Pergamon

Tetrahedron Letters 44 (2003) 3245–3247

TETRAHEDRON
LETTERS

Formation of aldehydes and ketones via reduction of alkyl monohalides by electrogenerated nickel(I) salen in dimethylformamide in the presence of water, oxygen, and light

Parichatr Vanalabhpatana and Dennis G. Peters*

Department of Chemistry, Indiana University, Bloomington, IN 47405, USA

Received 18 February 2003; revised 4 March 2003; accepted 6 March 2003

Abstract—Addition of a stoichiometric amount of a primary alkyl monohalide (1-bromooctane) to a solution of electrogenerated nickel(I) salen in dimethylformamide containing water, followed by irradiation with a xenon arc lamp and brief exposure to air, results in the formation of an aldehyde (1-octanal). Analogous experiments with a secondary alkyl monohalide (2-bromohexane) afford a ketone. Other products are alkanes, alkenes, and dimers that arise from classic radical coupling and disproportionation of alkyl radicals. © 2003 Published by Elsevier Science Ltd.

Previous work from our laboratory has dealt with the catalytic reduction of alkyl monohalides by nickel(I) salen electrogenerated at a carbon electrode in dimethylformamide (DMF).[1–5] For example, electrolysis of a 1 mM solution of nickel(II) salen at a reticulated vitreous carbon cathode held at −0.24 V versus SCE in DMF containing 0.10 M tetramethylammonium perchlorate and 20 mM 1-chloro-5-iodopentane (with a nonreducible carbon–chlorine bond) results in the production of 1,10-dichlorodecane (82%), 1-chloropentane (18%), and 5-chloro-1-pentene (3%).[3] This product distribution can be readily rationalized on the basis of well established reactions involving the coupling and disproportionation of catalytically formed alkyl radicals, as well as hydrogen atom abstraction from the solvent by those radicals.

Recently, however, we have discovered that, when a catalytically reducible alkyl monohalide (1-bromooctane) is injected in stoichiometric amount into an oxygen-free solution of electrogenerated nickel(I) salen in DMF containing deliberately added water and when the resulting mixture is exposed to light and air, an aldehyde (1-octanal) is formed in substantial yield, along with other products arising from classic reactions involving alkyl radicals. Typical results are compiled in Table 1. For these experiments (and others discussed later), the procedure entailed the following steps: (a) controlled-potential reduction of nickel(II) salen in oxygen-free DMF containing 0.10 M tetramethylammonium tetrafluoroborate ($TMABF_4$) and various concentrations of added water at a reticulated vitreous carbon cathode held at −0.34 V versus SCE to generate nickel(I) salen; (b) injection of 1-bromooctane (or another substrate); (c) a second electrolysis at −0.34 V versus SCE, accompanied by a 15-min irradiation of the solution in the cell with a 150-W xenon arc lamp; and (d) opening of the electrochemical cell to expose the solution to air (ordinarily for 1 min), prior to ether workup and product analysis by means of gas chro-

Table 1. Effects of UV–vis light and water on product distributions obtained from the reaction between 4 mM 1-bromooctane and 2 mM nickel(I) salen in DMF containing 0.10 M $TMABF_4$

UV–vis light	H_2O (M)[b]	Product distribution (%)[a]				
		1	**2**	**3**	**4**	Total
No	–	43	12	1	12	68
Yes	–	38	5	2	19	64
Yes	0.15	39	6	2	25	72
Yes	0.75	42	5	1	33	81
Yes	1.50	49	7	1	29	86

[a] Each entry represents the average of at least three separate experiments.

[b] Concentration of added water.

1 = hexadecane; **2** = octane; **3** = 1-octene; **4** = 1-octanal.

Keywords: alkyl monohalides; nickel(I) salen; aldehydes; ketones; catalytic reduction.

* Corresponding author. Tel.: +1-812-855-9671; fax: +1-812-855-8300; e-mail: peters@indiana.edu

0040-4039/03/$ - see front matter © 2003 Published by Elsevier Science Ltd.
doi:10.1016/S0040-4039(03)00634-8

Table 2. Effects of water concentration and of the substrate–catalyst ratio on product distributions obtained from the reaction between 1-bromooctane and 2 mM nickel(I) salen in DMF containing 0.10 M $TMABF_4$

1-Bromooctane (mM)	H_2O (M)[b]	Product distribution (%)[a]				
		1	**2**	**3**	**4**	Total
4	0.75	42	5	1	33	81
2	1.00	25	4	1	51	81
1	1.25	9	4	2	65	80
0.5	2.00	2	2	1	74	79

[a] Each entry represents the average of at least three separate experiments.

[b] Concentration of added water.

1 = hexadecane; **2** = octane; **3** = 1-octene; **4** = 1-octanal.

matography. This procedure has been designed to maximize the yield of aldehyde. In some instances, the last step of the procedure was replaced by actual bubbling of air through the solution for up to 15 min, but no significant difference in the yield of aldehyde was observed. Other aspects concerning experimental technique can be found in previous publications.[2,6,7]

As revealed by the first two entries in Table 1, the yield of 1-octanal increased from 12% in the presence of only ambient laboratory light to 19% when the electrolysis cell was irradiated with the xenon arc lamp. For the last three experiments in Table 1, we probed the effect of deliberately added water; the concentration of residual water in DMF from a freshly opened bottle is typically 40 mM.[8] Accordingly, when the water concentration was increased from 0.15 to 0.75 to 1.50 M, the yield of octanal passed through a maximum at 33% for a water concentration of 0.75 M. In trying to account for the fact that the total yield of all products is less than 100%, we postulate that the missing material might be 1-octanal which has undergone aldol condensation in the presence of electrogenerated base. Another process that can account for missing product is alkylation of nickel salen during the catalytic reduction; in related (but not yet published) work in our laboratory, evidence has been acquired by means of LC–MS experiments that mono- and dioctylation of nickel salen takes place during the catalytic reduction of 1-iodooctane.

