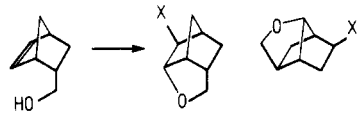
Table I. Oxidation of Olefins with Sodium Bismuthate in Acetic Acid

olefin	reacn[a] time	products	yield[b,c]
1-phenylcyclohexene	3	*cis*-2-acetoxy-1-phenylcyclohexanol	37
1-methylcyclohexene	8	1-methyl-2-acetoxycyclohexanol	21
methylenecyclohexane	7	1-(acetoxymethyl)cyclohexanol	40
α-methylstyrene	3	1-acetoxy-2-phenyl-2-propanol	39 (62)
		acetophenone	9
		α-acetoxyacetophenone	1
2,6-dimethyl-2-octene	7	2,6-dimethyl-3-acetoxy-2-octanol	21 (42)
cyclohexene	4	2-acetoxycyclohexanol	25
		3-acetoxycyclohexene	8
(*E*)-3-hexene	10	*erythro*-4-acetoxy-3-hexanol	18 (41)
(*Z*)-3-hexene	10	*threo*-4-acetoxy-3-hexanol	18
1-decene	21	1-acetoxy-2-decanol	10
		nonanal	5

[a] Reaction time in days at room temperature. [b] Yield of product (%) isolated by preparative thin-layer chromatography or distillation. [c] Isolated yield (%) corrected for recovered olefin is indicated in parentheses.

Table II. Oxidation of *endo*-2-(Hydroxymethyl)-5-norbornene



1 2 3

reagents	yield, % 2	3	X	ref
$Hg(OAc)_2$/MeOH	>95		HgOAc	*a*
Tl_2O_3/HOAc		46	OAc	*b*
$Tl(OAc)_3$/HOAc	21	42	OAc	*c*
$Pb(OAc)_4/C_6H_6/CaCO_3$	37	0	OAc	*d*
$NaBiO_3$/HOAc	10	35	OAc	*c*
$C_6H_5CO_3H$	>90		OH	*e*

[a] H. B. Henbest and B. Nicholls, *J. Chem. Soc.*, 227-36 (1959). [b] R. M. Moriarty and H. Gopal, *Tetrahedron Lett.*, 347-50 (1972). [c] Results of the present study. [d] R. M. Moriarty and K. Kapadia, *Tetrahedron Lett.*, 1165-9 (1964). [e] H. B. Henbest and B. Nicholls, *J. Chem. Soc.*, 221-6 (1959).

between these two paths, we oxidized *endo*-2-(hydroxymethyl)-5-norbornene (1). If epoxidation is the exclusive pathway, we would expect to obtain only tricyclic ethers **2** (X = OH, OAc), whereas if oxymetalation is intervening, we would expect predominantly the rearranged tricyclic ether **3** (X = OAc, OH). It is clear from the results in Table II that oxymetalation of **1** initially affords the cyclic ether **2** (X = $M(OAc)_n$) which, depending on the strength of the metal–carbon bond, either can be isolated (M = Hg) or can decompose to generate a carbonium ion at the metalated carbon. In nonpolar solvents such as benzene, the carbonium ion is short-lived (if ever fully generated), affording predominantly the ether acetate **2**, while in polar, ionizing solvents such as acetic acid, the carbonium ion can rearrange to the ether acetate **3**. This latter path is the predominant one followed in the sodium bismuthate oxidation. Thus the chemistry of sodium bismuthate in acetic acid resembles that of the acetates of the neighboring fifth-row $3d^{10}$ oxidants mercury, thallium, and lead.

The heterogeneous nature of the reaction and the mild, room-temperature conditions offer advantages over the more traditional reagents, lead tetraacetate and thallium triacetate. Even though the yields are only moderate, when they are corrected for recovered starting material, they are competitive with the alternate oxymetalation reagents.

(10) Such a sequence would require a hydroxy-metalated intermediate, since if acetoxy metalation were occurring, one would expect diacetate to be present as a reaction product.

