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Hydrogenation Via Photochemically Generated Diimide

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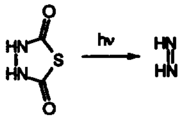
Abstract: Diimide is a well-known reagent for hydrogenating multiple bonds with very high stereospecificity. However, all of the methods for generating diimide require somewhat rigorous conditions. We show here that 1-thia-3,4-diazolidine-2,5-dione (TDADH) can be used to photochemically produce diimide at room temperature under neutral conditions. The diimide thus produced can hydrogenate multiple bonds in high yields.

INTRODUCTION

Diimide (HN=NH) has been the subject of interest and speculation for many years.[1] It is the prototype azo compound and is recognized for its ability to hydrogenate multiple bonds.[2] Its selectivity (functional and stereo) makes diimide hydrogenations a useful alternative to catalytic hydrogenation.[3] Diimide hydrogenation is always highly stereospecific with the hydrogens adding in a syn configuration. These results have led to a suggested mechanism involving a concerted transfer of hydrogens from *cis*-diimide to alkenes. Theoretical calculations have supported this pericyclic mechanism.[4]

Thiele first produced diimide via the acid hydrolysis of the potassium azodiformate,[5] and this method is still the most prevalent.[1b,6] Other methods of production, hydrazine oxidation,[7] thermal decomposition of arenesulfonyl hydrazides,[7,8] the base-catalyzed decomposition of hydroxylamine-*O*-sulfonic acid or chloramine,[9] thermal decomposition of anthracene-9,10-bisimine[10] all involve harsh conditions: either acid, base or high temperature. Because these conditions have limited diimide's synthetic value, the creation of diimide at room temperature under neutral conditions would broaden the utility of this reagent.

Recently our group has developed a milder pathway to azo compounds via photochemical irradiation of 1-thia-3,4-diazolidine-2,5-dione (TDADH)-adducts.[11] These results suggested the exciting possibility that the parent TDADH would produce the prototype azo compound, diimide (Figure 1). We have confirmed this potential of readily synthesized TDADH[12] and have used the photochemically generated diimide for hydrogenation of various alkenes.



TDADH

Figure 1

RESULTS AND DISCUSSION

Hydrogenation Via Photolysis of TDADH/Alkene Mixtures. When 1.3 mL of a 2-methoxyethyl ether solution of norbornene (3.8 mM) and TDADH (7.8 mM) was photolyzed at 254 nm using a Rayonet-type photoreactor, GC analysis revealed that hydrogenation occurred and a quantitative yield of norbornane resulted after eleven minutes. Acetonitrile, tetrahydrofuran or methanol could also be used as solvents in this reaction but they interfered with GC analysis of the reaction mixture.

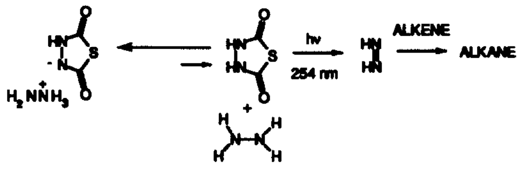
When a solution of TDADH and cyclohexene in 2-methoxyethyl ether was photolyzed at 254 nm, no hydrogenation took place. Instead a white precipitate formed during the photolysis and there was a strong smell of hydrazine. The solid was isolated (m.p. = 118-121°) and the ^{13}C NMR spectra showed one resonance at 166.4 ppm. Photolysis at 254 nm of a solution of TDADH in 2-methoxyethyl ether with no alkene present resulted in formation of the same precipitate that was identified as a hydrazine - TDADH salt; a consequence of hydrazine produced by diimide disproportionation reacting with the relatively acidic TDADH (pKa=3.5). The absence of cyclohexene hydrogenation is not surprising since cyclohexene is 500 times less reactive to diimide hydrogenation than norbornene.[2b] Thus disproportionation prevails when diimide is produced via direct photolysis of less-reactive alkene/TDADH mixtures.

Continuous Addition of TDADH to Irradiated Alkene Solutions. To minimize disproportionation a low continuous concentration of diimide relative to the alkene is necessary. To achieve this we continuously added a dilute solution of one equivalent of TDADH to a cyclohexene solution that was being irradiated at 254 nm. Unlike direct irradiation of cyclohexene/TDADH solutions this method does produce cyclohexane. The yields of the cyclohexane were generally low but increased as the flow rate was lowered. This suggests that the steady-state concentration of diimide and thus the relative amounts of disproportionation versus hydrogenation could be controlled by the rate of addition of TDADH.

The yields of cyclohexene could be improved by increasing the amount of TDADH added. However, even when an excessive amount of TDADH was used, hydrogenation yields were modest (~75%) even though all the cyclohexene had disappeared. The same result was found for cycloheptene and 1-heptene which gave ~75% hydrogenation yields when a ten molar excess of TDADH was used. The absence of 100% mass balance in all these reactions suggests that these alkenes are undergoing photoreactions that lead to their destruction. Photoreaction and photoisomerization of alkenes under these irradiation conditions are well known.[13] These alkene photoreactions resulted in a large decrease in the yield of the desired hydrogenation product, because the alkene was subjected to irradiation during the entire course of our experiments.

Thus we became interested in establishing conditions that minimized alkene photoreactions. We attempted to produce diimide from TDADH with longer wavelength light to avoid absorption by the alkene. Unfortunately when TDADH was continuously added to a norbornene solution with simultaneous irradiation with light of λ > 333 or even 285 nm, no hydrogenation of norbornene was seen.

