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Substituted Xanthenylidene Enols. The Importance of β-Ar–C=C Conjugation in the Stabilization of Aryl-Substituted Enols[†,1]

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Abstract: 9-Xanthenecarboxaldehyde (**7a**) and methyl (**7b**), mesityl (**7c**), 2,4,6-triisopropylphenyl (Tip) (**7d**), and *tert*-butyl (**7e**) 9-xanthenyl ketones were prepared and found to be ketonic in $CDCl_3$. In DMSO-d_6, **7a**, **7c**, **7d**, and diphenylacetaldehyde **16** are in rapid equilibrium with the enols **15a**, **15c**, **15d**, and **17**, respectively. Keto $\rightleftharpoons$ enol equilibrium constants, K_{enol}, were measured in DMSO-d_6 at various temperatures. The values at 294 K are **7a** (101) > **16** (5.06) > **7d** (1.1) > **7c** (0.48). The $\Delta H°$ values are -2.0 to -4.4 kcal mol^{-1}, and the $\Delta S°$ values are -9.1 to -11.8 cal mol^{-1} K^{-1}. From the decrease of δ(OH) values on increasing the temperature, the association constants, K_{assoc}, of the enols with DMSO-d_6 and the derived ΔH_{assoc} and ΔS_{assoc} values were obtained. The qualitative rates of formation of the enol acetates in DMSO-pyridine/Ac_2O follow the K_{enol} values. X-ray diffraction data for **7b**, **7c**, and **18c**—the acetate of **15c**—gave the Ar—C=C and Mes—CO dihedral angles and showed that the xanthenyl moiety had a butterfly conformation. Several triarylethanones PhCH(Ar^1)COAr^2 (Ar^1 = Ph, Ar^2 = Mes, Tip; Ar^1 = Ar^2 = Mes) also isomerize in DMSO-d_6 to the ketone–enol mixtures. The increase of K_{enol} by planarization of the β-aryl groups is reflected by the K_{enol}(**7a**)/K_{enol}(**16**) ratio of 20 at 294 K. Lower ratios for the α-aryl derivatives are K_{enol}(**15c**)/K_{enol}(Ph$_2$CHCOMes) = 2 and 13.2 for the α-Tip analogues. These ratios were discussed in terms of ArC=C and ArC=O conjugation in the enols and ketones. β,β-Dimesityl substitution increased K_{enol} more than did β,β-diphenyl substitution due to steric effects. α-Alkyl substitution decreased K_{enol} strongly due to the higher stability of the ketones. The K_{enol}(DMSO-d_6)/K_{enol}(H$_2$O) ratio was 46 for **16** at 294 K. This first such ratio measured for a simple enol is ascribed to higher hydrogen bond acceptance by the DMSO-d_6. Solvation of the enol is an important contributor to K_{enol}. The thermodynamic parameters resemble those for the nonsimple stable enol of acetylacetone rather than for the simple but much less stable enol, $H_2C{=}C(OH)Me$.

Several decades ago Fuson and co-workers prepared a series of stable aryl-substituted enols.[2,3] Most of them were substituted by two bulky aryls, nearly always mesityl (Mes). Comparison with the thermodynamic and kinetic instability of simple aliphatic enols indicates that the bulky aryl substituents confer kinetic and thermodynamic stability to the former enols. Recently, we measured the keto $\rightleftharpoons$ enol equilibrium constants K_{enol} (eq 1) for several of these and related enols in hexane.[4] The increased bulk

$$Ar^1Ar^2CHCOR \xrightleftharpoons{K_{enol}} Ar^1Ar^2C{=}C(OH)R \qquad (1)$$

of the α-aryl group in enols **1** indeed increased the thermodynamic stability,[4a,c] and the increased bulk of the alkyl group in enols **2** mainly increased the kinetic stability.[5] However, the increased bulk of an aliphatic R in enols **3** reduced K_{enol}.[4b] Consequently,

$$\underset{\mathbf{1}}{Mes_2C{=}C(OH)Ar} \qquad \underset{\mathbf{2}}{Z\text{—}MesC(R){=}C(OH)Mes}$$

$$\underset{\mathbf{3}}{Mes_2C{=}C(OH)R}$$

electronic effects also contribute to the stability of the enols. Meta- and para-substituted α-aryls in enols **1** gave a log K_{enol}–σ^+ relationship with $\rho^+ = 0.65$, indicating that electron donation by the α-aryl group decreases K_{enol}.[4c] Analysis had shown[2,4d] that a major effect contributing to the K_{enol} values is the Ar—C=C conjugation since the enol is stabilized by two β-Ar—C=C conjugation interactions, each amounting to 4.5–5 kcal mol^{-1} for Ar = Ph or Mes at full planarity,[4c] with no counterparts in the ketone. In contrast, the α-R—C=C stabilization in the enol (R = Alkyl, Ar) is usually more than compensated by an α-R—C=O conjugative interaction. When R = Ar, this factor will favor the ketone by ca. 2 kcal mol^{-1} at full planarity, and the effect will decrease on increasing the α-Ar—C=X (X = O, C) torsional angles. Consequently, a delicate steric–conjugation balance influences K_{enol}. Bulkier β-aryl groups sterically stabilize the enol relative to the ketone, but the simultaneous increase in the Ar—C=C torsional angles destabilize the enol due to the decreased conjugation.

Table I. Ar—C=C Torsional Angles for Several $Ar_2C{=}C$-Substituted Compounds

compd	method	ϕ, deg	cos ϕ	ref
$Ph_2C{=}C{=}CPh_2$	X-ray	27, 29.3, 35.0, 38.6[a]	0.85	6
$Ph_2C{=}CH_2$	MM calculation	40	0.77	7
$Mes_2C{=}CH_2$	X-ray	50, 58[b]	0.60	7
$Mes_2C{=}C{=}O$	X-ray	49, 57[c]	0.59	8

[a] Values for four different molecules in the unit cell. [b] Values for two different molecules in the unit cell. [c] Two different MesC=C angles for one molecule.

Table II. pK_{enol} Values for Several β-Aryl-Substituted Enols

enol	solvent	T, °C	pK_{enol}	ref
$H_2C{=}CHOH$	H_2O	25	6.23	9
$H_2C{=}C(OH)Ph$	H_2O	25	7.96	10
(E)-PhCH=CHOH	H_2O	25	3.35	11
(Z)-PhCH=CHOH	H_2O	25	3.07	11
$Ph_2C{=}CHOH$	H_2O	25	0.98	12
AnC(Me)=CHOH[a]	DMSO	60	1.17	13
p-$O_2NC_6H_4C(Me){=}CHOH$	DMSO	60	0.002	13
$Mes_2C{=}CHOH$	n-C_6H_{14}	80.6	−1.3	4a
In=CHOH[b]	H_2O	25	3.84	15
Fl=CHOH[c]	H_2O	25	−1.25	14

[a] An = p-Anisyl. [b] In = Indan-2-ylidene. [c] Fl = Fluorenylidene.

[†] Dedicated to Professor Hiroshi Taniguchi and Yuho Tsuno on the occasion of their sixtieth birthdays.

(1) Stable Simple Enols. Part 31. For Part 30, see: Nadler, E. B.; Zipori, E. S.; Rappoport, Z. *J. Org. Chem.* **1991**, *56*, 4241. Presented in part at the 10th IUPAC Conference on Physical Organic Chemistry, Haifa, Israel, August 5–10, 1990, p 27 Abstr. A-13.

(2) For example, see: (a) Fuson, R. C.; Corse, J.; McKeever, C. H. *J. Am. Chem. Soc.* **1940**, *62*, 3250. (b) Fuson, R. C.; Maynert, E. W.; Tan, T.-L.; Trumbull, E. R.; Wassmundt, F. W. *Ibid.* **1957**, *79*, 1938 and papers in the series in between a and b.

(3) For an extensive review on aryl-substituted enols including Fuson's work, see: Hart, H.; Rappoport, Z.; Biali, S. E. In *The Chemistry of Enols*; Rappoport, Z., Ed.; Wiley: Chichester, England, 1990; Chapter 8, pp 481–589.

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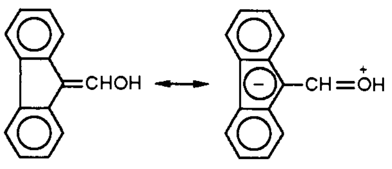
These considerations lead to an interesting conclusion concerning the stability of Fuson-type enols. A less bulky aryl group could stabilize the enol more than a more sterically demanding one, provided that the Ar—C=C system in the former case is more planar. Consequently, a β-phenyl-stabilized enol may become as stable or even more stable than a β-mesityl-stabilized enol. The importance of this effect can be deduced from Table I, which shows the crystallographically determined Ar—C=C torsional angles (ϕ) in molecules where the Ph_2C= and the Mes_2C= moieties are in the least sterically encumbered environment. The values are lower for Ph_2C= (27–40°)[6,7] than for Mes_2C= (average 53°).[7,8] Assuming a cos ϕ dependent conjugation, this will stabilize =CPh_2- compared with =$CMes_2$-stabilized enols by ca. 2 kcal mol^{-1}.

Recent studies on β-aryl-substituted systems are consistent with this suggestion. Table II compares the pK_{enol} ($-\log K_{enol}$) values for eight β-aryl-substituted systems with the values for vinyl alcohol (6.23 in H_2O)[9] and acetophenone enol (7.97 in H_2O).[10] The single β-phenyl substituent in phenylacetaldehyde enol already reduces pK_{enol} by 4.6–4.9 units in water.[11] The two phenyl groups of diphenylacetaldehyde lead to a pK_{enol} of 0.98,[12] which should make this enol observable in water. Steric effects are still important since the K_{enol} of dimesitylacetaldehyde[4a] in hexane is 200 times higher than that of diphenylacetaldehyde in water. Ahlbrecht et al. studied the 2-arylpropanol $\rightleftharpoons$ (*E*/*Z*)-2-arylpropen-1-ol equilibria for 11 compounds in DMSO and found the LFER $\log K_{enol} = 0.76\sigma^- - 0.97$.[13] This suggests an important dipolar contribution to the enol ground state having a negative charge on the β-aryl group. In spite of the presence of only a single β-aryl group, the enols are sufficiently stable in DMSO to be directly observable (6.3% and 49.8% for the *p*-MeO and the *p*-NO_2 derivatives) by ^1H NMR. In contrast, the *p*-NO_2-substituted enol was not observed in less hydrogen bond accepting solvents such as CCl_4, C_6H_6, and even $MeNO_2$.[13]

Finally, when two β-phenyl groups are forced to near planarity by incorporation into a ring, as in the enol of 9-formylfluorene (**4a**), the enol becomes thermodynamically more stable: K_{enol} = 17 in water.[14] As with other β-phenyl-[15] or β-mesityl-substituted systems,[4b] an α-Me or α-Ph substitution in this system reduces K_{enol} by several orders of magnitude.[16]

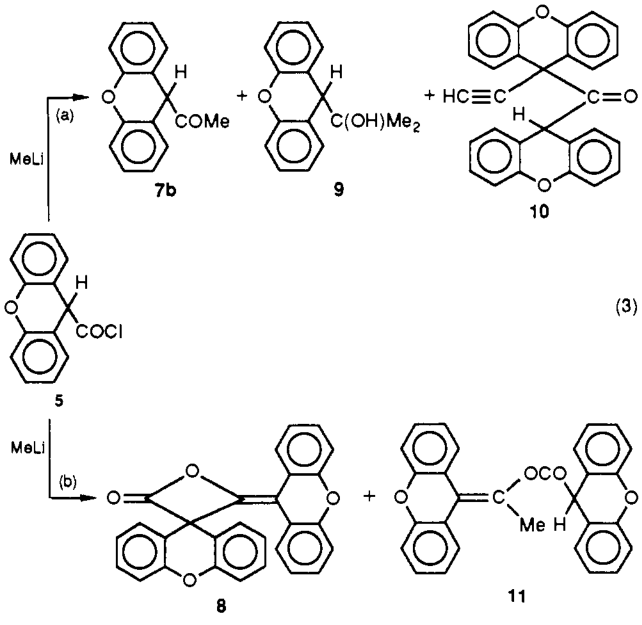
Comparison of K_{enol} values for Ph_2CHCHO[12] and 9-formylfluorene[14] shows that planarization increases K_{enol} by at least 130-fold. However, in view of the σ^- dependence on $\log K_{enol}$-(ArC(Me)=CHOH), it is possible that this is partly due to the contribution of the dipolar structure **4b** (eq 2). Consequently, we decided to study xanthenylidene-substituted systems, where planarity is still forced on two β-aryl rings but the expected dipolar contribution is much lower.



4a **4b** (2)

Results

Synthesis. The most convenient route to stable β,β-diaryl-substituted enols such as **1** and **3** involves addition of organometallic reagents or $LiAlH_4$ reductions of the stable diarylketene. Hence, we attempted to obtain the 9-carbonylxanthene (**6**) from the known[17] 9-xanthenecarbonyl chloride (**5**). However, we were unable to isolate **6** or even to observe its C=C=O stretching absorption by IR, although we obtained evidence for its intermediacy in the reaction of **5** with MeLi. When **5** was added to a 2 molar equiv solution of MeLi in THF, the main product was methyl 9-xanthenyl ketone (**7b**), whereas in the reverse addition of MeLi to an equimolar solution of **5**, both the ketene dimer **8** and the ester **11** were formed (eq 3).[18] Both reactions gave several additional products. In the former reaction 2-(9-xanthenyl)-propan-2-ol (**9**) was obtained by apparent addition of MeLi to the initially formed **7b**. Also formed was <1% of a compound whose high-resolution mass spectrum and ^1H and ^{13}C NMR spectra were consistent with the acetylenic derivative **10**, but it lacked a C≡C stretching frequency in the IR and was not investigated further. The ester (**11**) was presumably formed from the reaction of the initially formed enolate of **7b** with either **5** or **6**. Precedents for such reactions are known.[1,4b] All the products, except for **10**, are accounted for by the initial formation of the ketene **6**, which dimerizes in the absence of excess nucleophile (eq 4). Evidence for the formation of the enol of **7b** was not obtained.



