conformation like that which may precede the elimination transition state of the alkoxide 2a (M = Li).

As summarized in Table I, other nucleophiles such as ethyllithium,¹³ hydride (LiAlH₄), (phenyldimethylsilyl)lithium, and (trimethylstannyl)lithium showed parallel behavior: i.e., good Felkin-Anh selectivity during the carbonyl addition and exclusive formation of a single enol ether isomer. With R groups such as phenyl and vinyl capable of modest carbanion stabilization the rate of elimination was much higher than for $R = CH_3$, being complete in at most a few hours at -78 °C. The rate difference between 2a and 2b was much smaller than for $R = CH_3$ (~7x for $R = C_6H_5$) so that both enol ethers were formed at 0 °C.

With R groups such as alkynyl and m-(trifluoromethyl)phenyl the stereoselectivity was still good during the carbonyl addition but the elimination was nonstereospecific. We believe that for these cases the elimination process has become E_{1cb} -like, i.e., a silvl migration to a stabilized siloxy carbanion with sufficient lifetime to lose stereochemical memory.

We have extended the process to silyl ketones with other substitution patterns. For example, reaction of methyllithium with 2-(phenylthio)-1-(dimethylphenylsilyl)-1propanone gave an 88/12 ratio of diastereomeric alcohols and a 98/2 E/Z ratio of the appropriate enol ethers.

The approach described above is not the only way to prepare alkoxides such as 2. The same intermediates could be generated by addition of $C_6H_5CH_2CH(SC_6H_5)Li$ to methyl trimethylsilyl ketone, or by addition of R₃SiLi to an α -phenylthio alkyl ketone.¹⁴ Table II summarizes the results obtained by these procedures, as well as those obtained by some more traditional methods for enol ether formation. It can be seen that both stereoisomers are now available with excellent stereocontrol and essentially complete regiocontrol (entries 6 and 7) simply by interchanging the role of silyl and alkyl groups as nucleophile or pendant group.

Acknowledgment. We thank the National Science Foundation for generous support of our work and J. J. Rusek for exploratory experiments.

(12) Anti elimination of hydroxide has been observed during a similar rearrangement-elimination studied by Hudrlik^{7c} and co-workers.

(13) Approximately 8% reduction (hydride addition, erythro/threo = 7/1) accompanied the ethyllithium addition product. n-BuLi, sec-BuLi, (14) Vedejs, E.; Arnost, M. J.; Eustache, J. M.; Krafft, G. A. J. Org.

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Ruthenium-Catalyzed Synthesis of Vinyl Carbamates from Carbon Dioxide, Acetylene, and Secondary Amines

Summary: RuCl₃·3H₂O catalyzed the reaction of CO₂, acetylene, and secondary amines giving vinyl carbamates $R_2NCO_2CH = CH_2$ with a small amount of 2-butadienyl carbamates $CH_2 = C(R_2NCO_2)CH = CH_2$.

Sir: The catalytic incorporation of CO₂ into organic compounds has been an attractive goal in recent years¹ in order to produce functionalized substrates with an inexpensive and stable reagent. However, few examples are known of such reactions involving industrially available chemicals and of particular importance concerning their application to industry besides butadiene and epoxides.

As for reactions of CO₂ affording carbamates, Inoue et al. recently reported the catalytic formation of carbamic esters from CO₂, amines, and epoxides using a metalloporphyrin catalyst.² We have also reported a novel synthesis of vinyl carbamate derivatives from CO₂, diethylamine, and hex-1-yne or phenylacetylene in the presence of $Ru_3(CO)_{12}$.³ $Ru_3(CO)_{12}$ showed very little activity toward acetylene. This was unfortunate as there is significant commercial interest in nonsubstituted vinyl carbamates (as precursor for varnish or agricultural chemicals⁴) previously obtained from vinyl chloroformate.⁵

We have now found that acetylene itself reacts with CO_2 and secondary amines in the presence of RuCl₃·3H₂O to give vinyl carbamates 2 in one step and in good yields. A small amount of 1-methylene-2-propenyl carbamate 3 was formed, as well.

