipylacetic acid. We therefore attempted the more tedious methods suggested by Akkerman[35] for the preparation of polyalkyl-substituted diphenylacetic acids starting from the diarylacetonitrile or from diarylmethyl methyl ether. In both routes ditipylmethanol **15** is an intermediate. The alcohol was prepared according to Scheme 1. Tipyllithium was prepared from tipyl bromide and butyllithium in ether and when reacted with excess of ethyl formate at 0 °C ditipylmethyl formate **16** was obtained in a relatively low (27%) yield. Likewise, several other hindered benzhydryl formates were isolated from Grignard reagents and aldehydes.[36] Reduction of **16** with $LiAlH_4$ gave **15** in 92% yield. This procedure is advantageous over the reaction of tipyl bromide with BuLi and 0.5 equivalent of ethyl formate which gave a low yield of **15** admixed with triisopropylbenzene, triisopropylbenzenecarboxaldehyde, and **16**. When gaseous HCl was bubbled through the solution of **15** in dry benzene,[37a] a solid, which was not crystallized due to its high solubility in all the solvents tried, was obtained. Its ^1H and ^{13}C NMR spectra, the immediate precipitation of AgCl on addition of ethanolic $AgNO_3$ solution, the development of deep purple color on absorption on SiO_2 (suggesting the formation of the diarylmethyl carbocation) and the formation of a methyl ether, unequivocally identified the compound as ditipylmethyl chloride **17**.

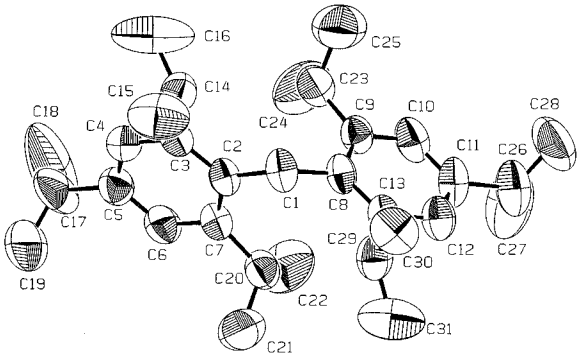


Figure 1. ORTEP drawing of **21**.

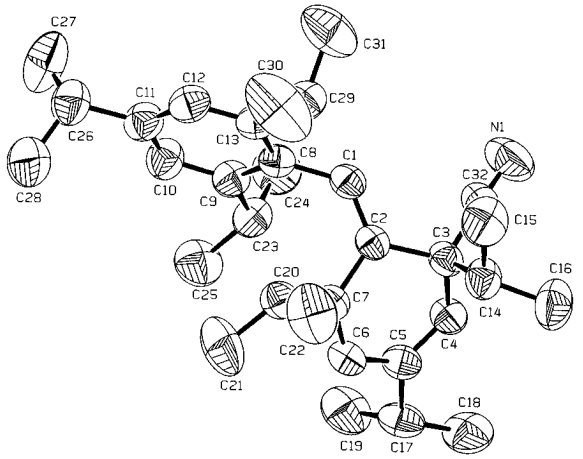
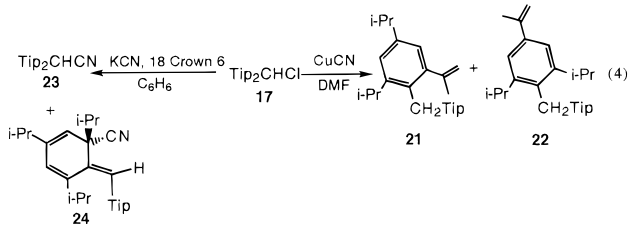


Figure 2. ORTEP drawing of the ipso-attack product **24**.

When solution of crude **17** in benzene was reacted with cuprous cyanide in DMF (eq 4) by the method of Lock and Riegler,[37b] no organic nitrile was isolated. Instead, two isomeric



aryl tipyl methanes **21** and **22** in which the aryl group was 2,6-diisopropyl-4-isopropenylphenyl and 2-isopropenyl-4,6-diisopropylphenyl, respectively, were isolated in a 1:3 ratio and characterized by ^1H,^{13}C NMR, mass spectra, and microanalysis. The structure of **21** was determined by X-ray diffraction, and its ORTEP drawing is shown in Figure 1 (C(17)−C(18) = 1.30 Å; dihedral angle between the two aryl groups 85.8°).[38]

In the reaction of **17** with a 18-crown-6/KCN complex in benzene >90% of **17** was hydrolyzed to **16**. The expected nitrile **23** was formed in only a 0.8% yield together with 2.5% of an cyclohexadienyl isomer **24** where the cyano group is attached to the ring. Both compounds were fully characterized, including an X-ray diffraction of **24** whose ORTEP drawing is given in Figure 2 (The C=C bonds are C(1)−C(2) = 1.329 Å; C(4)−C(5) = 1.322 Å; C(6)−C(7) = 1.336 Å).[38] We ascribe the formation of **24** to a reaction of the Tip_2CH^+ carbocation, formed from **17**, with the cyanide ion at a ring position. Precedents for ipso capture of relatively stable substituted benzyl

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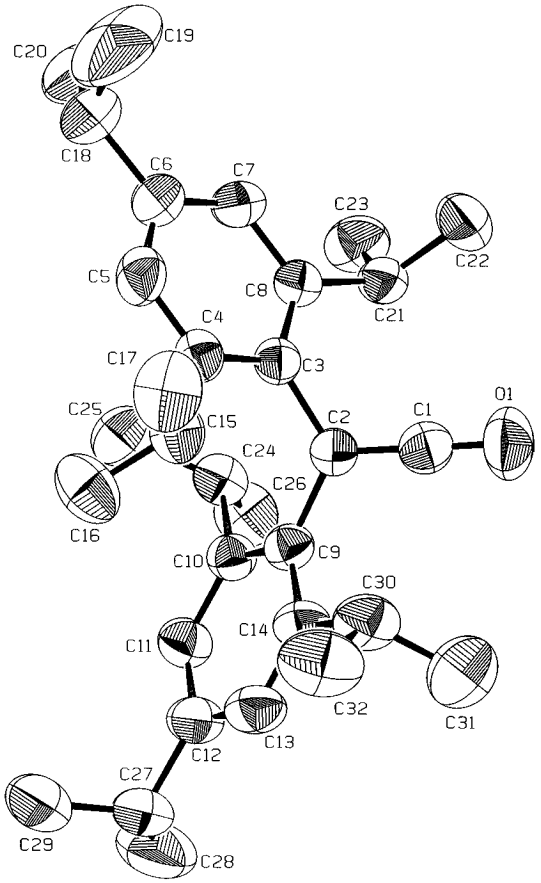


Figure 3. ORTEP Drawing of ditipyl ketene **20**.

cations are known.[39] Due to the low yield of the nitrile an alternative method based on the known benzylic C−O cleavageof benzyl and benzhydryl ethers by alkali metals[35,40] was applied.

Dry methanol and **17** in benzene gave the methyl ether **18** in 95% yield. Cleavage of **18** with Na/K alloy in ether with sonication under argon, followed by passing dry carbon dioxide into the red solution of the anion gave ditipylacetic acid **19** in 73% yield. The sonication, known to accelerate the reduction reaction[40c] reduced the reaction time and increased the yield of the acid over those of analogous reactions.[35] When thionyl chloride, trace of pyridine, and **19** were refluxed in dry benzene, ditipylketene (**20**) was obtained in 89% yield. It was stable enough for purification by chromatography on a silica column, and it was identified by NMR, FTIR, mass spectra, microanalysis, and X-ray diffraction. The ORTEP drawing of **20** is given in Figure 3 and its stereoview in Figure 4. Selected bond lengths and angles are given, together with those of dimesitylketene **13**[41] in Table 1.

In contrast to 1,1-ditipylvinyl systems which adopt a frozen propeller conformation ≤ room temperature,[32,33] the derivatives **15**−**19** show two 12H *o*-i-Pr signals in the ^{1}H NMR spectra and the more symmetrical ketene **20** showed a 24H signal, which

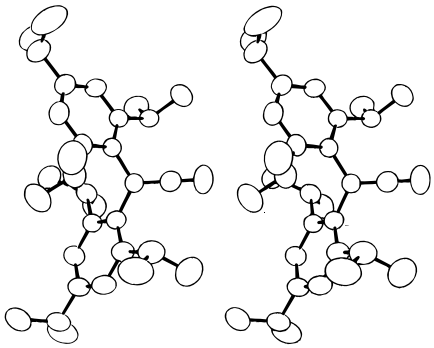


Figure 4. Stereoview of ditipyl ketene **20**.

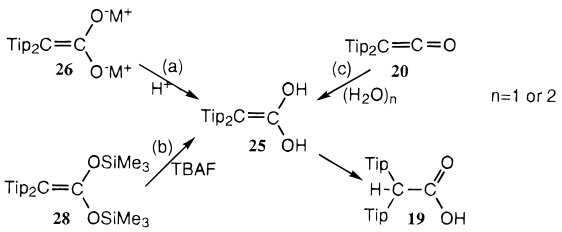
did not broaden on cooling (in acetone) down to 180 K. Hence, the aryl groups in **15**−**20** freely rotate around the Ar−C bonds at room temperature.

Synthesis of 1,1-Enediols. Most earlier studies on "observable" carboxylic acid enols were kinetic measurements using UV spectroscopy.[19−21,28,29] The enediol was formed in very low concentration (ca. 10^{-5} M), its isolation was impractical, and its purity impossible to asses. Capon[42] emphasized the difference between "generation" and "synthesis" of unstable enols which also applies for enediols. When generating unstable enediols for spectroscopic and kinetic studies, Capon's question could be rephrased as "*has the enediol been generated in the absence of its acid-tautomer?*". In contrast, conventional synthesis is interested in the purity and the yield of the enediol.

The methods used so far to generate 1,1-enediols were inspired by the two basic successful approaches for the generation of stable simple enols: (a) using reactions of reactive precursors containing the enediolic C=C(OR)$_2$ skeleton (e.g., O-protonation of endiolates or solvolysis of O-protected enediols) and (b) a rapid generation from non-enediolic precursors. In order to enable the isolation of 1,1-enediols, their formation ought to be much faster than their destruction. As discussed above, 2,2-ditipylethene-1,1-diol **25**, i.e., the enol of ditipylacetic acid **19**, seems a proper candidate. Moreover, if formed, it should be easily detected and monitored since a pair of *o*-i-Pr methyl signals appears at a high field in the ^{1}H NMR spectrum of *gem*-ditipylvinyl systems. Scheme 2 summarizes the three different synthetic methodologies attempted.

(a) Careful Protonation of the Dimetal Enediolates Tip$_2$C=C(O$^-$M$^+$)$_2$ 26. Carboxylic acids yield metal enediolates[43] (Ivanov reagents[44]) with organometallic reagents. Several structures of enediolates of phenylacetic acids have been

Scheme 2



(38) For crystallographic data see the supporting information section.

(39) (a) E.g., Richard, J. P. *J. Am. Chem. Soc*., **1989**, *111*, 6735. *Tetrahedron Lett*. **1989**, *30*, 23. (b) Tidwell, T. T. *J. Am. Chem. Soc*. **1986**, *108*, 3470. (c) For reaction of photogenerated triarylvinyl cations with cyanide ion, see: Kitamura, T.; Murakami, M.; Kobayashi, S.; Taniguchi, H. *Tetrahedron Lett.* **1986**, *27*, 3885.

