

COMMUNICATIONS

LETTERS

Organic Sonochemistry. Ultrasonically Accelerated Hydrogenation of Olefins Using Palladium-Hydrazine

Dae Hyun Shin and Byung Hee Han†

Department of Chemistry, College of Science, Chungnam National University, Daejeon 300-31, Korea
(Received March 28, 1985)

The catalytic transfer hydrogenation (CTH)¹ process has received considerable attention as a useful synthetic method for the reduction of nitro compounds², carbonyl compounds³, olefins⁴, hydrogenolysis of protected peptides⁵ and carbohydrates⁶.



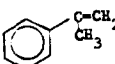
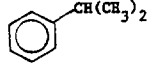
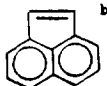

Basically, the CTH process¹ utilizes cyclohexene, 1,3-cyclohexadiene, and formic acid as a hydrogen donor in the presence of solubilized catalysts (Pd⁷, Rh⁸, Ru⁹) and heterogeneous metal catalysts (Ni¹⁰, Pd¹¹) to effect hydrogen transfer to an organic substrates. The successful utilization of this methods, however, requires the proper quantity and type of catalyst, concentration of the substrate, temperature, and hydrogen donors. The popularity of donors reflects their commercial availability, conversion effectiveness, and convenience on handling.¹² Recently, we reported that ultrasonic accelerated hydrogen transfer with formic acid-palladium catalyst constituted a rapid hydrogenation of olefins at room temperature and atmospheric pressure, and particularly useful for the complete hydrogenation

of olefin compounds without touching other functional group¹³.

In a research for more active hydrogen donors for transfer hydrogenation under sonic waves, we found that hydrazine-palladium couple¹⁴ is a very efficient hydrogen donor at room temperature and that in the presence of sonic waves, the rate of hydrogenation is significantly enhanced. In a brief study of the reaction rate of magnetically stirred, refluxed, and sonicated reaction of diphenylacetylene were also compared.

These results are summarized in Table and Diagram. Surprisingly, the rate enhancements induced by ultrasound were shown as good as reflux. According to the earlier work,¹⁵ sonication was the unique way to improve the yield. Typical procedure for the present reactions are as follows: A dry nitrogen filled 100 ml single neck round bottom flask was charged with 2.35×10^{-4} mol (0.5g) of palladium on carbon (5%), 6 mmol of olefin, 24 mmol of anhydrous hydrazine, and 8 ml of absolute ethanol (Runs 2, 4, and 7 required an additional 8 ml of benzene to dissolve the olefin). The reaction vessel was placed in a common ultrasound laboratory cleaner (Branson Model 220, 117V, 150W, 50/60 Hz, 55Kc) so that the liquid level inside flask matched that of the bath water and in the location that produced the maximum cavitation in the flask. A strong agitation of the mixture results from the cavitation phenomenon produced a lot of gases (presumably H₂ and N₂ from the decomposition of hydrazine) and hydrogenation reaction went to com-

TABLE I: Ultrasound-Accelerated Hydrogenation of Carbon-Carbon Bonds by Hydrazine-Palladium Couple

	Olefin	Product	Yield
1.	$C_6H_{13}CH=CH_2$	$n-C_8H_{18}$	95
2.	$t-Ph-CH=CH-Ph$ ^b	$Ph-CH_2CH_2-Ph$	90
3.	$n-C_4H_9OCH=CH_2$	$n-C_4H_9OCH_2CH_3$	88
4.	$Ph-C#C-Ph$ ^b	$Ph-CH_2CH_2-Ph$	100
5.			95
6.			85
7.			100

^a Reaction times are not optimized. All runs were sampled after 1 hr, found to be complete by NMR, and work up. All of our reactions were run at room temperature and an atmosphere of nitrogen in 8 ml ethanol using 2.35×10^{-4} ; 6×10^{-3} ; 2.4×10^{-3} mol of palladium: olefin: hydrazine; ^b Runs 2, 4, and 7 required an additional 8 ml of benzene to dissolve the olefin. Run 4 required 2 hour for completion.

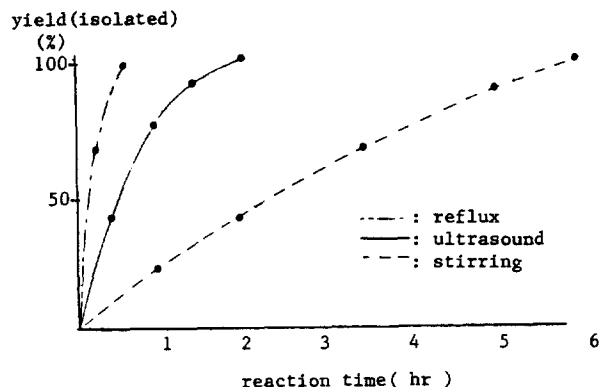


Diagram: Hydrogenation of Diphenylacetylene by Palladium-Hydrazine.

pletion within one hour. Reactions were run under a nitrogen atmosphere and bath temperature were maintained at 25°C by using a cooling coil. Product isolation was straightforward.

The reaction mixture were filtered to remove catalyst and carbon. The filtrates were concentrated on a rotary evaporator. The residual solid was recrystallied in ethanol-pentane to give the corresponding hydrogenated product. The fractional distillation was done in case of liquid. The products were characterized by comparison of their physical and chemical properties with those of authentic samples.