(a) Local excess of MeLi
(b) Local excess of **5**

Reaction of **5** with other organometallic reagents also gave only the ketones **7** and none of the enols (eq 5).

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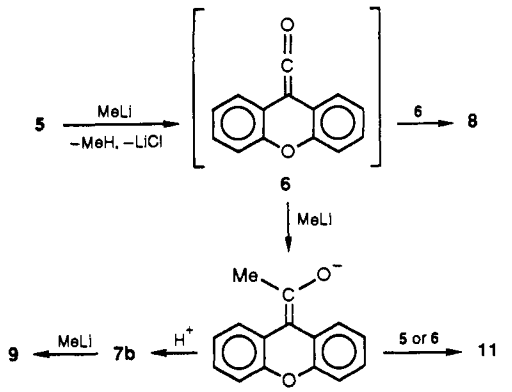
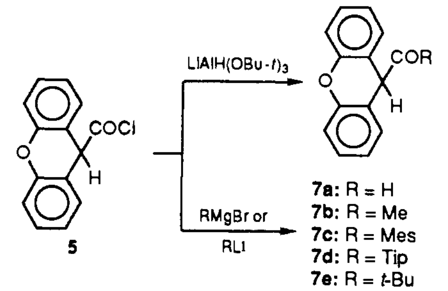
[18] For information on ketene dimers, see: Blake, P. In *The Chemistry of Ketenes, Allenes and Related Compounds*; Patai, S., Ed.; Wiley: Chichester, England, 1980; Chapter 9, pp 331–334 and other chapters in this monograph.



(4)



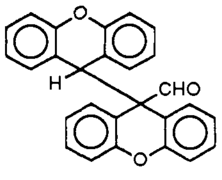
(5)

Aldehyde **7a** was obtained by the reduction of **5** with tri-*tert*-butoxylithium aluminum hydride. In solution and even in the solid state, it undergoes an easy oxidative cleavage to xanthone, causing difficulties in the purification of **7a**. A few crystals of an additional compound, whose NMR and mass spectra are consistent with 9-(9-xanthenyl)-9-xanthenecarboxaldehyde (**12**), are also formed in the reduction.

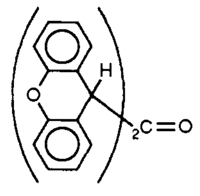
7a gives a bisulfite adduct with $NaHSO_3$ in aqueous EtOH, which on addition of Na_2CO_3 gives nearly pure **7a**.

The α-aryl ketones **7c** and **7d** were prepared from **5** and mesitylmagnesium bromide or TipLi in 52% and 7.7% yields, respectively. They also develop to xanthone on standing in DMSO-d_6, DMF-d_7, and Me_2CO-d_6.

tert-Butyl 9-xanthenyl ketone (**7e**) was obtained in 8% yield according to eq 5 together with di-9-xanthenyl ketone (**13**). The ^1H NMR signals of **13** were also observed when a solution of **7c** in DMSO-d_6 stood for a few days in air. Ketone **7e** also undergoes oxidative cleavage to xanthone on standing.



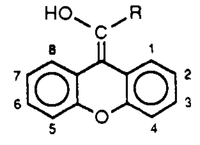
12



13

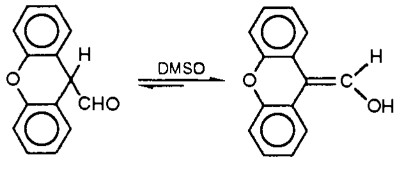
The relatively high enol content of **7a** and **7c** in DMSO (see below) suggested that the enols may be isolated by pouring their solutions in DMSO into water since their water-insolubility would reduce the rapid reketonization. However, these expectations were not borne out.

Keto ⇌ Enol Equilibria. When aldehyde **7a** or the aryl-substituted ketones **7c** and **7d** were dissolved in good hydrogen bond accepting solvents such as DMSO-d_6 or DMF-d_7 without an added catalyst, new signals were rapidly and spontaneously developed at the expense of the signals of the carbonyl compounds. The new signals that are ascribed to the enols are given in Table III, and the labeling of H1, H2, and H8 is according to structure **14**. Integration of the signals enabled the determination of K_{enol} values (see below).



14

The spectrum of the formyl derivative **7a** in $CDCl_3$ is that of an aldehyde, with CH and CHO doublets at 4.75 and 9.47 ppm. In DMSO-d_6, **7a** displays almost completely new doublets at δ 7.29 and 10.15, as well as new xanthenyl hydrogen multiplets of δ 6.95–7.26 (6 H) and doublets of doublets at ca. δ 7.44 and 8.22 (Figure 1). The two latter multiplets are characteristic for coupling of the peri hydrogens H1 and H8 with H2 and H3 and H7 and H6, respectively, and they appear together in the spectrum of the analogous xanthone. The rapid and clean reaction, its reversibility when the solution in DMSO-d_6 is poured into water, and analogy with the other reactions reported below strongly suggest that the new signals are due to enol **15a** (eq 6). The disappearance of the signal at δ 10.15 on addition of D_2O identifies it as the OH signal. Its rapid disappearance together with the small signal at δ 5.10 (H9 of **7a**, see below) or its absence in the reisolated **7a** indicates that the equilibrium of eq 6 is rapidly established.



7a **15a**

(6)

Additional signals with very low intensity were also observed in DMSO-d_6. The two doublets at δ 5.10 and 9.58 (J = 1.27 Hz; they disappear by irradiation) were ascribed to **7a** due to their close δ values to those of **7a** in $CDCl_3$. This enabled us to calculate K_{enol} values by repeated integration of the H and CHO signals of **7a** and the vinylic H and OH signals of **15a** in relatively concentrated solutions. The average percentage of **7a** from four measurements was 0.98 ± 0.01%, giving a K_{enol} value of 101 ± 13. Changes in the relative signal intensities on raising the temperature were within the experimental error. In addition, the OH signal of **15a** was shifted to higher field and broadened, and together with the CH signal it became a singlet: δ(OH) = 10.15 (d), 10.07, 10.02, 9.96, 9.74 (s) at 293, 304, 314, 324, and 357 K, respectively.

In order to compare the effect of two independent and two mutually tied phenyl groups, the enolization of diphenylacetaldehyde **16** was investigated. Dissolution of **16** in DMSO-d_6 rapidly gave a mixture of two species, which were identified as **16** (δ 5.14 (CH), 9.95 (CHO), both d, J = 1.5 Hz) and the enol **17** (δ 6.97 (=CH), 9.50 (OH), both d, J = 5.7 Hz; cf. Table III).[19] The aromatic signals of both species appear at δ 7.12–7.41. The equilibrium (eq 7) was already established after <5 min at room temperature, the measurement time of the first experimental point by ^1H NMR. The signals of **17** at δ 9.50 and of **16** at δ 5.14 exchanged rapidly with D_2O, indicating that the equilibrium of eq 7 is achieved rapidly.

$$\underset{\mathbf{16}}{Ph_2CHCHO} \xrightleftharpoons{DMSO} \underset{\mathbf{17}}{Ph_2C{=}CHOH} \qquad (7)$$

On raising the temperature, δ(OH) shifted to lower values, and the percentage of **17** decreased and that of **16** increased regularly, although in the range investigated **17** was always in excess. For example, 83.5% and 54.8% of **17** were observed at 294 and 364 K, respectively. The percentage of **17** and the derived K_{enol} values are given in Table IV. A plot of ln K_{enol} vs $1/T$ is linear (Figure 2), giving $\Delta H°$ −4.4 kcal mol^{-1} and $\Delta S°$ = −11.8 cal mol^{-1} K^{-1}. In acetone-d_6, signals for both **16** and **17** are observed, but the mixture consists of only 7% **17**, giving a K_{enol} value of ca. 0.075 at 296 K.

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[19] On increasing the temperature or on an increase in the amount of adventitious water in the DMSO, both doublets are converted to singlets, apparently due to a rapid exchange process.

Table III. δ Values (ppm) in the ^{1}H NMR Spectra of the Enols and Their Derivatives at Room Temperature

substr	solv	H1 (dd)[a]	H8 (dd)[a]	H2 (m)[a]	H2–H7 (m)[b]	OH	α-Ar	α-Alk(H)	*o*-Me	*p*-Me
15a	DMSO-d_6	7.46	8.20[c]		6.95–7.20	10.15 (d)		7.29 (d)		
18a	$CDCl_3$	7.52	8.09[c]		7.03–7.33			7.80 (s)		
18b	$CDCl_3$	7.42, 7.53[c]			7.06–7.29			2.18 (s)		
15c	DMSO-d_6	6.23	8.12	6.55	6.95–7.14	9.24 (s)	6.89 (s)		2.12	2.25
18c	$CDCl_3$	6.51	8.04	6.69	7.11–7.34		6.83 (s)		2.20	2.28
15d	DMSO-d_6	6.22 (d)	8.11	6.50	6.93–7.36	9.24 (s)			0.84, 1.21[d]	
16	DMSO-d_6	*e*	*e*		7.12–7.42	9.51 (d)		6.96 (d)		
16-OAc	$CDCl_3$	*e*	*e*		7.28–7.33			7.62 (s)		
8		6.75	8.12	6.53	6.99–7.44					
xanthone	$CDCl_3$		8.35		7.35–7.78					

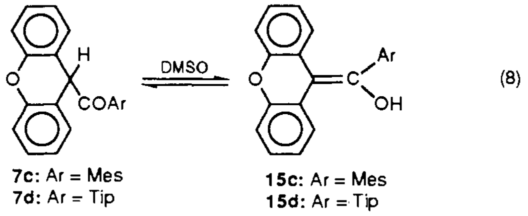
[a] See structure **14** for numbering. [b] H3–H7 for the α-Ar derivatives. [c] Assignment of H1 and H8 was not made or is only tentative. [d] *o*-C*H* (m) 3.14; *p*-C*H* (m) 2.88. [e] Appear together with H2–H7.

Table IV. Percent Enol at equilibrium, K_{enol}, and δ(OH) Values in DMSO-d_6 at Various Temperatures

ketone	*T*, K	% enol	K_{enol}	δ(OH)	ketone	*T*, K	% enol	K_{enol}	δ(OH)
7c	295	32.4	0.48	9.25		296	21.9	0.28	
	300	34	0.52	9.22		298	23.1	0.3	9.31
	307	31	0.45	9.16		310	21.9	0.28	9.22
	316	28.8	0.405	9.10		320	20.6	0.26	9.14
	327	26.5	0.36	9.04		330	18.7	0.33	9.06
	338	24.2	0.32	8.98	**7d**	294	52.4, 44.1	1.1[c] (0.79)[d]	9.23
	348	22.5	0.29	8.92		314	45.7, 42.5	0.84[c] (0.74)[d]	9.13
	358	21.9	0.28	8.86		334	43.8, 37.5	0.78[c] (0.60)[d]	9.02
	368	19.4	0.24	8.80		354	35.5,[c] 30.6	0.55[c] (0.44)[d]	8.91
	379	18.7	0.23	8.74		373	34,[c] 26.5	0.52[c] (0.36)[d]	8.80
	389	17.4	0.21	8.67		380	29.6, 25.4	0.42[c] (0.34)[d]	8.76
	399	15.3	0.18	8.63	**16**	294	83.5	5.06	9.48
7c[a]	214			9.84		304	79.6	3.9	9.42
	223			9.79		314	75.3	3.05	9.35
	233	35.5	0.55[b]	9.72		324	70.6	2.4	9.28
	243	35	0.54[b]	9.66		334	66.7	2.0	9.21
	253	34	0.52	9.59		344	62.3	1.65	9.15
	263	32.9	0.49	9.52		354	56.0	1.38	9.08
	292	25.4	0.34	9.34		364	54.8	1.21	9.03

[a] In DMF. [b] Due to slow equilibration these values probably do not amount to the correct equilibrium ratio. [c] Based on integration of H1 and H8, the OH of **15d**, and the CH of **7d**. [d] Based on integration of the *i*-Pr methyl signals of **7d** and **15d**.

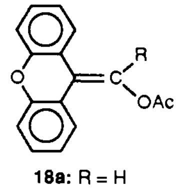
The effect of the α-substituent on the keto ⇌ enol equilibria was investigated for three alkyl (R = Me, *t*-Bu, 9-xanthenyl) and two bulky aryl (Ar = Mes, Tip) groups (eq 8). The five compounds, **7b–e** and **13**, are exclusively ketonic (by ^{1}H NMR) in $CDCl_3$. When the α-mesityl ketone **7c** is dissolved in DMSO (δ CH 5.56), it develops in <5 min additional new signals ascribed to the enol **15c**: δ 9.25 (OH), 8.14 (H1), 6.22 (H8), and *p*-Me and *o*-Me signals (Table III). The ^{1}H NMR spectrum of the **7c**/**15c** mixture is shown in Figure 3. The enol acetate **18c**, whose solid-state structure is discussed below, is obtained nearly quantitatively from **7c** in pyridine/Ac_2O. The similarity of the ^{1}H NMR spectra of **18c** and **15c** (Table III) serves as strong evidence for the structure of **15c**, whereas the rapid exchange of the signals at δ 9.25 and 5.56 (H9 of **7c**) with added D_2O indicates that the reversible **7c**–**15c** equilibrium is rapidly established.



