1 h. Then the reaction mixture was treated with warm water containing a small amount of hydrochloric acid, and the insoluble part was collected, washed with water, and dried. The crude product (13.5 g) was refluxed with 600 g of chlorobenzene for 2 h, and the insoluble material was removed by hot filtration. The filtrate was evaporated to dryness, giving 3.00 g of brown solid. It was sublimated under vacuum (10^{-3}–10^{-4} torr) at 150 °C and then 280–320 °C to give 0.486 g of recovered **5a** and 1.968 g of brown sublimates, respectively. The latter was recrystallized from chlorobenzene, giving 1.004 g of **3** which melted at 330–331 °C (lit.[2,4] orange-red needles, mp 331 °C, UV λ_{max} (C_6H_6) 482 nm). The mother liquor was chromatographed on alumina and eluted with chlorobenzene. The products, obtained by evaporation of successive fractions, were purified by recrystallization and vacuum sublimation to give 66 mg of **2** (2%) (lit.[5] yellow needles, mp 331 °C, UV λ_{max} (C_6H_6) 444 nm), 175 mg of **3** (total 1.179 g, 38%), 51 mg of recovered **5a** (total 537 mg, 10.7%), and 140 mg of **4** (4.5%) (lit.[2] brown-yellow needles, mp 307 °C, UV λ_{max} (C_6H_6) 471 nm).

In addition, the use of zinc dust, instead of copper powder,[6] afforded comparable results to those described above when the reaction mixture was heated at 180–200 °C for 30 min.

Condensation of 3-Chlorobenzanthrone (5b). A mixture of 2.00 g of **5b**, 2.0 g of zinc dust,[7] 10 g of zinc chloride, and 2 g of sodium chloride was kept at 220–230 °C for 1 h, and the reaction mixture was worked up in a manner similar to that used for **5a**, giving 13 mg of **2** (1%), 333 mg of **3** (26%), 35 mg of **4** (2.7%), and 418 mg of recovered **5b** (20.9%).

Acknowledgment. We express our thanks to Professor Hiroo Inokuchi and Dr. Hidemasa Takaya of The Institute for Molecular Science for their kind advice.

Registry No. 2, 191-53-7; 3, 191-46-8; 4, 190-93-2; 5a, 81-96-9; 5b, 6409-44-5.

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[6] The use of zinc dust is undesirable for **1** because of forming tarry matter.

[7] Copper powder was of little use to force this condensation reaction.

On the Mechanism of Imide Formation in the Thermolysis of ^{18}O-Labeled *N*-Butylphthalamic Acid

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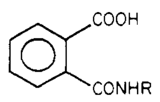
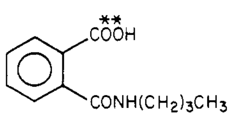
The thermal dehydration of phthalamic acids has long been a well-known method for the preparation of phthalimides;[1] however, the mechanism of imide formation in this reaction has not been elucidated. We have recently shown that the relative proportions of imide and anhydride obtained in thermolysis of a series of *N*-alkyl-substituted phthalamic acids **1** are very sensitive to the steric bulk of the alkyl residue on nitrogen.[2] Specifically, the amount of imide formed in the thermolysis of these compounds decreases dramatically with the number and size of branching groups on the carbon atom attached to nitrogen. Although there is evidence to suggest that isoimides are intermediates in the formation of imides,[3,4] we were unable to observe their formation in our study. We were able to show, however, that isoimides rearranged rapidly to imides under our conditions and thus the intermediacy of isoimides in the formation of imides remains a mechanistic possibility.



1

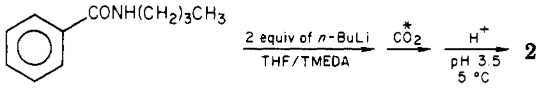


2

In evaluating the mechanistic implications of our observation of a steric inhibition to imide formation, we were interested in determining the "nucleophilic–electrophilic" relationship between the acid and amide functions in this ring closure reaction. In order to address this question experimentally, we have prepared the oxygen-18-labeled phthalamic acid **2** and examined by mass spectrometry the ^{18}O content of the phthalimide obtained from its thermolysis. The results of our examination are reported here.

Results and Discussion

The ^{18}O-labeled phthalamic acid **2** was chosen as a model compound because we had previously shown that *N*-*n*-butylphthalamic acid gives only imide upon thermolysis. Additionally, on the basis of an analysis of the mechanistic possibilities leading to imide formation, the labeled compound **2** might allow us to determine the "nucleophilic–electrophilic" relationship between the amide and acid functions in this ring closure reaction based on the ^{18}O content of the imide obtained from its thermolysis. The labeled phthalamic acid **2** was prepared by the ortho lithiation of *n*-butylbenzamide[5] and reaction of the resultant dianion with solid CO_2 (99.9% ^{18}O) (eq 1). The oxygen–18 content of the phthalamic acid prepared in this manner was evaluated by field-desorption mass spectrometry.



