

## Rieke zinc as a reducing agent for common organic functional groups

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**Abstract**—The ability of Rieke zinc to reduce common organic functional groups has been studied. Nitrobenzene, conjugated aldehydes, arylacetylenes, and phenylpropiolates are readily reduced under mild conditions. Benzonitrile, alkylacetylenes, ketones, unconjugated aldehydes, and alkenes are not reduced.  
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In the early 1970s, Rieke developed a process for making highly reactive metal powders. In the intervening years these Rieke metals have found wide application in numerous organic syntheses, most notably in the preparation and reaction of novel organometallic reagents.<sup>1</sup> However, little information on the use of these metals as possible reducing agents for organic compounds could be found in the literature. The reduction of organic compounds is an essential reaction in many synthetic schemes. It is acknowledged that there are a number of reagents available for conducting these reductions. However, there continues to be a need for new reducing agents; particularly those that are effective under mild conditions so that there is less likelihood of altering other functional groups present in the molecule besides the group being reduced. We have found that Rieke zinc is able to reduce conjugated aldehydes, alkynes, esters, and nitro compounds under very mild reaction conditions in high yields. These reductions are performed in a mixture of THF, the solvent in which Rieke zinc is prepared, and a proton donor such as water or methanol or both.

The compounds in [Table 1](#) were reduced by a procedure patterned after that used by White.<sup>2,3</sup> The compounds were added as methanol solutions to a slurry of Rieke

zinc in THF. Water was then slowly added and the resulting mixture heated at reflux for the indicated times. Products were isolated by extraction with ether from the reaction mixture.

The mechanism involved in zinc reductions, including Rieke zinc, of alkynes and other functional groups is assumed to be a dissolving metal reduction<sup>4–6</sup> much the same as that proposed for the reductions of alkynes with sodium metal. This mechanism ([Scheme 1](#)), as studied by Olah,<sup>4</sup> involves both the formation of a radical anion and a radical; it accounts for the trans product predominating unless the reaction is conducted at high temperatures.

Olah also notes that, though studied less thoroughly, other dissolving metal reductions are believed to occur via a similar mechanism. He further states that: ‘interestingly, activated zinc in the presence of a proton donor (alcohol) although a dissolving metal reagent, reduces disubstituted alkynes to *cis*-alkenes’.<sup>4</sup>

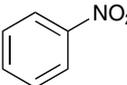
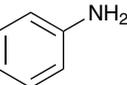
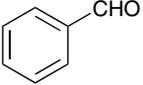
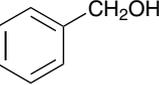
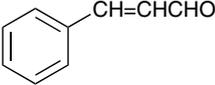
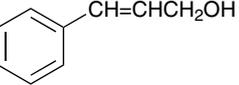
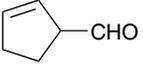
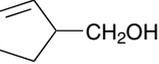
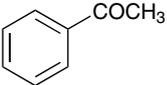
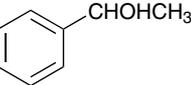
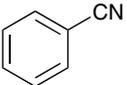
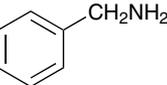
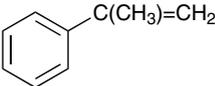
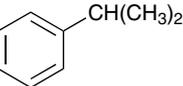
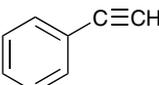
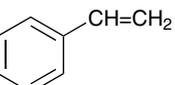
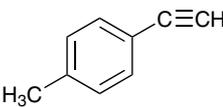
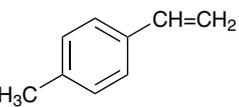
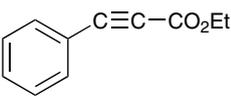
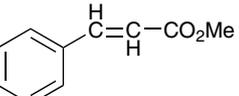
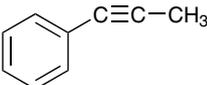
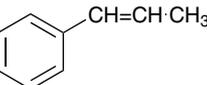
Our results are consistent with the dissolving metal model because we were able to reduce only conjugated functional groups as shown in [Table 1](#). Whether it is the anion radical or the radical that is formed in the rate determining step, both would be more stabilized in a conjugated system. Evidently, in the absence of that conjugation, reduction with zinc is not possible.

Our most intriguing Rieke reduction results were found in the reduction of alkynes. The only previous attempts

**Keywords:** Rieke; Zinc; Reduction; Alkenes; Aldehydes; Ketones; Esters; Alkynes; Nitro; Conjugated.

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**Table 1.** Reduction of compounds with Rieke zinc

