Organic Process Research & Development **1997**, *1,* 226–232

# Synthesis of Aldehydes by Rosenmund Reduction

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## Abstract:

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**Important perfumery aldehydes such as 10-undecenal could be synthesized by Rosenmund reduction. This reduction by hydrogen is usually effected in the presence of a supported Pd catalyst. The main by-product is the alcohol, and it is formed by the subsequent reduction of the aldehyde. This can be prevented by the use of a catalyst poison or regulator. The regulator deactivates the catalyst for the desired reaction and renders the repeated use of the catalyst difficult. However, reuse of the catalyst is of great industrial relevance, because the incidence of cost due to catalyst may be prohibitive if it is used for only a single run. Therefore, attempts to dispense with the use of a regulator acquire considerable significance. It may be possible to obtain very high selectivities to the aldehyde even in the absence of a regulator, provided that the temperature employed is about 30−40 °C and the reduction is carried out at atmospheric pressure, at which the rate of hydrogenolysis is acceptable. The present work is an attempt in this direction. Under this condition it was possible to obtain 10-undecenal conforming to perfumery industry specifications.**

## Introduction

Important perfumery aldehydes such as 10-undecenal (**3**), having extensive commercial use, could be synthesized from comparatively cheaper raw material, viz., 10-undecenoic acid (**1**), a castor oil based product, by conversion to the acyl chloride (**2**) followed by Rosenmund reduction. This reduction by hydrogen is effected in the presence of a supported Pd catalyst. The chemistry of this reduction is well-known, and the various possible side products as reported in the literature[1,2] are represented in Figure 1. The main by-product is the alcohol (**4**), and it is formed by the subsequent reduction of the aldehyde (**3**). This can be prevented by the use of a catalyst poison or regulator[3−11] such as quinoline−sulfur which selectively deactivates the catalyst, whereby the formation of the alcohol is suppressed, thereby increasing the selectivity to the aldehyde. Quinoline−sulfur deactivates the catalyst for the desired reaction and renders the repeated use of the catalyst difficult. However, reuse of the catalyst is of great industrial relevance, because the incidence of cost due to catalyst may be prohibitive if it is used for only a single run. Therefore, attempts to dispense with the use of quinoline−sulfur acquire considerable significance. It may be possible to obtain very high selectivities to the aldehyde (**3**) even in the absence of a regulator such as quinoline−sulfur, provided that the temperature employed is almost at the threshold and the reduction is carried out at atmospheric pressure, at which the rate of hydrogenolysis is acceptable.

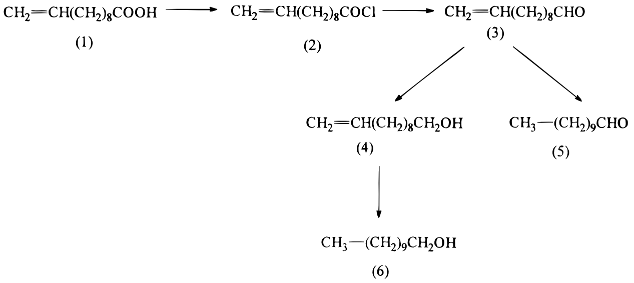

***Figure 1.*** **Reaction Scheme: undecenoic acid (1); 10-undecenoyl chloride (2); 10-undecenal (3); 10-undecenol (4); undecanal (5); undecanol (6).**

The present work is an attempt in this direction. In addition to the conventional catalyst, viz., Pd/C, Pd/polymer, the polymer being poly(*p*-phenylene terephthalamide) (PPTA), was also used. Under this condition it was possible to obtain 10-undecenal (**3**) conforming to perfumery industry specifications (Figure 2).

## Experimental Section

**Materials.** 10-Undecenoyl chloride, *p*-anisoyl chloride, terephthaloyl chloride, 5% Pd/polymer, PPTA (prepared in the laboratory), 5% Pd/C (from Aurora Mathews, Calcutta, India), acetone, ethyl acetate, toluene, *N*,*N*-dimethylaniline, and *p*-phenylenediamine (laboratory grade, procured from S. D. Fine Chemicals, Bombay, India) were used for the above study.

**Synthesis of Acyl Chloride.** The carboxylic acid (1 mol), thionyl chloride (1.5 mol), and 2 mL of *N*,*N*-dimethylformamide were taken into the reactor. The reaction mixture was refluxed at 80 °C in a water bath for 4 h. Gaseous sulfur dioxide, hydrochloric acid, and unreacted thionyl chloride escaping from the condenser were trapped in the water and the alkali traps. After the completion of the reaction, the unreacted thionyl chloride was removed under vacuum. After that, 25 mL of toluene was added and the mixture of toluene and thionyl chloride was removed under vacuum. This