Experimental Section

The following procedure for the oxidation of α-methylstyrene is representative. To a 250-mL Morton flask with a stirbar were added 5.92 g (0.05 mol) of α-methylstyrene, 100 mL of glacial acetic acid, and 16.62 g (0.05 mol) of sodium bismuthate. The reaction was permitted to stir at room temperature for 3 days. The reaction mixture was poured into ether and extracted with water followed by extraction with saturated $NaHCO_3$ until all of the acetic acid had been removed. The ether layer was then rinsed with brine, dried over anhydrous magnesium sulfate, and filtered, and the ether was removed under reduced pressure to afford 7.96 g of crude product. Column chromatography on 60 g of silica gel using hexanes and methylene chloride in an increasing gradient gave, from 1.00 g of crude product, 0.48 g (39%) of 1-acetoxy-2-phenyl-2-propanol: ^1H NMR ($CDCl_3$) δ 7.7-7.1 (m, 5 H, ArH), 4.25 (s, 2 H, CH_2OAc), 2.70 (br s, 1 H, OH), 2.02 (s, 3 H, $COCH_3$), 1.55 (s, 3 H, CCH_3).

Acknowledgment. The authors thank Dr. Danne Smith for mass spectral analysis, Mr. George Babbitt for NMR analysis, and Dr. Divakaran Masilamani for a generous gift of the trideuterio-α-methylstyrene.

Registry No. **1**, 15507-06-9; **2** (X = OAc), 16479-71-3; **3** (X = OAc), 35359-71-8; 1-phenylcyclohexene, 771-98-2; 1-methylcyclohexene, 591-49-1; methylenecyclohexane, 1192-37-6; α-methylstyrene, 98-83-9; 2,6-dimethyl-2-octene, 4057-42-5; cyclohexene, 110-83-8; (*E*)-3-hexene, 13269-52-8; (*Z*)-3-hexene, 7642-09-3; 1-decene, 872-05-9; *cis*-2-acetoxy-1-phenylcyclohexanol, 23313-43-1; 1-methyl-2-acetoxycyclohexanol, 72331-74-9; 1-(acetoxymethyl)cyclohexanol, 72331-75-0; 1-acetoxy-2-phenyl-2-propanol, 72331-76-1; 2,6-dimethyl-3-acetoxy-2-octanol, 72331-77-2; 2-acetoxycyclohexanol, 22241-34-5; 3-acetoxycyclohexene, 14447-34-8; *erythro*-4-acetoxy-3-hexanol, 64833-03-0; *threo*-4-acetoxy-3-hexanol, 72346-78-2; 1-acetoxy-2-decanol, 72331-78-3; $NaBiO_3$, 12232-99-4.

Cycloaddition of (Trimethylsilyl)ketene with Tetraalkoxyethylenes

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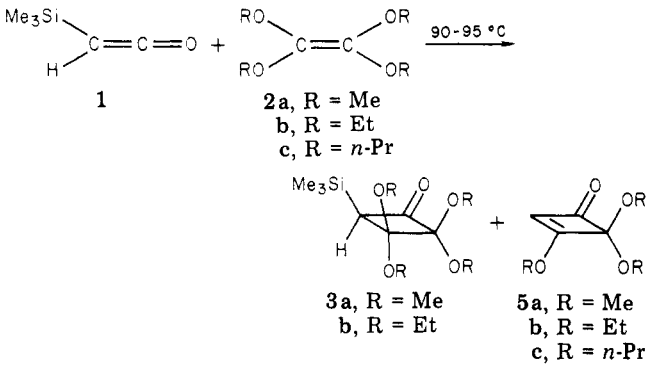
We have recently reported on the cycloaddition of (trimethylsilyl)ketene with aldehydes.[1] The cycloaddition of this ketene with ketene dimethyl and diethyl acetals has also been described.[2] However, the attempted (2 + 2)

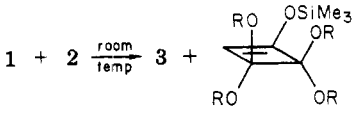
(1) Brady, W. T.; Saidi, K. *J. Org. Chem.* **1979**, *44*, 733.
(2) Zaitseva, G. S.; Baukov, Y. I.; Mal'tsev, V. V.; Lutsenko, I. F. *Zh. Obshch. Khim.* **1974**, *44*, 1415.

