at 20–21 °C. (In this case, the temperature increases up to 31–33 °C and then decreases as soon as 1 hydrogen equivalent has been absorbed). Indeed, we found that conducting these semihydrogenations in thermostated flasks at +10 °C, –6 °C, or –20 °C generally resulted in a poorer selectivity without significant improvement of the stereoselectivity. However, hydrogenation of diphenylacetylene appeared to be an exception. Indeed, in this case, the temperature effect was found to be more important, at least with some solvent combinations. For example, in EtOH/THF (1/1) mixtures, the following results were obtained (T °C, Z/E/saturated): +21 °C, 95.4/2.9/1.7; +10 °C, 96.6/2.2/1.2; –20 °C, 97.2/1.6/1.2. However, it must be noted that a comparable result could be obtained at 21 °C by changing the solvent in EtOH/THF (3/5) mixtures (Table I).

Pdc thus appears as very selective and stereoselective. A direct comparison with some of the best catalysts reported so far is possible, owing to a recent, careful, study by Friedlin et al.[18] of the semihydrogenation of diphenylacetylene. Among the many group VIII metal catalysts studied, these authors found that the more selective and stereoselective were Lindlar Pd and $[PtCl_2(SnCl_3)]^{2-}$, this latter being reported as the only one that allows a self-terminating semihydrogenation. The results summarized in the scheme clearly indicate that Pdc is superior to the above catalysts, both for selectivity and stereoselectivity.

A comparison of Pdc with P_2Ni[9] is also important since P_2Ni often appeared more stereoselective than Lindlar Pd.[19] In the cases where a direct comparison is possible,[9] it is clear that Pdc is at least as stereoselective as P_2Ni, and above all, more selective.[20]

In conclusion, the present work shows that Pdc, very easy to obtain with a high reproducibility, from NaH, t-AmOH, and $Pd(OAc)_2$ may be presently considered as one of the best catalysts for the semihydrogenation of simple acetylenes to (Z)-alkenes. Extension of these results to more complex substrates is being pursued and will be reported later.

Experimental Section

Fluka sodium hydride (50–60% in oil)[21] was used and washed twice with THF in the reaction flask under nitrogen. Badische Anilin reagent grade THF was distilled from benzophenone–sodium couple before use. (The absence of peroxides was tested before each run). Fluka palladium acetate was dried under vacuum for 24 h at 80 °C. t-AmOH (2-methyl-2-butanol) was distilled from sodium. All acetylenes were commercial (Fluka or Aldrich). They were purified (distillation, recrystallization, or column chromatography) just before use. In each case they were checked by GLC analysis and found to be free of any possible hydrogenation product. Synthetic quinoline was distilled just before use. Nitrogen R, argon U, and hydrogen (L'Air Liquide) were used. GLC analyses (SE-30 or Carbowax capillary columns) were performed with a 7100 Spectra Physics apparatus (flamme ionization detector) equipped with a 4100 SP computing integrator. In all the cases studied, all compounds likely to be formed were available and GLC analyses were performed in such conditions that they all gave base-line separated signals.

Preparation and Storage of the Catalyst. Pdc was prepared from NaH (60 mmol), t-AmOH (20 mmol), and $Pd(OAc)_2$ (10 mmol) in THF (50 mL) following the procedure previously reported for the preparation of Nic.[11] Addition of t-AmOH was started at 40 °C as it was very important not to exceed 45 °C during either step of the preparation. After 3 h of stirring at 45 °C, the catalyst was ready for use. It was syringed and stored under argon in air-tight bottles in which was placed a magnetic stirrer in order to homogenize the suspension before each sampling (1 mL, 0.2 mmol catalyst).

