J. Am. Chem. Soc. 1987, 109, 2112–2127

Stable Simple Enols.[1] Polar and Resonance Substituent Effects of α-Aryl Groups on Keto ⇌ Enol Equilibria of Stable Enols

Ella B. Nadler and Zvi Rappoport*

Contribution from the Department of Organic Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel.

Received July 7, 1986

Abstract: Seven enol/ketone pairs of 1-aryl-2,2-dimesitylethenols $Mes_2C{=}C(OH)Ar$ (**1a–g**)/1-aryl-2,2-dimesitylethanones $Mes_2CHCOAr$ (**2a–g**) were synthesized, and their spectral properties were determined. The λ_{max}, ϵ values, and $\delta(^{13}C)$ shifts of the ketones are linearly correlated with those of the corresponding acetophenones with slopes of 0.77–1.11. The structures of the 1-phenyl enol (**1d**) and the 1-(4-methoxyphenyl)-, 1-phenyl-, and 1-(3,5-dibromophenyl) ketones, **2b**, **2d**, and **2g** were determined by X-ray crystallography. **1d** has a propeller structure with Ar—C=C dihedral angles of 33.3° (α-Ph), 62.4° (β-mesityl), and 65.7° (β′-mesityl). The Ar–CO dihedral angles of **2b**, **2d**, and **2g** are 3.5°, 18° (in excellent agreement with that calculated from the UV spectra), and 22.6°, respectively. Keto ⇌ enol equilibrium constants were determined in hexane at 367.6 K. They increase with the electron withdrawal of the α-aryl group, e.g., $K_{enol} = 0.32$ for **2b** and 3.6 for **2g**. The log K_{enol} vs. σ^+ plot is linear with $\rho^+ = 0.65$. Ab initio calculations and literature data showed a small substituent dependence of the Ar—C=C stabilization energy. Ab initio calculations and literature data on equilibria in addition to ArCOR derivatives or on Ar–CO rotational barriers show that the substituent-dependent Ar—C=O stabilization energy is appreciable. Consequently, the change in the K_{enol} values is mainly due to a decrease in stabilization of the ketone by electron-withdrawing substituents. The roles of the polar effect and the conformation-dependent conjugation effect on K_{enol} are discussed. The ρ^+ value is compared with $\rho(K_{enol})$ for other aryl-substituted systems. Comparison with K_{enol} for mono- and other triaryl-substituted systems in conjunction with the Ar–CO and Ar—C=C stabilization energies suggests that the high K_{enol} values are not mainly due to conjugation effects. Steric effects should be mainly responsible for the high values.

Keto ⇌ enol equilibria and kinetics have been under active investigation for over 70 years.[2] When an electron-withdrawing group, e.g., ester or carbonyl, is present β to the C=O group as in acetylacetone or ethyl acetoacetate,[3] both keto and enol species are present in appreciable quantities in the equilibrium mixture. Accurate determination of the equilibrium constant (K_{enol}) for the equilibrium (eq 1, 2) is then possible. The enol form in these

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

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

cases is stabilized by intramolecular hydrogen bonding, and solvent effects on the stability are opposite to those expected for simple enols.[4] Not much is known about substituent effects in these cases. In contrast, although several techniques were used for determination of K_{enol} values for simple enols,[5-8] which are defined as those where R^1, R^2, R^3 are hydrogen, alkyl, or aryl groups,[9] until recently the K_{enol} values determined were subject to large errors. This results from the fact that the percentage of the enol at equilibrium is so small that the determination of K_{enol} values is very sensitive to impurities, and assumptions are required for their calculations.

Three recent developments improve the situation regarding the accuracy and the number of K_{enol} values. First, Toullec and Dubois[7h-j] improved the old halogen titration method by working under conditions where halogen addition is part of the rate-determining step. In the present context, it is important that K_{enol} values for a series of aryl-substituted acetophenones in water were determined with great accuracy. It was found that K_{enol} increases on electron withdrawal by the aromatic substituent.[7i] The value obtained for PhCOMe was lower than that obtained by Guthrie's kinetic estimation method[8] which involves certain assumptions and is apparently less accurate. A drawback of the method is that the bimolecular diffusion rate constant enters into the calculation. Consequently, when a better value was recently measured, the K_{enol} values had to be slightly revised.[7j]

A second remarkable development is the actual preparation of aliphatic enols, e.g., vinyl alcohol and its mono- and dimethyl-substituted derivatives by Capon's[10] and Kresge's[11] groups. From the known enolization rates of the corresponding ketones and the

---

[1] Part 15 in a series. For previous paper, see: Uggerud E.; Drewello, T.; Schwarz, H.; Nadler, E. B.; Biali, S. E.; Rappoport, Z. *Int. J. Mass Spectrom. Ion Processes* **1986**, *71*, 287.

[2] For a recent review, see: Toullec, J. *Adv. Phys. Org. Chem.* **1982**, *18*, 1.

[3] For early reviews dealing with enols stabilized by β-electron-withdrawing substituents, see: (a) Wheland, G. W. *Advanced Organic Chemistry*, 3rd ed.; Wiley: 1960; Chapter 14, pp 663–702. (b) Forsén, S.; Nilsson, M. In *The Chemistry of the Carbonyl Group*; Zabicky, J., Ed.; Interscience, New York, 1970; Vol. 2, p 157.

[4] In these systems, K_{enol} increases on decreasing the polarity of the solvent, whereas for simple enols K_{enol} should increase by intermolecular hydrogen bonding to the solvent. Roughly, more polar solvents are better hydrogen bond acceptors.

[5] Calculations: (a) Hehre, W. J.; Lathan, W. A. *J. Chem. Soc., Chem. Commun.* **1972**, 771. (b) Bouma, W. J.; Poppinger, D.; Radom, L. *J. Am. Chem. Soc.* **1977**, *99*, 6443. (c) Bouma, J. W.; Radom, L. *Aust. J. Chem.* **1978**, *31*, 1167, 1649. (d) Noack, W. E. *Theor. Chim. Acta* **1979**, *53*, 101. (e) Bouma, W. J.; Radom, L.; Rodwell, W. R. *Theor. Chim. Acta* **1980**, *56*, 149. (f) Franking, G.; Heinrich, N.; Schmidt, J.; Schwarz, H. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 1597. (g) Heinrich, N.; Koch, W.; Frenking, G.; Schwarz, H. *J. Am. Chem. Soc.* **1986**, *108*, 593.

[6] Thermochemical calculations: (a) Hine, J.; Arata, K. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 3085, 3089. (b) Guthrie, J. P.; Cullimore, P. A. *Can. J. Chem.* **1979**, *57*, 240.

[7] Halogen titration methods: (a) Meyer, K. H. *Chem. Ber.* **1912**, *45*, 2843. (b) Schwarzenbach, G.; Wittwer, C. *Helv. Chim. Acta* **1947**, *30*, 669. (c) Gero, G. *J. Org. Chem.* **1954**, *19*, 469, 1960; **1961**, *26*, 3156. (d) Walisch, W.; Dubois, J. E. *Chem. Ber.* **1959**, *92*, 1028. (e) Dubois, J. E.; Barbier, G. *Bull. Soc. Chim. Fr.* **1965**, 682. (f) Bell, R. P.; Smith, P. W. *J. Chem. Soc. B.* **1966**, 241. (g) Novak, M.; Loudon, G. M. *J. Am. Chem. Soc.* **1976**, *88*, 3591. (h) Dubois, J. E.; Toullec, J. *Tetrahedron* **1973**, *29*, 2859. (i) Dubois, J. E.; Toullec, J.; El-Alaoui, M. *J. Am. Chem. Soc.* **1981**, *103*, 5393. (j) Toullec, J. *Tetrahedron Lett.* **1984**, *25*, 4401.

[8] Kinetic estimation: Guthrie, J. P. *Can. J. Chem.* **1979**, *57*, 797.

[9] For reviews on simple stable enols, see: (a) Hart, H. *Chem. Rev.* **1979**, *79*, 515. (b) Hart, H.; Sasaoka, M. *J. Chem. Educ.* **1980**, *57*, 685.

[10] (a) Capon, B.; Rycroft, D. S.; Watson, T. W. *J. Chem. Soc., Chem. Commun.* **1979**, 724. (b) Capon, B.; Rycroft, D. S.; Watson, T. W.; Zucco, C. *J. Am. Chem. Soc.* **1981**, *103*, 1761. (c) Capon, B.; Zucco, C. *Ibid.* **1982**, *104*, 7657. (d) Capon, B.; Siddhanta, A. K. *J. Org. Chem.* **1984**, *49*, 255.

[11] (a) Chiang, Y.; Kresge, A. J.; Walsh, P. A. *J. Am. Chem. Soc.* **1982**, *104*, 6122. (b) Chiang, Y.; Kresge, A. J.; Tang, Y. S.; Wirz, J. *Ibid.* **1984**, *106*, 460. (c) Chiang, Y.; Kresge, A. J.; Wirz, J. *Ibid.* **1984**, *106*, 6392.

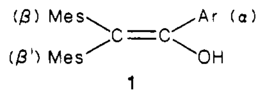
0002-7863/87/1509-2112$01.50/0

newly determined ketonization rates of the enols, accurate K_{enol} values were obtained from the rate constants ratios. Definite conclusions which could be deduced from the data are that a change α-H → α-Me decreases K_{enol},[10c,11b] whereas the change β,β-H_2 → β,β-Me_2 increases K_{enol}.[10c,11a] The former result is also corroborated by MO calculations.[5] No other reliable data are available.

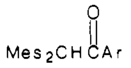
The third development is our work, which extended an old work of Fuson[12] to the preparation of a series of stable β,β-dimesityl-α-substituted enols. We measured K_{enol} values directly from both sides in hexane and found that in the α-aliphatic substituted series K_{enol} decreases along the series H > Me > Et > *i*-Pr > *t*-Bu. Moreover, a LFER between $\Delta G°$ for equilibria 1 and E_s values was obtained.[13] In contrast, in the aromatic series K_{enol} increased on increasing the bulk of the α-aryl group.[14] K_{enol} for trimesitylethenol (79 in hexane)[15] is ca. two orders of magnitude larger than K_{enol} for β,β-dimesityl-α-phenylethenol (see below).

Four questions therefore arise: (i) What is the reason for the different behavior of α-aliphatic and α-aromatic substituents in the β,β-dimesityl-substituted systems? Why do more electron-donating and bulkier alkyl groups reduce K_{enol}, whereas with bulky aromatic groups with *o*-methyl substitution it increases? In other words, why do steric effects apparently operate in opposite directions in the aliphatic and the aromatic case? (ii) Are there no appreciable electronic contributions of the α-alkyl substituents to the K_{enol} values as judged by $\Delta G° - E_s$ linearity, or are they hidden by or compensated for by steric or conjugation effects? (iii) Could the heavily substituted β,β-dimesityl derivatives serve as models for electronic/conjugation/steric effects for K_{enol}'s of simple aliphatic systems? What are the Ar—C=C and Ar—C=O torsional angles in the ketone and the enol series, and how do they affect (by changing the conjugation contribution) the response of K_{enol} values to the substituent? (iv) Could data in hexane be compared with data in aqueous or aqueous–organic solvents?

In order to assist in answering questions (i)–(iii) and to delineate the polar/resonance effects of aryl substituents on K_{enol} values we decided to prepare, study, and determine K_{enol} values for α-meta- and para-substituted-aryl-β,β-dimesitylethenols **1** and their keto analogues **2**.[16] One pair of the isomeric α,β-dimesityl-β-aryl-substituted systems (**3** and **4**)[12a] was studied briefly earlier.



1

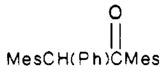


$Mes_2CHC(=O)Ar$

2

$MesC(Ph){=}C(OH)Mes$

3



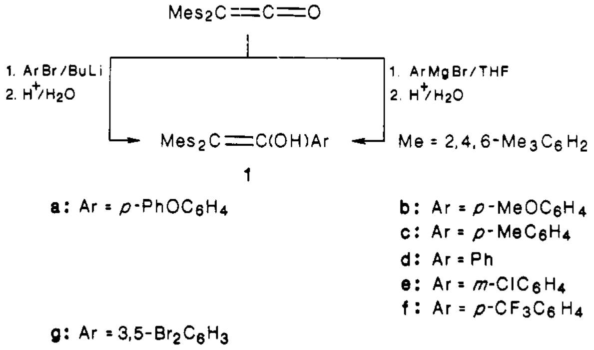
$MesCH(Ph)C(=O)Mes$

4

Mes = 2,4,6-$Me_3C_6H_2$ (mesityl); Ar = meta- and para-substituted phenyl

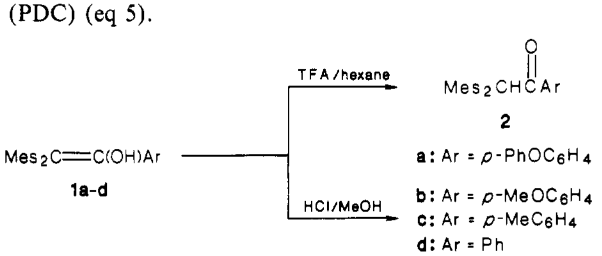
Results

Synthesis. Enols **1b–f**, of which only **1d** was known,[12b] were prepared by addition of the arylmagnesium bromide to dimesitylketene.[12b] 1,3,5-Tribromobenzene gave no Grignard reagent, and when $BrCH_2CH_2Br$ was added, the Mg reacted but the proceeding reaction gave several products which were not separated. Use of the corresponding lithium reagent gave enol **1g** in 56% yield. Preparation of the *p*-phenoxy-substituted enol **1a** via ArMgBr gave low yields, and purification was difficult, but addition of ArLi gave better yields and was the method of choice (eq 3).

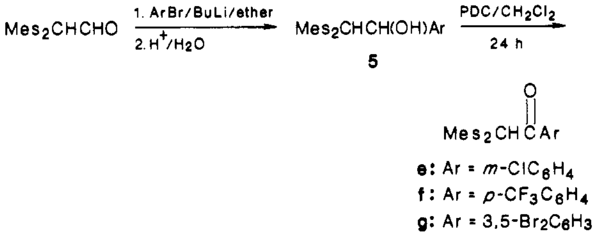


(3)

The ketones **2a–g** were obtained by two methods. Acid-catalyzed (TFA, HCl) isomerization of **1a–d** gave the keto/enol equilibrium mixtures from which **2a–d** were separated (eq 4). Ketones **2e–g** with electron-attracting substituents on the α-aryl ring were obtained by addition of the corresponding aryllithium reagent to dimesitylacetaldehyde,[15] isolation of the 2,2-dimesityl-1-arylethanols **5**, and their oxidation by pyridinium dichromate (PDC) (eq 5).



(4)



(5)

The UV, IR, ^1H NMR, and mass spectra of the ketones and enols are given in Table I. In the IR spectra of the enols, an O–H stretching at ca. 3520 cm^{-1} (in Nujol), which was not very sensitive to the nature of the α-aryl substituent, was observed. The UV spectra show two maxima. The wavelength of the maximum at 239–254 nm increases from the electron-donating to the electron-withdrawing substituents although not always regularly. The higher $\lambda_{\max}$ at 311–326 nm which has a somewhat lower ϵ than that of the lower $\lambda_{\max}$ shows a similar behavior.

The position of the OH stretching was determined accurately by FT IR in CCl_4. The OH absorption appeared in most cases as a sharp absorption and a shoulder at 4–5 cm^{-1} lower wavenumber with a lower intensity. In two cases the two absorptions appeared as a doublet with almost equal intensities. The position of the higher wavenumber absorption is given in Table I, and it is apparent that it is only very slightly substituent-dependent, being at 3518–3524 cm^{-1}. For **1a**, where intermolecular hydrogen bonding between the α-PhO group and the OH is a possibility, the concentration-dependence of the position of the OH band was determined. In the concentration range of 0.01–0.08 M the absorption remained nearly constant at 3522 ± 2 cm^{-1} with no apparent trend.

The ^1H NMR of the enols at room temperature shows a coalescence phenomenon.[17] The six methyl groups of the two β-

---

(12) For representative examples, see: (a) Fuson, R. C.; Armstrong, L. J.; Kneisley, J. W.; Shenk, W. J. *J. Am. Chem. Soc.* **1944**, *66*, 1464. (b) Fuson, R. C.; Armstrong, L. J.; Chadwick, D. H.; Kneisley, J. W.; Rowland, S. P.; Shenk, W. J.; Soper, Q. F. *Ibid.* **1945**, *67*, 386. (c) Fuson, R. C.; Chadwick, D. H.; Ward, M. L. *Ibid.* **1946**, *68*, 389. (d) Fuson, R. C.; Maynert, E. W.; Tan, T. L.; Trumbull, R. E.; Wassmundt, F. W. *Ibid.* **1957**, *79*, 1938 and references therein.

(13) Nugiel, D. A.; Rappoport, Z. *J. Am. Chem. Soc.* **1985**, *107*, 3669.

(14) Rappoport, Z.; Biali, S. E. 6th IUPAC Conference on Physical Organic Chemistry, Louvain, La Neuve, Belgium, July 11-16, 1982. Abstract: *Bull. Soc. Chim. Belg.* **1982**, *91*, 388.

(15) Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1985**, *107*, 1007.

(16) A preliminary report had appeared: Nadler, E. N. B.; Rappoport, Z. The 51th Annual Meeting, The Israel Chemical Society, October 9-10, 1985, Haifa, Israel, Abstract p 56 O1.

