OXIDATION OF PRIMARY ALCOHOLS TO ALDEHYDES CATALYZED

BY RUTHENIUM COMPOUNDS

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The RuCl₃ and RuO₂·nH₂O catalyzed oxidation of alkanes, aromatic fatty acids, alcohols, citronellol, and hydroxycitronellol by NaOCl was studied in the diphase system CCl₄—aqueous NaOCl at pH 13-13.5. At 60-65°C, using 1-2 mole % of catalyst and a 1.5-fold molar excess of NaOCl, primary alkanols (hexanol-1, 2-ethylhexanol-1, decanol-1, hexadecanol-1) benzyl and 3-phenyl-propyl alcohols, and hydroxycitronellol are converted to the corresponding aldehydes with a selectivity of 70-90% and a yield of over 75%.

The oxidation of primary alcohols to aldehydes is one of the most important reactions in organic syntheses. Oxidizing agents and catalysts capable of inducing this reaction with a high degree of selectivity are transition metal compounds [1], especially chromium(VI). Compounds widely used in the laboratory include chromic acid (Jones's reagent), pyridinium chlorochromate, pyridinium dichromate (Corey's reagent), etc. [2]. The most serious drawback of all reagents based on chromium(VI) is that they must be used in excess or at least in stoichiometric amounts, and thus are highly toxic. Thus the exploration for selective reagents to convert alcohols to aldehydes continues. Effective catalytic oxidizing systems are sought in which transition metal compounds act as catalysts. The following systems have been proposed: $RuCl_3-NaBrO_3$ [3], pyridinium dichromate- $(Me_3SiO)_2$ [4], Bu_4NRuO_4-N -methylmorpholino-N-oxide (MMO) [5], $RuCl_3-Ca(OCl)_2$ or $NaIO_4$ [6], $[Ru_2O_6(py)_4]-MMO$, $[RuO_2(py)_4]^{2+}-$ MMO [7], $RuCl_2(PPh_3)_3$ combined with $(Me_3SiO)_2$ [4], H_2O_2 , tert-butyl hydroperoxide [8], MMO [9], PhJ(OAc)_2 [10], tris(cetylpyridinium)-12-phosphotungstate-H_2O_2 [11].

The aim of the present work was to investigate the use of sodium hypochlorite, one of the cheapest and most readily available oxidizing agents, as a cooxidant in the conversion of alcohols to aldehydes catalyzed by ruthenium compounds.

We investigated the RuCl₃ catalyzed oxidation of decanol-1 (I) to decanal (II), including the following factors: molar ratios of oxidizer/substrate and catalyst/substrate, concentrations of NaOCl solutions, sodium ion concentrations, and a few other factors.

 $\begin{array}{c} C_{9}H_{1\nu}CH_{2}OH \xrightarrow{\text{RuCl}_{9}-\text{NaOCI}} C_{9}H_{1\nu}CHO \\ (1) & (1) \end{array}$

The oxidation was carried out in a diphase system of about equal volumes of CCl_4 and aqueous NaOCl (pH of the aqueous medium, 13-13.5), with effective mixing of the reaction mass, at 60-65°C using catalytic amounts of RuCl₃ (1-5%). The latter is converted almost immediately to hydrated ruthenium dioxide (HRD, RuO₂·nH₂O), which is practically insoluble in water or CCl_4 [12]. During vigorous mixing HRD is dispersed throughout the reaction mixture as a finely divided black suspension. At the end of the reaction HRD was removed quantitatively from the other products by routine filtration and was washed with CCl_4 and water. Its catalytic activity was almost fully preserved, and no significant differences were observed in results obtained with RuCl₃ and those obtained with fresh or regenerated HRD. The reaction was stopped when over 75% of compound (I) was oxidized. Results of the oxidation of compound (I) to (II) are shown in Table 1.