(40) (a) Maercker, A. *Angew. Chem., Int. Ed. Engl*. **1987**, *26*, 972. (b) Fish, R. H.; Dupon, J. W. *J. Org. Chem*. **1988**. *53*, 5230. (c) Karaman, R.; Kohlman, D. T.; Fry, J. L. *Tetrahedron Lett.* **1990**, *31*, 6155. (d) Azzena. U.; Fenude, E.; Fina, C.; Melloni, G.; Pisano, L.; Sechi, B. *J. Chem. Res. (S)* **1994**, 108.

(41) Biali, S. E.; Gozin, M.; Rappoport, Z. *J. Phys. Org. Chem.* **1989**, *2*, 271.

(42) Capon, B. In *The Chemistry of Enols*; Rappoport, Z., Ed.; Wiley: Chichester, 1990; Chapter 5, p 307.

(43) (a) Rasmussen, J. K. *Synthesis* **1977**, 91. (b) Petragnani, N.; Yonashiro, *Synthesis* **1982**, 521.

(44) Ivanov, D.; Vassilev, G.; Panayotov, I. *Synthesis* **1975**, 83 and references cited therein.

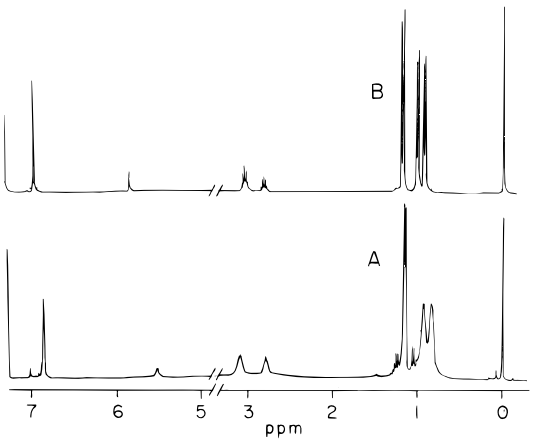


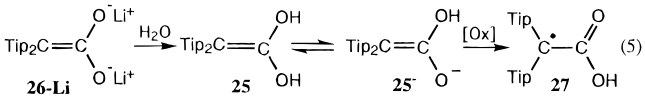
Figure 5. ^{1}H NMR spectra in $CDCl_3$ of (A) the quenching product of the enediolate **26-Li** and (B) the acid **19**.

determined by NMR,[45] and they showed normal enolate reactions with electrophiles.[46]

O-Protonation of enolates is widely used for generating enols of β-ketoesters and β-diketones which ketonize relatively slowly[47] but less in the case of simple enols. Sufficiently rapid mixing of the enolate solution with the water is required so that the O-protonation will be completed before further ketonization. We prepared a solution of dilithium 2,2-ditipylethene-1,1-diolate (**26-Li**) in THF by injecting 2 equiv of *n*-BuLi in hexane into a THF solution of ditipylacetic acid. The bright yellow solution was stirred under argon at room temperature and when quenched with water or D_2O after 10 min it turned orange-red. The solvents were evaporated, $CDCl_3$ was added, and an ^{1}H NMR spectrum of the deep red solution was immediately taken. The spectrum which is compared with that of acid **19** in Figure 5 displayed several persistent broad signals even upon heating or cooling, thus excluding the occurrence of a dynamic process on the NMR time scale as the reason for the broad signals. When a catalytic amount of CF_3COOH was added to the red sample or when the enediolate solution was quenched with an aqueous NH_4Cl solution, the spectrum of acid **19** was immediately observed.

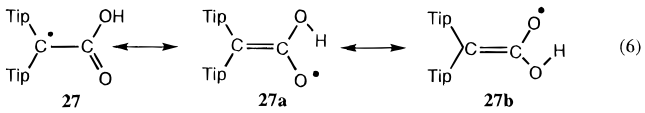
When solutions of **26-Na** or **26-K** generated by heating **19** with dimsyl sodium or with *t*-BuOK in DMSO-d_6 were quenched with water or D_2O, a similar spectrum with broad signals was obtained. Addition of iodine or bromine solutions in CCl_4 to ditipylethene-1,1-diol **25** resulted in a similar broad ^{1}H NMR spectrum, suggesting the formation of some oxidized form of **25**. The broadening of only several of the signals is reminiscent of spectra of stable radicals or of solutions displaying a rapid equilibrium of radicals with nonradical species.[48] Hegarty[49] has noted that the bulky α-acyldiaryl radicals formed by oxidation of his enediols are indefinitely stable as solids and do not dimerize or react with oxygen.

The solid obtained on quenching **26-Li** by water was chromatographed on a silica column, and the red solid isloated displayed an identical NMR spectrum to that shown in Figure 5. Since the yellow color of a solution of **26-Li** persists after standing for 1 h at room temperature in an argon atmosphere and only after adding water the solution turns red, we suggest that the monoenolate **25**$^-$ rather than the enediolate **26** is the species oxidized by air to the α-carboxy radical **27**. Moreover, 1,1-enediols ionize substantially even in neutral solutions and since a base is formed on quenching, we suggest that on quenching **26-Li** by water, the ditipylethene-1,1-diol monoanion **25**$^-$ is formed and then oxidized by air to **27** (eq 5).



(5)

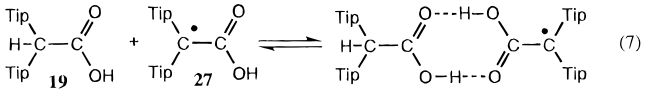
The ESR spectrum of **27** showed a broad signal with g = 2.0047, consistent[49] with the carboxyl conjugated radical structure proposed. We ascribe the relatively high *g*-value, which resembles those reported for α-acyl radicals,[28,49] to a spin density delocalization on the oxygen[50] as depicted in **27a** and **27b** (eq 6). **27** shows an IR $\nu_{C=O}$ at 1675 cm^{-1} (25 cm^{-1} lower than in **19**) indicating an increased single bond character of the carbonyl moiety (cf. **27a** and **27b**).



(6)

The ^{13}C NMR spectrum of **27** is also affected by the delocalization of the radical. The C=O and α-CH resonances which appear at 180.9 and 48.3 ppm for **19** have disappeared, presumably by broadening whereas the rest of the spectrum of **27** is slightly shifted upfield compared with that of **19**. The *ipso*- and *ortho*-ring carbons and the *ortho*-isopropyl carbons are also broadened as expected from their proximity to the radical center in line with the peak broadening observed in the ^{1}H NMR spectrum.

Examination of Figure 5 raises questions. If the radical has structure **27** which is the proton appearing at 5.7 ppm? Why are some signals sharp if a radical should broaden the whole NMR spectrum due to its paramagnetism? We suggest that this is due to an association phenomenon. When an "NMR invisible" radical associates with a "NMR detectable" nonradical species, broadening of hydrogen signals in a close proximity to the paramagnetic center should be observed. If radical **27** and acid **19** associate (eq 7), in analogy with the association of carboxylic acids only the α- and the *m*-H and the *o*-i-Pr of the



(7)

"dimer" should broaden while the *p*-i-Pr will remain unchanged. To test this hypothesis, we added dimesitylacetic acid to a sample of **27** assuming that acid-radical association would significantly broaden the usually sharp ^{1}H NMR signals of dimesitylacetic acid. Such a broadening was indeed observed. Moreover, when the sample was kept for three days at room temperature its color had almost faded and only a slight broadening was observed in the ^{1}H NMR spectrum. This suggest that broadening is due to the presence of the radical **27** which is slowly lost by hydrogen abstraction from the solvent. If radical **27** formed from enediol **25** abstract an hydrogen from the solvent to yield ditipylacetic acid **19**, this adds an additional

(45) Mladenova, M.; Blagoev, B.; Gaudemar, M.; Dardoize, F. *Tetrahedron* **1981**, *37*, 2153.

(46) (a) Mladenova, M.; Blagoev, B.; Gaudemar, M.; Gaudemar-Bardone, F.; Lallemand, J. Y. *Tetrahedron* **1981**, *37*, 2157. (b) Toullec, J.; Mladenova, M.; Gaudemar-Bardone, F.; Blagoev, B. *J. Org. Chem.* **1985**, *50*, 2563.

(47) (a) Knorr, L. *Ann. Chem.* **1899**, *306*, 363. (b) Meyer, K. H. *Chem. Ber.* **1912**, *45*, 2864.

(48) Günther, H. *NMR Spectroscopy*; Wiley: Chichester, 1980; p 327 and references cited therein.

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(50) Dobbs, A. J. *Electron Spin Resonance Spectroscopy*, Specialist Periodical Reports, Vol. 2, The Chemical Society: London, 1974; Chapter 10, p 281.

route from **25** to **19** which does not involve keto−enol tautomerization and should be considered in a complete kinetic analysis of the **25** ⇌ **19** process.

Both Kresge and Wirz reported problematic results in basic solutions: (i) Analysis of the highly colored product mixtures indicated that more than one product was formed in the photoprocesses at pH > 8 or 9.[19b] (ii) In flash photolytic processes conducted at high pH several transients are detected as deduced from the different observed rates of decay.[18a] Radical formation and destruction at these low concentrations should be considered in these cases.

(b) Fluoride Ion Catalyzed Cleavage of the Bis(trimethylsilyl) Ketene Acetal 28. Tetrabutylammonium fluoride (TBAF, "naked fluoride"),[51] is a well-known silylation/desilylation reagent.[52] We prepared ditipylketene bis(trimethylsilyl) acetal **28** and attempted its *in situ* fluoride catalyzed cleavage by using TBAF both in THF solutions or as a suspension while adsorbed on SiO_2, in an NMR tube in THF-d_8. The NMR spectrum of the red solution formed immediately after addition of TBAF, resembled that shown in Figure 5. This is not surprising since the F^-/THF solutions are very basic[53] and the enediol is more prone to oxidize in basic media. We note that this method was used by Hegarty in his first communication on generation of 2,2-diarylethene-1,1-diols in solution[28] but not in his later studies.

(c) Uncatalyzed Hydration of Ditipylketene 20. We finally succeeded in generating 2,2-ditipylethene-1,1-diol **25** by hydration of ditipylketene **20** under neutral conditions.[54] The ketene is insoluble in water in the 10^{-2} M concentration range, and an organic−water mixture had to be used. When a drop of water was added to a solution of **20** in $CDCl_3$, no reaction was observed even after 3 days, presumably due to the low solubility of water in $CDCl_3$. Hence, for a successful *in situ* hydration the organic cosolvent should fulfill five prerequisites: (a) dissolve the ketene, (b) be water miscible, (c) be unreactive toward the ketene, (d) be commercially available in its polydeuteriated form, for enabling an NMR study, and (e) be a good hydrogen-bond acceptor since the analogous 2,2-diarylethenols are stabilized by hydrogen bonding to hydrogen bond accepting solvents.[55] The first prerequisite is very restrictive since the solubility of **20** in the good aprotic hydrogen bond accepting solvents DMSO-d_6, DMF-d_7, Me_2CO-d_6, or MeCN-d_3 is so poor that we were unable to prepare samples of 10 mg of **20** in 0.5 mL of these solvents at room temperature. Heating or sonication achieved total dissolution, but on further addition of 30 μL of water the ketene was immediately precipitated. If the sample was then heated, the solution turned deep orange and its NMR spectrum displayed signals of a mixture of **19**, **20**, and a new compound having a doublet at 0.1−0.3 ppm which is 2,2-ditipylethene-1,1-diol **25** (*vide infra*). The products ratio was dependent on the duration of the heating. However, after 5 min some ketene had precipitated again. We finally found that the water miscible THF-d_8 dissolves **20** at room temperature and even at 243 K. More important, **20** is soluble in mixtures of THF-d_8 (at least 10% v/v) with DMF-d_7, DMSO-d_6, Me_2CO-d_6, or MeCN-d_3 containing a few percent of water. However, dissolving samples of **20** in either of these mixtures by heating induced a rapid formation of **19**, even before all the ketene had reacted. Hence, the hydration was conducted at lower temperatures in order to retard the highly temperature-dependent ketonization.