(17) The rotational process leading to coalescence will be discussed elsewhere. It depends on the nature and the bulk of the α-substituent in β,β-dimesityl-α-substituted ethenols.[18]

Table I. Spectral Data for Enols **1** and Ketones **2**

compd	$\lambda_{\mathrm{max}}^{\mathrm{C_6H_{14}}}$ (nm) ε	ν_{max} (Nujol), $\mathrm{cm^{-1}}$	δ ^{1}H NMR ($\mathrm{CDCl_3}$)	*m/z* (% rel abundance, assignment)
1a	243 (22 800), 313 (17 800)	3524 (s),[a] 2980–2820 (w), 1570–1610 (m)	1.62–2.65 (18 H,[c] including 3 sharp s, [1.91, 2.19, 2.27], Me), 5.16 (1 H, s, OH), 6.68–7.36[d] (13 H,m, Ar-H + Mes-H)	448 (100, M), 251 (28, $\mathrm{Mes_2CH}$), 236 (4, $\mathrm{Mes_2CH}$-Me), 221 (10, $\mathrm{Mes_2CH}$-2Me), 206 (12, $\mathrm{Mes_2CH}$-3Me), 197 (97, $\mathrm{PhOC_6H_4CO}$), 119 (6, Mes), 91 (7, $\mathrm{C_7H_7}$), 77 (21, Ph)
1b	239 (18 400), 311 (16 000)	3524 (s),[a] 2940–2880 (w), 1600–1610 (m), 1590 (s)	1.64–2.65 (18 H,[c] including 3 sharp s, [1.90, 2.20, 2.27], Me), 3.76 (3 H, s, MeO), 5.12 (1 H, s, OH), 6.67–6.70[d] (4 H, d, Mes-H + half AB q of Ar-H), 6.89 (2 H, br, Mes-H), 7.24–7.28[d] (2 H, d, *J* = 9 Hz, half AB q of Ar-H)	386 (87, M), 371 (10, M-Me), 356 (6, M-2Me), 251 (39, $\mathrm{Mes_2CH}$), 235 (7, $\mathrm{Mes_2C}$-Me), 221 (7, $\mathrm{Mes_2CH}$-2Me), 135 (100, AnCO)
1c	244 sh (15 000), 313 (12 500)	3523 (s),[a] 2960–2840 (w), 1605 (s), 1600 (s)	1.64–2.63 (21 H,[c] including 4 sharp s, [1.90, 2.19, 2.27, 2.28], Me), 5.12 (1 H, s, OH), 6.67 (2 H, s, Mes-H), 6.90, 6.97 (4 H, d, *J* = 8 Hz, Mes-H + half AB q of Tol), 7.20, 7.22 (2 H, d, *J* = 8.1 Hz, half AB q of Tol)	370 (15, M), 251 (3, $\mathrm{Mes_2CH}$), 221 (4, $\mathrm{Mes_2CH}$-2Me), 206 (10, $\mathrm{Mes_2CH}$-3Me), 185 (15), 119 (100, TolCO), 91 (45, $\mathrm{C_7H_7}$
1d	246 (16 800), 314 (11 600)	3521 (s),[a] 2960–2840 (w), 1610–1590 (m)	1.61–2.65 (18 H,[c] including 3 sharp s [1.90, 2.19, 2.28], Me), 5.17 (1 H, s, OH), 6.67 (2 H, s, Mes-H), 6.89 (2 H, br, Mes-H), 7.12–7.34[d] (5 H, m, Ph)	356 (100, M), 341 (32, M-Me), 326 (8, M-2Me), 251 (15, $\mathrm{Mes_2CH}$), 236 (6, $\mathrm{Mes_2CH}$-Me), 221 (13, $\mathrm{Mes_2CH}$-2Me), 105 (18, PhCO), 91 (6, $\mathrm{C_7H_7}$)
1e	250 (19 100), 319 (12 000)	3518 (s),[a] 2960–2840 (w), 1610 (s), 1590 (s)	1.67–2.72 (18 H,[c] including 3 sharp s [1.91, 2.20, 2.28], Me), 5.18 (1 H, s, OH), 6.69 (2 H, s, Mes-H), 6.91 (1 H, br, Mes-H), 6.99–7.18 (3 H, m, Ar-H), 7.41 (1 H, m, Ar-H)	392, 390 (35, 100, M), 377, 375 (7, 20, M-Me), 360 (4, M-2Me), 347 (6, M-$\mathrm{C_3H_7}$), 251 (49, $\mathrm{Mes_2CH}$), 221 (11, $\mathrm{Mes_2CH}$-2Me), 206 (10, $\mathrm{Mes_2CH}$-3Me), 141, 139 (4, 8, *m*-$\mathrm{ClC_6H_4CO}$), 119 (10, Mes), 91 (8, $\mathrm{C_7H_7}$)
1f	249 (21 600), 325 (13 700)	3518 (s),[a] 2980–2820 (w), 1610 (s)	1.61–2.83 (18 H,[c] including 3 sharp s [1.89, 2.21, 2.28], Me), 5.21 (1 H, s, OH), 6.69 (2 H, s, Mes-H), 6.91 (s, br, Mes-H), 7.42 (4 H, AB q, *J* = 9 Hz, Ar-H)	424 (100, M), 409 (70, M-Me), 394 (12, M-2Me), 381 (22, M-$\mathrm{C_3H_7}$), 251 (26, $\mathrm{Mes_2CH}$), 236 (5, $\mathrm{Mes_2CH}$-Me), 221 (14, $\mathrm{Mes_2CH}$-2Me), 206 ($\mathrm{Mes_2CH}$-3Me), 173 (17, $\mathrm{CF_3C_6H_4CO}$), 91 (8, $\mathrm{C_7H_7}$)
1g	254 (22 500), 326 (12 400)	3520 (s),[a] 2970–2840 (w), 1610–1590 (m)	1.65–2.65 (18 H,[c] including 3 sharp s [1.91, 2.22, 2.28], Me), 5.17 (1 H, s, OH), 6.72 (2 H, s, Mes-H), 6.90 (1 H, br, Mes-H), 7.34 (2 H, m, Ar-H), 7.46 (1 H, m, Ar-H)	516, 514, 512 (50, 100, 49, M), 500, 501, 499, 497 (13, 3, 8, 7, M-Me), 251 (23, $\mathrm{Mes_2CH}$), 235 (6, $\mathrm{Mes_2CH}$-Me), 221 (8, $\mathrm{Mes_2CH}$-2Me), 91 (5, $\mathrm{C_7H_7}$)
2a	228 (24 000), 270 (21 000)	2960–2840 (w), 1678 (m),[b] 1600–1570 (m)	2.02 (12 H, s, *o*-Me), 2.24 (6 H, s, *p*-Me), 6.11 (1 H, s, CH), 6.78 (4 H, s, Mes-H), 6.87, 6.92, (2 H, d, half AB q, *J* = 9 Hz, Ar-H), 7.04–7.09 (2 H, m, PhO-H), 7.09–7.26[d] (1 H, m, PhO-H), 7.34–7.42 (2 H, m, PhO-H), 7.85, 7.89 (2 H, d, *J* = 9 Hz, half AB q, Ar-H)	448 (12, M), 251 (67, $\mathrm{Mes_2CH}$), 221 (17, $\mathrm{Mes_2CH}$-2Me), 206 (11, $\mathrm{Mes_2CH}$-3Me), 197 (100, $\mathrm{PhOC_6H_4CO}$), 141 (22), 115 (18), 91 (6, $\mathrm{C_7H_7}$), 77 (19, Ph)
2b	228 sh (15 100), 270 (18 500), 281 (14 600)	2940–2860 (w), 1677 (m),[b] 1590–1610 (m)	2.02 (12 H, s, *o*-Me), 2.24 (6 H, s, *p*-Me), 3.83 (3 H, s, OMe), 6.13 (1 H, s, CH), 6.78 (4 H, s, Mes-H), 6.838, 6.844 (2 H, d, *J* = 9 Hz, half AB q, Ar-H), 7.87, 7.90 (2 H, d, *J* = 9 Hz, half AB q, Ar-H)	386 (9, M), 251 (50, $\mathrm{Mes_2CH}$), 236 (3, $\mathrm{Mes_2CH}$-Me), 221 (9, $\mathrm{Mes_2CH}$-2Me), 135 (100, $\mathrm{MeOC_6H_4CO}$), 91 (3, $\mathrm{C_7H_7}$)
2c	231 sh (22 200), 249 (17 800)	2960–2840 (w), 1679 (m),[b] 1605–1595 (m)	2.02 (12 H, s, *o*-Me), 2.24 (6 H, s, *p*-Me), 2.37 (3 H, s, Ar*Me*), 6.15 (1 H, s, CH), 6.78 (4 H, s, Mes-H), 7.15, 7.19 (2 H, d, *J* = 8 Hz, half AB q, Ar-H), 7.79, 7.83 (2 H, d, *J* = 8 Hz, half AB q, Ar-H)	370 (7, M), 251 (100, $\mathrm{Mes_2CH}$), 236 (3, $\mathrm{Mes_2CH}$-Me), 221 (14, $\mathrm{Mes_2CH}$-2Me), 206 (8, $\mathrm{Mes_2CH}$-3Me), 119 (33, TolCO), 91 (10, $\mathrm{C_7H_7}$)
2d	232 (20 200), 244 (14 700)	2960–2840 (w), 1687 (m),[b] 1605 (s), 1590 (s)	2.02 (12 H, s, *o*-Me), 2.24 (6 H, s, *p*-Me), 6.18 (1 H, s, CH), 6.79 (4 H, s, Mes-H), 7.64–7.91 (5 H, m, Ph)	356 (12, M), 252 (81, $\mathrm{Mes_2CH_2}$), 251 (100, $\mathrm{Mes_2CH}$), 236 (9, $\mathrm{Mes_2CH}$-Me), 221 (39, $\mathrm{Mes_2CH}$-2Me), 206 (24, $\mathrm{Mes_2CH}$-3Me), 105 (33, PhCO), 91 (9, $\mathrm{C_7H_7}$), 77 (32, Ph)
2e	238 sh (13 800), 243 sh (11 500), 269 (2000)	2920–2800 (w), 1687 (m),[b] 1590 (s)	2.01 (12 H, s, *o*-Me), 2.24 (6 H, s, *p*-Me), 6.10 (1 H, s, CH), 6.79 (4 H, s, Mes-H), 7.29[d] (1 H, br, m, Ar-H), 7.47–7.51 (1 H, m, Ar-H), 7.68–7.72 (1 H, m, Ar-H), 7.93–7.95 (1 H, m, Ar-H)	392, 390 (6, 18, M), 377, 375 (1, 4, M-Me), 251 (100, $\mathrm{Mes_2CH}$), 236 (7, $\mathrm{Mes_2CH}$-Me), 221 (33, $\mathrm{Mes_2CH}$-2Me), 206 (23, $\mathrm{Mes_2CH}$-3Me), 141, 139 (5, 12, *m*-$\mathrm{ClC_6H_4CO}$), 119 (6, Mes), 91 (10, $\mathrm{C_7H_7}$)
2f	239 sh (13 500), 272 (2600)	2960–2840 (w), 1692 (m),[b] 1610 (s)	2.01 (12 H, s, *o*-Me), 2.25 (6 H, s, *p*-Me), 6.14 (1 H, s, CH), 6.80 (4 H, s, Mes-H), 7.63, 7.67 (2 H, d, *J* = 8.2 Hz, Ar-H), 7.99, 8.03 (2 H, d, *J* = 8.2 Hz, Ar-H)	424 (2 M), 251 (100, $\mathrm{Mes_2CH}$), 236 (14, $\mathrm{Mes_2CH}$-Me), 221 (39, $\mathrm{Mes_2CH}$-2Me), 206 (19, $\mathrm{Mes_2CH}$-3Me), 173 (9, $\mathrm{F_3CC_6H_4CO}$), 145 (20, $\mathrm{C_6H_4CF_3}$), 91 (6, $\mathrm{C_7H_7}$)
2g	228 sh (30 500), 243 sh (9000), 253 (7900), 285 (2000)	2960–2840 (w), 1692 (m),[b] 1610 (s)	2.01 (12 H, s, *o*-Me), 2.25 (6 H, s, *p*-Me), 6.01 (1 H, s, CH), 6.80 (4 H, s, Mes-H), 7.79–7.81 (1 H, m, *p*-Ar-H), 7.90–7.91 (2 H, m, *m*-Ar-H)	516, 514, 512 (2, 4, 2, M), 265, 263, 261 (2, 5, 2, ArCO), 251 (100, $\mathrm{Mes_2CH}$), 236 (6, $\mathrm{Mes_2CH}$-Me), 221 (25, $\mathrm{Mes_2CH}$-2Me), 206 (15, $\mathrm{Mes_2CH}$-3Me)

[a] Determined in $\mathrm{CCl_4}$ solution. [b] Determined in $\mathrm{CH_2Cl_2}$ solution. [c] Broad envelope due to coalescence of *o*-Me groups. [d] Determination of the accurate position of (some of) the signal(s) or of *J* is difficult due to overlap by the solvent.

Table II. ^{13}C NMR[j] of $Mes_2CHCOAr$

X	δ (Mes-Me)[a]			δ (Mes-C)[a]				δ (Ar-C)					
in Ar	*p*-Me	*o*-Me	δ (*C*H)	C(1) or C(4)		C(2,6)	C(3,5)	C(1)	C(2,6)	C(3,5)	C(4)	δ (C=O)	δ (others)
p-MeO	20.70	21.31	55.35	134.34	136.08	137.45	130.35	130.18	130.90	113.78	160.23	199.80	54.93[b]
p-PhO	20.70	21.34	55.05	134.16	136.14	137.41	130.41	130.19	132.29	117.07	161.86	199.79	120.38, 124.65, 129.99, 155.25[c]
p-Me	20.70	21.34	55.11	134.29	136.12	137.46	130.38	135.30	129.36	123.10	143.60	200.84	21.61[d]
H	20.72	21.36	55.19	134.13	136.23	137.44	130.41	137.63	128.68	127.99	132.92	201.22	
m-Cl	20.68	21.31	55.33	133.58	136.93	137.30	130.52	139.07	128.04[e]	130.02[g]	132.89	199.85	
									125.97[f]	135.02[h]			
p-CF_3	20.73	21.36	55.60	133.46	136.64	137.40	130.61	140.11	128.38	125.79	125.86	200.24	*i*
m,*m*-Br_2	20.72	21.34	55.38	132.94	136.66	137.22	130.61	140.27	129.76	123.46	138.13	198.52	

[a] Assignment based on relative integration. [b] *p*-MeO signal. [c] Signals for the *p*-PhO group. [d] *p*-Me signal. [e] C(2). [f] C(6). [g] C(5). [h] C(3). [i] The CF_3 signal was not observed. [j] δ values in ppm.

mesityl groups are divided into two sub-groups. Two sharp singlets are for the two *p*-Me groups, and one sharp singlet is for two *o*-Me groups. The other two *o*-Me groups appear as very broad signals on which the singlets are superimposed. This is unfortunate since the two methyl groups at the two extremes of the Me region are the most sensitive probes for the conformation of the α-aryl group. The ^{1}H NMR was measured both at 353 K, where the coalescence is complete and only four methyl lines are observed, and at 200 K, well below the coalescence temperature, where all six methyl signals are separated.

The OH signal appears as a sharp singlet, and its position at δ 5.1–5.2 is only slightly affected by the α-aryl group and not in an apparently regular manner.[20] Two of the aromatic mesityl protons show partial broadening whereas the other two are sharp, and the substituent effects on four of them are small.

The mass spectral cleavage of the enols in relation to the kinetic energy release is discussed in detail elsewhere.[1] In the present work we found that the base peak is not identical throughout the series. For the electron-withdrawing substituted enols as well as for **1a** it is the molecular peak. The peaks at m/z 251 (Mes_2CH^+) are 26 ± 3%, and the peaks for ArCO are relatively small (except for **1a** where it is 97%). In contrast, for enols **1b** and **1c** with electron-withdrawing α-substituents the base peak is for ArCO, whereas the peaks at m/z 251 or the molecular peaks are of moderate or small intensities.

The ketones show a conjugated carbonyl absorption of medium intensity at 1677–1692 cm^{-1} in CH_2Cl_2 and no apparent OH absorption. Qualitatively, the change in the position of the C=O stretching is monotonous in the expected direction, although the Hammett-type correlation shows a considerable scatter. The most electron-donating *p*-MeO-substituted **2b** absorbs at the lowest wavenumber, whereas the *p*-CF_3 and the *m*,*m*-dibromo derivatives **2f** and **2g** absorb at the highest wavenumber.

The UV spectra show two or three maxima, which sometimes overlap to give shoulders enabling only an approximate determination of the position of the maxima. The positions of the bands are substituent-dependent, and the band with ϵ = 9000–21 000 (the B band according to Forbes et al. in acetophenones)[21] is shifted by the substituent according to the approximate values given by Williams and Fleming.[22] Low intensity maxima (ϵ = 2000–2600) are observed at 269–285 nm only for the electron-withdrawing substituted systems **2e–g**. This resembles the C band observed for similarly substituted acetophenones.[21] In the region of the higher λ_{max} of the enols the ketones show no appreciable absorption, and the UV method could therefore be used for evaluating the K_{enol} values.

The ^{1}H NMR show free rotation of the mesityl groups on the NMR time scale at room temperature: 3 singlets, one for the 4 *o*-Me groups, one for the 2 *p*-Me groups, and one for the 4 aromatic protons, whose positions are substituent-independent are observed. The shift in the position of the CH proton is <0.2 ppm between the extremes (Table I).

The δ (C) values in the proton decoupled ^{13}C NMR spectra of the ketones in $CDCl_3$ are given in Table II. The positions of the *o*-Me and *p*-Me carbons of the mesityl groups and of the methine (*C*H) carbon are α-substituent independent. All compounds show eight aromatic carbon signals except for **2a** and **2e** which, as expected, show additional signals. In the absence of labeled derivatives to assist the assignments, it was assumed that the ring carbons of the mesityl groups should be very little affected by the α-substituent. Indeed, four signals with δ's at 130.47 ± 0.10, 133.84 ± 0.44, 136.40 ± 0.29, and 137.38 ± 0.07 ppm were found and assigned to the β-mesityl groups. The assignments of the aryl group signals were based on analogy with the variation of the ^{13}C spectra of the ring carbons of acetophenones in 1:1 $CHCl_2F$–$CHClF_2$ where the major change is in δ (C-4) and the smallest is for δ (C-2, C-6).[23] Four-points plots of δ (C-1), δ (C-4), δ (C-2, C-6), and δ (C-3, C-5) for the corresponding series gave approximately linear plots with slopes of 1.06 (r = 0.9967), 1.04 (r = 0.9752), 0.84 (r = 0.9262), and 0.77 (r = 0.9100), respectively. The δ (C-1) values are correlated with Hammett's σ^+ values with ρ^+ = 6.18 (0.9623, excluding the point for *p*-PhO) or ρ^+ = 6.95 (r = 0.9453 for all points), similar to the correlation for acetophenones in 1:1 $CHCl_2F$–$CHClF_2$[23] where ρ^+ = 6.70 (r = 0.9618).

The change in δ (C=O) is 2.70 ppm between the extremes and 1.45 ppm if the point for **2g** is excluded. As for the unsubstituted acetophenones the C=O of the unsubstituted compound appears at the lowest field, and a five-points plot of δ (C=O) for **2** vs. δ (C=O) for acetophenones in $CDCl_3$[24] gives a linear plot with a slope of 0.95 (r = 0.9671). When the deviating point for *p*-MeO is excluded, the slope is 0.87 (r = 0.9907).