In attempting to optimize the yield of 1-octanal, we examined the effects of the concentration of added water and of the 1-bromooctane-to-nickel(II) salen concentration ratio. Table 2 shows the results of these experiments; for each run, the reaction mixture was irradiated and exposed to air, as mentioned earlier. For each concentration of 1-bromooctane, we determined from a separate set of experiments what concentration of water was needed to maximize the yield of 1-octanal; these water concentrations are indicated in Table 2. As the concentration of 1-bromooctane is decreased, the yield of 1-octanal increases dramatically, whereas the quantity of the dimeric product (hexadecane) diminishes substantially; these trends are probably related to the smaller amount of radical coupling which takes place at low substrate concentrations, thereby permitting more 1-octanal to be formed. It is interesting to note in Table 2 that, for a smaller substrate concentration, the concentration of added water must be increased to afford 1-octanal in maximal yield.

We have extended this investigation to include other primary alkyl bromides and iodides, as indicated in Table 3. For all of the substrates examined, a significant amount of the aldehyde product was formed. However, in these preliminary studies, we did not attempt to optimize conditions to obtain the highest yield of aldehyde; in particular, we chose arbitrarily to employ a water concentration of 1.0 M, because this quantity of water maximized the yield of aldehyde from 1-bromooctane (Table 2). Interestingly, it appears that the yield of aldehyde obtained from a primary alkyl bromide is higher than that produced from a primary alkyl iodide.

In some experiments involving 1-bromoheptane, we attempted to trace the source of the oxygen atom in the resulting 1-heptanal by adding $H_2{}^{18}O$ to the system. In two separate experiments in which 2.5 mM nickel(I) salen was treated with 2.5 mM 1-bromoheptane in DMF containing 0.10 M $TMABF_4$ and 0.84 M $H_2{}^{18}O$, we found by means of mass spectrometry that the 1-heptanal contained 51% and 39% of oxygen-18, respectively. Further work is planned with $H_2{}^{18}O$ and ${}^{18}O_2$ to gain more insight into the source of the aldehydic oxygen.

Table 3. Product distributions from the reaction of 2 mM concentrations of different primary alkyl monohalides with 2 mM nickel(I) salen in DMF containing 0.10 M $TMABF_4$ and 1.0 M water

Alkyl halide	Product distribution (%)[a]				
	1	**2**	**3**	**4**	Total
$C_5H_{11}Br$	22	3	Trace	58	83
$C_6H_{13}Br$	24	2	1	38	65
$C_7H_{15}Br$	27	5	1	50	83
$C_{10}H_{21}Br$	34	4	1	30	69
$C_6H_5(CH_2)_3Br$	49	5	1	27	82
$C_8H_{17}I$	46	5	1	25	77
$C_{10}H_{21}I$	51	9	1	16	77

[a] Each entry represents the average of at least three separate experiments.

1 = dimer; **2** = alkane; **3** = 1-alkene; **4** = aldehyde.

Preliminary work has been done with a secondary alkyl bromide (2-bromohexane) as substrate. Although we have so far accounted for only a fraction (26%) of the starting material, the identified products are 2-hexanone (6%), hexane (12%), 1-hexene (3%), *trans*-2-hexene (2%), *cis*-2-hexene (1%), and 5,6-dimethyldecane (2%); the last species actually consists of a mixture of (5*R*,6*R*)-, (5*S*,6*S*)-, and (5*R*,6*S*)-5,6-dimethyldecane.

It is interesting to compare our findings with some results previously obtained for systems involving the photodecomposition of alkylcobalt(III) species in the presence of oxygen. For example, Hogenkamp[9] reported that photolysis of methylcobalamin in the presence of excess oxygen affords formaldehyde in 76% yield, whereas Hayashi and co-workers[10] found that octaethylporphycenecobalt(III) chloride catalyzes the addition of alcohols to vinyl ethers under aerobic conditions to produce two acetals, namely those of β-formylacetaldehyde and β-hydroxyacetaldehyde. For earlier studies, as well as for the present work, the aldehyde that is obtained bears the same number of carbon atoms as the starting material. On the other hand, several publications have dealt with the production of aldehydes with one more carbon atom than the original alkyl halide. Vanhoye and co-workers[11] found that electrochemical reduction of a mixture of $Fe(CO)_5$ and ethyl iodide at a platinum cathode in THF, followed by introduction of CO and a work-up procedure with acetic acid, affords propanal in up to 70% yield (based on consumption of starting material). In subsequent research, Yoshida and co-workers[12,13] discovered that electrolysis of mixtures of 1-bromoalkanes and $Fe(CO)_5$ at stainless-steel or platinum cathodes in acetonitrile containing a tetraalkylammonium salt results (after hydrolysis in an acidic medium) in the formation of aldehydes in yields of at least 80% (based on consumption of starting material).

In summary, a procedure has been unexpectedly discovered that allows us to synthesize an aldehyde in up to 74% yield from a stoichiometric reaction involving a primary alkyl monohalide, electrogenerated nickel(I) salen, and oxygen in the presence of light and water. However, knowledge about the mechanism of the process is lacking at this time, so conditions required to optimize the yield of the aldehyde require further investigation. These, and other questions raised by this work, will be subjects for future inquiry in our laboratory.

Acknowledgements

Appreciation is expressed to the Anandamahidol Foundation (under the royal patronage of His Majesty the King of Thailand) for a continuing fellowship awarded to P.V.

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