

Regenerable *N*-Alkylamide Hydroperoxide for Catalytic Substrate Oxidation

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The use of *N*-methylpyrrolidinone in a catalytic cycle employing O_2 and H_2 in the presence of transition metal catalysts provides a regenerative hydroperoxide system. When treated with O_2 at $75^\circ C$, *N*-methylpyrrolidinone is converted into the corresponding hydroperoxide, 5-hydroperoxy-1-methylpyrrolidin-2-one. This stable hydroperoxide undergoes reactions similar to those of *tert*-butyl hydroperoxide, yielding *N*-methylsuccinimide as the product. By using either heterogeneous or homogeneous catalysts, *N*-methylsuccinimide can be reduced with H_2 under mild conditions to the hydroperoxide precursor, *N*-methylpyrrolidinone. The steps in the conversion of the hydroperoxide into *N*-methylsuccinimide were elucidated by study of the oxidation of PPh_3 to $OPPh_3$. Oxygen-atom transfer from the hydroperoxide to the phosphine produces the amido alcohol intermediate, 5-hydroxy-1-methylpyrrolidin-2-one. In the presence of O_2 , the amido alcohol intermediate undergoes rapid oxidation to *N*-methylsuccinimide.

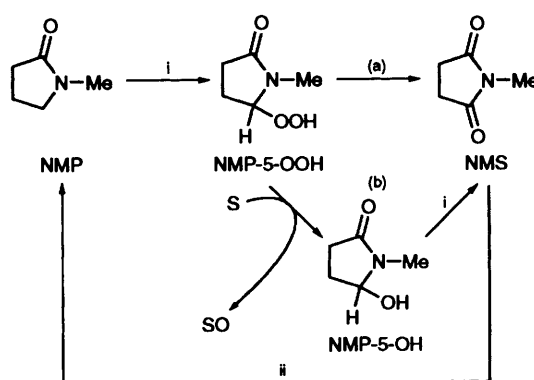
The use of various oxidants, with and without transition metal catalysts, has been reported to oxidize amides to their corresponding imides.¹⁻⁵ In an earlier report, the direct reaction of the lactam (cyclic amide) *N*-methylpyrrolidinone, NMP, with O_2 at $75^\circ C$ was shown to yield an approximately 2 mol dm^{-3} concentration of an oxidizing agent that was characterized by ^{13}C NMR spectroscopy and GLC-MS to be 5-hydroperoxy-1-methylpyrrolidin-2-one, NMP-5-OOH.⁶ This hydroperoxide decomposes at elevated temperatures or in the presence of transition metal catalysts to the cyclic imide, *N*-methylsuccinimide, NMS. The reaction to produce hydroperoxide exhibits an induction period of 24 h and reaches maximum hydroperoxide concentration in the next 24 h. Attempts to increase the yield and rate of formation of hydroperoxide by increasing the temperature were unsuccessful. Instead, less hydroperoxide and an increased rate of conversion into NMS occur.

Another interesting aspect of the chemistry of amides and imides is the difficulty of hydrogenating cyclic imides to their corresponding lactams. A nickel⁷ or platinum oxide⁸ catalyst did not give pyrrolidin-2-one. The reduction of succinimide to the corresponding amide is possible at high pressures of H_2 and elevated temperatures^{9,10} by using various transition metals supported on carbon or silica gel.

Our interest in the oxidation and hydrogenation reactions of these materials involved using NMP catalytically in a cycle that used only H_2 and O_2 to effect monooxygenate-type substrate oxidation. NMP reacts with O_2 to form NMP-5-OOH, which can be used to oxidize selectively a variety of organic substrates, thereby producing NMS as a by-product [Scheme 1, path (a)].¹¹ Hydrogenation of NMS would regenerate NMP allowing it, in effect, to function as a catalyst for the oxidation of substrates using only H_2 and O_2 . We report mild conditions for the hydrogenation of NMS to NMP with a variety of homogeneous or heterogeneous catalysts. These findings prompted further investigation of the reaction of NMP with O_2 and the reaction sequence that leads to the formation of NMS after the oxygen-atom transfer from the hydroperoxide to the organic substrate.

