

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

entry	secondary amine	products (isolated yield, %) ^b	
		2a (46)	3a (2)
1	pyrrolidine (1a)	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)

^a CH₃CN (50 mL), RuCl₃·3H₂O (2 mmol), amine (100 mmol), acetylene (320 mmol), CO₂ (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.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.

Acknowledgment. We are grateful to the C.N.R.S.-S.N.P.E. "Groupement Scientifique CO₂", which supported this investigation.

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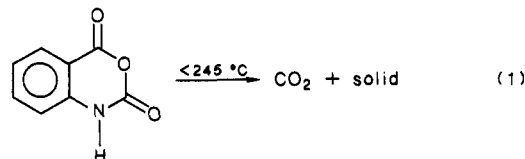
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Decarboxylation of Isatoic Anhydride in the Crystalline State

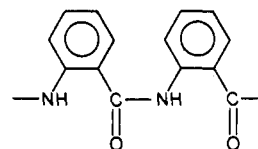
Summary: Isatoic anhydride when heated below its melting point decarboxylates to form a thermally stable polyamide. Gel permeation chromatography, kinetics, microscopy, dopant studies, etc. were carried out to characterize the reaction.

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



CO₂, 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 H₂SO₄. 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_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.

(1) Paul, I. C.; Curtin, D. Y. *Acc. Chem. Res.* 1973, 6, 217.

(2) Gavezzotti, A.; Simonetta, M. *Chem. Rev.* 1982, 82, 1.

(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 III. 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 anhydride minus CO₂" 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. *Handbook of Analysis of Synthetic Polymers and Plastics*; Halsted: New York, 1977; pp 21-22.

Similar time curves were obtained for the following sieve cuts: <210, 250-297, and >420 μm . No difference in kinetics was observed between silitated and unsilitated glassware or between the presence and absence of an N_2 purge. Decarboxylation could not be induced photochemically (450-W Hanovia medium-pressure bulb for 24 h in an argon atmosphere).

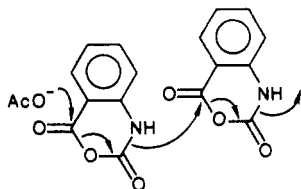
Microscopy. A single isatoic anhydride crystal was heated to 200 $^\circ\text{C}$ while viewed under 40 \times magnification (Vickers polarizing microscope). Photomicrographs taken periodically show no evidence of a "reaction front". Instead, small bits of solid break off from the crystal as the surface becomes progressively more pitted. After 25 min, the original "chunk" appears completely amorphous—although most of the isatoic anhydride has yet to react. Visual inspection suggests, therefore, that the reaction initiates at the surface (in apparent conflict with the rate insensitivity to particle size).

Thermal Stability of Product. The product, a remarkably stable organic solid, softens to the touch of a probe at $T_g = 254$ $^\circ\text{C}$ and melts with discoloration at $T_m = 354$ $^\circ\text{C}$. A thermal stability curve was secured by heating the product at 300 $^\circ\text{C}$ (ambient atmosphere) and plotting "percent weight loss vs. time". There is only about a 11% weight loss after 5 h; an additional 13 h of heating does not further diminish the weight. By way of comparison, the polyamide formed from terephthalyl chloride and *p*-phenylenediamine loses 7.4% of its weight at 300 $^\circ\text{C}$ for 40 h.⁷

Solution Chemistry. Isatoic anhydride in DMF (1.1 M), dioxane (1.1 M), or diglyme (0.6 M) was heated at 220 $^\circ\text{C}$ for 24 h in a sealed glass tube purged with nitrogen. Starting material was recovered in >90% yield. In contrast to the crystalline state, the solution phase lacks the molecular constraints necessary for a rapid oligomerization reaction. In current parlance, the reaction is under "lattice control".⁸

N-Methylisatoic Anhydride. *N*-Methylisatoic anhydride (recrystallized 3 \times from EtOH, mp 170-178 $^\circ\text{C}$) does not decompose when heated at 160-185 $^\circ\text{C}$ as a solid or a melt. In fact, no decomposition was observed at 270 $^\circ\text{C}$, a marked difference in reactivity from the *N*-protonated analogue.

Catalysis by Dopants. Isatoic anhydride (100 mg) was added to a solution or slurry of a dopant (1 mg) in 5 mL of water. The water was then removed with the aid of a rotary evaporator. Isatoic anhydride, "doped" in this manner, was dried over P_2O_5 and subjected to 200 $^\circ\text{C}$ for 20 min. Samples doped with anthranilamide and sodium acetate expelled 14% and 81% of the theoretical CO_2 volume, respectively, compared to only 2% for undoped isatoic anhydride. The catalysis could be "physical", arising from irregularities or local melting produced in the crystal lattice. Alternatively, the catalysis could be "chemical" with the dopant (included or otherwise in the lattice) serving as a nucleophilic initiator:



Not only does sodium acetate accelerate the decarboxylation, it affects the molecular weight distribution of the

product. Thus, 1% sodium acetate increases the weight average M_w from 740 to 1280. Moreover, the "polydispersity index" (defined as the weight average M_w /number average M_n) increases almost 3-fold; this means that the sodium acetate induced product has a much broader range of molecular weights.

Crystal Structure. The crystal structure of isatoic anhydride has been reported previously.⁹ Each unit cell contains four molecules. These are arranged as two pairs of centrosymmetric dimers engaged in intermolecular amide-amide hydrogen bonding. An analysis using published X-ray data⁵ in conjunction with the SHELXTL MOLECULAR GEOMETRY program (Nicolet, Inc.) shows that 6.79 \AA separates the nitrogens from their nearest electrophilic carbonyl carbon. Obviously, coupling between two molecules in the course of oligomer formation would require a major disruption of lattice organization (including H-bond cleavage). Hence, it is likely that loci of crystalline disorder provide intermolecular contacts which initiate the reaction. This is consistent with the observed rate sensitivity to impurities and dopants.

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Reactions of Diisopropyl Tartrate Modified Allyl- and (*E*)- and (*Z*)-Crotylboronates with β -Alkoxy- α -methylpropionaldehydes: A Reagent Based Solution to the Acyclic Dipropionate Problem

Summary: Compounds 5, 6, 7, 9, and 10 are now available each with a minimum of diastereoselectivity of 87% from the reactions of β -alkoxy- α -methylpropionaldehyde 4 and the diisopropyl tartrate modified crotyl- and allylboronates 1-3.

Sir: The development of concise, highly stereoselective methods for the synthesis of the 1,3-dimethyl-2-hydroxy or 1,3-dihydroxy-2-methyl stereochemical relationships present in macrolide, ansamycin, and other natural products of propiogenic/acetogenic biosynthetic origin is a topic of considerable current interest.¹ Many studies have focused on the construction of synthetic equivalents of 5-10. Although several ingenious but multistep solutions have been reported,^{1a-f} until now a general one-step protocol for elaboration of a chiral aldehyde (e.g., 4) with a family of suitable enolates or allylmetal reagents has been lacking.²

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