In the mass spectra the base peak for the ketones with electron-donating α-substituents (**2a**, **2b**) is for the ArCO fragment, with an appreciable signal for m/z 251. For the other ketones m/z 251 is the base peak, whereas the intensity of the signal for ArCO is of relatively low intensity. More detailed discussion is given in ref 1.

Crystallographic Data. (a) Ketones. Since the conformation of the ketones in solution is relevant to our analysis of substituent effects, the solution data were supplemented by determination of the solid-state conformations of three ketones by X-ray crystallography. These include the parent **2d** and ketones **2b** and **2g** with the most electron-donating and -withdrawing substituent(s). The solid state structures show many similarities and few differences in spite of the fact that **2b** and **2d** crystallized in space group $P2_1/n$

---

(18) Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1984**, *106*, 477.

(19) Nugiel, D. A.; Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1984**, *106*, 3357.

(20) In contrast, the position of the OH is strongly dependent on the solvent: Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1984**, *106*, 5641.

(21) Forbes, W. F.; Mueller, W. A.; Ralph, A. S.; Templeton, J. F. *Can. J. Chem.* **1957**, *35*, 1049.

(22) Williams, D. H.; Fleming, I. *Spectroscopic Methods in Organic Chemistry*; McGraw Hill: 1973; p 26.

(23) Drakenberg, T.; Sommer, J. M.; Jost, R. *Org. Magn. Reson.* **1976**, *8*, 579.

(24) Bromilow, J.; Craik, D. J.; Fiske, P. R.; Rowe, J. E.; Sadek, M. *J. Chem. Soc., Perkin Trans. 2* **1981**, 753.

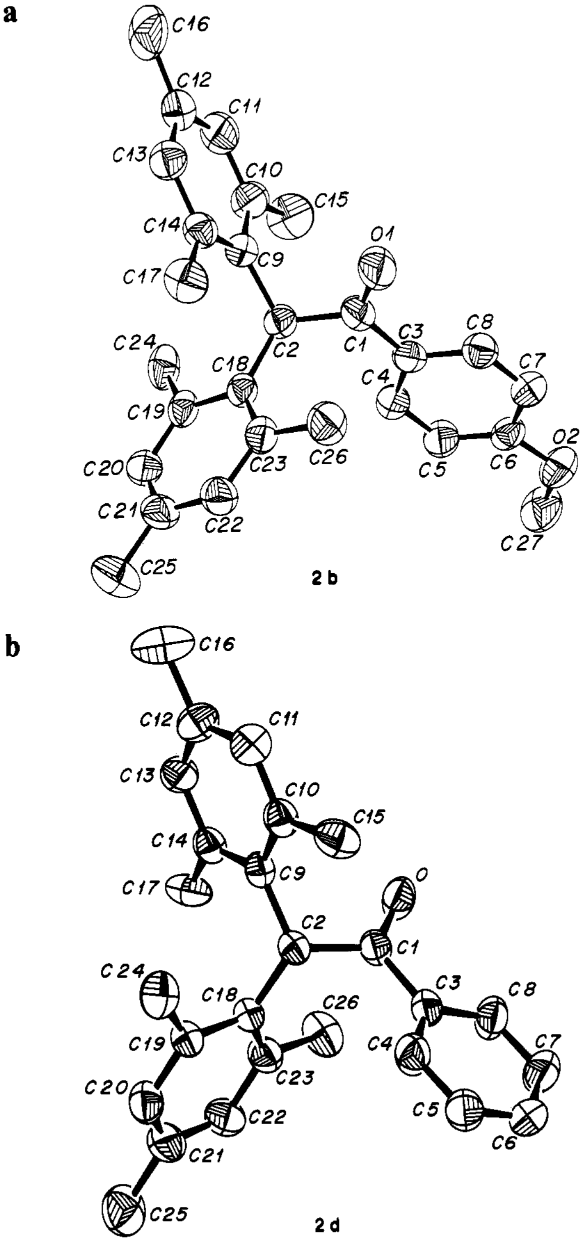


Figure 1. ORTEP drawings and numbering schemes for **2b** and **2d**.

whereas **2g** crystallized in the $P\bar{1}$ space group. Hence, only the ORTEP drawings and the numbering schemes for **2b** and **2d** are given in Figure 1. In **2g**, C(5) is attached to Br(1) and C(7) to Br(2). The important bond lengths and angles and the dihedral angles are given in Table III, and the rest of the crystallographic data are given in supplementary Tables S1–S12. The stereoviews of **2b**, **2d**, and **2g** and the ORTEP drawing of **2g** are given in the supplementary Figures S1–S4.

Bond lengths and angles around the carbonyl group or around C(2) are identical or nearly so. The C(9)–C(2)–C(18) angles relfect the interaction between the two bulky β-mesityl groups, by their opening to 117.4° for **2b**, to 119.8° for **2d**, and to 121.4° in **2g**. In the analogous ketones **4** and trimesitylethanone **6** these angles are close to the tetrahedral angles, being 114.4° and 116.0°, respectively.[25]

$Mes_2CHCOMes$
6

An important feature is that while the bond lengths within the α-aryl ring are normal, 11 of the 12 bond lengths from the ipso carbon of the β- or β′-mesityl group to the ortho carbon atoms

Table III. Bond Lengths and Angles for 1-Aryl-2,2-dimesitylethanones **2**

bond length, Å	**2b**	**2d**[g]	**2g**	angle, deg[h]	**2b**	**2d**	**2g**	dihedral angle[i] deg	**2b**	**2d**	**2g**
O–C(1)	1.220 (3)	1.217 (4)	1.221 (6)	O–C(1)–C(2)	120.7 (3)	121.3 (3)	121.4 (5)	α-Ar—C=O	3.50	161.94	22.62
C(1)–C(2)	1.538 (4)	1.542 (5)	1.547 (6)	O–C(1)–C(3)	120.2 (3)	120.3 (3)	120.3 (6)	β-Ar—C=O[k]	89.36	84.54	98.01
C(1)–C(3)	1.479 (4)	1.496 (4)	1.498 (8)	C(1)–C(2)–C(9)	109.6 (3)	111.4 (3)	110.8 (5)	β′-Ar—C=O[k]	94.79	106.94	104.59
C(2)–C(9)	1.534 (4)	1.523 (4)	1.528 (7)	C(1)–C(2)–C(18)	116.8 (3)	113.9 (3)	113.9 (5)	α-Ar–β-Ar[k]	86.02	77.60	75.71
C(2)–C(18)	1.544 (5)	1.542 (5)	1.528 (6)	C(9)–C(2)–C(18)	117.4 (2)	119.8 (3)	121.4 (5)	α-Ar–β′-Ar[k]	93.73	76.64	102.69
C–C(α-Ar)[a,b]	1.369 (4)– 1.398 (4)	1.372 (5)[e]– 1.391 (4)	1.367 (9)– 1.393 (7)	C(2)–C(1)–C(3)	119.0 (3)	118.2 (3)	118.2 (5)	β-Ar–β′-Ar[k]	90.05	92.11	95.47
C(9)–C(10)	1.414 (5)	1.413 (5)	1.420 (8)	C(9)–C(14)–C(17)	123.7 (3)	123.7 (4)	124.7 (5)	β-Ar–B	38.61	31.88	148.50
C(9)–C(14)	1.403 (4)	1.404 (5)	1.405 (9)	C(13)–C(14)–C(17)	117.2 (3)	116.6 (3)	116.6 (5)	β′-Ar–B	68.93	109.41	103.34
C–C(β-Mes)[a,c]	1.381 (6)– 1.396 (4)	1.380 (5)– 1.395 (4)	1.39 (1)– 1.398 (9)	C(2)–C(9)–C(10)	116.7 (3)	115.9 (3)	115.3 (5)	A–B	121.94	54.48	53.06
C(18)–C(19)	1.426 (3)	1.415 (4)	1.410 (6)	C(2)–C(9)–C(14)	124.7 (3)	125.9 (3)	125.5 (5)	H(2)–C(2)–C(1)–C(3)	–46.42	42.94	–40.76[j]
C(18)–C(23)	1.400 (4)	1.395 (4)	1.415 (7)	C(21)–C(22)–C(23)	122.0 (4)	123.0 (5)	123.2 (6)	O–C(1)–C(2)–C(9)	20.85	–20.83	27.62
C–C(β′ ring)[a,d,f]	1.373 (5)– 1.387 (6)	1.375 (6)– 1.395 (6)	1.368 (9)– 1.394 (7)	C(18)–C(23)–C(26)	125.0 (3)	124.9 (3)	123.4 (6)	O–C(1)–C(2)–C(18)	–120.10	118.46	–109.08
				C(22)–C(23)–C(26)	115.7 (3)	115.8 (4)	117.6 (5)	C(3)–C(1)–C(2)–C(9)	–156.69	155.17	–150.03
				C(2)–C(18)–C(23)	125.6 (3)	125.7 (3)	124.7 (6)	C(3)–C(2)–C(1)–C(18)	62.36	–65.54	73.27
				C(2)–C(18)–C(19)	115.9 (3)	116.2 (4)	116.5 (5)				
				C(11)–C(12)–C(13)	116.7 (3)	117.6 (4)	117.6 (4)				

[a] All aromatic bond lengths within the rings except for those specified. [b] α-ring: C(3)–C(4)–C(5)–C(6)–C(7)–C(8). [c] β-ring: C(9)–C(10)–C(11)–C(12)–C(13)–C(14). [d] β′-ring: C(18)–C(19)–C(20)–C(21)–C(22)–C(23). [e] C(5)–C(6) = 1.390 Å. [f] C(22)–C(26) = 1.406 Å. [g] Br(1)–C(5) = 1.899 (7) Å; Br(2)–C(7) = 1.906 (5) Å. [h] Of the internal aromatic bond angles only those that for at least one ketone are >123° or <117° are given. [i] C=O plane: O–C(1)–C(2)–C(3); plane A: C(1)–C(2)–O; plane B: C(9)–C(2)–C(18). [j] Approximate value. [k] Angle between the planes of the two groups.

---

(25) Kaftory, M.; Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1985**, *107*, 1701.

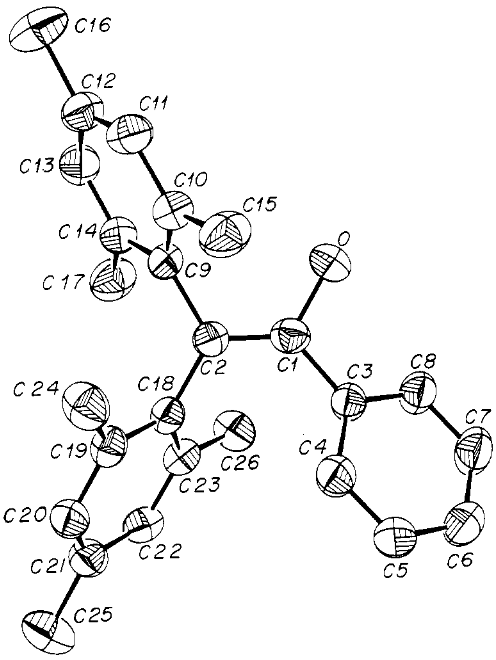


Figure 2. An ORTEP drawing and numbering scheme for **1d**.

are long. There is regularity in that the C(9)–C(10) and the C(18)–C(19) bonds are much longer, being 1.413 (5)–1.420 (8) and 1.410 (6)–1.426 (3) Å, respectively, whereas the elongation of the other two bonds (with one exception) is less pronounced. The bond angles within the nine aryl groups of the three ketones change from 116.7° to 123.2°. In the mesityl groups the angles near the *p*-methyl group (C(11)–C(12)–C(13) and C(20)–C(21)–C(22)) are the smallest (116.7–118.3°) whereas the two angles neighboring to it are wider (121.7–123.2°). The angles from C(2) to the aryl groups (C(2)–C(ipso)–C(ortho)) are not symmetrical. One is 115.3–116.7°, and the other is 124.7–125.9°. The two mesityl groups are nearly perpendicular to one another. The dihedral angles between the two β-mesityl groups are 90.05° for **2b**, 92.11° for **2d**, and 95.47° for **2g**.

The most interesting angle for our studies is the dihedral angle between the α-Ar and the C=O planes. In **2d** it is 161.94° in perfect agreement with the value of 19° (161°) calculated in solution from the UV spectra.[15] The dihedral angle is only slightly higher for **2g** (22.6°), but the ArCO moiety of **2b** is nearly planar, the dihedral angle being only 3.50°. These values should be compared with the Ar—C=O dihedral angles of 66.6° and 47.7° for **4** and **6**, respectively.[25] Compounds **2d** and **6** are isomeric, and the difference in the dihedral angles demonstrates the importance of the steric interaction when the bulky group is directly attached to the carbonyl.

The conformations of the three ketones do not differ much. Although the positions of the methine (H(2)) hydrogens were determined only approximately, the bond angles H(2)–C(2)–C(18) and H(2)–C(2)–C(9) are close to tetrahedral, being 103.9 ± 1.1° and 105.5 ± 1.3°, respectively. The H(2)–C(2)–C(1) angle is smaller, being 99.5 ± 2.3° (with the smallest value of 95.9° for **2g**). In contrast to **6** where the C=O and the C–H bonds are in an anti relationship, i.e., the H(2)–C(2)–C(1)–O angle is close to 180°, in **2b**, **2d**, and **2g** these angles are 136.9°, 133.1°, and 131.1°. The β-mesityl group and the carbonyl are in a periplanar relationship with torsional angles of 20.8–27.6°, whereas the corresponding angles for the β′-mesityl groups are 109–120.1°. The α-Ar is gauche to H(2) and the β′-mesityl.

(b) 1d. The conformation of the parent enol **1d** in the solid state was also determined by X-ray diffraction. Bond lengths and angles around the central bond and few others, together with the dihedral angles of the aryl groups in relation to the double bond plane and the twist angle of this bond, are given in Table IV. The ORTEP drawing of **1d** is given in Figure 2. The rest of the crystallographic data are given in supplementary Tables S13–S16,

Table IV. Bond Lengths and Angles for **1d**

bond	length, Å	bond	length, Å	angle	deg	angle	deg	dihedral angle	deg
C(1)–C(2)	1.339 (4)	C(18)–C(19)	1.413 (4)	O–C(1)–C(2)	121.0 (4)	C(9)–C(14)–C(17)	122.3 (4)	α-Ar–OC(1)C(2)C(3)	33.34
C(1)–O	1.394 (4)	C(18)–C(23)	1.417 (6)	O–C(1)–C(3)	109.9 (4)	C(18)–C(19)–C(24)	122.9 (4)	β-Ar–OC(1)C(2)C(3)	117.57
C(1)–C(3)	1.479 (5)	C–C(α-ring)	1.372 (5)–1.393 (5)	C(1)–C(2)–C(9)	118.0 (4)	C(18)–C(23)–C(26)	123.9 (4)	β′-Ar–OC(1)C(2)C(3)	65.69
C(2)–C(9)	1.509 (5)	C–C(β-ring)[a]	1.384 (6)–1.397 (5)	C(1)–C(2)–C(18)	121.5 (4)	CCC(α-ring)[c]	118.0 (4)–121.3 (4)	OC(1)C(3)–C(9)C(2)C(18)	170.69
C(2)–C(18)	1.503 (5)	C–C(β′-ring)[b]	1.375 (6)–1.400 (5)	C(9)–C(2)–C(18)	120.4 (4)	CCC(β-ring)[c]	118.2 (4)–122.6 (4)		
C(9)–C(10)	1.418 (6)			C(2)–C(1)–C(3)	129.1 (4)	CCC(β′-ring)[c]	117.4 (4)–122.7 (4)		
C(9)–C(14)	1.405 (5)			C(9)–C(10)–C(15)	123.5 (4)				

[a] Except for C(18)–C(19) and C(18)–C(23). [b] Except for C(9)–C(10) and C(9)–C(14). [c] Intra-ring angles.

Table V. K_{enol} Values for 1-Aryl-2,2-dimesityl Systems in Hexane at 367.6 K[a]

			K_{enol} (HPLC analysis)				K_{enol} (NMR analysis)			
X	equilbrm	time,[b] h	from enol side	from keto side	average	% enol at equilbrm	from enol side	from keto side	% enol at equilbrm	$\Delta G°$, kcal mol^{-1}
p-PhO	**1a** ⇌ **2a**	5.5	0.54 ± 0.02	0.59 ± 0.02[c]	0.57 ± 0.02	36 ± 2				0.41 ± 0.03
p-MeO	**1b** ⇌ **2b**	2	0.34 ± 0.01	0.31 ± 0.01[d]	0.32 ± 0.02	24 ± 1	0.42 ± 0.05[g]	0.39 ± 0.03[g]	28	0.83 ± 0.05
p-Me	**1c** ⇌ **2c**	4.5[e]	0.74 ± 0.02	0.71 ± 0.04	0.72 ± 0.02	42 ± 1.5	0.66 ± 0.06[h]	0.66 ± 0.06[h]	40	0.23 ± 0.02
H	**1d** ⇌ **2d**	5	1.06 ± 0.07	0.98 ± 0.06	1.02 ± 0.07	50 ± 2	1.0 ± 0.1[i]	0.99 ± 0.05[j]	50	−0.01 ± 0.04
m-Cl	**1e** ⇌ **2e**	3	2.16 ± 0.04	2.17 ± 0.06	2.17 ± 0.06	68.5 ± 1	(3.6 ± 0.2[k])		78	−0.56 ± 0.02
p-CF_3	**1f** ⇌ **2f**	10	2.9 ± 0.1	2.8 ± 0.1	2.85 ± 0.15	74 ± 1	3.7 ± 0.2[l]	3.6 ± 0.1[l]	78	−0.76 ± 0.01
m,m-Br_2	**1g** ⇌ **2g**	1.7[f]	3.7 ± 0.2	3.5 ± 0.3	3.6 ± 0.2	78 ± 1	3.3 ± 0.5[m]		77	−0.93 ± 0.04

[a] [Substrate] = 0.04 mmol; catalyst 0.22% CF_3COOH (TFA) (0.13 mmol) in the HPLC-analyzed experiments and 1.1% TFA in the NMR-analyzed experiments unless otherwise stated. [b] Time at which the last point was taken and where the [**1**]/[**2**] ratio resembles that of the preceding point. [c] Taken after 9.5 h. [d] Taken after 10 h and with 0.44% TFA catalyst after 11 h. [e] With 0.44% TFA catalyst. Similar values were obtained with 0.22% and 1.1% TFA. [f] With 0.88% TFA. Similar values were obtained from the ketone side with 0.22% and 0.44% TFA. [g] Identical values were obtained after 6 and 10 h. Decompositions of 2% and 7% from the enol and the keto sides were observed after 6 h; 11% decomposition from both after 10 h. [h] Measured after 19.5 h. Decomposition of 35% from the enol side and 41% from the keto side. [i] Measured after 19 h, when decomposition amounts to 13%. K_{enol} = 1.02 ± 0.04 after 41 h, and decomposition amounts to 17%. [j] Measured after 11 h (20% decomposition). After 8 h K_{enol} = 1.02 ± 0.09, and 12% decomposition was observed. [k] Value after 7 or 11 h, when the decomposition is 9%. [l] Value after 10 h with 0.22% TFA. [m] Value after 11 h, with 12% decompostion. After 9 h K_{enol} = 3.6 ± 0.6 with 12% decomposition.

and the stereoview is given in the supplementary Figure S5.

