*Anal.* Calcd for $C_5H_6O_2$: C, 61.22; H, 6.16. Found: C, 61.25; H, 6.13.

**Registry No.**—**1**, 930-60-9; **2**, 3859-41-4; zinc, 7440-66-6; palladium, 7440-05-3.

**Acknowledgments.**—We would like to express our thanks to the National Research Council of Canada for financial support, to Mr. D. Hill for technical assistance, and to Dr. K. G. Rutherford for helpful discussions.

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## Preparation of Acyclic Isoimides and Their Rearrangement Rates to Imides

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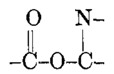
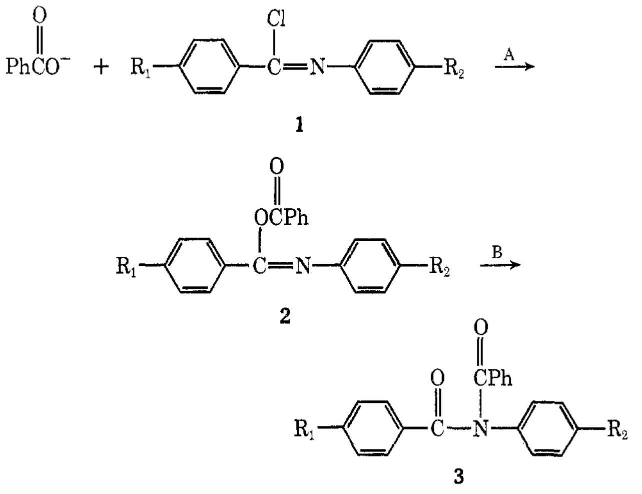
The 1,3(O-N) acyl transfer of the acyl imidate group (a) in a Mumm rearrangement[1–4] (reaction B of Scheme I) proceeds by an intramolecular process. To examine the possibility of carrying out intermolecular acylations with such a structure, a series of isoimides **2** were prepared to study the relative ease of formation and measure the rate of rearrangement to imide **3**. If the intramolecular rearrangement rate could be inhibited, intermolecular acyl transfer might occur. Intramolecular analogies to this have been found many times when an additional acylatable group is present in the isoimide.[5–9]



$$-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{N-}{|}}{C}-$$

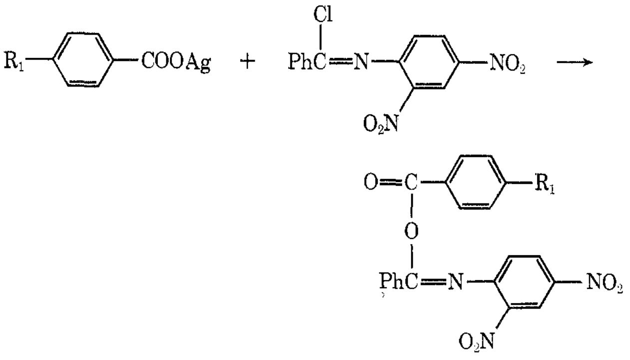
a

SCHEME I



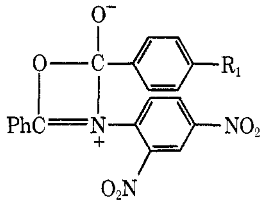
| | $R_1$ | $R_2$ | | $R_1$ | $R_2$ |
|---|---|---|---|---|---|
| **a** | H | Me | **d** | Me | H |
| **b** | H | H | **e** | Cl | H |
| **c** | H | Cl | **f** | H | $NO_2$ |

It has long been known that imidoyl chlorides react with carboxylate anions to form imides. It had been suspected that isoimides were intermediates in this reaction (Mumm rearrangement), but early attempts to prepare these intermediates were unsuccessful due to the rapid rearrangement to imide. Finally, by careful work at room temperature and below, Curtin and Miller[2,3] were able to prepare isoimides stabilized by two nitro groups by the following method.



**4**

They were able to establish that the rearrangement of isoimide **4** to imide was first order in isoimide and that $\rho$-para for the migrating group was about +0.6. From these facts and the fact that more polar solvents increased the rate, they proposed the reaction as proceeding through a four-membered ring transition state (or intermediate)[10] **5**.