Semihydrogenation of Acetylenes. All experiments were conducted with a classical apparatus for atmospheric pressure hydrogenations equipped with the modified hydrogenation vessel we have previously described.[11b]

Hydrogenations were performed on a 10-mmol substrate scale (catalyst/substrate ratio; 1/50). Reactants were introduced into the reaction vessel in the following order: solvent (6 mL), quinoline (2 mL), Pdc (0.2 mmol). Then hydrogen was introduced after purging the apparatus 3 times and stirring was then started. After 10 min of stirring (2500 rpm monitored by a stroboscope), the acetylene (10 mmol) with 2 mL of solvent was syringed in the reaction vessel through a septum cap. The progress of the hydrogenation was then followed in a classical manner. All others experimental details may be found in the previous publications on Nic.[11,12]

Acknowledgment. This work was supported by the Centre National de la Recherche Scientifique, France (ATP: Messagers Chimiques), which is gratefully acknowledged.

Registry No. Pd, 7440-05-3; t-AmOH, 75-85-4; $Pd(OAc)_2$, 3375-31-3; NaH, 7646-69-7; $C_6H_5C{\equiv}CH$, 536-74-3; $C_6H_5CH{=}CH_2$, 100-42-5; $H_2C{=}CH(CH_2)_5CH_3$, 111-66-0; (Z)-$C_6H_5CH{=}ChCH_3$, 766-90-5; (E)-$C_6H_5CH{=}CHCH_3$, 873-66-5; (Z)-$H_3CCH{=}CHCH_2CH_2CH_3$, 7688-21-3; (E)-H,3CCH=$CHCH_2CH_2CH_3$, 4050-45-7; (Z)-$C_6H_5CH{=}CHC_6H_5$, 645-49-8; (E)-$C_6H_5CH{=}CHC_6H_5$, 103-30-0; $C_6H_5CH_2CH_3$, 100-41-4; $H_3C(CH_2)_6CH_3$, 111-65-9; $C_6H_5CH_2CH_2CH_3$, 103-65-1; $H_3C(CH_2)_4CH_3$, 110-54-3; $C_6H_5CH_2CH_2C_6H_5$, 103-29-7; 1-octyne, 629-05-0; 2-hexyne, 764-35-2; 1-phenylpropyne, 673-32-5; diphenylacetylene, 501-65-5; quinoline, 91-22-5.

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(19) Semihydrogenation of alkynes over Lindlar Pd often led to large amounts of E isomers. See, for example: Dobson, N. A.; Eglington, G.; Krishnamurti, M.; Raphael, R. A.; Willis, R. G. *Tetrahedron* **1961**, *16*, 16.

(20) It can be inferred from results reported in ref 9 that P_2Ni generally led to the formation of 2–4% of overhydrogenated compounds.

(21) Titration of each batch before use was carried out by classical techniques. See: Plesek, J.; Hermanek, S. "Sodium Hydride"; Iliffe: London, 1968.

Syntheses of Macrocyclic Acetals via Cyclization of α,ω-Diols with an Intermediate from Diphenyldiazomethane and 2,3-Dichloro-5,6-dicyanobenzoquinone

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There are numerous procedures available for the syntheses of acetals.[1,2] Conventional methods include the conversion of aldehydes and ketones into their corresponding acetals by use of alcohols in the presence of acidic catalysts such as p-toluenesulfonic acid.[3] These well-known methods, however, fail completely or give low yields when the product is a strained cyclic acetal or an acetal of unusually low stability.

Recently, we developed a new synthetic method for cyclic and noncyclic diphenyl acetals and macrocyclic crown ether acetals that makes use of a redox reaction of diphenyldiazomethane (DDM) with 2,3-dichloro-5,6-di-

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(2) Bergstrom, R. G. In "The Chemistry of Ethers, Crown Ethers, Hydroxy Groups and Their Sulphur Analogues"; Patai, S., Ed.; Wiley: Chichester, 1980; Chapter 20.