Results and Discussion

The preparation of 5-hydroperoxy-1-methylpyrrolidin-2-one, NMP-5-OOH, from the direct reaction of NMP and O_2 at $75^\circ C$ makes it an inexpensive, easily obtainable source of



Scheme 1 Catalytic *N*-methylpyrrolidinone cycle for oxidation of substrate (S). Reagents: i, O_2 ; ii, H_2 .

hydroperoxide.¹¹ It was of interest to compare the stability of this hydroperoxide with that of a commercially available hydroperoxide. The stability of a solution of NMP-5-OOH was compared with that of a solution of *tert*-butyl hydroperoxide of comparable hydroperoxide concentration under ambient conditions by iodometric titration. As seen in Fig. 1, the stability of NMP-5-OOH, a secondary hydroperoxide, is comparable to that of *tert*-butyl hydroperoxide.

Generation of the Hydroperoxide.—An improved synthesis of NMP-5-OOH involves increasing the conversion of NMP into this product and eliminating the induction period. A series of experiments were carried out to accomplish these objectives. The formation of hydroperoxide as a function of time is shown in Fig. 2 for the uncatalysed, direct reaction with O_2 . An autoxidation mechanism is suggested because of the observed induction period.

As shown in Fig. 2 the hydroperoxide reaches a maximum concentration of $\sim 1.4 \text{ mol dm}^{-3}$. The reaction of NMP with O_2 (50 psig)[†] at $75^\circ C$ was analysed at various time intervals by ^{13}C and 1H NMR spectrometry, along with iodometric titrations. The integration 1H NMR spectra and the corresponding iodometric titrations of the periodically drawn samples showed that the concentration of hydroperoxide remained constant after 48 h, but that the concentration of NMS increased steadily.

[†] 1 psig = 51.715 mmHg.

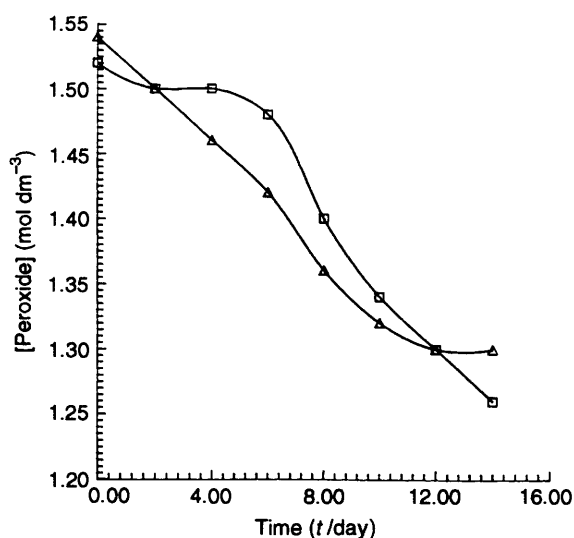


Fig. 1 Stability comparison of 5-hydroperoxy-1-methylpyrrolidin-2-one (Δ) and *tert*-butyl hydroperoxide (\square)

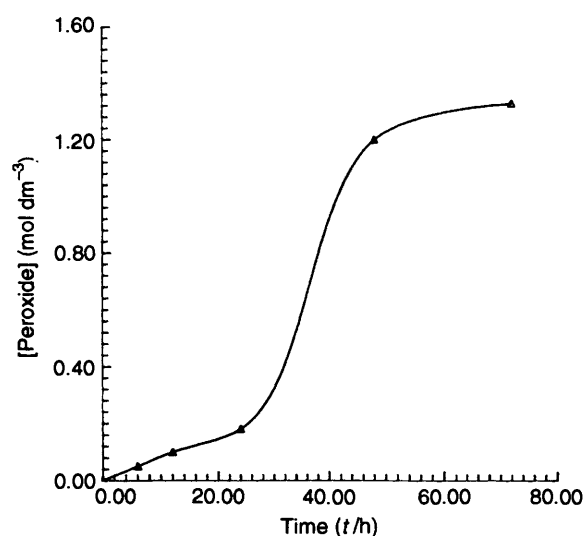


Fig. 2 Uncatalysed oxidation of 1-methylpyrrolidin-2-one with oxygen (50 psig) at 75 °C.

Table 1 Formation of ROOH in water or acetonitrile^a

NMP/water (v/v)	[ROOH] _{final} (mol dm ⁻³)	NMP/MeCN (v/v, %/%)	[ROOH] _{final} (mol dm ⁻³)
100/0	1.33		
90/10	1.00	90/10	1.12
50/50	0.010	50/50	0.46
10/90	0	10/90	0.06

^a Reaction conditions: O₂ at 50 psig; 75 °C; total solution volume 50 cm³. Reaction time: 72 h.

