Three- and Four-Carbon Elongating Ring Expansion of Cyclic Acetals to Medium-Sized Dioxacycloalkenones. Use of the Intramolecular Formation of Oxonium Ylides

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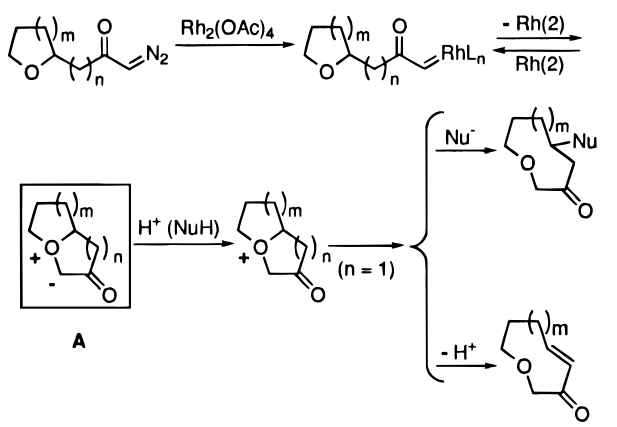
The Rh(II)-catalyzed reaction of 2-(3′-diazo-2′-oxopropyl)-2-methyldioxolane (**1**) in the presence of a protic nucleophile (NuH) such as AcOH resulted in effective ring enlargement to give the 8-membered 3-acetoxydioxocanone **4a** (41%) and dioxocan-2-en-1-one **3** (46%). Similar treatment of 2-(4′-diazo-3′-oxobutyl)-2-methyldioxolane (**9**) with AcOH gave 4-acetoxydioxonanone **10** (67%), which was readily hydrolyzed on silica gel to a tautomeric mixture of hydrolysis products **16a** and **16b** (total yield 46%). In contrast, similar treatment of 2-(5′-diazo-4′-oxopentyl)-2-methyldioxolane (**19**) gave 2,5-dioxa-1-methyldecalin-7-one (**20**, 24%), and the yield increased to 61% in the absence of AcOH, by Stevens rearrangement. The reaction of 1,3-dioxane homologues **26** and **31** gave similar results. All of these reactions can be explained in terms of the intermediacy of bicyclooxonium ylides, which undergo either a Stevens rearrangement or, after protonation by a NuH, ring enlargement through release of the strain of the bicyclic ylides. Evidence of the reversible formation of oxonium ylides is also provided.

Ethereal oxonium ylides continue to elude spectroscopic identification.[1] Nevertheless, their presence has been frequently proposed and verified indirectly[2] in carbene reactions in which singlet carbenes are properly generated in ethereal solvents or in the presence of ethereal substrates.[3] However, in comparison with carbonyl ylides, which have been extensively studied,[4] the use of ethereal ylides for synthetic purposes has been limited. This lack is mainly due to the lability of the ylides, which exist as extremely short-lived components in equilibrium with the parent carbenes. In an effort to further develop the synthetic utility of ethereal oxonium ylides,[5] we recently designed[6] an intramolecular reaction of carbenes with cyclic ethereal substituents to form ethereal bicyclooxonium ylides, the kinetically formed products, which is followed by release of the strain of the constrained bicyclic intermediates to give open-ring products. This ring-enlargement reaction may be of synthetic interest (Scheme 1). We adopted three conditions for this reaction: (1) use of medium-sized cyclic ethers as intramolecular nucleophiles toward carbenes; (2) diazo ketone side chains whose transition-metal carbenoids can form entropically favorable, albeit short-lived, 5- and 6-membered oxonium ylide intermediates,[7] and ylide formation must be followed by fast, irreversible reactions such as protonation or intramolecular proton shift; and (3) the presence of ylide-stabilizing groups, such as carbonyl groups. In this regard, Clark and his group[8] have extensively studied other types of ring expansion, i.e., (2,3)-sigmatropic rearrangement of vinyltetrahydrofuranonium ylide systems,[9] which are synthetically interesting.

Scheme 1



The limitation we encountered with diazocarbonyl-substituted cyclic ether systems was the length of the diazocarbonyl side chain:[6] as the chain was elongated to more than $n = 1$, the desired ring enlargement did not take place and a ring-switching reaction took place instead. We presumed that if a cation-stabilizing group was positioned adjacent to the bridgehead carbon of both the ylides and oxonium ions, cleavage of the central bond would be facilitated. The present study deals with cyclic

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(1) (a) Padwa, A.; Hornbuckle, S. F. *Chem. Rev.* **1991**, *91*, 263. (b) Tomioka, H.; Kobayashi, N.; Murata, S.; Ohtawa, T. *J. Am. Chem. Soc.* **1991**, *113*, 8771.

(2) (a) Kirmse, W.; Kapps, M. *Chem. Ber.* **1968**, 994. (b) Ando, W.; Kondo, S.; Nakayama, K.; Ichibori, K.; Kohoda, H.; Yamato, H.; Imai, I.; Nakaido, S.; Migita, T. *J. Am. Chem. Soc.* **1972**, *94*, 3870. (c) Friedrich, K.; Jansen, U.; Kirmse, W. *Tetrahedron Lett.* **1985**, *26*, 193. (d) Kirmse, W.; Chiem. P. V. *Ibid.* **1985**, *26*, 197.

(3) (a) Iwamura, H.; Imahasi, Y. *Tetrahedron Lett.* **1975**, 1401. (b) Olah, G. A.; Doggweiler, H.; Felberg, J. D. *J. Org. Chem.* **1984**, *49*, 2116. (c) Baird, M. S.; Baxter, A. G. W.; Hoorter, A.; Jefferson, I. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2575. (d) West, F. G.; Eberlein, T. H.; Tester, R. W. *J. Org. Chem.* **1992**, *57*, 3479. (e) Doyle, M. P.; Griffin, J. H.; Chinn, M. S.; van Leusen, D. *J. Org. Chem.* **1984**, *49*, 1917. (f) Pirrung, M. C.; Brown. W. L.; Rege, S.; Laughton, P. *J. Am. Chem. Soc.* **1991**, *113*, 8561.

(4) (a) Padwa, A.; Hornbuckle, S. F. *Chem. Rev.* **1991**, *91*, 263. (b) Padwa, A.; Krumpe, K. E. *Tetrahedron.* **1992**, *48*, 5385.

(5) Oku, A. *J. Synth. Org. Chem. Jpn.* **1995**, 18.

(6) Oku, A.; Ohki, S.; Yoshida, T.; Kimura, K. *J. Chem. Soc., Chem. Commun.* **1996**, 1077.

(7) (a) Hamaguchi, M.; Ibata, T. *Tetrahedron Lett.* **1974**, 4475. (b) Ibata, T.; Toyoda, J. *Bull. Chem. Soc. Jpn* **1985**, *58*, 1787.

(8) For examples of the [2,3]-sigmatropic rearrangement of oxonium ylides, see: (a) Clark, J. S.; Dossetter, A. G.; Whittingham, W. G. *Tetrahedron Lett.* **1996**, *37*, 5603. (b) Clark, J. S.; Whitlock, G. A. *Tetrahedron Lett.* **1994**, *35*, 6381.

(9) Pirrung, M. C.; Werner, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 6060.

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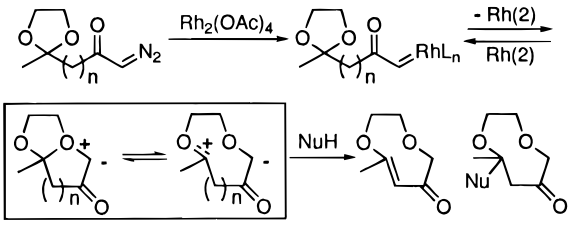
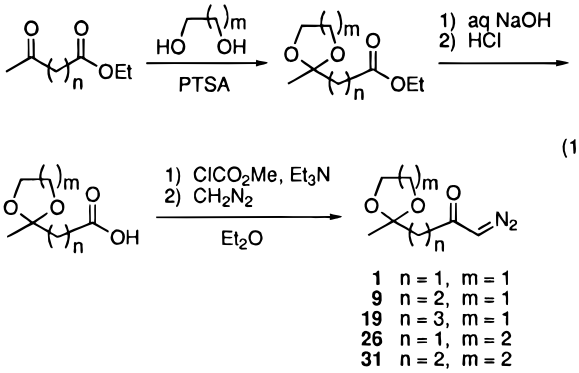
Scheme 2



acetal systems instead of cyclic ethers in the hope of demonstrating the anticipated bond-cleaving effect (Scheme 2).