(1)

This technique was chosen because other techniques such as electron impact result in rapid and complete conversion to imide. The field-desorption spectrum showed an isotopically uncomplicated ion cluster for the protonated molecule $(M + H)^+$ at *m*/*e* 226 completely consistent with clean incorporation of the labeled CO_2. Loss of label by exchange during the acid workup was therefore not observed. This point was further supported by our observation that unlabeled *N*-*n*-butylphthalamic acid failed to exchange its oxygens in ^{18}O-enriched water (60% ^{18}O) at pH 3 at 80 °C after 48 h. At pH values less than 3, oxygen scrambling was observed.

Heating in situ of the field-desorption emitter to about 200 °C resulted in imidization of the amic acid followed by observation of a molecular ion at *m*/*e* 205 for the product imide. The pattern observed for this ion was also isotopically uncomplicated, thereby indicating that imidization occurred exclusively with retention of a single ^{18}O label.

A second experiment involving imidization on the solids probe (200 °C) followed by analysis by electron-impact mass spectrometry provided an identical result. In both of these reactions the imidization reaction was solvent free

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[1] Chapman, E.; Stephens, H. *J. Chem. Soc.* **1925**, *127*, 1793. Sherrill, M. L.; Schaeffer, F. L. *J. Am. Chem. Soc.* **1928**, *50*, 475.

[2] Verbicky, J. W.; Williams, L. *J. Org. Chem.* **1981**, *46*, 175.

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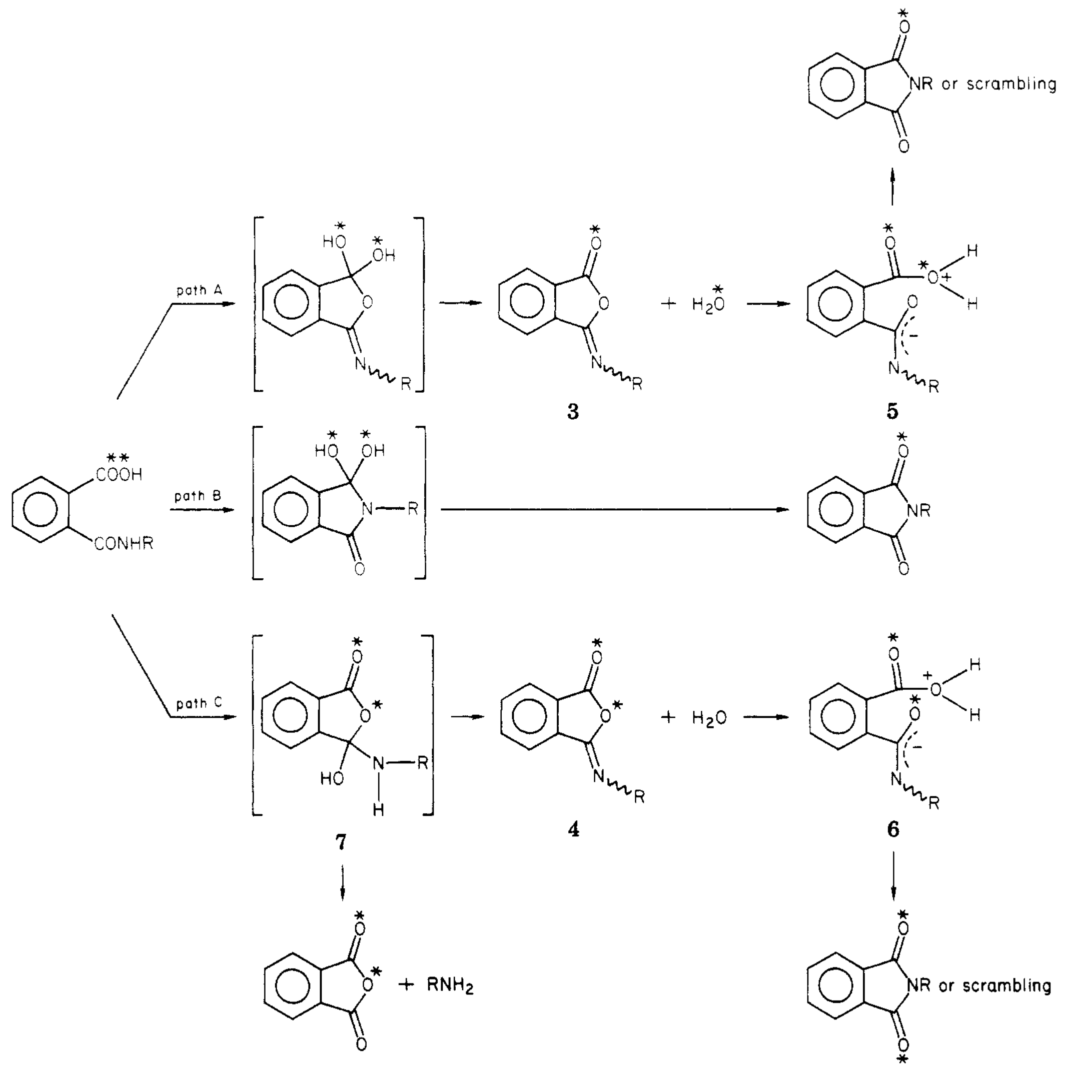
[5] For a review of ortho-lithiation reactions, see Gschwend, H. W.; Rodriguez, H. *Org. React.* **1979**, *26*, 1.