7c: Ar = Mes
7d: Ar = Tip

15c: Ar = Mes
15d: Ar = Tip

(8)



18a: R = H
18b: R = Me
18c: R = Mes

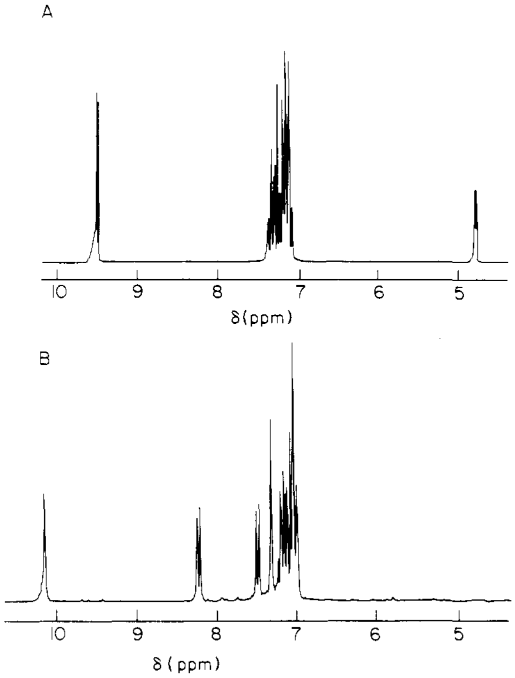


Figure 1. ^{1}H NMR spectra of solutions of **7a** in (A) $CDCl_3$ (**7a**) and (B) DMSO-d_6 (**15a**).

On raising the temperature of a solution of **7c** in DMSO-d_6, the percentage of the enol decreases (Table IV). The ketone predominates in the equilibrium from 295 (68% **7c**) to 399 K (85% **7c**). The behavior of **7c** in DMF-d_7 parallels that in DMSO-d_6. However, below 263 K the enolization becomes so slow that

Table V. Thermodynamic Parameters for the Ketone-Enol Equilibria

enol	solvent	K_{enol} (294 K)	$\Delta H°$, kcal mol^{-1} [a]	$\Delta S°$, cal mol^{-1} K^{-1} [a]	ref
$Ph_2C{=}CHOH$	DMSO-d_6	5.06	-4.4	-11.8	this work
Xan=C(OH)Mes[b]	DMSO-d_6	0.48	-2.4	-9.5	this work
	DMF-d_7	0.32	-2.0	-9.1	this work
Xan=C(OH)Tip[b]	DMSO-d_6	1.1	-2.6	-9.1	this work
MeCOCH=C(OH)Me	DMSO-d_6	3.65	-1.6	-12.4	30
$H_2C{=}C(OH)Me$	CD_3CN	1.1×10^{-8}	8.7	7.4	28

[a] Estimated errors: $\Delta H° = \pm 0.3$ kcal mol^{-1} and $\Delta S° = 1$ cal mol^{-1} K^{-1}, except for **15d**, where the estimated errors are twice these values. [b] Xan = Xanthenylidene.

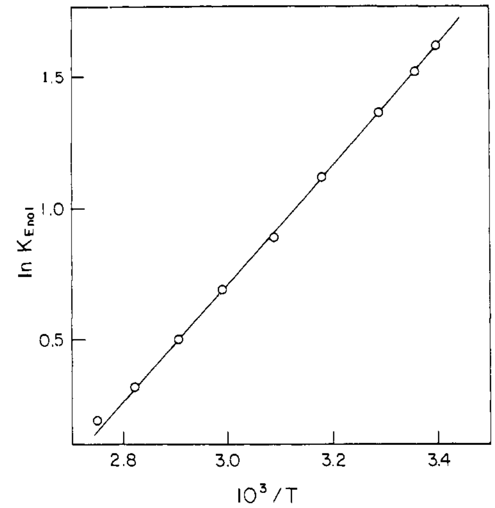


Figure 2. ln K_{enol}(DMSO-d_6) vs $1/T$ plot for Ph_2CHCHO (**16**).

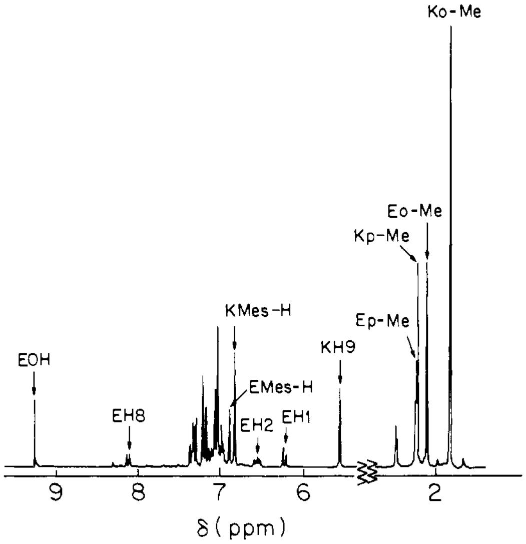


Figure 3. ^{1}H NMR spectrum of a solution of **7c** in DMSO-d_6 at 295 K. Main signals for **7c** (K) and **15c** (E) are indicated.

equilibrium is not achieved during the measurement, and the corresponding K_{enol} values reported in Table IV are probably not the equilibrium values. Indeed, the log K_{enol} vs $1/T$ plot is linear only in the range 330–263 K. In pyridine-d_5 both **7c** and **15c** were observed, and K_{enol} = 0.27 at 295 K. Lower concentrations of **15c** were observed in acetone-d_6, and K_{enol} was estimated to be 0.06. In CCl_4, $CDCl_3$, C_6D_6, CD_3CN, and $C_6D_5NO_2$ solutions only **7c** was observed. The thermodynamic parameters derived from the data of Table IV are given in Table V.

Attempts to isolate **15c** by pouring the equilibrium mixture into D_2O gave only **7c**, **13**, and xanthone, whereas only **7c** was obtained when the mixture was poured into dilute AcOH.

The α-Tip ketone **7d** was studied only briefly (eq 8). In DMSO it rapidly develops the signals of enol **15d** at δ 3.14 (m, $CHMe_2$), 6.22 (d, H1), 6.46–6.54 (m, H2), 8.10, 8.13 (dd, H8), and 9.24 (s, OH) in a 2/1/1/1 ratio. Other signals (Table III) partially overlap those for **7d**.

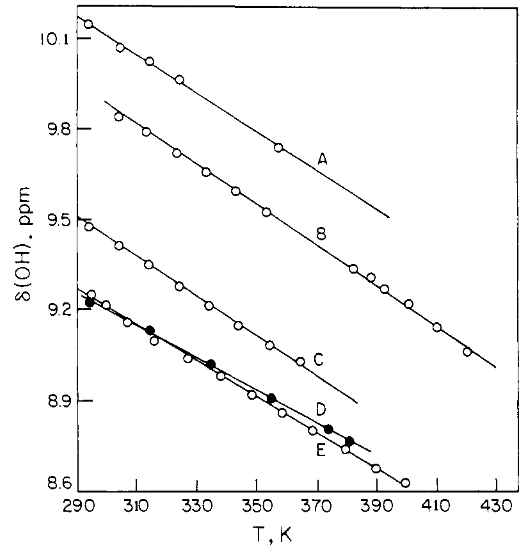


Figure 4. Plots of the observed δ(OH) of the enols against temperature: (A) **15a** in DMSO-d_6; (B) **15c** in DMF-d_7; (C) **17** in DMSO-d_6; (D) **15d** in DMSO-d_6; (E) **15c** in DMSO-d_6.

Integration of the H1, H8, and OH signals of **15d** and the CH signal of **7d** gave a set of equilibrium constants which were higher than those calculated by integration of the isopropyl methyls of **7d** and **15d** by 20–25% (Table IV). Both sets gave parallel log K_{enol} vs $1/T$ slopes, with deviations larger than for **7c**. K_{enol} decreases from 1.1 at 294 K to 0.42 at 380 K. Ketone **7d** shows broadening of the *i*-Pr signals due to a coalescence process, which will be reported elsewhere. Since this broadening may be responsible for the discrepancy of the different integrations, only the first set of data was used for comparisons. The diastereotropism of the *o*-*i*-Pr groups in both **7d** and **15d** results in three isopropyl doublets for each of them.

Solutions of the α-alkyl ketones **7b**, **7e**, and **13** in DMSO-d_6 did not show an OH signal which could be ascribed to the corresponding enol. However, in the spectrum of **7b** two very small doublets of doublets, which resemble those for H1 and H8 of the acetate **18b**, appear at δ 7.56 and 7.74. Integration of both relative to the CH signal of **7b** at δ 5.12 gave a ratio of 0.02. Hence, the maximum value of K_{enol} is 0.01.

Evaluation of the Hydrogen Bond Strength to DMSO. The downfield shift of δ(OH) on increasing the temperature (Table IV) is linear with the temperature for **15a**, **15c**, **15d**, and **17** in DMSO-d_6 and for **15c** in DMF-d_7 (Figure 4). Such shifts may provide information on the energetics of hydrogen bond association with the solvent (eq 9), provided that (a) the observed shift is due to a change of the equilibrium constants with the temperature for association of the enol with the solvent S (K_{assoc}), and (b) the δ(OH) of both the free and associated enol are nearly completely temperature independent in the temperature range studied.

$$\text{enol} + S \xrightleftharpoons{K_{assoc}} \text{enol}\cdots S \qquad (9)$$

Under these conditions δ(OH) is given by eq 10, where δ_f and δ_a are the chemical shifts of the free (nonassociated) and the

Table VI. Regression Parameters of Eq 13

enol	solvent	A	C^a	δ_f	δ_a	ΔH_{assoc}, kcal mol^{-1}	ΔS_{assoc}, cal mol^{-1} K^{-1}	K_{assoc} (294 K), M^{-1}	f_a (294 K)	$\Delta\Delta H$,^{b} kcal mol^{-1}	$\Delta\Delta S$,^{b} cal mol^{-1} K^{-1}
15a	DMSO-d_6	1300.0	−1.62	4.00	10.50	−2.6	−8.5	1.3	0.95		
15c	DMSO-d_6	953.5	−1.61	5.81	9.92	−1.9	−8.5	0.4	0.84	−0.5	−1.0
15c	DMF-d_7	822.6	−0.99	4.00	10.15	−1.6	−7.0	0.5	0.87	−0.4	−2.1
15d	DMSO-d_6	1210.1	−1.74	5.16	9.61	−2.4	−8.7	0.7	0.91	−0.2	−0.4
17	DMSO-d_6	1355.7	−3.25	7.47	9.99	−2.7	−11.7	0.3	0.80	−1.7	−0.1

[a] Calculated from $C = \Delta S_{assoc}/R - \ln [S]$; in pure DMSO-$d_6$ [S] = 14.14 M, and in pure DMF-d_7 [S] = 12.85 M. [b] $\Delta\Delta H = \Delta H° - \Delta H_{assoc}$; $\Delta\Delta S = \Delta S° - \Delta S_{assoc}$, where $\Delta H°$ and $\Delta S°$ are values for the keto–enol equilibria.

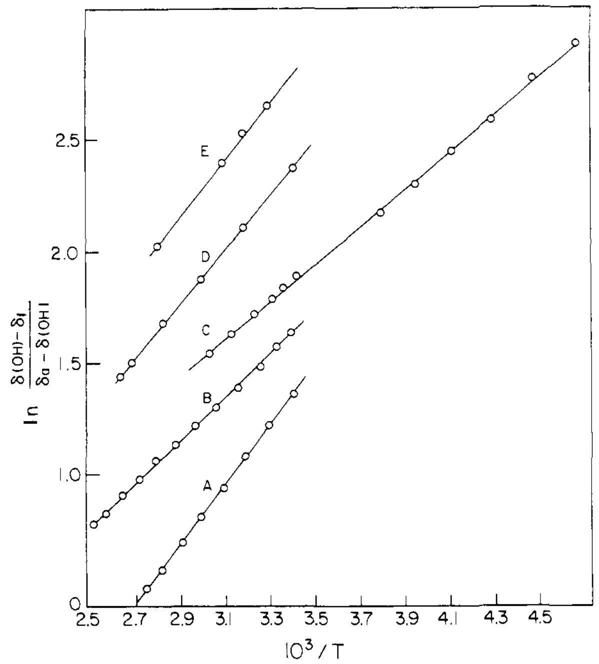


Figure 5. Plots of ln [(δ(OH) − δ_f)/(δ_a − δ(OH)] against $1/T$: (A) **17** in DMSO-d_6; (B) **15a** in DMSO-d_6; (C) **15c** in DMF-d_7; (D) **15d** in DMSO-d_6; (E) **15c** in DMSO-d_6.

associated enols, respectively, and the f's are the corresponding fractions of these species. Since $f_a + f_f = 1$, eqs 9 and 10 lead to eq 11, where [S] is the solvent concentration. Using expression

$$\delta(OH) = f_f\delta_f + f_a\delta_a \tag{10}$$

$$K_{assoc} = f_a/\{(1 - f_a)[S]\} = (\delta(OH) - \delta_f)/\{(\delta_a - \delta(OH))[S]\} \tag{11}$$

12 where $A = \Delta H_{assoc}/R$ and $B = \Delta S_{assoc}/R$ (ΔH_{assoc}, ΔS_{assoc} are the thermodynamic parameters of association), the temperature dependence of δ_{obsd} is given by eq 13,

$$K_{assoc} = e^{-(A/T+B)} \tag{12}$$

$$\delta = \delta_a e^{(A/T+B)} + \delta_f/(1 + e^{(A/T+B)}) \tag{13}$$

Since A, B, δ_f, and δ_a are a priori unknown, their best values are obtained by the so-called[20] Wood–Fickett–Kirkwood (WFK) method.[21] In spite of reservations concerning this method (see the Discussion), we calculated the parameters of eq 13 using the nonlinear least-squares regression program SAS-NLIN, with the MARQUARDT variant. Starting with reasonable values of ΔH_{assoc} and ΔS_{assoc}, δ_f and δ_a gave a rapid convergence. The derived parameters are given in Table VI.