A steady-state concentration of hydroperoxide is attained in this system when the rates of formation and decomposition of hydroperoxide become equal.

An attempt was made to decrease the observed induction period by carrying out the reaction of NMP with O₂ (50 psig) for 4 h at 100 °C and then decreasing the temperature to 75 °C for the remainder of the reaction. Although the induction period was decreased when using the higher initial reaction temperature, a lower maximum concentration of hydroperoxide resulted.

The uncatalysed reaction of NMP with O₂ in the presence of other solvents (water or MeCN) was investigated to determine if any hydroperoxide would form. Both systems were found to form the corresponding hydroperoxide; however, a lower steady-state concentration of hydroperoxide was attained than was observed in the oxidation of neat NMP (Table 1).

Experimental results given in Table 1 indicate that the organic solvent, MeCN, has a greater ability to form the hydroperoxide than does water as the solvent. After reaction for 72 h no further increases in the concentration of hydroperoxide were observed, an indication of the attainment of a steady-state concentration of hydroperoxide.

Catalytic Formation of Hydroperoxide.—Attempts were made to eliminate the induction period observed in the uncatalysed autoxidation of NMP by using various homogeneous transition metal complexes,⁶ such as Co(octoate)₂ (where octoate = 2-ethylhexanoate), Co(BPI) [where BPI = 1,3-bis(2-pyridylimino)isoindoline], and Mn(TPP)Cl (where TPP = tetraphenylporphyrin) which are known to catalyse Class IV radical chain reactions.¹² In all cases, the induction

Table 2 Heterogeneous oxidation of *N*-methylpyrrolidinone^a

Time (t/h)	[Hydroperoxide] (mol dm ⁻³)				
	Blank	Na-Y*	CoNa-Y**	FeNa-Y**	MnNa-Y**
0	0	0	0	0	0
6	0.05	0.08	0.50	1.15	0.25
12	0.10	0.11	1.62	0.72	0.66
24	0.18	0.20	2.07	1.35	1.56
48	1.20	0.42	2.30	1.92	2.97
72	1.33	0.50	2.35	2.14	3.00

^a Reaction conditions: O₂ at 50 psig; 75 °C; NMP (50 cm³). In all cases except FeNa-Y, samples (0.25 g) of catalyst were employed. With FeNa-Y, the sample was 0.38 g.

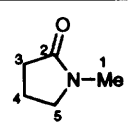
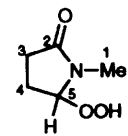
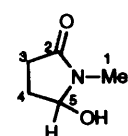
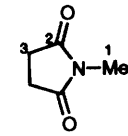
period was eliminated, but extensive decomposition of the *N*-alkylamide hydroperoxide to NMS was observed.

Additional attempts focused on metal-ion-exchanged zeolites, such as CoNa-Y, FeNa-Y and MnNa-Y. When the heterogeneous catalyst CoNa-Y was used to oxidize NMP, the reaction occurred at a faster rate and to a greater extent than that observed for the uncatalysed reaction.⁶ The 24 h induction period observed for the uncatalysed reaction of this heterocyclic amide was eliminated, with minimal decomposition of hydroperoxide occurring.

A comparison of the formation of hydroperoxide with and without metal-ion-exchanged zeolite catalysts is shown in Table 2. In contrast to CoNa-Y, Na-Y decreased the amount of hydroperoxide formed in solution. This result shows that cobalt(II), with its hindered accessibility, plays a key role in catalysing formation of the hydroperoxide. Other metal-ion-exchanged zeolites, such as FeNa-Y and MnNa-Y, also eliminate the induction period and catalyse the reaction, increasing the concentration of hydroperoxide relative to the uncatalysed reaction.

Decomposition of Hydroperoxide and Oxygen-atom-transfer Ability.—The decomposition and reaction of NMP-5-OOH with various substrates results in the formation of NMS.¹⁻⁶ The amido alcohol, 5-hydroxy-1-methylpyrrolidin-2-one, NMP-5-OH, is expected to form in the first step of an oxygen-atom transfer from NMP-5-OOH [Scheme 1, path (b)]. We propose that NMS forms as a result of the ready oxidation of the alcohol.