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	Catalyst, mole %	Sodium hypochlorite ^C			Yield of		
Experi- ment No.		n moles per mole (I)	method and concentra- tion, moles/ liter	Na salt concentra- tion, moles/ liter	Conver- sion of (I), %	(II), mole % with re- spect to (I) ^d	
Catalyst RuCl ₃							
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16	$ \begin{array}{c} 1 \\ 1 \\ 2 \\ 5 \\ 1 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2$	1 1 1 1 1 1 1,5 1,5 1,5 1,5 1,5 1,5		$\begin{array}{c} 4,7\\ 4,7\\ 1.0\\ 4,7\\ 4,7\\ 4,7\\ 4,7\\ 4,7\\ 1.0\\ 0,5\\ 1.0\\ 1.5\\ 2.0\\ 2.5\\ 3,7\\ 5,0\end{array}$	70 83 90 89 86 80 50 66 77 80 89 95 93 90 88 90	$\begin{array}{c} 86\\ 30\\ 50\\ 90\\ 88\\ 87\\ 66\\ 84\\ 82\\ 87\\ 75\\ 75\\ 75\\ 70\\ 65\\ 60\\ 50\\ \end{array}$	
Catalyst $RuO_2 \cdot nH_2O$							
17 18 19 20 21 22 23 24	$ \begin{array}{c} 2 \\ $	1 1,3 1,5 1,5 1,5 1,7 2,1	B 0.20 B 0.10 B 0.10 A 0.10 A 0.20 A 0.36 B 0.10 A 1.80	$\begin{array}{c} 4.7 \\ 1.0 \\ 0.2 \\ 0.5 \\ 1.0 \\ 1.0 \\ 5.0 \end{array}$	50 73 85 90 90 84 100 40	95 89 82 73 74 68 66 95	

TABLE 1. $RuCl_3$ - or $RuO_2 \cdot nH_2O$ -Catalyzed Oxidation of Decanol-1 (I)^a to Decanal (II) by Sodium Hypochlorite in CCl_4 -Aqueous NaOCl at 20°C(experiments 1-8 and 17) and 60-65°C (remaining experiments)^b

- ^a Concentration of (I), mmoles: 1 (experiments 1-5) and 20 (remaining experiments).
- ^b Reaction time: 15-30 min (experiments 2-5, 13-16, and 18-24), 60-90 min (experiments 1, 6, 9-12, 17), and 120 min (experiments 7-8).
- ^c Method for obtaining NaOC1: A) reaction of chlorine with aqueous NaOH; B) electrolysis of aqueous NaC1. pH of NaOC1 solutions: 10 (experiment 2), 12 (experiment 3), 13-13.5 (remaining experiments).
- ^d Based on GLC data.

Using optimal conditions for the conversion of (I) to (II), in subsequent experiments we studied the oxidation of alkanols with molecular weights larger or smaller than (I) (hexanol-1, 2-ethylhexanol-1, hexadecanol-1); α , β , and γ -phenylalkanols, cinnamic alcohol, citronel-lol, and hydroxycitronellol (Table 2).

In the presence of fresh or regenerated HRD the oxidation of (I) to (II) could be carried out at room temperature (experiments 1-8 and 17, Table 1). However, in experiments where the NaOCl and sodium ion concentrations reached 0.25 and 4.7 moles/liter, respectively, further oxidation of alcohol virtually ceased after 50-66% conversion despite the presence of NaOCl in the aqueous phase (experiments 7 and 8, Table 1). This results from catalyst inactivation due to decreased solubility of sodium decanoate at 20°C. Sodium decanoate is a side product in the oxidation of (I) by NaOCl-Ru. It is partially displaced from the aqueous layer to the interphase boundary and to the organic layer, where it emulsifies the catalyst and prevents its contact with the reagents, thus decreasing or completely suppressing its catalytic activity. Catalyst inactivation is suppressed when the reaction is carried out above 60°C. Thus at 60-65°C a smooth, rapid, and highly selective conversion of (I) to (II) is obtained using 0.01-0.02 equiv. of RuCl₃ or HRD and 1.5-fold molar concentration of 0.1-0.6 M aqueous NaOCl

Experiment No.	Alcohol	Alcohol conversion, %	Selectivity of conversion of alcohol to aldehyde, % ^b
1 2 3 4 5 6 7 8 9	hexanol-1 (IV) 2-Ethylhexanol-1 (V) Hexadecanol-1 (VI) Benzyl (VIIa) 2-Phenylethanol-1 (VIIb) 3-Phenylpropanol-1 (VIIc) Cinnamic (VIII) Citronellol (IX) 3,7-Dimethyloctanediol-1,7 (hydrowycitronellol) (XI)	85 95 66 99 83 90 90 85 90	90 90 88 75 24 c 70 d 26 80

TABLE 2. Oxidation of Alcohols by Sodium Hypochlorite, Catalyzed by $RuCl_3$ or $RuO_2 \cdot nH_2O$, in CCl_4 -Aqueous NaOCl (60-65°C)^a

