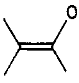
thylisobutenyl ether (**2**). The rate of hydrolysis of this substance in aqueous solution has not been measured, but an estimate of its hydrogen ion catalytic coefficient can be made by combining the specific rate of hydrolysis of ethyl isopropenyl ether (**3**) with the deactivating effect of two β-methyl 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**.



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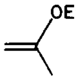

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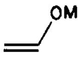

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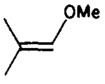

5

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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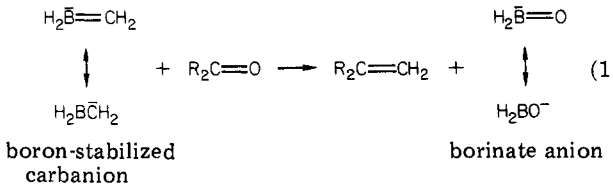
(5) Salomaa, P.; Nissi, P. *Acta Chem. Scand.* **1967**, *21*, 1386.

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 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.

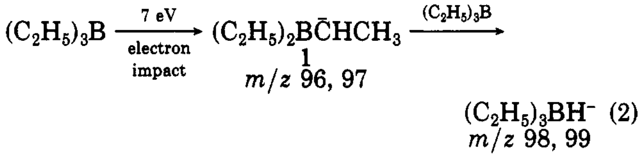


(1)

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

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.



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

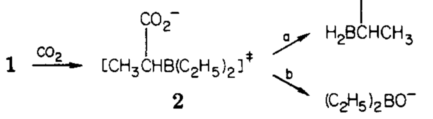
Ion **1** reacts with a variety of oxygenated compounds to yield diethylborinate anions, $(C_2H_5)_2BO^-$, which are observed at m/z 84 and 85. Reaction with water or with molecular oxygen is rapid, and both reactions are estimated to be very exothermic, as shown in reactions 3 and 4.

ΔH calcd for
R = R′ = H

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

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

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



(6)

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

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

(2) Pelter, A.; Singaram, B.; Wilson, J. W. *Tetrahedron Lett.* **1983**, *24*, 635–636, and references contained therein.

(3) Hinde, A. L.; Pross, A.; Radom, L. *J. Comput. Chem.* **1980**, *1*, 118–128.

(4) Wilkins, C. L.; Gross, M. L. *Anal. Chem.* **1981**, *53*, 1661A–1676A.

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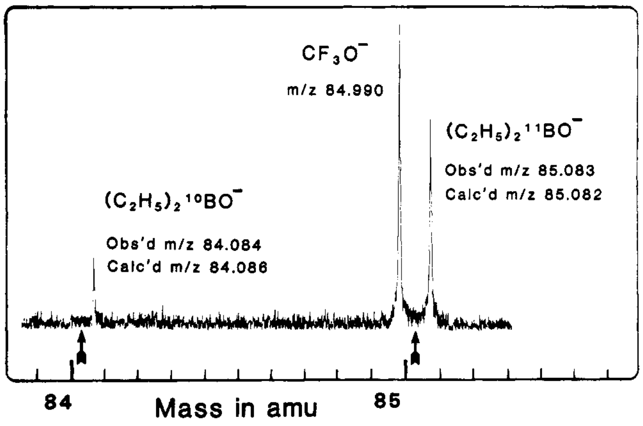

Figure 1. Fourier transform mass spectrum at 3 T of products from reaction of anion 1 with carbon dioxide and molecular oxygen at a total pressure of 10^{-7} torr. Boldface arrows indicate where ions with molecular formula $C_3H_6BO_2^-$ would have been observed, had they been present. Resolution=14 500.

dioxide by the carbanionic center to form carboxylate **2** can be estimated to be on the order of 10 kcal/mol exothermic. Subsequent expulsion of two ethylene molecules or of a butene molecule would yield $H_2BCH(CH_3)CO_2^-$, which has the same nominal mass as diethylborinate.

High-resolution mass measurements can distinguish between the alternative pathways of reaction 6. The isobaric products actually differ in exact mass by 0.036 amu, and base-line resolution of this difference is well within the capability of FTMS.[4] Figure 1 shows a high-resolution FTMS spectrum of the products from reacting **1** with carbon dioxide. The mass scale is calibrated with the CF_3O^- ion from perfluorokerosene. Molecular oxygen was also present in the reaction mixture. Reaction of **1** with oxygen unquestionably yields diethylborinate, and the reaction products of **1** with carbon dioxide are observed at exactly the same masses. No ion is seen above the base line at the masses corresponding to $H_2BCH(CH_3)CO_2^-$, and we conclude that reaction 5 is indeed taking place. We interpret this to mean that the intermediate adduct ion **2** (which is not observed) decomposes via path b shown in reaction 6. Of course, the neutral product is not directly identified, but we note that methylketene is the most stable C_3H_4O isomer.[5]

Wittig reaction of carbon dioxide to yield a ketene has not, to our knowledge, been previously reported. We observe it as a reaction of free boron-stabilized carbanions in the absence of counterions. But there is no apparent reason why this same reaction should not also proceed in solution. We foresee that FTMS may provide useful approaches for exploring reaction pathways of potential synthetic utility.

