Table I. Correlations of NMR Shifts and Coupling Constants of Trifluoroacetic Acid Complexes of HBA Bases in CCl_4

no.	X in substrate *n*-BuX	π^* [b]	β [b]	$\delta_{C=O}$	δ_{CF_3}	$^1J_{CF_2}$	$^2J_{CF_3}$
1	*n*-Bu	−0.08	0.00	163.47	114.79	283.6	43.0
2	Cl	0.39	0.00	163.04	114.80	283.6	43.2
3	$CH{=}CH_2$	0.08	0.07[c]	163.01	114.83	285.1	43.3
4	NO_2	0.75	0.25	160.38	115.05	285.4	42.7
5	SCH_3	0.34	0.26[c]	160.35	115.05	285.1	42.2
6	CH=O	0.60	0.41	159.22	115.28	286.3	42.6
7	$COCH_3$	0.65	0.48	158.72	115.34	286.5	43.6
8	$COOCH_3$	0.50	0.45	158.81	115.39	286.5	41.7
9	OCH_3	0.27	0.48	158.69	115.44	285.8	41.8
10	CN	0.65	0.35	158.65	115.30	285.9	41.9

[a] HBA bases in 1.0 M solution in CCl_4 containing 1 mol equiv of CF_3COOH. [b] Most π^* and β values were estimated from corresponding values for related compounds (usually lower homologues). [c] Kamlet, M. J.; Doherty, R. M.; Abboud, J.-L. M.; Abraham, M. H.; Taft, R. W. *J. Pharm. Sci.*, in press.

Table II. Estimation of New β Values

no.	X in substrate *n*-BuX	est. π^*	$\delta_{C=O}$	β_1	δ_{CF_3}	β_2	β_3	β_{av}
1	SO_2Me	0.85	158.65	0.41	115.31	0.42		0.42
2	$SCOCF_3$	0.30	162.09	0.11	114.89	0.10		0.11
3	$OCOCF_3$	0.35	161.58	0.16	114.93	0.12	(0.19)[b]	0.16
4	$OCSCH_3$	0.40	160.69	0.25	115.08	0.24		0.25
5	$SCOCH_3$	0.40	159.11	0.43	115.27	0.38	0.43[a]	0.41
6	$SCSCH_3$	0.30	161.43	0.18	114.98	0.16		0.17

[a] From equation for $RCOCH_3$ compounds: $\beta = 0.40 - 0.56\sigma_I - 0.20\sigma_{R^+}$.[2] [b] Value reported[2] for ethyl trifluoroacetate.

and COOH, are assembled in Table I, as are the relevant π^* and β values of the HBA bases. Because the hydrogen bond donor compounds are excluded and because we are dealing with family-independent properties, we do not include the α and ξ parameters, and correlations are by eq 2.

$$XYZ = XYZ_0 + s\pi^* + b\beta \quad (2)$$

The correlations by eq 2 for the $\delta_{C=O}$ and δ_{CF_3} ^{13}C shifts are given by eq 3 and 4. As expected, the effects of base HBA basicity and dipolarity/polarizability are greater for the carbon atom closer to the hydrogen bonding site. The

$$\delta_{C=O} = (163.48 \pm 0.23) - (1.40 \pm 0.54)\pi^* - (8.91 \pm 0.78)\beta \text{ ppm} \quad (3)$$

$$n = 10,\ r = 0.9869,\ \text{sd} = 0.336 \text{ ppm}$$

$$\delta_{CF_3} = (114.77 \pm 0.03) - (0.02 \pm 0.07)\pi^* + (1.32 \pm 0.12)\beta \text{ ppm} \quad (4)$$

$$n = 10,\ r = 0.9829,\ \text{sd} = 0.053 \text{ ppm}$$

precision of eq 3 and 4 is sufficiently good that we can use them to back calculate new β values. The insignificant dependence on π^* in eq 4 is of particular interest, because it allows a back calculation that is independent of our estimate of this parameter. The statistical quality of the correlation equations for the coupling constants, eq 5 and 6, is significantly poorer, and we now consider these results to be inadequate for back calculational purposes.