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S1083-6160(96)00024-2 CCC: $14.00
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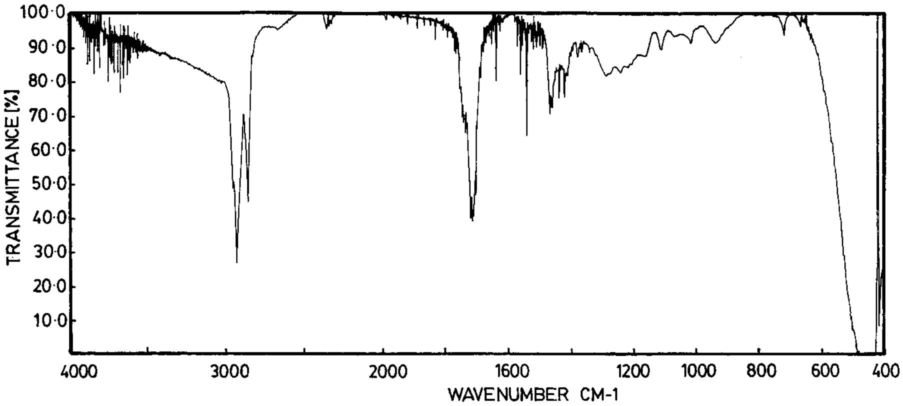

***Figure 2.*** **FTIR of 10-undecenal.**

***Table 1.*** **Physical properties of chemicals synthesized in the laboratory**

| chemicals | physical properties |
|---|---|
| terephthaloyl chloride | lit. mp, 84 °C<br>obsd mp, 84 °C |
| 10-undecenoyl chloride (**2**) | lit. bp, 270 °C<br>obsd bp, 270 °C |
| *p*-anisoyl chloride | product distilled under vacuum and its purity checked by Volhard's method, purity = 100% |
| 10-undecenal (**3**) | product isolated by vacuum distillation and confirmed by IR spectroscopy, its purity was checked using GC |
| *p*-anisaldehyde | confirmed by GC |

process was repeated 4−5 times to remove traces of thionyl chloride, whose presence might affect the activity of the catalyst used in the Rosenmund reduction. Finally, 10-undecenoyl chloride and *p*-anisoyl chloride were distilled under vacuum and terephthaloyl chloride was recrystallized from hexane (Table 1).

**Preparation of 5% Pd/polymer. (A) Preparation of Poly(*p*-phenylene terephthalamide) (PPTA).** A mixture of 0.03 mol (3.24 g) of *p*-phenylenediamine, 0.05 mol (2 g) of sodium hydroxide in 300 mL of distilled water, and sodium lauryl sulfate (0.5 g) was taken into a reactor. This mixture was cooled to −10 °C. Terephthaloyl chloride, 0.025 mol (5.1 g), dissolved in 200 mL of cyclohexanone was added instantly in one portion. The reaction mixture was stirred at −10 °C for 1 h. Then the reaction mixture was filtered. The precipitate thus obtained was washed initially with distilled water and then with a mixture of distilled water and acetone (1:1) until the filtrate was free of brown colour. The solid polymer was dried under vacuum at 80 °C.

The polymer was analyzed by IR spectroscopy, which showed the presence of NH and CO groups at 3325 and 1660 $\mathrm{cm}^{-1}$.

The inherent viscosity ($\eta$) was calculated as follows:

$$\eta_{\mathrm{inh}} = \frac{\ln(t/t_0)}{C}$$

where $t = 258.02$ s, flow periods for polymer solution; $t_0 = 213.1$ s, flow periods for sulfuric acid (95% w/w); $C$ = concentration (0.5 g/100 mL); and $\eta_{\mathrm{inh}} = 38.25$.

The molecular weight ($M$) of the polymer was determined by using the formula

$$M = (\eta_{\mathrm{inh}}/K)^{1/\alpha}$$

where $K = 7.9 \times 10^{-4}$ and $\alpha = 1.06$. The molecular weight obtained was 26 295. $K$ and $\alpha$ are in cgs units.

**(B) Deposition of Palladium Chloride on PPTA.** For preparing 5 g of the catalyst, 0.42 g of palladium chloride was dissolved in 70 mL of a glacial acetic acid/water mixture (1:9) in a conical flask at 60 °C and the solution was charged to a four-necked reactor maintained at room temperature. The temperature of the reaction mixture was brought down to room temperature, and the support was added with good stirring. After the addition of the polymer, the stirring was continued at room temperature for 6 h.

The absence of palladium in the mother liquor was checked by using an alcoholic solution of dimethylglyoxime.[12] All palladium chloride was found to be dispersed on the support. Further, this catalyst was activated in a hydrogen flow of 30 mL/min for 4 h at 210 °C in a specially designed reactor as shown in Figure 3.

**Experimental Set-Up.** Rosenmund reduction of acid chloride at atmospheric pressure was carried out in a borosilicate glass reactor, 5 cm i.d., provided with a six-bladed turbine impeller through a glass tube, baffles, sparger, thermometer pocket, and a condenser as shown in Figure 4. The desired temperature of the reaction mixture was maintained by immersing the reactor in a constant temperature bath. The hydrogen gas was bubbled into the reaction mass through a trap containing the solvent used in the reactor at the same temperature. This was necessary to saturate the gas with the solvent vapours. An autoclave made of hastalloy was used for hydrogenations conducted under pressure. In this case, the hydrogen passed into the reactor was not saturated with the solvent used.

