(155 mm). Glpc analysis using a 10 ft × 0.375 in. Carbowax 20M column programmed at 1°/min from 80 to 105° after a post injection delay of 20 min and at 10°/min from 105 to 160° with an upper limit delay of 20 min revealed 4 major and 12 minor components using a helium flow of 56 ml/min. Nmr spectra of the major components eluting at 27.5 and 42 min showed them to be bicyclo[2.2.2]octa-2,5-diene [nmr (CCl_4) τ 3.90 (p, 4 H, CH=), 6.50 (m, 2 H, bridgehead), and 8.78 (m, 4 H, bridge)][6] and bicyclo[2.2.2]octa-2,5,7-triene [nmr (CCl_4) τ 3.50 (structured pentet, 6 H, CH=) and 5.40 (m, 2 H, bridgehead)],[2] respectively. The two other major eluents had retention times of 54.5 and 60.5 min and were not further characterized. Two of the minor components eluting at 13 and 20 min were identified as benzene and bicyclo[2.2.2]oct-2-ene, respectively. The percentages of 1 and 2 estimated on the basis of total eluted materials were approximately 17 and 32%. Preparative glpc separation of 2.0 g of distillate afforded 0.24 g of barrelene for a yield of 2% based on bicyclo[2.2.2]octene.

Equipment.—Nmr spectra were taken using a Jeol C-60HL spectrometer. Analytical and preparative glpc were conducted using a Hewlett-Packard Model 5750 vapor phase chromatograph equipped with a Model 5797 A collection unit.

Registry No.—Barrelene, 500-24-3; 1-bromobicyclo[2.2.2]octane, 7697-09-8.

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An Improved Preparation of 1,3-Cyclopentanedione

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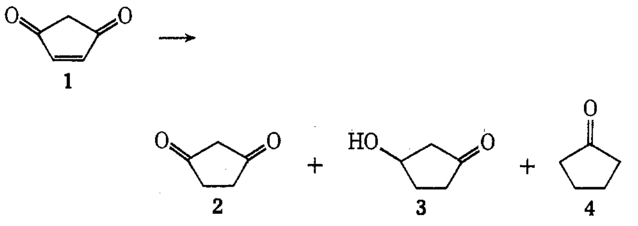
During the course of other investigations, we required a source of relatively large amounts of 1,3-cyclopentanedione (2). Although this compound and its alkylated derivatives have been used in the synthesis of many materials of varying degrees of complexity,[1] methods for its preparation, particularly on a large scale, are limited. The most widely quoted method[2] suffers from large solvent volumes, difficult isolation, and erratic yields. Other methods give unacceptably low yields.[3] Catalytic hydrogenation and zinc–acetic acid reduction of 4-cyclopentene-1,3-dione (1) have been reported.[4] Low yields of 2 were obtained, but the choice of catalyst and reaction conditions for these reactions did not appear to be optimal. Therefore we decided to reinvestigate the reduction of 1 as an attractive route to 2.

It is well established that the selective hydrogenation of olefins in the presence of carbonyl functions occurs best when palladium rather than platinum catalysts are employed.[5] Whereas the use of Adams' catalyst in the hydrogenation of 1 afforded only 2% of 2 in addition to large amounts of 3 and 4,[4] employing a palladium catalyst resulted in the continuous absorption of in excess of 1 equiv of hydrogen and the formation of a 3:2 mixture of 2 and 3, which could be separated by distillation. No cyclopentanone was formed. Variation of the solvent from 95 to 75% ethanol drastically reduced the rate of reduction, but did not change the product distribution substantially.



The reduction of conjugated diketones with zinc in acetic acid is a well-documented process,[6] but the reported yield[4,7] of 2 from the reduction of 1 was low. We verified these results, but found that *the use of activated zinc*[8] afforded 2 *in 75–77% yield* after recrystallization. Purification by sublimation at pressures greater than 0.02 mm reduced the yield to less than 60%. The ready availability of 4-cyclopentene-1,3-dione[9] coupled with the simplicity and high yield of this reduction clearly make this route the method of choice for the preparation of 2. Whether the use of activated zinc in other reductions of this type will result in a similar improvement in yield remains to be investigated.

Experimental Section

Infrared spectra were taken on a Beckmann IR 12 spectrometer in chloroform solution; nmr spectra were recorded on a JEOLCO C60HL spectrometer in deuteriochloroform and are reported in parts per million from an internal standard (TMS = 0). Melting points are uncorrected. Microanalyses were performed by A. B. Gygli, Toronto, Ontario.