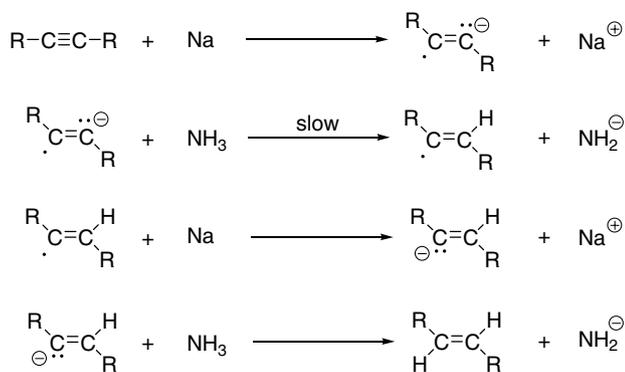
Entry	Reactant	Product	% Yield <sup>a</sup>	Reaction time (h)
1			90	3
2			100	3
3			100	3
4			nd	3
5			nd	12
6			nd	24
7			nd	24
8			nd	24
9	$\text{HC}\equiv\text{C}(\text{CH}_2)_5\text{CH}_3$	$\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_5\text{CH}_3$	nd	24
10			100	4
11 <sup>b</sup>	$\text{Fec}-\text{C}\equiv\text{CH}$	$\text{Fec}-\text{CH}=\text{CH}_2$	100	0.5
12			100	4
13 <sup>c</sup>			100	3
14	$\text{EtO}_2\text{C}-\text{C}\equiv\text{C}-\text{CO}_2\text{Et}$	$\text{EtO}_2\text{C}-\text{CH}_2\text{CH}_2-\text{CO}_2\text{Et}$	100	3
15			nd	24

nd = Not detected spectroscopically, all starting material recovered.

<sup>a</sup> Yields of the crude reaction product were determined by proton NMR (300 MHz).

<sup>b</sup> Fec represents the ferrocenyl group.

<sup>c</sup> 100% Trans stereochemistry observed. Also note that transesterification occurred.



**Scheme 1.** Mechanism of dissolving metal reduction of alkynes.

to use Rieke zinc to reduce alkynes were propargylic alcohols, 1,3-diyne, and 1,3-enynes; *cis*-alkenes were the major products of this work done by White.<sup>2</sup> It is of interest to note that we obtained the *trans*-alkene in contrast to the *cis*-isomer suggested by Olah and obtained by White. For example, ethyl phenylpropiolate was reduced by Rieke zinc in quantitative yield to *trans*-ethyl cinnamate.

Of additional interest, we noted that both phenylacetylene and *p*-methylphenylacetylene were readily and quantitatively reduced to their respective alkenes (entries 10 and 12 in Table 1), while 1-phenylpropyne showed no reaction with Rieke zinc (entry 15 in Table 1). In all three of these alkynes, the triple bond is conjugated with a phenyl group and so might be expected to react similarly. It may be that the small electron releasing tendency of the methyl group directly attached to the triple bond in 1-phenylpropyne destabilizes the radical or radical ion just enough to prevent this molecule from being reduced. However, it might also be argued that the *para*-methyl group in *p*-methylphenylacetylene should have a similar effect.

While it is true that ‘regular’ powdered zinc can be used to achieve many of the same reductions as Rieke zinc,<sup>7</sup> it should be noted that much milder reaction conditions can be employed with Rieke zinc.<sup>6</sup> For example, proton donors as weak as water or methanol can be used with Rieke zinc, whereas stronger acids such as hydrochloric acid, phosphoric acid or acetic acid are needed for regular powdered zinc. For instance, ethyl phenylpropiolate was quantitatively reduced to its alkene with

Rieke zinc using water/methanol, while powdered zinc gave no reaction with this alkyne under similar conditions. Thus, an attractive feature of using Rieke zinc for organic reductions is that it can be used under conditions that would less likely alter other acid sensitive functional groups in compounds being reduced.

### Acknowledgements

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### References and notes

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2. Chou, W.-N.; Clark, D. L.; White, J. B. *Tetrahedron Lett.* **1991**, *32*, 299–302.
3. The general procedure for dissolving zinc metal reduction: A three-necked flask, fitted with a reflux condenser and septa, was purged with Ar for 15 min. The Rieke zinc/THF slurry (purchased from Rieke Metals, Inc., 1001 Kingbird Road, Lincoln, NE 68521) was then transferred to the flask via syringe. After the Zn suspension was heated to reflux, a methanol solution of the organic compound to be reduced was added, followed by addition of water. The ratio of THF:methanol:water used was 7:5:1. A representative reduction: To 8.0 mL of a stirred suspension of 5% Rieke zinc,  $6.12 \times 10^{-3}$  mol, a solution of  $4.08 \times 10^{-3}$  mol of phenylacetylene dissolved in 5.70 mL of methanol was slowly added followed by dropwise addition of 1.10 mL of water. After refluxing for 2.5 h under argon, the solution was cooled and flooded with 150 mL of ether. The resulting mixture was filtered through Celite and extracted successively with 10% ammonium chloride (25 mL), 10% sodium bicarbonate (25 mL), and saturated sodium chloride (25 mL). After drying over anhydrous magnesium sulfate, the solvents were stripped by rotary evaporation. The yield and composition of the resulting crude product was determined by proton NMR.
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7. See, for instance; Durant, A.; Delplancke, J. L.; Libert, V.; Reisee, J. *Eur. J. Org. Chem.* **1999**, 2845–2851.