$$^1J_{CF} = (283.88 \pm 0.28) + (0.44 \pm 0.65)\pi^* + (4.76 \pm 0.95)\beta \text{ Hz} \quad (5)$$

$$n = 10,\ r = 0.9315,\ \text{sd} = 0.44 \text{ Hz}$$

$$^2J_{CF} = (43.02 \pm 0.41) + (0.35 \pm 0.98)\pi^* - (2.06 \pm 1.42)\beta \text{ Hz} \quad (6)$$

$$n = 10,\ r = 0.513,\ \text{sd} = 0.66 \text{ Hz}$$

β_i values back-calculated from eq 3 and 4 are assembled in Table II, together with several β_i values from other sources and resulting average β values for a number of additional *n*-BuX derivatives. Table II contains no surprises. Thus, Abboud[7] has determined β values of 0.40 and 0.55 for $HCSNMe_2$ and $Me_2NCSNMe_2$, compared with 0.69 and 0.80 for $HCONMe_2$ and $Me_2NCONMe_2$, i.e., decreases of 0.29 and 0.25 on replacing C=O by C=S. These accord reasonably well with the β_{av} values of 0.25 for $BuOCSCH_3$ compared with 0.45 for $BuOCOCH_3$ and of 0.17 for $BuSCSCH_3$ compared with 0.41 for $BuSCOCH_3$. The β_i values for $BuSCOCH_3$ agree quite well with a value calculated from an earlier reported[2] multiple substituent parameter equation for β of R_1COR_2 compounds (the latter β_i being included in the β_{av} result).

Registry No. $CH_3(CH_2)_6CH_3$, 111-65-9; BuCl, 109-69-3; $CH_3(CH_2))_3CH{=}CH_2$, 592-41-6; $BuNO_2$, 627-05-4; $BuSCH_3$, 628-29-5; $CH_3(CH_2)_3CHO$, 110-62-3; $CH_3(CH_2)_3COCH_3$, 591-78-6; $CH_3(CH_2)_3COOCH_3$, 624-24-8; $BuOCH_3$, 628-28-4; $CH_3(CH_2)_3CN$, 110-59-8; $BuSO_2Me$, 2976-98-9; $BuSC(O)CF_3$, 760-47-4; $BuOC(O)CF_3$, 367-64-6; $BuOC(S)CH_3$, 55613-69-9; $BuSC(O)CH_3$, 928-47-2; $BuSC(S)CH_3$, 69380-59-2; CF_3CO_2H, 76-05-1.

(7) Prof. J.-L. M. Abboud, Universidad de Leon, private communication.

Acid-Catalyzed Hydrolysis of Benzophenone Crown Ether Acetals and Analogous Open Chain Acetals

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The hydrolysis of acetals has received much attention in recent years.[1,2] The generally accepted mechanism involves a fast preequilibrium protonation of the acetal,

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(2) (a) Bergstrom, R. G. In *The Chemistry of Ethers, Crown Ethers, Hydroxy Groups and Their Sulphur Analogues*; Patai, S., Ed.; Wiley: Chichester, 1980; Chapter 20. (b) Burt, R. A.; Chiang, Y.; Kresge, J. *Can. J. Chem.* **1980**, *58*, 2199. (c) Jensen, J. L.; Carr, M. D.; Yamaguchi, K. S. *Int. J. Chem. Kinet.* **1983**, *15*, 235.