Scheme I



and the water evolved can reasonably be assumed to be rapidly removed by the high vacuum ($\sim 1 \times 10^{-7}$ torr).

The formation of imide in the thermolysis of amic acids can be envisioned as proceeding by any of three mechanistic pathways outlined in Scheme I. The presentation of the mechanistic outline shown in Scheme I is only meant for the purposes of this discussion to distinguish nucleophilic attack by the amide or carboxylic acid functions and is not meant to imply the formation of discrete or transient cyclic tetrahedral species, although their existence has been postulated.[6] Proton transfers prior to or accompanying such ring closures are not shown since these mechanistic details are not known. Reaction by both path A and B involves the ambident amide function acting as the nucleophilic component, while path C involves nucleophilic attack of the carboxylic acid function on the amide. Reaction by path B involving nucleophilic attack by the amide nitrogen should clearly lead to the formation of imide containing a single ^{18}O label, which is consistent with the results obtained here. Futhermore, steric inhibition to imide formation via this pathway would be understandable in terms of *F* strain.[7] Reaction by paths A and C proceeds through the intermediacy of isoimides and should give rise to the singly and doubly labeled isoimides **3** and **4**, respectively. Rearrangement of the isoimides **3** and **4** according to the mechanism proposed by Ernst and Schmir[8] and later corroborated by Sauers et al.,[9] involving nucleophilic catalysis by the water of cyclization, should proceed through species such as **5** and **6**, respectively. Attack of the labeled water on the imino carbon of **3** would result in scrambling of the oxygen labels. If proton transfer between the incoming water molecule and the leaving amide anion in **5** occurs, the starting material would be regenerated, while proton transfer between the labeled oxygens of **5** prior to rearrangement and ring closure should result in the formation of imide containing a single ^{18}O label. Thus, the rearrangement of **3** catalyzed by the water of cyclization can result in the formation of imide containing a single label or a mixture of labels. Only the former case is consistent with the results obtained here. Attack of the unlabeled water on the imino carbon of **4** will regenerate the starting material. Proton transfer between the incoming water molecule and the labeled carbonyl oxygen or the leaving amide anion in **6** prior to rearrangement and ring closure would result in scrambling of the oxygen labels. If proton transfers do not occur prior to rearrangement and ring closure, then only imide containing two oxygen labels will be formed. Thus, the rearrangement of **4** catalyzed by the water of cyclization can result in the formation of imide containing two ^{18}O labels

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(6) Bender, M. L.; Chow, Y. L.; Chloupek, F. *J. Am. Chem. Soc.* **1958**, *80*, 5380.

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J. Org. Chem. 1981, 46, 3925–3928

or a mixture of labels, neither of which is consistent with the results obtained here.

It is therefore clear that in the formation of imides by the thermal dehydration of amic acids, the amide function serves as the nucleophilic component in the ring closure reaction and that the nature of the steric inhibition to imide formation previously observed does not reflect a partitioning of a species such as **7** between the formation of anhydride and the isomide **4** based on the relief of steric interactions in such an intermediate. Furthermore, on the basis of the results obtained here, we cannot distinguish between imide formation by paths A or B or a combination of these. We can, however, state that if path A is operative in this reaction, the rearrangement of the isomide **3** must occur with specific nucleophilic assistance proceeding by attack of water at the carbonyl carbon of the isoimide. This observation is consistent with the previously proposed mechanism for this reaction.[8,9] It has also been suggested that isoimides rearrange to imides under "substantially anhydrous" conditions;[10] however, a consideration of this possibility does not alter the conclusions drawn in this work.

Experimental Section

Melting points were determined on a Melt-Temp apparatus and are uncorrected. Mass spectral analyses were performed on a Varian MAT 731 field desorption mass spectrometer.