Results and Discussion

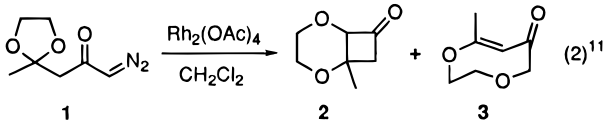
Preparation of Diazocarbonyl-Substituted Cyclic Acetals. Diazocarbonyl-substituted cyclic acetals **1**, **9**, **19**, **26**, and **31** were prepared from keto esters as reported elsewhere (eq 1).[10, 17−19]



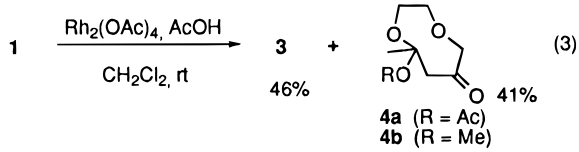
(1)

1 n = 1, m = 1
9 n = 2, m = 1
19 n = 3, m = 1
26 n = 1, m = 2
31 n = 2, m = 2

Rh(II)-Catalyzed Reaction of 2-(3′-Diazo-2′-oxopropyl)-2-methyldioxolane (1) in the Presence of Acetic Acid. Roskamp and Johnson[11] first reported that the Rh-catalyzed reaction of **1** in benzene yielded bicyclo[4.2.0]-2,5-dioxaoctanone **2** (68%) together with a small amount of 4,7-dioxocan-2-en-1-one (**3**, 16%) (eq 2). A



(2)[11]

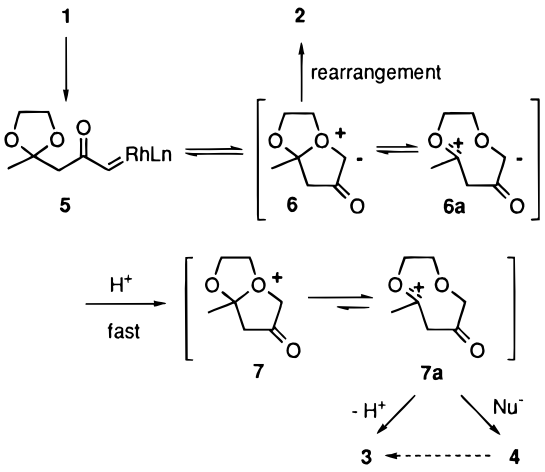


(3)

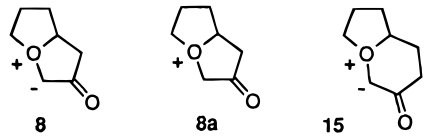
4a (R = Ac)
4b (R = Me)

similar 1,2-shift in oxonium ylides has been reported by Brogan and co-workers.[12] We thought that the ring-enlarged **3** would become a major product if the formation of Stevens rearrangement product **2** could be suppressed by protonating the plausible bicyclooxonium ylide **6** with

Scheme 3

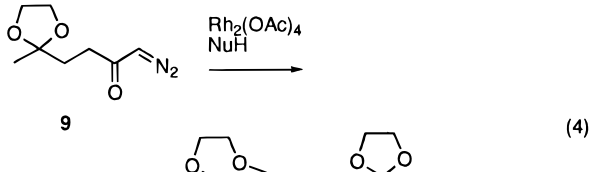


a protic nucleophile (NuH). Indeed, when the analogous reaction was carried out in CH_2Cl_2 in the presence of acetic acid, ring-enlargement products **3** and **4a** were formed in high yields (46 and 41%, respectively, overall 87%) (eq 3). Thus, acetic acid dramatically facilitated the ring-enlargement process. This facilitation is assumed to be due to (1) faster protonation of ylide **6** than its rearrangement to **2** (Scheme 3) and (2) stabilization of bicyclooxonium ylide **6** and its ring-opened monocyclic zwitterion structure **6a** by charge-delocalization in two-oxygen systems and similar stabilization of protonated oxonium ion **7** and its ring-opened structure **7a** (Scheme 3). In this sense, the ring-opening of **7** should be facilitated more than that of the related tetrahydrofuranonium system **8a**.[13]



Even a weak acid such as methanol can protonate ylide **6** before rearrangement occurs. Thus, when methanol was used in place of acetic acid, a similar ring-enlargement reaction gave **4b** (47%) but not **3**. This indicates that dioxolane ylide **6** is longer-lived than the tetrahydrofuran ylide **8**[6] and can be protonated by methanol whereas **8** cannot.

Reaction of 2-(4′-Diazo-3′-oxobutyl)-2-methyldioxolane (9). On the basis of the anticipated facilitation of the enlargement of two-oxygen systems, we expected that the elongation of the diazocarbonyl side chain by a one-methylene unit would also enable a similar reaction to occur. Indeed, the analogous reaction of dioxolanyl diazo ketone **9** in the presence of acetic acid produced ring-enlargement product **10** (67%) in addition to nonrearrangement product **11** (6%) (eq 4).

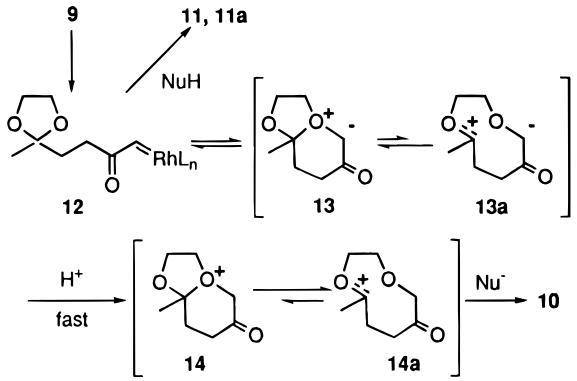


(4)

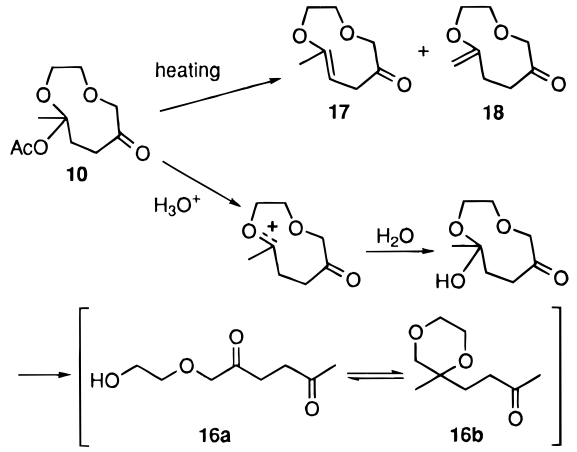
10 (Nu = OAc) **11** (Nu = OAc)
11a (Nu = OMe)

(10) Thus, L.; Smeets, F. L. M.; Cillissen, P. J. M.; Harmsen, J.; Zwanenburg, B. *Tetrahedron.* **1980**, 36, 2141.
(11) Roskamp, E. J.; Johnson, C. R. *J. Am. Chem. Soc.* **1986**, *108*, 6062.
(12) Brogan, J. B.; Bauer, C. B.; Rogers, R. D.; Zercher, C. K. *Tetrahedron Lett.* **1996**, *37*, 5053.
(13) Kamada, T.; Ge-Quing, Abe, M.; Oku, A. *J. Chem. Soc., Perkin Trans. 1* **1996**, 413.

