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An improved protocol for aerobic oxidation of acetals to esters catalyzed by *N*-hydroxy phthalimide (NHPI) and lipophilic Co(II) complexes

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Professor Habib Firouzabadi on the occasion of his 61st birthday

Abstract

In this work the effect of lipophilization of Co(II) ions on the rate of the aerobic oxidation of acetals to esters in the presence of *N*-hydroxy phthalimide (NHPI) was investigated. The catalysts that were used in this work are $Co(OAc)_2$ (**1a**), $Co(OCOC_5H_{11})_2$ (**1b**), $Co(OCOC_6H_5)_2$ (**1c**), $Co(OCOC_9H_{19})_2$ (**1d**), $Co(OCOC_{17}H_{35})_2$ (**1e**). It has been found that among the described Co(II) salts, both **1b** and **1c** were better suited than the other cobalt carboxylates in catalyzing of aerobic oxidation of acetals in the presence of NHPI. The probable role of the carboxylate ligands were also briefly discussed.

Keywords: Acetals; Oxidation; *N*-hydroxy phthalimide; O_2; Co(II) complexes

1. Introduction

Direct oxidation of acetals to the corresponding esters is an interesting transformation in organic chemistry as testified by a large number of reagents that have been developed for this purpose [1,2]. This transformation was traditionally carried out using stoichiometric Cr salts [3], peracetic acid [4], DDQ [5], sodium perborate [6], halogen-based reagents [7], oxone [8], $VO(OAc)_2$ [9], etc. However, many of these protocols lead to expensive processes and toxic by-product. Some other methods, based on especially the use of inexpensive reagents such as H_2O_2, *t*-BuOOH were also developed for this purpose. These includes H_2O_2 and HCl [10], MTO-H_2O_2 [11], *t*-BuOOH/Pd(II) [12], O_3 [13], and V_2O_5-H_2O_2 [14]. With rare exceptions, most of these protocols also suffer from drawbacks such as use of excess of reagent, drastic conditions, and tedious work-up and in many instances the methods afforded the corresponding esters in low yields. Therefore, from the standpoint of the so-called green and sustainable chemistry, another approach to construct a cleaner catalytic system for this reaction is demanded. Along this line, the utilization of molecular oxygen as final oxidant in oxidation process has been becoming increasingly attractive in recent years. Unfortunately, despite the importance and attractiveness of this opinion, less attention has been paid to the development of new protocols for efficient oxidations of acetals to the corresponding ester using molecular oxygen [15].

The efficient aerobic oxidation of various types of organic compounds has been effectively achieved using *N*-hydroxy phthalimide (NHPI) as a key radical generator [16]. Quiet recently, Ishii and his co-workers showed that the use of lipophilic NHPI instead of NHPI itself has an extraordinary effect on both selectivity and total yields of the air oxidation of alkanes in the absence of organic solvents [17]. They also found that the use of lipophilic NHPI as catalyst is superior than that of NHPI from the standpoint of turnover number of the catalyst. However, to our knowledge there is no systematic investigation on the effect of lipophilization

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of Co(II) ions on the oxidation reactions in the presence of NHPI.

2. Experimental

2.1. General remarks

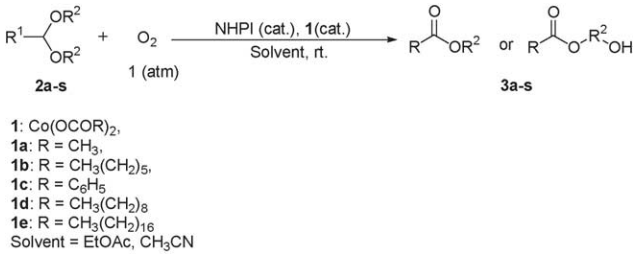
Chemicals were either prepared in our laboratories or purchased from Merck, Fluka and Aldrich Chemical Companies. All yields refer to isolated products unless otherwise stated. The products were characterized by comparison of their physical data with those of known samples or by their spectral data. ^{1}H and ^{13}C NMR spectra were recorded on a 500 MHz spectrometer in $CDCl_3$ as the solvent and TMS as internal standard. UV–vis spectra were recorded on a Varian (Cary 100) spectrophotometer. Most of the products are known and all of the isolated products gave satisfactory IR and NMR spectra.