$$R_{2}NH + CO_{2} + HC \equiv CH \xrightarrow{\text{RuCl}_{3} \cdot 3H_{2}O}$$

$$1 \qquad \qquad CH_{3}CN, 90 \text{ °C} \qquad \qquad CH_{2}$$

$$R_{2}NCO_{2}CH = CH_{2} + R_{2}NCO_{2}CCH = CH_{2}$$

$$2 \qquad 3$$

$$R_{2}N = \boxed{N, ON, ON, and Et_{2}N}$$

$$a \qquad b \qquad c \qquad d$$

Acetonitrile (50 mL), RuCl₃·3H₂O (2 mmol), pyrrolidine 1a (100 mmol), and acetylene (320 mmol) were successively placed in a 500-mL autoclave and stirred under CO₂ pressure (15 atm) at 90 °C for 20 h. The resulting solution was concentrated, and 200 mL of ether was added. After washing with 50 mL of dilute HCl solution (3%) several times, the organic layer was concentrated and distilled under reduced pressure. The primary product (6.5 g) and the secondary product (0.4 g) were identified as [(N,Ntetramethylenecarbamoyl)oxy]ethylene (2a) and 2-[(N,Ntetramethylenecarbamoyl)oxy]buta-1,3-diene (3a), respectively by IR, NMR, and GC-MS analyses.⁶ The yields, based on pyrrolidine, were 46% and 2%, respectively. Secondary amines such as piperidine (1b), morpholine (1c), and diethylamine (1d), under similar con-

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(6) The boiling points and the analytical data of the products are as follows. 2a: 49 °C (0.5 mmHg); ¹H NMR (CDCl₃) δ 1.8 (m, 4 H), 3.4 (m, 4 H), 4.5 (m, 2 H), 7.2 (m, 1 H); IR (neat) 1720 cm⁻¹; mass spectrum, m/e141 (M⁺). 3a: ¹H NMR (CDCl₃) δ 1.9 (m, 4 H), 3.4 (m, 4 H), 4.9 (s, 2 H) 141 (M⁺). **3a**: ¹H NMR (CDCl₃) δ 1.9 (m, 4 H), 3.4 (m, 4 H), 4.9 (s, 2 H), 5.2 (m, 2 H), 6.2 (m, 1 H); IR (neat) 1720 cm⁻¹; mass spectrum, m/e 167 (M⁺). **2b**: 53 °C (0.6 mmHg); ¹H NMR (CDCl₃) δ 1.5 (m, 6 H), 3.4 (m, 4 H), 4.5 (m, 2 H), 7.2 (m, 1 H); IR (neat) 1715 cm⁻¹; mass spectrum, m/e155 (M⁺). **3b**: ¹H NMR (CDCl₃) δ 1.5 (m, 6 H¹), 3.5 (m, 4 H), 4.9 (s, 2 H), 5.2 (m, 2 H), 6.2 (m, 1 H); IR (neat) 1715 cm⁻¹; mass spectrum, m/e181 (M⁺). **2c**: 56 °C (0.7 mmHg); ¹H NMR (CDCl₃) δ 3.5 (m, 8 H), 4.5 (m, 2 H), 7.2 (m, 1 H); IR (neat) 1718 cm⁻¹; mass spectrum, m/e 157 (M⁺). **2d**: 41 °C (3 mmHg); ¹H NMR δ 1.1 (t, 6 H), 3.3 (q, 4 H), 4.5 (m, 2 H), 7.2 (m, 1 H); IR (neat) 1718 cm⁻¹; mass spectrum, m/e 143 (M⁺). **3d**: ¹H NMR (CDCl₃) δ 1.2 (t, 6 H), 3.4 (q, 4 H), 4.9 (s, 2 H), 5.2 (m, 2 H), 6.2 (m, 1 H); IR (neat) 1718 cm⁻¹; mass spectrum, m/e 169 (M⁺). (m, 1 H); IR (neat) 1718 cm⁻¹; mass spectrum, m/e 169 (M⁺)