Scheme 4



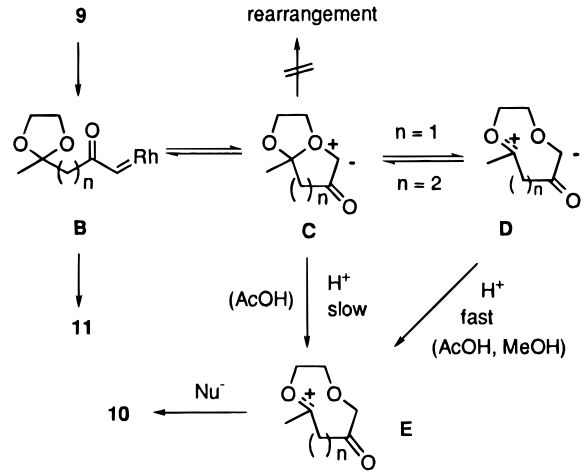
Scheme 5



In contrast to the reaction of **1**, the formation of a small amount of **11** from **9** implies that cyclization of the linear carbenoid **12** to the 1,7-dioxabicyclo[4.3.0]nonanone-type oxonium ylide **13** may not be as favorable as that of **5** to **6**. Therefore, a minor amount of **12** that is formed either directly from **9** or reversibly from the ylide[14] could be trapped by a protic nucleophile (NuH) to give **11** or **11a** (Scheme 4). Most of **12** underwent cyclization to form ylide **13** and finally resulted in the formation of **10**, which is analogous to the result with **6**. In a previous study in which we postulated the formation of a 1-oxabicyclo[4.3.0]-octanone-type oxonium ylide (**A** in Scheme 1, $m = 1$, $n = 2$),[6] the ylide did not undergo cleavage of the central bridging bond, in contrast to the behavior of **13**. This difference can be attributed to the stabilizing effects of the second acetal oxygen atoms in ylide **13** (or its zwitterion **13a**) and oxonium ion **14** (or **14a**).

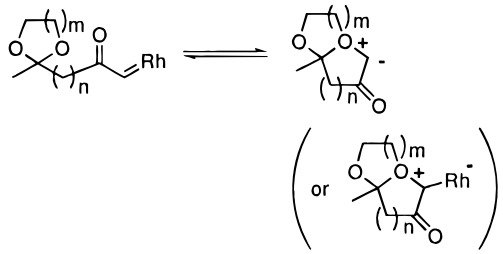
Acetoxydioxocanone **10** is labile under weakly acidic conditions, such as in silica gel chromatography. For example, under treatment with aqueous MeOH and even on a silica gel TLC plate, **10** undergoes hydrolysis to give an equilibrium mixture of **16a** and its isomer **16b** (Scheme 5).[15] The structure of **16a** was determined by ^{1}H-NMR after its transformation to the corresponding silyl ether. Compound **10** is also thermally labile (e.g., under VPC analysis conditions) and is readily trans-

Scheme 6



formed into a mixture of the endo- and exo-isomers of cyclic enol ether **17** and **18**.

In the presence of MeOH, the outcome of the reaction of **9** was different from that of **1** (*vide supra*). The nonrearrangement product **11a** was obtained exclusively instead of the expected ring-enlargement products. This observation provides additional evidence concerning the reversibility of oxonium ylide formation between keto-carbenoids and ethereal oxygen atoms (eq 5).[14,16] In the



(5)

reaction of **9**, MeOH traps the *initially* produced linear carbenoid **12** in a nucleophilic manner and prevents its cyclization. A strong acid but a weak nucleophile, such as AcOH, waves the protonation of **12** to help its cyclization. Our rationale for explaining this discrepancy is shown in Scheme 6. When $n = 1$, carbenoid **B** forms the bicyclic ylide **C**, which, due to its strain energy, prefers to exist as the monocyclic zwitterion structure **D**. We presume that **D** can be protonated much faster than **C** due to its charge separation, thereby enabling protonation even using methanol. When $n = 2$, the ylide may prefer the less-strained and electronically more-stable bicyclic form **C** to the monocyclic form **D**. The rate of protonation of **C** may be slower than the rate of the reversion back to carbenoid **B**. The subsequent formation of products **10** and **11** can be explained in terms of these intermediates.[6]

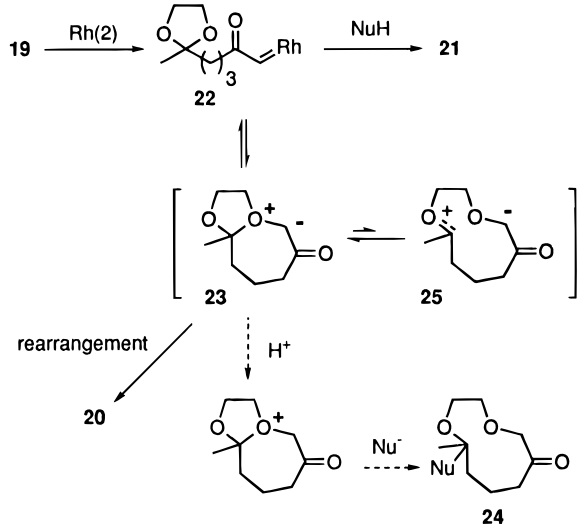
Reaction of 2-(5′-Diazo-4′-oxopentyl)-2-methyldioxolane (19). The reaction of **19**, which has a longer diazocarbonyl side chain than **1** by two methylene units, in the presence of nucleophiles such as MeOH, AcOH, *p*-$NO_2C_6H_4OH$, and PhCOOH was also examined. Two products identified as 5′-substituted 2-methyl-2-(4′-oxopentyl)dioxolane **21** and 2,5-dioxa-1-methyldecahydronaphthalen-7-one (**20**) were formed. Decalone **20** was pro-

(14) (a) Naito, I.; Oku, A.; Otani, N.; Fujiwara, Y.; Tanimoto, Y. *J. Chem. Soc., Perkin Trans. 2* **1996**, 725. (b) West, F. G.; Eberlein, T. H.; Tester, R. W. *J. Chem. Soc., Perkin Trans. 1* **1993**, 2857.

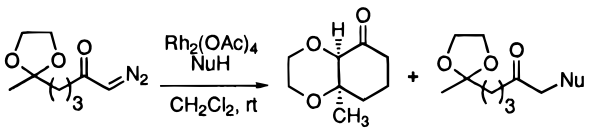
(15) We identified **16a** and **16b** by silylation. The mixture of **16a** and **16b** was treated with dimethyl-*tert*-butylsilyl chloride and imidazole in dimethylformamide at room temperature for 18 h. 9-[(*tert*-Butyldimethylsilyl)oxy]-7-oxanonane-2,5-dione was obtained in 46% yield.

(16) Very recently, Sueda and Ochiai reported evidence of reversible ylide formation between free alkylidenecarbenes and ethers. Sueda, T.; Nagaoka, T.; Goto, S.; Ochiai, M. *J. Am. Chem. Soc.* **1996**, *118*, 10141−10149.

Scheme 7



duced by Stevens rearrangement (eq 6), and its yield increased to 61% in the absence of a nucleophile.

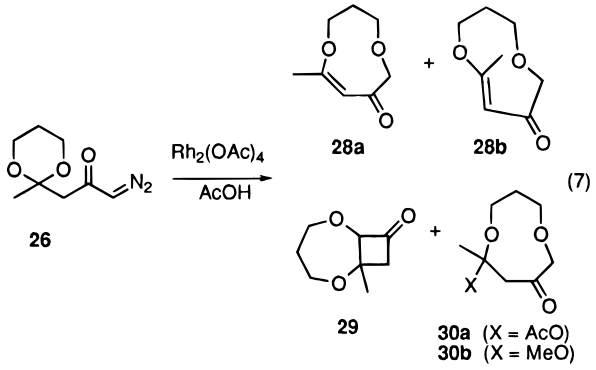


NuH:	20	21
none	61%	–
MeOH	6%	53%
AcOH	24%	41%
$PhCO_2H$	47%	24%

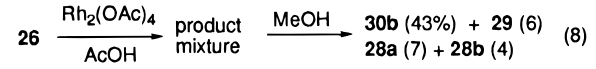
(6)

Although the anticipated ring-enlargement product **24** was not obtained, the formation of **20** as the major product unequivocally supports the intermediacy of bicyclo[5.3.0]dioxadecanone-type oxonium ylide **23** as the key intermediate that possesses a less-strained bicyclo-[5.3.0] structure (Scheme 7). As noted in Scheme 6, ylide **23** (= **C**, $n = 3$) may prefer a less strained and more stable bicyclic structure to zwitterion structure **25** and, therefore, undergoes a rapid Stevens rearrangement to the less-strained decalone **20** much faster than protonation by a strong acid such as benzoic acid. The reversible interconversion of **23** to **22** is also possible, and the formation of **21** from **22** seems to be dependent on the nucleophilicity of the NuH rather than the acidity.