2.2. General procedure for aerobic oxidation of acetals to esters using NHPI/Co(II) system under O_2 (1 atm)

A solution of NHPI (1 mmol, 10 mol%) and cobalt hexanoate (**1b**, 0.05 mmol, 0.5 mol%) in CH_3CN or EtOAc (50 ml) was prepared in a two-necked flask. To this solution acetal (10 mmol) was added and the resulting pale yellow solution was stirred at room temperature under an oxygen atmosphere (1 atm, balloon filled) for the indicated optimized time in table. After completion of the reaction, the excess of solvent was removed under reduced pressure; the products were purified by chromatography through a short pad of silica gel to give the corresponding ester.

3. Results and discussion

Very recently, we have developed a novel method for oxidation of a variety of structurally diverse acetals with molecular oxygen using NHPI combined with $Co(OAc)_2$ under mild reaction conditions [18]. Although, this system was successfully applied to a range of benzylic and aliphatic acetals, the reaction time is prohibitively long and the loading of the catalysts required to advance the reaction to high conversion were high. In continuation of this study, herein, we wish to disclose our recent finding on the effect of various types of lipophilic Co(II) salts on the rate of oxidation of acetals (Scheme 1).



Scheme 1.

During the course of our investigations into the aerobic oxidation of acetals, we prepared a number of cobalt carboxylate by the direct reaction of the corresponding sodium carboxylate with a saturated aqueous solution of cobalt sulfate. The resulting precipitate were collected and washed thoroughly with a large volume of cold distilled water and dried in a vacuum desiccator. The yields of the cobalt carboxylates were almost quantitative in most cases.

We first investigated the oxidation of benzaldehyde dimethylacetal **2a** as a model substrate using O_2 (1 atm) in the presence of NHPI (10 mol%) and various types of cobalt carboxylates (**1a**–**1e**, Scheme 1, 0.5 mol%) in either CH_3CN or EtOAc as solvent at room temperature.

As can be seen, in CH_3CN total yields of methyl benzoate **3a** increased with the increase of number of carbon in carboxylate ligands up to seven carbon atoms within a limited time interval 45 min (Table 1, entries 1–4). It is interesting to note that under similar reaction conditions, the system consisting NHPI combined with $Co(OAc)_2$ (**1a)** lead to low conversion of **2a**, even at higher loading of the catalysts and prolonged reaction time (Table 1, entry 2).

Table 1
NHPI-catalyzed aerobic oxidation of benzaldehyde dimethylacetal **2a**[a]

Entry	Catalyst	Product distribution (%)[b,c]							
		3a		Benzaldehyde		Others[d]		Selectivity	
		CH_3CN	EtOAc	CH_3CN	EtOAc	CH_3CN	EtOAc	CH_3CN	EtOAc
1	**1a**[e]	54	–	None	–	None	–	100	–
2	**1a**[e,f]	65	44	0.3	None	None	10	99	87
3	**1b**	89	75	None	0.3	None	1.5	100	96
4	**1c**	85	52	2.3	0.3	None	8	97	86
5	**1d**	77	55	2.0	0.4	None	3.5	97	93
6	**1e**	48	59	3.7	0.4	None	12	93	83

[a] BDMA (1 mmol) – NHPI: cobalt salts ratios were 1:0.1:0.005 in 5 ml solvent and reaction times in CH_3CN and EtOAc were 45 min and 1 h, respectively.
[b] The numbers in parenthesis referred to the yields of the products in EtOAc as solvent.
[c] GC yields.
[d] Unidentified by-products.
[e] The reaction time was 10 h.
[f] NHPI (20 mol%) and $Co(OAc)_2$ (1 mol%) was used.