Hydrogenation Via Continuous Addition of Alkenes to an Irradiated TDADH-salt Solution. In early experiments we noted that further photolysis after addition of the TDADH solution was complete often produced an increase in the yields of hydrogenation. This puzzling result could be explained if formation of the salt of TDADH and the hydrazine produced by disproportionation was reversible. In this case the salt would continuously release TDADH in low concentrations. This TDADH could photochemically produce diimide which would hydrogenate the alkenes that remain in the solution after the TDADH addition was complete (Scheme 1).



Scheme 1

If a salt can be used to continuously produce TDADH, an interesting point arises. If the salt acting as a reservoir of TDADH could be used as a continuous source of a low concentration of diimide then excessive amounts of disproportionation could be avoided and even more importantly the alkene could be continuously added to a salt solution during photolysis and thus avoid alkene photoreaction.

In fact when we continuously added for 8 hours 0.5 mL of a 0.01 M solution of cycloheptene in 2-methoxyethyl ether to 0.3 mL of a 2-methoxyethyl ether solution containing 20 equivalents of the hydrazine salt of TDADH and photolyzed at 254 nm during this time, we found a 65% yield of cycloheptane while 18% of cycloheptene remained. The amount of free TDADH in solution is controlled by the salt - TDADH equilibrium that will depend upon the strength of the base used to form the salt. By varying the base strength the steady state concentration of TDADH and thus of the diimide could possibly be controlled. We have shown this to be true with the triethylamine - TDADH salt. The stronger base, triethylamine, should release less free TDADH from its salt and should result in a lower hydrogenation yield. When the same procedure described above was performed using the triethylamine salt of TDADH, a lower hydrogenation yield (58%) was in fact seen. Presumably varying the salt base, raising the concentration and/or lowering the addition rate would increase the relative amount of diimide continuously present and even higher hydrogenation yields could be obtained with this method.

Table 1. Hydrogenations with Diimide Produced Photochemically from TDADH: Continuous Addition of a TDADH and Alkene Solution[14]

Alkene (0.01M)	TDADH:Alkene Ratio	Alkene after addition (%)	Alkane yield after addition (%)	Alkane yield after a further 16 hr of photolysis (%)
Cycloheptene	2:1	81	16	---
Cycloheptene	5:1	76	23	---
Cycloheptene	10:1	42	41	---
Cycloheptene	20:1	22	78	100
Cycloheptene	40:1	---	98	---
Norbornene	1:1	0	100	---
1-Heptene	20:1	32	67	96
cis-2-Heptene	20:1	37[a]	28	---

a. 7% of *trans*-2-heptene was also present.

Hydrogenation Via Continuous Addition of TDADH/Alkene Mixtures. While using the salt as a continuous low level source of TDADH seems to be a viable approach, an easier option to avoid alkene photoreactions is to add the alkene along with the TDADH (Table 1).[14] Because disproportionation competes with hydrogenation, a TDADH:alkene ratio near to the ratio of the relative rates of disproportionation and hydrogenation would be expected to be needed. When a 40:1 cycloheptene - TDADH solution is added to the photolyzed tube over a 17 hour period a 98% hydrogenation yield results. When a solution of TDADH and cycloheptene in a ratio of 20:1 was added over an eight hour period, a 78% yield of cycloheptane was produced while 23% cycloheptene remained immediately after addition. Photolysis of the solution for sixteen additional hours resulted in a quantitative hydrogenation yield. Presumably diimide produced from the salt formed during the reaction is again responsible for this additional hydrogenation. When this same method was applied to 1-heptene in a TDADH:alkene ratio of 20:1, a 96% hydrogenation yield of n-heptane resulted (Table 1).

Internal acyclic alkenes. Hydrogenation of internal acyclic alkenes was examined using our initial method of continuous addition of a 2-methoxyethyl ether solution containing two equivalents of TDADH to an irradiated solution of *cis*-2-heptene. This gave very disappointing results. Only 2% hydrogenation occurred and was accompanied by a large amount of alkene isomerization (50% *trans*-2-heptene). However when a

20:1 TDADH:*cis*-2-heptene solution is continuously added during irradiation much better results are obtained (Table 1). Even higher hydrogenation yields with little isomerization could be obtained with internal alkenes if higher TDADH/alkene ratios and slower addition rates were used.

SUMMARY

We have shown that photochemical production of diimide from TDADH can lead to hydrogenation of multiple bonds at room temperature under neutral conditions thereby avoiding the harsh conditions necessary to produce diimide from previous precursors. Alkenes reactive toward hydrogenation can be hydrogenated simply by photolyzing a mixture of TDADH and the alkene. Less reactive alkenes may often photoreact or isomerize so that hydrogenation with these alkenes must be carried out by adding the alkene slowly to the irradiated solution. When this is done, good hydrogenation yields can be obtained either by adding the alkene to a TDADH salt solution or by simply adding excess TDADH along with the alkene to an irradiated solution. The mild reaction conditions used here to make diimide should significantly increase the synthetic utility of this reagent.

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14. In a typical procedure 0.5 mL of a degassed 2-methoxyethyl ether solution 0.01M in the alkene and with the indicated number of equivalents of TDADH added was syringed slowly (0.07 mL/hr) into a quartz tube containing 0.5 mL of 2-methoxyethyl ether which was stirred. After addition was complete the solution was analyzed by GC on a J&W DB-5 capillary column. Sometimes the sample was redegassed, photolyzed for a further period of time and reanalyzed by GC.

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