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Table I. Product Distribution in the DDM–DDQ–Diols Systems

run[a]	diols (rel equiv)	n (no. of CH_2 groups)	products,[b] % yield 2	3	4	5[c]
1	**1a** (3)	2	81	0	0	0
2	**1b** (3)	3	84	0	0	0
3	**1b** (3)	3	76	0	0	0
4	**1c** (3)	4	75	0	0	0
5	**1d** (1)	5	21	18	0.9	30
6	**1e** (1)	6	0	42	0	12
7	**1e** (1)	6	0	32	0	17
8	**1f** (1)	7	0	20	0	43
9	**1g** (1)	8	0	35	0	30
10	**1h** (1)	9	0	19	0	49
11	**1i** (1)	10	0	23	0	50
12	**1j** (1)	12	0	13	0	40
13	**1j** (1)[d]	12	0	18	0	44

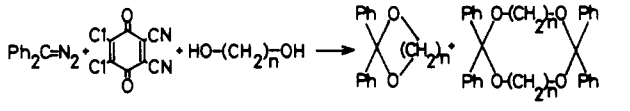
[a] Runs 1, 2, 4, and 7 were carried out in 1,2-dichloroethane, others in benzene. [b] Unless otherwise noted, based on DDM used. [c] Based on diols used. [d] Added over 1 h into the reaction mixture of DDM and DDQ.

cyanobenzoquinone (DDQ) in the presence of suitable alcohols and oligo ethylene glycols.[4,5]

The aim of this paper is to present the possible application of these redox systems to the synthesis of large-ring acetals by employing α,ω-diols, to point out the noticeable difference between α,ω-diols and oligo ethylene glycols, and to discuss the effects of chain length on the product distributions.

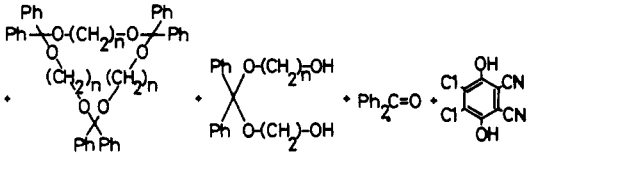
Results and Discussion

Product and Mechanistic Studies. Reaction of DDM with DDQ in the rpesence of an excess or an equimolar amount of α,ω-diols **1** in dry 1,2-dichloroethane or benzene at 20–25 °C gave three types of cyclic acetals, **2**, **3**, and **4** together with noncyclic acetals (**5**) (eq 1). This reaction



DDM DDQ 1 2 3

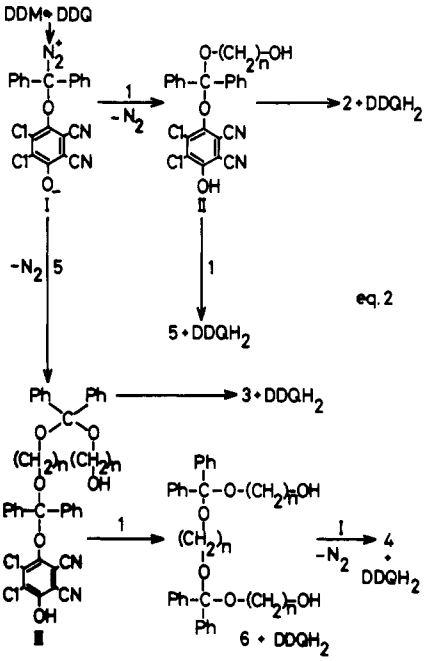
eq 1



4 5 $DDQH_2$

provided benzophenone (20%) as a byproduct and almost quantitative amounts of 2,3-dichloro-5,6-dicyanohydroquinone ($DDQH_2$). These product distributions were dependent on the chain length of α,ω-diols (Table I). The diols with short chain length such as **1a–c** gave only monomeric cyclic acetals in good yields, while the use of 1,5-pentanediol provided dimeric and a small amount of trimeric cyclic acetal together with noncyclic acetal and monomeric acetal. However, the monomeric acetals were no longer obtained in the higher homologous series for which dimeric and noncyclic acetals were obtained in moderate yields. In the case of 1,3-propanediol and 1,6-hexanediol, solvent variation brought about no essential change in the product distributions.