**Experimental Procedure.** The acid chloride in a suitable solvent and the catalyst were taken into the reactor. The temperature of the reaction mixture was raised to the desired value. Then hydrogen gas was bubbled through the reaction mixture at a slow constant rate at atmospheric pressure. It was ensured that there was always a positive flow of hydrogen at the outlet of the reactor. At regular time intervals, samples were withdrawn for the estimation of the conversion to the product by gas chromatography (GC).

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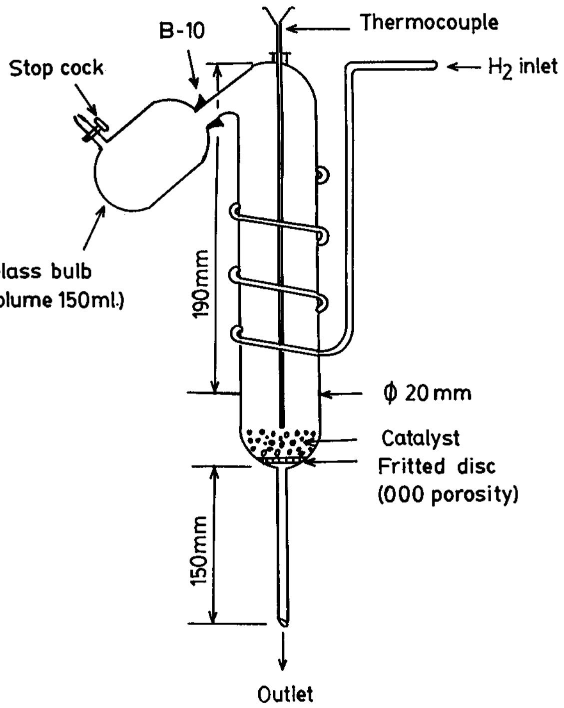

***Figure 3.*** **Catalyst reducer assembly (not to scale).**

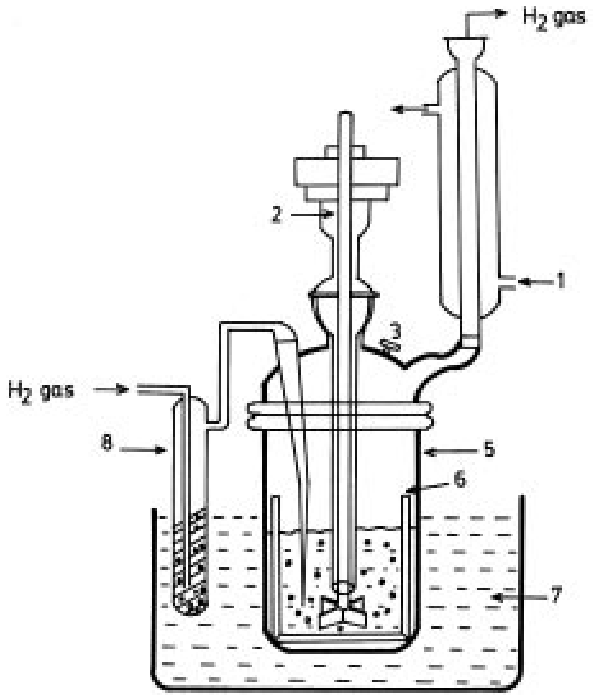

***Figure 4.*** **Experimental set-up: 1, condenser; 2, stirrer; 3, sample point; 4, sparger; 5, reaction vessel; 6, baffles; 7, constant temperature bath; 8, trap.**

After completion of the reaction the mixture was filtered to separate the catalyst. The catalyst was washed with the solvent. The filtrate and the washings were mixed and used for the estimation of the overall conversion of the acid chloride.

## Analysis

**Estimation of Overall Conversion and Yield.** The samples from the reaction mixture were taken at regular time intervals, and unsaturated aldehyde (**3**) and other by-products present in the sample were analyzed by gas chromatography. However, on the assumption that all of the by-products have been determined by gas chromatography, the overall conversion of the acyl chloride could be calculated. Each run was carried out for a predetermined period of time. After the run was completed, the overall conversion was also determined by estimating the unconverted acyl chloride. The overall conversion calculated on this basis agreed with that obtained on the basis of conversion to product and other by-products.

***Table 2.*** **Material balance using catalyst, 5% Pd/C**[a]

| | mol | % |
|---|---|---|
| undecenoyl chloride taken | 0.088 89 | 100 |
| undecenoyl chloride recovered | 0.041 98 | 47.2 |
| 10-undecenal obtained | 0.044 64 | 48.3 |
| unaccounted | 0.002 27 | 4.5 |
| total | 0.088 89 | 100 |

[a] Undecenoyl chloride, 18 g, 1.679 × $10^{-4}$ mol $mL^{-1}$; catalyst, 5% Pd/C; catalyst loading, 4.4 g, 0.83 × $10^{-2}$ g $mL^{-1}$; solvent, acetone, 530 mL; temperature, 27 °C; time, 7200 s; speed of agitation, 1100 rpm.