The calculated δ_f values vary appreciably (by 3.47 ppm), with that for 2,2-diphenylethenol being the highest. The variation of δ_a values is lower, being 0.9 ppm between the extremes. The fraction of the associated enol $f_a = (\delta(OH) - \delta_c)/(\delta_a - \delta_f)$ is 0.8–0.95 at 294 K. The δ_a and δ_f values were used to calculate K_{assoc} values of 0.3–1.3 at 294 K from eq 11. When they were plotted against $1/T$, linear plots (Figure 5) were obtained. When the parameters of Table VI were used for drawing δ(OH) vs T plots, the deviations from the experimental plots (Figure 4) were less than 0.01 ppm.

Table VII. K_{enol} and δ(OH) Values for **15c**^{a} in CCl$_4$/DMSO-d_6 Mixtures at 293 K

[DMSO-d_6], M	K_{enol}	δ(OH), ppm	f_a
14.14	0.48	9.25	0.84
11.53	0.48	9.18	0.82
7.7	0.42	9.03	0.78
5.26	0.35	8.93	0.76
3.53	0.30	8.85	0.74
2.02	0.20	8.75	0.72
1.19	0.14	8.65	0.69
0.55	0.04	b	
0.35	0.03	b	
0.18	c	c	

[a] 0.023–0.026 M. [b] The OH signals for **15c** were not observed. K_{enol} was calculated from the integration of the Mes methyl signals. [c] Signals for **15c** were not observed.

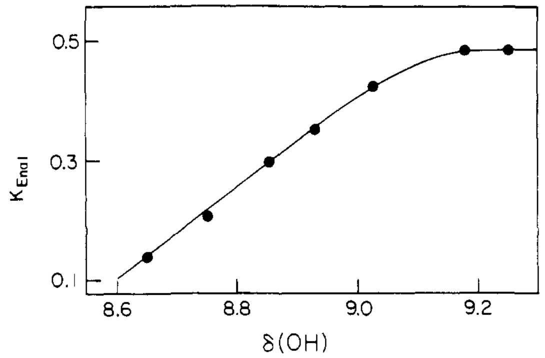


Figure 6. Plot of K_{enol} against δ(OH) for **7c** in CCl$_4$/DMSO-d_6 mixtures.

The differences between the thermodynamic parameters for the enolization (Table V) and the association (Table VI), i.e., $\Delta\Delta H = \Delta H° - \Delta H_{assoc}$ and $\Delta\Delta S = \Delta S° - \Delta S_{assoc}$, are given in Table VI. Except for a $\Delta\Delta H$ value of 1.7 kcal mol^{-1} for 2,2-diphenylethenol, the other values are rather small.

K_{enol} and δ(OH) in CCl$_4$/DMSO-d_6 Mixtures. In order to find out if K_{enol} and δ(OH) change in the same direction when parameters other than the temperature are changed (Table IV), the changes in K_{enol} and in δ(OH) caused by diluting the DMSO-d_6 with CCl$_4$ were measured for **7c**/**15c** in several CCl$_4$/DMSO-d_6 mixtures containing 0.18–11.53 M DMSO-d_6 at 293 K (Table VII). At low DMSO-d_6 concentrations, the OH signal was not observed but K_{enol} could still be evaluated by integration of the more intense signals. In general, both δ(OH) and K_{enol} decreased on decreasing [DMSO-d_6], and **15c** was not observed when [DMSO-d_6] ≤ 0.18 M. The K_{enol} vs δ(OH) plot is linear at 1.19–7.7 M DMSO-d_6 but gives a plateau at high [DMSO-d_6] (Figure 6). The fraction f_a of the enol associated with DMSO-d_6 was calculated from $f_a = (\delta(OH) - 5.81)/4.11$, which is based on eq 10 and the δ_a and δ_f values of Table VI, assuming the absence of medium effects. It decreases from 0.84 to 0.69 when the DMSO-d_6 concentration changes by 12-fold.

Crystallographic Data for 7b, 7c, and 15c. The Ar—C=C and Ar—C=O dihedral angles are important for analyzing the effect of conjugation on the K_{enol} values.[4c] For a complete analysis, the

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(20) Joshua, H.; Gans, R.; Mislow, K. *J. Am. Chem. Soc.* **1968**, *90*, 4884.

(21) Wood, W. W.; Fickett, W.; Kirkwood, J. G. *J. Chem. Phys.* **1952**, *20*, 561.

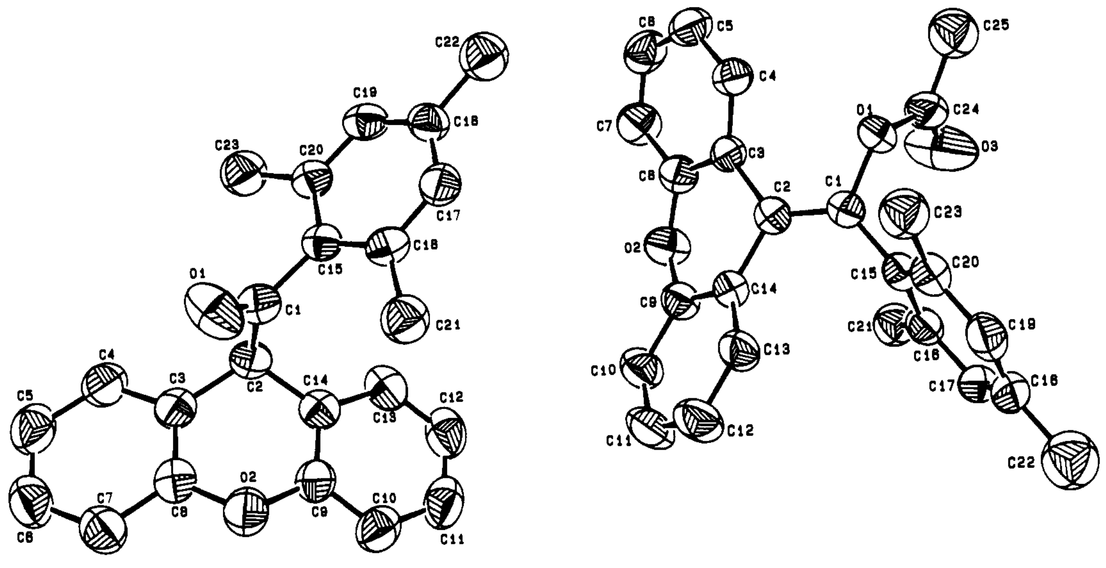

Figure 7. ORTEP plots of (A) **7c** and (B) **15c**.

Table VIII. Crystallographic Data for Methyl (**7b**) and Mesityl 9-Xanthenyl Ketone (**7c**) and for 9-(Acetoxymesitylmethylene)xanthene (**18c**)

	length, Å				deg		
bond	**7b**	**7c**	**18c**	angle	**7b**	**7c**	**18c**
C1–C2	1.549 (3)	1.544 (4)	1.342 (4)	C1C2C3	111.7 (2)	110.1 (2)	125.2 (3)
C1–O1	1.210 (3)	1.211 (4)	1.418 (3)	C1C2C14	106.3 (2)	108.6 (2)	122.1 (3)
				O1C1C15	122.2 (2)	119.7 (3)	113.4 (2)
C1–C15	1.499 (3)	1.505 (4)	1.483 (4)	C3C2C14	109.4 (2)	110.1 (2)	112.5 (2)
				C2C1C15	116.7 (2)	119.8 (2)	128.7 (3)
2 C15–C_o		1.407 ± 0.002	1.402 (4) ± 0.003	C1C15C16		119.4 (2)	120.8 (2)
				O1C1C2	121.1 (2)	120.4 (3)	117.8 (3)
2C_o–C_m		1.382 (4) ± 0.003	1.396 (5)	C1C15C20		120.1 (3)	119.3 (3)
2C_m–C_p		1.386 (4) ± 0.007	1.385 (5) ± 0.005	ring CCC[a]	119.9 (2) ± 1.0	119.9 (3) ± 1.0	119.8 (3) ± 1.6[b]
3 Mes C–Me		1.523 (4) ± 0.005	1.506 (5) ± 0.008	6 CCMe		120.4 (3) ± 1.1	120.8 (3) ± 0.9
2 O2–CAr	1.390 (2), 1.394 (2)	1.385 (3), 1.390 (4)	1.383 (4) ± 0.002	C3C2C14	109.4 (2)	110.1 (2)	112.5 (2)
2 C2–C(Xan)	1.516 (3) ± 0.004	1.514 (4) ± 0.007	1.481 (4) ± 0.001	O2C9C10	116.1 (2)	116.3 (3)	116.3 (2)
12 C–C(Xan)	1.391 (4) ± 0.004	1.390 (4) ± 0.004	1.390 (5) ± 0.010	O2C8C7	116.6 (2)	116.3 (3)	115.7 (3)
				C8O2C9	116.4 (2)	117.0 (2)	116.7 (2)
				C2C3C4	122.8 (2)	122.8 (3)	126.2 (3)
				C2C14C13	123.5 (2)	123.2 (3)	124.7 (3)

[a] 14 angles for **7b**; 20 angles for **7c** and **18c**. [b] C6C7C8: 116.6 (3)°; C9C14C13: 116.8 (3)°.

geometry of at least two ketone/enol pairs, e.g., **7a**/**15a** and **16**/**17**, is required. Unfortunately, none of the enols of the present work is isolable; **16** is a liquid and **7a** is a low-melting solid. Consequently, we obtained crystallographic data for ketone **7c** and for the vinyl acetate **18c**, which is taken as a model for enol **15c** on the basis of the similarity of the crystallographic data for enol **2** (R = Ph) and its acetate.[22] Data for ketone **7b** was collected in order to see if its nonobserved enolization is due to geometrical differences from **7c**. Unfortunately, good crystals of acetate **18b**, which is valuable for a complete study, could not be obtained.

The ORTEP drawings for **7c** and **18c** are given in Figure 7. The numbering for **7b** resembles that for **7c**, except that the carbon of the vinylic methyl group, C15, and C16-23 are absent. Its ORTEP drawing and the stereoscopic views of the three species are given in Figures S1–S4, contained in the supplementary material. Selected bond lengths and angles for **7b**, **7c**, and **18c** are given in Table VIII, and the complete lists of bond lengths and angles, positional and thermal parameters, and structure factors are given in Tables S1–S15, contained in the supplementary material.

The bond lengths and angles of the two ketones are very similar and do not display any unusual features. The interesting features of the acetate **18c** are the bond angles: the MesC1C2 angle is the widest (128.7°) followed by the C1C2C3 angle (125.2°). The O1C1C15 angle of 113.4° is closer to a tetrahedral than to a trigonal bond angle, in spite of the sp^2 hybridization of C1. These features resemble those of β,β-dimesityl-α-substituted ethenols.[7,22a]

Table IX. Torsional Angles in the Xanthene Derivatives

	torsional angle, deg			
definition of plane	between planes	**7b**	**7c**	**18c**
plane 1: O1 C1 C2 C15	1,2	78.09	91.13	170.72
plane 2: C3–C8 O2 C2	1,3		81.87	154.66
plane 3: C2 C3 C8 O2 C9 C14	2,3		11.96	29.85
plane 4: C9–C14 O2 C2	1,4	76.99	74.14	35.20
plane 5: Mes (C1 C21 C22 C23)	2,4	149.89	25.73	149.70
plane 6: C3 C8 C9 C14	3,4		14.02	150.12
	1,5		106.99	119.00
	2,5		25.90	67.48
	3,5		37.68	38.19
	4,5		51.61	118.74
	1,6	89.29		153.66
	2,6	164.80		25.62
	3,6			15.02
	4,6	14.92		165.09
	3,6			49.58

More informative are the dihedral angles (Table IX). The xanthene moiety is nonplanar, and the angles between the planes of the two tied phenyl rings are 26–30°, with no appreciable effect of the different α-substituent in **7b** and **7c** or the substitution of C9 by the exo double bond on this angle. The xanthene moiety has a butterfly conformation rather than the propeller conformation found for enols with two unconnected β-aryl groups.[4c,7,22a] Consequently, the angles of the β-aryl ring with the C3C8C9C14

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[22] (a) Kaftory, M.; Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1985**, *107*, 1701. (b) Biali, S. E.; Rappoport, Z. Unpublished results.

[23] Fuson, R. C.; Armstrong, L. J.; Kneisley, J. W.; Shenk, W. J. *J. Am. Chem. Soc.* **1944**, *66*, 1464.

plane are 13–15°. The central ring has a boat conformation (cf. **19**), with O and C2 being 0.27 and 0.4 Å in **7b**, 0.28 and 0.36 Å in **7c**, and 0.26 and 0.34 Å in **18c**, respectively, above the C3C8C9C14 plane. The strain in the enol acetate **18c** is shown by the nonplanarity of the double bond, which has a torsional angle of 9.3°. The α-Mes—C=C torsional angle is 61°.

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In the ketones, the xanthene ring is close to perpendicular to the carbonyl group plane. The carbonyl group of **7c** is above the xanthenyl plane. The Mes—C=O dihedral angle is 73°. Due to the conformation of the ring, the two phenyl groups of the xanthenylidene moiety of **18c** are not symmetrical in relation to the double bond. The β-Ar—C=C dihedral angles are 9.3° and 35.3°, respectively.