The exclusive source of hydrogen, hydrazine was shown when *t*-stilbene was recovered quantitatively from a reaction mixture in which hydrazine was omitted. Using activated charcoal only or simply hydrazine and olefin gave no reaction with heating or sonication. The catalyst can be activated prior to the reaction by exposing it to sonic waves. However, the rates of hydrogenation were increased only by 5% when stirring. The short reaction times, mild condition, and complete hydrogenation observed in these sonic induced heterogeneous reaction may be from increased surface area of the catalyst caused by sonic fragmentation of the carbon support, or sonic activation of the palladium surface. We are presently investigating reduction of nitro group with metal-hydrazine and will report on them in due course.

Acknowledgement. This research was supported by a grant from the Korea Science and Engineering Foundation.

References

- (1) For a review, see. G. Brieger and T. J. Nestruck, *Chem. Rev.*, **74**, p. 567 (1974).
- (2) N. A. Cortese and R. P. Heck, *J. Org. Chem.*, **42**, 3491 (1977).
- (3) G. A. Brieger and T. H. Fu, *J. Chem. Soc., Chem. Comm.*, 757 (1976).
- (4) G. A. Olah and G. K. Surya Prakash, *Synthesis*, 397 (1978). G. A. Olah, G. K. Surya Prakash and S. C. Narang, *ibid.*, 825 (1978).
- (5) G. A. Anantharamaiah and K. M. Sivanandaiah, *J. Chem. Soc., Perkin Trans.* **1**, 490 (1977). S. A. Khan and K. M. Sivanandaiah, *Synthesis*, 750 (1978). B. ElAmin, G. M. Anantharamaiah, G. P. Royer and G. E. Means, *J. Org. Chem.*, **44**, 3442 (1979); A. M. Felix, E. P. Heimer, T. J. Lambros, C. Tzougraki, and J. Meienhofer, *J. Org. Chem.*, **43**, 4194 (1978).
- (6) S. Hanessian, T. J. Kiak and B. Vanasse, *Synthesis*, 396 (1981); V. S. Rao and A. S. Perlin, *Carbohydr. Res.*, **83**, 175 (1980).
- (7) H. Imai, T. Nishigucho, and K. Fukuzumi, *J. Org. Chem.*, **42**, 431 (1977).
- (8) T. Nishiguchi and K. Fukuzumi, *J. Amer. Chem. Soc.*, **96**, 1983 (1974).
- (9) M. E. Vol'pin, V. P. Kukolev, V. O. Chernyshev, and I. S. Kolomonokov, *Tetraheron Lett.* 4435 (1971). S. Regen and G. M. Whitesides, *J. Org. Chem.*, **37**, 1832 (1972).
- (10) M. J. Andrews and C. N. Pillai, *Indian J. Chem. Sect. B.* **16B**, 465 (1978). *Chem. Abstract.* 90, 55151. *ibid.*, **91**, 39053 (1979).
- (11) W. H. Chiu and M. E. Wolff, *Steroids*, **34**, 361 (1979). V. S. Rao and A. S. Perlin, *Carbohydr. Res.*, **83**, 175 (1980). G. Brieger, T. J. Nestruck and T. H. Fu., *J. Org. Chem.* **44**, 1876 (1979). R. T. Coutts and J. B. Edwards, *Can. J. Chem.*, **44**, 2009 (1966).
- (12) R. L. Augustine, "Catalytic Hydrogenation, Techniques and Applications in Organic Synthesis" Marcel Dekker, N. Y. (1965). M. Freifelder, "Practical Catalytic Hydrogenation", Wiley-Interscience, N. Y. (1971). P. N. Rylander, "Catalytic Hydrogenation in Organic Synthesis", Academic Press, N. Y. (1979).
- (13) P. Boudjouk and B. H. Han, *J. Catalysis*, **79**, 489 (1983).
- (14) For a review, see. C. E. Miller, *J. Chem. Edu.*, 254 (1965). S. Hung, H. R. Muller and W. Thier, *Angew. Chem. Inter. Edition*, Vol 4, No. 4 271 (1965).
- (15) B. H. Han and P. Boudjouk, *J. Org. Chem.*, **47**, 751 (1982). *ibid.*, **47**, 5030 (1982).

New Synthesis of Solid Catalyst for Ethylene Dimerization

Jong-Rack Sohn[†] and Hong-Jae Kim

Contribution from the Department of Industrial Chemistry, Engineering College, Kyungpook National University, 635 Taegu, Korea (Received March 9, 1985)

Ethylene dimerization is an important reaction and worthy of study.¹⁻⁴ We have synthesized a new catalyst which is very active for ethylene dimerization even at room temperature.

The catalyst was prepared as follows. The coprecipitate of Ni(OH)₂-Ti(OH)₄ was obtained by adding aqueous ammonia slowly into a mixed aqueous solution of nickel chloride, titanium tetrachloride, and hydrochloric acid at room temperature with stirring until the pH of mother liquid reached about 7. The

precipitate thus obtained was washed thoroughly with distilled water until chloride ion was not detected, and was dried at room temperature. The dried precipitate (2g) was powdered below 100 mesh and was treated with 30ml of 1N H₂SO₄ followed by drying. It was used as catalyst after decomposing at different evacuation temperature for 1.5 h.

The catalytic activities for the reaction of ethylene dimerization were examined and the results are shown as a function of