All the three aryl groups are twisted appreciably from the plane of the double bond but not in a symmetrical way. The dihedral angle of the α-phenyl ring is 33.34°, whereas those for the two mesityl rings are much larger: 62.43° for the β-ring (cis to α-phenyl) and 65.69° for the β'-ring. The double bond itself is twisted by 9.3°.

This arrangement is reminiscent of the dihedral angles of Z-(**3**), the positional isomer of **1d**, where the dihedral angle of the β-phenyl ring is 38.3° whereas those for the α- and the β-mesityl rings are 79.0° and 74.4°, respectively.[25] Apparently, the smaller α-phenyl ring achieves more coplanarity with the double bond than the bulkier mesityls. However, both isomers have a three-blade propeller conformation.

The steric interaction between the cis aryl groups is reflected by opening of the bond angle near the α-aryl group, C(1)–C(2)–C(3), to 129.1° at the expense of the O–C(1)–C(3) angle which is only 109.9°. The other bond angles around the double bond are normal.

As in the ketones, the two bonds from the ipso-mesityl carbons to their neighboring ring carbons are longer than other ring C–C bonds. The angles from these ipso-carbons to the o-methyl groups are slightly wider than 120°.

Equilibration Studies. The keto–enol equilibria were studied in hexane at 367.6 K in the presence of trifluoroacetic acid. The amount of acid was more than catalytic since the use of very low concentrations required relatively long reaction times for the equilibration. Initial experiments with **1b–g**, **2b–d**, and **2f** and 1.1% TFA were analyzed by ^{1}H NMR where both species were detected. Equilibrium ratios were recorded when two consecutive points gave the same **1**/**2** ratios starting either from **1** or from **2**. By comparison with the HPLC data it was found that the reaction times used in these experiments were much longer than required for equilibration. Decomposition products, which were shown as aromatic multiplets in the NMR but were not identified, were observed. The **1**/**2** ratios were determined by several integrations of each point: (1) of the high field enol Me's compared with the ketone Me signals, (2) of the enol (OH + aryl) signals compared with the ketone (C-H + aryl) signals, and (3) of specific signals, e.g., the MeO's of **1b** and **2b**. Although the average integration ratios were similar starting from **1** and **2** they contain an error due to the decomposition products. The error probably amounts to several percent of each component, although it is difficult to estimate it due to known and unknown overlap of the signals and to the observed peak broadening which may be due to overlap, superimposed on broadening due to exchange processes.[26]

Consequently, analysis by HPLC, where the enols and ketones peaks are sufficiently separated from each other and from peaks due to decomposition products, was used for all the systems. The conditions are given in the Experimental Section, and the reaction times at which equilibration was already achieved are given in Table V. The decision when equilibrium was achieved was based on the two criteria described above for the ^{1}H NMR analysis, and the times required were found to be shorter than those used for the initial NMR experiments. The TFA concentration in the standard experiments was 0.22%, and a two- or fivefold increase in this value did not affect the equilibrium ratio indicating that partial selective protonation of either **1** or **2** does not contribute to K_{enol}. However, a 10-fold increase in the [TFA] indeed changed the equilibrium ratio. Hence, the 0.22% TFA used in all the experiments is regarded as "catalytic".

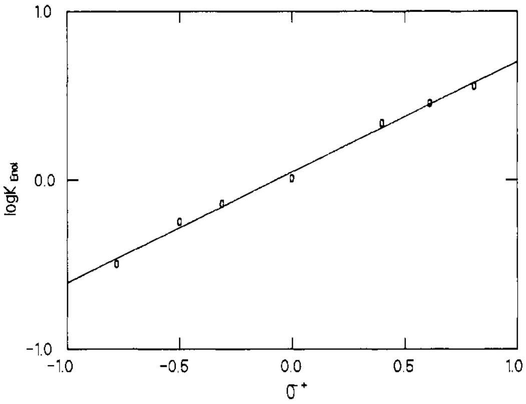


Figure 3. A plot of log K_{enol} values vs. σ^+ values for **1**/**2**.

The NMR- and the HPLC-derived data are summarized in Table V. Inspection of the percentage of enol at equilibrium calculated by the two methods shows that the agreement between them is generally good. The K_{enol} values obtained by both methods are almost identical for **1d**/**2d** and **1g**/**2g** and slightly different for **1b**/**2b** and **1c**/**2c**. The difference is larger for **1f**/**2f** and for **1e**/**2e**. In the latter case it was shown that the value given by NMR (and measured only from the enol side) is for a point where equilibrium was not yet reached, but no further study was conducted. We note that since K_{enol} is the ratio of the two species which are determined from the same data in the NMR method, a small error in the concentration is magnified in K_{enol} calculated by this method. For the reasons discussed above, we consider the HPLC-derived values to be more accurate, and the K_{enol} values used for the correlations and the derived $\Delta G°$ values are based on the HPLC-derived values.

A log K_{enol} vs. Hammett's σ values,[27] using $\sigma_{p\text{-PhO}} = -0.32$,[28] gives $\rho = 0.87$ ($r = 0.9635$) and the point for p-MeO deviates.

---

(26) Occasional broadening of the OH signal may be due to exchange with residual traces of TFA.

(27) The σ and σ^+ values were taken from the critical compilation of Exner: Exner, O. In *Correlation Analysis in Chemistry*; Chapman, N. B., Shorter, J., Eds.; Plenum: New York, 1978, Chapter 10, p 439.

When $\sigma_{p\text{-PhO}} = 0.05$[28] is used, $\rho = 0.95$ ($r = 0.9459$). The correlation is improved by using σ^+ values[27]: $\rho^+ = 0.65$ ($r = 0.997$) when ${\sigma^+}_{p\text{-PhO}} = -0.5$[28] (Figure 3), and $\rho^+ = 0.64$ ($r = 0.9949$) when using ${\sigma^+}_{p\text{-PhO}} = -0.56$. A dual-parameter equation $\log K_{\text{enol}} = \sigma^n\rho^n + \rho^r(\sigma^+ - \rho^n) + i$ gave $\rho^n = 0.60 \pm 0.07$, $\rho^r = 0.75 \pm 0.14$ ($R = 0.9955$) when $\sigma = -0.32$, $\sigma^+ = -0.56$ values for *p*-PhO were used.

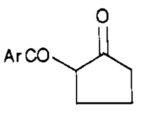
For comparison with literature data[7] we attempted to obtain data in more aqueous media. A preliminary experiment on the equilibration of **1b**/**2b** in 1:1 THF–H_2O (v/v), a medium where the substrates are soluble, was conducted under the conditions of Table V. However, decomposition was appreciable even before equilibration was achieved and reactions in this medium were not investigated further.

Discussion

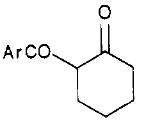
The main contribution of the present work is the direct determination of K_{enol} values for the series of α-aryl-substituted enols **1** and their isomeric ketones **2** in a nonpolar solvent. Viewed more generally, ketones **2** are a subgroup of the family of meta- and para-substituted α-substituted acetophenones $ArCOCHR^1R^2$ where $R^1 = R^2$ = Mes, and our K_{enol} values are complementary to those found for other three subgroups of this generalized family. These are (a) the "simple" and highly unstable enols of acetophenones **7**, where the enols cannot be directly detected, and hence K_{enol} values were determined indirectly,[7i] and (b) the benzoylcyclopentanones **8** and benzoylcyclohexanones **9**, which are stable due to the electron withdrawal by the β-carbonyl group, where both species are detected in the equilibrium mixture.[29,30] Semiquantitative data are also available for benzoylacetones **10**.[31] Our system resembles both **7**, **8**, and **9** since the enols are "simple" but are present in appreciable concentrations at equilibria. Another aspect is that various types of solvents were applied in the equilibria investigated: the nonpolar hexane for **2**, MeOH for **8** and **9**,[29,30] and water for **7**.[7i]

ArCOMe

7



8



9

ArCOCH$_2$COMe

10

In spite of these differences the substituent effects on K_{enol} in all the series are qualitatively similar (see below). It seems therefore logical to start the discussion with the influences that meta- and para-substituted aryl groups have on the keto–enol equilibria which are common to all the series. Then we will discuss special features in our systems, such as the possibility that steric effects may cause deviation from planarity with a consequent reduced conjugation which may quantitatively affect the K_{enol} values. Comparison will then be made with the behavior of **7**–**9**, and other systems and conclusions concerning the possible reasons for the stability of polyaryl-substituted enols will be drawn.

The substituent effects on equilibria are the differences in the substituent effects on each side of the equilibria. Consequently, the substituent effects on K_{enol} in our systems are determined by the differences in the substituent effects on the stabilization of the enols and ketones. In the following discussion these will be treated separately for model reactions, in terms of Hammett-type correlations.

Stabilization of Enols by an α-Aryl Group. The common structural moiety of all the enols is the 2,2-dimesitylethenolyl ($Mes_2C{=}C(OH){-}$) group. The hydroxy group as well as both mesityl groups stabilize the double bond. From equilibrium data on enol ethers (which are the best models for the enols) it was evaluated that a β-phenyl substituent stabilizes the enol ether by 3.6 kcal mol^{-1},[32] a value which should be compared with the 4.3-kcal mol^{-1} stabilization energy ($\pi(C{=}C)-\pi(Ph)$) in styrenes.[33] The difference is not large, and we therefore believe that the *differential* effect of the α-aryl group on the enol stability could be estimated with reasonable accuracy from the effect of meta and para substituents on the stabilization of the styrene moiety Ph—C=C. Data from (i) equilibrium values in solution which give the contributions of both the polar and resonance effects and (ii) MO calculations on isolated molecules which give mainly the $\pi(C{=}C)-\pi(Ph)$ conjugation energy from the difference in energy between the planar and the orthogonal conformations[34] were used for evaluating the substituent effects.

Five reaction series supply the appropriate data. Hine and Skoglund[35] used Bushby and Ferber's data[36] for the equilibria of eq 6 in 1:8 Et_2O–NH_3 at 25 °C for evaluating the stabilization

$$\textit{trans}\text{-}PhCH_2CH{=}CHAr \xrightleftharpoons{K_{eq}} \textit{trans}\text{-}PhCH{=}CHCH_2Ar \qquad (6)$$

energy of a double bond by an Ar compared with a Ph group, where the Ar–C(sp^3) and Ph–C(sp^3) stabilization energies serve as the reference. The stabilization energies for X = *p*-Me_2N, *p*-Me, *p*-F, and *o*-Me in XC_6H_4 were 5.07, 4.62, 4.38, and 3.99 kcal mol^{-1}, respectively, and the $\Delta\Delta G° = \Delta G°(Ar) - \Delta G°(Ph)$ values change by 0.70 kcal mol^{-1} between the extreme para substituents studied.[37] We correlated the data with Hammett's σ values and obtained ρ of 0.44 ($r = 0.962$) and σ^+ ($\rho^+ = 0.27$, $r = 0.983$) for eight points. A combination of σ and σ_R gave no improvement: $\rho = 0.30$, $\rho^r = 0.24$ ($r = 0.983$).

The equilibrium addition of the AcOH solvent to 10 meta- and para-substituted styrenes (eq 7, S = Ac)[38] gave the adducts **11**, S = Ac in percentages which changed from 80.2% for Ar = *p*-$MeOC_6H_4$ ($K_{eq} = 4.1$) to 96% for *p*-$O_2NC_6H_4$ ($K_{eq} = 24$). We

$$ArCH{=}CH_2 + SOH \xrightleftharpoons{K_{eq}} \underset{\textbf{11},\ S\,=\,H,\ Ac}{ArCH(OS)CH_3} \qquad (7)$$

calculated a ρ value of 0.60 ($r = 0.943$) for all the substituents and $\rho = 0.62$ ($r = 0.979$) when points for *p*-Br and *m*-Br are excluded. A plot vs. σ^+ gave $\rho^+ = 0.45$ ($r = 0.936$) and $\rho^+ = 0.48$ ($r = 0.981$, *p*-Br, *m*-Br excluded). The equilibrium (acid-catalyzed) addition of water to 10 styrenes in water (eq 7, S = H) gave adducts **11**, S = H.[39] Even excluding the deviating point for *m*-Me resulted in poor correlations with $\rho = 1.17$ ($r = 0.869$) and $\rho^+ = 0.81$ ($r = 0.857$). When the points for *m*-Br and *p*-Br were also excluded, the correlations were improved and gave $\rho = 1.32$ ($r = 0.952$) and $\rho^+ = 0.94$ ($r = 0.956$).[40]

---

(28) Appreciable differences exist for σ and σ^+ values for *p*-PhO obtained from different sources: $\sigma = -0.32$ (based on pK_a of the benzoic acid) and $\sigma = 0.05 \pm 0.13$ (average value) are given in ref 27. $\sigma^+ = -0.5$ is an average value,[27] and $\sigma^+ = -0.56$ was determined in a search for reliable values (Clementi, S.; Linda, P. *J. Chem. Soc. Perkin Trans. 2* **1973**, 1887) as an average value based on several electrophilic substitution reactions.

(29) Campbell, R. D.; Harmer, W. L. *J. Org. Chem.* **1963**, *28*, 379.

(30) (a) Campbell, R. D.; Gilow, H. M. *J. Am. Chem. Soc.* **1960**, *82*, 2389. (b) Campbell, R. D.; Gilow, H. M. *Ibid.* **1962**, *84*, 1440.

(31) Lowe, J. U., Jr.; Ferguson, L. N. *J. Org. Chem.* **1969**, *30*, 3000.

(32) Taskinen, E.; Ylivainio, P. *Acta Chem. Scand.* **1975**, *B29*, 1. The reduced stabilization of the double bond in vinyl ethers by a β-phenyl group is ascribed to reduced double bond character due to the delocalization

$$\ddot{O}{-}C{=}C \leftrightarrow \overset{+}{O}{=}C{-}\overset{-}{C}$$

(33) This value is based on hydrogenation of ethylene and styrene (Kistiakowsky, G. B.; Romeyn, H.; Ruhoff, J. R.; Smith, H. A.; Vaughan, W. E. *J. Am. Chem. Soc.* **1935**, *57*, 65. Dolliver, M. A.; Gresham, T. L.; Kistiakowsky, G. B.; Vaughan, W. E. *J. Am. Chem. Soc.* **1937**, *59*, 831). It is close to the value of 4.5 kcal mol^{-1} estimated in ref 35 from equilibration of allylbenzene and *trans*-propenylbenzene (Ela, S. W.; Cram, D. J. *J. Am. Chem. Soc.* **1966**, *88*, 5791).

(34) These calculations were performed by Dr. M. Karni and Prof. Y. Apeloig of the Technion, Haifa, Israel, to whom we are gratefully indebted.

(35) Hine, J.; Skoglund, M. J. *J. Org. Chem.* **1982**, *47*, 4766.

(36) Bushby, R. J.; Ferber, G. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1683.

(37) The values quoted are probably for complete conjugation since it is likely that for para-substituted systems both species in eq 6 are coplanar with the double bond.

(38) Mollard, M.; Torck, B.; Hellin, M.; Coussemant, F. *Bull. Soc. Chim. Fr.* **1966**, 83.

(39) Durand, J.-P.; Davidson, M.; Hellin, M.; Coussemant, F. *Bull. Soc. Chim. Fr.* **1966**, 43.

(40) The acid-catalyzed hydration of five styrenes (Schubert, W. M.; Lamm, B.; Keefe, J. R. *J. Am. Chem. Soc.* **1964**, *86*, 4727) was studied at different acidities. The scatter of equilibrium values found for each substituent and the small difference between the *K*'s for the various substituents made a Hammett-type correlation meaningless.

The equilibrium addition of MeOH to eight meta- and para-substituted-α-methoxystyrenes (ranging from *p*-MeO to *m*-NO_2) (eq 8)[41] should be a better model for the enols stabilization due to the presence of the vinylic ether group. The K_{eq}'s differ by a small factor, from 42.5 for *p*-MeO to 75.8 for *m*-NO_2. The data were analyzed by the authors by using the Young–Jencks' modification[42a,b] of the Yukawa–Tsuno equation[42c] and gave $\rho° = 0.28 \pm 0.05$ ($r = 0.964$) and $\rho^r = 0.08 \pm 0.06$.

Finally, equilibrium 9 was studied for two systems in cyclohexane. For the **12** ⇌ ***E*-13** and the **12** ⇌ ***Z*-13** equilibria the $\Delta\Delta G° = \Delta G°(\text{Ph}) - \Delta G°(p\text{-MeC}_6\text{H}_4)$ values were -0.06 ± 0.04 and -0.31 ± 0.07 kcal mol^{-1}, respectively.[43]

$$\text{ArC(OMe)}{=}\text{CH}_2 + \text{MeOH} \xrightleftharpoons{K_{eq}} \text{ArC(OMe)}_2\text{CH}_3 \qquad (8)$$

$$\underset{\textbf{12}}{\text{ArCH}_2\text{C(OMe)}{=}\text{CH}_2} \rightleftharpoons \underset{\boldsymbol{E}\textbf{-13}}{E\text{-ArCH}{=}\text{C(OMe)Me}} \rightleftharpoons \underset{\boldsymbol{Z}\textbf{-13}}{Z\text{-ArCH}{=}\text{C(OMe)Me}} \qquad (9)$$

Ab initio calculations using the split-valence 3-21G basis set[44] were performed for the fully conjugated planar and for the orthogonal (Ar—C=C dihedral angles of 0° and 90°, respectively) conformations of styrene and its *p*-OH and *p*-O_2N derivatives.[34] The geometry of styrene was optimized[45] except for the inter-ring angles in both conformations, and the same geometry was used for the two derivatives together with the appropriate additional parameters for OH and NO_2.[46] The energy differences between the two conformers which reflect the $\pi(\text{Ar}) - \pi(\text{C}{=}\text{C})$ conjugation energies were 1.90, 1.78, and 1.74 kcal mol^{-1} for X = OH, H, and NO_2 in *p*-$XC_6H_4CH{=}CH_2$, respectively. The derived $\Delta\Delta G° = \Delta G°\ (\pi(p\text{-HOC}_6\text{H}_4)/\pi(\text{C}{=}\text{C})\text{ interaction}) - \Delta G°(\pi(p\text{-O}_2\text{NC}_6\text{H}_4)/\pi(\text{C}{=}\text{C})\text{interaction})$ is 0.11, leading to a ρ value of ca. 0.1 for the stabilization.