Acknowledgment. This work was supported by grants from the Research Corp. (T.H.M.) and by NSF Grant CHE 80-18245 (C.L.W. Co-P.I. with M. L. Gross, University of Nebraska). The UCR departmental FTMS facility was purchased with the help of NSF departmental research instrumentation Grant No. CHE 82-17610 and of Grant No. BRSG SO7 RR07010-18 awarded by the Biomedical Research Grant Program, Division of Research Resources, National Institutes of Health.

Registry No. 1, 86120-54-9; CO_2, 124-38-9; $(C_2H_5)_3B$, 97-94-9; $(C_2H_5)_3BH^-$, 75338-98-6; $(C_2H_5)_2BO^-$, 86120-55-0; $CH_3CH{=}C{=}O$, 6004-44-0.

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Received May 3, 1983

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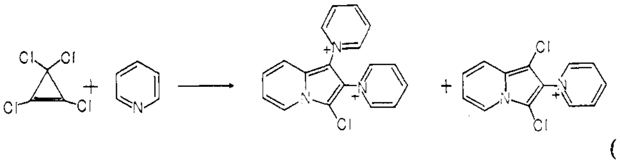
(5) Schiess, P.; Radimerski, P. *Helv. Chim. Acta* **1974**, *57*, 2583–2597.

An Offbeat Reaction of Pyridine with Tetrachlorocyclopropene: A New Synthesis of Indolizines

Summary: Pyridine reacts with tetrachlorocyclopropene to give indolizine derivatives.

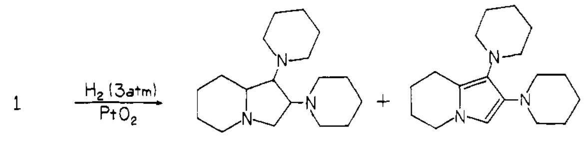
Sir: During investigations of cyclopropenium systems derived from tetrachlorocyclopropene (TCC),[1] we observed an unexpected reaction with pyridine. When pyridine was added to a methylene chloride solution of TCC at 0 °C, a purple color occurred instantly. With time the color faded and a green-brown precipitate formed. This solid, **1**, was washed with CH_2Cl_2 and recrystallized from aqueous acetonitrile to yield yellow sheets, soluble in water and insoluble in nonpolar organic solvents. Two additional compounds were isolated from washes and supernatant. One was pyridinium hydrochloride; the other, isolated as its tetraphenylborate salt, was a bright orange, multifaceted solid, **2**. The proposed structures of **1** and **2** are indicated in eq 1.[2]



(1)

1 2

The structures were deduced primarily from UV–vis (H_2O; λ, nm [log ε]: 219 [4.36], 264 [3.96], 390 [3.42])[3] and ^1H NMR (Table I). In addition, **1** was hydrogenated to a complex mixture from which column chromatography ($CHCl_3$–CH_3OH) provided a 60% yield of material indicated by NMR and mass spectroscopy to be a 72:28 mixture of **3** and **4**.



3 4

Assignment of protons of **1** was facilitated by carrying out the reaction with 4-picoline, which gave the corresponding methyl-substituted products and the expected changes in intensity/coupling patterns [H_6 (δ 7.01, d of d);

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(1) (a) Tobey, S. W.; West, R. *J. Am. Chem. Soc.* **1966**, *88*, 2481. (b) Tobey, S. W.; West, R. *Tetrahedron Lett.* **1963**, 1179. This preliminary report of TCC synthesis is especially interesting in that pyridine was investigated as a base to convert pentachlorocyclopropene to TCC.

(2) **1** (as monohydrate): Anal. Calcd for $C_{18}H_{14}N_3Cl_3 \cdot H_2O$: C, 54.50; H, 4.06; N, 10.59; Cl, 26.81. Found: C, 54.35; H, 4.07; N, 10.55; Cl, 26.58. **2**: Anal. Calcd for $C_{37}H_{29}N_2Cl_3B$: C, 76.18; H, 5.01; N, 4.80; Cl, 12.15. Found: C, 76.11, H, 5.08; N, 4.82; Cl, 12.03.

(3) Compare: Katriztsky, A. R. "Physical Methods in Heterocyclic Chemistry"; Academic Press: New York, 1963; Vol. II.