- ^a 10-20 mmoles alcohol, 75-150 ml of 0.2 M NaOCl, pH 10 (experiments 4 and 7) and 13 (remaining experiments), 0.1-0.2 mmole catalyst, 25-50 ml CCl₄.
- ^b Based on GLC data.
- ^c Benzaldehyde (yield, 40%) is formed in addition to phenylacetaldehyde. Oxidation products of (VIIb) in NaOCl at pH 10 (yield in %): phenylacetaldehyde (11), benzaldehyde (8), benzyl chloride (3), benzoic acid (25), phenylacetic acid (35).
- ^d Cinnamaldehyde was not found in the oxidation product. Identified oxidation products of (VIII) (yield in %): benzaldehyde (40), cinnamic acid (trace), benzoic acid (40).

at pH 13-13.5. In less basic NaOC1 solutions the selectivity decreases sharply: to 30% at pH 10 and 50% at pH 12 (experiments 2 and 3, Table 1). The selectivity decreases from 75 to 50% when the NaOC1 concentration is raised from 0.6 to 2 moles/liter (experiments 10-16, Table 1).

Ruthenium-catalyzed oxidation of organic compounds by various oxidizing agents, including NaOCl, is based on the high oxidizing capacity of high-valent oxoruthenium intermediates formed in the reaction. Three basic types of such intermediates are known: ruthenium(VIII) tetroxide (RuO_4), tetraoxoperruthenate(VII) (RuO_4 -), and tetraoxoruthenate(VI) (RuO_4^{2-}) [12]. In alkaline media ruthenium(VIII) tetroxide is readily reduced to RuO_4^- and then much more slowly to RuO_4^{2-} [13]. All of these intermediates oxidize primary alcohols, but highly selective conversion of alcohols to aldehydes is obtained only with RuO_4^- [5].

The high selectivity of the conversion of (I) to (II) under our conditions leads us to assume that compound (I) is oxidized primarily by RuO_4 , which is then converted to H_2RuO_4 :

 $(I) + RuO_4^- \rightarrow (II) + II_2RuO_4^-,$

The reduction of $H_2RuO_4^-$ to HRD and the regeneration of RuO_4^- is described by reactions (1)-(4):

$$2H_2RuO_4^- \rightarrow RuO_2 + RuO_4^{2-} + 2H_2O$$
⁽¹⁾

$$H_2 RuO_4^- + RuO_4^2^- \rightarrow RuO_2 + RuO_4^- + 20H^-$$
⁽²⁾

$$2RuO_2 + 4NaOCI \rightarrow 2RuO_4 + 4NaCl$$
(3)

$$2\mathrm{RuO}_4 + 2\mathrm{OH}^- \rightarrow 2\mathrm{RuO}_4^- + \frac{1}{2}\mathrm{O}_2 + \mathrm{H}_2\mathrm{O}$$

$$3H_2RuO_4^- + 4NaOCl \rightarrow 3RuO_4^- + 4NaCl + \frac{1}{2}O_2 + 3H_2O$$
 (4)

It should be noted that oxidation of (I) to (II) is accompanied by the formation of a small amount of decyl hypochlorite (2-3%). When compound (II) is isolated from the reaction mixture by distillation, the latter decomposes to (II) and HCl, which results in the quantitative conversion of (II) (2-4 h after distillation) to the cyclotrimer 2,4,6-trinonyltrioxane-1,3,5 (III). This conversion can be eliminated by treatment of the reaction product with triethylamine prior to distillation.

Under optimal conditions for the oxidation of (I) to (II), lower and higher analogs of (I)-hexanol-1 (IV), 2-ethylhexanol-1 (V), and hexadecanol-1 (VI) - are oxidized to the corresponding alkanals with a high degree of selectivity (88-90%) and a conversion of 66-95% (experiments 1-3, Table 2).

Phenylalkanols $C_6H_5(CH_2)_nOH$ (VIIa-c) — where n = 1 (a), 2 (b) and 3 (c) — and cinnamic alcohol (VIII) (experiments 4-7, Table 2) were oxidized under similar conditions. Of these alcohols only (VIIa, c) were converted to the corresponding aldehydes with a high degree of selectivity (70-80%) and a conversion of 90-99%. In the case of (VIIb) phenylacetaldehyde was obtained in a yield of only 24% at 83% conversion, and no cinnamaldehyde was detected in the oxidation product of (VIII). It should also be noted that the oxidation of these alcohols is accompanied by cleavage of their carbon chains, with the formation of benzaldehyde, benzyl chloride, and benzoic acid from (VIIb) and of benzaldehyde and benzoic acid from (VIII) (experiments 5 and 7, Table 2).

