38.96; H, 6.44; N, 6.59; F, 35.12.

Solutions of **3** in Me$_2$SO-d_6 decompose within minutes due to the presence of traces of water; **3** is also readily hydrolyzed in aqueous solution to give the diformate.

B. A suspension of the cis/trans mixture of **2a** in DMF, prepared as described under A, is diluted with 500 mL of water and the resulting milky suspension is extracted with methylene chloride. The extracts are again shaken with water to remove DMF, dried, and concentrated. Vacuum distillation gives 31.4 g (79%) of the diformate of 1,4-bis(hydroxymethyl)cyclohexane, bp 94 °C (0.1 mm); spectroscopic data (IR, ^{1}H and ^{13}C NMR) confirm the structure of the compound.

C. A suspension, prepared as described under B, is heated for 2 h at 60–70 °C whereby the solid **2a** dissolves and a cis/trans mixture of 1,4-bis(chloromethyl)cyclohexane is formed. After removal of DMF by distillation at reduced pressure (10–12 mm), the product is distilled in vacuo, bp 65–70 °C (0.1 mm), yield 32.7 g (90%); IR and ^{1}H NMR spectroscopic data confirm the structure of the compound.

Registry No. *cis*-**2a**, 86217-95-0; *trans*-**2a**, 86217-96-1; **3**, 86217-98-3; $CH_3(CH_2)_5CH_2Cl$, 629-06-1; $CH_3(CH_2)_8CH_2Cl$, 1002-69-3; $CH_3(CH_2)_{10}CH_2Cl$, 112-52-7; $CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_2Cl$, 59485-81-3; $PhOCH_2CH_2Cl$, 622-86-6; $CH_3(CH_2)_3CH(C_2H_5)CH_2Cl$, 123-04-6; $ClCH_2(CH_2)_8CH_2Cl$, 2162-98-3; $ClCH_2C{\equiv}CCH_2Cl$, 821-10-3; $CH_3(CH_2)_5CH_2OCOCl$, 33758-34-8; $CH_3(CH_2)_8CH_2OCOCl$, 55488-51-2; $CH_3(CH_2)_{10}CH_2OCOCl$, 24460-74-0; $CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_2OCOCl$, 86217-99-4; $PhOCH_2CH_2OCOCl$, 34743-87-8; $CH_3(CH_2)_3CH(C_2H_5)CH_2OCOCl$, 24468-13-1; $ClCOOCH_2(CH_2)_8CH_2OCOCl$, 56757-75-6; $ClCOOCH_2C{\equiv}CCH_2OCOCl$, 16669-40-2; DMF, 68-12-2; *cis*-1,4-bis(chloromethyl)cyclohexane, 53188-14-0; *trans*-1,4-bis(chloromethyl)cyclohexane, 86218-00-0; 1,4-bis(chloromethyl)benzene, 623-25-6; decahydro-2,5-bis(chloromethyl)-4,7-methanoindene, 86218-01-1; *cis*-1,4-cyclohexanediyldimethylene bis(chloroformate), 86218-02-2; *trans*-1,4-cyclohexanediyldimethylene bis(chloroformate), 46744-84-7; 1,4-phenylenedimethylene bis(chloroformate), 10362-03-5; decahydro-2,5-bis[(chlorocarbonyloxy)methyl]-4,7-methanoindene, 86218-03-3; *cis*-1,4-bis(hydroxymethyl)cyclohexanediformate, 86218-04-4; *trans*-1,4-bis(hydroxymethyl)cyclohexanediformate, 86218-05-5.

Vinyl Ether Hydrolysis. 16. 2-Cyclohexylidene-3,3-dimethyloxetane

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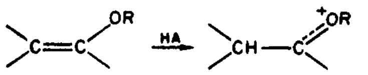
Received December 3, 1982

The acid-catalyzed hydrolysis of simple vinyl ethers is a process whose reaction mechanism is well characterized: the first step is known to be rate determining and to consist of proton transfer from the catalyst to the β-carbon atom of the carbon–carbon double bond system (eq 1).[1]



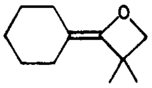
(1)