Table 3 ^{13}C NMR results for oxidation of PPh_3^a

	Carbon	δ_{O}
	1	28.6
	2	173.6
	3	30.3
	4	17.4
	5	48.6
	1	26.8
	2	174.6
	3	29.6
	4	23.1
	5	94.2
	1	26.0
	2	173.1
	3	28.2
	4	27.8
	5	83.8
	1	24.2
	2	177.5
	3	28.1

^a Resonances for OPPh_3 were also observed.

Table 4 Reduction of *N*-methylsuccinimide^a

Catalyst	Solvent (cm^3)	Products (%)
$\text{RuCl}_2(\text{PPh}_3)_3$	Toluene (5.0)	0
$\text{RuCl}_2(\text{PPh}_3)_3$ (Et_3N added)	Toluene (5.0)	0
$\text{RuCl}_2(\text{PPh}_3)_3$	1,4-Dioxane (5.0)	0
$\text{RuCl}_2(\text{PPh}_3)_3$ (Et_3N added)	1,4-Dioxane (5.0)	0
$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$	Water (100)	NMP (21)
$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$	Toluene-EtOH (50:50, 10)	0
<i>cis</i> - RuCl_2 (dmsO) ₄	Toluene-EtOH (50:50, 10)	NMP (23)
<i>cis</i> - RuCl_2 (dmsO) ₄	EtOH (10)	NMP (8)
$[\text{Ru}(\text{dmp})_2(\text{H}_2\text{O})_2][\text{PF}_6]_2$	Toluene-EtOH (50:50, 10)	NMPD ^b (< 1) NMP (28)
$[\text{Ru}(\text{dmp})_2(\text{H}_2\text{O})_2][\text{PF}_6]_2$	Water (100)	0
5% Pd on C	Water (100)	NMP (< 1)
5% Ru on silica gel	Water (100)	NMP (36)
5% Ru on C	Water (100)	NMP (57)*
5% Ru on C	Water (100)	NMP (> 99)**

^a The runs were performed under H_2 (100 psig) at 100 °C. In the first four systems listed the amount of substrate used was 8.8×10^{-3} mol; 4.4×10^{-5} mol of catalyst was added; and (when added) 4.4×10^{-4} mol of triethylamine. In the next six systems, the amount of substrate used was 4.0×10^{-3} mol and the amount of catalyst was 4.0×10^{-5} mol. Reactions were followed for 24 h. In the last four reactions, the amount of substrate used was 4.0×10^{-3} mol. The amount of catalyst, and reaction times, were: for 5% Pd on C (0.30 g), 24 h; for 5% Ru on silica gel (0.59 g), 72 h; for 5% Ru on C (0.30 g), 24 h* and 48 h**. ^b NMPD = *N*-methylpyrrolidine.

To test this, a pregenerated solution of NMP-5-OOH in NMP was treated with an equimolar amount of PPh_3 under an inert atmosphere at 0 °C for 6 h. A quantitative yield of OPPh_3 was produced, as shown by ^{31}P NMR spectroscopy. The ^{13}C NMR spectrum of the solution after reaction showed resonances due to both the solvent (NMP) and OPPh_3 , as well as five new peaks for the amido alcohol, NMP-5-OH (Table 3). No ^{13}C resonances were detected in this solution for either the hydroperoxide, NMP-5-OOH, or for NMS.

Exposure of the solution containing the amido alcohol

intermediate to O_2 at room temperature for 24 h resulted in the further oxidation of NMP-5-OH to NMS [Scheme 1, path (b)].

The combined results of the ^{13}C and ^{31}P NMR studies of this reaction indicate that oxygen-atom transfer occurs with this hydroperoxide *via* nucleophilic attack on the peroxide. In the absence of O_2 , NMP-5-OH results. In the presence of O_2 , this product is not observed, for it is oxidized to NMS by O_2 under the reaction conditions.

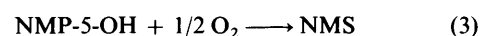
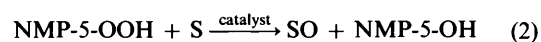
Reduction of *N*-Methylsuccinimide.—The utility of NMP-5-OOH towards catalytic oxidation of organic substrates would be enhanced by the regeneration of the NMP from the hydroperoxide decomposition product, NMS (Scheme 1).¹¹ This would provide a recyclable hydroperoxide precursor with the NMP becoming a co-catalyst for a net reaction utilizing H_2 and O_2 . Several homogeneous and heterogeneous methods for this stage of the catalytic cycle were studied. Since there are no literature reports on the homogeneous reduction of NMS with H_2 , our initial work involved this system.