With respect to the formation of these cyclic and noncyclic acetals, we can describe the similar sequence of process as was pictured for the case of oligo ethylene glycols (eq 2).[5] The nucleophilic attack of diols **1** toward an



eq 2

initially formed diazonium betaine (I) provides II. Because of the strong electron withdrawal of the DDQ moiety, the diphenylmethylene site of II was most likely subject to the internal nucleophilic displacement and/or the external attack of another diol. Thus, monomeric cyclic acetals **2** and noncyclic acetals **5** can be produced by the respective internal and external acetalization process, both leaving $DDQH_2$. As to dimeric cyclic acetals **3**, it is assumed that because of the presence of two OH end groups, **5** further reacts with I and then the resulting III leads to dimeric cyclic acetals and $DDQH_2$ by the internal reaction. This assumption was confirmed by finding that the treatment of **5** with 2 equiv of DDM and DDQ gave the dimeric acetals in 60–80% yields (see Experimental Section). Similarly, trimeric cyclic acetal **4d** may be constructed by the action of I toward noncyclic acetal **6d**, possibly arising from the reaction of III and **1d**. As expected, the formation of benzophenone is responsible for the unfavorable hydrolysis of such intermediates as I, II, and III by residual water, so it is necessary to carefully dry reagents and reaction equipment.

Effects of Chain Length. Figure 1 shows a plot of yields of **2**, **3**, and **5** as a function of the number (n) of methylene units in the diols and of the number (N) of ring atoms. The lower diols **1a–c** gave only monomeric cyclic acetals of five–seven ring size in spite of the presence of three-fold excess of diols. This is indicative of the preferential ocurrence of intramolecular cycloacetalization of II prior to the attack of these diols, mainly because of the higher ring-closure probabilities for these common ring. However, on going from 1,6-hexanediol to 1,12-dodecanediol, the corresponding monomeric acetals of ring size 9–15 were no longer detected on careful analysis of the reaction mixtures. These result from the lower ring-closure reactivity of II for medium 8- to 11-membered ring region and beyond owing to the large ring strain and/or lower probabilities of cyclization.[6]

(4) Oshima, T.; Nishioka, R.; Nagai, T. *Tetrahedron Lett.* **1980**, *21*, 3919.

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(6) (a) Galli, C.; Illuminati, G.; Mandolini, L.; Tamborra, P. *J. Am. Chem. Soc.* **1977**, *99*, 2591. (b) Mandolini, L. *J. Am. Chem. Soc.* **1978**, *100*, 550.

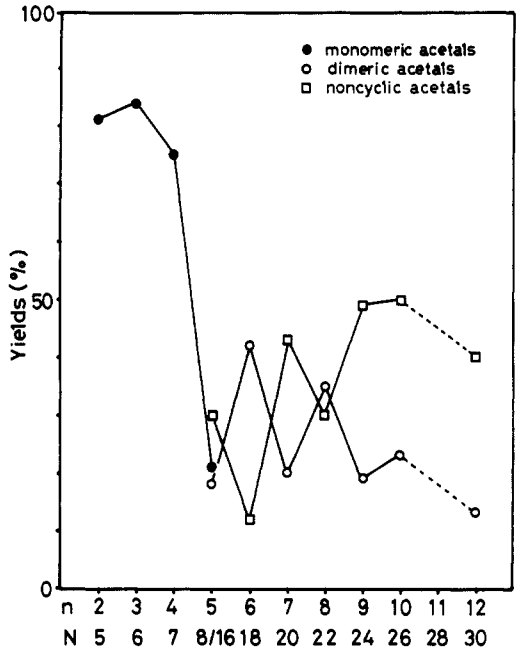

Figure 1. Yields of monomeric (**2**), dimeric (**3**), and noncyclic acetals (**5**): N = total number of atoms in ring; n = number of CH_2 groups in each polymethylene.

Here, an interesting question is raised on the ease of cycloaceatalization of **5** into **3**, because these noncyclic aceatls have a diol structure with chain length of more than 13 atoms. This can be easily answered by considering the enhancement of ring closure of a long-chain bifunctional compound by the presence of a number of groups composing the chain itself held in the form suitable for ring closure.[7] The bulky *gem*-diphenyl group located in the midst of the chain of **5** was considered as an example of a structural moiety fitting these requirements with the aid of ajacent two ether bonds.