Optimization of the reaction conditions led to the following procedure: to a solution of 10 mg of **20** in 0.05 mL of THF-d_8, a mixture of 0.42 mL of DMF-d_7, and 0.03 mL of water ([**20**] = 0.045 M; 75-fold molar excess of water) was added at 273 K, and the reaction progress was monitored by ^{1}H NMR. After 90 min the solution consisted of ca. 1.5% of **20** and >98% of a new compound having an ^{1}H NMR spectrum almost identical with that of the bis(trimethylsilyl)ketene acetal **28** except that the $SiMe_3$ signals are replaced by a signal at δ 9.65 ppm, a position reminiscent of the δ(OH) signals of $Ar_2C{=}CHOH$ in hydrogen bond accepting solvents[55] (Figure 6). The new compound was therefore identified as the enediol **25**. Its NMR spectrum remained unchanged after 1 week at −18 °C, while after standing overnight at room temperature or rapidly upon addition of a catalytic amount of TFA, the spectrum of pure acid **19** was obtained. Slower formation of **25** was observed by its ^{1}H NMR spectrum, in a binary 47:3 THF-d_8:water mixture at 273 K and in ternary solvent mixtures of THF-d_8:water with DMSO-d_6 (at 298 K), Me_2CO-d_6, or MeCN-d_3 (at 273 K) at a solvent:water:THF v/v ratio of 42:5:3. Yet, only in DMF-d_7 and in THF-d_8 at 273 K, formation of **25** was almost complete in <6 h without any apparent tautomerization; in Me_2CO-d_6 and MeCN-d_3 the hydration at 273 K was very slow, e.g., in acetone < 10% of **25** were formed after 6 h before tautomerization to **19** had started. Tautomerization became important at 298 K, and the ternary mixture **20**:**25**:**19** was observed in all solvents. The reaction mixtures were orange-red, but no additional spectral indication for formation of radical **27** was found.

Spectroscopic Characterization of 2,2-Ditipylethene-1,1-diol (25). Since **25** was not isolated its identification is based on its way of preparation, its tautomerization to **19**, and unequivocally on its spectroscopic characterization.

(a) ^{1}H NMR. The ^{1}H NMR spectrum of **25** in 42:5:3 DMF-d_7:THF-d_8:H_2O at 273 K (compared in Figure 6 with that of its precursor **20**) displays features characteristic of other symmetrical *gem*-ditipylvinyl systems $Tip_2C{=}CR_2$ (R = H, $OSiMe_3$). The presence of a longitudinal C_2 symmetry axis reduces the number of magnetically unequivalent sites by half. The diastereotopic *o*-i-Pr methyls appear as four separate doublets, 2 Me each (J in Hz) at 0.14 (6.5), 0.93 (6.8), 1.26 (6.5), and 1.34 (6.8) ppm and a doublet with double integration at 1.19 ppm (J = 6.8 Hz) is assigned to two accidentally equivalent *p*-i-Pr methyls. The i-Pr methines appear as two heptets in a 2:1 ratio at 2.83 (J = 6.8 Hz) and 3.43 (J = 6.6 Hz) ppm, but it is unclear whether the larger peak represents two accidentally isochronous *o*-i-Pr methines or an overlap of one *o*- and one *p*-methine heptets. Two different 2H aromatic protons appear at 6.79 and 7.07 ppm and another 2H signal at 9.65 ppm is assigned to the OH group. From the number of the *o*-i-Pr and Ar-H signals we conclude that the rotation round the Tip-C=C bonds of **25** is slow on the NMR time scale at 273 K. Consequently, the molecule adopts a chiral conformation and judging by the X-ray data of other diaryl and triarylethylenes,[56] including *gem*-ditipyl derivatives[32,33] this is a propeller confor-

(51) Concerning the controversy about this terminology, see: Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 292.

(52) For a short review, see: Larson, G. L. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1989; Chapter 11, pp 789−793.

(53) (a) Hayami, J.; Ono, N.; Kaji, A. *Tetrahedron Lett.* **1968**, 1385. (b) Corey, E. J.; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190.

(54) We tried to apply this approach in 1984 for generating a 1,1-enediol by adding water to dimesitylketene followed by neutralization with aqueous NH_4Cl solution. However, we isolated dimesitylacetamide, presumably formed by the reaction of **13** with ammonia and we did not pursue the study.

(55) (a) Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1984**, *106*, 5641. (b) Rappoport, Z.; Nugiel, D. A.; Biali, S. E. *J. Org. Chem.* **1988**, *53*, 4814. (c) Nadler E. B.; Rappoport, Z. *J. Am. Chem. Soc.* **1989**, *111*, 213.

(56) Kaftory. M.; Nugiel, D. A.; Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1989**, *111*, 8181.

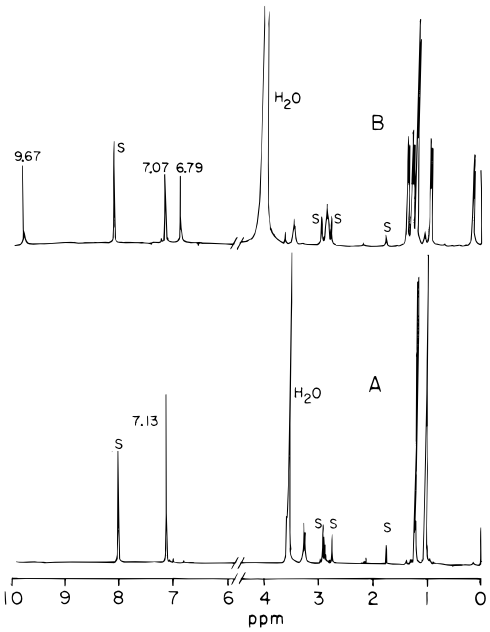


Figure 6. ^{1}H NMR spectra of (A) ketene **20** (obtained 3 min after its dissolution in DMF:THF:D_2O/residual H_2O) and (B) enediol **25** in DMF-d_7:THF-d_8:H_2O at 273 K. The signals marked S are the solvent signals.

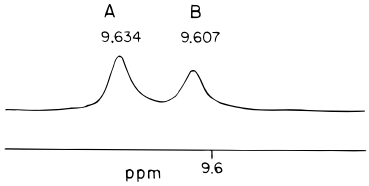


Figure 7. ^{1}H NMR spectrum of the OH region of partially O-deuteriated **25** in DMF:THF:H_2O:D_2O spectrum: (A) O-H of **25** and (B) O-H of **25-D**.

mation, cf. **29**. Since heating to 298 K does not cause peak broadening we calculate that the activation barrier for enantiomerization is >14.2 kcal mol^{-1}. This value should be compared with the barrier of 15.9 kcal mol^{-1} in DMSO for the sterically close 1,1-ditipylpropen-2-ol **30**. An accurate determination of the rotation barrier by DNMR is impractical since the coalescence temperature (T_c) of the diastereotopic Tip-H signals with $\Delta\nu$ = 108.9 Hz (at 400 MHz) in 42:5:3 DMF:THF:H_2O should be higher than 298 K (it is 331 K for **30** for which $\Delta\nu$ = 101.8 Hz in DMSO at 400 MHz) and **25** starts to isomerize to **19** > 273 K.

That the low field singlet is due to the enediolic hydroxyl was corroborated by an OH/OD exchange experiment. To a >95% pure sample of **25** in a 42:5:3 DMF-d_7:THF-d_8:H_2O mixture at 273 K, 0.05 mL of D_2O was added, and the new NMR spectrum was immediately recorded. Interestingly, in contrast with the usual fast deuteron-hydron OH exchange of alcohols leading to an immediate disappearance of the OH signal, we did not detect any spectral changes. Only when the spectrum was recorded again after keeping the sample at −18 °C for 3 days did a new signal at 0.027 ppm higher field appear side by side with the old OH signal [integration ratio:1 (old): 0.65(new) (Figure 7)]. We ascribe the slow exchange to hydrogen bonding of the OH groups to the good hydrogen bond accepting solvent DMF. Since deuterium is electron donating compared with hydrogen,[57] the new high field signal was assigned to the OH group of the monodeuteriated enediol

(57) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; p 18.

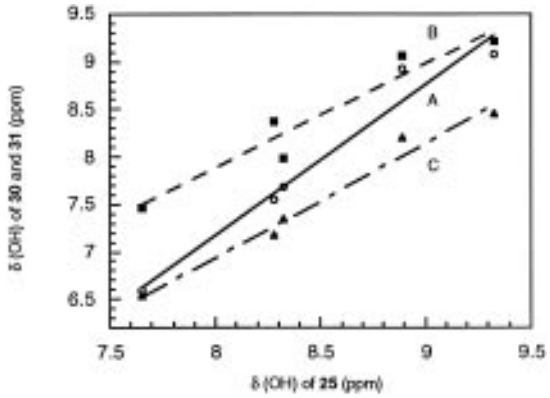


Figure 8. Plots of (A) δ(OH) of enol **31** in the pure solvent vs δ(OH) of enediol **25** in 42:5:3 solvent:THF-d_8:H_2O solvents (●), (B) δ(OH)[**31**] vs δ(OH)[**25**] in 42:5:3 solvent:THF-d_8:H_2O (■) and (c) δ(OH)-[**30**] vs δ(OH)[**25**] in 42:5:3 solvent:THF-d_8:H_2O (▲). All data at 298 K.

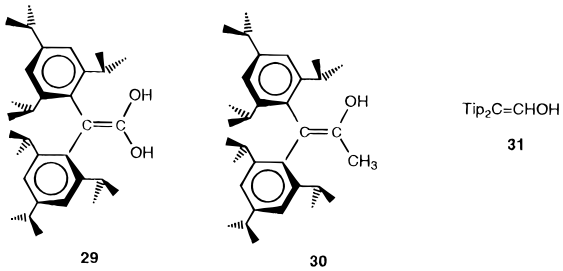
$Tip_2C{=}C(OH)(OD)$ (**25-D**) (eq 8a). Even after correcting the integration ratio for the different numbers of protons in the two species, i.e., [**25**]/[**25-D**] = 0.65:1, the extent of exchange is unknown since the doubly exchanged enediol $Tip_2C{=}C(OD)_2$ (**25-D$_2$**) is not detected in the OH region.

$$\underset{\mathbf{25}}{Tip_2C{=}C(OH)_2} \xrightarrow{D_2O} \underset{\mathbf{25\text{-}D}}{Tip_2C{=}C(OH)OD} + \underset{\mathbf{25\text{-}D_2}}{Tip_2C{=}C(OD)_2} \qquad (8a)$$

$$\underset{\mathbf{20}}{Tip_2C{=}C{=}O} \xrightarrow{1:1\ D_2O/H_2O} \mathbf{25} + \mathbf{25\text{-}D} + \mathbf{25\text{-}D_2} \qquad (8b)$$

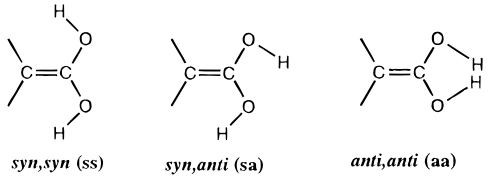
This appearance of separate OH signals for **25**, **25-D**, and water as well as the sharp water signal in all the **25**-containing mixtures corroborates the slow exchange on the NMR time scale of the enediolic OH groups with water.