"Spontaneous" Enolization of Other Triarylethanones. The rapid enolization of **7c** and **7d** in DMSO-d_6 suggested a search for uncatalyzed enol formations of other triarylethanones. Indeed, after ketones **20a–c** were dissolved in DMSO-d_6, the spectra of their enols **21a–c** were obtained (eq 14). The assignment of the enol structure to **21a** and **21b** is based on the similarity of their spectra, especially δ(OH), to those of **15c** and **15d**, whereas enol **21c** is known.[19] The equilibrium for **20a**/**21a** is attained after 24 h and K_{enol} = 0.24 at 295 K. The enolization of **20b** gives a **21b**/**20b** ratio of ca. 0.06 after both 40 min and 48 h, but it is not clear if complete equilibration was achieved. One day was required until the signals of **21c** were observed and, since **21c** should be preferred at equilibrium with **20c**,[24] the enolization seems very slow.

$$\mathrm{PhCH(Ar^1)COAr^2} \overset{\mathrm{DMSO}}{\rightleftharpoons} \mathrm{PhC(Ar^1){=}C(OH)Ar^2} \quad (14)$$

20a: Ar^1 = Ph, Ar^2 = Mes 21a: Ar^1 = Ph, Ar^2 = Mes
20b: Ar^1 = Ph, Ar^2 = Tip 21b: Ar^1 = Ph, Ar^2 = Tip
20c: Ar^1 = Ar^2 = Mes 21c: Ar^1 = Ar^2 = Mes

Acetylation of 7a–c, 16, and 20a. The extent of enolization could be qualitatively estimated from the rate of acetylation of the 9-xanthenylidene carbonyl derivatives, **7a–e**, and of **16** under similar conditions. The acetylation rate with Ac_2O/pyridine at reflux followed the observed or estimated order of K_{enol} values.

Acetylation of **7a** to the enol acetate **18a** was complete after 3 min and that of **16** was complete after 15 min, whereas **7c** gave **18c** completely after 2 h. The reaction of the "open" analogue of **7c**, i.e., **20a**, was complete only after refluxing overnight. The α-Me ketone **7b** reacted much more slowly, giving a 1/2 mixture of unreacted **7b** and the acetate **18b** after 72 h. The *tert*-butyl ketone **7e** did not give any vinyl acetate even after 60 h of refluxing, but partial cleavage to xanthone took place. The base peak or a peak of high abundance in the mass spectra of these vinyl acetates is M − CH_2=C=O.

NMR Characteristics of the Xanthenylidene Enols. The identification of the nonisolated enols **15** depends on proper assignment of the ^{1}H NMR spectra. Fortunately, the presence of an exo double bond (C=C or C=O) at C9 of the xanthene moiety results in characteristic patterns of the peri protons H1 and H8 and with the α-aryl derivatives also of H2, which differ from those in ketones **7**. This enables integration of nonoverlapping signals of both species. Examples are shown in Figures 1 and 3.

The similarity of the xanthenylidene protons patterns for enols **15** and their acetates **18** (Table III) justifies the use of the conformation of solid **18c** as a model for the conformation of enol **15c**.

The ^{1}H NMR of the xanthenylidene moiety **14** is characterized by a 6 H multiplet of H2–H7 at δ 6.95–7.33 for α-H and α-alkyl species. In the α-Ar enols, H2 on the ring cis to the α-Ar appears separately at a higher field than H3–H7, suggesting that like H1 it is in the shielding range of a perpendicular α-Ar ring, as shown in the crystal structure of **18c**. H1 and H8 appear as two multiplets at a lower field than the major xanthenyl signals in **15a** and **18a**, but they are at higher and lower fields, respectively, than the latter in the α-aryl enols **15c** and **15d** and their acetates.

Only the spectrum of 2,2-diphenylvinyl acetate differs somewhat from that of enol **17**, in that the vinylic hydrogen is at a lower field than the aromatic protons whereas it is at a higher field in **17**. In contrast, the xanthenyl signals of the carbonyl compounds display a single 8 H multiplet at δ 6.91–7.37.

Discussion

Several new aspects of the chemistry of aryl-substituted enols were revealed in the present work. These include the effect of planarization of the β-Ph_2C= moiety on K_{enol} values when dipolar contributions are minor, the measurement of thermodynamic parameters for the keto $\rightleftharpoons$ enol equilibria of simple enols, the comparison of K_{enol} values in H_2O and DMSO, the contribution of association of the enol with the solvent to K_{enol} values, and the spontaneous enolization of several triarylethanones in DMSO.

β-Xanthenylidene vs β,β-Diphenyl: Effect on K_{enol}. Our results corroborate the assumption that increased planarity of the β-Ar_2C= moiety in the enol will increase K_{enol}. From our data K_{enol}(**7a**)/K_{enol}(**16**) = 20 at 294 K, i.e., $\Delta\Delta G°$ = 1.8 kcal mol^{-1}. Data for comparison with 9-formylfluorene are unavailable, but if its K_{enol} is affected by the change from water to DMSO in the same way that K_{enol}(**16**) changes (see below), then K_{enol}(9-formylfluorene)/K_{enol}(**7a**) = 7.3 in DMSO. This ratio is consistent with an expected higher planarity of the fluorenylidene derivative and a possible modest contribution of structure **4b** to K_{enol}. However, a quantitative evaluation of such a contribution is impossible due to lack of data.

A second comparison is between the corresponding α-aryl analogues: at 294 K K_{enol}(**7c**)/K_{enol}(**20a**) = 2 and K_{enol}(**7d**)/K_{enol}(**20b**) = 18.3 in DMSO-d_6. The difference, and especially the much lower value for **7c**/**20a** than for **7a**/**16**, should be rationalized by comparison of the α-Ar—C=O, α-Ar—C=C, and β-Ar_2C= conjugative interactions in the four species.

Unfortunately, the ground-state geometry, and hence the contribution of the various conjugation terms, is known experimentally only for **7c**. A drawback is that the solid-state geometry does not necessarily reflect the conformation in solution. In the absence of the enol, the conformation of the enol acetate **18c** is taken as a model for **15c** since the ^{1}H NMR spectra of **15c** and **18c** are similar and the crystallographically determined Ar—C=C torsional angles of **21c** and its acetate are very similar.[22]

The Mes—C=C torsional angle of 61° in **18c** gives a Mes—C=C conjugation energy of 2.3 kcal mol^{-1} when 4.8 kcal mol^{-1} is taken as the value at full planarity.[4c,25] The higher Mes—C=O torsional angle of 73° in **7c** amounts to a 2.0 kcal mol^{-1} conjugation energy if 6.9 kcal mol^{-1} is assumed as the value at full planarity.[4c] The conjugation by the α-mesityl should, therefore, increase K_{enol} 2-fold compared with **7a**/**15a**.

In spite of the oxygen bridge between the ortho positions of the two phenyl rings, the xanthenylidene moiety of **18c** is nonplanar. The butterfly shape with the dihedral angles of 15.0° in relation to the average plane of the central ring and the twist of the double bond itself, reduce the conjugation. Nevertheless, the conjugation between the xanthenyl moiety and the double bond is still extensive and amounts to 8.1–8.6 kcal mol^{-1} (based on 4.5 kcal mol^{-1} at full Ph—C=C conjugation[25]). This is absent in ketone **7c**.

The conjugation term in **15a** should be similar to, or somewhat higher than, that for **15c**. In contrast, the value for 2,2-diphenylethenol **17** is lower. The calculated values of 40° for the Ph—C=C angles in 1,1-diphenylethylene (Table I) should be a good representation for the value in **17**, resulting in a 7 kcal mol^{-1} conjugation energy.

Consequently, the **7a**/**16** ratio seems to result mainly from the conjugation effect of the β-aryl groups in the enols. The effect of the α-mesityl group on the K_{enol}(**7c**)/K_{enol}(**20a**) ratio will be accounted for by conjugation if α-mesityl conjugation stabilizes

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enol **21a** more than it stabilizes enol **15a**, or it stabilizes **20a** less than it stabilizes **7c**, or both. It is difficult to evaluate these parameters since the Mes—C=O angles in $Mes_2CHCOAr$ are lower, being 47.7°,[22a] 22.6°,[4c] 19°,[4c] and 3.5°[4c] for Ar = Mes, 3,5-$Br_2C_6H_3$, Ph, and *p*-MeOPh, respectively, but only slightly lower in MesCH(Ph)COMes, **21c** (67°).[22a] However, the bulkier α-Tip is apparently twisted much more than the α-mesityl in all species since the similarity of K_{enol}(**7d**)/K_{enol}(**20b**) and K_{enol}(**7a**)/K_{enol}(**16**) ratios can be interpreted as due to very low α-Tip—C=O and α-Tip—C=C conjugations in the four species involved in determining the ratio.

β,β-Dimesityl/β,β-Diphenyl Ratio. K_{enol} for Mes_2CHCHO is 20 in hexane at 353.6 K.[4a] The present work gives K_{enol} for Ph_2CHCHO as ca. 1.38 at 353 K in DMSO-d_6. Consequently, even without correction for a solvent effect, K_{enol} for the β,β-dimesityl derivative is still 14.5-fold higher than for the β,β-diphenyl derivative. If a factor of 650 is taken for the hexane → DMSO-d_6 change (see below), the β,β-dimesityl/β,β-diphenyl ratio becomes 9.4×10^3 in DMSO-d_6. Even if the phenyl groups are forced to planarity as in **4** (R = H), the β,β-dimesitylvinyl system of **3** with β-Mes—C=C angles of 50.2° and 56.7°[26] still gives a more stable enol.

A similar result arises by comparison of K_{enol} = 79 at 353 K for trimesitylvinyl alcohol in hexane[4a] with K_{enol} = 0.28 for **15c** at 358 K and K_{enol} = 0.24 for **21a** at 295 K in DMSO-d_6. The preference for the β,β-dimesityl enol with average β-Mes—C=C dihedral angles of 52° and 56.4°[22a] over the β-xanthenyl enol with β-"Ph" torsional angles of 15° is 1.8×10^5 after correction for the solvent effect. Consequently, both Ar—C=C conjugation effects and steric effects in the enols, and presumably also in the ketones, are important in determining K_{enol} values.

Other β-Substituent Effects on K_{enol}. Comparison of the K_{enol} value of 2.0 for Ph_2CHCHO in DMSO at 334 K with a K_{enol} of 0.095 for PhCH(Me)CHO at 333 K in DMSO[13] gives a β-Ph/β-Me ratio of 21. Unfortunately, the value could not be compared with data from the same source for changes in $K_{enol}(H_2O)$ from CH_2=CHOH (pK_{enol} = 6.23)[9] to PhCH=CHOH (pK_{enol} = 3.35(*E*), 3.07(*Z*))[11] and to MeCH=CHOH (accurate value unavailable) in water. If a DMSO/H_2O ratio of 50 for K_{enol} is assumed (see below), K_{enol} for (PhC(Me)=CHOH) is 0.002 in water, a value which is 2.5–4.7-fold higher than for PhCH=CHOH, suggesting a small β-methyl stabilization of the enol.

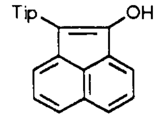
Effect of α-Alkyl and α-Aryl Substituents. Whereas the α-H system **7a**/**15a** is completely enolic in DMSO, the α-alkyl derivatives are nearly completely ketonic. The K_{enol} value for **7b**/**15b** is ≤ 0.01 and that for **7e**/**15e** or for **13** is lower since no trace of the enol is observable by NMR. A comparison with K_{enol} for **7a** shows that alkyl substitution reduces K_{enol} by $>10^4$-fold. The α-H → α-Me change in the fluorenylidene enol **4** reduces K_{enol} by a smaller ratio of 3.6×10^3-fold. The α-H → α-Me and α-H → α-*t*-Bu changes reduce K_{enol} for enols **3** by 31 and 3.4×10^3-fold.[4b] This was ascribed to higher stabilization of the carbonyl derivative than of the alkene by alkyl groups[4b] and was corroborated by calculation.[27] A similar explanation holds in the present case.

K_{enol} values for **7b** and **7e** are unknown, but their order is obtained from their relative rates of acetylation to the enol acetates. For the three cases of known K_{enol} values and for **7b** and **7e**, the acetylation rate qualitatively follows K_{enol}. This may reflect a parallel between the kinetic rate of formation and the thermodynamic stability of the enols, and in this case the order of K_{enol} values is **7b** > **7e**, as found for **3** (R = Me, *t*-Bu).[4b]

Another comparison is between the α-H and α-Ar derivatives. At 294 K, K_{enol}(**7a**)/K_{enol}(**7c**) = 206, K_{enol}(**7a**)/K_{enol}(**7d**) = 129 (92), K_{enol}(**16**)/K_{enol}(**20a**) = 22.1, and K_{enol}(**16**)/K_{enol}(**20b**) = 84 in DMSO, whereas K_{enol}(**3**, R = H)/K_{enol}(**1**, Ar = Mes) $\approx$ 0.25 in hexane.[4b] Clearly, α-H increases K_{enol} compared with α-Ar in the β,β-diphenyl, xanthenyl, and β,β-dimesityl systems, except for the most bulky trimesityl systems. This represents the operation of steric and conjugation effects in opposite directions.