**5**

In the present study isoimides were prepared by allowing triethylammonium benzoate to react with the appropriate imidoyl chloride **1** in chloroform solution at about 0°. The reactions were rapid and exothermic except in the case of the nitro-substituted imidoyl chloride, where no significant concentration of isoimide accumulated because it rearranged approximately as fast as it was formed (Table I).

The rates of rearrangement of the isoimides once formed were measured without prior isolation because isolation of compounds this labile would have required very special handling. Instead the half-lives were determined in the solution in which they were formed by an infrared comparison method explained in the Experimental Section. From our data (Table I),

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(1) O. Mumm, H. Hesse, and H. Volquartz, *Ber.*, **48**, 379 (1915).

(2) D. Y. Curtin and L. L. Miller, *J. Amer. Chem. Soc.*, **89**, 637 (1967).

(3) D. Y. Curtin and L. L. Miller, *Tetrahedron Lett.*, 1869 (1965).

(4) J. W. Schulenberg and S. Archer, *Org. React.*, **14**, 31 (1965).

(5) E. Taschner, B. Rzeszotarska, and L. Lubienska, *Chem. Ind. (London)*, 402 (1967).

(6) D. S. Kemp and R. B. Woodward, *Tetrahedron*, **21**, 3019 (1965).

(7) R. B. Woodward and R. A. Olofson, *J. Amer. Chem. Soc.*, **83**, 1007 (1961).

(8) R. B. Woodward, R. A. Olofson, and H. Mayer, *ibid.*, **83**, 1010 (1961).

(9) G. Gokel, G. Luedke, and I. Ugi in "Isonitrile Chemistry," I. Ugi, Ed., Academic Press, New York, N. Y., 1971, p 145.

(10) The four-membered ring mechanism had been briefly alluded to but not formally depicted by C. L. Stevens and M. E. Munk, *J. Amer. Chem. Soc.*, **80**, 4069 (1958).

TABLE I

RATES OF FORMATION AND REARRANGEMENT OF ISOIMIDES 2

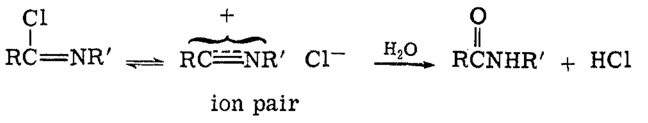
| Run | Isoimide | $R_1$ | $R_2$ | Formation[a] time, min, ca. 0° | Half-life,[b] min, 19.6° |
|---|---|---|---|---|---|
| 1 | **2a** | H | Me | 3 | 15.5 ± 1.0 (18) |
| 2 | **2b** | H | H | 5 | 22.8 ± 1.4 (12) |
| 3 | **2c** | H | Cl | 45 | 45.6 ± 2.7 (19) |
| 4 | **2c** | H | Cl | | 44.4 ± 3.0 (3)[c] |
| 5 | **2d** | Me | H | 4 | 13.4 ± 1.1 (22) |
| 6 | **2e** | Cl | H | 20 | 41.3 ± 2.4 (26) |
| 7 | **2f** | H | $NO_2$ | ~36 hr | 3.7 hr[d] |

[a] Measured by time of maximum attainment of enol ester carbonyl band in the ir. [b] Numbers in parentheses refer to number of measurements in the average. [c] Starting isoimide concentration 0.1 *M* with excess triethylammonium benzoate (0.314 *M*). [d] Calculated using data of runs 1 through 3.

the $\rho$-para was $-1.27$ for each ring studied as calculated by the least squares method.

These negative $\rho$ values lend support to the intermediacy of **5**, although the values might have been expected to be higher in view of the great amount of charge developed. A possible explanation for these low $\rho$ values might be that the positive charge in the transition state (or intermediate) can be distributed between both the nitrogen and the oxygen of the four-membered ring.

It is clear that the nucleophilic substitution reaction to form the isoimide is promoted by electron-donating groups ($R_1$, $R_2$) in the imidoyl halide ($\rho$ is clearly negative) with substantial positive charge development on the trigonal carbon. The mechanism of displacement probably bears a strong relationship to that of hydrolysis of imidoyl chlorides, where Ugi, Beck, and Fetzer[11] also find rate enhancement by electron-donating groups. They propose that hydrolysis in acetone–water proceeds by the following pathway.

