

The First Acid and Ester Enols: 2,2-Bis(pentamethylphenyl)ethene-1,1-diol and 1-t-Butoxy-2,2-bis(pentamethylphenyl)ethenol, and Their Oxidation to Stable Free Radicals

Patrick O'Neill and Anthony F. Hegarty*

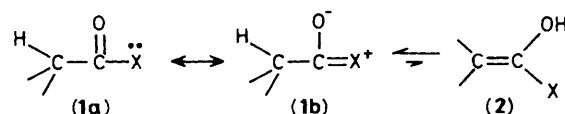
Chemistry Department, University College Dublin, Belfield, Dublin 4, Ireland

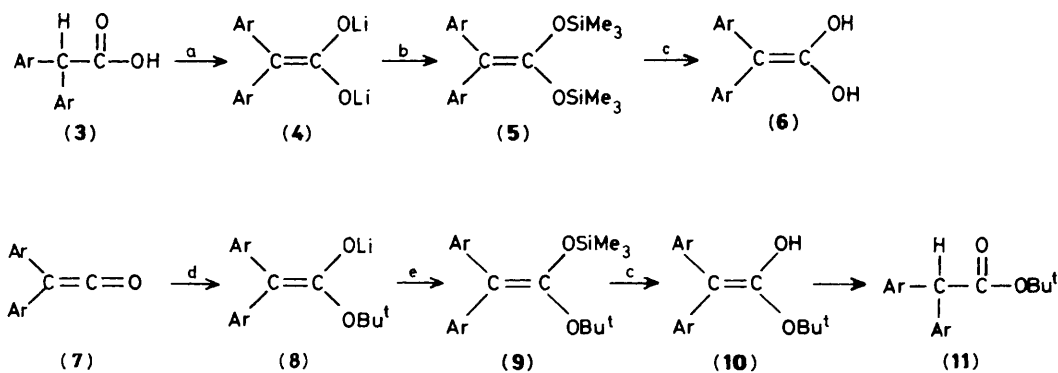
Desilylation of the ketene acetals (**5**) and (**9**) provides the ene-1,1-diols (**6**) and (**10**) which undergo relatively slow ketonisation and are oxidized to stable free radicals in basic solution.

There has been considerable interest in the enolisation of carbonyl compounds for many years¹ and excellent methods exist for the generation of simple enols of aldehydes and ketones in solution.² These enols, although thermodynamically unstable with respect to their carbonyl isomers, exist for long enough to be detected by conventional methods. On the other hand, the enol forms of simple carboxylic acids (**2**, X = OH) and derivatives such as esters (X = OR), amides (X = NR₂), thioesters (X = SR), and anhydrides (X = OCOR) have never been detected in solution. The relative instability of these enols can be attributed to resonance stabilisation of the keto isomers [(**1a**) ↔ (**1b**)]. A recent theoretical study³ has calculated that the energy difference between acetic acid and ethene-1,1-diol is 10 kcal mol⁻¹ (1 cal = 4.184 J) greater

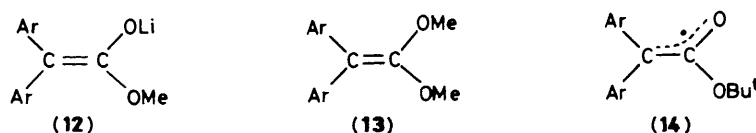
than that between acetaldehyde and ethenol. This suggests that enols of carboxylic acids (and their derivatives) would have much lower intrinsic stability than enols of aldehydes and ketones.

Enols can, however, be dramatically stabilized by the introduction of bulky groups, such as mesityl, onto the carbon α to the carbonyl group;^{4,5} in some cases the enol may then be the thermodynamically stable tautomer.⁶ We have found that





Scheme 1. Reagents: a, BuⁿLi (2 equiv.), THF, 30°C; b, Me₃SiCl (2 equiv.); c, TBAF; d, LiOCMe₃, THF, 0°C; e, Me₃SiCl.



the novel pentamethylphenyl group, whose effective bulk is increased by the buttressing effect of the *m*-methyl groups, provides the necessary stability for enediols (2, X = OH or OR).