These diverse data lead to three general conclusions. First, electron donation by a meta or a para substituent increases the stabilization of the styrene.[47] Second, the effect is small as shown by the ρ values. Third, mostly the correlation with σ is marginally better than with σ^+ (or the ρ^r value is negligible in comparison with ρ) in spite of the inclusion of strongly resonative electron-donating substituents in the correlations. The substituent effect is therefore mainly polar.[48]

Stabilization of a Carbonyl Group by an α-Aryl Group. Three different probes were used for estimating the effect of α-aryl substituents on the stability of a carbonyl group: (a) rotational barriers around the Ar–CO bonds, (b) MO calculations, and (c) equilibration data for additions to the ArCOR system.

Rotational Barriers Around Ar–CO Bonds. The resonance contribution to the Ar–CO interaction should be reflected by the rotational barrier around the Ar–CO bond. The rotational barrier measures the energy difference between the ground state which is presumably completely planar (torsional angle 0°) in benzaldehydes and ortho- and para-substituted acetophenones (see below) and the perpendicular conformer (torsional angle 90°) which is presumably the highest point on the potential energy surface for the rotation.

The most suitable data for our purpose are the rotational barriers for ketones **2a–g** which should reflect the effect of the bulky Mes_2CH group on the extent of ground-state Ar–CO conjugation.[49] Unfortunately these values are not available since even at the lowest temperature at which the ketones are still soluble, peak broadenings were not observed.

Rotational barriers around the Ar–CO bond were obtained by NMR and IR techniques for both benzaldehydes and acetophenones.[50] Most of the NMR data come from the same laboratory,[23,51] but the $\Delta G^\ddagger$ values from different laboratories usually differ by only 0.1–0.3 kcal mol^{-1}.[50,52] The barriers estimated by IR[53] are lower than those obtained by DNMR, but it seems[51b] that the latter values show a better internal consistency, and the most reliable ones are based on ^{13}C DNMR.[23,51] The barriers decrease with the increase in the electron withdrawal by the substituent from 10.5 kcal mol^{-1} for *p*-Me_2N to 6.8 kcal mol^{-1} for *p*-CF_3 in ArCHO[51b] and from 8.3 kcal mol^{-1} for *p*-Me_2N to 4.7 kcal mol^{-1} for *p*-CF_3 for ArCOMe.[23] The $\Delta G^\ddagger$ values showed significantly better correlations with σ^+ than with σ, and the slopes (for $\Delta G^\ddagger$ in kcal mol^{-1}) were 1.61 ± 0.07 ($r = 0.994$, $n = 10$) for ArCHO and 1.5 ± 0.07 ($r = 0.992$, $n = 8$) for ArCOMe.[51b,54] Of the various Taft's dual parameter equations the best correlations were with σ_I,σ_R^+ with $\Delta G^\ddagger = -1.16\sigma_I - 1.78\sigma_R^+ + 7.6$ for ArCHO and $\Delta G^\ddagger = -1.12\sigma_I - 1.70\sigma_R^+ + 5.38$ for ArCOMe.[51b,54]

There are three noteworthy features of these data. First, the similar slopes for the ArCHO and the ArCOMe are mostly due to the electron donation by the Me group in the latter, but steric effects may also be important since the Ph/COMe steric interaction is ca. 1.5 kcal mol^{-1} higher than the Ph/CHO steric interaction.[51b,55] However, since the aryl and the carbonyl moieties in benzaldehydes are coplanar in solution,[56] the identity of the Hammett slopes suggest that the acetophenones are also planar. This is consistent with all of the crystallographic data (see below) and with most of the data in solution.[57] However, some data,[57] and especially a recent dipole moment and Kerr effect study, suggest that whereas acetophenone and *p*-methylacetophenone are planar the twist angles for several derivatives, e.g., *p*-chloroacetophenone, may be appreciable.[58] Second, when the $\Delta G^\ddagger$ vs. σ^+ plot for acetophenones is scaled to a log *k* vs. σ^+ plot, the ρ^+ value of 1.1 resembles the ρ^r values obtained from the equilibrium additions to ArCOR (see below). Third, as the dual parameter analysis indicates the rotational barrier is not deter-

---

(41) Toullec, J.; El-Alaoui, M. *Tetrahedron Lett.* **1979**, 3085.

(42) (a) Young, P. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 8238. (b) Young, P. R.; Jencks, W. P. *Ibid.* **1979**, *101*, 3288. (c) Yukawa, Y.; Tsuno, Y. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 971.

(43) Taskinen, E.; Kuusisto, M. *Acta Chem. Scand.* **1985**, *B39*, 495.

(44) The GAUSSIAN80 series of programs were used: Binkley, J. S.; Whitesides, R. A.; Krishnan, R.; Seeger, R.; De Frees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. Program QCPE **1980**, *13*, 406. Indiana University, Bloomington, IN; 3-21G: Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

(45) For the method of optimization (using the gradient technique), see: Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214. Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem.* **1978**, *14*, 545.

(46) The geometry of NO_2 was taken from trinitrobenzene (Whitesides, R. A.; Frisch, M. J.; Pople, J. A. *The Carnegie-Mellon Quantum Chemistry Archive*). The geometry of OH (attached to a phenyl group) was taken from Yamabe, S.; Minato, J.; Arai, T. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2143.

(47) The frequent predominance of one of the species in the equilibria discussed above results in relatively high error in several values and is probably responsible for the relatively low correlation coefficients.

(48) These conclusions are also relevant to solvolysis of α-arylvinyl derivatives where the Ar—C=C ground state stabilization is replaced by an orthogonal Ar-C^+ transition state stabilization (Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. *Vinyl Cations*; Academic Press: 1969; Chapter 6). The ρ^+ in the solvolysis is therefore predominantly due to transition-state stabilization.

(49) The higher the Ar–CO torsional angle, the lower the rotational barrier if the rotational process involves passage through a conformation with a 90° Ar–CO torsional angle.

(50) For a collection of data, references and calculations, see: Antypas, W. G., Jr.; Siukola, L. V. M.; Kleier, D. A. *J. Org. Chem.* **1981**, *46*, 1172.

(51) (a) Drakenberg, T.; Jost, R.; Sommer, J. *J. Chem. Soc., Chem. Commun.* **1974**, 1011. (b) Drakenberg, T.; Sommer, J. M.; Jost, R. *J. Chem. Soc., Perkin Trans. 2* **1980**, 363.

(52) The much earlier $\Delta G^\ddagger$ values of Anet (Anet, A. L.; Ahmad, M. *J. Am. Chem. Soc.* **1964**, *86*, 119) for ArCHO are consistently higher by 0.3–0.5 kcal mol^{-1} than those of Drakenberg et al.[22,51]

(53) Miller, F. A.; Fateley, W. G.; Witkowski, R. E. *Spectrochim. Acta, Part A* **1967**, *23*, 891 gave values of 3.1 and 3.5 kcal mol^{-1} for the rotational barrier in *p*-XC_6H_4COMe, X = H, CF_3, respectively. The values were higher for the benzaldehydes, *p*-XC_6H_4CHO, e.g., 4.66 (X = H), 3.6 (X = *p*-F) (Fateley, W. G.; Harris, R. K.; Miller, F. A.; Witkowski, R. E. *Spectrochim. Acta* **1965**, *21*, 231).

(54) Note that the slopes are given here in units of kcal mol^{-1} for a better comparison with the kinetic data, and they therefore differ from those given in ref 51b in kJ mol^{-1}.

(55) A lower value of ca. 1 kcal mol^{-1} was previously estimated on the basis of an estimated lower torsional barrier for acetophenone (Grindley, T. B.; Katritzky, A. R.; Topsom, R. D. *J. Chem. Soc., Perkin Trans. 2* **1974**, 289. *Tetrahedron Lett.* **1972**, 2643).

(56) Mirarchi, D.; Ritchie, G. L. D.; Williams, A. J. *Aust. J. Chem.* **1982**, *35*, 663.

(57) Barthelemy, J.-F.; Jost, R.; Sommer, J. *Org. Magn. Reson.* **1978**, *11*, 438.

(58) Mirarchi, D.; Ritchie, G. L. D. *Aust. J. Chem.* **1981**, *34*, 1443.

mined solely by Ar–CO conjugation. Large contribution to $\Delta G^{\ddagger}_{\text{rot}}$ is due to a polar effect, and $\lambda = \rho_R{}^+/\rho_I = 1.5$, to the surprise of Drakenberg and his co-workers.[51b]

MO Calculations. Ab initio calculations using the split-valence 3-21G basis set were performed for the fully planar and for the orthogonal p-XC_6H_4CHO, X = OH, H, NO_2.[34,44,45] The geometry of benzaldehyde was optimized except for the inter-ring angles in both conformations, and the same geometry was used for the substituted benzaldehydes.[46] The energy differences between the conformers were 12.3, 11.2, and 10.2 kcal mol^{-1} for p-XC_6H_4CHO, X = OH, H, and p-O_2N, respectively. These values reflect the Ar–CO rotational barriers and the corresponding log K vs. σ plot gives $\rho = 1.25$ ($r = 0.974$) and a better correlation with σ^+ with $\rho^+ = 0.87$ ($r = 0.999$).

Aromatic Substituent Effects on Equilibrium Additions to ArCOR. Several equilibrium additions of nucleophiles to ring-substituted benzaldehydes and acetophenones were investigated, and the results were analyzed by LFER's. For example, the equilibrium addition of SO_3^{2-} [59] in water or of semicarbazide in 25% EtOH[60] to ArCHO (eq 10, Nu = SO_3^{2-} or $H_2NCONHNH_2$)

$$\text{ArCHO} + \text{NuH (or Nu}^- + \text{H}^+) \overset{K_{\text{eq}}}{\rightleftharpoons} \text{ArCH(OH)Nu} \qquad (10)$$

gave ρ^+ values of 1.25, and a better correlation with σ^+ ($\rho^+ = 1.04$)[61] than with σ was obtained for the addition of HCN (eq 12, Nu$^-$ = CN$^-$).[61,62] This is not always the case: for addition of MeOH to form the hemiacetal (eq 10, NuH = MeOH) correlation with σ^0 was excellent ($\rho = 2.0$) although p-MeO deviated.[63,64] For acetal formation (eq 11) in 95% MeOH–5% H_2O the correlation with σ gave $\rho = 2.14$ ($r = 0.957$), but the correlation was not improved by using other σ scales.[65] The situation is better for formation of anionic adducts (eq 12). For Nu$^-$ = OMe$^-$ good correlation with σ^0 ($\rho = 3.2$) was observed.[63,64] For Nu$^-$ = OH$^-$ the correlation with σ ($\rho = 2.76$, $r = 0.994$;[66,67] $\rho = 2.24$ for electron-withdrawing substituents only[68]) was better than with σ^+ ($\rho^+ = 2.19$, $r = 0.939$) in spite of the deviation of the p-MeO derivative.[66,67] For Nu$^-$ = CN$^-$ in the presence of 18-crown-6 the correlation was better with σ ($\rho = 1.3$) in Me_2SO[69] but better with σ^+ ($\rho^+ = 1.49$) in water.[62]

$$\text{ArCHO} + 2\text{MeOH} \overset{K_{\text{eq}}}{\rightleftharpoons} \text{ArCH(OMe)}_2 \qquad (11)$$

$$\text{ArCHO} + \text{Nu}^- \overset{K_{\text{eq}}}{\rightleftharpoons} \text{ArCH(Nu)O}^- \qquad (12)$$

Equilibrium data for nucleophilic addition to acetophenones are scarcer than for addition to aldehydes. For addition of bisulfite (eq 13) the log K vs. σ^+ correlation ($\rho^+ = 1.1$) is better than with σ or σ^0.[42a] In this case Young and Jencks[42b,70] suggested a dual parameter equation (eq 14) which is a modification of the Yukawa–Tsuno equation,[42c] and the correlation was excellent ($\rho = 1.2$, $\rho^r = 0.95$, $r = 0.999$).

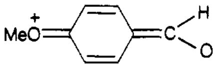
$$\text{ArCOCH}_3 + \text{HSO}_3^- \rightleftharpoons \text{ArC(OH)(SO}_3^-)\text{CH}_3 \qquad (13)$$

$$\log(k/k_0) = \sigma^n\rho + \sigma^r\rho^r \qquad (14)$$

Toullec et al.[71] applied the Young–Jencks' analysis to the equilibrium formation of dimethyl acetals of acetophenones in MeOH, H_2O, and dodecane (eq 15). Excellent correlations ($r = 0.993 - 0.999$) with relatively solvent-independent ρ^r values of 0.90–1.06 but a solvent-dependent ρ^n value (1.73, 1.81, and 0.99 in MeOH, dodecane, and water, respectively) were obtained. The analysis was extended to six additions to aldehydes with the conclusions that the fit to eq 14 was excellent and that ρ^r was nearly reaction- and solvent-independent, whereas ρ^n was reaction- and solvent-dependent. Consequently, the interaction expressed in ρ^r reflects the loss of π(Ar)–π(C=O) conjugation which should be reaction-independent, whereas the dependence of ρ^n on the reaction and solvent reflect the differential polar effects of the substituents on the trigonal carbonyl precursor and the tetrahedral adduct.

$$\text{ArCOMe} + 2\text{MeOH} \rightleftharpoons \text{ArC(OMe)}_2\text{Me} + \text{H}_2\text{O} \qquad (15)$$

In conclusion, the three probes used for the evaluation of the Ar–CO interaction lead to a similar conclusion. The ρ (ρ^+,ρ^r) for the π(Ar)–π(C=O) conjugative interaction *in the planar ArCO moiety* is ca. unity. The positive sign of ρ reflects an increased stabilization of the ArCO moiety by electron-donating substituents due to contribution of hybrids such as **14** to the ground-state structure. A contribution from the polar effect of the substituents reflected by the ρ value is also important.


14

Conformations of 1 and 2. The π(Ar)–π(C=C) and π(Ar)–π(C=O) conjugative stabilization energies given above are for the fully planar systems. Since crowding in our systems is responsible for an appreciable contribution to the large K_{enol} values, the extent of planarity of the Ar—C=C moieties in **1** and of the Ar—C=O moieties in **2** in solution should be evaluated before analysis of the K_{enol} values.

Conformations of 1a–g. Data are available both in the solid state and in solution. Table IV shows that the three dihedral angles in **1d** are large, and the same situation prevails for all the triarylvinyl systems studied so far in the solid state.[25] We believe that since the differential stabilization of the C=C bond by the aryl group is small (vide supra) all enols **1** will have the same conformations in solution, although they may be slightly modified in the solid state due to crystal packing forces. By taking the α-Ar—C=C dihedral angle of 33.34° for **1d** from Table IV a π(Ph)–π(C=C) stabilization energy of 4.5 kcal mol^{-1}, and applying eq 16 which relates the energy of the conformer at a dihedral angle θ, i.e., $E(\theta)$ to the energy of the fully planar system $E(0)$,[72] the stabilization energy due to the α-Ph—C=C interaction is 3.1 kcal mol^{-1}. Even if this angle changes by a few degrees for other enols **1**, it is most reasonable that the ρ term for this interaction (i.e., ca. 0.3–0.6, vide supra) will be reduced by a factor of 0.7 = $E(0)/E(\theta)$, and the expected ρ value for this interaction in **1** is ca. 0.2–0.4.

$$E(\theta) = 0.5E(0)(1 + \cos 2\theta) \qquad (16)$$

Although the information concerning the Ar—C=C dihedral angle in solution is embodied in the UV spectra of **1a–g** (Table I), we are unable to obtain the necessary data without an appropriate planar model. Even for the simpler triphenylethylene, for which the stilbenes were taken as models,[73a] only a qualitative conclusion that all the rings are twisted from the double bond plane could be deduced from the UV spectrum.[74] However, the cal-

---

(59) Gentese, P.; Lamaty, G.; Roque, J. P. *Recl. Trav. Chim. Pays-Bas* **1972**, *91*, 188.

(60) Anderson, B. M.; Jencks, W. P. *J. Am. Chem. Soc.* **1960**, *82*, 1773. Sayer, J. M.; Pinsky, B.; Schonbrunn, A.; Washtien, W. *J. Am. Chem. Soc.* **1974**, *96*, 8005.

(61) Okano, V.; do Amaral, L.; Cordes, E. H. *J. Am. Chem. Soc.* **1976**, *98*, 4201.

(62) Ching, W.-M.; Kallen, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 6119.

(63) Crampton, M. J. *J. Chem. Soc., Perkin Trans. 2* **1975**, 185.

(64) Equilibria 12 and 14 were also studied with various electron-withdrawing substituents, but no Hammett correlation was attempted. (Arora, M.; Cox, B. G.; Sørensen, P. E. *J. Chem. Soc., Perkin Trans. 2* **1979**, 103.

(65) Davis, T. S.; Feil, P. D.; Kubler, D. G.; Wells, D. J. *J. Org. Chem.* **1975**, *40*, 1478.

(66) Bover, W. P.; Zuman, P. *J. Chem. Soc., Perkin Trans. 2* **1973**, 786.

(67) No Hammett-type correlation was attempted in a similar study by using electron-withdrawing substituents in water (Bell, R. P.; Sørenson, P. E. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1594.

(68) Greenzaid, P. *J. Org. Chem.* **1973**, *38*, 3164.

(69) Gold, V.; Wassef, W. N. *J. Chem. Soc. Perkin Trans. 2* **1984**, 1431.

(70) (a) Young, R. P.; Jencks, W. P. *J. Am. Chem. Soc.* **1978**, *100*, 1228. (b) Young, P. R.; McMahon, P. E. *Ibid.* **1979**, *101*, 4678.

(71) Toullec, J.; El-Alaoui, M.; Kleffert, P. *J. Org. Chem.* **1983**, *48*, 4808.