0022-3263/80/1945-0727$01.00/0

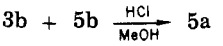
Scheme I



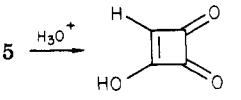
Scheme II



Scheme III



Scheme IV



cycloadditions of (trimethylsilyl)ketene with a variety of simple olefins and dienes has been unsuccessful.[3] We now wish to describe the facile cycloaddition of this isolable and stable ketene with the electron-rich tetraalkoxyethylenes.

The addition of equimolar quantities of (trimethylsilyl)ketene (1) and tetraethoxyethylene (**2b**) under a nitrogen atmosphere at 90–95 °C resulted in a loss of all the ketene and afforded a 68% yield of 2-(trimethylsilyl)-3,3,4,4-tetraethoxycyclobutanone (**3b**) after 2 h (Scheme I). The infrared spectrum of **3b** revealed the carbonyl band at 1770 cm^{-1} and the NMR spectrum a singlet at 0.05 ppm, a triplet at 1.05 ppm, a singlet at 2.80 ppm, and a quartet at 3.50 ppm. In addition to the cyclobutanone, a 10% yield of 3,4,4-triethoxy-2-cyclobutenone (**5b**) was found. The amount of **5b** varied significantly, depending upon the temperature and the rate of distillation. When a mixture of 90% **3a** and 10% **5a** was injected into the gas chromatograph, the ratio changed to 57 and 43%, respectively. The cycloaddition of **1** with **2c** was allowed to proceed overnight at 90–95 °C, and **5c** was the only isolated product in a 50% yield.

The addition of equimolar quantities of (trimethylsilyl)ketene (1) and tetraalkoxyethylene (**2**) under a nitrogen atmosphere at room temperature afforded a 70% yield of 2-(trimethylsilyl)-3,3,4,4-tetraalkoxycyclobutanone (**3**) after several days (Scheme II). An infrared spectrum of the reaction mixture during the cycloaddition revealed a band at 1680 cm^{-1} which was assigned to the silyl enol ether 3,3,4,4-tetraalkoxy-1-(trimethylsiloxy)cyclobutene (**4**). The cyclobutanone rearranged to the corresponding silyl enol ether by a silyl migration from carbon to oxygen as evidenced by the 1680-cm^{-1} band in the infrared spectrum.[4]

It is proposed that the cyclobutanone is intially formed regardless of the reaction conditions, either at room temperature or at elevated temperature. When the reaction is run at room temperature, some of the cyclobutanone undergoes a silyl migration to oxygen, thus yielding the silyl enol ether. During the distillation process, elimination of the silyl and ethoxy groups from the silyl enol ether occurs, thus yielding the cyclobutenone. Hence, the silyl enol ether was thermally sensitive and not isolable by distillation. However, at the higher reaction temperature the cyclobutanone undergoes silyl migration to the silyl enol ether which, being susceptible to heat, immediately undergoes elimination to yield the cyclobutenone. The silyl enol ether was not observed when the reaction was run at elevated temperature. An analogous elimination has been reported in the literature.[5]

When a mixture of **3b** and **5b** were treated with absolute methanol containing a few drops of concentrated hydrochloric acid under a nitrogen atmosphere, 3,4,4-trimethoxy-2-cyclobutenone (**5a**) was isolated in quantitative yield. None of the silyl enol ether was observed in this reaction (Scheme III).

Treatment of **5b** with *n*-propyl alcohol resulted in exchange to yield **5c**. Apparently, the acid conditions promote the silicon migration and the elimination process. The methoxy exchange is, of course, expected under the acid conditions.