Reaction of 2-(3′-diazo-2′-oxopropyl)-2-methyl-1,3-dioxane (26). An important factor in ylide formation is the nucleophilicity of the acetal oxygen atom. In general, the nucleophilicity of cyclic ethers varies in the order THF > THP > Et_2O, and we assume a similar order of nucleophilicity with cyclic acetals in that 1,3-dioxane will be next to 1,3-dioxolane. In addition, adoption of a 1,3-dioxane ring rather than a dioxolane ring will enable a larger ring-expansion reaction, thereby extending the synthetic utility of the reaction. In this regard, the analogous reaction of the dioxane-substituted diazo ketone **26** in the presence of acetic acid was examined, and we found that an isomeric mixture of ring-enlargement products **28a**(cis) and **28b**(trans) (overall 55%) was formed in addition to the Stevens rearrangement product **29** (6%) (eq 7). In the absence of AcOH, the amount of enlargement product **28b** decreased to 10% (**28a** was not formed), whereas **29** increased to 50%. In the presence



(7)



(8)

of MeOH (instead of AcOH), **29** (47%) was the major product in addition to the ring-enlargement products **30b** (X = MeO, 4%) and **28b** (6%). When MeOH was added to the reaction mixture immediately after the reaction with AcOH was complete, the yield of ring-enlargement product **30b** increased to 43% and compounds **28a** (7%), **28b** (4%), and **29** (6%) were also present (eq 8). These findings indicate that protonation of the intermediate ylide **27** or **27a** is essential to suppress rearrangement to **29** (Scheme 8).

The mechanisms for the formation of the two isomeric products **28a** and **28b** appear to be different, on the basis of the following observations: (1) eq 8 indicates that the major product **30a** is labile enough to react with MeOH, and (2) in the absence of a NuH, enone **28b** (10%) was the only enlargement product besides rearrangement product **29**, indicating that **28b** must be formed by an intramolecular proton shift but not via intermediate **30**. This result also indicates that in the absence of a NuH ylide **27** mostly undergoes Stevens rearrangement. Therefore, the formation of **28a** in the presence of AcOH may follow a different route, such as via the elimination of labile intermediate **30a** (X = AcO).

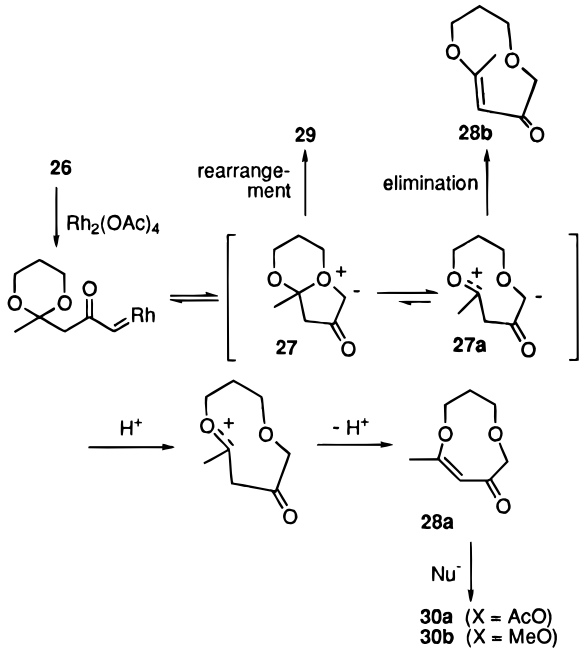
Reaction of 2-(4′-Diazo-3′-oxobutyl)-2-methyl-1,3-dioxane (31). Elongation of the diazoalkyl side chain of the dioxane series also disfavored the expected enlargement reaction as with the dioxolane series **9** and **19**. Thus, when **31** was treated under analogous conditions in the presence of AcOH, 10-hydroxy-7-oxadecane-2,5-dione **35** (25%) was obtained in addition to the Stevens rearrangement product **33** (12%) and the non-rearranged product **34** (10%) (eq 9). The expected ring-enlargement product **36a** was not obtained. When MeOH was used in place of AcOH, ring-enlargement product **36b** (X = OMe) (10%) was obtained in addition to **34** (34%); when a mixture of AcOH and MeOH was used, **36b** (12%), **35** (13%), **33** (7%), **34** (7%), and its MeO-derivative (15%) were obtained. In the absence of nucleophiles, **33** was the only product isolated. Although ring-enlargement products were not isolated with AcOH, **35** was evidently formed from the ring-enlargement intermediate **36a**, which in turn was derived from **32a** (Scheme 9).

The rearrangement product **33** was labile under acidic conditions and quantitatively gave the ring-opened cyclopentenone **37** (eq 10).

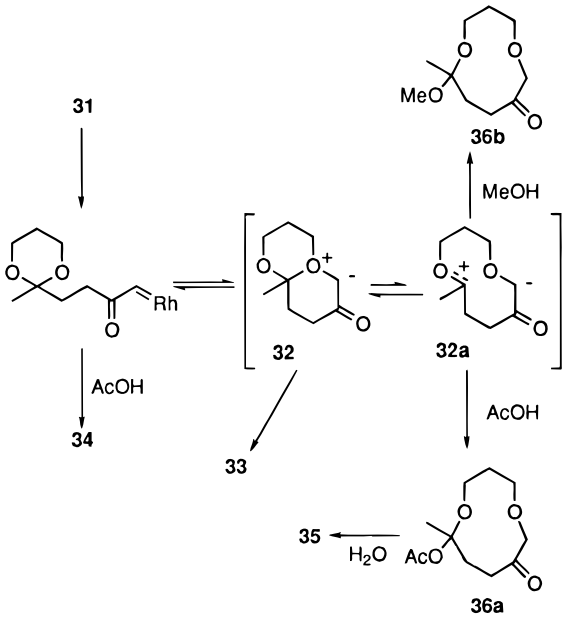
Conclusions

The expected ring-enlargement reaction (Scheme 2) was realized in four of the systems examined (**1**, **9**, **26**,

Scheme 8

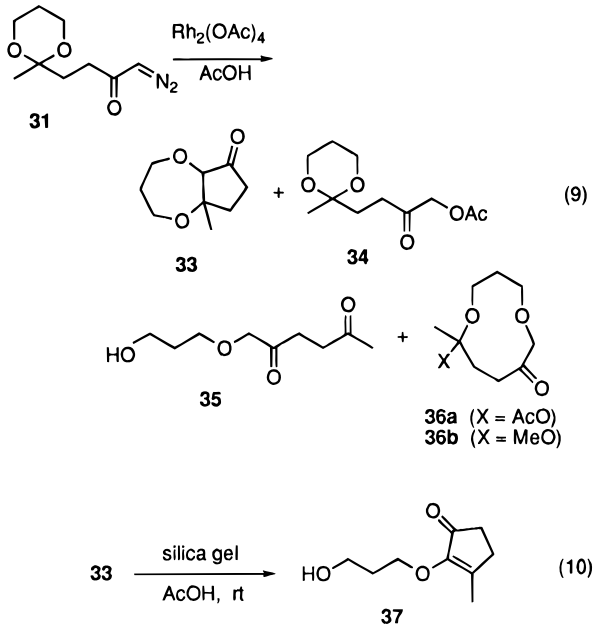


Scheme 9



and **31**) but was unsuccessful with substrate **19**. The formation of strained bicyclooxonium ylide intermediates (e.g., **C** in Scheme 6) and the stability of both the ylides and their ring-opened monocyclic zwitterion (e.g., **D** in Scheme 6) seem to be the dominant factors in facilitating the ring-enlargement reaction. The presence of the second oxygen atom in the acetal ring evidently stabilizes the zwitterion structure sufficiently to enable enlargement of the bicyclo[3.4.0]- and [4.4.0]-ylide systems **13** and **32**, but not that of the corresponding tetrahydrofuranyl (**15**) and tetrahydropyranyl systems.[6]

To summarize, when AcOH is adopted as a nucleophile and acid, the product ratios can be adequately explained by the equilibrium between **B** and **C** for open chain vs other products and between **C** and **D** for Stevens rearrangement products vs ring-enlargement products (Scheme 6 and also Schemes 3, 4, and 7−9). When one adopts MeOH, which is a weaker acid and a stronger nucleophile than AcOH, the reaction behavior of the rhodium carbenoids can be classified into two types according to the length of the side chain, i.e., (a) $n = 1$ for **1** and **26** and (b) $n = 2$ (or 3) for **9**, **19**, and **31**. Thus, with **1** or **26** ($n = 1$), strained bicyclic ylide **C** is formed faster than with $n = 2$, and this undergoes ring opening to zwitterion **D** faster than the reversible reaction, due to strain release, and D is protonated by MeOH. With **9** or **31** ($n = 2$), a less-strained bicyclic ylide is formed more slowly than with $n = 1$ and, therefore, the open-chain carbenoids **B** are trapped by the strong nucleophile MeOH before cyclization. In addition, even after **C** is formed, a reversible reaction from **C** to **B** occurs in competition with other reactions, which are slower than those with $n = 1$ due to the lower strain of **C**, and **B** is trapped by MeOH. However, the effect of ring-size (dioxolane vs dioxane) on the reversible process between open-chain carbenoid (e.g., **B**) and bicyclic ylide (e.g., **C**) is not as significant as the side-chain effect.