The oxidation of (VIIb), similar to the one-electron oxidation of β -arylalkanols by Ag(II) ions [14], indicates that under our conditions the alcohols are oxidized by RuO₄⁻ ions, which have properties of one-electron oxidizing agents [15], with the generation of alkoxyl radicals:

 $\mathrm{RCH}_{2}\mathrm{OH} + \mathrm{RuO}_{4}^{-} \rightarrow \mathrm{RCH}_{2}\dot{\mathrm{O}} + \mathrm{HRuO}_{4}^{-}.$

Alcohol (VIIb) gives rise to β -phenylethoxyl radicals, which are very susceptible to fragmentation with cleavage of the β -C-C bond [16]:



In reactions with phenylalkanols evidence that electron transfer occurs from the hydroxyl group to RuO_4^- without participation of the benzene ring is provided by the very similar reaction rates for the competitive oxidation of (VIIc) and nonanol-1 (see experimental section). If the electron would be transferred from the benzene ring, compound (VIIc) would be oxidized at a much higher rate, as exemplified by one-electron oxidations of secondary and tertiary β - and γ -phenylalkanols by sulfate anion radicals, whose rate is 20-25 times higher than that of the analogous reaction with isopropanol [16].

The conditions ensuring highly selective conversion of (I) to (II) were unsuitable for the conversion of unsaturated aliphatic alcohols such as, for example, citronellol (IX) and hexene-3-ol-1. Under these conditions the latter compound was practically inert, and citronellol was converted to citronellal (X) with a low degree of selectivity (26%). In this respect the hydration product of (IX) - 3,7-dimethyl-1,7-octanediol (XI) (hydroxycitronellol) - 3,7-dimethyl-7-hydroxyoctanal (XII) - with the same degree of selectivity as compound (I) and other saturated alkanols (cf. experiments 1-3 and 9, Table 2). Thus, unlike the C=C bond in alcohol (IX), the tertiary hydroxyl group is not oxidized under these conditions.

The low reactivity in the case of hexene-3-ol-1 is typical for homoallyl alcohols in reactions of this type [9]. It is assumed that this is due to the formation by these alcohols of stable alkoxyolefin complexes with ruthenium ions, which do not catalyze alcohol oxidation.

EXPERIMENTAL

GLC analysis was carried out using a LKhM-8MD chromatograph with a flame-ionizing detector in a nitrogen stream (30 ml/min) and columns (stainless steel, 200×0.3 cm) with 5% OV-17 on Inerton Super (0.125-0.160 mm). PMR spectra of the organic compounds in CDCl₃ were recorded on a Jeol-FQ-90Q spectrometer with TMS as internal standard.

Analytically pure ruthenium trichloride, containing 47.18% Ru, was used. Analytically pure decanol-1 and the other alcohols (hexanol-1, 2-ethylhexanol-1, hexadecanol-1, benzyl alcohol, 2-phenylethanol, 3-phenylpropanol, cinnamic alcohol, citronellol, and hydroxycitro-nellol) were vacuum distilled prior to use. Carbon tetrachloride and chloroform (analytically pure) were purified by standard methods [17]. In the case of CCl_4 such purification did not produce a noticeable improvement in the results; consequently, in most of the experiments CCl_4 was used without additional purification.

Aqueous NaOCl solutions were prepared using two methods: A) by bubbling chlorine through 5 M aqueous NaOH according to the method in [18]; B) by electrolysis of alkaline (0.125 mole NaOH per liter) 5% and saturated aqueous NaCl solutions (0.85 and 4.7 moles/liter) at 20°C using platinum electrodes. Solution A contained 2.0 moles NaOCl per liter and had a pH of 13.5; solution B contained 0.1-0.25 mole NaOCl per liter and had a pH of 13-13.3. To obtain solutions with different NaOCl concentrations, solution A was diluted with distilled water or 0.1 N NaOH.