Hydrolysis of any of the cyclobutenones in dilute hydrochloric acid yields the biologically interesting compound 3-hydroxy-3-cyclobutene-1,2-dione [semisquaric acid (**6**)] (Scheme IV). This highly oxidized cyclobutene has been recently prepared from the cycloaddition products of aldoketenes and tetramethoxyethylenes.[6]

Experimental Section

The proton NMR spectra were recorded on a Perkin-Elmer R-24B nuclear magnetic resonance spectrometer, employing CCl_4 as the solvent and $CHCl_3$ as the internal standard. Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6E double-focusing mass spectrometer and on a Finnigan GC/MS 3200 with a Data System 6100.

Commercially available ether, heptane, glyme, and tetraglyme were dried and purified by distillation from sodium–potassium alloy prior to each run. These solvents were used for the preparation of (trimethylsilyl)ketene and tetraalkoxyethylenes. (Trimethylsilyl)ketene was prepared from (trimethylsilyl)ethoxyacetylene by a procedure similar to that used by Ruden.[3] (Trimethylsilyl)ethoxyacetylene was prepared from ethoxyacetylene which was commercially available and was also synthesized from ethyl vinyl ether. The tetraalkoxyethylenes were synthesized from dialkoxy-(*p*-chlorophenoxy)methane by treatment with sodium hydride.[7] The dialkoxy-(*p*-chlorophenoxy)methanes were prepared from the appropriate dialkoxymethyl acetates which were synthesized from the necessary alkyl orthoformates.[8,9]

Cycloaddition of (Trimethylsilyl)ketene with Tetramethoxyethylene. (a) 3,3,4,4-Tetramethoxy-2-(trimethylsilyl)cyclobutanone (3a). A 1.54-g (13.4 mmol) portion of 1 was added dropwise to a stirred solution of 2 g (13.5 mmol) of **2a** under a nitrogen atmosphere. After completion of the addition, the

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(5) Danishefsky, S.; Etheredge, S. J. *J. Org. Chem.* **1978**, *43*, 4604.

(6) (a) Bellus, D. *J. Am. Chem. Soc.* **1978**, *100*, 8026. (b) Bellus, D.; Fischer, H.; Greuter, H.; Martin, P. *Helv. Chim. Acta* **1978**, *61*, 1784. (c) Bellus, D. *J. Org. Chem.* **1979**, *44*, 1208.

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(9) Ohme, R.; Schmitz, E. *Justus Liebigs Ann. Chem.* **1968**, *716*, 207.

reaction mixture was heated at 90 °C until the ketene had been consumed, as evidenced by the disappearance of the ketene band at 2080 cm^{-1} in the infrared spectrum, about 2 h. There was obtained 2.3 g (65%) of the cyclobutanone at 58–62 °C at 0.25 mm by using a short-path distillation apparatus: IR 1770 cm^{-1} (C=O); NMR (CCl_4 with $CHCl_3$ as a reference) δ 0.1 (s, 9 H), 2.85 (s, 1 H), 3.3 (s, 12 H); mass spectrum, *m/e* (relative intensity) parent peak 262 (no M found), 247 (17, M–15), 189 (68), 127 (71), 95 (100), 93 (84.3).

Anal. Calcd for $C_{11}H_{22}O_5Si$: C, 50.38; H, 8.4. Found: C, 49.98; H, 8.66.

(b) 3,4,4-Trimethoxy-2-cyclobutenone (5a). A 2.3-g (8.7 mmol) portion of the cyclobutanone **3a** was heated about 24 h at 95 °C to give 1.39 g (80%) of the cyclobutenone **5a** at 58–62 °C (0.25 mm): IR and NMR data were consistent with the literature;[6b] mass spectrum, *m/e* (relative intensity) 158 (3.3, M, parent peak), 143 (100, M - 15), 127 (20, M - 31), 115 (63), 99 (43).

Cycloaddition of (Trimethylsilyl)ketene with Tetraethoxyethylene. (a) 3,3,4,4-Tetraethoxy-2-(trimethylsilyl)-cyclobutanone [3b]. This cycloaddition was accomplished by employing the same procedure as described above. From 3.0 g (26 mmol) of the ketene and 5.3 g (26 mmol) of **2b** there was obtained 5.6 g (68%) of **3b** at 75–80 °C (0.15 mm): IR 1770 cm^{-1} (C=O); NMR (CCl_4 with $CHCl_3$ as reference) δ 0.05 (s, 9 H), 1.05 (t, 12 H), 2.80 (s, 1 H), 3.50 (q, 8 H); mass spectrum *m/e* (relative intensity) parent peak 318 (no M found), 303 (3.4, M - 15), 289 (100, M - 29), 273 (15.3), 245 (6.8), 217 (15.3), 215 (42.4), 187 (39.0), 171 (69.5).