Using the present method, similar ring-enlargement reactions may be possible with other diazoalkyl-substituted cyclic acetals with rings larger than 1,3-dioxane, such as dioxepanes and dioxocanes, and several medium-sized dioxacycloalkanone derivatives may become available through the generation of bicyclo[n.3.0]- and [*n*.4.0]-oxonium ylide intermediates ($n > 3$).

Experimental Section

General Methods. ^{1}H and ^{13}C NMR spectra were expressed in ppm (δ) using residual $CHCl_3$ (δ 7.26) and $CDCl_3$ (δ 77.00) as the internal standard. Flash column chromatography was performed using silica gel (Wakogel C-300) or alumina (Merck aluminum oxide 90 active basic). Solvents were dried and distilled before use. Dirhodium tetraacetate was dried in vacuo before use. HRMS analyses were performed on most of the key products (liquid) instead of elemental analyses.

Preparation of Diazo Ketones. Diazo ketones **1** and **26** were prepared from ethyl acetoacetate, **9** and **31** from ethyl 4-oxo pentanoate, and **19** from ethyl 5-oxohexanoate according to eq 1 by utilizing conventional methods: i.e., acetalization,[17] alkaline hydrolysis,[18] methoxycarbonylation,[19] and diazom-

(17) Daignault, R. A.; Eliel, E. L. *Organic Syntheses* **1973**, *Col. Vol. 5*, 303.

(18) (a) Johnson, J. R.; Hanger, F. D. *Org. Synth.* **1941**, *Col. Vol. 1*, 351. (b) Warren, C. K.; Weedon, B. C. L. *J. Chem. Soc.* **1958**, 3972.

ethylation.[19] Overall yields of diazo ketones from the corresponding starting esters were **1** (44%), **9** (52%), **19** (54%), **26** (48%), and **31** (41%).

Spectroscopic data of diazo ketones and the corresponding precursors are as follows.

2-[(Ethoxycarbonyl)methyl)-2-methyldioxolane: ^{1}H NMR (300 MHz, $CDCl_3$) 1.19 (t, J = 7.2 Hz, 3H), 1.42 (s, 3H), 2.59 (s, 2H), 3.90 (s, 4H), 4.07 (q, J = 7.2 Hz, 2H); IR (liquid film) 1740 (s) cm^{-1}. **2-(Carboxymethyl) analogue:** ^{1}H NMR (300 MHz, $CDCl_3$) 1.48 (s, 3H), 2.69 (s, 2H), 3.97 (s, 4H), 10.15 (brs, 1H); IR (liquid film) 2400−3400 (br), 1720 (s) cm^{-1}.

2-(3′-Diazo-2′-oxopropyl)-2-methyldioxolane (1): ^{1}H NMR (300 MHz, $CDCl_3$) 1.39 (s, 3H), 2.63 (s, 2H), 3.94−3.97 (m, 4H), 5.46 (s, 1H); ^{13}C NMR (75.6 MHz, $CDCl_3$) 24.2, 50.5, 55.6, 64.6, 107.8, 190.8; IR (liquid film) 2100 (s), 1640 (s) cm^{-1}.

2-[2′-(Ethoxycarbonyl)ethyl]-2-methyldioxolane: ^{1}H NMR (300 MHz, $CDCl_3$) 1.24 (t, J = 7.2 Hz, 3H), 1.31 (s, 3H), 2.00 (d, J = 7.5 Hz, 1H), 2.02 (d, J = 7.8 Hz, 1H), 2.36 (d, J = 7.8 Hz, 1H), 2.40 (d, J = 7.5Hz, 1H) 3.90−3.95 (m, 4H), 4.12 (q, J = 7.2 Hz, 2H); IR (liquid film) 1740 (s) cm^{-1}. **2′-Carboxy analogue:** ^{1}H NMR (300 MHz, $CDCl_3$) 1.33 (s, 3H), 2.03 (d, J = 7.2 Hz, 1H), 2.05 (d, J = 7.8 Hz, 1H), 2.43 (d, J = 7.8 Hz, 1H), 2.45 (d, J = 7.2, 1H), 3.90−4.00 (m, 4H), 10.58 (brs, 1H); IR (liquid film) 2400−3400 (br), 1720 (s) cm^{-1}.

2-(4′-Diazo-3′-oxobutyl)-2-methyldioxolane (9): ^{1}H NMR (300 MHz, $CDCl_3$) 1.32 (s, 3H), 1.99−2.04 (m, 2H), 2.40−2.44 (m, 2H), 3.89−3.99 (m, 4H), 5.24 (brs, 1H); ^{13}C NMR (75.6 MHz, $CDCl_3$) 23.6, 33.4, 35.0, 54.1, 64.4, 108.9, 194.4; IR (liquid film) 2100 (s), 1640 (s) (m) cm^{-1}.

2-[3′-(Ethoxycarbonyl)propyl]-2-methyldioxolane: ^{1}H NMR (300 MHz, $CDCl_3$) 1.22 (t, J = 7.2 Hz, 3H), 1.29 (s, 3H), 1.60−1.76 (m, 4H), 2.29 (t, J = 7.2 Hz, 2H), 3.85−3.95 (m, 4H), 4.09 (q, J = 7.2 Hz, 2H); IR (liquid film) 1740 (s) cm^{-1}. **3′-carboxy analogue:** ^{1}H NMR (300 MHz, $CDCl_3$) 1.32 (s, 3H), 1.66−1.79 (m, 4H), 2.36−2.40 (m, 2H), 3.88−3.98 (m, 4H); IR (liquid film) 2400−3700 (br), 1710 (s) cm^{-1}.

2-(5′-Diazo-4′-oxopentyl)-2-methyldioxolane (19): ^{1}H NMR (300 MHz, $CDCl_3$) 1.30 (s, 3H), 1.62−1.77 (m, 4H), 2.35−2.39 (m, 2H), 3.89−3.94 (m, 4H), 5.24 (brs, 1H); ^{13}C NMR (75.6 MHz, $CDCl_3$) 19.6, 23.7, 38.2, 40.7, 54.3, 64.6, 109.7, 194.8; IR (liquid film) 2100 (s), 1640 (s) cm^{-1}.

2-[(Ethoxycarbonyl)methyl]-2-methyl-1,3-dioxane: ^{1}H NMR (300 MHz, $CDCl_3$) 1.23 (t, J = 7.2 Hz 3H), 1.52 (s, 3H), 1.63−1.73 (m, 2H), 2.77 (s, 2H), 3.84−3.97 (m, 4H), 4.12 (q, J = 7.2 Hz, 2H); IR (liquid film) 1740 (s) cm^{-1}. **2-Carboxy analogue:** ^{1}H NMR (300 MHz, $CDCl_3$) 1.56 (s, 3H), 1.56−1.66, (m, 1H), 1.84−1.98, (m, 1H), 2.78 (s, 2H), 3.91−4.06 (m, 4H); IR (liquid film) 2400−3700 (br), 1720 (s) cm^{-1}.

2-(3′-Diazo-2′-oxopropyl)-2-methyl-1,3-dioxane (26): ^{1}H NMR (300 MHz, $CDCl_3$) 1.50 (s, 3H), 1.50−1.58 (m, 1H), 1.81−1.92 (m, 1H), 2.70 (s, 2H), 3.84−4.01 (m, 4H), 5.53 (bs, 1H); ^{13}C NMR (75.6 MHz, $CDCl_3$) 20.3, 25.2, 50.7, 55.3, 59.6, 97.8, 190.6; IR (liquid film) 2100 (s), 1640 (s) cm^{-1}.