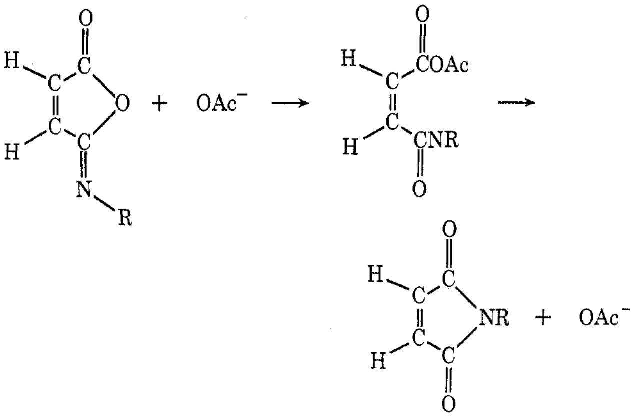


$$\overset{\displaystyle Cl}{RC}{=}NR' \rightleftharpoons \underset{\text{ion pair}}{\overset{+}{RC{\equiv}NR'}\ Cl^-} \xrightarrow{H_2O} \overset{\displaystyle O}{\overset{\|}{RC}}NHR' + HCl$$

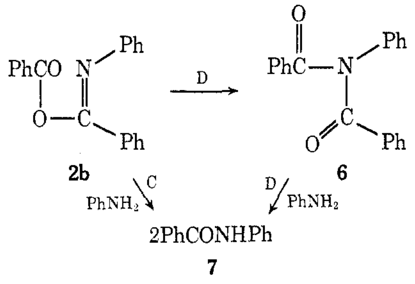
In the present case, an ion pair as depicted above would explain the relative rate data for the preparation of isoimides.

Although carboxylate anions have been implicated in the mechanism of the rearrangement of cyclic isoimides (Scheme II),[12] they do not appear to participate in any measurable way in the rearrangement of acyclic isoimides. This can be seen from the fact that **2c** rearranged at the same rate within experimental error whether benzoate ion was added or not.

SCHEME II



SCHEME III



To investigate the possibility of intermolecular acylation with one of these isoimides, two experiments were run in which aniline was treated at 0° with a freshly prepared chloroform solution of benzoyl *N*-phenylbenzimidate (**2b**). This particular combination of reactants was chosen since the product of any acylation would be the same as the by-product from the acylating agent. The acylation could then proceed by two possible routes (C and/or D, Scheme III). The progress of the reactions was followed by ir, and it was found that, in the run where an equimolar amount of aniline was used, only dibenzoylaniline (**6**) was isolated. In the second run where ten times the equimolar amount of aniline was used, it appeared (ir monitoring) that the isoimide was consumed by rearrangement in the control experiment as fast as it was consumed in the presence of aniline. After rearrangement to imide was essentially complete at 0°, the reaction mixture with aniline was allowed to stand at room temperature overnight. From this reaction then, benzanilide (**7**) was the only product isolated. From this experiment, it is clear that the predominant pathway to benzanilide is *via* the imide. This is not completely unexpected, since Stevens and Munk[10] have shown that intermolecular acylation of amines with imides can be used preparatively.

The failure to achieve intermolecular acylation with an isoimide in this case may be due to the relative instability of the isoimide used toward rearrangement or the low nucleophilicity of aniline. Further work with more stable isoimides together with more reactive amines is indicated to see whether this failure to achieve acyl transfer is general for this type of potential acylating agent.

## Experimental Section[13]

**Preparation of Imidoyl Chlorides.**—These compounds were prepared by refluxing the appropriate anilide either with an excess of thionyl chloride or with 1 mol of phosphorus pentachloride in a benzene slurry. The volatile constituents were removed under vacuum, and purification was effected by vacuum distillation, vacuum sublimation, or recrystallization. The melting ranges are tabulated in Table II.

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(11) I. Ugi, F. Beck, and U. Fetzer, *Chem. Ber.*, **95**, 126 (1962).

(12) C. K. Sauers, *J. Org. Chem.*, **34**, 2275 (1969), and references cited therein.

(13) All infrared spectra were taken on a Perkin-Elmer Model 137. The benzoic acid was sublimed and the triethylamine was passed through an alumina column before use. Chloroform was freed of the ethanol preservative by passing through an alumina column and was found to be quite stable in this condition as long as light was rigorously excluded. All melting ranges are uncorrected. Rates were determined at 19.6 ± 0.1° (corrected).

