

Palladium-Catalyzed and Sonically Accelerated Hydrogenations of Olefins Using Formic Acid as a Hydrogen Transfer Agent

The formic acid/palladium-on-carbon couple was found to be an effective hydrogenating system. Ten olefins, including terminal and internal alkenes, a diene, a vinyl ether, and an α,β -unsaturated ketone, were hydrogenated in high yields at room temperature and atmospheric pressure. Sonication of the reaction mixtures accelerated the reactions as did heating to reflux. Cyclopropylbenzene and diphenylacetylene were reduced quantitatively to *n*-propylbenzene and bibenzyl, respectively.

INTRODUCTION

Formic acid and its derivatives have been used only occasionally to hydrogenate olefins (1-5). Lukes and Cervinka reduced a series of tetrahydropyridines in high yields with the $\text{HCO}_2\text{H}/\text{H}_2\text{CO}_2\text{K}$ couple at 150°C in 6 h (1). Using a variety of homogeneous precious metal catalysts, Vol'pin and co-workers found formic acid and its derivatives to be only moderately effective in hydrogenating 1-octene at 100°C (2). In contrast, Blum *et al.* were able to use homogeneous ruthenium and iridium catalysts to hydrogenate the double bond in α,β -unsaturated ketones quantitatively at 97°C with formic acid as the hydrogen donor (3). More relevant to the work we present here are the report by Nishiguchi and co-workers (4) that supported palladium catalyzed the transfer of hydrogen from formic acid to one of the double bonds in methyl linoleate in 55% yield and the study by Cortese and Heck (5) demonstrating that a trialkylammonium formate-palladium system will hydrogenate a variety of olefins in 37-93% yields at 100°C with reaction times of 1.3 to 48 h.

In this paper (6) we report that, in the presence of palladium on carbon, formic acid is a very efficient hydrogen donor at room temperature and that, in the presence of sonic waves, the rate of hydrogenation is significantly enhanced (7).

METHODS

Formic acid was obtained from Matheson, Coleman and Bell (Reagent, ACS) and used without further purification. The palladium catalyst was 10% Pd on activated carbon and was used as obtained from Aldrich (lot No. 2123 TE). Absolute ethanol was used from stock without further purification. The reagents listed in the table were obtained commercially and used as purchased only if >97% pure as determined by NMR and GLC. When needed the reagents were purified by distillation or crystallization to at least 97% purity. NMR spectra were obtained on a Varian EM-390 spectrometer. Infrared spectra were taken on a Perkin-Elmer 257. Product analyses were carried out on a Varian Model 920 gas chromatograph.

General procedure for small-scale hydrogenations. A dry nitrogen-filled 100-ml flask was charged with 6 mmol of olefin, 24 mmol of HCO_2H , 0.50 g of 10% Pd on carbon (0.47 mmol), and 8 ml of absolute ethanol (Runs 4 and 5 required an additional 8 ml of benzene to dissolve the olefins) and placed in a common laboratory ultrasonic cleaner (Bransonic Model 220). Reactions were run under a nitrogen atmosphere and at ~25°C. Bath temperatures were maintained at ~25°C by means of a 4-in muffin fan mounted on the side of the cleaner. After 1 h of sonication the reaction vessel was

removed from the bath, the contents were filtered, and the collected solid was washed with chloroform or pentane. The combined filtrates were placed on a rotary evaporator and the volatiles were removed. NMR spectra of the residue showed only the hydrogenated product. Spectra of the products obtained from these reactions were identical to those of authentic samples in the Aldrich Library of NMR Spectra. The high level of purity of the products from these reactions was verified by both NMR and GLC. Yields were based on the amount of olefin used.

Hydrogenation of trans-stilbene. To a dry, nitrogen-filled 250-ml single-necked round bottom flask fitted with a nitrogen inlet and magnetic stirring bar we added 11.8 g (65.5 mmol) of stilbene, 11 g (240 mmol) formic acid, 5 g of 10% Pd on activated carbon (4.7 mmol Pd), 60 ml of absolute ethanol, and 100 ml of dry benzene. The reaction vessel was placed in a sonicator so that the liquid level inside the flask matched that of the bath water and in the location that produced the maximum cavitation in the flask. After 1 h the flask was removed and the contents were filtered. The solid was washed with chloroform and the combined filtrates were concentrated on a rotary evaporator. The residual solid was recrystallized (ethanol-pentane) to give 11.03 g (92.5% yield) of bibenzyl, mp 51–51.5°C (lit. 52.2) (8).

RESULTS AND DISCUSSION

A variety of unsaturated compounds, including cyclic and alicyclic olefins, a diene, a vinyl ether, and an α,β -unsaturated ketone, were hydrogenated in very high yields at room temperature using formic acid, 10% palladium on charcoal as the catalyst, and ethanol as solvent. Typical olefin:formic acid:catalyst mole ratios were 1:4:0.08. When the reactions were carried out in a common ultrasound laboratory bath cleaner the hydrogenations were complete within 1 h. While accurate rate data were not taken,

it was observed that when stirring the reagents for 1 h without ultrasound the reactions progressed to $\geq 70\%$ completion. Two hours was usually enough to give $>90\%$ yield. Thus sonic waves, while beneficial, are not necessary. We also investigated the effects of heating without sonication on the hydrogenations of nonene, *trans*-stilbene, and acenaphthene and found quantitative conversion to product when the reaction mixtures were refluxed for 0.25 h. Our results with olefins are summarized in Table 1.