Thermodynamic Parameters. The thermodynamic parameters measured for a few enols in the present work enables two types of comparison: with the unstable simple aliphatic enols and with the stable but not simple enols of β-dicarbonyl compounds (Table V). Values for simple aliphatic enols are rare, but the recent value of Kresge for 1-propen-2-ol in MeCN shows an appreciable *positive* $\Delta H°$ of 8.7 kcal mol^{-1} and a positive $\Delta S°$ of 7.4 cal mol^{-1} K^{-1}.[28] For cycloalkanones, $\Delta H°$ = 8–10.4 kcal mol^{-1} and $\Delta S°$ = –0.3 to –4.5 cal mol^{-1} K^{-1} in water.[29] In contrast, for the enolization of acetylacetone in DMSO where the K_{enol} of 3.65 is similar to that for **16**, $\Delta H°$ = –1.6 kcal mol^{-1} and $\Delta S°$ = –12.4 cal mol^{-1} K^{-1}.[30] Comparison with $\Delta H°$ = –2.0 to –4.4 kcal mol^{-1} and $\Delta S°$ = –9.1 to –11.8 cal mol^{-1} K^{-1} for our three enols shows that they resemble acetylacetone rather than the simple aliphatic enols. The K_{enol} values of both types of stable enols are controlled by negative $\Delta H°$, which is compensated by negative entropy. Whether the agreement between the values for our enols, where the hydrogen bonds are intermolecular, and acetylacetone, where the hydrogen bond is probably intramolecular, is fortuitous requires the study of additional systems. For the simple unstable enols the positive $\Delta H°$ clearly controls the equilibrium in spite of a favorable entropy for 1-propen-2-ol.[28] The negative entropy in all of the cases, except one, is mainly due to hydrogen bonding to the enolic OH in these species. For the α-aryl-substituted systems it may also reflect a higher loss of rotational freedom around the α-Ar–C bond in the enols than in the ketones, as judged by the higher rotational barrier for trimesitylethenol[31] than for trimesitylethanone.[4a]

Solvent Effects. From extensive data, K_{enol} values for β-diketones and related species are appreciably higher in hydrogen bond accepting solvents than in other solvents.[32] K_{enol} values for simple enols are mainly available in three solvents: in water for the simple aliphatic enols,[33] in hexane for the polyaryl-substituted enols,[4] and in DMSO for ArCH(Me)CHO[13] and the presently studied systems. For simple enols the only comparative data are for 2-(2,4,6-triisopropylphenyl)acenaphthen-1-ol (**22**) where K_{enol}(DMSO) $\geq$ 650K_{enol}(hexane).[34]



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Comparison between our K_{enol} value for diphenylacetaldehyde in DMSO-d_6 and Kresge's value (pK_{enol} 0.98)[12] in water gave K_{enol}(DMSO-d_6)/$K_{enol}(H_2O)$ ratios of 46 and 50 at 298 and 294 K, respectively. We ascribe the much higher K_{enol} value in DMSO-d_6 to stabilization of the enol by hydrogen bonding between its OH and the DMSO-d_6, which serves as a hydrogen bond acceptor. We had shown previously that such interaction is appreciable. For example, the association constants K_{assoc} for the 1:1 associate of **3** (R = H) with DMSO, DMF, and acetone are 7.4, 4.6, and 0.61, respectively.[35c] The hydrogen bond accepting ability of water is much lower than that of DMSO as judged by the Kamlet–Taft hydrogen bond accepting parameter, β, which

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is 0.76 (DMSO), 0 (hexane), and 0.14 (H_2O),[36] and with $\Delta G°$ values for association of *p*-fluorophenol with these solvents.[36] This observation is consistent with the order of K_{assoc} values for **3** (R = H) in these solvents.[35a,c]

The K_{enol} values for **7c** follow the order DMSO > DMF > pyridine > Me_2CO > $PhNO_2$, C_6H_6, $CDCl_3$, CCl_4, which is the order of β values for these solvents.[36]

If a similar $K_{enol}(DMSO)/K_{enol}(H_2O)$ ratio applies for other simple enols with $K_{enol}(H_2O) \approx 10^{-3}$, which are unobservable in water, these enols may be observed in DMSO. This is under investigation.

Hydrogen Bond Strengths. The hydrogen bond strength was evaluated from the shift of δ(OH) with temperature (Tables IV and VI), and the interpretation of results obtained by this method deserves comment. The two basic assumptions of the method were previously criticized. Lambert et al.[37] argued that the main reason for the shift in δ(OH) with the temperature in many cases is not due to changes in K_{assoc}, but to simultaneous changes in the viscosity of the solution and a deshielding effect due to stronger van der Waals forces when the temperature changes. A different argument[38] is that the δ's of both species in the equilibrium are temperature-dependent due to changes in the population of the vibrational levels of the OH group with temperature. According to Mislow and co-workers,[20] the main problem is related to the accuracy of the measurements and the method of calculation. The values of the calculated parameters of eq 13 could be appreciably changed without a major change in the statistical quality of the correlation. The functions calculating the residual sum of squares seem not to have a sharp minimum in our cases.[20] Attempts at improvement are meaningless since the accuracy of the measurements does not justify them. Consequently, we regard the reliability of the values of Table VI as being in doubt. Nevertheless, it is interesting to consider whether the values are reasonable in comparison with those in related systems. The δ_a values are higher by ca. 1 ppm than the δ(OH) values found for enols **1** in DMSO,[35c] whereas the δ_f values for enols **1** in CCl_4, deduced from data similar to that in Table VII, are at ca. 5 ppm.[35c] Since the values should be sensitive to the conformation of the system, to the nature of α- and β-substituents, and especially to the solvent (DMSO vs CCl_4), the only exceptional δ_f value is 7.47 for **17**. The K_{assoc} values are appreciably higher for enols **1** than those calculated for enols **15** and **17**. For example, the value for **1** (Ar = Mes) is 1.82, and for **3** (R = H) is 7.4,[35c] i.e., 4.5–5.7-fold higher for the β,β-dimesityl derivatives. The ΔS_{assoc} values of -10 ± 1.5 eu are consistent with the association of two neutral molecules, and the ΔH_{assoc} values are also reasonable for a moderate association. An interesting observation is the similarity of the $\Delta H°$ and $\Delta S°$ values for the keto $\rightleftharpoons$ enol equilibria with the ΔH_{assoc} and ΔS_{assoc} values, as shown by the small values of the differences, $\Delta\Delta H$ and $\Delta\Delta S$, in Table VI. Due to the reservation raised above, further discussion is unwarranted.

Experimental Section

General Methods. Melting points were determined with a Thomas-Hoover apparatus and are uncorrected. UV spectra were taken with a Uvikon-930 spectrometer and IR spectra with a Perkin-Elmer Model 157G spectrometer. EI mass spectra were recorded with a MAT-311 instrument at 70 eV, CI spectra with a Finnigan 4021 spectrometer, and high-resolution spectra with a MAT-711 instrument. ^1H NMR spectra were recorded on a Brucker WP 200 SV pulsed F1 spectrometer operating at 200.133 MHz, and ^{13}C NMR spectra were recorded on a Bruker WP 200 SV spectrometer operating at 50.32 MHz, with TMS as a reference. In the mass spectral assignments, Xan is xanthenylidene, $C_{13}H_8O$.

Solvents and Materials. THF was stored over benzophenone ketyl, and ether was kept over $LiAlH_4$. Both solvents were distilled before use under argon. CCl_4 was dried over 4A molecular sieves. Other solvents, including deuterated ones (DMSO-d_6, DMF-d_7, $(CD_3)_2CO$, pyridine-d_5 Aldrich; $CDCl_3$, Merck), 9-xanthenecarboxylic acid, and Tip bromide were commercial samples and were used without further purification. Commercial solutions (Aldrich) of MeLi (1.4 M in ether), *n*-BuLi (1.6 M in hexane or 1.7 M in pentane), MesMgBr (1 M in THF) and $LiAlH_4(OBu\text{-}t)_3$ (0.5 M in diglyme) were handled in an inert atmosphere. Ketones **20a–c** were available from previous studies.

9-Xanthenecarbonyl Chloride (5). To a suspension of 9-xanthenecarboxylic acid (7.65 g, 3.38 mmol) in dry benzene (50 mL) was added thionyl chloride (4 mL, 54.8 mmol), and the mixture was refluxed with stirring. After 30 min the solution became homogeneous, indicating the end of the reaction since the acid is insoluble in benzene. The benzene and most of the $SOCl_2$ were evaporated in vacuo, leaving a yellow solid. Dry benzene (100 mL) was then added, and the benzene with the remaining thionyl chloride was evaporated, leaving a light-yellow solid (8.02 g, 97%). Crystallization from dry hexane gave colorless needles (7.75 g, 94%) of 9-xanthenecarbonyl chloride (**5**): mp 87–88 °C (lit.[17] mp 86–88 °C); IR (Nujol) ν_{max} 1785, 1760 (C=O, s), 1265, 1250 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.41 (1 H, s, CH), 7.10–7.43 (8 H, m, XanH); mass spectrum (EI, 70 eV, 50 °C), *m/z* (relative abundance, assignment) 246, 244 (3, 8 ($M(^{37}Cl,^{35}Cl)$)), 182 (51, $XanH_2$), 181 (XanH, B), 152 (63, $(C_6H_4)_2$), 126 (13), 90 (23, C_7H_6), 76 (21, C_6H_4). Anal. Calcd for $C_{14}H_9ClO_2$: C, 68.72; H, 3.71. Found: C, 68.59; H, 3.73.

9-Xanthenecarboxaldehyde (7a). A 0.5 M solution of tri-*tert*-butoxylithium aluminum hydride in diglyme (24.6 mL) was added dropwise over 2.5 h to an acetone/dry ice cooled, stirred solution of 9-xanthenecarbonyl chloride (**5**) (3 g, 12.3 mmol) in diglyme (15 mL) at a temperature less than −68 °C, and stirring was continued for an additional 30 min at −76 °C. TLC showed the disappearance of **5** and formation of a main product (**7a**) and a minor product (**12**). The solution was poured with vigorous stirring into a mixture containing a solution of HCl (3.5 mL) and saturated aqueous NaCl (11 mL) and ice (4 g), and the phases were separated. The aqueous phase was extracted three times with ether (150 mL), and the organic phase was dried ($MgSO_4$) and filtered and the ether was evaporated, giving a yellow oil containing 9-xanthenecarboxaldehyde and diglyme. Further purification was achieved by two methods.

(a) The diglyme was distilled at 1 Torr. TLC on silica of the remaining yellow oil showed mainly **7a**, but also an additional new spot with R_f identical to that of xanthone. The yellow oil was chromatographed rapidly on a silica under N_2 pressure, with a 1:1 CH_2Cl_2/petroleum ether eluent. 9-Xanthenecarboxaldehyde (**7a**) (2.04 g, 79%) was obtained as a yellow oil at room temperature, which solidified on standing at 0 °C. On standing in contact with air it slowly gave xanthone and HCOOH (according to ^1H NMR). **7a**: IR (Nujol) ν_{max} 2825, 2720 (CH, m), 1730 (C=O, s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.76 (1 H, d, J = 3.3 Hz, H9), 7.08–7.37 (8 H, XanH), 9.48 (1 H, d, J = 3.3 Hz, CHO). Anal. Calcd for $C_{14}H_{10}O_2$: C, 79.98; H, 4.79. Found: C, 80.27; H, 4.90.

The chromatography gave a few crystals of an additional solid whose NMR, IR, and mass spectra are consistent with 9-(9-xanthenyl)-9-xanthenecarboxaldehyde (**12**): IR (Nujol) ν_{max} 1720 (C=O, s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.96 (1 H, s, H9), 6.57–7.33 (16 H, m, XanH), 9.66 (1 H, s, CHO); mass spectrum (CI, methane), *m/z* (relative abundance, assignment) 391 (9, MH), 210 (7, $XanH_2CO$), 209 (21, XanHCO), 180 (B, Xan-2H).

(b) When the yellow oil (2.17 g) obtained after evaporation of the ether was poured with vigorous stirring into a saturated $NaHSO_3$ solution (40 mL) in H_2O/EtOH, a white bisulfite adduct precipitated after 20 min. After stirring for an additional 2 h, it was filtered and washed with ether (100 mL), giving white crystals which decompose at 114–5 °C. The adduct is soluble in water, insoluble in most organic solvents, and slightly soluble in DMSO, and separation from unreacted $NaHSO_3$ is difficult due to their similar solubility. Attempted crystallization from EtOH resulted in decomposition: IR (Nujol) ν_{max} 3510, 3410 (OH, m) cm^{-1}; ^1H NMR (DMSO-d_6) δ 3.94–3.98 (1 H, dd, J_1 = 5.9 Hz, J_2 = 2.8 Hz, CH), 4.57 (1 H, d, J = 2.8 Hz, H-9), 5.17 (1 H, d, J = 5.9 Hz, OH, disappears in D_2O), 6.93–7.63 (8 H, m, XanH); mass spectrum (EI, eV), *m/z* (relative abundance, assignment) 181 (B, XanH), 152 (16, $(C_6H_4)_2$), (CI, CH_4) 211 (B, M − SO_3Na), 182 (1), 181 (14, XanH), 65 (4).

The adduct decomposes when dissolved in aqeuous Na_2CO_3 or K_2CO_3 solution. After extraction with ether (150 mL), drying ($MgSO_4$), and evaporation of the solvent, nearly pure **7a** (1.83 g, 71% based on **5**) admixed with traces of xanthone is obtained.

