

COMMUNICATIONS TO THE EDITOR

Reduction of Aromatic Nitro Compounds with Hydrazine Catalyzed by Activated Zinc-Copper

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It is well demonstrated that hydrazine reduces aromatic nitro group to the amino group in the presence of Pd-C, Pt-C, Raney Nickel.¹ Alternative methods using FeCl₃,² Raney Nickel/ClCH₂CH₂Cl-C₂H₅OH³, Fe-C⁴ also afford elegant routes to aromatic amines or to partially reduced dinitro aromatic compounds.⁵ However, these methods suffer from such disadvantages as cumbersome workup procedures, use of expensive catalysts, relatively high temperature and long reaction times.

Recently, we reported convenient reduction methods which circumvent all the above disadvantages.⁶ These successes led us to investigate the effects of various catalysts on the reduction of aromatic and aliphatic nitro compounds in the presence of hydrazine hydrate. In this communication, we now report that activated Cu-Zn catalyzes the reduction of aromatic nitro compounds to amino compounds by hydrazine hydrate.

Our results are summarized in Table 1. The preparation of the Cu-Zn catalyst was extremely simple. CuSO₄·5H₂O (25 g 0.1 mol) and Zn powder (13g, 0.2 mol) were added to distilled water (200 ml). After being stirred for one hour, the blue color had disappeared and a finely divided black powder was formed.

The solution was filtered to remove water and zinc sulfate, and the black powder was washed with absolute ethanol and was dried under suction. This catalyst was good enough to use in the reduction reaction without further treatment. In a typical experiment, a 100 ml round bottom singleneck flask was charged with 0.01 mol of aromatic nitro compound, 2 g of Zn-Cu catalyst and 7 ml of absolute ethanol. A mixture of 0.04 mol of hydrazine monohydrate and 3 ml of ethanol was added dropwise to the above solution with stirring. Exothermic reaction was observed in most cases and gas (presumably H₂, N₂) was evolved.

Product isolation was straightforward. The reaction mixture was filtered and washed with ethanol. The combined filtrate was concentrated on a rotary evaporator. The residue was flash chromatographed to give the corresponding amino compounds. The products were characterized by comparison of their physical and chemical properties with those of authentic samples. When the same reaction was carried out with commercially purchased Zn-Cu couple in the case of nitrobenzene, only 7% of aniline was realized by GC.

Table 1. Activated Zinc-Copper Catalyzed Reduction of Aromatic Nitro Compounds to Aromatic Amino Compounds with Hydrazine Hydrate at 25 °C in Ethanol^a

Nitro Compounds	Products	Time (h)	Yields (%) ^b
C ₆ H ₅ -NO ₂	C ₆ H ₅ -NH ₂	2	86
<i>o,m,p</i> -CH ₃ C ₆ H ₄ -NO ₂	<i>o,m,p</i> -CH ₃ C ₆ H ₄ -NH ₂	2	90,90,92
<i>o,p</i> -HOC ₆ H ₄ -NO ₂	<i>o,p</i> -HOC ₆ H ₄ -NH ₂	2	88,92
<i>p</i> -HOCH ₂ C ₆ H ₄ -NO ₂	<i>p</i> -HOCH ₂ C ₆ H ₄ -NH ₂	2	92
<i>o,p</i> -ClC ₆ H ₄ -NO ₂	<i>o,p</i> -ClC ₆ H ₄ -NH ₂	4	92,95
<i>o,p</i> -CH ₃ OC ₆ H ₄ -NO ₂	<i>o,p</i> -CH ₃ OC ₆ H ₄ -NH ₂	2	90,92
<i>p</i> -N≡CC ₆ H ₄ -NO ₂	<i>p</i> -N≡CC ₆ H ₄ -NH ₂	4	46 ^c
6-Nitroquinoline	6-Aminoquinoline	2	90
8-Nitroquinoline	8-Aminoquinoline	2	88
1-Nitronaphthalene	1-Aminonaphthalene	4	90
<i>m</i> -O ₂ NC ₆ COOCH ₃	<i>m</i> -H ₂ NC ₆ H ₄ C(=N)NH ₂ CH ₃	2	80

^a All reactions were stirred under nitrogen. ^b Isolated. ^c GC yield.

Attempted reduction of nitropropane or benzonitrile under same conditions resulted in recovery of the starting materials.

Under the same conditions, other metal-hydrazine combinations proved less effective. Thus, using activated Fe-Cu-NH₂NH₂·H₂O, nitrobenzene was reduced to aniline in only 71% yield, while no reaction was detected with commercially available iron and copper.