The GC column and conditions used were as follows: column, S.S., 3.2 mm i.d., 2 m length; stationary phase, 10% OV-17 on Chromosorb-W; carrier gas, rate, $N_2$, 0.138 MPa; detector, FID; oven temperature, 80 °C, 1 min isothermal, ramp, 10 °C/min to 300 °C; injector temperature, 300 °C; detector temperature, 300 °C.

**Estimation of Unreacted Acid Chloride.** The reaction mixture was filtered, and the catalyst was washed with the solvent. The filtrate was made alkaline using 10% sodium hydroxide solution and refluxed for 4 h. Acetone was distilled off under vacuum, and the residue was made acidic by addition of dilute hydrochloric acid. 10-Undecenoic acid formed was extracted in diethyl ether. The ether layer was washed twice with water and dried using anhydrous sodium sulfate. The ether was distilled under vacuum, the residue was diluted with methanol to 50 mL in a volumetric flask, and a 10 mL sample was taken for each titration. It was titrated with 0.1 N methanolic sodium hydroxide solution using phenolphthalein as an indicator.

## Results and Discussion

**Material Balance.** A typical run was carried out on a relatively large scale using suitable reaction conditions with a view to ascertaining the material balance. The crude product was isolated, and its purity was determined by gas chromatography as discussed earlier. It was possible to account for 95.5% of 10-undecenoyl chloride (**2**) consumed (Table 2).

**Effect of Support.** In addition to the use of the conventional catalyst system comprising Pd supported on activated charcoal, barium sulfate, etc., there are a few references[13] on the use of Pd supported on polymers. In this work, therefore, Pd supported on poly(*p*-phenylene terephthalamide) (PPTA), a polymer which could be conveniently prepared and might be suitable for the purpose, was also employed, and its performance was critically assessed in comparison with that of the conventional catalyst.

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[13] Gaimpietro, C.; Gallo, R.; Galvango, S.; Spadaro, A.; Vitarelli, P. *J. Chem. Technol. Biotechnol.* **1984**, *34A*, 416.

*Table 3.* **Effect of support[a]**

| catalyst | 5% Pd/C | 5% Pd/PPTA |
|---|---|---|
| time, h | 2 | 6 |
| % overall conversn | 52.8 | 56 |
| % conversn to 10-undecenal | 50.1 | 50 |
| % conversn to 10-undecenol | 2.7 | 1.5 |
| % conversn to undecanal | | 4.5 |
| % yield of 10-undecenal | 94.9 | 89.9 |

[a] Undecenoyl chloride, 1.7 g, 1.679 × $10^{-4}$ mol $mL^{-1}$; catalyst loading, 0.44 g, 0.83 × $10^{-2}$ g $mL^{-1}$; solvent, acetone, 50 mL; temperature, 27 °C; time, 7200 s; speed of agitation, 1100 rpm.

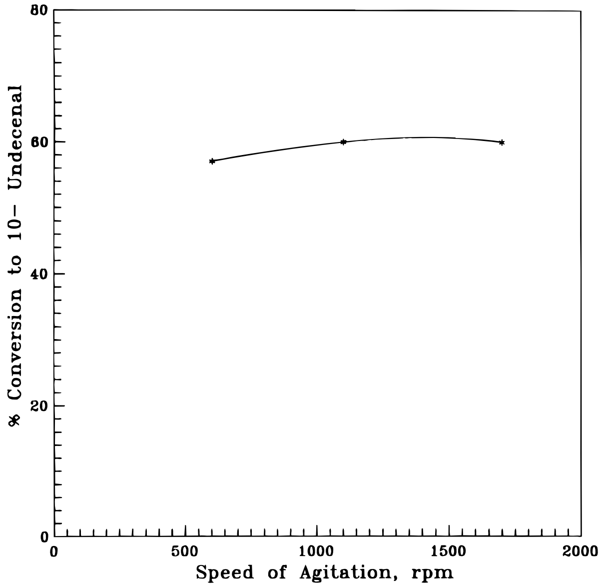

*Figure 5.* **Effect of speed of agitation: 10-undecenoyl chloride, 1.7 g, 1.679 × $10^{-4}$ mol $mL^{-1}$; catalyst, 5% Pd/C; catalyst loading, 1.6 × $10^{-2}$ g $mL^{-1}$; acetone, 50 mL; temperature, 27 °C; time, 10 800 s.**

*Table 4.* **Effect of catalyst loading on yield of the product[a]**

| catalyst loading × $10^{-2}$, g $mL^{-1}$ | 0.8 | 1.2 | 1.6 | 2.4 |
|---|---|---|---|---|
| % overall conversn | 48 | 54 | 60 | 64.3 |
| % yield of 10-undecenal | 100 | 98.1 | 100 | 93.2 |

[a] Undecenoyl chloride, 1.7 g, 1.679 × $10^{-4}$ mol $mL^{-1}$; catalyst, 5% Pd/C; solvent, acetone, 50 mL; temperature, 27 °C; time 7200 s; speed of agitation, 1100 rpm.