Table I. Rates of Hydrolysis of 2-Cyclohexylidene-3,3-dimethyloxetane in Aqueous Hydrochloric Acid Solution at 25 °C[a,b]

10^2[HCl], M	10^2k_{obsd}, s^{-1}
0.60	1.47, 1.43, 1.47, 1.45
1.00	2.39, 2.34, 2.41
1.50	3.53, 3.61, 3.58, 3.71
2.00	4.72, 4.47, 4.85, 4.47
2.50	6.06, 5.93, 5.88, 6.08
3.00	7.09, 7.34, 7.10
4.00	9.10, 9.14, 9.18

[a] Ionic strength maintained at 0.10 M by adding NaCl.
[b] $k_{obsd} = (1.21 \pm 0.62) \times 10^{-3} + (2.30 \pm 0.03)[HCl]$.

This process is therefore especially well suited to investigating the effect of structure on chemical reactivity. A particular example which is perhaps of more than usual interest is the hydrolysis of 2-cyclohexylidene-3,3-dimethyloxetane (**1**) inasmuch as the vinyl ether functional group in this substance is a part of two separate rings of different size. The hydrolysis reaction converts an sp^2-hybridized carbon atom of the six-membered ring into an sp^3-hybridized atom, which is a process known to be favored over the corresponding change in an acyclic system,[2] but it also introduces a partial double bond into a four-membered ring, and, since small unsaturated rings are highly strained,[3] this change would be disfavored over the corresponding transformation in a similar acyclic system.



1

It is of interest to determine which of these two opposing effects dominates, i.e., whether **1** is more or less reactive than an analogous acyclic vinyl ether. We have therefore measured the rate of hydrolysis of **1** and report our results herein.

Experimental Section

Materials. 2-Cyclohexylidene-3,3-dimethyloxetane was prepared as described before.[4] Hydrochloric acid solutions were made from deionized water purified further by distillation from alkaline permanganate.

Kinetics. Rates of hydrolysis were measured spectroscopically by following the decrease in absorbance of the vinyl ether functional group at λ = 210 nm. Measurements were made by using a Cary 118 C spectrometer with cell compartment thermostated at 25.0 ± 0.05 °C. The data conformed well to the first-order rate law, and first-order rate constants were evaluated as slopes of plots of ln $(A - A_\infty)$ vs. time.

Results and Discussion

Rates of hydrolysis of 2-cyclohexylidene-3,3-dimethyloxetane were measured in dilute HCl solutions over the concentration range 0.006–0.04 M. The observed first-order rate constants so obtained are accurately proportional to acid concentration, and least-squares analysis of the data (Table I) give the hydrogen ion catalytic coefficient $k_{H^+} = 2.30 \pm 0.03$ M^{-1} s^{-1}.

An appropriate simple acyclic analogue of 2-cyclohexylidene-3,3-dimethyloxetane (**1**) might be ethyl α-me-

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[3] Greenberg, A.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978; p 94.

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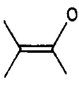
thylisobutenyl ether (**2**). The rate of hydrolysis of this



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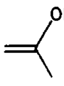

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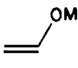

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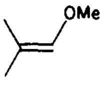

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substance in aqueous solution has not been measured, but an estimate of its hydrogen ion catalytic coefficient can be made by combining the specific rate of hydrolysis of ethyl isopropenyl ether (**3**) with the deactivating effect of two β-methyl groups. The latter, as measured by the catalytic coefficients for methyl vinyl ether (**4**; $k_{H^+} = 0.76$ $M^{-1}\ s^{-1}$)[1b] and methyl isobutenyl ether (**5**; $k_{H^+} = 0.025\ M^{-1}\ s^{-1}$)[5] amounts to a factor of 0.033, and combination of that with $k_{H^+} = 580\ M^{-1}\ s^{-1}$ for **3**[1b] leads to an estimate of $k_{H^+} = 19\ M^{-1}\ s^{-1}$ for **2**.

This estimate is nearly an order of magnitude greater than the rate constant determined here for the hydrolysis of 2-cyclohexylidene-3,3-dimethyloxetane. This shows that the latter is less reactive than its acyclic analogue, which indicates that the deactivating effect of introducing a double bond into a four-membered ring is stronger in the present case than the activating effect of converting an sp^2- to an sp^3-hybridized carbon atom in a six-membered ring.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for its financial support of this work.