In our previous syntheses of crown ether acetals,[5] both monomeric and dimeric cyclic aceatls were obtained together with noncyclic ones. This acetalization was successfully achieved in the glycols which formaly correspond to the α,ω-diols of 5, 8, 11, 14, and 17 methylene units. The yields of monomeric products were improved by the stepwise addition of glycols into the reaction mixture of DDM and DDQ, where free glycols are present in very low concentration relative to I (or its polymerized form). This dilution technique was applied to 1,12-dodecanediol in order to make a large-ring monomeric acetal, but no essential change was found in the product distributions (runs 12 and 13). This result implies that the intermediate II of the long-chain diol resists the intramolecular cycloacetalization and preferably undergoes the external attack of diol even if the forcing condition is particularly designed to buildup a monomeric acetal. Ultimately, the marked difference in the reaction fashion between oligo ethylene glycols and α,ω-diols may be attributed to the oxgen atom effect[8] by which transannular –CH···HC– repulsions in the polymethylene chain can be relieved.

It is of interest that the dimeric acetals **3** derived from diols with an even number of methylene units (n = 6, 8, 10) were formed in higher yield than those from diols with an odd number of methylene units (n = 5, 7, 9). The melting points of dimeric acetals also showed the similar zig–zag profiles (Figure 2). However, the opposite alternation was found in the yields of noncyclic acetals **5**, except

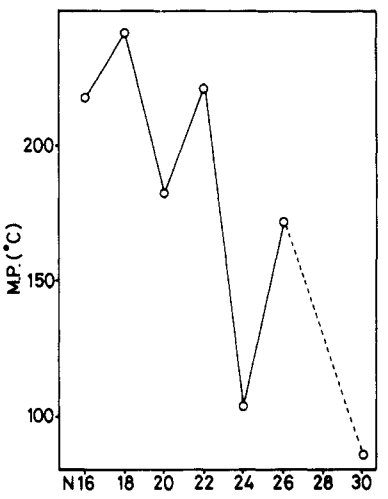

Figure 2. Melting points of dimeric acetals (**3**): N = number of ring atoms.

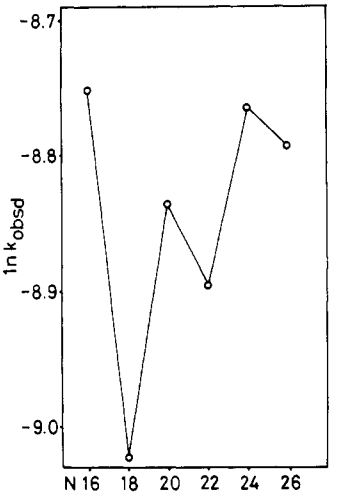

Figure 3. Rate profiles vs. ring size for the hydrolysis of dimeric acetals (**3**) at 30 °C in 95% 1,4-dioxane–0.1 N hydrochloric acid (v/v). Observed rate constants (k_{obsd}) were determined according to eq 3 and had values of 1.58×10^{-4} s^{-1} (**3d**), 1.21×10^{-4} (**3e**), 1.45×10^{-4} (**3f**), 1.37×10^{-4} (**3g**), 1.56×10^{-4} (**3h**), and 1.52×10^{-4} (**3i**).

for a small inversion in nonanediol and decanediol, strongly supporting the participation of **5** as a precursor of **3**. Such alternating effects in the yield data have been widely observed in the various cyclization reactions of bifunctional polymethylene compounds.[9-11]

Borgen[12] has already reported that *gem*-dimethyl-substituted dimeric acetals of ring size 16–24 show a similar alternation in yield profiles and melting points as our new *gem*-diphenyl-substituted ones. He explained the feature by means of conformational stabilities of the compounds with 1,3-dioxa groups. We attempted a kinetic study of acid-catalyzed hydrolysis of these dimeric acetals to make an experimental justification of the conformational stabilities. The results shown in Figure 3 strongly suggest the alternation in the conformational stabilities.

Experimental Section

Materials and instruments used were described elsewhere.