2-[2′-(Ethoxycarbonyl)ethyl]-2-methyl-1,3-dioxane: ^{1}H NMR (300 MHz, $CDCl_3$) 1.25 (t, J = 7.2 Hz, 3H), 1.39 (s, 3H), 1.50−1.60 (m, 1H), 1.71−1.84 (m, 1H), 2.00−2.06 (m, 2H), 2.41−2.46 (m, 2H), 3.81−3.96 (m, 4H), 4.11 (q, J = 7.2 Hz, 2H); IR (liquid film) 1735 (s) cm^{-1}. **2′-Carboxy analogue:** ^{1}H NMR (300 MHz, $CDCl_3$) 1.43 (s, 3H), 1.47−1.56 (m, 1H), 1.79−1.91 (m, 1H), 2.00 (d, J = 7.2 Hz, 1H), 2.03 (d, J = 7.5 Hz, 1H), 2.53, (dd, J = 4.5, 7.5 Hz, 1H), 2.56 (dd, J = 4.5, 7.2 Hz, 1H), 3.83−4.01 (m, 4H); IR (liquid film) 2400−3700 (br), 1720 (s) cm^{-1}.

2-(4′-Diazo-3′-oxobutyl)-2-methyl-1,3-dioxane (31): ^{1}H NMR (300 MHz, $CDCl_3$) 1.32 (d, J = 3.0 Hz, 3H), 1.45−1.52 (m, 1H), 1.62−1.78 (m, 1H), 1.93 (dd, J = 3.0, 8.0 Hz, 1H), 1.96 (dd, J = 3.0, 8.0 Hz, 1H), 2.39 (br, 2H), 3.73−3.90 (m, 4H), 5.23 (brs, 1H); ^{13}C NMR (75.6 MHz, $CDCl_3$) 20.6, 25.3, 33.5, 34.8, 54.2, 59.7, 98.3, 195.0; IR (liquid film) 2100 (s), 1640 (s) cm^{-1}.

General Procedure of $Rh_2(OAc)_4$-Catalyzed Reaction of Diazo Ketones. To a CH_2Cl_2 solution (10 mL) of $Rh_2(OAc)_4$ (2.2 mg, 1.0 mol % equivalent) were added a protic nucleophile NuH (0.706 mmol, 1.3 equiv) and diazo ketone (0.50 mmol) dissolved in CH_2Cl_2 (3.0 mL) at one time under an argon atmosphere at ambient temperature. The reaction mixture was stirred for 30 min, in general, until the diazo ketone was not detectable on a TLC plate. After workup with 8 mL of saturated aqueous $NaHCO_3$ solution, the solvent was removed and the residue was chromatographed through a flash column, in general, on silica gel or basic alumina in the cases where certain products **4a**, **10**, **30a**, **33**, and **36a** were proved labile on silica gel. Some products (**17** and **18**) were isolated by distillation under vacuum.

Spectroscopic data of the products are as follows.

3-Methyl-4,7-dioxocan-2-en-1-one (3):[11] ^{1}H NMR (300 MHz, $CDCl_3$) 1.98 (s, 3H), 3.94−3.98 (m, 2H), 4.05 (s, 2H), 4.14−4.17 (m, 2H), 5.01 (s, 1H); ^{13}C NMR (75.6 MHz, $CDCl_3$) 23.4, 67.6, 72.2, 74.7, 100.9, 168.7, 201.3; IR (liquid film) 1740 (s), 1620 (s) cm^{-1}; HRMS (EI) calcd for $C_7H_{10}O_3$ (M^+) 142.0629, found 142.0633.

7-Acetoxy-7-methyl-3,6-dioxocan-1-one (4a): ^{1}H NMR (300 MHz, $CDCl_3$) 1.70 (s, 3H), 2.06 (s, 3H), 3.01 (d, J = 11.4 Hz, 1H), 3.58−3.72 (m, 3H), 3.84 (d, J = 18.3 Hz, 1H), 4.15 (d, J = 18.3 Hz, 1H), 4.22−4.31 (m, 1H); ^{13}C NMR (75.6 MHz, $CDCl_3$) 22.0, 24.4, 45.9, 64.3, 73.4, 78.5, 104.3, 168.9, 211.0; IR (liquid film) 1740 (s), 1720 (s) cm^{-1}.

7-Methoxy analogue 4b: ^{1}H NMR (300 MHz, $CDCl_3$) 1.34 (d, J = 0.9 Hz, 3H), 2.38 (d, J = 11.1 Hz, 1H), 3.21 (s, 3H), 3.46−3.62 (m, 2H), 3.60 (d, J = 11.1 Hz, 1H), 3.81 (dd, J = 0.3, 18.3 Hz, 1H), 3.93−3.99 (m, 1H), 4.17 (d, J = 18.3 Hz, 1H), 4.24−4.29 (m, 1H); ^{13}C NMR (75.6 MHz, $CDCl_3$) 21.9, 47.7, 48.4, 62.4, 73.8, 78.9, 100.2, 212.2; IR (liquid film) 1750 (s), 1380 (s), 1220 (s), 1170 (s) cm^{-1}; HRMS (EI) calcd for $C_8H_{14}O_4$ (M^+) 174.0891, found 174.0900.

7-Acetoxy-7-methyl-3,6-dioxonan-1-one (10): ^{1}H NMR (300 MHz, $CDCl_3$) 1.72 (s, 3H), 2.02 (s, 3H), 2.29−2.34 (m, 1H), 2.44−2.47 (m, 1H), 2.63 (d, J = 10.8 Hz, 1H), 2.70 (d, J = 10.8 Hz, 1H), 3.64−3.75 (m, 4H), 4.00 (d, J = 15.6 Hz, 1H), 4.11 (d, J = 15.6 Hz, 1H); ^{13}C NMR (75.6 MHz, $CDCl_3$) 22.1, 22.3, 34.7, 34.9, 64.1, 72.9, 81.6, 106.7, 169.3, 210.7; IR (liquid film) 1730 (s), 1720 (s) cm^{-1}.

2-(4′-Acetoxy-3′-oxobutyl)-2-methyldioxolane (11): ^{1}H NMR (300 MHz, $CDCl_3$) 1.31 (s, 3H), 2.00 (d, J = 7.2 Hz, 1H), 2.03 (d, J = 7.5 Hz, 1H), 2.16 (s, 3H), 2.47 (d, J = 7.5 Hz, 1H) 2.49 (d, J = 7.2 Hz, 1H), 3.86−3.97 (m, 4H), 4.67 (s, 2H); ^{13}C NMR (75.6 MHz, $CDCl_3$) 20.5, 23.9, 32.4, 33.4, 64.7, 67.9, 109.0, 170.3, 203.4; IR (liquid film) 1750 (s), 1725 (s) cm^{-1}; HRMS (CI) calcd for $C_{10}H_{17}O_5$ (MH^+) 217.1075, found 217.1065.

4′-Methoxy analogue (11a): ^{1}H NMR (300 MHz, $CDCl_3$) 1.32 (s, 3H), 2.01 (t, J = 7.2 Hz, 4H), 2.51 (t, J = 7.2 Hz, 2H), 3.41 (s, 3H), 3.90−3.95 (m, 4H), 4.03 (s, 2H); ^{13}C NMR (75.6 MHz, $CDCl_3$) 23.7, 32.2, 33.2, 59.1, 64.5, 77.3, 109.0, 208.0; IR (liquid film) 1720 (s) cm^{-1}; HRMS (CI) calcd for $C_9H_{17}O_4$ (MH^+) 189.1126, found 189.1119.