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Table I. Formation of Carbamates from CO₂, Acetylene, and Secondary Amines

entry 1	secondary amine	products (isolated yield, %) ^b	
		2a (46)	3a (2)
2	piperidine (1b)	2b (34)	3b (4)
3	morpholine (1c)	2c (20)	not analyzed
4	diethylamine (1 d)	2d (10)	3d (2)

^aCH₃CN (50 mL), RuCl₃·3H₂O (2 mmol), amine (100 mmol), acetylene (320 mmol), CO₂ (15 atm), 90 °C, 20 h. ^bBased on amines. The yield of 3 was determined by GLC analysis of the distillate of high boiling point which mainly consisted of 3. High molecular weight products were not analyzed.

ditions lead to the vinvl carbamates 2b, 2c, and 2d, respectively, with a small amount of derivatives 3 as shown in Table I.

Little of the unreacted amines were recovered and a substantial amount of polymeric products were obtained as residue in all the cases. This may be caused by the polymerizations of acetylene, the carbamate monomers, and/or some monomers formed by reactions of acetylene with amines.

Although the reaction conditions are not determined as optimum for each of the secondary amines, those of low steric hindrance and high basicity seem to be favorable for the formation of carbamates. Primary amines did not undergo this reaction.

The reaction mechanism may involve a nucleophilic attack of the ammonium carbamate to acetylene coordinated on ruthenium. 1-Methylene-2-propenyl carbamates are considered to be formed via vinylacetylene resulting from the in situ dimerization of acetylene catalyzed by RuCl₃·3H₂O. Vinylacetylene is known to react with carboxylic acids to give 1-methylene-2-propenyl carboxylates.⁷

This novel synthesis of simple vinyl carbamates presents the advantage over the multistep synthesis based on phosgene, to result in one step from the nontoxic reagent CO₂.

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Decarboxylation of Isatoic Anhydride in the **Crystalline State**

Sir: Sometimes one pursues a laboratory observation that is unrelated to any personal interest or experience of the past. Intuition, memory, analogy, and testimony play no role: mere curiosity motivates the decision to experiment further. Thus we were curious about an unexpected observation made during the course of our work: Isatoic anhydride decarboxylates when heated at temperatures below its melting point of 245 °C (eq 1). Crystals eject



 CO_2 , often shattering in the process. What is the main product of this solid-state reaction? What are the mechanistic details? Is the solid-state reactivity^{1,2} different from that in solution? These and other questions are addressed herein.³

Product. The product is a high-melting amorphous material. It is insoluble in all common organic solvents; appreciable solubility was noticed only in concentrated H_2SO_4 . Elemental analyses correspond closely to that of isatoic anhydride minus CO₂.⁴ Gel permeation chromatography (column = micro Bondagel; solvent = hexafluoro-2-propanol)⁵ gave a weight-average molecular weight $M_{\rm w}$ equal to five times that of isatoic anhydride. These facts, plus IR data and flame tests,⁶ all point strongly toward an oligomeric polyamide:



Kinetics. Reaction rates were monitored gravimetrically and by gas volume measurements; the two methods agree. Plots of "percent conversion vs. time" are sigmoidal. displaying an induction period prior to a steep rise in rate. Perhaps when a crystal defect appears at a reaction site, further reaction is facilitated at that location; the process is thereby autocatalytic. Curiously, the yield at "infinity" was always a few percent less than theoretical. A small amount of isatoic anhydride, which could be leached from the product by a DMF wash, resists decarboxylation. Rates of decarboxylation depend upon the purity of the isatoic anhydride. Thus, 4× recrystallized isatoic anhydride (EtOH + activated carbon) reacts 2-3 times more slowly than once recrystallized material. All work was carried out on highly purified isatoic anhydride. Reaction times are also sensitive to temperature. For example, about 90% of the isatoic anhydride was unreacted after 60 min at 210 °C, whereas only 12% remained after 60 min at 220 °C. Particle size is, on the other hand, not a factor.

Summary: Isatoic anhydride when heated below its melting point decarboxylates to form a thermally stable polyamide. Gel permeation chromatography, kinetics, microscopy, dopant studies, etc. were carried out to characterize the reaction.

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