Anal. Calcd for $C_{15}H_{30}O_5Si$: C, 56.60; H, 9.43. Found: C, 56.83; H, 9.38.

(b) 3,4,4-Triethoxy-2-cyclobutenone (5b). Heating 5.6 g (17.6 mmol) of **3b** as described above resulted in the formation of 3.0 g (86%) of **5b** at 90–95 °C (0.1 mm) [lit.[6b] 75 °C (0.02 mm)]; the IR and NMR data were consistent with that reported in the literature; mass spectrum, parent peak at *m/e* 200.

3,4,4-Tri-*n*-propoxy-2-cyclobutenone, 5c. A 2.0-g (17.54 mmol) portion of the ketene was added dropwise to 4.56 g (17.54 mmol) of tetra-*n*-propoxyethylene. When the addition was complete, the reaction mixture was heated at 90–95 °C overnight. There was obtained 2.1 g (50%) of **5c** at 90–95 °C (0.1 mm): IR 1770, 1585, 1470, 1340, 1200, 1080 cm^{-1}; NMR δ 1.19 (m, 9 H), 1.3 (m, 6 H), 3.35 (t, 4 H), 3.9 (t, 2 H), 5.15 (s, 1 H); mass spectrum, *m/e* (relative intensity) 242 (1.7 M parent peak), 199 (5.9), 157 (27.1), 115 (100), 103 (9.3), 99 (24.5), 87 (7.6), 69 (93.2).

Anal. Calcd for $C_{13}H_{22}O_4$: C, 64.5; H, 9.1. Found: C, 64.76; H, 9.03.

Conversion of a Mixture of 3b and 5b to 5a. A 1.0-g mixture of **3b** and **5b** in 20 mL of absolute methanol containing a few drops of concentrated HCl was stirred overnight under a nitrogen atmosphere. Upon evaporation of the solvent, the distilled product was only **5a** as evidenced by comparison of spectral data.

(c) 3-Hydroxy-3-cyclobutene-1,2-dione, 6. Semisquaric Acid. To a solution containing 1 g (6.3 mmol) of **5a** in 20 mL of THF was added 15 mL of 18% HCl. This solution was stirred for 1 h at 45 °C. All of the liquids were removed under reduced pressure, and the residual solid was purified by sublimation to give 0.62 g (100%) of product: mp 145–150 °C dec (lit.[6] mp 145–150 °C dec); IR and NMR data were identical with those in the literature.[10]

The NMR spectrum of **6** in acetone-d_6 revealed two singlets at 2.1 and 8.7 ppm in a ratio of 1.

Semisquaric acid was also obtained from **5b** as described above for **5a**.

Typical Procedure for the Reaction of (Trimethylsilyl)-ketene with Tetraalkoxyethylene at Room Temperature. A 1.0-g (8.7 mmol) portion of (trimethylsilyl)ketene was added dropwise to a solution of 1.29 g (8.7 mmol) of **2a** under a nitrogen atmosphere and stirred at room temperature for 3–5 days, depending on the tetraalkoxyethylene.

Acknowledgment. The authors express appreciation to the Robert A. Welch Foundation and to the North Texas State University Faculty Research Committee for support of this investigation.

Registry No. 1, 4071-85-6; **2a**, 1069-12-1; **2b**, 40923-93-1; **2c**, 40923-94-2; **3a**, 72332-21-9; **3b**, 72332-22-0; **5a**, 68057-55-6; **5b**, 68057-58-9; **5c**, 72332-23-1; **6**, 31876-38-7.

(10) Scharf, H. D.; Frauenrath, H.; Pinske, W. *Chem. Ber.* **1978**, *111*, 168.