Registry No. 2-Cyclohexylidene-3,3-dimethyloxetane, 60931-02-4.

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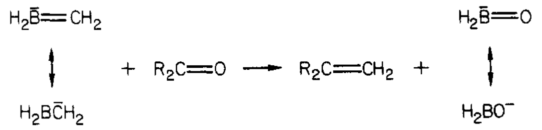
Communications

Wittig Reaction of a Boron-Stabilized Carbanion with Carbon Dioxide in the Gas Phase[1]

Summary: Boron-stabilized carbanions react with carbon dioxide in the gas phase to yield borinate anions. Neutral ketenes must be produced concurrently via a Wittig-type reaction.

Sir: The boron Wittig reaction, known for more than a decade, has been a subject of recent interest.[2] From reported ab initio calculations,[3] the metathesis shown in reaction 1 can be estimated to be very exothermic. In this



(1)

boron-stabilized carbanion

borinate anion

calcd $\Delta H = -34$ kcal/mol

reaction, a boron-stabilized carbanion is converted to a borinate anion, and the strength of the newly formed boron–oxygen bond drives the reaction to the right.

We report evidence that carbon dioxide also undergoes the boron Wittig reaction. Using Fourier Transform Mass Spectrometry (FTMS), we observe that boron-stabilized carbanions react with carbon dioxide at pressures on the order of 10^{-7} torr to yield borinate anions. With FTMS, ions can be stored for up to several seconds in a static ion trap before mass analysis. In this way, products from reactions between gaseous ions and neutral molecules can be observed at very low pressures.[4]

Our reagent ion, **1**, is derived from electron impact on triethylboron, as reaction 2 depicts. In the absence of other reagents, **1** reacts slowly with triethylboron by hydride transfer to produce gaseous triethylborohydride ion. The masses of all observed boron-containing ions agree with the natural abundance of the two stable isotopes, ^{10}B and ^{11}B.

$$(C_2H_5)_3B \xrightarrow[\text{electron impact}]{7\ \text{eV}} \underset{\substack{1\\ m/z\ 96,\ 97}}{(C_2H_5)_2B\bar{C}HCH_3} \xrightarrow{(C_2H_5)_3B} \underset{m/z\ 98,\ 99}{(C_2H_5)_3BH^-} \quad (2)$$

Ion **1** reacts with a variety of oxygenated compounds to yield diethylborinate anions, $(C_2H_5)_2BO^-$, which are observed at *m/z* 84 and 85. Reaction with water or with molecular oxygen is rapid, and both reactions are estimated to be very exothermic, as shown in reactions 3 and 4.

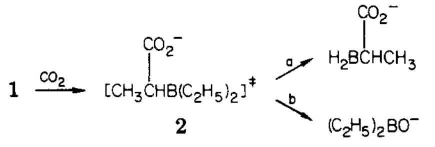
ΔH calcd for
R = R' = H

$$R_2B\bar{C}HR' + H_2O \rightarrow R_2BO^- + R'CH_3 \qquad -42\ \text{kcal/mol} \qquad (3)$$

$$R_2B\bar{C}HR' + O_2 \rightarrow R_2BO^- + R'CHO \qquad -110\ \text{kcal/mol} \qquad (4)$$

$$R_2B\bar{C}HR' + CO_2 \rightarrow R_2BO^- + R'CH{=}C{=}O \qquad +0.6\ \text{kcal/mol} \qquad (5)$$

Reaction between **1** and carbon dioxide is slower but also yields ions at *m/z* 84 and 85. We have taken some care to ensure that this observation is not due to trace impurities of air or water. Two different molecular formulas could correspond to these product ion masses. As reaction 5 shows, the Wittig reaction to yield diethylborinate yields a ketene as well. Thermochemical estimates do not show this reaction to be exothermic. An alternative is drawn as path a in reaction 6. Nucleophilic attack of carbon



(6)

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[1] Presented at the 31st Annual Conference on Mass Spectrometry and Allied Topics, Boston, MA, May 11, 1983.

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