Whereas the general appearance of the *gem*-ditipylvinyl moiety is identical in all solvents, the δ(OH) value is strongly solvent and temperature dependent (Table 2), as observed for other di- and triaryl ethenols[55] including the structurally related **30** and ditipylethenol **31**. A plot of the δ(OH) values of **31** in five ternary solvent mixtures (42:5:3 solvent:THF-d_8:water) against the δ(OH) values of **25** in the pure solvents at 298 K is linear with a slope of 1.59 (R = 0.9812, SD = 0.18) (Figure 8A). However, when **31** was dissolved in the same ternary solvent mixtures its OH shifted downfield by 0.13−1.20 ppm. A plot of δ(OH)[**31**] versus δ(OH)[**25**] in the five ternary mixtures at 298 K gave an approximate linear correlation with a slope of 1.10 (R = 0.9622, SD = 0.18) (Figure 8B).



The sensitivity to changes of the medium are reflected by the different slopes in the two media. A slope close to unity in the ternary solvent mixture indicates a similar interaction of **25** and **31** with the medium. The addition of 6% water and 10% THF to the solution of **31** results in small $\Delta\delta$(OH) values of 0.12−0.14 ppm in the good hydrogen bond accepting solvents DMF and DMSO and a more substantial $\Delta\delta$(OH) value in poorer hydrogen bond acceptors acetonitrile and acetone (0.81−

Scheme 3



1.20 ppm). This is attributed to a combined change of the polarity and the hydrogen bond accepting ability of the medium caused by the addition of water which is more important for the less hydrogen bond accepting solvent.[58] The better an hydrogen bond acceptor is the solvent, the more attenuated will be the effect of the added water.

The slight difference in solvation of **31** and **25** may result from the different steric bulk of the α-OH and α-H. Hence, we measured the δ(OH) values for the α-Me enol **30** in the five ternary solvent mixtures, since OH is closer in size to Me than to H. The plot of δ(OH) [**30**] vs δ(OH)[**25**] is close to linear with a slope of 1.20 (R = 0.9891, SD = 0.11) (Figure 8C) indicating only a slightly higher sensitivity of δ(OH)[**30**] to the medium changes. The small steric effect is consistent with a previous conclusion that α-substituents in α-alkyl-β,β-dimesitylethenols influence the association with the solvent mainly by a polar rather than a steric effect.[55b]

The solvent dependent shift of the δ(OH) values in various di- and trimesityl substituted ethenols[55] have been interpreted in terms of different associations of the OH group. An anti-type conformation of the enol moiety in hydrogen bond accepting solvents is stabilized by hydrogen bonding, whereas a syn-planar conformation is stabilized by an intramolecular O−H···π(Ar) hydrogen bond involving the aromatic ring cis to the hydroxyl prevails in non-hydrogen-bond accepting solvents. The same interactions should be also important for **25**.

Conformation of the C═C−O−H Moieties. The appearance of a single OH signal have a bearing on the conformation of the C═C−OH moieties of the enediol. Since the OH group was never hitherto experimentally "observed" a brief review is in order. Several *ab initio* calculations on ethene-1,1-diol are available. Early STO-3G/STO-3G calculations[2] indicated that out of three possible conformations of the hydroxy groups (Scheme 3) the syn,syn (ss) and syn,anti (sa) conformations are stable, the sa being preferred by 2 kcal mol^{-1} whereas the anti,-anti (aa) confomer is a saddle point on the potential energy surface. The relative destabilization of the ss conformer was ascribed to repulsion between the vinylic and hydroxylic hydrogens. The preference of the sa conformer is shown also by 3-21G//3-21G, 6-31G*//3-21G,[7] 6-31G**/6-31G** [59] and recently by high level 10-in-10/6-31G* CASSCF calculations.[8] The sa conformer is also the most stable for 1-cyclopropane- and 3-cyclopropenecarboxylic acids.[7]

These results could not be *a priori* assumed to apply for **25** for three reasons. (i) The steric interactions are much larger in **25** than in the parent enediol. (ii) Hydrogen bonding of each OH group to the tipyl group cis to it could lower the energy of the ss conformation. (iii) In the hydrogen bond accepting solvents used, especially DMF, the conformation may be anti, as suggested for the analogous enols.[55] The position of the OH signal and the δ(OH)[**30**] vs δ(OH)[**31**] correlation strongly suggest that solvation is important. Since space filling models show that there is no space for an associating solvent molecule

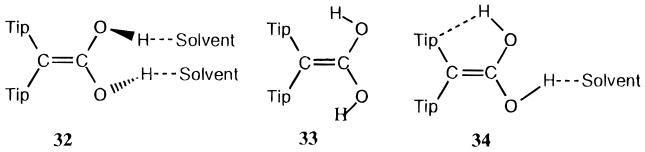
(58) Marcus, Y. *Chem. Soc. Rev.* **1993**, 409.
(59) Rodler, M. *Chem. Phys.* **1986**, *105*, 345.

Table 1. Selected Structural Parameters for Ketenes **20** and **13**[a]

structural parameter	**20**	**13**
Bond Lengths (Å)		
C(1)−O	1.166(2)	1.18(1)
C(1)−C(2)	1.298(3)	1.29(1)
Bond Angles (deg)		
O-C(1)−C(2)	179.5(2)	176(1)
C(1)−C(2)−C(3)	118.1(2)	115.5(8)
C(1)−C(2)−C(9)	118.7(2)	119.3(8)
C(3)−C(2)−C(9)	121.3(1)	125.0
Dihedral Angles (deg)		
Ar-C(2)−C(1)	55.88[b]	48.8
Ar-C(2)−C(1)	54.13[c]	56.8
Ar-C(2)−Ar	85.98	82.1

[a] The parameters for **13** are taken from ref 45 or calculated from it. The numbering scheme has been adapted to that of **20** in Figure 3. [b] Ar = C(3)−C(8). [c] Ar = C(9)−C(14).

in a syn-type conformer, we believe that an anti arrangement of both groups, i.e., as in the solvated aa conformation **32**, is implicated.



The two OH groups in the sa conformer should display two different ^{1}H NMR signals. The observation of a single OH signal is consistent with either a symmetrical conformation, ss (**33**) or aa (**32**), or with an sa (**34**) conformation whose two OH hydrogens exchange rapidly on the NMR time scale. The appearance of separate signals for enols[55a] or for **25** and water suggest that such exchange is slow. A better tool for analyzing the C═C−O−H dihedral angle of the ═C(OH)$_2$ moiety of **25** is the ^4J(HOCOH) coupling constant. That it was not observed could corroborate the existence of the symmetrical **32** conformation. Since hydrogen bonding stabilize the C═C−O−H moiety, we tentatively suggest that each OH group is hydrogen bonded as depicted in **32**. Furthermore, for steric reasons, and in analogy with the enols,[55] the C═C−O−H moieties are not periplanar but clinal, cf. **32**.

The δ(OH) values of the 1,1-ethenediols **10** and **8** which were prepared by the ketene hydration method in DMF:THF:water mixtures at 273 K (see below) are 9.63 and 9.44 ppm, respectively, compared with 9.65 ppm for **25**.

(b)^{13}C NMR. Additional corroboration for the structure of **25** is obtained from the ^{13}C NMR spectra,[60] at 273 K in THF-d_8:H$_2$O and in DMF-d_7:THF-d_8:H$_2$O which display 17 separate signals completely assigned by a gated decoupled ^{13}C NMR spectrum (Table 3), in accord with a chiral propeller structure **29** having a C_2 symmetry. In acetone-d_6:THF-d_7:H$_2$O, however, where hydration and tautomerization rates are comparable, the spectrum display signals for a mixture of **19**, **20**, and **25** and a complete assignment is hampered. Nevertheless, C$_\alpha$ and C$_\beta$ were unequivocally assigned in a gated decoupled ^{13}C NMR spectrum.

Comparison of δC$_\alpha$ and δC$_\beta$ of **25** with those of **31** (δ(C$_\alpha$) = 144.02(143.69) and δ(C$_\beta$) =110.93 (110.48) at room temperature (or 240 K) in CDCl$_3$[61] and 144.70 and 108.62 ppm,

(60) For a review on NMR spectra of enols, see: Floris, B. In *The Chemistry of Enols*; Rappoport, Z., Ed.; Wiley: Chichester, 1990; Chapter 4, p 147.

Table 2. δ(OH) Values (ppm) for $Tip_2C{=}C(OH)R$ in Several Solvent Mixtures[a]

solvent[b]	**25**		**31**		**30**	
T (K)	273	298	273	298	273	298
DMSO-d_6	*c*	8.89	*c*	9.06	*c*	8.20
			c	8.92[d]		
DMF-d_7	9.65	9.33	9.45	9.21	8.68	8.45
			9.31[d]	9.08[d]		
THF-d_8	8.50	8.28	8.70	8.38	7.50	7.18
			7.76[d]	7.54[d]		
Me_2CO-d_6	8.58	8.32	8.76	7.98	7.67	7.34
			7.95[d]	7.68[d]		
MeCN-d_3	7.92	7.65	7.79	7.46	6.87	6.54
			6.59[d]	6.59[d]		

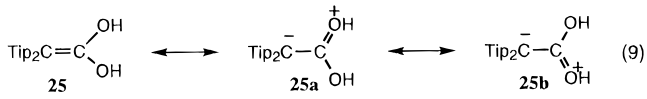
[a] Chemical shifts are relative to internal TMS standard. [b] Solvent used: solvent given: THF-d_8: water in a 42:5:3 v/v ratio. [c] Not determined since the solvent freezes. [d] δ(OH) value in the neat solvent.