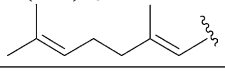
Furthermore, under the same reaction conditions, upon the further increasing of the length of carboxylate ligands to 10 and 18 carbon in $Co(O_2CC_9H_{19})_2$ (**1d**) and $Co(O_2CC_{17}H_{35})_2$ (**1e**), respectively, the yields of **3a** decreased considerably (Table 1, entries 5 and 6). On the other hand, in ethyl acetate as solvent, it is rather difficult to explain rationally the effect of the size of carboxylate ligands on the aerobic oxidation of **2a**. Although, the oxidation of **2a** using NHPI combined with $Co(O_2CC_5H_{11})_2$ (**1b**) instead of **1a** was markedly accelerated, replacing **1b** by $Co(O_2CC_6H_5)_2$ (**1c**) resulted in significant decrease in the reaction rate. It is also worth mentioning that under the same reaction conditions, replacing of **1c** with more lipophilic **1d** and **1e** gave nearly the same results as those obtained with **1c** and slightly better than that with **1a**. Moreover, in the course of the oxidation of **2a**, among different catalyst listed in Table 1, NHPI combined with **1b** is also turned out to be the most suitable catalytic system in term of product **3a** selectivity (Table 1, entry 3).

Inspection of the data in Table 1 also shows that, in general, both NHPI/**1b** and NHPI/**1c** systems in CH_3CN are better suited as catalyst considering both conversion and product selectivity. However, we have chosen NHPI/**1b** system for the subsequent studies, although NHPI/**1c** gave nearly the same results in most cases. Therefore, **2a** (1 mmol) was allowed to react in the presence of NHPI (10 mol%) and **1b** (0.5 mol%) under O_2 atmosphere (1 atm) in CH_3CN. Under these circumstances, **2a** was almost entirely converted (more than 99% by GC) into **3a** within 2 h giving 93% isolated yield (Table 2, **2a**, entry 1). This result is noteworthy, because similar transformation using a catalytic system consisting NHPI (20 mol%) and **1a** (1 mol%) in CH_3CN afforded the corresponding ester **3** after much longer (20 h) reaction time, although the loading of the catalyst was twice as the NHPI/**1b** system [18].

To ensure that optimum conditions were selected, several other reaction variables were also evaluated. Reducing the NHPI and **1b** to 5 and 0.25 mol%, respectively, led to an anticipated slower oxidation with only 52% conversion after 24 h (Table 2, **2a**, entry 2). Changing the solvent of the reaction to hexane, toluene, and CH_2Cl_2 resulted in a very poor conversion accompanied with formation of complex mixture of products after prolonged (24 h) reaction time.

To show the generality of this new protocol, various types of substituted benzylic open-chain acetals were allowed to react in the presence of a catalytic amount of NHPI (10 mol%) and **1b** (0.5 mol%) under O_2 (1 atm) in either CH_3CN or EtOAc at room temperature. As can be seen, the aerobic oxidation of acetals in all cases furnished the corresponding esters in excellent yields within relatively short reaction time (Table 2, **2b**–**e**). However, acetals bearing one strong withdrawing group on aromatic rings are resisted against the described reaction conditions (Table 2, **2f**). Under similar reaction conditions, the aerobic oxidation of heptanal diethyl acetals as a model substrate for aliphatic open-chain acetals also afforded the corresponding ethyl heptanoate in high yields (Table 2, **2g**). In all cases, the catalyst system NHPI/**1b** turned out to work better than that of NHPI combined with the other

Table 2
Aerobic oxidation of acetals to esters using NHPI/**1b** at room temperature