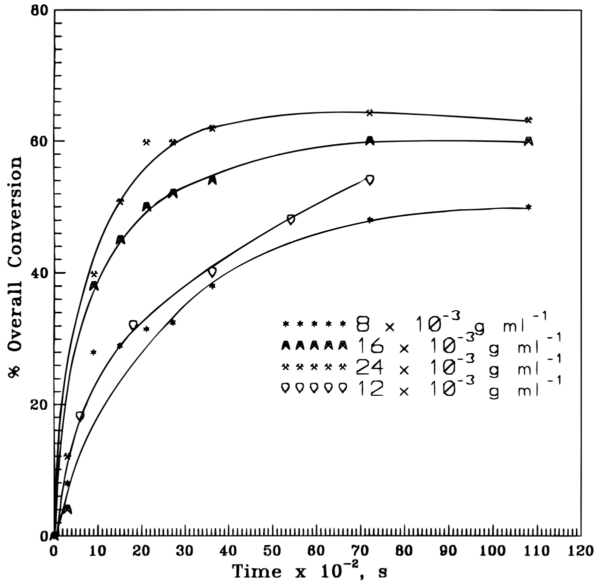

*Figure 6.* **Effect of catalyst loading, 5% Pd/C: 10-undecenoyl chloride 1.7 g, 1.8 × $10^{-4}$ mol $mL^{-1}$; speed of agitation, 1100 rpm; acetone, 50 mL; temperature, 27 °C.**

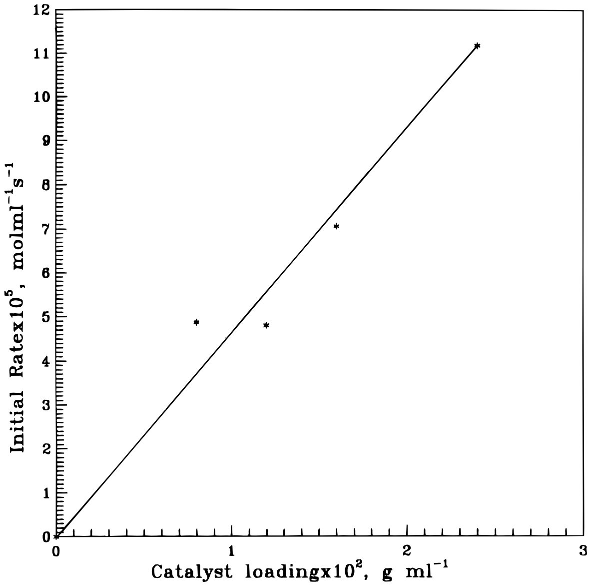

*Figure 7.* **Effect of catalyst loading.**

It was observed that 5% Pd supported on carbon was more active than 5% Pd supported on PPTA. The catalyst 5% Pd/C gave 53% overall conversion in 2 h while a comparable conversion of 56% was obtained in 6 h when 5% Pd/PPTA was used (Table 3). It may be interesting to note that, with 5% Pd/C, the major side product was the unsaturated alcohol (**4**) whereas with 5% Pd/PPTA the side product was saturated aldehyde (**5**).

**Effect of Speed of Agitation.** The effect of speed of agitation was studied in the range 600−1700 rpm. Above 1100 rpm, there was no significant difference in the overall conversion of acid chloride, which indicates the absence of external mass transfer resistance (Figure 5).

**Effect of Catalyst Loading.** The effect of catalyst loading, expressed as g $mL^{-1}$ of reaction volume, on conversion to and yield of the aldehyde was studied at four different catalyst loadings, viz., 8 × $10^{-3}$, 12 × $10^{-3}$, 16 × $10^{-3}$, and 24 × $10^{-3}$, using 5% Pd/C as catalyst (Table 4, Figure 6). The initial reaction rate was found to be directly proportional to catalyst loading (Figure 7). This fact in corroboration with the observation that, beyond the speed of agitation of 1100 rpm, the conversion was not affected indicated that the effects of mass transfer from the gas phase to the gas liquid interface are completely eliminated. For the catalyst size and the conditions employed, an estimate of the mass transfer coefficient indicated that the mass transfer from the liquid to the catalyst surface is unlikely to play an important role. Therefore, the data obtained represented the intrinsic kinetics of the process.