Reaction of DDM with DDQ in the Presence of α,ω-Diols. The general procedure is represented by the case of 1,5-penta-

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(12) Borgen, G. *Acta Chem. Scand., Ser. B* **1975**, *B29*, 265.

nediol. To a stirred suspention of DDQ (1.18 g, 5.2 mmol) and 1,5-pentanediol (0.54 g, 5.2mmol) in benzene (20 mL) was added dropwise over 10 min at 20–25 °C a benzene solution (10 mL) of DDM (1.0 g, 5.2 mmol). After the mixture was stirred for 2 h, $DDQH_2$ was filtered off and was washed with benzene (20 mL × 3). The filtrate parts and the washing were combined, washed with 5% aqueous sodium carbonate (10 mL × 5) and then with NaCl saturated water (10 mL × 5), dried over anhydrous sodium sulfate, and concentrated in vacuo to give a pasty residue. The residue was chromatographed on alumina (300 mesh). Elution gave monomeric acetal **2d** (296 mg, 21%), dimeric acetal **3d** (240 mg, 18%), trimeric acetal **4d** (12 mg, 0.9%), and benzophenone (140 mg, 15%) with a light petroleum–benzene mixture (1:20–1:1) and noncyclic acetal **5d** (260 mg, 30%) with benzene–methanol (100:1). In the case of 1,6-hexanediol and 1,12-dodecanediol, dimeric acetals were partly filtered off together with $DDQH_2$; however, these dimers were cleanly recovered by dissolving $DDQH_2$ in a minimum amount of acetone. The structures of monomeric, dimeric, and trimeric cyclic acetals were determined by IR, NMR, mass spectra, and elemental analyses.

2,2-Diphenyl-1,3-dioxolane (2a): mp 54–55 °C (from ether); IR (KBr) 2800, 1450, 1085, 1000 cm^{-1}; NMR ($CDCl_3$) δ 4.0 (s, 4 H, OCH_2CH_2O), 7.1–7.6 (m, 10 H, Ph); MS, *m/e* 226 (M^+). Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.68; H, 6.24.

2,2-Diphenyl-1,3-dioxane (2b): mp 113–115 °C (from ether); IR (KBr) 2970, 1450, 1100, 1005 cm^{-1}; NMR ($CDCl_3$) δ 1.7–2.0 (m, 2 H, CH_2), 4.03 (t, 4 H, OCH_2, J = 6.0 Hz), 7.1–7.7 (m, 10 H, Ph); MS, *m/e* 240 (M^+). Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.96; H, 6.72. Found: C, 79.88; H, 6.65.

2,2-Diphenyl-1,3-dioxepane (2c): mp 124–126 °C (from ether); IR (KBr) 2880, 1450, 1090, 700 cm^{-1}; NMR ($CDCl_3$) δ 1.5–1.8 (m, 4 H, CH_2CH_2), 3.6–3.9 (m, 4 H, OCH_2), 7.1–7.7 (m, 10 H, Ph); MS, *m/e* 254 (M^+). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.19; H, 7.03.

2,2-Diphenyl-1,3-dioxocane (2d): mp 41–42 °C (from ether); IR (KBr) 2920, 1440, 1090, 1025 cm^{-1}; NMR ($CDCl_3$) δ 1.5–1.8 (m, 6 H, $(CH_2)_3$), 3.55 (t, 4 H, OCH_2, J = 6.3 Hz), 7.0–7.6 (m, 10 H, Ph); MS, *m/e* 268 (M^+). Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.79; H, 7.49.

2,2,10,10-Tetraphenyl-1,3,9,11-tetraoxacyclohexadecane (3d): mp 217–218 °C (from benzene); IR (KBr) 2930, 1440, 1080, 1020 cm^{-1}; NMR ($CDCl_3$) δ 1.2–1.9 (m, 12 H, $(CH_2)_3$), 3.23 (t, 8 H, OCH_2, J = 6.0 Hz), 7.0–7.7 (m, 20 H, Ph); MS, *m/e* 536 (M^+). Anal. Calcd for $C_{36}H_{40}O_4$: C, 80.56; H, 7.51. Found: C, 80.60; H, 7.50.