Substrate	Product	R^1	R^2	Time (h)		Yield (%)[a,b,c]	
				CH_3CN	EtOAc	CH_3CN	EtOAc
2a	**3a**	Ph	Me	2.00	2.50	93	89
2a	**3a**	Ph	Me	10	–	52	–[d]
2b	**3b**	Ph	Et	2.00	2.75	93	87
2c	**3c**	4-ClC_6H_4	Et	3.25	3.25	90	89
2d	**3d**	4-$(MeO)C_6H_4$	Et	1.00	1.00	93	91
2e	**3e**	3-$(MeO)C_6H_4$	Et	2.75	3.00	95	93
2f	**3f**	4-$(NO_2)C_6H_4$	Et	20	–	NR	–
2g	**3g**	*n*-C_6H_{13}	Et	5.00	7.25	96	94
2h	**3h**	Ph	$-(CH_2)_2-$	2.50	3.50	91	89
2i	**3i**	4-ClC_6H_4	$-(CH_2)_2-$	2.00	2.50	90	90
2j	**3i**	4-$(MeO)C_6H_4$	$-(CH_2)_2-$	2.00	2.00	90	89
2k	**3k**	3-$(MeO)C_6H_4$	$-(CH_2)_2-$	4.00	4.75	95	92
2l	**3l**	Ph	$-(CH_2)_3-$	5.00	5.25	91	89
2m	**3m**	4-BrC_6H_4	$-(CH_2)_3-$	4.00	4.50	90	87
2n	**3n**	3-$(MeO)C_6H_4$	$-(CH_2)_3-$	5.00	5.00	90	86
2o	**3o**	4-$(MeO)C_6H_4$	$-(CH_2)_3-$	2.00	4.50	91	85
2p	**3p**	*n*-C_6H_{13}	$-(CH_2)_2-$	5.00	5.00	96	94
2q	**3q**	*n*-C_6H_{13}	$-(CH_2)_3-$	6.00	8.00	91	90
2r	**3r**	4-$(NO_2)C_6H_4$	$-(CH_2)_3-$	20	–	NR	–
2s	**3s**		$-(CH_2)_2-$	4.25	–	–[e]	–

[a] Isolated yields.
[b] The ratios of substrate – NHPI: **1b** are 1:0.1:0.005.
[c] The numbers in parentheses refer to the reactions in EtOAc as solvent.
[d] The ratio of substrate – NHPI: **1a** are 1: 0.05: 0.0025.
[e] The reaction was completed within the indicated time; however, a mixture of unidentified products was formed.

cobalt salts from standpoint of both reaction times, product selectivity. Furthermore, it is also clear that oxidations better take place in CH_3CN than EtOAc as solvent. Clearly, this observation is in consisting of the data embodied in Table 1.

On the other hand, the oxidation of cyclic acetals like 1,3-dioxolanes and 1,3-dioxanes is of interest because it represents a route to selectively prepare the corresponding diol monoesters. Although, there is a limited number of procedures on the oxidation of cyclic acetals by H_2O_2, *t*-BuOOH, and stoichiometric oxidizing agents [3–14], in particular, their oxidations with O_2 via a radical process is rarely reported [15]. Thus, we decided to expand the domain of this new protocol over the oxidation of various types of cyclic acetals. Along this study, we found that the aerobic oxidation of different types of aromatic 1,3-dioxolane and 1,3-dioxane as well as aliphatic counterparts afforded the corresponding diol monoesters in good to excellent yields (Table 2, **2h**–**q**). Once again, in the case of cyclic acetals bearing electron-withdrawing groups such as 4-nitrophenyl survived intact under the described reaction conditions (Table 2, **2r**). It is also noteworthy that acetals containing double bonds are not suitable substrate for this oxidation and gave a complex mixture of unidentified products. It is presumably owing to the reaction of radical intermediate with their double bonds (Table 2, **2s**).

The precise role of hexanoate (or benzoate) ligand is not clear at present and its effect must be further studied in detail. However, at this time there is some plausible explanation, which seems to be in accord with experimental evidences.

(a) Solubility of cobalt salts: We found that the solubility of cobalt salts increased dramatically with increasing of carboxylate ligand's size to rich a maximum in **1b** and **1c** and the reaction solution became clear under the operated reaction conditions. On the other hand, the reactions involving **1a**, **1d**, and **1e** were turbid under the similar reaction conditions. Whereas, it is difficult to explain exactly the effect of lipophilic carboxylate ligands on overall aerobic oxidation of acetals exclusively in term of solubility factor alone, with the above observation this effect cannot be neglected.

(b) Formation of complex [Co-NHPI]: Fig. 1 shows the UV–vis spectrum of NHPI/**1a** (spectrum b), and NHPI/**1b** (spectrum a) in acetonitrile according to their actual concentration under operated oxidation condition after 2 h. As can be seen, the solution of both NHPI/**1a** and NHPI/**1b** shows a band at $\lambda_{max} = 420$ nm.