The selective reduction of carbonyl functionalities in several heterocyclic compounds to methylene groups is reported in the literature.¹³ The catalyst $\text{RuCl}_2(\text{PPh}_3)_3$ was reported by Lyons to hydrogenate succinic anhydride to 4-butyrolactone upon reaction with H_2 under mild conditions.¹³ Using this catalyst, several unsuccessful attempts were made to reduce NMS to NMP in different solvents (Table 4). The addition of Et_3N to these reactions did not improve matters. Reports of the use of Ru catalysts in the hydrogenation of ketones prompted investigation of other Ru complexes and/or solvents.^{14,15} As seen in Table 4, the activities of the catalyst appear to be solvent dependent and, in some cases, show high selectivities to NMP, but with low yields.

The hydrogenation of succinimide to the corresponding amide has been reported to occur in the presence of ammonia when using various metal catalysts supported on carbon or silica gel.⁹ The reduction of succinimide to the corresponding cyclic amide by using a supported Pd catalyst and H_2 in aqueous solution is also described.¹⁰ All of the reported hydrogenations were run under higher H_2 pressures and temperatures than were employed in our experiments.

By using 5% Pd on activated carbon as catalyst, only trace amounts of NMP were detected from hydrogenation in an aqueous solution. This catalyst is not effective for hydrogenation of ketones.¹⁵ Of the three commercially available catalysts investigated, 5% Ru on activated carbon showed the highest yield of the corresponding cyclic amide, NMP (Table 4). In both of the Ru-catalysed reactions, a high selectivity for the formation of NMP was observed.

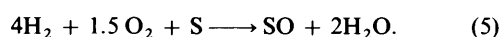
Conclusions.—This research has shown that, with the CoNa-Y catalyst, 2 mol dm^{-3} solutions of the alkyl hydroperoxide, NMP-5-OOH, can be easily generated. This provides a convenient and inexpensive source of hydroperoxide for the oxidation of organic substrates and for the initiation of radical reactions. The oxidative reactions involve the net reactions (1)–(3), where S is substrate.



In a separate step, the NMS can be hydrogenated to NMP [equation (4)].



For applications in which NMP-5-OOH is a reactant, this sequence in effect makes NMP a co-catalyst for the oxidation of substrate with the net reaction being equation (5).



Experimental

N-Methylpyrrolidinone (HPLC grade), *N*-methylsuccinimide, and triphenylphosphine were obtained from Aldrich Chemical Company and were used as received. $\text{RuCl}_2(\text{PPh}_3)_3$ was obtained from Strem Chemicals. All other reagents and solvents were obtained from Fischer Scientific and were used as received.

^1H and ^{13}C NMR spectra were run on a General Electric QE-300 Fourier Transform Spectrometer operating at 300 and 75 MHz, respectively. The samples were run in [$^2\text{H}_6$]benzene or deuteriochloroform with Me_4Si as internal reference. ^{31}P NMR spectra were run on a Varian VXR 300 Fourier Transform Spectrometer operating at 121 MHz. The samples were run in [$^2\text{H}_6$]benzene with H_3PO_4 (85%) as external reference.

Unless otherwise indicated, all reactions were run in a Parr Pressure Apparatus at the indicated temperature and pressure.

CAUTION! Extreme care should be taken when working with a pressurized apparatus at or above room temperature. Appropriate shields must be used and fire extinguishers should be nearby. For elevated temperatures, the reaction solution should be cooled to room temperature before disassembly of the pressure apparatus.

A Varian 3700 GC with an FID and a Hewlett Packard 3390A integrator was used to analyse the oxidation and hydrogenation reactions. The substrate(s) and product(s) were identified and quantified by using known standards.

Concentrations of peroxide were measured by removing samples (0.5–2.0 cm^3) from the pressure bottles with a 12 in stainless steel needle. The iodometric titration was performed immediately.¹⁶

CAUTION! Many hydroperoxides are shock/temperature sensitive and the hydroperoxide derived from NMP should be treated as potentially explosive.

The catalysts *cis*- $\text{RuCl}_2(\text{dmsO})_4$ ¹⁷ and $[\text{Ru}(\text{dmp})_2(\text{H}_2\text{O})_2][\text{PF}_6]_2$ ¹⁸ were prepared by literature methods.