0022-3263/86/1951-2131$01.50/0

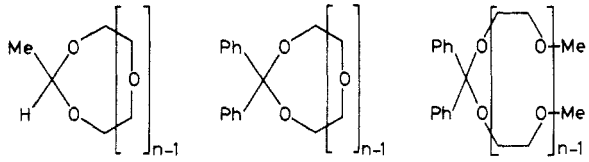
Table I. Rate Constants (k) and Activation Parameters for the Hydrolysis of 2a–g and 3a–d in 80% Dioxane–Water

acetal	number of oxygen atoms (N)	10^2k, dm^3/mol·s				$\Delta H^{\ddagger}$, kJ/mol[a]	$\Delta S^{\ddagger}$, J/mol·K[a]
		20 °C	30 °C	40 °C	50 °C		
2a	2	0.30	0.97	3.36		88.9	12.9
2b	3		2.92	10.2	30.6	93.2	33.1
2c	4		14.2	45.6	146	92.3	43.1
2d	5		13.8	43.8	131	89.1	32.3
2e	6		34.0	103	277	83.0	19.7
2f	7		17.7	57.2	169	89.3	35.1
2g	8		11.6	35.6	107	88.2	28.1
3a	2		7.01	23.3	77.8	95.5	47.8
3b	4		3.50	12.0	39.8	96.6	45.7
3c	6		6.79	22.1	67.7	91.1	33.1
3d	8		7.62	23.8	71.4	88.6	25.9

[a] Values at 30 °C.

an unimolecular rate-determining decomposition of the conjugate acid (SH^+) to a resonance-stabilized oxocarbenium ion (C^+), and the subsequent multistep degradation into carbonyl compound and alcohol by the action of water.

One part of the experimental evidences for the above A1 mechanism is provided from the investigation of the structure reactivity relationship.[1] A great deal of information has been collected for the polar effects in the hydrolyses of cyclic or open chain acetals having the substituents on the carbonyl or alkyl moieties.[1] However, only one case is known for the hydrolysis of cyclic acetals with the poly(oxyethylene) moiety (**1**), so-called crown ether acetals, probably because of the difficulty in the synthesis.[3] Recently, we discovered the facile synthetic methods of benzophenone crown ether acetals (**2**) by means of the reaction of diphenyldiazomethane (DDM) with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) under the influence of oligoethylene glycols.[4] This situation prompted us to report the results for the hydrolysis of the title crown ether acetals and to compare the reactivities with those of the corresponding acetals of acetaldehyde (**1**). Hydrolysis of the noncyclic acetals **3** was also made in the same conditions to know the effects of structural change in the oxyethylene unit moiety on the hydrolytic behavior of these acetals.



1a-f 2a-g 3a-d

a; n=1 e; n=5
b; n=2 f; n=6
c; n=3 g; n=7
d; n=4

Results and Discussion

The rate constants and the activation parameters for the HCl-catalyzed hydrolysis of 2,2-diphenyl-1,3-dioxolane (**2a**) and benzophenone crown ether acetals **2b–g** and open chain acetals **3a–d** with oxyethylene units in 80% dioxane–water are collected (Table I).

In the case of cyclic acetals of 5–23-membered rings, rate constants rise rapidly with increasing ring size, reach a maximum in 17-membered ring, and finally decrease moderately with further increasing ring size. In the open chain acetals, however, a marked effect of chain length was not observed though the number of oxyethylene units varied from zero to six. Similar hydrolytic behavior as observed for our benzophenone cyclic acetals has been given by Gold et al. for the HCl-catalyzed hydrolysis of acetaldehyde crown acetals **1a–f** with one to six oxyethylene units in 60% dioxane–water.[3] As seen in the plots of log k vs. the number of oxygen atoms (Figure 1), both series of these crown ether acetals exhibited very similar dependence of rates on the ring size except that the maximum rate for the acetaldehyde series was obtained in the one oxyethylene unit shorter acetal, 14-membered ring, than in our benzophenone acetals. They did not mention the reason of this rate profile with the maximum rate in the 14-membered ring size. We want to describe the effects of the number of oxyethylene units on the hydrolysis reactivity of our benzophenone acetals by considering the contribution of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ on the rate constants.