Reaction of 5 with MeLi. (1) Methyl 9-Xanthenyl Ketone (7b). (A) To a stirred solution of MeLi (19.3 mL of a 1.4 M solution in ether, 27.1 mmol) was added slowly over 1.5 h a solution of 9-xanthenecarbonyl chloride (3 g, 12.3 mmol) in dry THF (25 mL) under argon at −10 °C. After 1 additional h of stirring, TLC showed the complete disappearance of **5** and formation of several new spots. The mixture was poured into a 4% HCl solution in ice-water (250 mL), extracted with ether (150 mL), washed with an aqueous $NaHCO_3$ solution (150 mL) and with

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water (150 mL), and dried ($\mathrm{MgSO_4}$), and the solvent was evaporated, leaving a brown-yellow oil (2.26 g, 82%) which was mainly **7b**. Chromatography on silica with a 1:1 $\mathrm{CH_2Cl_2}$/petroleum ether (40–60 °C) eluent gave a yellow solid. Recrystallization from hexane gave colorless needles of methyl 9-xanthenyl ketone (**7b**) (1.81 g, 66%): mp 69–70 °C; UV (hexane) λ_{max} (log ϵ) 203 nm (4.66), 253 (3.97); IR (Nujol) ν_{max} 1700 (C=O, s) cm^{-1}; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 1.91 (3 H, s, Me), 4.88 (1 H, s, CH), 7.05–7.32 (8 H, m, XanH); ^{13}C NMR ($\mathrm{CDCl_3}$) δ 25.7 (Me), 54.3 (C-9), 117.2, 118.3, 123.6, 128.9, 129.3, 150.8 (Ar—C), 205.6 (C=O); mass spectrum (EI, 70 eV, 30 °C), *m/z* (relative abundance, assignment) 224 (7.2, M), 182 (81, $\mathrm{XanH_2}$), 181 (B, XanH), 152 (81, $\mathrm{(C_6H_4)_2}$), 151 (28), 127 (16), 126 (17), 77 (11, Ph), 43 (24, MeCO). Anal. Calcd for $\mathrm{C_{15}H_{12}O_2}$: C, 80.34; H, 5.39. Found: C, 80.13; H, 5.30.

Two other compounds were obtained from the chromatography in small yields. The first one, which eluted before the ketone (mp 221–222 °C, 24 mg, 0.9%), could have structure **10**. There was not enough material for microanalysis and it was not investigated further: IR (Nujol) ν_{max} 3280 ($\mathrm{HC\equiv C}$, m), 1720 (C=O, s) cm^{-1}; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 2.75 (1 H, s, $\mathrm{HC\equiv}$), 5.23 (1 H, s, CH), 5.67–7.53 (16 H, m, XanH); ^{13}C NMR ($\mathrm{CDCl_3}$) δ 48.1, 54.5 (C-9), 76.0, 77.2 ($\mathrm{C\equiv C}$), 117.0, 117.3, 118.5, 120.4, 122.6, 124.2, 127.7, 128.6, 130.1, 130.5, 150.6, 152.2 (XanC), 198.7 (C=O); mass spectrum (DCI, isobutane) *m/z* (relative abundance, assignment) 471.2 (8, M + $\mathrm{C_4H_9}$), 415.2 (43, MH), 387.2 (5, M − CO), 181.1 (B, XanH), CID 415 → 181, HR 415.1282 (1.4, $\mathrm{C_{29}H_{19}O_3}$), 205.0646 (59, $\mathrm{C_{15}H_9O}$, $\mathrm{XanC\equiv CH}$), 181.0671 (B, xanthene).

(2) 2-(9-Xanthenyl)propan-2-ol (9). The second compound that eluted as colorless needles was **9** (0.21 g, 7%): mp 110–112 °C; IR (Nujol) ν_{max} 3430, 3550 (OH, m) cm^{-1}; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 1.09 (6 H, s, Me), 3.89 (1 H, s, H9), 7.06–7.32 (8 H, m, XanH) (the OH signal is not observed); ^{13}C NMR ($\mathrm{CDCl_3}$) δ 26.0 (Me), 51.6 (C-9), 74.6 (*C*(OH)), 116.5, 122.87, 122.95, 128.05, 130.3, 153.3 (XanC); mass spectrum (high resolution), *m/z* (relative abundance, assignment) 240.1173 (M, $\mathrm{C_{16}H_{16}O_2}$, 1.4), 225.0921 (20, M − Me), 152.0622 (B, $\mathrm{C_{12}H_8O}$), CI (isobutane) 279.2 (73, M + $\mathrm{C_4H_9}$ − $\mathrm{H_2O}$), 265.2 (64, M + $\mathrm{C_3H_5}$ − $\mathrm{H_2O}$), 241.1 (29, MH), 223.1 (B, MH − $\mathrm{H_2O}$), 197.1 (48, xanthoneH$^+$), 182 (77, $\mathrm{XanH_2}$), 181 (40, XanH), CID 241 − $\mathrm{H_2O}$ → 223; 241 − MeCOMe → 183, EI *m/z* 225 (3, M − Me), 181 (B, XanH), 152 (40, $\mathrm{C_{12}H_8}$). Anal. Calcd for $\mathrm{C_{16}H_{16}O_2}$: C, 79.97; H, 6.71. Found: C, 79.66; H, 6.62.

(B) When procedure A was repeated in dry THF (20 mL) with the same order of addition of reagents, but with a MeLi (8.6 mL of 1.4 M MeLi in ether, 12 mmol)/9-xanthenecarbonyl chloride (2.45 g, 10 mmol) ratio of 1.3, **7b** was not formed and the main product (1.37 g, 63.4%) was the ester 1-(9-xanthenylidene)ethyl 9-xanthenecarboxylate (**11**): mp 162–164 °C (from hexane/benzene); IR (Nujol) ν_{max} 1740 (C=O, s) cm^{-1}; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 2.02 (3 H, s, Me), 5.11 (1 H, s, H-9), 6.60–7.40 (16 H, m, XanH); ^{13}C NMR ($\mathrm{CDCl_3}$) δ 18.5 (Me), 45.9 (C-9), 116.14, 116.19, 117.11, 117.16, 117.47, 121.60, 122.23, 122.59, 122.90, 123.36, 127.22, 127.47, 127.78, 128.27, 128.96, 129.32, 141.55, 151.26, 152.19, 153.49 (XanC), 169 (COO); mass spectrum (EI), *m/z* (relative abundance, assignment) 432 (2.7, M), 388 (2, M − MeCHO), 224 (12, Xan=C(Me)OH), 223 (52, XanCOMe), 195 (31, $\mathrm{XanCH_2}$), 181 (B, XanH), 180 (38, Xan), 152 (61, $\mathrm{(C_6H_4)_2}$). Anal. Calcd for $\mathrm{C_{29}H_{20}O_4}$: C, 80.54; H, 4.66. Found: C, 80.63; H, 4.58.

(C) To **5** (2.45 g, 10 mmol) dissolved in dry THF (20 mL) was added MeLi (1.4 M in ether, 7.2 mL, 10 mmol) (1:1 ratio), slowly under argon with vigorous stirring. On workup as described in procedure A, both **11** (1.31 g, 61%) and **8**, a dimer of 9-carbonylxanthene (112 mg, 5.4%), were obtained. Crystallization of **8** from hexane/benzene gave a solid: mp 199–200 °C; IR (Nujol) ν_{max} 1840 cm^{-1}; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 6.58–6.98 (1 H, m, J_{21} = 8.0 Hz, J_{23} = 6.3 Hz, J_{24} = 2.4 Hz, H-2), 6.73–6.77 (1 H, m, J_{12} = 8.0 Hz, J_{13} = 4.0 Hz, H1), 6.99–7.44 (13 H, m, XanH), 8.10–8.15 (1 H, m, J_{86} = 1.7 Hz, J_{87} = 7.9 Hz, H8); mass spectrum (EI, 70 eV, 155 °C), *m/z* (relative abundance, assignment) 416 (4, M), 389 (93, MH − CO), 388 (B, M − CO), 371 (26, M − COOH), 360 (91, M − 2CO), 359 (36, M − 2CO − H), 358 (38, M − 2CO − 2H), 208 (27, Xan=C=O), 180 (94, Xan), 152 (72, $\mathrm{(C_6H_4)_2}$); ^{13}C NMR ($\mathrm{CDCl_3}$) δ 66.2 (C-9), 106.8, 114.5, 116.56, 116.72, 117.16, 117.69, 118.35, 122.81, 123.42, 124.35, 125.16, 126.92, 128.43, 128.88, 129.65, 130.83, 145.28, 150.30, 150.90, 151.15 (XanC, C=C), 168.9 (C=O); mass spectrum (EI, 70 eV), *m/z* (relative abundance, assignment) 416 (3.6, M), 389 (93), 388 (B, M − CO), 371 (26, M − COOH), 360 (91, M − 2CO), 208 (27), 194 (32, $\mathrm{XanCH_2}$), 180 (94, Xan), 152 (72, $\mathrm{(C_6H_4)_2}$). Anal. Calcd for $\mathrm{C_{28}H_{16}O_4}$: C, 80.76; H, 3.87. Found: C, 80.37; H, 3.88.

Mesityl 9-Xanthenyl Ketone (7c). To a solution of mesitylmagnesium bromide (Aldrich, 9 mL of 1 M solution in THF, 9 mmol) was added a solution of 9-xanthenecarbonyl chloride (2.2 g, 9 mmol) in dry ether (10 mL) under argon. The precipitated MgClBr was separated, and the solution was stirred for 3.5 h at 20 °C. Ice (5 g) and 5% HCl (50 mL) were added under argon, the solution was extracted with ether (100 mL), and the organic phase was washed with 5% $\mathrm{NaHCO_3}$ (100 mL) and water (200 mL), dried ($\mathrm{MgSO_4}$), and evaporated. The remaining yellow oil became dark green on exposure to air. ^{1}H NMR analysis showed the presence of mesitylene and mesityl 9-xanthenyl ketone in an ca. 1:1 ratio. Crystallization (EtOH) or chromatography on silica with a 1:1 $\mathrm{CH_2Cl_2}$/petroleum ether eluent gave pure mesityl 9-xanthenyl ketone (**7c**) (1.53 g, 52%): mp 119 °C; UV (hexane) λ_{max} (log ϵ) 202.5 nm (4.86), 280.0 (3.82), 321.5 (3.52); IR (Nujol) ν_{max} 1690 (C=O, s) cm^{-1}; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 1.91 (6 H, s, *o*-Me), 2.27 (3 H, s, *p*-Me), 5.24 (1 H, s, CH), 6.78 (2 H, s, MesH), 6.97–7.31 (8 H, m, XanH); ^{13}C NMR ($\mathrm{CDCl_3}$) δ 19.1, 21.1 (Me), 54.6 (CH), 116.8, 119.0, 123.2, 128.4, 128.8, 129.2, 133.9, 136.8, 138.8, 152.7 (Ar-C), 204.4 (C=O); mass spectrum (EI, 70 eV), *m/z* (relative abundance, assignment) 181 (43, XanH), 147 (100, MesCO), 119 (19, Mes); (CI, $\mathrm{CH_4}$) 357 (12, $\mathrm{MC_2H_5}$), 329 (100, MH), 181 (31, XanH), 147 (51, MesCO). Anal. Calcd for $\mathrm{C_{23}H_{20}O_2}$: C, 84.12; H, 6.14. Found: C, 83.85; H, 6.04.

Tip 9-Xanthenyl Ketone (7d). To a solution of Tiplithium prepared from 1-bromo-2,4,6-triisopropylbenzene (4.12 g, 14.5 mmol) in ether (50 mL) and BuLi solution (9.1 mL, 1.6 M in hexane, 14.6 mmol) at −20 °C was added 9-xanthenecarbonyl chloride (3.55 g, 14.5 mmol) in ether (50 mL). The mixture was stirred for 12 h at room temperature under argon and then poured into a 5% HCl solution (150 mL) with ice (50 g); the phases were separated, and the organic phase was washed with a 5% aqueous $\mathrm{NaHCO_3}$ solution (150 mL) and then with water (2 × 100 mL), dried ($\mathrm{MgSO_4}$), and evaporated. Crystallization from ethanol gave Tip 9-xanthenyl ketone (**7d**) (0.46 g, 7.7%): mp 142–3 °C; IR (Nujol) ν_{max} 1680 (C=O, s) cm^{-1}; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 1.07 (12 H, br d, due to a dynamic process, *o*-*i*-Pr-*Me*), 1.26 (6 H, d, *p*-*i*-Pr-*Me*), 2.34 (2 H, m, *o*-*i*-Pr-C*H*), 2.89 (1 H, *p*-*i*-Pr-C*H*), 5.17 (1 H, s, Xan-H9), 6.91–7.31 (10 H, m, Tip + XanH); ^{13}C NMR ($\mathrm{CDCl_3}$) 22.7, 24.0, 26.1 (Me, indicating residual diastereotropism), 31.8, 34.3 ($\mathrm{CHMe_2}$), 55.7 (CH), 116.8, 119.3, 120.8, 123.2, 128.7, 129.5, 134.7, 144.8, 152.6 (Ar-C), 205.1 (C=O); mass spectrum (EI, 70 eV, 120 °C), *m/z* (relative abundance, assignment) 296 (71, M − 2*i*-Pr − 2Me), 295 (12, M − 2*i*-Pr − 2Me − H), 231 (63, TipCO), 230 (80, TipCO − H), 218 (B, TipCO − CH), 216 (15, TipCO − Me), 182 (95, $\mathrm{XanH_2}$), 181 (20, XanH), 180 (64, Xan), 151 (22, $\mathrm{C_6H_4C_6H_3}$), 128 (15), 88 (86). Anal. Calcd for $\mathrm{C_{29}H_{32}O_2}$: C, 84.43; H, 7.82. Found: C, 83.56; H, 7.49.