2,2,11,11-Tetraphenyl-1,3,10,12-tetraoxacyclooctadecane (3e): mp 241–243 °C (from $CHCl_3$); IR (KBr) 2930, 1445, 1090, 1020 cm^{-1}; NMR ($CDCl_3$) δ 1.3–1.9 (m, 16 H, $(CH_2)_4$), 3.21 (t, 8 H, OCH_2, J = 7.5 Hz), 7.1–7.6 (m, 20 H, Ph); MS, *m/e* 564 (M^+). Anal. Calcd for $C_{38}H_4O_4$: C, 80.81; H, 7.85. Found: C, 80.63; H, 7.86.

2,2,12,12-Tetraphenyl-1,3,11,13-tetraoxacycloeicosane (3f): mp 181–183 °C (from benzene); IR (KBr) 2930, 1445, 1090, 1025 cm^{-1}; NMR ($CDCl_3$) δ 1.2–1.8 (m, 20 H, $(CH_2)_5$), 3.21 (t, 8 H, OCH_2, J = 6.6 Hz), 7.2–7.7 (m, 20 H, Ph); MS, *m/e* 592 (M^+). Anal. Calcd for $C_{40}H_{48}O_4$: C, 81.04; H, 8.16. Found: C, 81.05; H, 8.14.

2,2,13,13-Tetraphenyl-1,3,12,14-tetraoxacyclodocosane (3g): mp 220–222 °C (from benzene); IR (KBr) 2940, 1445, 1090, 1030 cm^{-1}; NMR ($CDCl_3$) δ 1.1–1.9 (m, 24 H, $(CH_2)_6$), 3.23 (t, 8 H, OCH_2, J = 6.3 Hz), 7.0–7.6 (m, 20 H, Ph); MS, *m/e* 620 (M^+). Anal. Calcd for $C_{42}H_{52}O_4$: C, 81.25; H, 8.44. Found: C, 81.43; H, 8.45.

2,2,14,14-Tetraphenyl-1,3,13,15-tetraoxacyclotetracosane (3h): mp 103–104 °C (from $CHCl_3$); IR (KBr) 2920, 1445, 1090, 1020 cm^{-1}; NMR ($CDCl_3$) δ 1.2–1.9 (m, 28 H, $(CH_2)_7$), 3.19 (t, 8 H, OCH_2, J = 6.8 Hz), 7.1–7.7 (m, 20 H, Ph); MS, *m/e* 648 (M^+). Anal. Calcd for $C_{44}H_{56}O_4$: C, 81.44; H, 8.70. Found: C, 81.31; H, 8.71.

2,2,15,15-Tetraphenyl-1,3,14,16-tetraoxacyclohexacosane (3i): mp 171–172 °C (from $CHCl_3$); IR (KBr) 2930, 1450, 1085, 1020 cm^{-1}; NMR ($CDCl_3$) δ 1.1–1.8 (m, 32 H, $(CH_2)_8$), 3.20 (t, 8 H, OCH_2, J = 6.2 Hz), 7.1–7.6 (m, 20 H, Ph); MS, *m/e* 676 (M^+). Anal. Calcd for $C_{46}H_{60}O_4$: C, 81.61; H, 8.93. Found: C, 81.79; H, 8.99.

2,2,17,17-Tetraphenyl-1,3,16,18-tetraoxacyclotriacosane (3j): mp 85–86 °C (from $CHCl_3$); IR (KBr) 2920, 1445, 1090, 1020 cm^{-1}; NMR ($CDCl_3$) δ 1.1–1.8 (m, 40 H, $(CH_2)_{10}$), 3.20 (t, 8 H, OCH_2, J = 6.5 Hz), 7.1–7.7 (m, 20 H, Ph); MS, *m/e* 733 (M^+). Anal. Calcd for $C_{50}H_{68}O_4$: C, 81.92; H, 9.35. Found: C, 81.62; H, 9.37.

2,2,10,10,18,18-Hexaphenyl-1,3,9,11,17,19-hexaoxacyclotetracosane (4d): mp 76–79 °C (from benzene–pentane); IR (KBr) 2940, 1450, 1080, 1020 cm^{-1}; NMR ($CDCl_3$) δ 1.1–1.9 (m, 18 H, $(CH_2)_3$), 2.9–3.4 (m, 12 H, OCH_2), 6.9–7.7 (m, 30 H, Ph); MS, *m/e* 804 (M^+). Anal. Calcd for $C_{54}H_{60}O_6$: C, 80.56; H, 7.51. Found: C, 80.60; H, 7.59.