Steady-state [ROOH] Studies.—NMP (50 cm^3 , 47 g, 4.7×10^{-1} mol) was placed in a 250 cm^3 Parr Pressure Bottle equipped with a magnetic stirrer. After the pressure apparatus had been assembled, the reactor was purged three times with O_2 (50 psig) and was then pressurized with O_2 (50 psig). The reactor was placed in a 75 °C oil-bath. Recharging with O_2 (50 psig) was performed as needed. Samples were periodically analysed by ^1H and ^{13}C NMR spectroscopy, and iodometric titration.

Comparisons of the Stability of Hydroperoxide.—A solution of 5-hydroperoxy-1-methylpyrrolidin-2-one was prepared by the reaction of NMP with O_2 (50 psig) at 75 °C. The concentration of hydroperoxide was determined by iodometric titration. The stability of this hydroperoxide solution was compared iodometrically with that of a *tert*-butyl hydroperoxide solution of comparable concentration of hydroperoxide under ambient conditions.

Formation of Hydroperoxide in other Solvents.—The appropriate amounts (see Table 1) of NMP and the solvent (water or MeCN) were placed in a 250 cm^3 Parr Pressure Bottle equipped with a magnetic stirrer. After the pressure apparatus had been assembled, the reactor was purged three times with O_2 (50 psig) and was then pressurized with O_2 (50 psig). The reactor was placed in a 75 °C oil-bath. Recharging with O_2 (50

psig) was performed as needed. Samples were withdrawn periodically and analysed by iodometric titration.

Oxidation of PPh_3 .—5-Hydroperoxy-1-methylpyrrolidin-2-one (1.5×10^{-2} mol; 15 cm^3 of a 1.0 mol dm^{-3} solution in NMP) and PPh_3 (4.0 g, 1.5×10^{-2} mol) were placed in a 100 cm^3 round-bottom flask equipped with magnetic stirrer, under N_2 , and cooled in an ice-bath. After the mixture had been stirred for several minutes at 0 °C, a colourless solution resulted. The reaction solution was then stirred at 0 °C for 6 h, when the solution was allowed to warm up slowly to room temperature. The reaction solution was analysed by ^{13}C and ^{31}P NMR spectroscopy.

Preparation of MNa-Y (M = Co^{2+} , Fe^{3+} or Mn^{2+}).—These heterogeneous catalysts were prepared by placing the appropriate chloride salt (2.0×10^{-2} mol) and distilled water (200 cm^3) in a 500 cm^3 Erlenmeyer flask equipped with a magnetic stirrer. Na-Y (10 g, Linde LZ Y-52) was added to the aq. metal-ion solution. The resulting reaction slurry was stirred at 70 °C (for M = Co^{2+}) or at room temperature (for M = Fe^{3+} or Mn^{2+}) for 24 h. After cation exchange, the slurry was filtered, and washed with distilled water until no chloride ions were detected with AgNO_3 solution. The solid catalyst was dried *in vacuo* at 150 °C for 48 h. After cooling to room temperature *in vacuo*, the catalyst was ready for use.

Catalytic Formation of Hydroperoxide.—NMP (50 cm^3 , 47 g, 4.7×10^{-1} mol) and MNa-Y (M = Co^{2+} or Mn^{2+} , 0.25 g; M = Fe^{3+} , 0.38 g) were placed in a 250 cm^3 Parr Pressure Bottle equipped with a magnetic stirrer. After the pressure apparatus had been assembled, the reactor was purged three times with O_2 (50 psig) and was then pressurized with O_2 (50 psig). The reactor was placed in a 75 °C oil-bath. Recharging with O_2 (50 psig) was performed as needed. Samples were withdrawn periodically and analysed by iodometric titration.

Reduction of NMS.—The appropriate catalyst, substrate and solvent(s) (see Table 4) were placed in a 250 cm^3 Parr Pressure Bottle equipped with a magnetic stirrer. After the pressure apparatus had been assembled, the reactor was purged three times with H_2 (100 psig) and was then pressurized with H_2 (100 psig). The reactor was placed in a 100 °C oil-bath. Recharging with H_2 (100 psig) was performed as needed. Samples were analysed by GLC using a 6 ft stainless steel column packed with FFAP (15%) on Chromosorb WA/W (80/100 mesh).

Acknowledgements

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