TABLE II

MELTING RANGES OF IMIDOYL CHLORIDES AND IMIDES

| | 1 | | 3 | |
|---|---|---|---|---|
| Comp | Mp, °C found | Mp, °C reported | Mp, °C found | Mp, °C reported |
| a | 54–57 | 52[a] | 146–146.5 | 142–144[e] |
| b | 42–45 | 39–41[b] | 162.5–164.5 | 163–164[f] |
| c | 62.5–64.5 | 68[c] | 158–159 | 159–160[g] |
| d | 52–54.5 | | 162–163.5 | 159[f] |
| e | 69.5–71.5 | 66–67[d] | 130–132 | |
| f | 114.5–117 | 118–120[b] | 209–210.5 | 203[h] |

[a] F. Just, *Ber.*, **19,** 980 (1886). [b] Reference 11. [c] H. Ley, *Ber.*, **31,** 241 (1898). [d] G. H. Coleman and R. E. Ryle, *J. Amer. Chem. Soc.*, **68,** 2007 (1946). [e] Reference 1. [f] M. P. Freunler, *Bull. Soc. Chim. Fr.*, **31,** 623 (1904). [g] S. Birtwell, *J. Chem. Soc.*, 2561 (1949). [h] O. Mumm, *Ber.*, **43,** 890 (1910).

**Preparation and Determination of Half-Lives of the Substituted Benzoyl *N*-Phenylbenzimidates (Isoimides).**—The isoimides were prepared in the following way. A chloroform solution of triethylammonium benzoate (10 ml, 1 *M*, 0°) was rapidly pipetted into a chloroform solution of the appropriate imidoyl chloride (5 ml, 2 *M*, 0°). The resulting solution was well mixed and kept in an ice bath while the reaction to form isoimide proceeded. With the faster reacting imidoyl chlorides, temperature rises of up to 8° were noted within a minute or two. The developing band in the infrared spectrum (*ca.* 1737 cm$^{-1}$ in $CHCl_3$) was observed during this period to ascertain when the isoimide had completely formed [maximum attainment of this band relative to the adjacent band (*ca.* 1680 cm$^{-1}$) of the $C{=}N$]. In all cases except that with *N*-*p*-nitrophenylbenzimidoyl chloride, the isoimide **2** formed completely before any rearrangement could be detected.

The half-lives of the isoimides were determined as follows. The isoimide solution as prepared above was allowed to stand at room temperature for several hours until rearrangement to imide was complete. A 5-ml aliquot was then accurately diluted to 25 ml with chloroform (solution 0.133 *M* in imide).

Now a fresh solution of isoimide was prepared as described above. A 5-ml aliquot of this isoimide solution was diluted accurately to 25 ml with chloroform thermostated at 19.6° (solution about 0.133 *M* in isoimide), and the diluted mixture was thermostated at 19.6° (solution A).

A 10-ml aliquot of the imide solution (thermostated at 19.6°) was mixed ($t = t_0$) with a 10-ml aliquot of the isoimide (solution A), and this mixture was thermostated at 19.6° (solution B). This solution then simulated solution A after rearrangement of half of the isoimide.

The infrared spectrum between 1800 and 1650 cm$^{-1}$ was determined for these two mixtures (A and B) every 1 to 3 min (depending on length of half-life) until the isoimide (*O*-acyl carbonyl) band became only a shoulder on the imide carbonyl band. In practice, the spectra were taken only with solution B at first until the isoimide band became a shoulder; then only solution A spectra were taken for the balance of the run.

The values for the half-lives were determined by measuring the time difference between identical solution A and solution B spectra using as a basis of comparison the distance between the isoimide maximum and the minimum between it and the adjoining carbonyl peak (*ca.* 1680 cm$^{-1}$), linearly interpolating as required. The results are tabulated in Table I.

**Preparation and Rearrangement of Benzoyl *N*-(*p*-Chlorophenyl)benzimidate (2c) in the Presence of Excess Benzoate.**—The general procedure described above was followed except that solution A was prepared in such a way that it was 0.1 *M* in isoimide and 0.314 *M* in triethylammonium benzoate. The results are tabulated in Table I.