The resinous noncyclic acetals showed the characteristic IR absorption assignable to hydroxyl groups (3350–3370 cm^{-1}) and ethereal bonds (1000–1200 cm^{-1}). The NMR spectra of these compounds revealed the presence of aromatic rings ($CDCl_3$, δ 7.1–7.6 ppm), hydroxyl groups (2–3 ppm), and three kinds of methylenes respectively assignable to central methylene moieties (1.2–1.8 ppm), OCH_2 (3.1–3.3 ppm), and CH_2OH (3.5–3.7 ppm). It is difficult to purify these resinous products so that further structural evidence was offered by the conversion into dimeric acetal when treated with excess DDM and DDQ (vide infra).

Reaction of DDM with DDQ Followed by Addition of 1,12-Dodecanediol. To a stirred suspension of DDQ (1.18 g, 5.2 mmol) in benzene (20 mL) was added dropwise over 10 min at 20 °C a benzene solution (10 mL) of DDM (1.0 g, 5.2 mmol). Introduction of an equivalent amount of powdered diol was made step by step over 1 h, causing gradually the precipitation of $DDQH_2$. After 1 h of stirring, usual workup of the reaction mixture provided **3j** (0.35 g, 18%) and **5j** (0.65 g, 44%).

Conversion of Noncyclic Acetals 5 into Dimeric Cyclic Acetals 3. This conversion was demonstrated in the case of noncyclic acetal **5g** of 1,8-octanediol by the use of 2 equiv of DDM and DDQ. To a stirred suspension of DDQ (0.59 g, 2.6 mmol) and **5g**, (0.6 g, 1.3 mmol) in benzene (10 mL) was added dropwise over 10 min at 20 °C a benzene solution (5 mL) of DDM (0.5 g, 2.6 mmol). After the mixture was stirred for 2 h, usual workup gave **2g** in 80% yield. The successful conversion of other noncyclic acetals also provided the corresponding dimeric acetals in over 60–80% yields.

Acid-Catalyzed Hydrolysis of Dimeric Actals 3d–i. Kinetic measurements were made by monitoring the decrease in the respective absorption of **3d–i** at 254 nm by means of high-performance liquid chromatography with methanol as an eluent.

A pseudo-first-order treatment of these analytical data gave the observed rate constants (k_{obsd}) for each of **3d–i** according to eq 3.

$$-\frac{d[3]}{dt} = k[H^+][3] = k_{obsd}[3] \quad (3)$$

Registry No. **1a**, 107-21-1; **1b**, 504-63-2; **1c**, 110-63-4; **1d**, 111-29-5; **1e**, 629-11-8; **1f**, 629-30-1; **1g**, 629-41-4; **1h**, 3937-56-2; **1i**, 112-47-0; **1j**, 5675-51-4; **2a**, 4359-34-6; **2b**, 786-03-8; **2c**, 77130-20-2; **2d**, 91491-62-2; **3d**, 91491-63-3; **3e**, 91491-64-4; **3f**, 91491-65-5; **3g**, 91491-66-6; **3h**, 91491-67-7; **3i**, 91491-68-8; **3j**, 91491-69-9; **4d**, 91491-70-2; **5d**, 91491-71-3; **5e**, 91491-72-4; **5f**, 91491-73-5; **5g**, 91491-74-6; **5h**, 91491-75-7; **5i**, 91491-76-8; **5j**, 91491-77-9; DDM, 883-40-9; DDQ, 84-58-2.

Ester Aminolysis in the Presence of Alkylammonium Carboxylate Reversed Micelles. On the Nature of the Rate-Limiting Step

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We have been interested in studying the mechanisms of reactions catalyzed by the reversed micelles[1] of alkyl-

(1) Reversed micelles are aggregates of surfactants in nonaqueous solvents. The central part or "core" of the aggregate is made of the hydrophilic groups of the surfactant and is the site of solubilization and chemical reactions.[2,3]

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