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 (trimethylstanny1)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 $R = CH₃$, being complete in at most a few hours at -78 *"C.* The rate difference between 2a and 2b was much smaller than for $R = CH_3 (\sim 7x \text{ for } R = C_6H_5)$ so that both enol ethers were formed at $0 °C$.

With R groups such as alkynyl and m -(trifluoromethy1)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 silyl 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 *881* 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,

and t-BuLi gave increasing amounts of reduction. **(14)** Vedejs, E.; Arnost, M. J.; Eustache, J. M.; Krafft, G. **A.** *J.* Org. *Chem.* **1982,47, 4384.**

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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 = $\text{C}(\text{R}_2\text{NCO}_2)\text{CH}$ = CH_2 .

Sir: The catalytic incorporation of $CO₂$ into organic compounds has been an attractive goal in recent years' 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 $CO₂$ 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.

$$
R_2NH + CO_2 + HC \equiv CH \frac{R_1C_1 + C_2}{R_1C_2 \cdot 3H_2O}
$$

\n
$$
R_2NCO_2CH = CH_2 + R_2NCO_2CCH = CH_2
$$

\n
$$
R_2N = \begin{bmatrix} R_1 & R_2 & R_1C & R_2 \cdot 3 & 3 \end{bmatrix}
$$

\n
$$
R_1N = \begin{bmatrix} R_1 & R_1 & R_2 & R_1 \cdot 3 & 3 \end{bmatrix}
$$

\n
$$
R_2N = \begin{bmatrix} R_1 & R_1 & R_2 & R_1 \cdot 3 & 3 \end{bmatrix}
$$

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$$
R_1N = \begin{bmatrix} R_1 & R_1 & R_2 & R_1 \cdot 3 & 3 \end{bmatrix}
$$

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R_2N = \begin{bmatrix} R_1 & R_2 & R_1 \cdot 3 & 3 \end{bmatrix}
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R_1N = \begin{bmatrix} R_1 & R_2 & R_1 \cdot 3 & 3 \end{bmatrix}
$$

\n
$$
R_2N = \begin{bmatrix} R_1 & R_2 & R_1 \cdot 3 & 3 \end{bmatrix}
$$

Acetonitrile (50 mL), RuC13.3H20 **(2** mmol), pyrrolidine la (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 HC1 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,N*tetramethylenecarbamoyl)oxy]ethylene $(2a)$ and $2-[N,N-1]$ **tetramethylenecarbamoyl)oxy]buta-1,3-diene** (3a), respectively by IR, NMR, and GC-MS analyses. 6 yields, based on pyrrolidine, were 46% and 2%, respectively. Secondary amines such as piperidine (lb), morpholine (IC), and diethylamine (ld), 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-'; maw **spectrum,** *m/e* 141 (M⁺). **3a**: ¹H NMR (CDCI₃) δ i.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 (CDCI₃) δ 1.5 (m (m, **1** H); IR (neat) **1718** cm-'; mass spectrum, m/e **169 (M').**

⁽¹⁾ Inoue, s.; Yamazaki, N. Organic and Bio-organic Chemistry *of* Carbon Dioxide; Kodansha; Tokyo, **1982.**

⁽²⁾ Kojima, F.; Aida, T.; Inoue, S. J. Am. Chem. Soc. 1986, 108, 391.
(3) Sasaki, Y.; Dixneuf, P. J. Chem. Soc., Chem. Commun. 1986, 790.
(4) Boivin, S.; Chettovf, A.; Hemerz, P.; Boileau, S. Polym. Bull. 1983,

^{9,} **114.**

Table **I.** Formation **of** Carbamates from **COz,** Acetylene, and Secondary Amines"

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

 $^{\circ}$ CH₃CN (50 mL), RuCl₃.3H₂O (2 mmol), amine (100 mmol), acetylene (320 mmol), CO_2 (15 atm), 90 °C, 20 h. ^b Based 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 vinyl 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.'

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 $CO₂$.

Acknowledgment. We are grateful to the C.N.R.S.- S.N.P.E. "Groupement Scientifique *C02",* which supported this investigation.

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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

COz, 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 **HzS04.** 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, 4X 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 OC, 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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(3) For full details, see: Kaiserman, H. B. "Part I. A Proton Transfer
Trajectory Study Utilizing a System of Known Angularity. Part II. Characterization of Phenyl Phosphonate **as** a Micellar Counterion. Part 111. The Solid State Thermal Decomposition of Isatoic Anhydride" Ph.D. Thesis, Emory University, Atlanta, **1984;** pp **87-179.**

⁽⁴⁾ The elemental analysis of product was found to be **69.15%** C, **4.09% H,** and **11.38%** N compared **to** values calculated for 'isatoic an- hydride minus COz" of **70.58%** C, **4.23% H,** and **11.76%** N.

⁽⁵⁾ Performed by Modchrom, Inc., Mentor, OH.

(6) Urbanski, J.; Czerwinski, W.; Janicka, K.; Majewska, F.; Zowall, H.

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