**Dibenzoylaniline.**—The chloroform solutions remaining from the experimental measurement of the rate of rearrangement of benzoyl *N*-phenylbenzimidate were combined and evaporated. The residue was extracted with benzene (125 ml). After filtration, the benzene solution was concentrated to about 40 ml. After being cooled to room temperature, the product was isolated by filtration, yield 6.8 g (45%), mp 162.5–164.5° (lit.[14] mp 163–164°).

**Acylation Tests Using Benzoyl *N*-Phenylbenzimidate.**—Two acylation experiments were run with varying amounts of aniline. The solution of the acylating agent was prepared in each case as follows. A solution of *N*-phenylbenzimidoyl chloride (5 ml of 2 *M* chloroform solution) at 0° was mixed with a solution of triethylammonium benzoate (10 ml of 1 *M* chloroform solution) at 0°. Within a few minutes the reaction to form isoimide was complete (ir) after a temperature rise of 8°. The mixture was cooled to 0° before adding to the aniline.

**Run 1.**—A 10-ml aliquot of the isoimide (*ca.* 6.67 mmol) was pipetted as soon as it had been formed into a tube containing aniline (0.621 g, 6.67 mmol) at 0°. This mixture, together with the remaining 5-ml solution of isoimide, was kept at 0° for the balance of the experiment. After 4 hr, the ir enol ester band was still the same intensity in each sample although a major portion of the isoimide had rearranged. After a total of 17 hr at 0°, the ir enol ester band had disappeared from each sample. The reaction mixture (isoimide–aniline) was treated with enough chloroform to dissolve the product which had precipitated during the last hours of standing. The resulting solution was extracted with water, 6 *N* HCl, water, saturated aqueous $NaHCO_3$, and finally water. The chloroform layer was dried ($Na_2SO_4$). The solution ir was identical with that of dibenzoylaniline. The chloroform was evaporated, and the residue was crystallized from benzene to yield pure dibenzoylaniline, yield 1.24 g (62%), mp 159–161.5°, ir ($CHCl_3$) identical with that of authentic dibenzoylaniline.

**Run 2.**—The procedure was the same as that of run 1 except as noted below. The aniline used was ten times that of run 1. Examination of the ir spectra of the two solutions periodically disclosed that the ir enol ester carbonyl band diminished at about the same rate in each solution and had completely disappeared after 8.5 hr at 0°. At this point the reaction containing aniline was removed from the ice bath and stored at room temperature overnight. Work-up was as in run 1. The chloroform solution was evaporated to dryness to yield benzanilide, yield 2.22 g (85%), mp 162–163.5°, ir ($CHCl_3$) identical with that of authentic benzanilide.

**Preparation of Imides.**—The chloroform solutions from the rate runs for each isoimide were combined after rearrangements were complete. The resulting solution was extracted with water twice, dried with anhydrous sodium sulfate, and taken to dryness. The resulting residue was crystallized from benzene. The melting ranges of the various imides are given in Table II.

**Registry No.**—**1d,** 34916-13-7; **2a,** 34916-14-8; **2b,** 34916-15-9; **2c,** 34934-83-3; **2d,** 34916-16-0; **2e,** 34916-17-1; **2f,** 34916-18-2; **3e,** 34916-19-3; **7,** 93-98-1.

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[14] M. P. Freundler, *Bull. Soc. Chim. Fr.*, **31,** 630 (1904).

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# Orbital Symmetry Control in the Cycloadditions of Ketenes to Norbornadiene

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*Received March 28, 1972*

Recent reports of orbital symmetry control in the cycloadditions of ketenes to cyclopentadiene[2] prompt us to communicate our results with cycloadditions of ketenes to norbornadiene. The cycloadducts of dichloroketene with norbornene and norbornadiene have

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(1) IAESTE Student, Summer, 1971.

(2) (a) W. T. Brady and R. Roe, Jr., *J. Amer. Chem. Soc.*, **92,** 4618 (1970); W. T. Brady and E. F. Hoff, Jr., *J. Org. Chem.*, **35,** 3733 (1970); (b) M. Rey, S. Roberts, A. Dieffenbacher, and A. S. Dreiding, *Helv. Chim. Acta*, **53,** 417 (1970); (c) P. R. Brook, J. M. Harrison, and A. J. Duke, *Chem. Commun.*, 589 (1970).