Thermally Induced Cyclobutyl–Cyclopropylcarbinyl-Type Rearrangement of 2-Oxabicyclo[4.2.0]octan-3-ones

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It has been well-known that cyclobutyl derivatives rearrange to cyclopropylcarbinyl ones through disrotatory opening of the cyclobutane ring.[1] More recently, the acid-catalyzed rearrangement of highly constrained polycyclic lactones such as cagelike compounds has been reported.[2] However, this type of thermally induced rearrangement is little known as yet.[3] In a continuation of studies on the transformation of readily available [*n*.3.2]propellanes into other important polycarbocyclic ring systems,[4] we previously reported the acid-catalyzed cyclobutyl–cyclopropylcarbinyl-type rearrangement of 2-oxabicyclo[4.2.0]octan-3-ones **2**, **8**, and **9** (δ-lactones) to the corresponding γ-lactones **11**, **14**, and **15** (Chart I) as a preliminary report.[4c] We describe here a novel thermally induced rearrangement of the δ-lactones **1–4**, **8**, and **9** to the γ-lactones **10–15** which may be considered to proceed in a concerted manner.[5] Interestingly, the obtainable γ-lactones in the present reactions will serve as useful intermediates for the synthesis of polycyclic substrates involving the spiro-α-methylene-γ-butyrolactone skeleton which have been shown to display antitumor activity.[6,7]

The δ-lactones **1–9** were prepared by the Baeyer–Villiger oxidation (H_2O_2/AcOH or MCPBA/$CHCl_3$) of the corresponding ketones in good yields. The thermal reaction was carried out by heating an *o*-dichlorobenzene solution of δ-lactones in a sealed tube at 240 °C for 72 h or passing a hexane solution of **1–9** through a Pyrex column heated at 350 °C (contact time ca. 20 s). The results are summarized in Table I along with those under the acidic conditions.

(1) Olah, G. A.; Schleyer, P. v. R. "Carbonium Ions"; Wiley-Interscience: New York, 1972; Vol. III, Chapter 26.

(2) (a) Büchi, G.; Goldman, I. M. *J. Am. Chem. Soc.* **1957**, *79*, 4741. (b) Hirao, K.; Miura, H.; Hoshino, H.; Yonemitsu, O. *Tetrahedron Lett.* **1976**, 3895. (c) Mehta, G.; Singh, V.; Duddeck, H. *Ibid.* **1978**, 1223.

(3) Only one example is known: Yamashita, Y.; Sato, K.; Mukai, T. "Abstracts of Papers", 37th Annual Meeting of the Chemical Society of Japan, Yokohama, Apr 1–4, 1978; Vol. 2, p 633.

(4) (a) Tobe, Y.; Kimura, K.; Odaira, Y. *J. Org. Chem.* **1979**, *44*, 639. (b) Tobe, Y.; Doi, A.; Kimura, K.; Odaira, Y. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 639. (c) Tobe, Y.; Kakiuchi, K.; Kawakami, Y.; Sakai, Y.; Kimura, K.; Odaira, Y. *Chem. Lett.* **1978**, 1027. (d) Sakai, Y.; Toyotani, S.; Tobe, Y.; Odaira, Y. *Tetrahedron Lett.*, **1979**, 3855.

(5) A concerted mechanism for this type of rearrangement has likewise been proposed for some highly strained compounds. References 2a and 3. McDonald, R. N.; Davis, G. E. *J. Org. Chem.* **1969**, *34*, 1916.

(6) (a) Rodriquez, E.; Towers, G. H. N.; Mitchell, J. C. *Phytochemistry* **1976**, *15*, 1573. (b) Grieco, P. A.; Noguez, J. A.; Masaki, Y.; Hiroi, K.; Nishizawa, M.; Rosowsky, A.; Oppenheim, S.; Lazarus, H. *J. Med. Chem.* **1977**, *20*, 71.

(7) For an example, we have prepared an α-methylene γ-lactone from **11** by the usual method,[6b] and its biological activity is now under investigation.

0022-3263/80/1945-0729$01.00/0