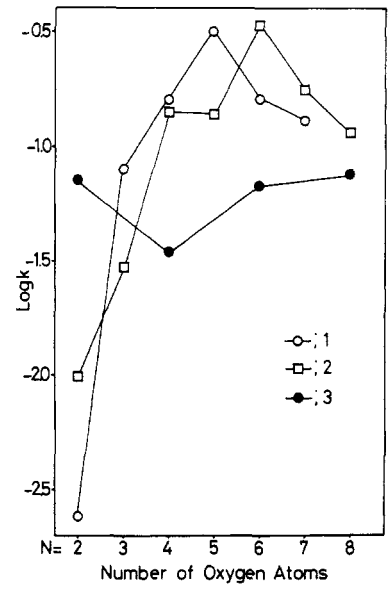


Figure 1. Plots of log k vs. the number (N) of oxygen atoms for hydrolyses of crown ether acetals **1a–f** and **2a–g** and open chain acetals **3a–d**. Log k values were calculated by using the values in 60% dioxane–water at 25 °C for 1 and in 80% dioxane water at 30 °C for **2** and **3**.

As shown in Figure 2, compensation relationships are generally found between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for both the crown and the open chain acetals. Interestingly, crown acetals showed sudden decrease of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ in the 17-membered ring, which has the maximum rate in the series, except for the 5-membered one. This is the marked difference from the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ profiles for open chain acetals **3a–d**, where these parameters substantially de-

(3) Gold, V.; Sghibartz, C. M. *J. Chem. Soc., Chem. Commun.* **1978**, 507.

(4) (a) Oshima, T.; Nishioka, R.; Ueno, S.; Nagai, T. *J. Org. Chem.* **1982**, *47*, 2114. (b) Oshima, T.; Nishioka, R.; Nagai, T. *Tetrahedron Lett.* **1980**, 3319.

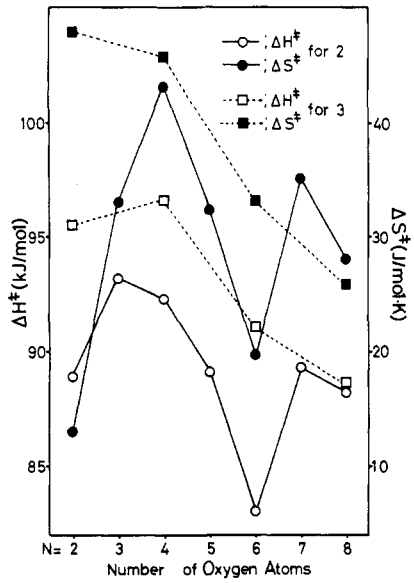
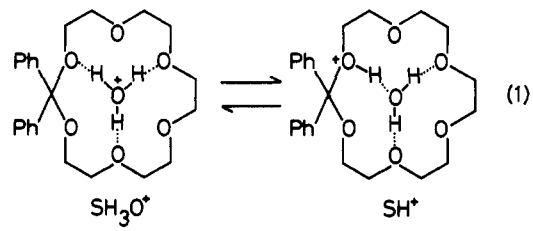


Figure 2. Plots of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ vs. the number (N) of oxygen atoms for hydrolyses of **2a–g** and **3a–d** at 30 °C.

creased monotonously with the increasing chain lengths.

Generally, in the hydrolysis of benzophenone acetals, the oxocarbenium ion intermediate (C^+) is stabilized by substantial resonance effects of *gem*-diphenyl group, and this makes the transition state closer to the conjugate acid (SH^+) according to the Hammond postulate.[1,5] This is the case with our crown ether acetals. As a characteristic property, crown acetals, especially the 17-membered **2e**, are expected to incorporate a H_3O^+ in light of the fact that dibenzo-18-crown-6 forms a more stable complex with H_3O^+ than with K^+.[6] In addition, various crown ethers are known to produce a stable tripod structure with H_3O^+.[7]

Accordingly, it is reasonable to assume that our crown acetals build up a similar three-hydrogen-bonded structure as illustrated for **2e** (eq 1). This hydronium ion complexed

