

Substituent Effects in the Acid-Catalyzed Hydrolysis of Cyclic Acetals of Benzophenones

Shinya UENO, Takumi OSHIMA, and Toshikazu NAGAI*

Institute of Chemistry, College of General Education, Osaka University,

Toyonaka, Osaka 560

(Received July 18, 1985)

Synopsis. Eight 2,2-diaryl-1,3-dioxanes were prepared and the kinetic substituent effects regarding acid-catalyzed hydrolysis were studied in 80% dioxane–water (v/v) at 30 °C. The log k were well correlated with the Yukawa-Tsuno equation; $\log k/k_0 = -2.92(\sigma^0 + 0.385\Delta\sigma_{R^+})(r=0.999)$.

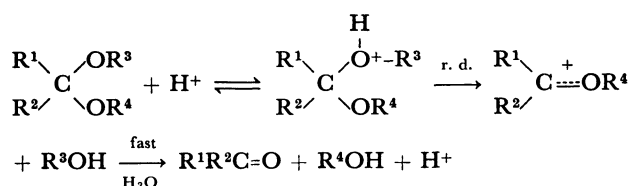
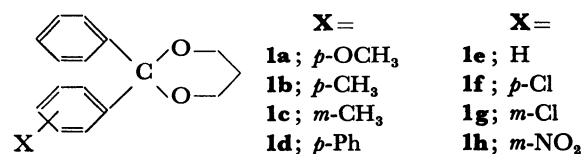
There have been numerous investigations on the acid-catalyzed hydrolysis of acetals from a mechanistic point of view.^{1–3)} It is generally accepted that the acetals hydrolyze by an A1 mechanism; pre-equilibrium protonation, rate-determining oxocarbenium ion formation, and fast degradation into carbonyl compound and alcohol (Scheme 1). As one part of the experimental evidence that supports the mechanism, a number of data have been collected related to kinetic substituent effects for the hydrolysis of a variety of acetals.²⁾ However, little is known about the cyclic acetals of benzophenones, especially with six-membered and higher ring sizes,⁴⁾ probably because of difficulties in a synthesis by traditional methods.⁵⁾

Recently, we have discovered a facile synthetic method for cyclic and acyclic acetals of benzophenone using a redox reaction of diphenyldiazo-

methane(DDM) with 2,3-dichloro-5,6-dicyanobenzoquinone(DDQ) in the presence of suitable alcohols.^{6–8)} This discovery prompted us to synthesize cyclic acetals of benzophenones with a series of substituents and to obtain further information concerning the structure-reactivity relationship regarding the hydrolysis of acetals.

Results and Discussion

The eight *m*- and *p*-substituted 2,2-diaryl-1,3-dioxanes (**1a–h**) were prepared and the rates of acid-catalyzed hydrolyses of these six-membered cyclic acetals were determined in 80% dioxane–water (by volume) at 30 °C (Table 1). When various values of



Scheme 1.

Table 1. Preparation and Hydrolysis of 2,2-Diaryl-1,3-dioxanes (**1a–h**)

Acetals	Substituents	Yields/% ^{a)}	Mp θ_m /°C	$10^4 k_{\text{obsd}} (s^{-1})^b$
1a	<i>p</i> -OCH ₃	62	52–53	51.0
1b	<i>p</i> -CH ₃	52	76–78	17.1
1c	<i>m</i> -CH ₃	61	67–69	6.96
1d	<i>p</i> -Ph	46	154–156	4.99
1e	H	84	113–115	1.36
1f	<i>p</i> -Cl	55	60–61	1.13
1g	<i>m</i> -Cl	56	75–77	0.311
1h	<i>m</i> -NO ₂	58	oil	0.0396

a) Isolated yields by column chromatography(Al₂O₃).

b) All rates were measured in 80% dioxane–water at 30 °C under the constant HCl concentration(0.2 mol dm⁻³).

log k were correlated with the standard Hammett σ and the Brown σ^+ , the σ substituent constants gave a better result ($\rho = -3.10$, $r = 0.997$) than σ^+ , ($\rho = -2.19$, $r = 0.974$). It can be corroborated, however, that the resonance substituent effects moderately contribute to the stabilization of the transition state as evaluated from the value of the resonance reaction constant ($R = 0.385$) in the satisfactory Yukawa-Tsuno equation.⁹⁾

$$\log k/k_0 = -2.92(\sigma^0 + 0.385\Delta\sigma_{R^+}) - 0.05 \quad (n=8, r=0.999)$$