(*tert*-Butyldimethylsilyl)oxy dErivative of 9-Hydroxy-7-oxanonane-2,5-dione (16a). Because **16a** and **16b** were not isolable in a pure state, an anomeric mixture of **16a** and **16b** was treated with *tert*-butyldimethylchlorosilane to be converted to the corresponding silyloxy derivative and analyzed: ^{1}H NMR (300 MHz, $CDCl_3$) 0.06 (s, 6H), 0.88 (s, 9H), 2.17(s, 3H), 2.68−2.77 (m, 4H), 3.58 (d, J = 5.7 Hz, 1H), 3.59 (d, J = 5.1 Hz, 1H), 3.77 (d, J = 5.1 Hz, 1H), 3.79 (d, J = 5.7 Hz, 1H), 4.15 (s, 2H); ^{13}C NMR (75.6 MHz, $CDCl_3$) −5.4, 18.3, 25.8, 29.8, 32.4, 36.5, 62.7, 73.1, 76.5, 206.8, 208.0; IR (liquid film) 1720 (s) cm^{-1}; HRMS (CI) calcd for $C_{14}H_{29}O_4Si$ (MH^+) 289.1834, found 289.1834.

4-Methylene-5,8-dioxonan-1-one (18): ^{1}H NMR (300 MHz, C_6D_6) 2.15−2.19 (m, 2H), 2.32−2.36 (m, 2H), 3.12 (t, J = 4.2 Hz, 2H), 3.45 (t, J = 4.2 Hz, 2H), 3.70 (s, 2H), 3.81 (d, J = 1.5 Hz, 1H), 4.00 (d, J = 0.6 Hz, 1H); ^{1}H NMR (300 MHz, in $CDCl_3$) 2.50−2.60 (m, 4H), 3.75 (d, J = 4.5 Hz 1H), 3.77 (d, J = 3.6 Hz, 1H), 4.03 (d, J = 3.6 Hz, 1H), 4.03 (s, 2H), 4.05 (d, J = 4.5 Hz, 1H), 4.08 (d, J = 1.8Hz, 1H), 4.26 (d, J = 1.8 Hz, 1H); ^{13}C NMR (75.6 MHz, $CDCl_3$) 33.2, 35.0, 71.9, 73.0, 81.9, 89.3, 164.1, 210.7; IR (liquid film) 1730 (s), 1710 (s), 1645 (m) cm^{-1}. HRMS (EI) calcd for $C_8H_{12}O_3$ (M^+) 156.0786, found 156.0794. Another isomer **17** was unstable under chromatographic conditions and, therefore, unable to be isolated. However,

(19) Padwa, A.; Fryxell, G. E.; Zhi, L. *J. Am. Chem. Soc.* **1990**, *112*, 3100.

their ^{1}H NMR (300 MHz, $CDCl_3$) were assigned as follows: 1.76 (d, J = 1.2 Hz, 3H), 3.31 (dd, J = 1.2 and 7.2 Hz, 2H), 3.65−3.68 (m, 2H), 3.90−3.94 (m, 2H), 3.97 (s, 2H), 4.88 (td, J = 1.2 and 7.2 Hz, 1H).

1-Methyl-2,5-dioxadecahydronaphthalen-7-one (20): ^{1}H NMR (300 MHz, $CDCl_3$) 1.44 (s, 3H), 1.63−1.75 (m, 2H), 1.93−2.08 (m, 1H), 2.14−2.29 (m, 2H), 2.51−2.58 (m, 1H), 3.46−3.72 (m, 2H), 3.77 (s, 1H), 3.90−4.00 (m, 2H); ^{13}C NMR (75.6 MHz, $CDCl_3$) 20.0, 22.6, 35.6, 40.1, 60.3, 62.2, 82.7, 207.4; IR (liquid film) 1720 (s) cm^{-1}; HRMS (EI) calcd for $C_9H_{14}O_3$ (M^+) 170.0942, found 170.0938. Anal. Calcd for $C_9H_{14}O_3$: C, 63.51, H, 8.29. Found: C, 63.23, H, 8.43.

2-(5′-Acetoxy-4′-oxopentyl)-2-methyldioxolane (21, Nu = AcO): ^{1}H NMR (300 MHz, $CDCl_3$) 1.30 (s, 3H), 1.61−1.78 (m, 4H), 2.16 (s, 3H), 2.44 (t, J = 6.9 Hz, 2H), 3.89−3.94 (m, 4H), 4.64 (s, 2H); ^{13}C NMR (75.6 MHz, $CDCl_3$) 17.7, 20.4, 23.6, 38.0, 38.5, 64.5, 67.9, 109.6, 170.1, 203.5; IR (liquid film) 1750 (s), 1725 (s) cm^{-1}; HRMS (EI) calcd for $C_{10}H_{15}O_5$ ($M^+ - CH_3$) 215.0919, found 215.0915.

5′-Methoxy analogue of 21 (Nu = MeO): ^{1}H NMR (300 MHz, $CDCl_3$) 1.29 (s, 3H), 1.59−1.75 (m, 4H), 2.43 (d, J = 6.9 Hz, 1H), 2.46 (d, J = 6.9 Hz, 1H), 3.39 (s, 3H), 3.89−3.94 (m, 4H), 3.99 (s, 2H); ^{13}C NMR (75.6 MHz, $CDCl_3$) 17.9, 23.5, 38.3, 38.6, 59.1, 64.4, 77.7, 109.0, 208.1; IR (liquid film) 1720 (s) cm^{-1}; HRMS (EI) calcd for $C_{10}H_{19}O_4$ (M^+) 203.1282, found 203.1289.

5′-Benzoyloxy analogue of 21 (Nu = PhCO$_2$): ^{1}H NMR (300 MHz, $CDCl_3$) 1.31 (s, 3H), 1.64−1.82 (m, 4H), 2.54 (t, J = 7.2 Hz, 2H), 3.90−3.95 (m, 4H), 4.88 (s, 2H), 7.43−7.49 (m, 2H), 7.56−7.62 (m, 1H), 8.07−8.11 (m, 2H); ^{13}C NMR (75.6 MHz, $CDCl_3$) 17.7, 23.7, 38.0, 38.6, 64.6, 68.4, 109.7, 128.4, 129.8, 130.1, 133.4, 165.8, 203.8; IR (liquid film) 3060 (w), 1730 (s), 1720 (s) cm^{-1}; HRMS (EI) calcd for $C_{16}H_{20}O_5$ ($M^+ - CH_3$) 277.1075, found 277.1083.

5′-*p*-Nitrophenoxy analogue of 21 (Nu = *p*-NO$_2$C$_6$H$_4$CO$_2$): ^{1}H NMR (300 MHz, $CDCl_3$) 1.31 (s, 3H), 1.63−1.81 (m, 4H), 2.60 (d, J = 6.9 Hz, 1H), 2.62 (d, J = 7.2 Hz, 1H), 3.89−3.95 (m, 4H), 4.67 (s, 2H), 6.94 (dd, J = 5.7, 10.5 Hz, 1H), 6.94 (d, J = 9.0 Hz, 2H), 8.21 (dd, J = 5.7, 10.5 Hz, 1H), 8.21 (d, J = 9.0 Hz, 1H); ^{13}C NMR (75.6 MHz, $CDCl_3$) 17.6, 23.6, 38.0, 38.8, 64.5, 72.7, 109.7, 114.6, 125.9, 142.2, 162.6, 204.9; IR (KBr) 3080 (m), 1730 (s), 1690 (s) cm^{-1}; HRMS (CI) calcd for $C_{15}H_{19}O_6N$ (MH^+) 310.1289, found 310.1299.

(*Z*)-3-Methyl-4,8-dioxonan-2-en-1-one (28a): ^{1}H NMR (300 MHz, $CDCl_3$) 1.87 (quint, J = 5.7 Hz, 2H), 2.08 (s, 3H), 3.67 (t, J = 5.7 Hz, 2H), 3.80 (t, J = 5.7 Hz, 2H), 4.05 (s, 2H), 5.72 (s, 1H); ^{13}C NMR (75.6 MHz, $CDCl_3$) 24.3, 32.1, 60.6, 69.8, 72.1, 97.1, 190.0, 192.4; IR (liquid film) 1730 (s), 1600 (s) cm^{-1}; HRMS (CI) calcd for $C_8H_{13}O_3$ (MH^+) 157.0864, found 157.0857.

(*E*)-Isomer 28b: ^{1}H NMR (300 MHz, $CDCl_3$) 1.92 (quint, J = 5.4 Hz, 2H), 1.99 (d, J = 0.9 Hz, 3H), 3.88 (t, J = 5.4 Hz, 2H), 4.19 (t, J = 5.4 Hz, 2H), 4.25 (s, 3H), 5.20 (s, 1H); ^{13}C NMR (75.6 MHz, $CDCl_3$) 18.0, 30.1, 68.5, 72.4, 78.7, 111.8, 166.4, 201.5; IR (liquid film) 1710 (m), 1640 (s) cm^{-1}; HRMS (CI) calcd for $C_8H_{13}O_3$ (MH^+) 157.0864, found 157.0859.