Catalytic Hydrogenation of 1.—To a solution of 1 g (0.01 mol) of 4-cyclopentene-1,3-dione[9] (1) in 25 ml of 95% ethanol was added a catalytic amount of 5% palladium on charcoal, and the mixture was hydrogenated at room temperature and pressure. Continuous absorption of hydrogen occurred until 1.6 molar equiv had reacted, at which point the reaction stopped. The solution was filtered free of catalyst, the solvent was evaporated, and the residue was distilled (90° bath temperature, 0.5 mm). Analysis of the distillate (0.37 g) by glc (8 ft × 0.25 in. 20% SE-30, 125°) showed the presence of two compounds, one of which had the same retention time as 2-cyclopentenone. No cyclopentanone was present. The spectra of the distillate identified the material as 3-hydroxycyclopentanone (3) from which the 2-cyclopentenone was formed by dehydration during glc analysis: ir 3610, 3450, 1737 cm^{-1}; nmr δ 4.6 (m, 1, CHOH), 3.58 (s, 1, -OH), 2.5–2.0 (m, 6). The residue from the distillation (0.6 g, 60%) was 1,3-cyclopentanedione (2), mp 151–152° (sublimed sample) (lit.[4] mp 149–150°).

Zinc Reduction of 1.—To a mixture of 500 ml of glacial acetic acid and 100 g (1.54 mol) of activated zinc[8] in a 2-l. flask equipped with a mechanical stirrer and maintained at 95° with an oil bath was added a solution of 20 g (0.21 mol) of 1 in 300 ml of glacial acetic acid over a period of 2 hr. The mixture was stirred at 95° for 1 hr, filtered, cooled to room temperature, and filtered again. Evaporation of the solvent at reduced pressure afforded a light yellow residue which gave 2 (15.5 g, 76%) on recrystallization from methanol–ethyl acetate (1:3) at −78°, mp 148–149°.

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(2) F. Merenyi and M. Nilsson, *Acta, Chem. Scand.*, **17**, 1801 (1963).

(3) J. H. Boothe, R. G. Williams, S. Kushner, and J. H. Williams, *J. Amer. Chem. Soc.*, **75**, 1732 (1953).

(4) C. H. DePuy and E. F. Zaweski, *ibid.*, **81**, 4920 (1959).

(5) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, New York, N. Y., 1965, p 10.

(6) See, for example, J. Elks, R. M. Evans, A. G. Long, and G. H. Thomas, *J. Chem. Soc.*, 451 (1954).

(7) H. O. House and G. Rasmusson, *J. Org. Chem.*, **28**, 27 (1963).

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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.

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Preparation of Acyclic Isoimides and Their Rearrangement Rates to Imides

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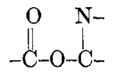
Received October 26, 1971

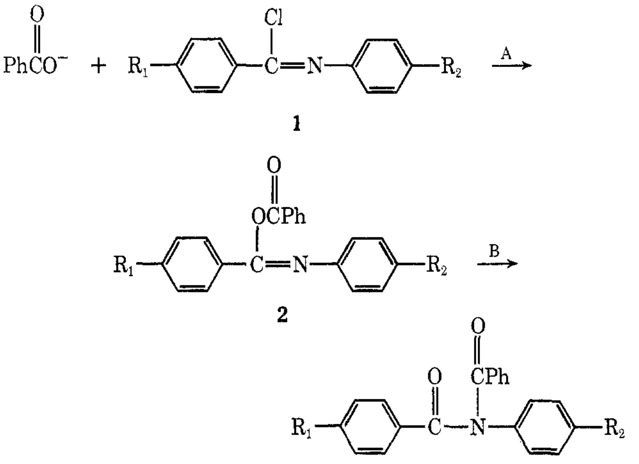
The 1,3(O-N) acyl transfer of the acyl imidate group (a) in a Mumm rearrangement[1-4] (reaction B of Scheme I) proceeds by an intramolecular process. To examine the possibility of carrying out intermolecular acylations with such a structure, a series of isoimides **2** were prepared to study the relative 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]



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

a

Scheme I



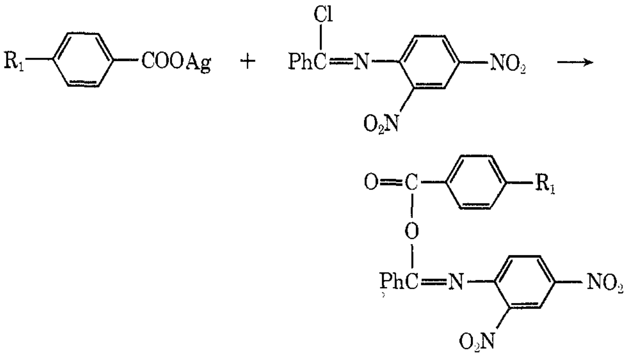
1

2

3

	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.



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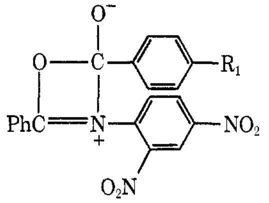
They were able to establish that the rearrangement of isoimide **4** to imide was first order in isoimide and that ρ-para for the migrating group was about +0.6. From these facts and the fact that more polar solvents increased the rate, they proposed the reaction as proceeding through a four-membered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



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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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(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).