**Effect of Type of Solvent and Temperature.** Generally the acyl chlorides of carboxylic acids have been converted to the corresponding aldehydes using xylene as a medium and a temperature of the order of 140 °C. More specifically Jethani[14] carried out the hydrogenation of 10-undecenoyl chloride (**2**) but produced polymeric materials, presumably

***Table 5.*** **Effect of type of solvent**[a]

| solvent | % overall conversn of undecenoyl chloride | % yield of 10-undecenal |
|---|---|---|
| acetone | 48 | 100 |
| toluene | 47.2 | 100 |
| ethyl acetate | 49.3 | 100 |

[a] Undecenoyl chloride, 1.7 g, 1.679 × $10^{-4}$ mol $mL^{-1}$; catalyst, 5% Pd/C; catalyst loading, 0.44 g, 0.83 g $mL^{-1}$; solvent, 50 mL; temperature, 27 °C; time, 7200 s; speed of agitation, 1100 rpm.

because of the use of high temperature leading to the polymerization of the thermally unstable 10-undecenal (**3**). Unlike this work, studies have been reported[15] where Rosenmund reduction was carried out at temperatures of 25−40 °C using toluene or acetone as solvents. More recently Peters and Bekkum[9] have also carried out the reaction at 28 °C for the synthesis of aliphatic and aromatic aldehydes. Another aspect worth examining is whether the reaction could be carried out at atmospheric pressure yet with reasonably high reaction rates. Perhaps atmospheric pressure and ambient temperature might enhance the selectivity with respect to unsaturated aldehyde (**3**) by minimizing the formation of alcohol (**4**) and saturated aldehyde (**5**). Further, in order to have better stripping conditions to ensure effective removal of hydrogen chloride, it may also be desirable to use a low-boiling solvent such as acetone or ethyl acetate and carry out the reaction under near-reflux conditions.

As mentioned above acetone and ethyl acetate were used as solvents, and the reaction was carried out at 27 °C and atmospheric pressure. Since these are low-boiling solvents, even at 30 °C there was a considerable vaporization which ensured stripping of hydrogen chloride formed in the reaction mixture to a considerable extent. The performance of both solvents was comparable (Table 5). In experiments with toluene, contrary to the comments made earlier, the reaction rate was found to be comparable with that obtained with acetone and ethyl acetate. This, however, may be due to lower solubility of hydrogen chloride in toluene as compared to that in acetone or ethyl acetate. An experiment was carried out at 90 °C, using toluene as the solvent. As expected, the reaction rate increased markedly and a similar conversion (48%) was obtained in 1800 s instead of 7200 s (Figure 8). The yield of the aldehyde was unaffected. No significant polymerization was observed. Thus, for the conversion of 10-undecenoyl chloride (**2**) to 10-undecenal (**3**), toluene may be used as the solvent as is commonly reported in the literature. However, the temperature employed should be in the range 30−90 °C.

**Effect of Substrate Concentration.** Kinetic runs carried out with different initial substrate concentrations were varied in the range of 0.49 × $10^{-4}$ to 3.4 × $10^{-4}$ mol $ml^{-1}$. At higher substrate concentrations, although the throughput was higher, the overall conversion of the acid chloride was lower (Figure 9).

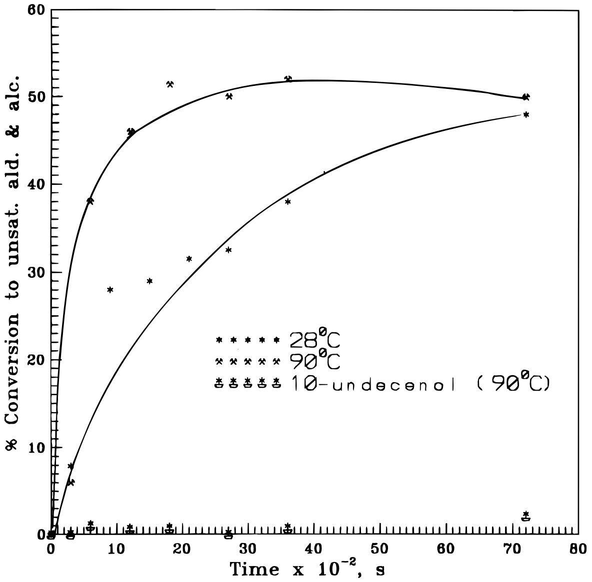

***Figure 8.*** **Effect of temperature, °C: 10-undecenoyl chloride, 1.7 g, 1.68 × $10^{-4}$ mol $mL^{-1}$; catalyst, 5% Pd/C; catalyst loading, 0.8 × $10^{-2}$ g $mL^{-1}$; toluene, 50 mL; speed of agitation, 1100 rpm.**