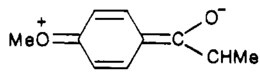
(72) This equation includes only the twofold component of a more general equation: Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 2371.

(73) Suzuki, H. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 389. (b) Suzuki, H. *Ibid.* **1960**, *33*, 379. (c) Suzuki, H. *Ibid.* **1960**, *33*, 410.

culated dihedral angle(s) for *cis*-stilbene is 28°,[73b] and from the UV spectra it is reasonable that the value for triphenylethylene is similar or higher. For $Ph_2C{=}CHPh$, λ_{max}(*n*-heptane) = 298.5 nm (ϵ 18 200), 242.5 sh (14 600), and 232 (17 600)[73a] and for p-$ClC_6H_4CH{=}CPh_2$, which presumably has the same conformation, λ_{max}(EtOH) = 234 (20 000), 320 (25 100).[75] The λ_{max} for **1a–g** are at longer wavelengths, probably due to the auxochromic OH, but the ϵ values (e.g., 11 800 ± 200 for **1d** and **1e**) are smaller, suggesting a larger loss of planarity in the enols than in triphenylethylene. We conclude that the dihedral Ar—C=C angle in solution cannot be much lower than in the solid state, and the conclusion reached above is therefore valid in solution.

It should be noted that there is an important difference between the UV spectra of the enols and those of possible models. For styrenes,[76a,b] α-substituted styrenes,[76b] and for stilbenes[73c,77] the longest wavelength λ_{max} is higher for both electron-donating and electron-withdrawing substituents compared with the unsubstituted compound. Hammett-type plots for styrenes and stilbenes should therefore be convex with a minimum for the unsubstituted compound. In contrast, the λ_{max} for **1a–g** is shifted monotonously to longer wavelengths on increasing the electron withdrawal by the α-aryl substituent, and plots of λ_{max} for the enols vs. σ and σ^+ are roughly linear with slopes of 15.3 (r = 0.969) and 9.8 (r = 0.950), respectively. The plots of $1/\lambda_{max}$ vs. σ and σ^+ are also linear with r's of 0.970 and 0.950, respectively. The plots of the lower wavelength maxima vs. σ^+ are better, with a slope of 7.8 (r = 0.979) for λ_{max}, and slope = −1.29 (r = 0.976) for a plot of $1/\lambda_{max}$. The reason for this behavior is not clear. The few values for E-p-$XC_6H_4C(Ph){=}CHPh$ may show a similar trend,[73b,78] but the data are in different solvents and too scarce to warrant a reliable conclusion.

Conformations of 2a–g. A main structural feature of the ketones in the solid state is that in spite of the bulk of the Mes_2CH group, the molecules achieve conformations with a relatively low Ar—C=O dihedral angle: 3.5°, 18.1°, and 22.6° for **2b**, **2d**, and **2g**, respectively. The increase of the angle follows the decreased electron donation of the para substituent and is consistent with a contribution of hybrid **15** to the ground state of **2b**. Since the Ar—C=O dihedral angle is soft and the difference between **2d** and **2g** is small, no quantitative treatment was attempted. However, the qualitative conclusions are that a Hammett-type treatment should include the σ^+ parameters and that other ketones **2** are not likely to have higher dihedral angles.



15

The dihedral angles should be compared with those known for the less crowded solid meta- and para-substituted acetophenones: 4-H, 2.9°;[79a] 4-H_2N, 3.0°;[79b] 4-OH, 8.1°;[79c] 4-O_2N, 1.5°;[79d] 4-(2-FC_6H_4), 1.5°;[79e] 4-Br(0°);[79f] and 3,5-Ac_2, 8.3°, 8.4° and 8.7°.[79g] All the acetophenones are therefore planar with no apparent trend in the values. Other conformational features are compared below with those of **6**.

Comparison of the ^{13}C NMR and the UV spectra of **2a–g** with those of acetophenones in solution lead to a similar conclusion. The ^{13}C shifts of the most sensitive C-1 and C-4 aromatic carbons and of the C=O carbon are linearly correlated with those of the corresponding acetophenones with slopes of 1.06, 1.04, and 0.95 (or 0.87, p-MeO excluded). To the extent that these shifts reflect an important contribution from conjugation effects,[80] the extents of conjugation in **2** and in the acetophenones do not differ very appreciably.

The Ar—C=O dihedral angle for **2d** was previously calculated from the UV spectrum by Braude's procedure as 19°.[15] This is in excellent agreement with the crystallographic value of 18.1°, suggesting that the conformations in solution resemble those in the solid state. UV spectra for the p-MeO, p-Me, m-Cl, and the unsubstituted acetophenone are available in cyclohexane,[21,81] and we correlated both the λ_{max} and the ϵ values for the B band of ketones **2** in hexane with those of the α-unsubstituted acetophenones.[21] Good linear correlations were observed with a slope of 1.05 (r = 0.990) for the λ_{max} vs. λ_{max} plot, and a slope of 1.11 (r = 0.958) for the ϵ vs. ϵ plot. Likewise λ_{max} (**2**) in hexane for the four compounds are similar, within 1–3-nm values with those of the acetophenones in MeOH.[71] The values of the slopes result from compensation of two opposing effects. Reduced planarity in **2** will result in a decrease in the ϵ values, a conclusion that is corroborated by the lower ϵ for **6**[15] compared with **2d** and presumably a decrease also in λ_{max}. On the other hand, the change $CH_3 \rightarrow CHMes_2$ is expected to increase both λ_{max} and ϵ as judged by comparison of the values for Mes_2CHO and **2d**.[15] Apparently, the second effect predominates since the slopes are higher than unity. We cannot estimate the Ar-CO dihedral angle from these correlations without knowing the quantitative contribution of the latter effect, but the linearity and the values of the slope strongly imply that the Ar-CO torsional angle in solution is not very high.

The conclusion from all the data is that in solution the Ar-CO torsional angle is not very high. The values found by X-ray crystallography in the solid state can be taken as a first approximation to the values in solution.

Substituent Effects on the 1 ⇌ 2 Equilibria. The substituent effect on the **1** ⇌ **2** equilibria differ from those for the equilibria in reactions of the carbonyl compounds discussed above in two respects. First, a priori a substituent-dependent conjugation interaction of the α-aryl group with a double bond (C=O or C=C) exists at both sides of the equilibria of eq 1, although to different extents. Second, these conjugation interactions are reduced by the steric effects of the β-mesityl substituents, again to a different extent.

When both polar and resonance interactions stabilize both species at equilibria, the ρ value (ρ_{eq}) should include the corresponding terms for substituent stabilization (ρ_{stab}) on each side. An equation with a combination of ρ and ρ^r seems appropriate, but since more data on ρ^+ are available we will use eq 17 for a

$$\rho_{eq} = \rho^+_{stab}(\mathbf{1}) - \rho^+_{stab}(\mathbf{2}) \qquad (17)$$

semiquantitative treatment, where ρ^+_{stab} reflects mainly the resonance contribution but also the polar contribution to ρ_{eq}. The discussion above indicates that for simple styrenes the polar contribution is the main one, and it will be more pronounced for the hydroxy-stabilized α-aryl twisted enols **1**. However, the effect of the substituents is small as judged by the data on Ar—C=C stabilization and the dihedral angles in **1d** given above. In contrast, the ρ's for the nucleophilic additions, the MO calculations, the

---

(74) (a) When it was assumed that one ring is coplanar with the double bond, the dihedral angles calculated for the other rings were ⩾40°, a value unreasonable according to Suzuki[73a] since it is higher than the calculated value for tetraphenylethylene. (b) For a discussion of the UV spectra of polysubstituted ethylenes, see: Jaffe, H. H.; Orchin, M. *Theory and Applications of Ultraviolet Spectroscopy*; Wiley: New York, 1962; Chapters 12 and 15.

(75) Bergmann, E. D.; Fischer, E.; Ginsburg, D.; Hirshberg, Y.; Lavie, D.; Magot, M.; Pullman, M. A.; Pullman, B. *Bull. Soc. Chim. Fr.* **1951**, *18*, 864.

(76) (a) Wheeler, O. H.; Covarrubias, C. B. *Can. J. Chem.* **1962**, *40*, 1224. (b) Gassman, P. G.; Harrington, C. K. *J. Org. Chem.* **1984**, *49*, 2258.

(77) Riezebos, G.; Havinga, E. *Recl. Trav. Chim. Pays-Bas* **1961**, *80*, 446.

(78) Eisch, J. J.; Hordis, C. K. *J. Am. Chem. Soc.* **1971**, *93*, 2974: λ_{max} X = Cl 299 nm (EtOH); X = MeO 305 nm (MeOH).

(79) (a) Tanimoto, Y.; Kobayashi, H.; Nagakura, S.; Saito, Y. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1973**, *B29*, 1822. (b) Haisa, M.; Kashino, S.; Yuasa, T.; Akigawa, K. *Ibid.* **1976**, *B32*, 1326. (c) Vainshtein, B. K.; Lobanova, G. M.; Gurskaya, G. V. *Kristallografiya* **1974**, *19*, 531. (d) Kim, J. K. S.; Boyko, E. R.; Carpenter, G. B. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1973**, *B29*, 1141. (e) Young, D. W.; Tollin, P.; Sutherland, H. H. *Ibid.* **1968**, *B24*, 161. (f) Gupta, Prasad, and Yadav (Gupta, M. P.; Prasad, S. M.; Yadav, S. R. P. *Curr. Sci.* **1974**, *43*, 509) reported an almost coplanar arrangement, although the parameters were not deposited with the Cambridge data base. (g) O'Connor, B. H.; Moore, F. H. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1973**, *B29*, 1893.

(80) Bromilow et al. (Bromilow, J.; Brownlee, R. T. C.; Craik, D. J.; Fiske, P. R.; Rowe, J. E.; Sadek, M. *J. Chem. Soc., Perkin Trans. 2* **1981**, 753) analyzed the ^{13}C shifts of many XC_6H_4COZ systems and concluded that inductive effects are the predominant factor.

(81) Bankowska and Jeargcwska (Bankowska, Z.; Jeargcwska, M. *Polish J. Chem.* **1979**, *53*, 2251) found very similar λ_{max} values to those in ref 20 but for a fewer number of substituents.

rotational barriers, and the Ar–CO angles for solid **2** indicate that the resonance stabilization is the main contributor of the carbonyl systems, especially when *p*-MeO is among the substituents studied (cf. **14** and **15**). All the probes used above gave $\rho^+_{\mathrm{stab}}(\mathbf{2})$ of 1.0 ± 0.1 at coplanarity of the Ar–CO moiety. Since all the ρ_{stab} terms are negative, *the first conclusion is that increased stability of α-aryl substituted stable enols with electron withdrawal by the α-aryl group is mainly due to increased destabilization of the keto form.*

The $\rho^+_{\mathrm{stab}}(\mathbf{2})$ term should be related to ρ^+_{stab} for Ar–CO at coplanarity (i.e., $\rho^{+0}_{\mathrm{stab}} = 1.0$) by eq 18 in analogy to eq 16. By using our $\rho_{\mathrm{eq}} \sim \rho^+_{\mathrm{stab}}(\mathbf{2}) = 0.65$ we obtain $\theta = 36°$, a value higher than those obtained from the X-ray data. Although this may be due to the neglect of polar effects, we note a general problem related to our analysis.

$$\rho^+_{\mathrm{stab}}(\mathbf{2}) = 0.5(1 + \cos 2\theta) \qquad (18)$$

In Hammett-type correlations it is usually implied that the conformation remains the same along the reaction series. This is true in most cases including our planar models ArCHO and ArCOMe (see above). However, for solid **2** the Ar–CO conformation is substituent-dependent: **2b** is almost planar, but **2d** and **2g** are nonplanar. This effect should enhance the stabilizing effect of the *p*-MeO group beyond that reflected by $\sigma^+_{p\text{-MeO}}$ at constant conformation, and since it is also proportional to σ^+, an overall linear log K_{enol} vs. σ^+ relationship is expected.[82] However, the derived ρ^+ value is not necessarily applicable for calculating the θ value from eq 18, which implicitly assumes an identical Ar–CO conformation for all substituents. *The second conclusion is therefore that distortion from planarity of the Ar–CO moiety in the keto form reduces the differential effects of meta and para substituents and leads to our relatively low ρ^+_{eq} value.*

Comparison of ρ_{eq} for α-Aryl-Substituted Keto/Enol Systems. ρ_{eq} values are now available for four series of α-aryl-substituted keto/enol pairs: the simple systems **2** and **7**[7i] and the activated systems **8** and **9**.[29,30] System **7** behaves analogously to **2** (better correlation with σ^+, no significant improvement by the Yukawa–Tsuno treatment[7i]). The main effect involved is again the C=O stabilization, as in nucleophilic addition to these species.[83] Although the K_{enol} for **7** in H_2O is ca. 10^8 times lower than for **1**/**2** in hexane, a plot of log K_{enol} for **1**/**2** vs. log K_{enol} for **7** is linear for the four common substituents with a slope of 0.75 ($r = 0.9997$).

Comparison with systems **8** and **9** is of interest. The K_{enol} values for **8** in MeOH are similar to those of our system[29] while those for system **9** are ca. 2 orders of magnitude lower.[30] The higher K_{enol} values for **8** and **9** compared with **7** are due to stabilization of the enols of **8** and **9** both by intramolecular hydrogen bonding and by formation of the β-hydroxy-α,β-unsaturated ketones with the complementary substituents on the double bond. For system **8** an approximate Hammett plot vs. σ values was found with $\rho = 0.934$.[29] A plot of log K_{enol} for **1**/**2** vs. log K_{enol} for **8** shows an excellent linearity with a slope of 1.27 ($r = 0.9965$). A similar plot vs. log K_{enol} for **9** shows severe deviation from linearity with a slope of 1.58 ($r = 0.8994$). When the deviating *m*-Cl point is excluded, the three points plot gives a slope of 5.1 (0.992).

An analysis similar to eq 17 should be also applicable to **8** and **9**. The lower response of K_{enol} to the aryl substituents in the aroylcycloalkanones is probably due to two reasons. First, the contribution of hybrid $\mathrm{ArC^+(OH)\text{–}C(O^-)\text{–}}$ increases ρ^+_{stab} for the enols of **8** and **9** compared with that for **1**. Second, deviation of the Ar–CO moiety from planarity is important, and this effect was invoked for explaining the lower response to substituents in **9** compared with **8**.[30b] A more accurate analysis requires ρ_{stab} values for the enols and X-ray data for both the enols and ketones. The two conclusions from the data are that the ρ_{eq} values are not very high and in the various series they do not correlate with K_{enol}.

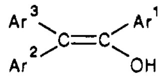
Factors Responsible for the High K_{enol} Values of Crowded Polyaryl Ethenols. The K_{enol} values of di- and trimesityl-substituted systems studied here and previously in hexane[13-15] are several orders of magnitude higher than those of simple noncrowded enols in water.[2,5-8,10,11] An extreme example is the ca. 10^{10} higher K_{enol} for trimesitylethanone[15] than for acetophenone.[7i] A large part of this difference is due to steric effects. However, for β,β-dimesityl-α-substituted systems a bulkier α-alkyl reduces K_{enol},[13] and a bulkier α-aryl increases it.[14,15] Polar, resonance, and hydrogen bonding effects also contribute to the high K_{enol} values. The present results assist in evaluating their contributions.

The linear dependence of $\Delta G°$ for equilibria 1 on E_s values for hydrogen and α-alkyl substituents may usually indicate the absence or the constancy of polar effects on K_{enol} values. However, the present results show that polar effects from the α-position are important. Consequently, their apparent absence for α-alkyl-substituted systems is due either to similar σ_{I} values for all the alkyl groups[84] (but the problem of the α-H still remains) or to nearly similar effects of these substituents on the enols and the ketones. This question could be better probed when data on K_{enol} for the MesCR=C(OH)Mes/MesCHRCOMes system (R = alkyl) will become available.[85]

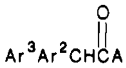
Our results show that polar effects of the *o*-Me groups on α-Ph and α-*p*-tolyl-β,β-dimesityl-substituted systems is small and opposite to that expected from steric effects. Assuming that $\sigma^+_{o\text{-Me}} \sim \sigma^+_{p\text{-Me}}$ and applying our $\sigma^+\rho^+$ relationship leads to $K_{\mathrm{enol}} = 0.25$ for trimesitylethanone (**6**)/trimesitylethenol (**16**), a value ca. 300 times smaller than the measured value of 79.[15] Intermolecular OH-π(α-Ar) hydrogen bonding is excluded by the concentration independence of the OH stretching band of **2a**. A *strong* α-substituent dependent OH-π(β′-Mes) intramolecular hydrogen bonding is excluded by the similarity of δ(OH) for all our enols and for **16**[20] in $CDCl_3$. The differential effect of the α-substituent on the solvation of **1a**–**g** and of **16** and of **2a**–**g** and **6** should be small in hexane since even in the good hydrogen bond accepting Me_2SO, the differences are small.[86]

$\mathrm{Mes_2C{=}C(OH)Mes}$

16



17



$\mathrm{Ar^3Ar^2CHC(=O)Ar^1}$

18

The high K_{enol} values, especially for **16** should therefore result from (a) steric interactions between geminal and vicinal groups in both the ketones and the enols and (b) their effects on the various conjugation interactions which are strongly conformation dependent.

Conjugation effects in triarylethenols **17** involve the three $\pi(\mathrm{Ar}^n)\text{–}\pi(\mathrm{C{=}C})$ interactions (n = 1–3) and the $p(\mathrm{OH})\text{–}\pi(\mathrm{C{=}C})$ interaction which amounts to ca. 5 kcal $\mathrm{mol^{-1}}$[87] and will be cancelled in all the comparisons since it is common to all the enols. For ketones **18** the single conjugative interaction is $\mathrm{Ar^1\text{—}C{=}O}$. There is no evidence for a through-space conjugation interaction of the $\mathrm{Ar^3Ar^2CH}$ and the C=O moieties,[15] which should have been detected in the UV spectrum of $\mathrm{Mes_2CHCHO}$. Since K_{enol} increases on stabilization of the enol and destabilization of the ketone, the higher the $\sum(\mathrm{Ar\text{—}C{=}C})\text{–}(\mathrm{Ar\text{—}C{=}O})$ interaction, the higher will be K_{enol}.