This band attributed to [Co-NHPI] complex (**4**) that formed upon the reaction of NHPI with cobalt salts [16g]. Very recently, Ishii and co-workers have been demonstrated that the formation of complex type **4** decreases the decomposition rate of formed alkylhydroperoxide by cobalt catalyst and thus affects the overall rate of oxidation reactions [16g,19]. They showed that addition of a molar excess of *m*-chlorobenzoic acid (MCBA, 10-fold excess with respect to Co salt) to the catalyst mixture of NHPI/**1a** decomposes

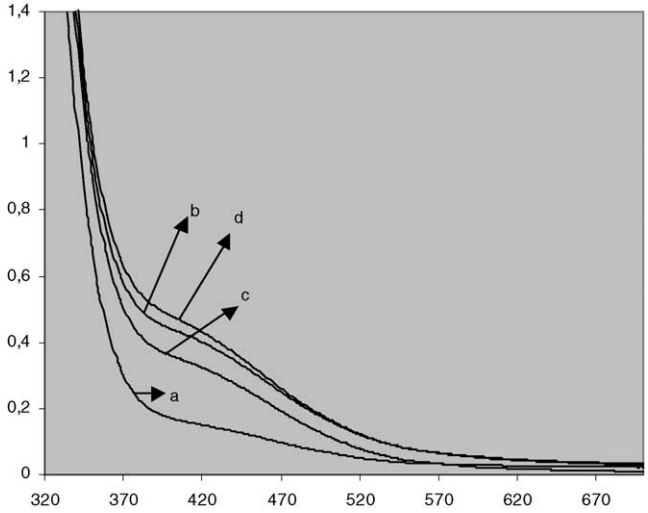


Fig. 1. (a) NHPI/**1b** after 2 h, (b) NHPI/**1a** after 2 h, (c) NHPI/**1b** after 6.5 h, and (d) NHPI/**1a** after 6.5 h.

the complex **4** which in turn facilitated the rate of aerobic oxidation of alcohols. Interestingly, it can be seen that the maximum absorption band concerning NHPI/**1a**, is certainly higher than that of NHPI/**1b** (Fig. 1).

Therefore, it is reasonable to assume that in our protocol, the extent of the formation **4** in NHPI/**1b** system is inherently lower than that of NHPI/**1a** without addition of any additives like MCBA. Based on these observation, the superior catalytic activity of NHPI/**1b** system in comparison with NHPI/**1a** is presumably due to the fact that in the former system hexanoate ligands (similar to MCBA in Ishii's procedure) strongly prevents the formation of **4** and thus accelerates the overall rate of aerobic oxidation process.

4. Conclusion

In conclusion, we have demonstrated that the use of NHPI combined with cobalt hexanoate is a superior catalytic system than that of NHPI/$Co(OAc)_2$ for the efficient and environmentally benign oxidation of a series of open-chain as well as cyclic acetals with molecular oxygen. The reactions are very clean and the yields of the products are excellent in most cases. Simplicity of the procedures, the use of clean molecular oxygen, easy work-up of the reaction products and mild reaction conditions can be considered as the advantages of the present protocol. Indeed, these altogether make this protocol as a green substituted for the existing traditional methods using stoichiometric and anxious oxidizing agents. To the best of our knowledge this is the first systematic study on the effect of lipophilization of Co(II) ions on the rate of aerobic oxidations using NHPI as radical generator. Further applications of this protocol for the oxidation of the other types of protecting groups are currently underway in our laboratories.

3h – ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.03–8.05 (d, J = 8.2 Hz, 2H), 7.52–7.56 (t, J = 8.2 Hz, ^{1}H), 7.40–7.43 (pseudo-t, J = 7.7 Hz, 2H), 4.42–4.44 (t, J = 4.7 Hz, 2H), 3.92–3.94 (t, J = 4.7 Hz, 2H), 2.70 (s, ^{1}H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 167.07, 133.22, 129.93, 129.74, 128.46, 66.67, 61.23.