As precursors for the acid and ester enols we have used the silylated ketene acetals (5) and (9) prepared as described in Scheme 1. Unlike most analogues,⁷ (5) and (9) are very stable and can be purified by chromatography on silica gel followed by recrystallisation from acetonitrile.† The silylated acetals can, however, be rapidly desilylated to the corresponding enols (6) and (10) by fluoride ion. Thus the acetals (5) and (9) show an absorption maximum λ_{max} at 258 nm in methanol (a solvent in which they are relatively stable). However, when an aliquot of a tetrahydrofuran (THF) solution of (5) or (9), is injected into MeOH containing tetrabutylammonium fluoride (TBAF) and a quantity of acetic acid [equimolar for (9), a two-fold excess for (5)], a new species with λ_{max} at 270 nm, identified as the corresponding acid or ester enol (6) or (10), respectively, is formed. The enols decay slowly in neutral solution at 25°C (with a half-life of several hours) to give the corresponding acid (3) and ester (11), respectively. This conversion is strongly buffer catalysed and acid catalysed at pH < 4.

When a THF solution of TBAF is added to a degassed solution of either (5) or (9) in CCl₄ (containing acetic acid as before) then the i.r. spectra recorded immediately shows a strong band at 1630 cm⁻¹ [characteristic of (6) and (10)]; (5) and (9) have absorptions at 1615 and 1607 cm⁻¹, respectively]. The dimethyl acetal (13) [formed exclusively on the methylation of the anion (12) with dimethyl sulphate] which is a model for the enols (6) and (10) also shows this characteristic ν(C=C) at 1630 cm⁻¹. On standing, the absorption observed for (6) and (10) is replaced by absorptions at 1700 and 1735 cm⁻¹, characteristic of the corresponding acid (3) and ester (11). ¹H N.m.r. evidence for the observation of enols (6) and (10) is complicated by (a) the similarity in the Me patterns to those of

their precursors and (b) partial overlapping with solvent (THF) and AcO⁻ peaks. The initial absence of the methine signal at δ 5.50 (ester) and 5.75 (acid) is significant. When the enol (10) is treated with base (n-butyl-lithium) in the presence of oxygen the purple α-t-butoxycarbonyl bis(pentamethylphenyl) methyl radical (14) is formed directly. These novel α-acyl radicals (14) are indefinitely stable as solids, do not react with oxygen or dimerise, and have i.r. and e.s.r. (g 2.0041) spectra consistent with considerable delocalisation of radical character onto the carbonyl oxygen. They have previously been implicated in enolate oxidation.^{8,9}

The ene-1,1-diols are also susceptible to oxidation to analogous stable radical species, particularly in basic solution. Although the oxidation is greatly slowed in dilute solution in the absence of oxygen, concentration of the solutions of (6) has led to the precipitation of mixtures of the radical and the acid.

In conclusion, the bis(pentamethylphenyl) substituent provides sufficient steric hindrance to stabilize these acid and ester enols kinetically but not thermodynamically. Detailed kinetic results for the tautomerism of these interesting species will be presented in a future report.

Received, 14th October 1986; Com. 1472

References

- H. O. House, 'Modern Synthetic Reactions,' 2nd edn., Benjamin, Menlo Park, California, 1972.
- Y. Chiang, A. J. Kresge, M. Capponi, and J. Wirz, *Helv. Chim. Acta*, 1986, **69**, 1137, 1331; B. Capon and C. Zucco, *J. Am. Chem. Soc.*, 1982, **104**, 7567.
- A. F. Hegarty and M. T. Nguyen, *J. Am. Chem. Soc.*, 1984, **106**, 1552.
- Z. Rappoport and S. Biali, *J. Am. Chem. Soc.*, 1984, **106**, 477.
- Z. Rappoport and S. Biali, *J. Am. Chem. Soc.*, 1985, **105**, 1701.
- A. R. Miller, *J. Org. Chem.*, 1976, **41**, 3599.
- C. Ainsworth, F. Chen, and Y. N. Kuo, *J. Organomet. Chem.*, 1972, **46**, 59, 73.
- J. K. Rasmussen, *Synthesis*, 1977, 91.
- N. Petraghani and M. Yonashiro, *Synthesis*, 1982, 521.

† Compounds (3), (5), (7), and (9) gave elemental analyses and spectral data (n.m.r., i.r.) consistent with the structures shown.