<u>RuCl₃-Catalyzed Oxidation of Decanol-1 (I) to Decanal (II) (Experiments 1-16, Table 1</u>). In experiments 1-5 RuCl₃ (0.01-0.05 mmole) was added to 3-4 ml aqueous NaOCl in a flask with a reflux condenser; when the RuCl₃ was dissolved, compound (I) (1 mmole) and dodecane (internal standard) in 2 ml CCl₄ were added. Almost immediately a black suspension appeared at the interphase boundary and, upon vigorous mixing, spread throughout the reaction mixture; simultaneously, the oxidation of (I) to (II) began. The reaction course was monitored by means of GLC; it was concluded when the conversion of (I) reached over 75% or, as happened in experiment 1, when the reaction stopped.

In experiments 6-8 RuCl₃ (0.1-0.2 mmole) was added to 20 ml aqueous NaOCl (5 mmoles); when the RuCl₃ was dissolved, compound (I) and dodecane in 40 ml CCl₄ were added. After 30 min another 60 ml of aqueous NaOCl (15 mmoles) was added dropwise, with vigorous mixing, at 20°C. The reaction mass was then mixed until 80% of compound (I) was converted (experiment 6) or until the reaction stopped (experiments 7 and 8).

In experiments 9-16 RuCl_3 (0.4 mmole) was added to 20-40 ml aqueous NaOCl (4-7 mmoles); when the RuCl_3 was dissolved, compound (I) and dodecane in 60 ml CCl₄ were added. The reaction mixture was heated, with efficient mixing, to 60-65°C and, after 10-30 min, another 60-160 ml of aqueous NaOCl (16-23 mmoles) was added at the same temperature. The reaction mixture was stirred at 60-65°C until 77-90% conversion of (I) was obtained.

When the specified degrees of conversion were obtained or when the reaction stopped, methanol (1-10 ml) was added for complete reduction of perruthenate and ruthenate ions in hydrated ruthenium dioxide (HRD), which was localized at the boundary between the aqueous and organic phases as a finely dispersed, black suspension. The HRD was separated from the aqueous and organic phases by means of a fine-pore glass filter or a filter consisting of a 1-cmthick celite (0.125-0.160 mm) layer capable of retaining the finely dispersed HRD particles. In this manner ruthenium could be extracted almost quantitatively from the reaction mixture; after washing the filter or celite layer with CCl_4 and water, the HRD could be reused as a catalyst. The conversion of (I) and the yield of (II) were determined by GLC analysis of the organic layer with the use of an internal standard (dodecane). The results are shown in Table 1.

Oxidation of (I) to (II) Catalyzed by Hydrated Ruthenium Dioxide (HRD) (Experiments 17-23, Table 2). In experiments 17-18 "fresh" HRD, formed from RuCl₃ in experiments 10-11, was used as catalyst; in experiments 19-24 the HRD was regenerated (once or several times) from experiments 17-23. The catalyst was transferred from the filter or celite layer to the flask by washing with aqueous NaOCl (4-6 mmoles), in which HRD is readily dissolved due to its oxidation to water-soluble RuO₄. Then compound (I) (20 mmoles) and dodecane in 60 ml CCl₄ were added to the flask, and the reaction was carried out as in experiments 6-16. The results are shown in Table 1.

In experiment 11 after separating the aqueous and organic phases and removing HRD, the aqueous phase was extracted with CCl_4 (2 × 20 ml); the extract was pooled with the organic phase and evaporated. A 1.97-g (63%) yield of compound (II) was isolated from the residue by flash chromatography [19]. PMR spectrum (δ , ppm): 0.85 t (3H, CH₃) 1.25 br.s (14H, CH₂), 2.37 m (2H, CH₂C=O), 9.73 s (1H, CHO). The dinitrophenylhydrazone (DNPH) of (II) had a mp of 106.5-107°C. Found: C 56.96; H 7.10; N 16.51%. $C_{16}H_{24}N_4O_4$. Calculated: C 57.13; H 7.19; N 16.66%.

<u>Preparative Methods for Obtaining Decanal (II).</u> The oxidation of (I) to (II) was carried out as in experiments 17-24 using 27 mmoles of (I), 0.4 mmole HRD, 40 mmoles of 0.2 M NaOCl (200 ml), and 60 ml CCl₄. Then methanol was added to the reaction mixture, the organic phase and HRD were separated, and the aqueous phase was extracted with CCl₄. The extract was pooled with the organic phase, and 1 ml of triethylamine was added (to decompose decyl hypochlorite and bind HCl). After 1 h the mixture was evaporated; the residue was dissolved in pentane and kept for 24 h in a refrigerator. Precipitated triethylamine chlorohydrate (0.092 g, 2.5%) was removed by filtration, and the filtrate was evaporated. Vacuum distillation of the residue afforded 2.6 g of compound (II) (60%); bp 98-100°C (10 mm), np^{20} 1.4283.