3l – ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.03–8.05 (d, J = 8.2 Hz, 2H), 7.55–7.58 (t, J = 7.8 Hz, ^{1}H), 7.46–7.42 (pseudo-t, J = 7.7 Hz, 2H), 4.48–4.50 (t, J = 6.1 Hz, 2H), 3.76–3.79 (t, J = 6.1 Hz, 2H), 2.13 (sb, ^{1}H), 1.98–2.03 (quin, J = 6.1 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 167.08, 133.11, 129.67, 128.66, 128.45, 61.89, 59.21, 30.38.

3i – ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.97–7.99 (d, J = 7.8 Hz, 2H), 7.39–7.41 (d, J = 7.8 Hz, 2H), 4.65 (s, ^{1}H), 4.44–4.46 (t, J = 4.7 Hz, 2H), 3.94–3.96 (t, J = 4.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 166.14, 139.70, 131.15, 128.83, 128.22, 66.78, 61.26.

3o – ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.96–7.98 (d, J = 8.9 Hz, 2H), 6.89–6.91 (d, J = 8.9 Hz, 2H), 4.43–4.45 (t, J = 6.2 Hz, 2H), 3.84 (s, 3H), 3.74–3.76 (t, J = 6.2 Hz, 2H), 2.44 (sb, ^{1}H), 1.97–2.00 (q, J = 6.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 166.88, 163.51, 131.70, 122.51, 113.70, 61.58, 59.15, 55.49, 32.01.

3j – ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.86–7.90 (d, J = 8.5 Hz, 2H), 6.75–6.78 (d, J = 8.5 Hz, 2H), 4.28–4.30 (t, J = 4.8 Hz, 2H), 3.81–3.83 (t, J = 4.8 Hz, 2H), 3.69 (s, 3H), 3.61 (sb, ^{1}H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 166.77, 163.46, 131.79, 122.23, 113.69, 66.30, 60.85, 55.34.

3k – ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.57–7.58 (d, J = 7.7 Hz, ^{1}H), 7.50 (m, ^{1}H), 7.23–7.26 (t, J = 7.7 Hz, ^{1}H), 7.01–7.03 (dd, J = 7.7, 2.7 Hz, ^{1}H), 4.35–4.37 (t, J = 9.6 Hz, 2H), 3.86–3.88 (t, J = 9.6 Hz, 2H), 3.75 (s, 3H), 3.32 (sb, ^{1}H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 166.89, 159.52, 131.19, 129.44, 122.07, 119.47, 114.31, 66.68, 60.92, 55.41.

3n – ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.55–5.56 (d, J = 7.4 Hz, ^{1}H), 7.51 (m, ^{1}H), 7.23–7.35 (t, J = 7.4 Hz, ^{1}H), 7.03–7.05 (dd, J = 7.4, 2.6 Hz, ^{1}H), 4.42–4.44 (t, J = 10.0 Hz, 2H), 3.74–3.76 (t, J = 10.0 Hz, 2H), 2.50 (sb, ^{1}H), 1.97–2.02 (quin, J = 10.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 166.71, 161.57, 130.98, 131.00, 129.40, 118.42, 115.37, 64.41, 59.33, 56.14, 32.86.

3m – ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.78–7.80 (d, J = 7.4 Hz, 2H), 7.47–7.49 (d, J = 7.4 Hz, 2H), 4.38–4.40 (t, J = 6.1 Hz, 2H), 3.70–3.72 (t, J = 6.1 Hz, 2H), 3.13 (sb, ^{1}H), 1.92–1.97 (quin, J = 6.1 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 166.24, 131.67, 131.10, 129.01, 128.19, 62.29, 58.93, 31.75.

3p – ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 4.13–4.15 (m, 2H), 3.74–3.76 (m, 2H), 2.24–2.30 (t, J = 7.5 Hz, 2H), 1.53–1.58 (m, 2H), 1.37 (sb, ^{1}H), 1.24 (mb, 6H), 0.81–0.84 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 173.56, 65.84, 61.98, 34.16, 31.43, 28.79, 24.83, 22.46, 13.97.