The $\pi(\mathrm{Ph})\text{–}\pi(\mathrm{C{=}C})$ conjugation energy of a planar system is 4.5 kcal $\mathrm{mol^{-1}}$,[85] and a *p*-Me group contributes an additional 0.1 kcal $\mathrm{mol^{-1}}$.[35] Assuming that *o*-Me contributes similarly the hypothetical planar MesC=C moiety is stabilized by 4.8 kcal $\mathrm{mol^{-1}}$. For the corresponding $\pi(\mathrm{Ar})\text{–}\pi(\mathrm{C{=}O})$ conjugation energies at full planarity we use the rotational barriers around the Ar—C=O bond of 5.4 (Ar = Ph) and 5.9 (Ar = $p\text{-MeC}_6\mathrm{H}_4$) kcal $\mathrm{mol^{-1}}$ in acetophenones.[88] Assuming again that *o*- and *p*-Me

---

[82] We are aware that the division of the conformation-dependent resonance effect to two "separate" effects is artificial, but it seems beneficial for the discussion when only one effect operates in the coplanar model. We are presently searching for a similar behavior in related systems.

[83] Jencks, W. P. *Prog. Phys. Org. Chem.* **1964**, *2*, 63.

[84] For a recent paper dealing with σ_{I}'s of alkyl groups and giving references to the question of their constancy, see: Hanson, P. *J. Chem. Soc., Perkin Trans. 2* **1984**, 101.

[85] This problem is now under preliminary investigation.

[86] Nadler, E. B.; Rappoport, Z., unpublished results.

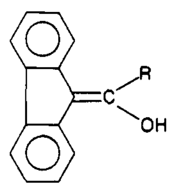
[87] Judged by the stabilization energy of 4.9 kcal $\mathrm{mol^{-1}}$ of the MeO—C=C moiety.

contribute similarly the value is 6.9 kcal mol^{-1} for Ar = Mes. Hence for planar acetophenone and its enol the differential conjugative stabilization favors the ketone by <1 kcal mol^{-1}. This is consistent with the fact that log K_{enol} of acetophenone (−7.92[7j]) differs only slightly from log K_{enol} of acetone (−8.22).[11b]

However, the steric deconjugation of the three Ar—C=C moieties in the triarylethenols is extensive as shown by the solid state data for **2d** and for **16**.[25] Due to this effect an *o*-tolyl is 0.5 kcal mol^{-1} less stabilizing than phenyl in the solid state.[89] Indeed, in five β,β-dimesityl-2-arylethenols,[90a] in dimesitylketene[90b] and in several 1,2-dimesityl-2-arylvinyl derivatives,[18,25] the Mes—C=C dihedral angles are ≥48°. These angles are 54.6° in solid tetramesitylethylene[91a] and 63° in solid (*Z*)-$Ph_2CHCH{=}C(Mes)$-OCOPh.[91b] The equilibrium data of (*E*)- and (*Z*)-MesCH=CHPh[92] show high Mes—C=C dihedral angle, Kerr constant studies give an angle of 65° for α-chloro-2,4,6-trimethylstyrene,[93] and UV data give an angle of 50° for 2,4,6-trimethylstyrene.[94] Consequently, a conservative estimate suggests that this dihedral angle will always be ≥50°. By applying this value to eq 16, we find that the π(Mes)–π(C=C) stabilization in "real" systems is only 41%, i.e., 2 kcal mol^{-1}, of the value in "planar Mes—C=C". A similar calculation for **16**, using the solid state angles, α,β,β' for the two forms (52.7°, 52.5°, and 54.6°; 55.0°, 51.4°, and 58.2°),[25] gives $\sum[\pi(\text{Mes})-\pi(\text{C=C})]$ stabilization energy of 4.95 ± 0.15 kcal mol^{-1}. A similar value is obtained for **1d** from the data of Table IV. The increased coplanarity of the Ph—C=C moiety is compensated by the increased twist of the Mes—C=C moiety.

In ketones **18** there is only one (Ar–CO) interaction and the experimental dihedral angle, and hence the conjugation energy is strongly substituent-dependent. From UV data the dihedral angle in acetylmesitylene MesCOMe is 63°,[94a] and in **6** it is 39° by UV[15] and 48° by crystallography.[25] The Ar–CO angle is 3.5° in **2b** and ca. 20° for **2d** and **2g** (Table III). By applying these values to eq 16 and taking the $E(0)$ values from the rotational barriers, the π(Ar)–π(CO) stabilization energies are 1.4 kcal mol^{-1} for acetylmesitylene, 4.2 or 3.1 kcal mol^{-1} for **6**, 4.8 kcal mol^{-1} for **2d**, and 6.7 kcal mol^{-1} for **2b** when taking $E(0)$ = 6.7 kcal mol^{-1}.[22] The $\sum(\pi(\text{Ar})-\pi(\text{C=C})) - (\pi(\text{Ar})-\pi(\text{CO}))$ energy difference contributes <0.6, 0.8 or 1.8, 0.1, and −1.9 kcal mol^{-1} to the stabilization of the enols MesC(OH)=CH_2, **16**, **1d**, and **1b**, respectively.

Consequently, the $\Delta\Delta G°$ of ca. 12 kcal mol^{-1} favoring K_{enol} in our system compared with the acetophenones[7j] cannot be mainly due to conjugation effects. However, these effects can explain the differences within the family of triarylethenols (**17**)/triarylethanones (**18**). The increase in K_{enol} of **1d** due to substitution of its α-phenyl ring by two *o*-Me groups to form **16** is mainly accounted for by the conjugation effects calculated above. Such analysis is also valuable in trying to extend the range of di- and triaryl-substituted stable enols. The enols benefit from having 2- or 3-π(Ar)–π(C=C) conjugation terms. However, due to the higher π(Ar)–π(C=O) compared with π(Ar)–π(C=C) stabilization, an α-aryl will reduce K_{enol} unless it is appreciably twisted in the ketone, and its absence may be beneficial. The high K_{enol} for $Mes_2C{=}CHOH$[15] is partially due to this effect. Interestingly, β-aryl groups *less bulky* than mesityl will *increase* K_{enol} more than β-mesityl groups due to a more extensive conjugation.[95] Increased planarity at C_β could be achieved by geometrical constraints, and we note in this respect that enol **19** was claimed to exist.[96]



19: R = Ph
20: R = Me

Moreover, the pK_{enol} for **20**[97] was recently measured as 2.3.[98] Complete planarity of the two phenyl groups in the absence of an α-phenyl group can contribute in the extreme case 9 kcal mol^{-1} (i.e., ca. 6 orders of magnitude in K_{enol}) conjugative stabilization. The increase of K_{enol} of **20** by 6 orders of magnitude over acetone[11b] could be accounted for by this effect.

Since the combination of polar conjugation and intramolecular hydrogen bonding effects[99] cannot account for the high K_{enol} values, steric effects—besides those connected with the conjugation—should also contribute appreciably to the K_{enol} values. In the analogous systems of arylacenaphthenones it was concluded that steric destabilization of the ketone is responsible for the high K_{enol} values.[100] It is difficult to evaluate these steric effects since the ketones and the enols are not directly comparable. Obviously, the tetrahedral geometry at the sp^3-hybridized $CHAr^3Ar^2$ group of the ketones **18** will cause higher steric interaction between bulky Ar^3, Ar^2, and Ar^1CO groups than in the ethenols **17** with the sp^2-geometry. Opening of the Ar^3CAr^2 angles to values close to those of the enols was indeed observed (Table III). However, the corresponding angle in the bulkier **6** is smaller. The bonds from the ipso to the two-ring carbons of the mesityls in **2** are elongated, but similar elongation was also found for the enol **1d**. The conformation of the apparently less crowded ketones **2b**, **2d**, and **2g** differ from that of **6** in that in the former the H(2)–C(2)–C(1)–O angle is 134 ± 3° whereas it is ca. 180° in **6**, but these changes are not necessarily associated with a large energy change. We see no specially short van der Waals distances, and the steric crowding is apparently relieved by a combination of changes in bond angles, dihedral angles, and bond lengths. The absence of large rotational barriers which are frequently observed in crowded molecules[101] is noticeable.

The enols are also crowded, as observed by the appreciable rotational barriers for a correlated rotation of all the three mesityl groups in **6** and its derivatives.[18] The propeller conformation found for **1d** is common to all polyarylethylenes. Opening of bond angles involving the double bond and the two cis bulky substituents, especially C(1)–C(2)–C(3), is an important feature. Increased opening of the corresponding angle for $Mes_2C{=}C(R)OH$ (R = alkyl) is accompanied by a decrease of K_{enol}[90a] so that this single mode cannot be a main contributor to the enols stability. We conclude that at present it is difficult to delineate a single bond length, angle, or distance which reflects strongly the steric effects and which can rationalize the high K_{enol} values. We note that the change of several structural parameters for the limited $Mes_2C{=}C(OH)R$ (R = alkyl) series can be used for a semiquantitative correlation of trends of K_{enol} values.[90a] We believe that extensive structural data on the ketones and the enols together with molecular mechanics calculations[85] may enable us to better understand the contribution of steric effects to the high K_{enol} values.

Conclusions. The present work substantially increases the number of stable simple enols. It is shown that electron withdrawal by an α-aryl group increases K_{enol} due mainly to destabilization

---

[88] This is justified by the excellent $\Delta G^{\ddagger}$ (rotation) vs. σ^+ correlations.[51]

[89] Hine, J.; Skoglund, M. J. *J. Org. Chem.* **1982**, *47*, 4758.

[90] (a) Kaftory, M.; Biali, S. E.; Rappoport, Z., unpublished results. (b) Biali, S. E.; Rappoport, Z., unpublished results.

[91] (a) Blount, J. F.; Mislow, K.; Jacobus, J. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1972**, *A28*, 812. (b) Pfluger, C. E.; Pinkus, A. G.; Wu, A.-B.; Hurd, P. W. *Tetrahedron* **1985**, *41*, 4417.

[92] Fischer, G.; Muszkat, K. A.; Fischer, E. *J. Chem. Sec. B* **1968**, 1156.

[93] LeFevre, R. J. W.; Radom, L.; Ritchie, G. L. D. *J. Chem. Soc. B* **1971**, *2100*.

[94] (a) Braude, E. A.; Sondheimer, F. *J. Chem. Soc.* **1965**, 3754. (b) Suzuki, H. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 619.

[95] That other effects are more important is shown by the higher K_{enol} for **6**[15] compared with **4**.[90b]

[96] Meyer, K. H.; Gottlieb-Billroth, H. *Chem. Ber.* **1921**, *54*, 575.

[97] Wislicenus, W.; Waldmüller, M. *Chem. Ber.* **1909**, *42*, 785.

[98] Argile, A.; Carey, A. R. E.; Fukata, G.; Harcourt, M.; More O'-Ferrall, R. A.; Murphy, M. G. *Isr. J. Chem.* **1985**, *26*, 303.

[99] Intramolecular hydrogen bonding of the OH to the β-mesityl group stabilizes the enol by ca. 1 kcal mol^{-1}.[19]

[100] Miller, A. R. *J. Org. Chem.* **1976**, *41*, 3599.

[101] For a discussion of the consequences of strain or various structural parameters, see: Rüchardt, C.; Beckhaus, H.-D. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 529.

of the ketone. The contribution of conjugation effects in determining the K_{enol} value was assessed. A combination of polar, resonance, and hydrogen bonding effects is not sufficient to account for the high K_{enol} values in most systems studied. Steric effects, apart from those associated with reduction of conjugation by reducing the coplanarity of interacting π moieties, should be important contributors to the high K_{enol} values.

Experimental Section

General Methods. Melting points were determined with a Thomas-Hoover apparatus and are uncorrected. Infrared spectra were taken with a Perkin-Elmer 157G spectrometer and accurate values of the O—H and C=O stretching frequencies were determined with a Nicolet MX-1 FT spectrometer. UV spectra were measured with a 2000 Baush and Lamb spectrometer. Mass spectra were recorded with a MAT-311 instrument at 70 eV.

^{1}H NMR spectra were recorded on a Bruker WH-300 and Bruker WP 200 SV pulsed FT spectrometers operating at 300.133 and 200.133 MHz, respectively. ^{13}C NMR spectra were recorded on a Bruker WP 200 SV spectrometer operating at 50.32 MHz. Tetramethylsilane was used as the reference.

Solvents and Materials. Spectroscopic hexane was used for the equilibrations. Compounds **1d** and **2d** were prepared according to Fuson.[12b]

X-ray Crystal Structure Analysis. Data were measured on a PW1100/20 Philips four circle computer-controlled diffractometer. Mo Kα (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 $12 \leqslant \theta \leqslant 14°$ for **2b**, of $10 \leqslant \theta \leqslant 14°$ for **1d** and **2d**, and of $12 \leqslant \theta \leqslant 15°$ for **2f**. Intensity data were collected by using the ω-2θ technique to a maximum of 2θ of 50°. The scan width, $\Delta\omega$, for each reflection was (1.00 + 0.35 tan θ) deg, with a scan speed of 3 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 nonhydrogen atoms were found by using the results of the MULTAN direct method analysis.[102] After several cycles of refinement[103] the positions of the hydrogen atoms were found and added with a constant isotropic temperature factor of 0.5 (for **2d**) and 0.05 (for **2b**, **2g**, and **1d**) Å^2 to the refinement process. Refinement proceeds to convergence by minimizing the function $\sum W(|F_o| - |F_c|)^2$. A final difference Fourier synthesis map showed several peaks less than 0.25 (for **1d**), 0.3 (for **2b** and **2d**), or 0.6 (for **2g**) Å^{-3} scattered about the unit cell without a significant feature.

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

Crystallographic Data. 2b: $C_{27}H_{30}O_2$, space group $P2_1/n$, a = 137.21 (2) Å, b = 15.749 (3) Å, c = 11.508 (2) Å, β = 112.86 (5)°, V = 2216.3 (8) Å^3, Z = 4, ρ_{calcd} = 1.16 g cm^{-3}, μ(Mo Kα) = 0.38 cm^{-1}, number of unique reflections 3816, reflections with $I \geqslant 2\sigma(I)$2763, R = 0.068, R_w = 0.084, $w = \sigma_F^{-2}$.

2d: $C_{26}H_{28}O$, space group $P2_1/n$, a = 18.062 (4) Å, b = 8.173 (2) Å, c = 15.368 (3) Å, β = 112.94 (4)°, V = 2089.2 (9) Å^3, Z = 4, ρ_{calcd} = 1.13 g cm^{-3}, μ(Mo Kα) = 0.35 cm^{-1}, number of unique reflections 2675, reflections with $I \geqslant 2\sigma(I)$ 2128, R = 0.063, R_w = 0.084, $w = (\sigma_F^2 + 0.000187F^2)^{-1}$.

2g: $C_{26}H_{26}O_2$, space group $P\bar{1}$, a = 11.547 (2) Å, b = 13.039 (3) Å, c = 8.526 (2) Å, α = 102.13 (4)°, β = 91.87 (4)°, γ = 70.58 (3)°, V = 1182.7 (6) Å^3, Z = 2, ρ_{calcd} = 1.44 g cm^{-3}, μ(Mo Kα) = 33.51 cm^{-1}, number of unique reflections 4057, reflections with $I > 2\sigma(I)$ 2842, R = 0.062, R_w = 0.083, $w = (\sigma_F^2 + 0.001696F^2)^{-1}$.

1d: $C_{26}H_{28}O$, space group $P\bar{1}$, a = 11.816 (2) Å, b = 12.219 (3) Å, c = 7.856 (1) Å, α = 107.41 (4)°, β = 107.56 (4)°, γ = 87.75 (4)°, V = 1030.2 (5) Å^3, Z = 2, ρ_{calcd} = 1.15 g cm^{-3}, μ(Mo Kα) = 0.35 cm^{-1}, number of unique reflections 2649, reflections with $I \geqslant 2\sigma(I)$ 2078, R = 0.066; R_w = 0.090, $w = (\sigma_F^2 + 0.000376F^2)^{-1}$.

1-Aryl-2,2-dimesitylethenols. (a) Enols 1b–f. Enols **1b–f** were prepared by addition of the arylmagnesium bromide to dimesitylketene[12b] according to the following procedure (which is a modification of Fuson's

Table VI. Analytic Data for Enols 1 and Ketones 2

	enol				ketone				analysis									
									calcd %				found % (enol)			found % (ketone)		
X	mp, °C	color	cryst solvent	yield,[a] %	mp, °C	color	cryst solvent	yield %	C	H	hal	formula	C	H	hal	C	H	hal
p-PhO	109	brown	petrlm ether 40–60 °C	35	119	cream	EtOH	45[b]	85.68	7.19		$C_{32}H_{32}O_2$	85.77	7.0		85.40	7.06	
p-MeO	128	light brown	EtOH	40	163	light yellow	EtOH	55[b]	83.90	7.82		$C_{27}H_{30}O_2$	83.96	7.69		83.74	7.94	
p-Me	131.5	white	EtOH	49	184	white	petrlm ether 60–80 °C	60[b]	87.52	8.16		$C_{27}H_{30}O$	87.60	8.46		87.31	8.20	
m-Cl	174	white	petrlm ether–ether	27	134.5	white	EtOH	55[c]	79.88	6.96	9.07	$C_{26}H_{27}ClO$	79.82	7.10	9.45	79.62	6.84	9.38
p-CF$_3$	169.5	greyish white	EtOH	27	162	white	petrlm ether 40–60 °C	55[c]	76.39	6.41	13.43	$C_{27}H_{27}F_3O$	76.20	6.60		76.43	6.62	13.0
m,*m*-Br$_2$	223	light brown	EtOAc	56	157	cream	EtOH–EtOAc	57[c]	60.72	5.10	31.07	$C_{26}H_{26}Br_2O$	60.64	4.92	31.4	60.53	5.23	

[a] Yield from dimesitylacetic acid. [b] Yield from the corresponding enol. [c] Yield from the 2,2-dimesityl-1-arylethanol.

---

(102) Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. MULTAN78 (a system of computer programs for the automatic solution of crystal structures from X-ray diffraction data); Universities of York, England, and Louvain, Belgium.

(103) All crystallographic computing was done on a CYBER 855 computer at the Hebrew University of Jerusalem, by using the SHELX1977 structure determination package.