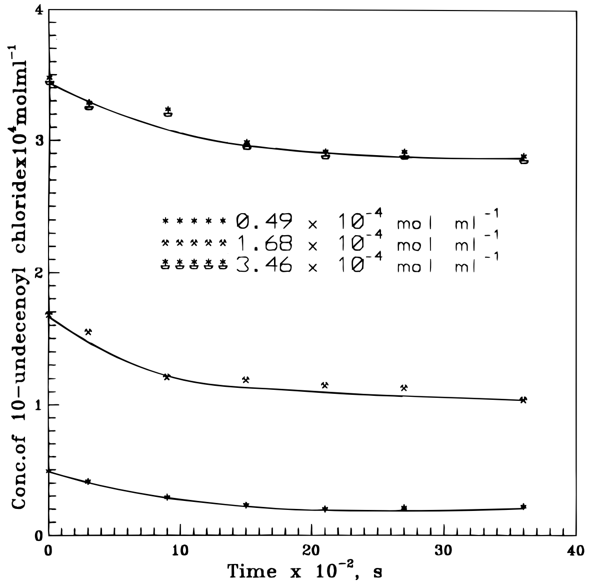

***Figure 9.*** **Effect of substrate concentration: speed of agitation, 1100 rpm; temperature, 27 °C; catalyst, 5% Pd/C; catalyst loading, 0.8 × $10^{-2}$ g $mL^{-1}$; acetone, 50 mL.**

**Effect of Pressure.** Though not explicitly mentioned, there are sufficient indications that the rate of hydrogenolysis of acyl chloride (**2**) to the aldehyde (**3**) may be relatively higher if hydrogen chloride is stripped off as soon as it is formed. By and large, for better output, hydrogenation of organic compounds including hydrogenolysis of acyl chloride is carried out under pressure. Even when high pressure is used, it may still be possible to minimize the amount of hydrogen chloride in the reaction system provided that an acid binding agent such as *N*,*N*-dimethylaniline is used. Therefore, certain reductions were carried out under pressure, with and without an acid binding agent such as *N*,*N*-dimethylaniline.

It was observed, in the absence of acid binding agent, that with an increase in pressure there was a decrease in the overall conversion of acid chloride (Figure 10). Better results

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(14) Jethani, K. R. Production of Aldehydes. M. Chem. Eng. Thesis, University Department of Chemical Technology, Bombay, 1980.

(15) Wagner, D. P.; Rachlin, A. I.; Gurien, H. *Organic Syntheses*; Wiley: New York, 1988; Collect. Vol. VI, 1007.

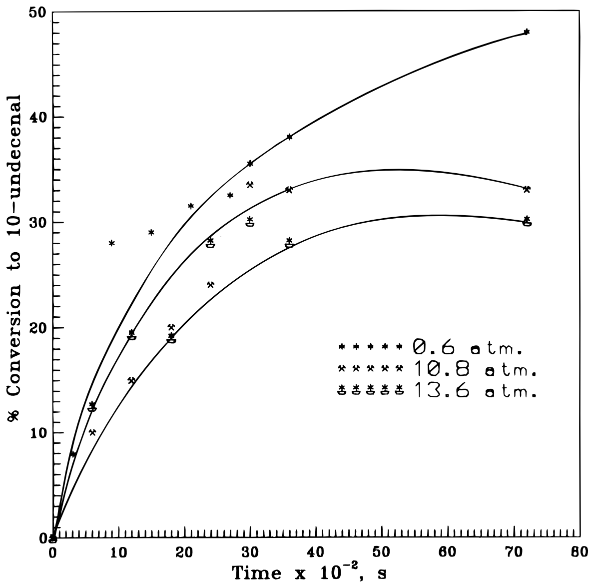

***Figure 10.*** **Effect of pressure without an acid binding agent: 10-undecenoyl chloride, 1.7 g, 1.68 × $10^{-4}$ mol mL$^{-1}$; catalyst, 5% Pd/C; catalyst loading, 0.8 × $10^{-2}$ g mL$^{-1}$; acetone, 50 mL; temperature, 27 °C; speed of agitation, 1100 rpm.**

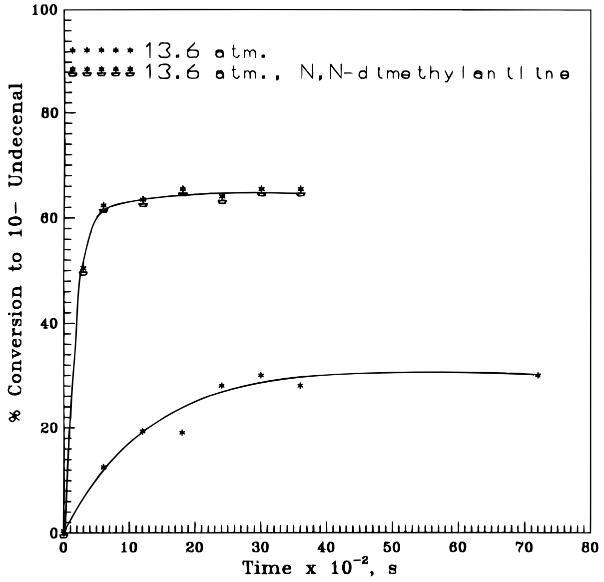

***Figure 11.*** **Effect of pressure with an acid binding agent: 10-undecenoyl chloride, 1.68 × $10^{-4}$ mol mL$^{-1}$; catalyst, 5% Pd/C; catalyst loading, 0.8 × $10^{-2}$ g mL$^{-1}$; acetone, 50 mL; temperature, 27 °C; speed of agitation, 1100 rpm; acid binding agent, *N,N*-dimethylaniline (1 mL).**

***Table 6.*** **Reusability of catalyst**[a]

| run no. | % overall conversn | % yield of 10-undecenal |
|---|---|---|
| 1 | 49 | 100 |
| 2 | 48 | 100 |
| 3 | 47 | 100 |
| 4 | 50 | 100 |
| 5 | 44 | 100 |

[a] Undecenoyl chloride, 9 g, 1.62 × $10^{-4}$ mol mL$^{-1}$; catalyst, 5% Pd/C; catalyst loading, 2.8 g, 1.02 × $10^{-2}$ g mL$^{-1}$; solvent, acetone, 275 mL; temperature, 27 °C; time, 7200 s; speed of agitation, 1100 rpm.