Table 3. ^{13}C NMR Chemical Shifts (in ppm) for **25** in Several Solvents at 273 K[a]

	solvent		
assignment	DMF-d_7	THF-d_8	Me_2CO-d_6[b]
i-Pr-Me	22.89	22.93	
	24.49	24.37	
	24.68	24.53	
	24.82	24.85	
	24.93	25.08	
	25.99	25.98	
i-Pr-CH	25.99	30.65	
	30.91	31.08	
	34.42	34.95	
C_β	80.40	80.45	81.16
m-Tip-C	121.63	121.64	
	122.63	122.72	
ipso-Tip-C	137.48	136.80	
p-Tip-C	148.98	149.18	
o-Tip-C	146.24	146.49	
	149.11	149.30	
C_α	157.02	156.68	156.36

[a] All chemical shifts vs internal TMS standard. [b] See text.

respectively, in DMSO at room temperature[61]) shows that C_α undergoes a substantial downfield shift of ca. 14 ppm and C_β a substantial upfield shift of ca. 29 ppm. This is ascribed to the contribution of degenerate structures **25a** and **25b** (eq 9) in which C_β is negatively charged and C_α is attached to a positively charged atom. In **31** there is only one parallel structure with a charge on the single OH group. This observation is reminiscent of the $\Delta\delta$(OH) that we have measured for $CCl_3CH(OH)_2$ and Cl_3CCH_2OH in DMF-d_7 at 298 K (respectively δ 96.46 vs 76.15 for C_α and 104.95 vs 99.22 for C_β) in spite of the absence of the double bond in these systems.



(9)

Another corroborating evidence for the 1,1-enediolic stucture with apparently identical two OH groups comes from a ^{13}C SIMPLE (Secondary Isotope Multiplets of Partially Labeled Entities) NMR experiment.[62] In a solvent containing a 1:1 mixture of H_2O and D_2O, the hydroxyl groups of ROH are 1:1 OH to OD due to proton-deuteron exchange (eq 8b). A noise-decoupled ^{13}C NMR spectrum of the mixture will then display isotopic split of all the signals for carbons that are within three bonds of the deuterium. The new signals are shifted upfield by 0.09−0.12 ppm in the case of a β-isotope effect (i.e., **C**-XD carbon) and by 0.07 ppm in the case of a γ-isotope effect (i.e., **C**-C-XD). This probe is applicable also for enols since when we added 50 μL of a 1:1 H_2O:D_2O mixture to enol **31** in 1:5 THF-d_8:$CDCl_3$ at 240 K we found in the ^{13}C NMR spectra two new signals shifted upfield relative to the original signals by 0.11 ppm for C_α and by 0.12 for C_β (Figure 9). Three isotopomers are expected for **25**, and when a 1:1 H_2O:D_2O mixture was added to **20** three resolved $^{13}C_\alpha(OL)_2$ (L = H, D) signals at 156.69, 156.60 and 156.52 ppm ascribed, respectively, to **25**, **25-D**, and **25-D_2** were indeed observed (Figure 9).[63] In contrast with **31**, we did not observe the splitting of the signal for C_β. The reason for the lower splitting of C_α (and C_β) of **25** compared with **31** is unclear.

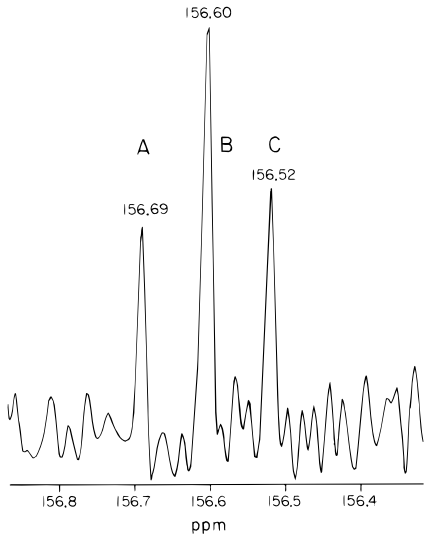


Figure 9. The C_α-OL (L = H, D) region in the ^{13}C NMR spectrum of **25**: (A) **25**; (B)**25-D**; and (C) **25-D_2**. Solvent: 42:5:3 DMF:THF:H_2O. The spectrum was obtained after 4 h acquisition time.

(c) ^{17}O NMR. Attempts to measure the ^{17}O NMR spectrum of **25** in aqueous THF, using natural abundance ^{17}O which was used successfully with 2,2-diarylethenols[61] had failed. Only signals of THF-^{17}O and $H_2{}^{17}O$ were observed. This may be due to the much larger concentration of the solvents compared with **25** and perhaps to a large line width of the signal for **25**, as found for the enols,[61] which may result in overlap of signals.[64]

(d) FTIR. Measurement of the IR sectra of enediols in the ν_{O-H} stretching region at 4000−3000 cm^{-1} is impractical since even at very low water concentration and with short optical path, the OH absorption around 3400 cm^{-1} is broad and total.[65] Likewise, the C=C stretching region is covered by the solvent peak.

Kinetic Stability of the 2,2-Diarylethene-1,1-diols. The low thermodynamic stabilities of 1,1-enediols reviewed above also applies to the bulky 1,1-enediol **25** which is transformed irreversibly within the NMR detection limit to the acid **19**. Likewise, a sample of **19** which was kept for 3 months at room temperature in DMSO-d_6 both in the presence or the absence

(61) Frey, J.; Eventova, I.; Rappoport, Z.; Müller, T.; Takai, Y.; Sawada, M. *J. Chem. Soc., Perkin Trans. 2* **1995**, 621.

(62) (a) Christofides, J. C.; Davies, D. B. *J. Am. Chem. Soc.* **1983**, *105*, 5099. (b) Reuben, J. *J. Am. Chem. Soc.* **1985**, *107*, 1756.

(63) The relative intensities of the three signals depend on the acquisition time of the spectra. This is probably associated with slow exchange rates of **25**, **25-D**, and **25-D_2** with H_2O, D_2O, and among themselves, which are likely to differ for each species. The spectrum in Figure 9 was taken after 4 h.

(64) We thank Prof. G. Cerioni from the University of Cagliari, Italy for this experiment.

(65) Perkins, W. D. *J. Chem. Educ.* **1987**, *64*, A296.

of a catalytic amount of TFA did not show any trace of **25**. Consequently, the "observed" stability conferred on **25** by the tipyl rings is only kinetic. A thermodynamic stabilization by several orders of magnitude compared with parent 1,1-ethenediol is expected by analogy with the kinetically and thermodynamically stabilized 2,2-dimesityl- and 2,2-ditipylethenols,[27,33] but it is unobservable by our detection technique.

The tautomerization $t_{1/2}$ values of the short lived 1,1-enediols of Kresge and Wirz were of the order of 10^{-6} s,[19−21] whereas those of Hegarty's 1,1-enediols in MeCN−H_2O were longer,[29] although rate constants were not given. By starting from a sample of >90% of **25** in 42:5:3DMF-d_7:THF-d_8:water at 303 K we conducted a qualitative kinetic analysis of the **25** → **19** transformation. From the build-up of the α-CH signal of **19** with time the reaction showed a first order behavior with a $t_{1/2}$ of ca. 98 min, while the first order decay of one or two of the aromatic signals of **25** gave $t_{1/2}$ = 93 min. Enediols **8** and **10** tautomerized faster with $t_{1/2}$ of ca. 9 and 7 min, respectively. The difference between them is much smaller than the reported[29] three- to four-fold decrease in the ketonization rate of **8** relative to **10**. However, our results are only semiquantitative.

The tautomerization of **25** to **19** in THF-d_8:water at 273 K is very slow. However, the reaction is accelerated by addition of a catalytic amount of TFA presumably due to a TFA-promoted ketonization when the formation of **19** obey first order kinetics with $t_{1/2}$ = ca. 60 min.

These lifetimes suggest that **25** should be regarded as the first rather relatively "long lived" carboxylic acid enol. Its kinetic stability, conferred by the bulky tipyl rings, allows the hitherto impossible unequivocal spectroscopic characterization of the 1,1-enediol intermediate in the ketene hydration reaction.

Solvent Effect on Hydration Rates and Equilibria. The hydration rate of **20** is highly solvent dependent. At 273 K in a DMF:THF:water mixture >98% of **20** had reacted after 90 min, in a THF:water mixture it took 6 h to obtain 95% **25** and in MeCN:THF:water and Me_2CO:THF:water <10% of **20** reacted after 10 h. The rate was higher at room temperature, but both **25** and **19** were formed. Hegarty[29] reported a low solvent sensitivity of the hydration rate of dimesitylketene **13** in MeCN, 1,4-dioxane, and *t*-BuOH and following Bothe et al.,[66] he suggested formation of a cyclic transition state of low polarity. Likewise, we ascribe the differences in hydration rates in different solvents to different solvation of both water and **20**.

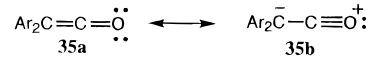
Since hydration of **20** is reversible and both **20** and its "hydrate" **25** are present in equilibrium[67] the more solvent stabilized the enediol, the less ketene is expected to be in the equilibrium. This is consistent with our finding that at 273 K ketene **20** is hydrated almost completely in the solvents with higher hydrogen-bond accepting ability parameter β[68] DMF and THF but not in MeCN and Me_2CO.

Ground State Structure of 20 as a Reason for Its Slow Hydration. The hydration rate of **20** was studied only qualitatively since a comprehensive kinetic analysis was prohibited by the high cost of the DMF-d_7 and THF-d_8. Half lives ($t_{1/2}$) of 130 min in a mixed THF-d_8:water solvent and of 40 min in a 42:5:3 DMF-d_7:THF-d_8:water mixture were measured at 273 K. Under the same conditions, hydrations of ketenes **11** and **13** were too fast to be followed although enediols **8** and **10** were observed at 273 K and their tautomerization rates measured (see above). Hence, **20** hydrates much slower than its dimesityl and bis(pentamethylphenyl) analogs previously studied.[29]

Increased steric bulk reduces significantly the hydration rate as shown, e.g., by comparing the rates for di-*tert*-butylketene with less hindered ketenes.[69] The steric bulk caused by the two geminal tipyl and mesityl rings on the ketene could be probed by comparing the solid state structures of **20** and of **13**[41] given in Table 1. The two different aryl-C=C dihedral angles of **13** differ slightly from those of **20**, presumably due to the repulsion of isopropyl groups at a spatial proximity. In both ketenes the two ring planes are close to perpendicular. The deviation of 4° of the C−C−O bond of **13** from linearity presumably results from crystal asymmetry.[41]

The difference in spatial proximity of the ketene's carbons and oxygen and the *ortho* methyls (in **13**) or the isopropyls (in **20**) could have been the reason for the substantial lower hydration rate of **20** relative to **13** by an in-plane nucleophilic attack at the ketene's C_α.[24] The nonbonded distances between the *ortho* methyls and the oxygen are 3.46−5.05 Å in **13** and 3.52−4.94 Å between the *o*-i-PrC-H carbon and the oxygen in **20**. The distances from C_α and C_β were 2.90−3.83 Å and 2.94−2.99 Å for **13**, 3.06−3.93 Å, and 2.97−3.03 Å for **20**, respectively. Since the tipyl C−H hydrogens in the crystal point toward the ketene moiety and the two methyls are directed backwards (Figure 3), the comparison of the nonbonded distances between the *ortho* substituents and the ketene moiety of the two ketenes is justified. These differences are not sufficiently significant to account for the considerable hydration rate difference between **20** and **13**. Inspection of the space filling models shows that the isopropyl methyls confer some additional steric hindrance on the ketene skeleton from a more remote position, and approach of water molecules in the C=O bond plane may become more encumbered due to the presence of some of the distant methyl groups.