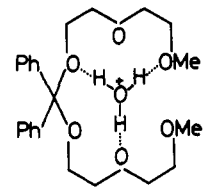


(1)

acetal (SH_3O^+) may be in rapid equilibrium with the conjugate acid form (SH^+) (eq 1). This SH_3O^+ has an ordered structure and is to be highly stabilized. Thus, low $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values for **2e** may be due to some contribution of these stable and ordered protonated structures to the conjugate acid, which is close to the transition state as mentioned above. On the other hand, the relatively low $\Delta H^{\ddagger}$ and very small $\Delta S^{\ddagger}$ for the 5-membered ring **2a** may be attributed to the ring strain and the restrictive freedom in the transition state due to small ring size.

In the case of 8-, 11-, 14-, 20-, and 23-membered ring acetals, the template ability toward H_3O^+ must be reduced on account of the smaller or larger ring sizes compared to the 17-membered ring. In case of Gold's series, the maximum rate constant is observed in just one oxyethylene unit shorter acetal (**1d**) compared to our case. If the same explanation mentioned above could be applied to Gold's acetals, the 17-membered acetaldehyde crown acetal should be most easily hydrolyzed. We have no apparent interpretation for this discrepancy;[8] however, it may be possible that Gold's 14-membered acetal forms more stable and ordered structure with H_3O^+ because of the loss of bulky *gem*-diphenyl group which will introduce steric hindrance and hydrophobicity in the crown ring, interfering in the interaction with H_3O^+.

As for the open chain acetals, both the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, which generally decreased with the increasing chain lengths, contributed to the free energies in such a way that the rates were little affected by the almost equal compensation. The simple decrease of these parameters is also indicative of the same participation of a stable and ordered hydronium ion incorporated structure (**4**) in the transition states of relatively long-chained acetals as illustrated for the cyclic acetal **2e**. Unlike **2**, compounds **3** have no valley in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ profiles, even in **3c** with the same six oxygen atoms as **2e**. This fact implies that the tripod conformation is also possible even in long chain **3d**.



4

Experimental Section

Materials Cyclic and noncyclic benzophenone acetals **2a–g** and **3a–d** were prepared by means of reaction of diphenyldiazomethane (DDM) and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) under the influence of corresponding oligoethylene glycols, oligoethylene glycol monomethyl ethers, and methanol.[4,9] General procedures were mentioned elsewhere.[4,9] The structures of newly prepared **2g** and **3b** were confirmed by IR, NMR, mass spectrum, and elemental analyses.

2,2-Diphenyl-23-crown-8 (2g): colorless oil; 58% yield; IR (neat) 2870, 1450, 1210, 1100, 1020, 700 cm^{-1}; NMR ($CDCl_3$) δ 3.3–3.8 (m, 28 H, OCH_2CH_2), 7.1–7.6 (m, 10 H, Ph); MS, m/e 490 (M^+). Anal. Calcd for $C_{27}H_{38}O_8$: C, 66.10; H, 7.81. Found: C, 66.24; H, 7.87.

6,6-Diphenyl-2,5,7,10-tetraoxaundecane (3b): colorless oil; 46% yield; IR (neat) 2880, 1450, 1210, 1090, 700 cm^{-1}; NMR ($CDCl_3$) δ 3.3–3.7 (m, 14 H, OCH_2CH_2), 7.1–7.6 (m, 10 H, Ph); MS, m/e 241 ($M^+ - OCH_2CH_2OCH_3$). Anal. Calcd for $C_{19}H_{24}O_4$: C, 72.12; H, 7.65. Found: C, 71.92; H, 7.42.