Using activated Cu-NH₂NH₂·H₂O, nitrobenzene gave only 42% of aniline (GC). The reducing abilities of various mixtures of Zn-Cu with BaCl₂, celite and silica gel were not significant. When a mixture of nitropropane and nitrobenzene was reduced by Zn-Cu-NH₂NH₂·H₂O under standard conditions, only 20% of aniline along with unchanged nitropropane and nitrobenzene was obtained. Under these conditions, nitrobenzene by itself was readily reduced to aniline in high yield, as shown in Table 1, so that nitropropane acts as an inhibitor.

Interestingly, hydrazine monohydrate was not decomposed by Zn-Cu in the presence of nitropropane. The surprising reactivity of activated Zn-Cu powder in the reduction of nitroarenes suggests that other abundant metals may be cox-

ed into a catalytic role, not only for reduction but for a wide variety of reactions. Application of this activated metal powder to the Simmons-Smith and Reformatsky reactions is currently under investigation.

Acknowledgement. We thank the Korea Science and Engineering Foundation for financial support.

References

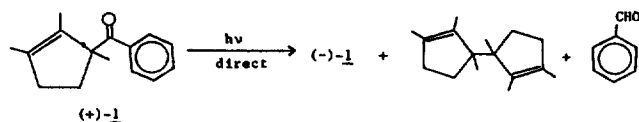
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Racemization vs. 1,3-Shift in the Excited State of 1-Methyl-2-Cyclohexenyl Phenyl Ketone

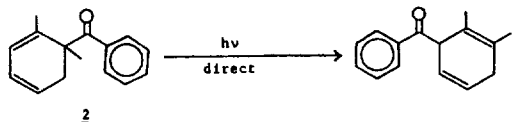
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The most β,γ -unsaturated ketones undergo 1,3-acyl migration under the direct irradiation and 1,2-acyl migration under the sensitized irradiation.¹ Schaffner² and coworkers have investigated the 3-benzoyl cyclopentene (1). Irradiation of optically active ketone 1 gave racemic mixture along with the α -cleavage, recombination products and benzaldehyde.

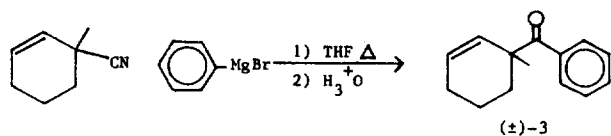


S. J. Lee³ have studied the photochemistry of benzoyl cyclohexadiene derivatives (2). The cyclic $\beta,\gamma,\delta,\epsilon$ -unsaturated ketone 2 are system in which 1,5-shift seems more likely. However, direct photolysis of 2 gave only the 1,3-shift product.



Since the benzoyl groups showed variety of photo-reaction depend upon the olefinic moiety, we have decided to investigate the migratory aptitude and the singlet-triplet reactivity of 1-methyl-2-cyclohexenyl phenyl ketone (3) which is analogous to the ketone 2.

The ketone 3 chosen for study was synthesized by the Grignard reaction of 1-cyano-1-methyl-2-cyclohexene.⁴



Direct irradiation of ketone 3 in ether at 350 nm for 40 min showed no significant change in nmr spectrum and GC

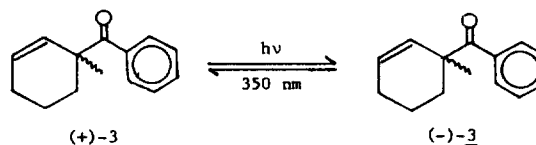
Table 1. Change in Optical Rotation During the Irradiation of (+)-Ketone 3

Time (min.)	Optical rotation, $[\alpha]$	$\ln[\alpha_0]/[\alpha_t]$
0	+36.474	0
5	+33.055	0.098
10	+30.775	0.170
20	+25.076	0.375
30	+21.657	0.521
40	+18.237	0.693

analysis. Nmr and GC analysis revealed that there were neither 1,3-shift nor decomposition during the 40 min irradiation. Over 60 min irradiation of ketone, however, produced products along with α -cleavage, recombination, and benzaldehyde.

The ($\pm$)-ketone 3 was resolved to see if the photo-racemization occurs under irradiation condition. The optical resolution of ($\pm$)-ketone 3 was performed by the selective ketalization⁵ of the ketone 3 with (2R, 3R)-2,3-butandiol and since the photo-racemization is first order kinetics, the optical purity and the absolute configurations were not determined.

Direct irradiation of the resolved ketone 3 at 350 nm showed racemization only and the quantum efficiency^{6,7} was calculated as 0.75 using the rate constant of first order kinetics, i.e. $\ln k = \frac{\alpha_0}{\alpha_t}$ where k 0.0171/min. (Table 1).



The photo-racemization of ketone 3 was quenched by the addition of trans-piperylene and linear Stern-Volmer relationships were observed as shown in Fig. 1.