***Table 7.*** **Synthesis of anisaldehyde**[a]

| | |
|---|---|
| % overall conversn of acid chloride | 44 |
| % conversn to anisaldehyde | 32 |
| % yield of anisaldehyde | 72.7 |
| % yield of alcohol | 27 |

[a] Anisoyl chloride, 2.04 g, 2.593 × $10^{-4}$ mol mL$^{-1}$; catalyst, 5% Pd/C; catalyst loading, 0.53 g, 1.06 × $10^{-2}$ g mL$^{-1}$; solvent, acetone, 50 mL; temperature, 27 °C; time, 7200 s; speed of agitation, 1100 rpm.

***Table 8.*** **Details of the best process**[a]

Yield of 10-undecenal = 7.5 g, 53%.
The product was isolated and purified by vacuum distillation.
Purity = 98% (GC).
IR spectroscopy showed strong peaks at 1716 and 2926 cm$^{-1}$, indicating the presence of a CHO group (Figure 2); the purity of the product was checked by GC.
Evaluation of the odour was carried out by M/s Beeta Chemicals, Saki Naka, Andheri, India.
Report: The odour was comparable with that of the authentic and commercial 10-undecenal.

[a] 10-undecenoyl chloride, 17 g, 1.679 × $10^{-4}$ mol mL$^{-1}$; catalyst, 5% Pd/C; catalyst loading, 4.4 g, 8.3 × $10^{-3}$ g mL$^{-1}$; solvent, acetone, 530 mL; temperature, 27 °C; time, 7200 s; speed of agitation, 1100 rpm.

were obtained when reductions were carried under pressure using an acid binding agent such as *N,N*-dimethylaniline (Figure 11). If an acid binding agent was used, its ease of recovery and its lack of adverse effect on the odour of the final product have to be ascertained. In the case of *N,N*-dimethylaniline, there was a problem of undesired odour in the product, which was retained even after the usual purification steps. Hence, reduction at atmospheric pressure without an acid binding agent may be preferred for the synthesis of perfumery aldehydes.

**Reusability of 5% Pd/C.** The catalyst could be reused four times with no significant effect on the conversion to and yield of 10-undecenal (**3**) (Table 6). When catalyst was used for the fifth time, there was a marginal decrease in the reactivity.

**Synthesis of *p*-Anisaldehyde.** As several aromatic aldehydes are used as perfumery chemicals, the present reaction conditions may be extended for the synthesis of such aromatic aldehydes.[16] Under identical reaction conditions using 5% Pd/C as catalyst, *p*-anisaldehyde was synthesized from its corresponding acyl chloride (Table 7). The major side product was the *p*-anisyl alcohol.

## Conclusions

The Rosenmund hydrogenolysis of 10-undecenoyl chloride (**2**) could be conveniently carried out at atmospheric pressure and in the temperature range 30−90 °C by using low-boiling solvents such as acetone and ethyl acetate in the presence of 5% Pd/C without an inhibitor like quinoline−sulfur with as high as 93% selectivity to the 10-undecenal (**3**). The catalyst 5% Pd/PPTA was also considered but was found to be less active. The use of acetone, ethyl acetate, and toluene gave comparable results.

If an acid binding agent was used, then the use of higher pressure gave better performance. However, in the absence of acid binding agent it is preferable to use atmospheric pressure. The product could be most suitably purified by

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(16) Mosettig, E. *Organic Reactions*; John Wiley & Sons: London, 1948; Vol. IV, pp 362−77.

vacuum distillation at 10 mm vacuum and the quality of the product matched with the commercial sample (Table 8, Figure 2).

The catalyst 5% Pd/C could be used four times with no significant effect on the conversion to and yield of the unsaturated aldehyde.

Under suitable reaction conditions (using 5% Pd/C as catalyst at a loading of $8.3 \times 10^{-3}$ g mL$^{-1}$, with acetone as solvent, at 1100 rpm and atmospheric pressure) an overall conversion of 52% with 93% selectivity towards 10-undecenal was obtained in 7200 s at 27 °C.

## Acknowledgment

V.G.Y. thanks the University Grant Commission for the award of a senior research fellowship.

Received for review August 15, 1996.⊗

OP960024J

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⊗ Abstract published in *Advance ACS Abstracts,* April 15, 1997.