The reactivity of the formic acid/palladium couple compares very favorably with related systems. For example, α -methylstyrene (Run 6) and the cyclic olefins are essentially quantitatively reduced using formic acid and palladium, whereas α -methylstyrene, cyclohexene, and methylcyclohexene are virtually untouched by formic acid in the presence of $(\text{Ph}_3\text{P})_3\text{RuHCl}$ (2). The facile conversion of methyl-oleate to methylstearate (Run 10) contrasts sharply with earlier attempts to hydrogenate unsaturated fatty acid methyl esters with formic acid and the apparently superior donor, indoline (4). Quantitative reduction of benzalacetone (*trans*-4-phenyl-3-buten-2-one) to 4-phenyl-2-butanone (Run 8) in 1 h at room temperature with $\text{HCO}_2\text{H}/\text{Pd}/\text{C}$ compares favorably with the 86% yield obtained in 2.5 h at 100°C using the tributylammonium formate-palladium couple (5) and avoids the use of tributylamine.



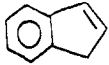
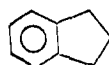
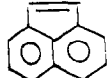
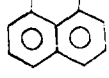
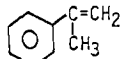
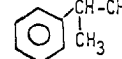


The results in Table 1 are for reactions run on 6 mmol of olefin and the yields were computed on the basis of isolated product that was $>97\%$ pure by GLC and NMR. To demonstrate feasibility of scaleup, 12 g of *t*-stilbene was hydrogenated and bibenzyl was isolated by crystallization in 93% yield. That formic acid is the exclusive source of hydrogen was shown when *t*-stilbene was recovered quantitatively from a reaction mixture in which formic acid was omitted.

The high yields, short reaction times, mild conditions, and simplicity of workup are noteworthy features of this system.

TABLE I

**Hydrogenation of Carbon–Carbon Double Bonds by Formic Acid
Catalyzed by Palladium on Carbon**

$$\text{>C=C<} \xrightarrow[\text{HCO}_2\text{H}]{\text{Pd/C}} \text{H-C-C-H} \text{ (% yield, isolated)}^a$$

Olefin	Product
1. $\text{C}_7\text{H}_{15}\text{CH}=\text{CH}_2^b$	C_9H_{20} (100%)
2. 	 (95%)
3. 	 (100%)
4. $\text{trans-PhCH}=\text{CHPh}^b$	$\text{PhCH}_2\text{CH}_2\text{Ph}$ (100%)
5. 	 (100%)
6. 	 (100%)
7. 	 (95%) ^c
8. $\text{trans-PhC}(\text{H})=\text{C}(\text{H})\text{C}(=\text{O})\text{CH}_3$	$\text{PhCH}_2\text{CH}_2\text{C}(=\text{O})\text{CH}_3$ (100%)
9. $n\text{-C}_4\text{H}_9\text{OCH}=\text{CH}_2$	$n\text{-C}_4\text{H}_9\text{OC}_2\text{H}_5$ (93%)
10. methyl 9-octadecenoate	methyl 9-octadecanoate

^a Reaction times are not optimized. All runs were sampled after 1 h, found to be complete by NMR, and worked up. Pd/C is required. Using activated charcoal only or simply formic acid and olefin gave no reaction with sonication or heating.

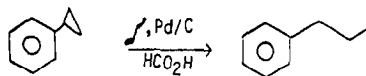
^b Quantitatively hydrogenated within 0.5 h when refluxed in the absence of sonic waves.

^c Trace benzene detected by NMR. In a separate experiment it was shown that when an ethanol solution of cyclohexene was sonicated in the presence of formic acid and palladium on carbon the cyclohexene was converted quantitatively to cyclohexane and benzene in a 2:1 ratio, respectively.

When the low cost and ease of handling of formic acid and the recyclability of the catalyst are also considered, the $\text{HCO}_2\text{H-Pd/C}$ couple is potentially very useful as a routine method of hydrogenating olefins.

The donor capabilities of $\text{HCO}_2\text{H-Pd/C}$ with respect to other organic systems were examined. Thus we found that cyclopro-

pylbenzene is converted to *n*-propylbenzene



quantitatively (no cumene detected) in less than 0.5 h at room temperature and that diphenylacetylene is reduced to bibenzyl in

>98% yield. Diphenylacetylene, however, was not hydrogenated at room temperature even with sonication. The reaction mixture must be refluxed for 0.5 h. We are presently exploring the ability of formic acid to donate hydrogen to a variety of functional groups in the presence of other metals and we are evaluating the effects of ultrasound on these reactions.

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