The analytic data of other benzophenone acetals are collected in elsewhere.[4,9]

Kinetic Measurements The rates of hydrolysis of acetals were measured in 80% dioxane–water (v/v) at acid (HCl) concentrations of 4.0×10^{-3} mol/dm^3 for **2b–g** and **3a–d** and of 2.0×10^{-1} mol/dm^3 for **2a**. The rates were measured spectrophotometrically with a JASCO 505 spectrophotometer by following the increase in absorption due to the benzophenone (λ_{max} = 340 nm). The reactions were generally followed up to 80% completion. The pseudo-first-order rate constants (k_{obsd}) were obtained from the slopes of plots of ln $[A_\infty - A_t]$ against time. The second-order rate constants (k) were obtained by dividing k_{obsd} by activity of H^+ (a_{H^+} = 0.00102 and 0.0104 mol/dm^3 respectively for the low and high HCl solutions), calculated according to Debye–Hückel equation.[10] Constant temperature was maintained in the kinetic

(5) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.
(6) Kolthoff, I. M.; Wang, W.-J.; Chantooni, M. K., Jr. *Anal. Chem.* **1983**, *55*, 1202.
(7) (a) Behr, J.-P.; Dumas, P.; Moras, D. *J. Am. Chem. Soc.* **1982**, *104*, 4540. (b) Chênevert, R.; Rodrigue, A.; Pigeon-Gosselin, M.; Savoi, R. *Can. J. Chem.* **1982**, *60*, 853. (c) Chênevert, R.; Rodrigue, A.; Beauchesne, P.; Savoie, R. *Can. J. Chem.* **1984**, *62*, 2293.
(8) In complexing with H_3O^+, 18-crown-6 is reported to have 2 log units higher complexation constant than 15-crown-5.
(9) Ueno, S.; Oshima, T.; Nagai, T. *J. Org. Chem.* **1984**, *49*, 4060.
(10) Debye, P.; Hückel, E. *Phys. Z.* **1923**, *24*, 185.

runs by circulating water from a Haake Model FE constant-temperature circulating bath.

Registry No. **2a**, 4359-34-6; **2b**, 77130-21-3; **2c**, 77130-22-4; **2d**, 81194-61-8; **2e**, 81194-62-9; **2f**, 81194-63-0; **2g**, 101858-70-2; **3a**, 2235-01-0; **3b**, 101858-71-3; **3c**, 81194-70-9; **3d**, 81194-71-0.

On the Hydrogen Peroxide/Sulfuric Acid Oxidation of Mesoporphyrin. Synthesis of Mesoporphyrindiones[1]

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Hans Fischer and his students reported in 1930 a novel method to obtain green-colored chlorins from porphyrins.[2] They reacted mesoporphyrin IX in concentrated sulfuric acid with hydrogen peroxide and yielded a product which was designated as "dioxymesoporphyrin" even though the elementary analysis results were ambivalent in showing whether one or two oxygen atoms had been added to mesoporphyrin. Indeed, they later concluded that the green product resulted from this acid medium contains only one extra oxygen atom and called it "anhydrochlorin".[3] The structure that they proposed, formulated as an epoxide ring across a pyrrole double bond, was again incorrect. Johnson[4,5] and Inhoffen,[6,7] about 20 years ago, independently reinvestigated such oxidation reaction using symmetrical etioporphyrin and octaethylporphryin (OEP) and established that the true identity of the major product from this hydrogen peroxide/sulfuric acid oxidation is a keto chlorin formed by a pinacol rearrangement of the intermediate diol or epoxide. By inference, Fischer's "dioxymesoporphyrin" must also be some sort of keto chlorins but the exact product(s) in mesoporphyrin oxidation is far from clear. For being an unsymmetrically substituted porphyrin, mesoporphyrin could produce up to eight isomeric ketones. Furthermore, as reported originally by Inhoffen and Nolte[6,7] and more recently by Chang[8] using OEP, the oxidation reaction does not stop at the monoketone level; diketones and even triketones arise almost simultaneously under the reaction condition optimized for the monoketone. With OEP, there are five diketones and four triketones identified; with mesoporphyrin, there could be 14 diketone regioisomers alone without counting the diastereomers! The sheer number of anticipated isomeric products from mesoporphyrin must have dissuaded attempts to reexamine this reaction for after more than a half century, Fischer's pioneering yet unsolved work stands unsettled.