Without treatment of the reaction product with triethylamine, after 2-4 h compound (II) was converted quantitatively to the cyclotrimer 2,4,6-trinonyltrioxane-1,3,5 (IV); mp 37-38°C. PMR spectrum (δ , ppm): 0.85 t (9H, CH₃), 1.25 m (42H, CH₂), 1.61 m (6H, CH₂, CH), 4.81 m (3H, CHO). Treatment with NaHCO₃ and Na₂CO₃ (in solution or solid form) and with acidified aqueous KI did not prevent the cyclotrimerization of (II) obtained by this method.

Oxidation of hexanol-1 (IV), 2-ethylhexanol-1 (V), and hexadecanol-1 (VI) was carried out as in the preparative method for obtaining compound (II). The results are shown in Table 2. The aldehydes were identified as their DNPH derivatives (shown below: aldehyde, its DNPH melting point, DNPH elemental analysis results, DNPH empirical formula, calculated DNPH composition): hexanal, 104-105°C, C 51.58, H 5.73, N 19.85%; $C_{12}H_{16}N_4O_4$, C 51.42, H 5.75, N 19.99%; 2ethylhexanal, 121°C, C 54.44, H 6.31, N 18.11%; $C_{14}H_{20}N_4O_4$, C 54.53, H 6.54, N 18.17%; hexadecanal, 104-105°C. In addition, the aldehydes were identified by their PMR spectra, especially by their singlet signal at 9.73 ppm, characteristic for aldehyde formyl groups.

<u>Oxidation of Phenylalkanols (VIIa-c) and Cinnamic Alcohol (VIII) (Experiments 3-7, Table 2)</u>. The oxidation of (VIIa-c) and (VIII) was carried out as for compound (I). The aldehydes were isolated by flash chromatography (as in experiment 11) and were identified as their DNPH derivatives (shown below: aldehyde, its DNPH melting point, DNPH elemental analysis results, DNPH empirical formula, calculated DNPH composition): benzaldehyde, 244°C, C 54.82, H 3.50, N 19.70%; $C_{13}H_{10}N_4O_4$, C 54.55, H 3.52, N 19.57%; phenylacetaldehyde, 120°C; 3-phenylpropanal, 158-159°C, C 57.31, H 4.39, N 17.92%; $C_{15}H_{14}N_4O_4$, C 57.32, H 4.49, N 17.83%. In addition, the aldehydes were identified by their PMR spectra.

Cinnamaldehyde was not found in oxidation product (VIII). It was shown that (VIII) was oxidized primarily to benzaldehyde (yield, 40%), cinnamaldehyde (trace), and benzoic acid (40%). In addition to phenylacetaldehyde, oxidation product (VIIb) in aqueous NaOC1 at pH 10 afforded benzaldehyde (8%), benzyl chloride (3%), benzoic acid (about 25%), and phenyl-acetic acid (about 35%).

Oxidation of citronellol (IX) and hydroxycitronellol (XI) was carried out as for compound (I). The results are shown in Table 2. Citronellal (X) and hydroxycitronellal (XII) were isolated by flash chromatography and identified as their DNPH derivatives (shown below: aldehyde, its DNPH melting point, DNPH elemental analysis results, DNPH empirical formula, calculated DNPH composition): (X), 77-80°C, C 57.23, H 6.82, N 16.96%; $C_{16}H_{22}H_4O_4$, C 57.47, H 6.63, N 16.76%; (XII), 85°, N 16.06%; $C_{16}H_{24}N_4O_5$, N 15.90%.

<u>Competitive Oxidation of Nonanol-1 and 3-Phenylpropanol-1 (VIIc)</u>. A 1.68-g portion of nonanol-1 (10.6 mmoles), 1.86 g of compound (VIIc) (13.4 mmoles), and undecane (internal standard) in 60 ml CCl₄ were added to 0.1 g RuCl₃ and 120 ml of 0.2 M aqueous NaOCl at pH 13, obtained according to method A. The reaction mixture was mixed vigorously at about 20° C, and samples were removed for determining the degree of alcohol conversion by means of GLC. According to the GLC results, after 20 and 80 min (5 and 24% for nonanol and 11 and 52% for (VIIc)) the oxidation rate ratio for nonanol-1 and 3-phenylpropanol (VIIc) was 1:2.5 at 20°C.

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