The hydration rate differences of several diarylketenes are also consistent with their ^{13}C and ^{17}O NMR spectra.[70] Table 4 summarizes the chemical shifts for four diaryl substituted ketenes in $CDCl_3$ at 298 K. The large ^{13}C upfield shifts of C_β relative to the average vinylic shifts at ca. 120 ppm reflect the high negative charge density on C_β as illustrated by structure **35b**. The bulkier the aryl substituent, the more upfield shifted the $^{13}C_\beta$ and ^{17}O resonances, with the exception of $^{13}C_\beta$ of **11** whose deviation is due to the inductive effect and/or the buttressing effect of its four *m*-Me groups. δC_α depends only moderately on steric hindrance.



The shielding of $^{13}C_\beta$ and ^{17}O is rationalized by the different oxygen hybridization in **35a** and **35b**.[70] The two lone pairs of the sp^2 hybridized oxygen in **35a** are relatively close to the substituents, whereas the single lone pair of the sp-hybridized oxygen of **35a** is further away from them. The observed shielding is therefore attributed to a larger contribution of **35b** having a lower steric requirement compared with **35a**. Consequently, the nucleophilic attack of water on C_α will be substantially slowed down the more significant the contribution of **35b**.

(66) Bothe, E.; Dessouki, A. M.; Schulte-Frohlinde, D. *J. Phys. Chem.* **1980**, *84*, 3270.
(67) Frey, J.; Rappoport, Z. *J. Am. Chem. Soc.* **1995**, *117*, 1161 and **1996**, *118*, 5182−5191.
(68) (a) Kamlet, M. J.; Abboud, J.-L. M.; Taft, R. *Prog. Phys. Org. Chem.* **1981**, *13*, 485. (b) For a list of recent β values, see: Kamlet, M. J.; Doherty, R. M.; Abraham, M. H.; Carr, P. W.; Doherty, R. F.; Taft, R. *J. Phys. Chem.* **1987**, *91*, 1996.
(69) Allen, A. D.; Tidwell, T. T. *J. Am. Chem. Soc.* **1987**, *109*, 2774.
(70) Cerioni, G.; Plumitallo, A.; Frey, J.; Rappoport, Z. *Magn. Res. Chem.* **1995**, *33*, 669.
(71) Nilsson, A. *Acta Chem. Scand*. **1967**, *9*, 21.

Table 4. ^{13}C and ^{17}O Chemical Shifts (ppm) of Diarylketenes $Ar_2C{=}C{=}O$[70]

ketene	$\delta\ ^{13}C^a$		$\delta\ ^{17}O^{b,c}$
	C=C=O	C=***C***=O	C=C=***O***
14	47.0	201.2	340(250)
13	38.9	191.4	310 (230)
11	41.9	191.3	301 (470)
20	33.4	191.5	292 (765)

[a] At 100.64 MHz. [b] At 40.66 MHz. [c] Values in parentheses are estimated half-height line widths in Hz.

The possibility that different extents of the reversibility of hydration for the various ketenes[67] contribute to the difference in hydration rates will be discussed in a future publication.

Could 1,1-Enediols be Isolated? Attempted Isolation of 25. The formation of ≥98% of enediol **25** in solution, coupled with its relatively long lifetime raises the question whether it could be isolated. We know that within the experimental error of the NMR detection probe **25** is "completely" converted to **19**, i.e., the pK_{enol} value is >2, although we believe that the value is much higher than 2. Nevertheless, we think that in spite of this it is feasible to isolate enediols structurally related to **25** although we failed so far in the attempted isolation of **25** due to a combination of inherent and practical reasons. The ketene hydration approach seems advantageous over the two other preparative approaches to 1,1-enediols of Scheme 2 due to the mild reaction conditions and the minimal side products formation when the only reagents are water and the ketene. The difficulties encountered in many attempts to isolate **25** include the need to work in the cold in order to prevent tautomerization which sometimes results in precipitation of the water, and high solubility of **25** which prevented its precipitation on adding excess water to the reaction mixture in either DMF or THF. Air oxidation to radical **27** took place under all conditions tested. Likewise, attempted isolation of **25** from a THF−water mixture by lyophilizing the solvents at low temperatures afforded only **27**.

These obstacles can be overcome, and, by using bulkier, or strongly electron withdrawing substituents, *isolation* of a 1,1-enediol is only a matter of time.

A General Comment. The unequivocal structural assignment of the hydration product of ketene **20** as the 1,1-enediol **25** and the similar, only much less studied, behavior of other diaryl ketenes, shows that hydration of these ketenes is initiated by addition of water to the C=O bond. This has a bearing on the mechanistic argument concerning the details of ketene hydration.[2,8,24] A relevant mechanistic point is that hydration of diarylketenes is reversible as shown in detail for the **20**/**25** system.[67] This and reactions of 1,1-enediol **25** which involve several reaction sites of **25** are discussed in the following paper (*J. Am. Chem. Soc.* **1996**, *118*, 5182−5191).[67b]

Conclusions. 2,2-Ditipylethene-1,1-diol was prepared in solution in ≥98% purity at 273 K as a sufficiently persistent species for spectroscopic characterization. Its structure was corroborated by ^1H and ^{13}C NMR techniques and exchange experiments. A symmetric arrangement of the C=C−O−H moieties, presumably anti, anti, with solvated OH groups, seems likely. On raising the temperature it tautomerizes to ditipylacetic acid. This is the longest-lived 1,1-enediol prepared so far.

Experimental Section

General Methods. Melting points were measured on a Thomas-Hoover apparatus and are uncorrected. UV spectra were measured on a Uvikon 930 spectrophotometer and FT infrared spectra on a Nicolet Impact 400 spectrometer. NMR spectra were recorded on Bruker WP 200 SY, WH-300, and AMX-400 pulsed FT spectrometers operating at 200.13, 300.13, and 400.13 MHz for ^1H and 50.32, 75.48, and 100.62 MHz for ^{13}C, respectively. The ESR spectrum of radical **27** was measured in the Institute for Fundamental Research of Organic Chemistry in Kyushu University, Japan on a Bruker ESP 300 spectrometer in microcapillary tubes without prior degassing of the sample in 9:1 THF:water. Electron impact (EI) and chemical ionization (CI) mass spectra were recorded on a MAT-311 and on Finnigan MAT 4600 spectrometers. High resolution mass spectral analyses (HRMS) were conducted at the Mass Spectrometry Center at the Technion, Haifa on a Finnigan MAT 711 apparatus. X-ray diffraction data of the single crystals were measured using a PW1100/20 Philips Four-Circle computer-controlled diffractometer. Mo Kα ($\lambda = 0.710\ 69$ Å) radiation with a graphite crystal monochromator in the incident beam was used. All crystallographic computing was done on a VAX 9000 computer using the TEXSAN structure analysis software.

Solvents and Materials. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl, ether was distilled from $LiAlH_4$ and benzene and ethyl formate were distilled from P_2O_5 immediately before use. CCl_4 was dried by standing over $MgSO_4$ for 30 min and was then filtered. All purchased reagents were the best commercial samples and were used without purification. Polydeuteriated solvents for NMR spectroscopy (Aldrich, except for DMF-d_7 from Ferak, Berlin, Germany) were dried over 4 Å (DMSO-d_6 and DMF-d_7) or 3 Å ($(CD_3)_2CO$ and CD_3CN) molecular sieves. Small portions of THF-d_8 were kept in separate sealed ampules. The solvents used for chromatography were not purified. 1,3,5-Triisopropylbenzene was kindly donated by Dr. Hartig from Huels AG, Germany.

1-Bromo-2,4,6-triisopropylbenzene was prepared according to Nilsson *et al.*[71]

Bis(2,4,6-triisopropylphenyl)methyl Formate (16). To a solution of 1-bromo-2,4,6-triisopropylbenzene (25 g, 88.25 mmol) in dry ether (150 mL) a 1.6 M solution of *n*-butyllithium in hexane (56 mL, 89.6 mmol) was added at room temperature. The reaction mixture was stirred in an argon atmosphere for 1 h and then cooled to 0 °C. Dry ethyl formate (20 mL, 248 mmol) was added dropwise over a period of 15 min, and the resulting mixture was stirred at 0 °C for 30 min and at room temperature for additional 12 h. The reaction was terminated by adding 10% aqueous HCl (100 mL). The organic phase was separated, washed with water, and dried ($MgSO_4$), and the solvent was evaporated. The residual yellowish oil was redissolved in methanol (50 mL), and the white suspension that immediatly formed was dissolved on heating. On cooling, white crystals of bis(2,4,6-triisopropylphenyl)methyl formate (5.5 g, 27%), mp 141−2 °C were isolated. ^1H NMR (200 MHz, $CDCl_3$) δ: 0.99 (12H, d, $J = 6.7$ Hz, *o*-i-Pr-Me), 1.06 (12H, d, $J = 6.7$ Hz, *o*-i-Pr-Me), 1.21 (12H, d, $J = 6.9$ Hz, *p*-i-Pr-Me), 2.84 (2H, m, $J = 6.9$ Hz, *p*-i-Pr-CH), 3.40 (4H, m, $J = 6.7$ Hz, *o*-i-Pr-CH), 6.97 (4H, s, Tip-H), 8.06 (1H, s, Tip_2CH), 8.20 (1H, s, CHO). ^{13}C NMR: (50.32 MHz, $CDCl_3$) δ: 23.89 (*p*-i-Pr-Me), 24.20 (*o*-i-Pr-Me), 29.01(*o*-i-Pr-CH), 33.95 (*p*-i-Pr-CH), 72.04 (Tip_2CH), 122.31 (*m*-Tip-C), 131.45 (*ipso*-Tip-C), 147.51 (*o*-Tip-C), 148.29 (*p*-Tip-C), 159.95(C=O). FTIR: ν_{max} cm^{-1} (Nujol): 1726 (s, C=O), 1610 (m, C=C). MS (EI, 70 eV, *m/z*, relative abundance, assignment): 464 (32%, M), 421 (50%, M − i-Pr), 375 (B, M − i-Pr − HCOOH), 337 (49%, M − i-Pr − 2MeCH=CH_2), 260 (59%, M − TipH), 232 (52%, TipCHO). Anal. Calcd for $C_{32}H_{48}O_2$: C, 82.70; H, 10.41. Found: C, 82.41; H, 10.39.