1-Methyl-2,6-dioxabicyclo[5.2.0]nonan-8-one (29): ^{1}H NMR (300 MHz, $CDCl_3$) 1.67 (s, 3H), 1.86−2.11 (m, 2H), 2.80 (dd, J = 4.2, 18.0 Hz, 1H), 2.90 (dd, J = 1.2, 18.0 Hz, 1H), 3.77 (td, J = 4.8, 12.6 Hz, 2H), 3.93 (ddd, J = 3.9, 9.0, 13.1 Hz, 1H), 4.02 (ddd, J = 3.9, 8.7, 12.5 Hz, 1H), 4.53 (dd, J = 1.2, 4.2 Hz, 1H); ^{13}C NMR (75.6 MHz, $CDCl_3$) 23.2, 33.8, 53.4, 56.1, 63.1, 66.9, 93.5, 219.7; IR (liquid film) 1790 (s) cm^{-1}; HRMS (EI) calcd for $C_8H_{12}O_3$ (M^+) 156.0786, found 156.0787.

8-Methoxy-8-methyl-3,7-dioxonan-1-one (30b): ^{1}H NMR (300 MHz, $CDCl_3$) 1.42 (d, J = 0.6 Hz, 3H), 1.65−1.88 (m, 2H), 2.13 (d, J = 12.3 Hz, 1H), 3.23 (s, 3H), 3.30 (td, J = 4.2, 11.0 Hz, 1H), 3.43 (ddd, J = 1.5, 5.4, 11.1 Hz), 3.73 (d, J = 16.2 Hz, 1H), 3.78 (d, J = 12.3 Hz, 1H), 3.90 (ddd, J = 1.8, 5.4, 10.2 Hz, 1H), 3.99 (d, J = 16.2 Hz, 1H), 4.15 (td, J = 4.2, 11.4 Hz, 1H); ^{13}C NMR (75.6 MHz, $CDCl_3$) 21.6, 28.3, 44.7, 48.5, 56.6, 67.4, 78.9, 101.2, 210.4; IR (liquid film) 1710 (s) cm^{-1}; HRMS (EI) calcd for $C_9H_{16}O_4$ (M^+) 188.1048, found 188.1046.

1-Methyl-2,6-dioxabicyclo[5.3.0]decan-8-one (33): ^{1}H NMR (300 MHz, $CDCl_3$) 1.43 (s, 3H), 1.82−1.99 (m, 3H), 2.07−2.28 (m, 2H), 2.38−2.51 (m, 1H), 3.66−3.85 (m, 3H), 3.83 (s, 1H), 3.99−4.06 (m, 1H); ^{13}C NMR (75.6 MHz, $CDCl_3$) 20.8, 33.0, 33.1, 33.5, 62.3, 66.5, 81.2, 88.3, 214.2; IR (liquid film) 1750 (s) cm^{-1}; HRMS (EI) calcd for $C_9H_{14}O_3$ (M^+) 170.0943, found 170.0950.

2-(4′-Acetoxy-3′-oxobutyl)-2-methyl-1,3-dioxane (34): ^{1}H NMR (300 MHz, $CDCl_3$) 1.39 (s, 3H), 1.45−1.52 (m, 1H), 1.76−1.92 (m, 1H), 2.00 (t, J = 7.2 Hz, 2H), 2.16 (s, 3H), 2.54 (t, J = 7.2 Hz, 2H), 3.77−3.97 (m, 4H); ^{13}C NMR (75.6 MHz, $CDCl_3$) 19.8, 25.4, 32.6, 33.2, 59.7, 68.0, 76.5, 98.1, 170.2, 203.8; IR (liquid film) 1750 (s), 1730 (s) cm^{-1}; HRMS (EI) calcd for $C_{10}H_{15}O_5$ ($M^+ - CH_3$) 215.0919, found 215.0922.

4′-Methoxy analogue of 34: ^{1}H NMR (300 MHz, $CDCl_3$) 1.39 (d, J = 0.9 Hz, 3H), 1.48−1.56 (m, 1H), 1.72−1.86 (m, 1H), 1.98 (d, J = 7.5 Hz, 1H), 2.01 (d, J = 7.2 Hz, 1H), 2.54 (d, J = 7.2 Hz, 1H), 2.56 (d, J = 7.5 Hz, 1H), 3.41 (d, J = 0.9 Hz, 1H), 3.79−3.96 (m, 4H), 4.04 (s, 2H); ^{13}C NMR (75.6 MHz, $CDCl_3$) 20.5, 25.4, 32.6, 32.8, 59.3, 59.7, 77.6, 98.3, 208.4; IR (liquid film) 1720 (s) cm^{-1}; HRMS (CI) calcd for $C_{10}H_{19}O_4$ (MH^+) 203.1283, found 203.1273.

10-Hydroxy-7-oxadecane-2,5-dione (35): ^{1}H NMR (300 MHz, $CDCl_3$) 1.84 (m, J = 5.7 Hz, 2H), 2.18 (s, 3H), 2.62 (d, J = 7.8 Hz, 1H), 2.63 (d, J = 6.6 Hz, 1H), 2.77 (d, J = 6.6 Hz, 1H), 2.79 (d, J = 7.8 Hz, 1H), 3.65 (t, J = 5.7 Hz, 2H), 3.80 (t, J = 5.7 Hz, 2H), 4.17 (s, 2H); ^{13}C NMR (75.6 MHz, $CDCl_3$) 29.7, 32.0, 32.1, 36.7, 60.5, 69.6, 75.7, 206.9, 207.8; IR (liquid film) 3700−3050 (br), 1720 (s), 1700 (s) cm^{-1}; HRMS (EI) calcd for $C_9H_{16}O_4$ (M^+) 188.1049, found 188.1046.

8-Methoxy-8-methyl-3,7-dioxecan-1-one (36b): ^{1}H NMR (300 MHz, $CDCl_3$) 1.34 (d, J = 0.6 Hz, 3H), 1.68 (dd, J = 5.4, 13.8 Hz, 1H), 1.71 (dd, J = 5.7, 13.8 Hz, 1H), 1.76−1.83 (m, 1H), 2.24−2.33 (m, 1H), 2.41−2.50 (m, 1H), 2.61−2.69 (m, 1H), 3.23 (s, 3H), 3.45−3.51 (m, 1H), 3.70−3.77 (m, 2H), 3.84−3.92 (m, 1H), 3.94 (d, J = 16.8 Hz, 1H), 4.07 (d, J = 16.8 Hz, 1H); ^{13}C NMR (75.6 MHz, $CDCl_3$) 20.8, 29.3, 32.5, 35.3, 48.9, 59.0, 70.1, 76.4, 101.8, 211.6; IR (liquid film) 1710 (s) cm^{-1}; HRMS (EI) calcd for $C_{10}H_{18}O_4$ (M^+) 202.1205, found 202.1201.

2-[(3′-Hydroxypropyl)oxy]-3-methylcyclopent-2-en-1-one (37): ^{1}H NMR (300 MHz, $CDCl_3$) 1.87 (quint, J = 5.7 Hz, 2H), 2.00 (s, 3H), 2.36−2.39 (m, 2H), 2.43−2.46 (m, 2H), 3.19 (brs, 1H), 3.81 (t, J = 5.7 Hz, 2H), 4.14 (t, J = 5.7 Hz, 2H); ^{13}C NMR (75.6 MHz, $CDCl_3$) 14.9, 27.2, 32.5, 32.8, 58.9, 67.7, 152.3, 156.9, 204.3; IR (liquid film) 3700−3100 (br), 1700 (s), 1640 (s) cm^{-1}; HRMS (EI) calcd for $C_9H_{14}O_3$ (M^+) 170. 0943, found 170.0941.

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Supporting Information Available: Copies of ^{1}H and/or ^{13}C NMR spectra for 21 compounds **1**, **9**, **26**, **31**, **4a,b**, **10**, **16a**, **18**, **17** + **18**, **20**, **21**, **28a**,**b**, **29**, **30b**, **33**, **35**, **36a**, and **37** (41 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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