***tert*-Butyl 9-Xanthenyl Ketone (7e).** To a solution of *t*-BuLi in pentane (1.7 M, 8 mL, 13.6 mmol) plus ether (15 mL) at −15 °C was added dropwise with vigorous stirring under argon a solution of 9-xanthenecarbonyl chloride (2.45 g, 10 mmol) in ether (20 mL) over 40 min. The solution turned cherry-red immediately. After an additional 3 h of stirring at −10 °C, the mixture was poured into concentrated HCl (15 mL) and ice (70 g). The green aqueous solution was extracted with ether (150 mL) and washed with 5% aqueous $\mathrm{NaHCO_3}$ (150 mL) and water (100 mL), and the organic phase was dried ($\mathrm{MgSO_4}$) and evaporated. TLC showed that the main product was 9-xanthenecarboxylic acid, together with several compounds formed in low yield. Chromatography on silica with a 1:1 $\mathrm{CH_2Cl_2}$/petroleum ether eluent gave two compounds: (a) di-9-xanthenyl ketone (**13**), mp 227–8 °C (with decomposition) (223 mg, 12% based on **5**) and (b) *tert*-butyl 9-xanthenyl ketone (**7e**) (211 mg, 8%), which was crystallized from hexane to colorless crystals, mp 118–119 °C.

7e: ^{1}H NMR ($\mathrm{CDCl_3}$) δ 1.20 (9 H, s, *t*-Bu), 5.41 (1 H, s, H-9), 6.99–7.30 (8 H, m, XanH); ^{13}C NMR ($\mathrm{CDCl_3}$) δ 27.05 (Me), 45.2 (*t*-Bu), 48.5 (C-9), 117.4, 120.7, 123.0, 128.1, 128.7, 152.0 (XanC), 213 (C=O); mass spectrum (EI, 60 °C, 70 eV), *m/z* (relative abundance, assignment) 182 (81, $\mathrm{XanH_2}$), 181 (B, XanH), 180 (8, Xan), 152 (66, $\mathrm{(C_6H_4)_2}$), 127 (11), 126 (9), 77 (6, $\mathrm{C_6H_4}$), 57 (30, *t*-Bu). Anal. Calcd for $\mathrm{C_{18}H_{18}O_2}$: C, 81.17; H, 6.81. Found: C, 80.88; H, 6.65.

13: IR (Nujol) ν_{max} 1710 (C=O) cm^{-1}; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 5.10 (1 H, s, H9), 6.35, 5.38 (2 H, 2d, XanH), 6.84–6.89 (2 H, dt, XanH), 7.15–7.29 (4 H, m, XanH); ^{13}C NMR ($\mathrm{CDCl_3}$) δ 51.7 (C9), 117.2, 118.6, 123.4, 129.0, 129.2, 151.7 (XanC), 203.3 (C=O); mass spectrum (EI, 60 °C, 70 eV), *m/z* (relative abundance, assignment) 390 (1.5, M), 362 (2, M − CO), 181 (B, XanH), 180 (14, Xan), 165 (1, Xan − Me), 152 (53, $\mathrm{(C_6H_4)_2}$), 127 (18), 126 (13), 91 (5, $\mathrm{C_7H_7}$); CI 408 (1.6, M + $\mathrm{H_2O}$), 391 (9, MH), 209 (4, XanCHO), 181 (B, XanH). Anal. Calcd for $\mathrm{C_{27}H_{18}O_3}$: C, 83.06; H, 4.65. Found: C, 82.97; H, 4.80.

Ketone **7e** decomposes on standing neat or in solution with formation of xanthone. The decomposition seems qualitatively most extensive in EtOH.

9-(Acetoxymethylene)xanthene (18a). To a solution of 9-xanthenecarboxaldehyde (**7a**) (92 mg, 0.44 mmol) in pyridine (1 mL) was added acetic anhydride (0.3 mL), and the mixture was heated rapidly. Analysis (TLC and NMR) after 3 min at reflux showed that **7a** had reacted completely with formation of a new compound. The mixture was poured into water (30 mL) and the vigorously stirred milky-white emulsion was neutralized with concentrated HCl to pH 4 and extracted with ether (50 mL), and the organic phase was washed with 5% $NaHCO_3$ (100 mL) and water (100 mL), dried ($MgSO_4$), and evaporated. The yellow solid obtained (93 mg, 84%) was, according to ^1H NMR, mainly **18a** admixed with a few percent of xanthone. Crystallization from hexane gave pure **18a** as a white solid (89 mg, 80%): mp 83–4 °C; ^1H NMR ($CDCl_3$) δ 2.30 (3 H, s, AcO), 7.03–7.33 (6 H, m, XanH), 7.80 (1 H, s, =CH), 7.52, 8.09 (2 × 1 H, 2dd, J_{12} = 8.0, 8.2 Hz, J_{13} = 1.6 Hz, H1 and H8); mass spectrum (EI, 70 eV), *m/z* (relative abundance, assignment) 252 (20, M), 210 (78, M – CH_2=C=O), 209 (23, M – MeCO), 197 (17, XanthoneH), 196 (28, Xanthone), 181 (B, XanH), 168 (14), 152 (30, $(C_6H_4)_2$). Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.17; H, 4.80. Found: C, 76.18; H, 4.79.

2,2-Diphenylvinyl Acetate. A mixture containing diphenylacetaldehyde (98 mg, 0.5 mmol) and acetic anhydride (0.3 mL) in pyridine (1 mL) was refluxed for 15 min. Sampling followed by TLC showed that the reaction was finished after this time. Workup as described for the preparation of **18a** gave, after evaporation of the ether, a colorless viscous liquid. Dissolution in a 3:2 CH_2Cl_2/petroleum ether (10 mL) mixture followed by slow evaporation of the solvent gave white crystals of 2,2-diphenylvinyl acetate (107 mg, 90%): mp 56–58 °C (lit.[39] mp 59 °C); ^1H NMR ($CDCl_3$) δ 2.12 (3 H, s, OAc), 7.28, 7.33 (10 H, 2s, Ph), 7.62 (1 H, s, =CH); mass spectrum (EI, 70 eV), *m/z* (relative abundance, assignment) 238 (4, M), 196 (24, M – CH_2=C=O), 182 (58, Ph_2CO), 166 (7, Ph_2C), 152 (7, $(C_6H_4)_2$), 105 (B, PhCO), 76 (58, C_6H_4).

9-(Acetoxymesitylmethylene)xanthene (18c). To a solution of **7c** (170 mg, 0.52 mmol) in pyridine (1 mL) was added acetic anhydride (0.3 mL), and the mixture was refluxed for 2 h, after which TLC showed that the reaction was complete. Workup similar to that described for the preparation of **18a** gave a yellow solid. Crystallization from hexane gave colorless crystals of **18c** (171 mg, 89%): mp 138–9 °C; ^1H NMR see Table III; mass spectrum (EI, 70 eV), *m/z* (relative abundance, assignment) 370 (39, M), 328 (B, M – CH_2=C=O), 327 (63, M – MeCO), 299 (11, M – COAc), 208 (10, XanC=O), 181 (92, XanH), 180 (93, Xan), 152 (21, $(C_6H_4)_2$), 147 (27, MesCO), 119 (25, Mes). Anal. Calcd for $C_{25}H_{22}O_3$: C, 81.06; H, 5.99. Found: C, 81.41; H, 5.89.

1-Mesityl-2,2-diphenylvinyl Acetate. To a solution of **20a** (154 mg, 0.49 mmol) in pyridine (1 mL) was added acetic anhydride (0.3 mL), and the mixture was refluxed for 15 h, after which the reaction was complete by TLC. Workup as described for the preparation of **18a** gave a yellow solid. Crystallization from hexane gave 1-mesityl-2,2-diphenylvinyl acetate as colorless crystals (127 mg, 73%): mp 102–4 °C; ^1H NMR ($CDCl_3$) δ 1.89 (3 H, s, AcO), 2.23 (3 H, s, *p*-Me), 2.27 (6 H, s, *o*-Me), 6.76 (2 H, s, MesH), 6.83–6.88 (2 H, m, Ph), 7.02–7.08 (3 H, m, Ph), 7.27–7.37 (5 H, m, Ph); mass spectrum (EI, 70 eV), *m/z* (relative abundance, assignment) 356 (28, M), 314 (B, M – CH_2=C=O), 223 (43, M – CH_2=C=O – C_7H_7), 194 (16, Ph_2C=O), 166 (31, Ph_2C), 165 (38, Ph_2C – H), 147 (43, MesCO), 119 (24, Mes), 91 (16, C_7H_7). Anal. Calcd for $C_{25}H_{24}O$: C, 84.23; H, 6.79. Found: C, 83.87; H, 6.68.

Attempted Isolation of Enol 15c. A solution of **7c** (40 mg) in DMSO (2 mL), which according to ^1H NMR is an equilibrium **7c**/**15c** mixture, was poured with vigorous stirring into D_2O (50 mL) and immediately extracted with ether (25 mL), dried, and rapidly evaporated. The ^1H NMR spectrum of the remainder showed a mixture of **7c** (66%), xanthone (23%), and di-9-xanthenyl ketone (**13**). The (xanthone + **13**)/**7c** ratio was similar to the initial **15c**/**7c** ratio. When the experiment was repeated but the mixture was poured into a dilute solution of AcOH (pH 4), only **7c** was observed by NMR.

Crystallographic Parameters. **7b**: $C_{15}H_{12}O_2$, MW = 224.3, space group $P2_1/n$, a = 15.197 (3) Å, b = 5.575 (1) Å, c = 14.772 (3) Å, β = 113.46 (2)°, V = 1148.1 (6) Å^3, Z = 4, ρ_{calcd} = 1.30 g cm^{-3}, μ (MoKα) = 0.48 cm^{-1}, No. of unique reflections = 1995, No. of reflections with $I \geqslant 2\sigma_1$ = 1573, R = 0.046, R_w = 0.060, $w^{-1} = \sigma_F{}^2$.

7c: $C_{23}H_{20}O_2$, MW = 392.5, space group $C2/c$, a = 30.591 (4) Å, b = 8.834 (1) Å, c = 13.630 (3) Å, β = 103.16 (2)°, V = 3586.7 (7) Å^3, Z = 8, ρ_{calcd} = 1.22 g cm^{-3}, μ (MoKα) = 0.42 cm^{-1}, No. of unique reflections = 3992, No. of reflections with $I \geqslant 2.5\sigma(I)$ = 2374, R = 0.063, R_w = 0.082, $w^{-1} = \sigma_F{}^2 + 0.000277F^2$.

18c: $C_{25}H_{22}O_3$, MW = 370.5, space group $C2/c$, a = 28.514 (6) Å, b = 7.425 (1) Å, c = 19.056 (5) Å, β = 97.87 (2)°, V = 3996.5 (8) Å^3, Z = 8, ρ_{calcd} = 1.23 g cm^{-3}, μ (CuKα) = 5.57 cm^{-1}, No. of unique reflections = 2390, No. of reflections with $I > 2\sigma(I)$ = 2142, R = 0.061, R_w = 0.113, $w^{-1} = \sigma_F{}^2 + 0.001116F^2$.

X-ray Crystal Structure Analysis. Data were measured on a PW1100/20 Philips Four-Circle Computer-Controlled diffractometer for **7b** and **7c** and on an ENGRAF-NONIUS CAD-4 diffractometer for **18a**. MoKα (λ = 0.71069 Å) radiation with a graphite crystal monochromator in the incident beam was used. The unit cell dimensions were obtained by a least-squares fit of 24 centered reflections in the range of $11 < \theta < 15°$ (**7b** and **7c**) or $25 < \theta < 29°$ (**18c**). Intensity data were collected using the ω–2θ technique to a maximum 2θ of 50° (**7b**) and 55° (**7c** and **18c**). The scan width, $\Delta\omega$, for each reflection was 1.00 + 0.35tan θ with a scan speed of 3.0 deg/min. Background measurements were made for a total of 20 s at both limits of each scan. Three standard reflections were monitored every 60 min. No systematic variations in intensities were found.

Intensities were corrected for Lorentz and polarization effects. All non-hydrogen atoms were found by using the results of the SHELXS-86 direct method analysis.[40] After several cycles of refinements,[41] the positions of the hydrogen atoms were calculated and added with a constant isotropic temperature factor of 0.08 Å^2 to the refinement process. Refinement proceeded to convergence by minimizing the fraction $\sum w(|F_0| - |F_c|)^2$. A final difference Fourier synthesis map showed several peaks less than 0.3 e/Å^3 scattered about the unit cell without a significant feature.

The discrepancy indices, $R = \sum||F_0| - |F_c||/\sum|F_0|$ and $R_w = [\sum w(|F_0| - |F_c|)^2/\sum w|F_0|^2]^{1/2}$ are presented above with other pertinent crystallographic data.

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Registry No. **5**, 26454-53-5; **7a**, 72240-47-2; **7b**, 72240-48-3; **7c**, 137144-18-4; **7d**, 137144-19-5; **7e**, 137144-20-8; **8**, 137144-32-2; **9**, 101168-99-4; **10**, 137144-21-9; **11**, 137144-22-0; **12**, 137144-23-1; **13**, 137144-24-2; **15a**, 137144-29-7; **15c**, 137144-25-3; **15d**, 137144-31-1; **16**, 947-91-1; **16**-OAc, 86846-73-3; **18a**, 137144-27-5; **18b**, 137144-30-0; **18c**, 137144-28-6; **20a**, 1889-68-5; 9-xanthenecarboxylic acid, 82-07-5; mesitylmagnesium bromide, 2633-66-1; 2,2-diphenylvinyl acetate, 86846-73-3; 1-mesityl-2,2-diphenylvinyl acetate xanthone, 137144-26-4; 1-bromo-2,4,6-triisopropylbenzene, 21524-34-5.

Supplementary Material Available: Tables S1–S4, S6–S9, and S11–S14 giving bond lengths, bond angles, and thermal and positional parameters of **7b**, **7c**, and **18c** and Figure S1 (ORTEP drawing of **7b**) and Figures S2–S4 giving the stereoscopic views of **7b**, **7c**, and **18c** (21 pages); Tables S5, S10, and S15 giving structure factors of **7b**, **7c**, and **18c** (35 pages). Ordering information is given on any current masthead page.

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