2,4,6,2′,4′,6′-Hexaisopropylbenzhydrol (15). (a) From Bis(2,4,6-triisopropylphenyl)methyl Formate. Bis(2,4,6-triisopropylphenyl)-methyl formate (5.9 g, 12.7 mmol) was dissolved in dry ether (75 mL). $LiAlH_4$ (1 g, 26.4 mmol) was added, and the resulting suspension was stirred under protection from air at room temperature for 2 h and then cooled to 0 °C, and the excess $LiAlH_4$ was destroyed with ethyl acetate (20 mL), followed by 5% aqueous HCl (30 mL). The organic layer was separated, washed with water (30 mL), dried ($MgSO_4$) and evaporated to dryness leaving a solid (5.6 g). Recrystallization from isopropyl alcohol−water afforded 5.1 g (92%) of white crystals of 2,4,6,2′,4′,6′-hexaisopropylbenzhydrol, mp 88−9 °C. ^1H NMR (200 MHz, $CDCl_3$) δ: 1.01 (12H, d, $J = 6.8$ Hz, *o*-i-Pr-Me), 1.07 (12H, d, $J = 6.8$ Hz, *o*-i-Pr-Me), 1.22 (12H, d, $J = 6.8$ Hz, *p*-i-Pr-Me), 1.74 (1H, d, $J = 4$ Hz, OH), 2.83 (2H, m, $J = 6.8$ Hz, *p*-i-Pr-CH), 3.54 (2H, m, $J = 6.8$ Hz, *o*-i-Pr-CH), 6.75 (1H, d, $J = 4$ Hz, Tip_2CH), 6.97 (4H, s, Tip-H). ^{13}C NMR: (50.32 MHz, $CDCl_3$) δ: 23.97 (*p*-i-Pr-

Me), 24.32 (*o*-i-Pr-Me), 24.60 (*o*-i-Pr-Me), 28.96 (*o*-i-Pr-CH), 34.00 (*p*-i-Pr-CH), 72.55 (Tip_2CH), 122.20 (*m*-Tip-C), 135.46 (*ipso*-Tip-C), 147.18 (*o*-Tip-C), 147.57(*p*-Tip-C). FTIR: ν_{max} cm^{-1} (Nujol): 3616 (w), 3411 (br, OH). MS (EI, 70 eV, *m/z*, relative abundance, assignment): 436 (3%, M), 375 (B, M − i-Pr − H_2O), 231 (90%, TipCO), 189 (22%, TipH − Me). Anal. Calcd for $C_{31}H_{48}O$: C, 85.25; H, 11.08. Found: C, 85.27; H, 10.93.

(b) From 1-Bromo-2,4,6-triisopropylbenzene and Ethyl Formate. To a stirred solution of 1-bromo-2,4,6-triisopropylbenzene (17 g, 60 mmol) in dry THF (150 mL) was added BuLi (1.2 M in hexane, 50 mL) in an argon atmosphere at −70 °C. After 20 min at −70 °C, ethyl formate (2 mL, 30 mmol) was added dropwise, and at the end of the addition the solution was allowed to reach room temperature. The mixture was then refluxed for 18 h and then poured into 10% aqueous NH_4Cl solution (250 mL). The solvent was evaporated, the residual suspension was extracted twice with CH_2Cl_2 (100 mL), the phases were separated, and the organic phase was washed with water (100 mL), brine (100 mL), water (100 mL), and dried ($MgSO_4$). The solvent was evaporated, and the residual oil was chromatographed on silica gel using petroleum ether (40−60 °C):ether as the eluent. 1,3,5-Triisopropylbenzene (6 g, 48%) was eluted first, followed by 2,4,6,2′,4′,6′-hexaisopropylbenzhydrol which was coeluted with a yellow unidentified compound. After several crystallizations from aqueous i-PrOH the pure benzhydrol (4.15 g, 32%) was obtained. The ^{1}H NMR spectrum of the crude product mixture indicated the presence of small quantities of bis(2,4,6-triisopropylphenyl)methyl formate and (2,4,6-triisopropylphenyl)carboxaldehyde, but these products were not isolated from the mixture.

Bis(2,4,6-triisopropylphenyl)chloromethane (17). A stream of HCl was passed for 30 min into a solution of 2,4,6,2′,4′,6′-hexaisopropylbenzhydrol **15** (5.6 g, 12.8 mmol) in dry benzene (75 mL) at room temperature. Dry ice (3 g) was then added to the solution followed by sodium carbonate (3 g). The mixture was allowed to reach room temperature, the solids were filtered, and the solvent was evaporated leaving a yellowish oily solid which we were unable to recrystallize due to its high solubility in all solvents investigated. On adsorption on SiO_2 TLC plate, the compound turned deep purple, but this color faded after ca. 1 min. When ethanolic $AgNO_3$ was added to the compound a white precipitate was immediately formed, indicating the presence of an easily released halide ion. This and the spectral properties suggest that the compound is bis(2,4,6-triisopropylphenyl)-chloromethane, and the compound was used as such without further purification. ^{1}H NMR (200 MHz, C_6D_6) δ: 1.07 (12H, d, J = 6.7 Hz, *o*-i-Pr-Me), 1.14 (12H, d, J = 6.7 Hz, *p*-i-Pr-Me), 1.16 (12H, d, J = 6.9 Hz, *o*-i-Pr-Me), 2.70 (2H, m, J = 6.9 Hz, *p*-i-Pr-CH), 3.76 (4H, m, J = 6.7 Hz, 2H, *o*-i-Pr-CH), 7.06 (4H, s, Tip-H), 7.26 (1H, s, Tip_2-CH). ^{13}C NMR: (50.32 MHz, C_6D_6) δ: 24.73 (*p*-i-Pr-Me), 25.10 (*o*-i-Pr-Me), 25.42 (*o*-i-Pr-Me), 30.21 (*o*-i-Pr-CH), 34.39 (*p*-i-Pr-CH), 59.40 (Tip_2CH), 123.57 (*m*-Tip-C), 134.57 (*ipso*-Tip-C), 148.66 (*p*-Tip-C), 149.32 (*o*-Tip-C).

Bis(2,4,6-triisopropylphenyl)acetonitrile (23). (a) With CuCN in DMF. A solution of ditipylchloromethane (2 g, 4.4 mmol) and CuCN (0.5 g, 5.6 mmol) in dry DMF (30 mL) was refluxed for 12 h. After cooling to room temperature, water (100 mL) was added, and the solution was extracted with benzene (5 × 50 mL). The combined organic phases were washed ten times with water and dried ($MgSO_4$), and the solvent was evaporated, leaving a yellow oil which showed no nitrile band around 2200 cm^{-1}. The ^{1}H NMR spectrum of the mixture showed a 1:3 ratio of (2,6-diisopropyl-4-isopropenyl)phenyltipylmethane **21** to (2,4-diisopropyl-6-isopropenyl)phenyltipylmethane **22**. The X-ray structure of **21** is given in Figure 1. The compounds were isolated in other experiments, and their characterization will appear elsewhere.

(b) With CuCN in Pyridine. A solution containing ditipylchloromethane (1 g, 2.2 mmol) and CuCN (0.5 g, 5.6 mmol) in dry pyridine (30 mL) was refluxed for 5 h. After 5 min the solution turned deep green, and the color changed gradually to deep red. The solution was cooled to room temperature and poured into a 10% HCl solution (50 mL), and concentrated HCl was then added until the pH was 2. After extraction thrice with ether (50 mL) the organic phase was washed with water (30 mL) and dried ($MgSO_4$), and the solvent was evaporated. The ^{1}H NMR of the crude product was identical with that obtained in *(a)* above and no IR band at 2200 cm^{-1} was observed.

(c) With KCN/18-Crown-6 in Benzene. A mixture containing a suspension of KCN (300 mg, 3.6 mmol), 18-crown-6 (100 mg, 0.38 mmol), and ditipylchloromethane (2 g, 4.4 mmol) in benzene (50 mL) was refluxed under constant argon flow. The reaction was followed by monitoring the disappearance of the purple color formed on absorption of ditipylchloromethane onto the silica gel of a TLC plate. After 6 h the mixture was cooled to room temperature and filtered, the solvent was evaporated, and the residual yellowish oil was chromatographed twice on silica gel using 30:1 high boiling petroleum ether: ether as eluent. The first fraction afforded a white solid, mp 114 °C after recrystallization from methanol (50 mg, 2.5%), identified as the nitrile **24**. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.66 (3H, d, J = 6.7 Hz, i-Pr-Me), 0.79 (3H, d, J = 6.8 Hz, i-Pr-Me), 0.97 (3H, d, J = 6.9 Hz, i-Pr-Me), 1.03 (3H, d, J = 6.9 Hz, i-Pr-Me), 1.06 (3H, d, J = 6.8 Hz, i-Pr-Me), 1.08 (3H, d, J = 6.7 Hz, i-Pr-Me), 1.09 (3H, d, J = 6.9 Hz, i-Pr-Me), 1.13 (3H, d, J = 6.7 Hz, i-Pr-Me), 1.20 (3H, d, J = 6.8 Hz, i-Pr-Me), 1.23 (6H, d, J = 6.9 Hz, i-Pr-Me), 2.00 (1H, m, J = 6.7 Hz, i-Pr-CH), 2.20 (1H, m, J = 6.7 Hz, i-Pr-CH), 2.34 (1H, m, J = 6.8 Hz, i-Pr-CH), 2.86 (2H, m, J = 6.9 Hz, i-Pr-CH), 3.18 (1H, m, J = 6.7 Hz, i-Pr-CH), 5.68 (1H, d, J = 1.2 Hz, HC═C-C═CH), 5.70 (1H, d, J = 1.2 Hz, HC═C-C═C**H**), 6.90 (1H, d, J = 1.6 Hz, Tip-H), 6.93 (1H, d, J = 1.6 Hz, Tip-H), 7.01 (1H, s, HC═C). ^{13}C NMR: (100.64 MHz, $CDCl_3$) δ: 18.43, 18.78, 20.33, 20.76, 21.95, 22.09, 22.78, 23.97, 24.13, 24.25, 25.48 (12 i-Pr-Me), 29.24, 29.48, 31.39, 32.76, 33.09, 34.24 (6 i-Pr-CH), 53.38 (*C*-C≡N), 119.41, 120.02, 120.63, 121.20 (4HC═C-C═CH), 121.13(TipCH═*C*) 129.92(C≡N), 131.52, 137.53, 142.58, 145.37, 145.70, 146.76, 148.20 (1 vinylic and 6 aromatic C). IR: ν_{max} cm^{-1} (Nujol): 1760 (m, C═N), 1620 (m, C═C). MS(CI, *i*-C_4H_{10}) *m/z* (relative abundance, assignment) 446 (3%, MH^+), 419 (B, M − CN), 402 (13%, M − i-Pr), 377 (5%, M − MeCH═CH_2 − CN). MS(EI) *m/z* (relative abundance, assignment): 402 (B, M − i-Pr), 360 (63%, M − i-Pr − MeCH═CH_2), 318 (13%, M − i-Pr − 2MeCH═CH_2), 200 (74%, M − Tip − i-Pr), 158 (14%, M − Tip − i-Pr − MeCH═CH_2). Anal. Calcd for $C_{32}H_{47}N$: C, 86.22; H, 10.62. Found: C, 86.35; H, 10.43. Crystal data: $C_{32}H_{47}N$, space group $P2_1/n$, a = 30.047(4) Å, b = 10.208(2) Å, c = 9.625(1) Å, β = 93.91(1), V = 1513.1(6) $Å^3$, Z = 4, ρ_{calc} = 1.01 g cm^{-3}, μ(Cu Kα) = 3.92 cm^{-1}, no. of unique reflections = 5594, no. of reflections with $I > 3\sigma_I$ = 3841, R = 0.053, R_w = 0.080.