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References

[1] (a) T.W. Greene, P.G.M. Wuts, Protective Groups in Organic Synthesis, 3rd ed., Wiley, New York, 1999;
(b) P.J. Kocienski, Protecting Groups, Thieme, New York, 1994.
[2] R.C. Larock, Comprehensive Organic Transformations, VCH, New York, 1999.
[3] N. Chidambaram, S. Bhat, S. Chandrasekaran, J. Org. Chem. 57 (1992) 5013.
[4] D.L. Heywood, B. Phillips, J. Org. Chem. 25 (1960) 1699.
[5] A.F. Sviridov, M.S. Ermolenko, D.V. Yashunsky, V.S. Borodkin, N.K. Kochetkov, Tetrahedron Lett. 28 (1987) 2835.
[6] S. Bhat, A.R. Ramesha, S. Chandrasekaran, Synlett (1995) 329.
[7] (a) J.D. Prugh, W.C. McCarthy, Tetrahedron Lett. (1966) 1351;
(b) R.G. Pearson, J. Chem. Soc. (1960) 1682;
(c) J.B. Wright, J. Am. Chem. Soc. 77 (1955) 4883;
(d) E.N. Marvell, M. Joncich, J. J. Am. Chem. Soc. 73 (1951) 973.
[8] M. Curini, F. Epifano, M.C. Marcotullio, O. Rosati, Synlett (1999) 777.
[9] B.M. Choudary, P.N. Reddy, Synlett (1995) 959.
[10] T. Takeda, H. Watanabe, T. Kitahara, Synlett (1997) 1149.
[11] J.H. Espenson, Z. Zhu, T.H. Zauche, J. Org. Chem. 64 (1999) 1191.
[12] T. Hosokawa, Y. Imada, S.I. Murahashi, J. Chem. Soc., Chem. Commun. (1983) 1245.
[13] (a) P. Deslongchamps, P. Atlani, Can. J. Chem. 52 (1974) 3651;
(b) P. Sundararaman, E.C. Walker, C. Djerassi, Tetrahedron Lett. (1978) 1627.
[14] R. Gopinath, A.R. Paital, B.K. Patel, Tetrahedron Lett. 43 (2002) 5123.
[15] E.M. Kuramshin, V.K. Gumerova, V.A. Dyachenko, L.G. Kulak, M.A. Molyavko, M.V. Kochinashvili, A.F. Mufteev, S.S. Zelotskii, D.L. Rakhmankulov, Zh. Obshch. Khim. 58 (1988) 1069;
E.M. Kuramshin, V.K. Gumerova, V.A. Dyachenko, L.G. Kulak, M.A. Molyavko, M.V. Kochinashvili, A.F. Mufteev, S.S. Zelotskii, D.L. Rakhmankulov, Chem. Abstr. 110 (1989) 192226h.
[16] (a) Y. Ishii, S. Sakaguchi, T. Iwahama, Adv. Synth. Catal. 343 (2001) 393;
(b) Y. Yoshino, Y. Hayashi, T. Iwahama, S. Sakaguchi, Y. Ishii, J. Org. Chem. 62 (1997) 6810;
(c) T. Iwahama, S. Sakaguchi, Y. Ishii, Chem. Commun. (1999) 727;
(d) T. Iwahama, S. Sakaguchi, Y. Ishii, Tetrahedron Lett. 39 (1998) 9059;
(e) S. Isozaki, Y. Nishiwaki, S. Sakaguchi, Y. Ishii, Chem. Commun. (2001) 1352;
(f) S. Sakaguchi, Y. Nishiwaki, T. Kitamura, Y. Ishii, Angew. Chem. Int. Ed. 40 (2001) 222;
(g) T. Iwahama, Y. Yoshino, T. Keitoku, S. Sakaguchi, Y. Ishii, J. Org. Chem. 65 (2000) 6502;
(h) S. Sakaguchi, T. Takase, T. Iwahama, Y. Ishii, Chem. Commun. (1998) 2037.
[17] N. Sawatari, T. Yokota, S. Sakaguchi, Y. Ishii, J. Org. Chem. 66 (2001) 7889.
[18] B. Karimi, J. Rajabi, Synthesis (2003) 2373.
[19] F. Haber, J. Weiss, Proc. R. Soc. Lond. Ser. A 147 (1934) 332.