In Table 2, the Hammett parameters have been collected for the hydrolysis of **1** and related cyclic acetals. The hydrolysis of **1** provided a larger negative ρ value, accompanied by increased resonance effects than that of the corresponding five-membered cyclic acetals, 2,2-diaryl-1,3-dioxolanes(**2**),¹⁰⁾ though a straightforward comparison is somewhat ambiguous because of the change in the solvent composition. Whereas, monoaryl substituted 1,3-dioxolanes(**3**) were more subject to both polar and resonance effects than **1**.¹¹⁾

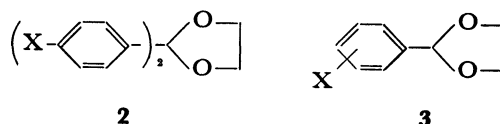


Table 2. Hammett Parameters for Hydrolysis of **1**, **2**, and **3**

Substrates	ρ	R	No. of substituents	Solvent	r	$T/^\circ\text{C}$	Ref.
1	-2.92	0.385	8	80% Dioxane	0.999	30	This work
2 ^{a)}	-2.08 ^{b)}	0.240 ^{b)}	4	20% Dioxane	0.998	25	10
3	-3.28 ^{b)}	0.457 ^{b)}	5	50% Dioxane	0.999	30	11

a) The σ^+ and σ^0 values used are the sums of the values for the two substituents. b) Original data were treated according to Yukawa-Tsuno equation.

Experimental

Materials. 1,4-Dioxane was refluxed over metal sodium and fractionated. The substituted diphenyldiazomethanes (DDMs) were synthesized by the oxidation of the corresponding benzophenone hydrazones with yellow mercury oxide as has been described.¹²⁾ Also, solid DDMs were purified by recrystallization from petroleum ether or ether. The melting points of these DDMs have been reported elsewhere.¹³⁾ The *m*-NO₂ substituted DDMs had a mp of 53–54 °C (lit.¹⁴⁾; oil). The acetals (**1a–h**) were produced by a reaction of DDMs with DDQ in the presence of 1,3-propanediol according to our previous methods.⁹⁾ The structures of **1a–h** were confirmed by IR, NMR, and elemental analyses. The yields and mp are collected in Table 1.

Kinetic Measurements. The rates of hydrolysis of **1a–h** were measured in 80% dioxane–water(v/v) at a constant acid(HCl) concentration(0.200 mol dm⁻³). The rates were measured spectrophotometrically with a JASCO UVIDEK 505 spectrophotometer by following the increase in absorption due to the benzophenone at constant temperature maintained by circulating water from a Haake constant temperature circulating bath. Pseudo-first-order rate constants (k_{obsd}) were determined from logarithmic plots of ($A_\infty - A_t$) against time. These were linear over 3 half-times.

References

- 1) E. H. Cordes, *Progr. Phys. Org. Chem.*, **4**, 1 (1967).
- 2) E. H. Cordes and H. G. Bull, *Chem. Rev.*, **74**, 581 (1974).
- 3) R. G. Bergstrom, "The Chemistry of Ethers, Crown Ethers, Hydroxy Groups and Their Sulphur Analogues," ed by S. Patai, John Wiley and Sons, London (1980), Chap. 20.
- 4) O. Ceder, *Arkiv. Kemi.*, **6**, 523 (1954).
- 5) E. Schmitz and I. Eichhorn, "The Chemistry of the Ether Linkage," ed by S. Patai, John Wiley and Sons, London (1967), Chap. 7.
- 6) T. Oshima, R. Nishioka, and T. Nagai, *Tetrahedron Lett.*, **1980**, 3319.
- 7) T. Oshima, R. Nishioka, S. Ueno, and T. Nagai, *J. Org. Chem.*, **47**, 2114 (1982).
- 8) S. Ueno, T. Oshima, and T. Nagai, *J. Org. Chem.*, **49**, 4060 (1984).
- 9) Y. Yukawa, Y. Tsuno, and M. Sawada, *Bull. Chem. Soc. Jpn.*, **39**, 2274 (1966).
- 10) R. H. DeWolfe, K. M. Ivanetich, and N. F. Perry, *J. Org. Chem.*, **34**, 848 (1969).
- 11) T. H. Fife and L. K. Jao, *J. Org. Chem.*, **30**, 1492 (1965).
- 12) L. I. Smith and K. L. Howard, *Org. Synth.*, Coll. Vol. III, 351.
- 13) T. Oshima, A. Yoshioka, and T. Nagai, *J. Chem. Soc., Perkin Trans. 2*, **1978**, 1283.
- 14) R. Curci, F. D. Furia, and F. Marcuzzi, *J. Org. Chem.*, **36**, 3374 (1971).