The second fraction contained 15 mg (0.8%) of a white crystalline solid identified as ditipylacetonitrile, **23**. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.05 (12H, d, J = 6.75 Hz, *o*-i-Pr-Me), 1.12 (12H, d, J = 6.75 Hz, *o*-i-Pr-Me), 1.20 (12H, d, J = 6.9 Hz, *p*-i-Pr-Me), 2.88 (2H, m, J = 6.9 Hz, *p*-i-Pr-CH), 3.49 (4H, d, J = 6.75 Hz, *o*-i-Pr-CH), 6.04 (1H, s, Tip_2CH), 7.00 (4H, s, TipH). ^{13}C NMR (50.32 MHz, $CDCl_3$) δ: 23.87, 23.99, 24.38 (*o*-i-Pr-Me + Tip_2CH), 29.75, 33.94 (*p*-i-Pr-CH), 122.0 (C≡N), 122.65 (*m*-Tip-C), 128.88 (*ipso*-Tip-C), 147.15 (*o*-Tip-C), 148.53 (*o*-Tip-C). IR ν_{max} cm^{-1} (Nujol): 2240 (m, CN), 1620 (m, C═C), 1560 (m, C═C). MS (CI, *i*-C_4H_{10}) *m/z* (relative abundance, assignment): 446 (39%, MH^+), 404 (B, MH^+ − MeCH═CH_2), 362 (41%, MH^+ − 2MeCH═CH_2), 320 (21%, MH^+ − 3MeCH═CH_2), 294 (3%, M − 3MeCH═CH_2 − CN), 215 (7%, M − Tip − HCN).

Bis(2,4,6-triisopropylphenyl)methyl Methyl Ether (18). Because of the difficulties encountered during the attempted purification of bis-(2,4,6-triisopropylphenyl)chloromethane, **17**, dry methanol was added *in situ* to the benzene solution of **17** at room temperature. After filtering the Na_2CO_3 and evaporation of the solvent a residual white solid remained. Recrystallization from methanol afforded 5.5 g (95%) of white crystals of bis(2,4,6-triisopropylphenyl)methyl methyl ether, mp 105−7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.99 (12H, d, J = 6.8 Hz, *o*-i-Pr-Me), 1.06 (12H, d, J = 6.8 Hz, *o*-i-Pr-Me), 1.21 (12H, d, J = 7.2 Hz, *p*-i-Pr-Me), 2.83 (2H, m, J = 7.2 Hz, *p*-i-Pr-CH), 3.43 (3H, s, OMe), 3.44 (4H, m, J = 6.8 Hz, *o*-i-Pr-CH), 6.13 (1H, s, Tip_2CH), 6.95 (4H, s, Tip-H). ^{13}C NMR: (100.64 MHz, $CDCl_3$) δ: 24.0 (*p*-i-Pr-Me), 24.4 (*o*-i-Pr-Me), 24.5 (*o*-i-Pr-Me), 28.8 (*o*-i-Pr-CH), 33.9 (*p*-i-Pr-CH), 57.6 (OMe), 81.1 (Tip_2CH), 122.1 (*m*-Tip-C), 133.7 (*ipso*-Tip-C), 147.3 (*p*-Tip-C), 147.6 (*o*-Tip-C). MS(EI, 70 eV, *m/z*, relative abundance, assignment): 449 (7%, M − H), 419 (34%, M − i-Pr − MeOH − Me), 407 (22%, M − i-Pr), 375 (B, M − i-Pr − MeOH), 360 (30%, M − i-Pr − MeOH − Me), 247 (26%, M -Tip), 246 (21%,

M- TipH), 231 (27%, M − TipH − Me), 215 (21%, TipC). Anal. Calcd for $C_{32}H_{50}O$: C, 85.27; H, 11.18. Found: C, 85.24; H, 10.96.

Bis(2,4,6-triisopropylphenyl)acetic Acid (19). To a solution of bis-(2,4,6-triisopropylphenyl)methyl methyl ether (4.56 g, 9.83 mmol) in dry ether (120 mL) in a three-necked, round-bottomed flask fitted with a reflux condenser, an argon inlet, and a closed gas bubbler, 4:1 potassium−sodium alloy (ca. 9 g) was added, and the resulting suspension was sonicated in a dry argon atmosphere. The solution became orange-red after ca. 1 h, and it turned darker with the progress of the reaction. After 6 h the sonication of the deep red solution was stopped, and a stream of carbon dioxide (dried over P_2O_5) was introduced into the solution through the gas bubbler until total decoloration. The solution was cooled to room temperature, ethanol was added to destroy the unreacted alloy, the solution was acidified to pH 2 with 10% aqueous HCl, and the organic phase was separated, washed twice with water (50 mL), and dried ($MgSO_4$). The solvent was removed in vacuo, leaving a white solid. Recrystallization from high boiling petroleum ether yielded 3.46 g (73%) of white crystals of bis(2,4,6-triisopropylphenyl)acetic acid, mp 212−3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.94 (12H, d, J = 6.6 Hz, *o*-i-Pr-Me), 1.02 (12H, d, J = 6.6 Hz, *o*-i-Pr-Me), 1.20 (12H, d, J = 6.9 Hz, *p*-i-Pr-Me), 2.83 (2H, m, J = 6.9 Hz, *p*-i-Pr-CH), 3.06 (4H, m, J = 6.6 Hz, *o*-i-Pr-CH), 5.82 (1H, s, Tip_2CH), 6.93 (4H, s,Tip-H). ^{13}C NMR (100.64 MHz, $CDCl_3$) δ: 23.93 (*o*-i-Pr-Me), 24.08 (*o*-i-Pr-Me), 24.17 (*p*-i-Pr-Me), 29.95 (*p*-i-Pr-CH), 33.92 (*o*-i-Pr-CH), 48.28 (Tip_2C), 122.34 (*m*-Tip-C), 131.83 (*ipso*-Tip-C), 147.43 (*o*-Tip-C), 147.48 (*p*-Tip-C), 180.86 (C═O). FTIR: ν_{max} cm^{-1} (Nujol): 2640 (br, COOH), 1695 (s, C═O), 1608 (m, C═C). MS(CI, *i*-C_4H_{10}) *m/z* (relative abundance, assignment): 464 (13%, M), 463 (7%, M − 1), 421 (3%, M − i-Pr), 303 (6%), 299 (4%), 261 (B, M − Tip), 260 (9%, M − TipH), 243 (4%, M − Tip − H_2O), 219 (3%, M − Tip − MeCH═CH_2), 217 (8%, M − TipH − i-Pr), 205 (5%), 203 (7%, Tip). Anal. Calcd for $C_{32}H_{48}O_2$: C, 82.70; H, 10.41. Found: C, 82.47; H, 10.36.

Bis(2,4,6-triisopropylphenyl)ketene (20). A solution containing bis-(2,4,6-triisopropylphenyl)acetic acid (1 g, 2.15 mmol), thionyl chloride (0.5 g, 4.3 mmol), and pyridine (two drops) in dry benzene (25 mL) was refluxed for 1 h in a flask protected from moisture by a $CaCl_2$ drying tube. The mixture was then decanted from the solid pyridinium chloride, and removal of the solvent left a yellow oil which was purified by chromatography on silica gel using low boiling petroleum ether as eluent. The first fraction, a bright yellow solid (880 mg), was recrystallized from hot acetonitrile, affording bright yellow crystals of bis(2,4,6-triisopropylphenyl)ketene (850 mg, 89%), mp 97 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.02 (24H, d, J = 6.8 Hz, *o*-i-Pr-Me), 1.22 (12H, d, J = 6.9 Hz, *p*-i-Pr-Me), 2.85 (2H, m, J = 6.9 Hz, *p*-i-Pr-CH), 3.23 (4H, m, J = 6.8 Hz, *o*-i-Pr-CH), 6.96 (4H, s,-Tip-H). ^{13}C NMR (50.32 MHz, $CDCl_3$) δ: 23.99 (*p*-i-Pr-Me), 24.16 (*o*-i-Pr-Me), 30.52 (*o*-i-Pr-CH), 33.49 (Tip_2C), 34.08 (*p*-i-Pr-CH), 122.18 (*m*-Tip-C), 125.85 (*ipso*-Tip-C), 148.25 (*p*-Tip-C), 148.73 (*o*-Tip-C), 191.51 (C═O). λ_{max} nm (ϵ) (CH_2Cl_2): 249 (19500), 290sh (530). FTIR: ν_{max} cm^{-1} (Nujol): 2096 (s, C═C═O). MS (CI, *i*-C_4H_{10}) *m/z* (relative abundance, assignment): 447 (24%, M + 1), 446 (9%, M), 243 (B, M − Tip), 153 (5%), 134 (2%). Anal. Calcd for $C_{32}H_{46}O$: C, 86.03; H, 10.38. Found: C, 86.06; H, 10.60. Crystal data: $C_{32}H_{46}O$, space group C_2/c, a = 19.390(2) Å, b = 17.978(4) Å, c = 15.597(2) Å, β = 107.10(1), V = 5863.0(8) Å^3, Z = 8, ρ_{calc} = 1.01 g cm^{-3}, μ(Cu Kα) = 4.12 cm^{-1}, no. of unique reflections = 4480, no. of reflections with $I \geq 3\sigma_I$ = 3738, R = 0.052, R_w = 0.089.

Bis(2,4,6-triisopropylphenyl)ketene Bis(trimethylsilyl)acetal (28). To a solution of bis(2,4,6-triisopropylphenyl)acetic acid (253 mg, 0.54 mmol) in THF (20 mL) was added *n*-butyllithium (1.6 M solution in hexane, 0.7 mL, 1.12 mmol) under argon at room temperature. The moisture-protected mixture was stirred for 3 h, chlorotrimethylsilane (0.3 mL, 2.6 mmol) was then added, and the resulting deep red mixture was kept overnight at room temperature. After evaporation of the solvent the residual red oil was redissolved in warm methanol (5 mL), and the white precipitate formed on cooling was filtered. Recrystallization from warm methanol afforded white crystals of bis(2,4,6-triisopropylphenyl)ketene bis(trimethylsilyl) acetal (95 mg, 29%), mp 88−9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.00 (18H, s, $SiMe_3$), 0.13 (6H, d, J = 6.7 Hz, *o*-i-Pr-Me), 1.03 (6H, d, J = 6.8 Hz, *o*-i-Pr-Me), 1.18 (12H, d, J = 6.9 Hz, *p*-i-Pr-Me), 1.22 (6H, d, J = 6.8 Hz, *o*-i-Pr-Me), 1.33 (6H, d, J = 6.5 Hz, *o*-i-Pr-Me), 2.79 (4H, m, J = 6.6 Hz, *o*-i-Pr-CH), 3.35 (2H, m, J = 6.5 Hz, *p*-i-Pr-CH), 6.71 (2H, d, J = 0.7 Hz, Tip-H), 6.94 (2H, d, J = 0.7 Hz, Tip-H). ^{13}C NMR (50.32 MHz, $CDCl_3$) δ: 0.4 ($SiMe_3$), 23.1, 24.1, 24.1, 24.2, 24.6, 25.7 (6 i-Pr-Me), 30.0, 30.5, 33.9 (3 i-Pr-CH), 95.2 (Tip_2C), 120.8, 122.1 (2 *m*-Tip-C), 135.2 (*ipso*-Tip-C), 146.5 (*p*-Tip-C), 147.6, 148.1 (2 *o*-Tip-C), 149.5 (═C($OSiMe_3$)$_2$). FTIR: ν_{max} cm^{-1} (Nujol):1623 (m, C═C). MS (CI, *i*-C_4H_{10}, *m/z*, assignment): 609 (M + 1). Anal. Calcd for $C_{38}H_{64}O_2$: C, 74.93; H, 10.59. Found: C, 74.77; H, 10.55.

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Supporting Information Available: Crystallographic summary for **20, 21**, and **24** including tables of crystal data, bond lengths and angles, and positional and thermal parameters and stereoviews for **21** and **24** (28 pages). Ordering information is given on any current masthead page.

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