Table VII. Spectral Data for $Mes_2CHCH(OH)Ar$

X in Ar	$\lambda_{max}^{C_6H_{14}}$ (nm), ϵ	λ_{max} (Nujol), cm^{-1}	δ ($CDCl_3$), ppm	*m/e* (rel abundance, assignment)
m-Cl	262 (740), 267 (880), 274 (700)	3500–3300 (w), 2970–2840 (w), 1610 (s), 1590 (s)	1.55[a] (1 H, s, OH), 2.08–2.23 (18 H,[b] Me), 4.80, 4.84 (1 H, d, *J* = 8.2 Hz, Mes_2CH), 5.72, 5.79 (1 H, dd, *J* = 8.2, 3.9 Hz, CHOH), 6.68 (1 H, s, Mes-H), 6.80 (1 H, s, Mes-H), 6.96–7.19 (4 H, m, Ar-H)	*e*, 251 (100, Mes_2CH), 236 (4, Mes_2CH-Me), 221 (15, Mes_2CH-2Me), 206 (8, Mes_2CH-3Me), 141, 139 (3, s, *m*-ClC_6H_4CO), 119 (3, Mes), 91 (4, C_7H_7), 77 (7, Ph)
p-CF_3	263 (900), 273 (540) (s)	3480–3200 (w), 2970–2840 (w), 1620–1610 (m)	1.56[a] (1 H, s, OH), 1.95–2.34 (18 H,[b] Mes-Me), 4.85, 4.89 (1 H, d, *J* = 8.2 Hz, Mes_2CH), 5.02–5.85 (1 H, dd,[c] *J* = 8.2 Hz, C*H*OH), 6.68 (2 H, s, Mes-H), 6.80 (2 H, s, Mes-H), 7.43–7.47[d] (2 H, d, *J* = 8.2 Hz, Ar-H)	409 (1, M-OH), 392 (73), 251 (100, Mes_2CH), 236 (9, Mes_2CH-Me), 221 (30, Mes_2CH-2Me), 206 (14, Mes_2CH-3Me), 173 (6, $CF_3C_6H_4CH_2CH_2$), 145 (10, $CF_3C_6H_4$), 119 (3, Mes), 91 (5, C_7H_7), 77 (3, Ph)
m,*m*-Br_2	269 (890)	3500–3300 (w), 2970–2840 (w), 1610 (s), 1580 (s)	1.57[a] (1 H, s, OH), 1.95–2.38 (18 H,[b] Mes-Me), 4.69, 4.73 (1 H, d, *J* = 8.5 Hz, Mes_2CH), 5.67–5.74 (1 H, dd, *J* = 8.5, 3.6 Hz, CHOH), 6.70 (2 H, s, Mes-H), 6.82 (2 H, s, Mes-H), 7.10–7.13 (2 H, m, Ar-H), 7.47–7.49 (1 H, m, Ar-H)	265 (2, Mes_2CHCH_2), 263 (2, Mes_2CHC), 251 (100, Mes_2CH), 221 (22, Mes_2CH-2Me), 206 (2, Mes_2CH-3Me), 237, 235, 233 (1.5, 3, 1.5, Ar), 158, 156 (7, 6, C_6H_5Br), 110 (11), 91 (8, C_7H_7), 77 (17, Ph)

[a] Overlaps a water signal in the $CDCl_3$. [b] Broad band due to coalescence of the *o*-Me groups. [c] It is difficult to determine the other *J* due to overlap. [d] The second half of the AB quartet is hidden by the $CDCl_3$. [e] Spectrum at 60 °C. Molecular peak with 1% intensity of the base peak was observed at 100-fold sensitivity at 80 °C.

Table VIII. Analytic Data for $Mes_2CHCH(OH)Ar$

					analysis						
					calcd %				found %		
X in Ar	mp, °C	color	cryst solvent	yield,[a] %	C	H	hal	formula	C	H	hal
m-Cl	164.5	white	EtOH	57	79.47	7.44		$C_{26}H_{29}ClO$	79.41	7.68	
p-CF_3	142	white	petrlm ether 40–60 °C	41	76.03	6.85	13.36	$C_{27}H_{29}F_3O$	76.14	6.69	12.7
m,*m*-Br_2	190	light brown	EtOH	61	60.48	5.47	30.95	$C_{26}H_{28}Br_2O$	60.59	5.39	31.35

[a] From Mes_2CHCHO.

method for preparation of **1d**).[12b] The yields and the analytic and the spectroscopic data are given in Tables I and VI.

The Grignard reagent is prepared in the regular manner. The amounts were the corresponding aryl bromide (10.1 mmol) in dry THF (25 mL) and Mg turnings (0.25 g, 10.1 mmol). The reaction is performed in a dry nitrogen or argon atmosphere. Initiation for **1e** and **1f** takes a long period (45 min), and the time is reduced by addition of both MeI and iodine. To the cooled Grignard reagent is added at room temperature dimesitylketene (prepared from dimesitylacetic acid (2 g, 6.75 mmol)) in dry THF (32 mL), and the mixture is refluxed overnight in an inert atmosphere. After cooling, the product is decomposed with saturated aqueous NH_4Cl, and the organic phase is extracted with ether (3 × 70 mL) and dried ($MgSO_4$). Evaporation of the ether leaves an oil which is crystallized from the appropriate solvent.

(b) Enols 1a and 1g. (1) Enol 1a. A solution of 1.6 M *n*-BuLi (6.6 mL, 10.55 mmol) is added to dry ether (30 mL) in an argon atmosphere, and the mixture is cooled to −15 °C. A solution of *p*-phenoxybromobenzene (2.36 mL, 10.55 mmol) in dry ether (20 mL) is added slowly with vigorous stirring which continues for an additional 2 h at −15 °C.[104] A cooled solution of dimesitylketene (1.36 g, 7.0 mmol) in dry ether (30 mL) is then added quickly, and stirring continues for an additional 90 min at −15 °C. The product is decomposed with an aqueous 0.5 N HCl solution, the reaction mixture is extracted with ether (3 × 70 mL) and dried ($MgSO_4$), and the ether is evaporated. The dark brown residue is chromatographed on a silica gel 60 (230–400 mesh) column under pressure with 97:3 petroleum ether/AcOEt as the eluant. The main fraction is collected and crystallized from petroleum ether.

(2) Enol 1g. A solution of 1,3,5-tribromobenzene (1.79 g, 5.4 mmol) in dry ether (50 mL) under an argon atmosphere is cooled to −77 °C. A solution of 1.6 M *n*-BuLi (3.38 mL, 5.4 mmol) is added dropwise with vigorous stirring which continues for 30 min at −77 °C.[105] A cooled solution of dimesitylketene (1 g, 3.6 mmol) in dry ether (35 mL) is then added quickly to the brown solution, and stirring continues for an additional 2 h at −77 °C. The workup is as described above in the preparation of **1a**. Purification is by crystallization from the appropriate solvent and not by chromatography.

1-Aryl-2,2-dimesitylethanones. (a) Ketones 2a–d. (1) 2a: To a solution of **1a** (400 mg, 0.89 mmol) in dry hexane (50 mL) was added TFA (0.1 mL). The solution was refluxed for 4 h, cooled, washed with an aqueous $NaHCO_3$ solution, dried ($MgSO_4$), and evaporated. The yellow oil was crystallized from EtOH. Analytic and spectroscopic data are given in Tables VI and I.

(2) 2b–d: These ketones were obtained by HCl isomerization of enols **1b–d** according to the following procedure: The enol (200 mg) was dissolved in MeOH (20 mL), and the solution was saturated with gaseous HCl and stirred for 48 h. A white precipitate was formed. The solvent was evaporated, and fractional crystallization of the ketone/enol mixtures yielded the ketone. Data for **2b** and **2c** are in Tables I and VI, whereas ketone **2d** was prepared previously.[12b]

(3) 2e–g. These ketones were obtained by addition of the corresponding aryllithium to dimesitylacetaldehyde,[15] isolation of the 2,2-dimesityl-1-arylethanols **5**, and oxidation by pyridinium dichromate (PDC) according to the following general procedure.

2,2-Dimesityl-1-arylethanols 5. (1) 5e: To a solution of 1.6 M *n*-BuLi (1.34 mL, 2.1 mmol) in dry ether (15 mL) in an argon atmosphere at −35 °C is added with vigorous stirring for 8–10 min[106] a solution of *m*-dichlorobenzene (0.25 g, 2.1 mmol) in dry ether (10 mL). During this time the solution acquires a yellowish tint. A cooled solution of dimesitylacetaldehyde (400 mg, 1.43 mmol) in dry ether (25 mL) is then added quickly, and the reaction mixture is stirred for 90 min at −35 °C. The solution turns dark orange. An aqueous solution of 0.5 N HCl is then added, and the solution is extracted with ether (100 mL), dried ($MgSO_4$), and evaporated. The residue is then crystallized from EtOH. Data are in Tables VII and VIII.

(2) 5f. To a solution of 1.6 M for *n*-BuLi (1.34 mL, 2.15 mmol) in dry ether (15 mL) in an argon atmosphere at −77 °C is added with vigorous stirring which continues for an additional 30 min at −77 °C *p*-bromobenzotrifluoride (0.3 mL, 2.15 mmol) in dry ether (10 mL). The temperature is slowly raised to 0 °C during 45 min.[107] Dimesitylacetaldehyde (400 mg, 1.43 mmol) in dry ether (25 mL) is then added. Stirring continues for 2 h at 0 °C. The color becomes dark brown. The workup is as for **5e**. Data are in Tables VII and VIII.

(3) 5g. The lithium reagent is synthesized as for **1a**. The amounts were the following: 1,3,5-tribromobenzene (2.02 g, 6.43 mmol), dry ether (50 mL), and 1.6 M *n*-BuLi (4.0 mL, 6.43 mmol). The dimesitylace-

---

(104) Gilman, H.; Goodman, J. J. *J. Org. Chem.* **1957**, *22*, 45.

(105) Chen, L. S.; Chen, G. J.; Tambroski, C. *J. Organomet. Chem.* **1981**, *215*, 281.

(106) Vogel, A. F. *Practical Organic Chemistry*, 3rd ed.; Longmans, Green and Co.: London, 1956; p 932.

(107) Ondons, T. A.; Christie, B. J.; Guy, R. W. *Aust. J. Chem.* **1979**, *32*, 2313.

taldehyde (1.2 g, 4.29 mmol) in dry ether (40 mL) is added. Stirring continues for 2 h at -77 °C. The workup is as for **5e**. Data are in Tables VII and VIII.

(b) Ketones 2e–g. A mixture of the corresponding 2,2-dimesityl-1-arylethanol **5** (0.51 mmol) and PDC (573 mg, 1.53 mmol) in dry DMF (5 mL) was stirred at room temperature for 24 h and then poured into water. The solid obtained was dissolved in ether, the layers were separated, and the organic phase was dried ($MgSO_4$) and evaporated. The ketone was crystallized. Yields, crystallization solvent, and analytical and spectroscopic data are in Tables I and VI.

Equilibration Conditions. (a) Samples of the substrate (15 mg) in hexane (AR) (10 mL) containing trifluoroacetic acid (0.05 mL) were kept at 367.6 K in pressure ampoules. Samples were withdrawn at a predetermined time and washed with an aqueous $NaHCO_3$ solution, the layers were separated, the organic phase was dried and evaporated, the remainder was dissolved in $CDCl_3$, and the enol/ketone ratios were determined by integration. Comparisons were made between the single $Mes_2\mathit{CH}$ proton, the four protons Mes-H singlet and the protons of the α-aryl group (which mostly show a low field doublet of ortho protons) of the ketones on the one hand, and the enolic OH, the two protons signals (one sharp and one broad) of the two Mes-H protons, and the aryl protons of the α-aryl group of the enol on the other. In the methyl region comparison was made between the two sharp *o*-Me and *p*-Me singlets of the ketones and three signals of the enols which are at the lower field side of the methyl region. Comparison of other signals, e.g., the MeO group of **1b**/**2b** was occasionally made. The average of all the ratios which sometimes includes 15 values is given in Table II. Sources of errors are peak overlap, and peak broadening resulting from coalescence of several *o*-Me and Mes-H signals of the enols due to the ring flip process. Broadening of the OH signal may be due to intermolecular exchange.

(b) Samples of approximately 20 mg (0.04 mmol) of the ketone or the enol were dissolved in 10 mL of hexane (AR) containing 0.01 mL of CF_3COOH in pressure tubes and kept at 367.6 K. After workup as described above, the enol/ketone ratio in the residue was determined by HPLC (Trakor 970 A) with the detector at 254 nm. For analysis of systems **1**,**2a–f** 10 μm, 250 mm × 4 mm CN-Lichrosorb column was used. The eluants were 9:1 hexane–CH_2Cl_2 (0.7 mL/min) for **1a**/**2a**, 8:2 hexane–CH_2Cl_2 (0.7 mL/min) for **1b**/**2b**, hexane (2 mL/min) for **1c**/**2c**, **1d**/**2d**, **1e**/**2e**, and hexane (1 mL/min) for **1f**/**2f**. A 5 μm, 150 mm/3 mm (Glass cartridge) Diol Lichrosorb column was used for **1g**/**2g** with hexane as the eluant (0.5 mL/min). The detection absorptions were calibrated by measuring the peak intensities of known enol/ketone ratios.

In spite of the shorter reaction times used for the HPLC analysis small impurity peaks were observed. Since their ϵ values are unknown, it was impossible to evaluate their percentages.

Acknowledgment. We are indebted to Ilana Cohen and D. Farin for technical assistance, to Dr. S. Cohen for the X-ray diffractions, to Dr. D. Kohn for help with the IR spectra, to Dr. Silvio Biali for discussions, to Prof. W. P. Jencks and Prof. F. Taskinen for correspondence, to Prof. A. Y. Meyer for assisting in the calculations, and to Prof. Y. Apeloig and Dr. M. Karni for the MO calculations. This work was supported by a grant from the United States–Israel Binational Science Foundation (BSF), Jerusalem, to which we are grateful.

Registry No. 1a, 106359-74-4; **1b**, 106359-75-5; **1c**, 106359-76-6; **1d**, 77787-80-5; **1e**, 106359-77-7; **1f**, 106359-78-8; **1g**, 106359-79-9; **2a**, 106359-80-2; **2b**, 106359-81-3; **2c**, 106359-82-4; **2d**, 77787-78-1; **2e**, 106359-83-5; **2f**, 106359-84-6; **2g**, 106359-85-7; **5e**, 106359-86-8; **5f**, 106359-87-9; **5a**, 106359-88-0; $Mes_2C{=}C{=}O$, 87871-33-8; *p*-$MeOC_6H_4Br$, 104-92-7; *p*-MeC_6H_4Br, 106-38-7; *m*-ClC_6H_4Br, 108-37-2; *p*-$F_3CC_6H_4Br$, 402-43-7; C_6H_5Br, 108-86-1; *p*-$PhOC_6H_4Br$, 101-55-3; 1,3,5-tribromobenzene, 626-39-1; *m*-dichlorobenzene, 541-73-1; dimesitylacetic acid, 5740-42-1; dimesitylacetaldehyde, 94203-58-4.

Supplementary Material Available: Tables S1–S16 giving the crystallographic data for compounds **2b**, **2d**, **2g**, and **1d**, Figures S1, S2, S3, and S5 giving the stereoviews of these compounds, and Figure S4 giving the ORTEP drawings of **2g** (16 pages). Ordering information is given on any current masthead page.

Exchange Rates of the Amide Protons of *d*-Biotin Sulfoxide Stereoisomers[†]

Terry L. Fox,*[‡] Peter A. Tipton,[§] W. W. Cleland,[§] and Albert S. Mildvan*[‡]

Contribution from the Department of Biological Chemistry, The Johns Hopkins University, School of Medicine, Baltimore, Maryland 21205, and the Department of Biochemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received October 14, 1986*

Abstract: The effects of pH on the exchange rates of the amide NH protons of *d*-biotin *d*-sulfoxide and of *d*-biotin *l*-sulfoxide with water have been measured by the transfer of saturation method. The NH exchange rates of both sulfoxides show typical first-order dependences on $[H^+]$, presumably due to the inability of the sulfoxide sulfur or oxygen to form a transannular bond to the protonated carbonyl group of the amide. A comparison of the second-order exchange rate constants of *d*-biotin *d*-sulfoxide with those of biotin indicates that base catalysis is fivefold faster and acid catalysis is 60-fold slower in the *d*-sulfoxide. The *l*-sulfoxide shows 1.2–1.8-fold inhibition of base catalysis and somewhat greater inhibition of acid catalysis (fivefold) when compared with biotin. These effects are qualitatively consistent with the differing orientations of the S^+–O^- dipole in the *d*- and the *l*-sulfoxides such that the partially positive sulfoxide sulfur stabilizes the anionic intermediate in base catalysis and destabilizes the cationic intermediate in acid catalysis, while the partially negative sulfoxide oxygen exerts opposite effects. A quantitative estimate of the electrostatic effects on the energy levels of the intermediates indicates that such effects, while in the right direction, are insufficient in magnitude to explain the observed differences in the relative exchange rates of the *d*- and *l*-sulfoxides of biotin, unless a significantly lower effective dielectric constant exists at the reaction center. Alternatively, entropic effects must be invoked to explain the relative rates.

In a previous paper[1] Fry et al. reported the unusual kinetics of the exchange of the 1′-NH proton of *d*-biotin, and its methyl ester, with water protons. Unlike all other amide NH protons, including the 3′-NH of *d*-biotin and its methyl ester, the exchange of the 1′-NH proton showed a second-order dependence on $[H^+]^2$ (Figure 1A). This unprecedented kinetic behavior required the presence of sulfur in biotin, since typical first-order dependences on $[H^+]$ were observed with O-heterobiotin, desthiobiotin, and imidazolidone. The second-order term in $[H^+]^2$ was ascribed to the formation of a doubly protonated form of biotin, facilitated

---

[†] Supported by National Institutes of Health Grants AM 28616 (A.S.M.) and GM 18938 (W.W.C.).

[‡] The John Hopkins University.

[§] University of Wisconsin.

(1) Fry, D. C.; Fox, T. L.; Lane, M. D.; Mildvan, A. S. *J. Am. Chem. Soc.* **1985**, *107*, 7659. **Note Added in Proof**: Recent measurements of the acid-catalyzed exchange of the NH protons of *d*-biotin and its methyl ester at the lower temperature of 10 °C (rather than 25 °C), where the decreased rates can be measured more accurately, reveal a kinetic order in $[H^+]$ at the 1′-NH of 1.23 ± 0.07, and 1.30 ± 0.06 (rather than 2.0), and a kinetic order in $[H^+]$ at the 3′-NH of 1.04 ± 0.05 and 0.96 ± 0.12, as originally found (E. H. Serpersu, T. Fox, D. C. Fry, M. D. Lane, and A. S. Mildvan, to be published).

0002-7863/87/1509-2127$01.50/0 © 1987 American Chemical Society