We have recently become interested in the dioxoisobacteriochlorins (porphinediones[1]) because we discovered that the green heme prosthetic group in the *cd*-type cytochrome prevailing in microbial denitrifiers may in fact possesses such a macrocyclic core structure.[9] In an effort to understand the intrinsic properties of the 2,4-porphinedione and particularly the difference between d_1 heme and protoheme, we need to obtain a copious supply of similarly structured model compounds. The H_2O_2/H_2SO_4 oxidation of mesoporphyrin therefore offered an attractive choice if the 2,4-mesoporphyrindione can be isolated.

Synthetically, a keto chlorin (porphinone[1]) sometimes can be produced in a stepwise manner: treating porphyrins with osmium tetraoxide[10] to generate a *vic*-dihydroxychlorin, which then undergoes pinacol rearrangement in acid. While this two-step reaction may offer some control over the unwanted monoketone isomers, it is not useful for producing the isobacteriochlorin derivatives. In the presence of excess amounts of osmium tetraoxide, only tetrahydroxybacteriochlorin was observed. Even deuteroporphyrin, which has built-in steric advantages, was found to react with an excess of OsO_4 to yield only the tetrahydroxybacteriochlorin without any trace of the isobacteriochlorin. This reaction pattern may be due to the preferred diagonal π-electron delocalization pathway present in all porphyrins, which prompts the saturation of the two isolated, diagonal pyrrole β,β'-double bonds with minimum loss of π-energy. Similar argument has been advanced to account for the exclusive diagonal reduction of tetraphenylporphyrin by diimide to yield bacteriochlorin.[11] In a medium of concentrated sulfuric acid, however, porphyrin would become doubly protonated, the influence of valence tautomerism would become insignificant, and isobacteriochlorin may be formed. Indeed, in the reaction of OEP with H_2O_2/H_2SO_4, the combined yield of the three dioxoisobacteriochlorins is better than that of the two dioxobacteriochlorins.[8] There is another element buttressing our optimism that the oxidation with mesoporphyrin may be simpler than it appears to be. The pinacolic rearrangement of the diols is dictated by very specific migratory aptitudes:[12] we have recently demonstrated that both ethyl and propionate side chains in a *vic*-dihydroxychlorin have a higher migratory aptitude as compared with the methyl group.[13] Furthermore, the epoxide or diol formation is highly sensitive to the size of the side chain. On the basis of these considerations, one would predict that the desired 2,4-mesoporphyrindione **3** is the favored product.

Thus, mesoporphyrin dimethyl ester dissolved in concentrated H_2SO_4 was reacted with H_2O_2, and after about 30 min the solution was neutralized by sodium acetate. The solid product, collected by filtration, contained most of the ketone products with intact propionic esters. Chromatography of this material on silica gel went surprisingly well, and nine different compounds, excluding the unreacted mesoporphyrin, were obtained (Scheme I); the total yield was about 30% (reproducible in three separate runs).[14] Structure identification in most cases was straightforward, aided by absorption and ^1H NMR spectra. The differentiation of the monoketones **1** and **2** and also

(1) The nomenclature of the ketone derivatives of porphyrins has not been standardized. Inhoffen called them geminiporphine-monoketone and -diketone[6,7] and Johnson used the name "oxochlorin".[4,5] The prefix "oxo-", however, could be confused with "oxyporphyrin" or "oxophlorin" which has an oxygen attached to the porphyrin meso position. Furthermore, we have discovered that these "oxo" derivatives have very little chemical properties in common with those of the parent chlorin, isobacteriochlorin, or bacteriochlorin.[21] We prefer to regard these ketones as "quinones" of porphyrin. The use of the suffix -one or -dione is both convenient and specific in that it allows the retention of the trivial name of the porphyrin precursor, as demonstrated by examples given in this paper.

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