Materials. All glassware was dried in vacuo at 140 °C and assembled under a dry nitrogen atmosphere. THF was freshly distilled from lithium aluminum hydride. *N*-Butylbenzamide and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) were distilled prior to use and stored over activated molecular sieves. ^{18}O-labeled carbon dioxide (Stohler 99.9% ^{18}O by mass spectral analysis) was used as purchased immediately after its mass spectral analysis.

Preparation of Labeled *N*-*n*-Butylphthalamic Acid (2). To a solution of 0.861 g (4.86 mmol) of *N*-butylbenzamide and 1.232 g (10.40 mmol) of TMEDA in 25 mL of dry TFH at 0 °C under a nitrogen atmosphere was added 6.5 mL (10.30 mmol) of a 1.6 molar solution of *n*-butyllithium in hexane. The *n*-butyllithium was added at a rate sufficient to maintain the reaction temperature between 0 and 10 °C. The reaction mixture was then allowed to stir at 0 °C for 4 h. The three-neck flask containing this reaction mixture was connected by means of a vacuum transfer line to a 250-mL round-bottom flask coontaining 0.500 g (11.3 mmol) of carbon dioxide (99.9% ^{18}O), which was cooled in liquid nitrogen to solidify the gas. The reaction mixture was then cooled to −78 °C in a dry ice–acetone bath and subsequently transferred to the flask containing the solid carbon dioxide. The reaction mixture was held at −78 °C overnight and then allowed to warm slowly to ambient temperature the next morning. Small aliquots (2 mL) were added to 25 mL of isooctane to precipitate the dilithium salt of the phthalamic acid. The precipitated salts were acidified in aqueous HCl to pH 3 at 5 °C and water was removed under vacuum at 0–5 °C. The solid residue was then extracted with cold acetone and filtered. Removal of the acetone solvent under vacuum at 0–10 °C provided the phthalamic acid **2**: mp 103 °C (lit.[2] mp 103 °C); field-desorption mass spectrum, *m/e* 226 (M + H). Thermolysis of the phthalamic acid on the emitter at 200 °C gave exclusively *N*-*n*-butylphthalimide, *m/e* 205 (M$^+$). Thermolysis of the phthalamic acid on the solids probe and analysis by electron-impact mass spectrometry gave the same result.

Acknowledgment. We express our gratitude to Professor Samuel Danishefsky, Dr. D. M. White, and Dr. H. M. Relles for many helpful discussions.

Registry No. 2, 78371-58-1; *N*-butylbenzamide, 2782-40-3.

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A Simple, Inexpensive Synthesis of Dipotassium Cyclooctatetraenide, $K_2C_8H_8$

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The cyclooctatetraenyl dianion, $C_8H_8^{2-}$, has proven to be important in many areas of chemistry.[2-4] It is of interest as a planar aromatic dianion, as a precursor to C_8 ring systems, and as a ligand in organometallic complexes of the transition, lanthanide, and actinide metals. More extensive use of the cyclooctatetraenyl dianion and the compounds derived from it is often not practical, however, due to the unavailability and/or expense of its precursor, 1,3,5,7-cyclooctatetraene.

As part of our general investigation of the nonaqueous reductive chemistry of the lanthanide metals,[5-9] we discovered that the relatively inexpensive *cis,cis*-1,5-cyclooctadiene (1,5-C_8H_{12}) can be converted to the cyclooctatetraenyl dianion at room temperature by the product of the reduction of $PrCl_3$ with 3 equiv of potassium.[6] To determine the importance of potassium vis-â-vis praseodymium in this reaction, we examined several reactions involving only potassium and 1,5-cyclooctadiene. Although no reaction occurred at room temperature, at higher temperatures the conversion of 1,5-C_8H_{12} to $K_2C_8H_8$ was observed. This reaction has proven to be an excellent synthetic route to $K_2C_8H_8$. We report here the details of this convenient preparation of $K_2C_8H_8$ and its conversion to 1,3,5,7-cyclooctatetraene (1,3,5,7-C_8H_8),[2] 9-phenyl-9-phosphabicyclo[4.2.1]nonatriene ($C_6H_5PC_8H_8$)[10-12] and uranocene ($U(C_8H_8)_2$).[13] Subsequent to our report,[6] an alternate synthesis of $C_8H_8^{2-}$ from 1,5-C_8H_{12} was briefly described using *n*-C_4H_9Li or C_6H_5Na in the presence of tetramethylethylenediamine (TMEDA).[14] Although these reactions are similar, our method is simpler since potassium rather than phenylsodium is required, and since the base free salt, $K_2C_8H_8$, is isolated rather than the TMEDA adduct, $Na_2C_8H_8 \cdot 2TMEDA$.

Results and Discussion

The primary reaction which occurs when potassium and 1,5-cyclooctadiene are heated to 100–150 °C in the absence of solvent is the isomerization of the diene to *cis*-bicyclo-

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