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Catalytic functionalization of methane

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A mixture of sodium vanadate and pyrazine-2-carboxylic acid (pcaH) efficiently catalyses the reaction of methane with molecular oxygen (from air) and hydrogen peroxide to give methyl hydroperoxide and, as consecutive products, methanol and formaldehyde. The reaction takes place under mild conditions (25–75 °C) either in aqueous or in acetonitrile solution. The complexes formed from the catalyst precursor and the co-catalyst (under the reaction conditions) have been isolated and characterized as the derivatives $[VO_2(pca)_2]^-$ (1) and $[VO(O_2)(pca)_2]^-$ (3). The implications of these species in the catalytic process are discussed.

Keywords: vanadium; methane; oxidation; peroxo complexes

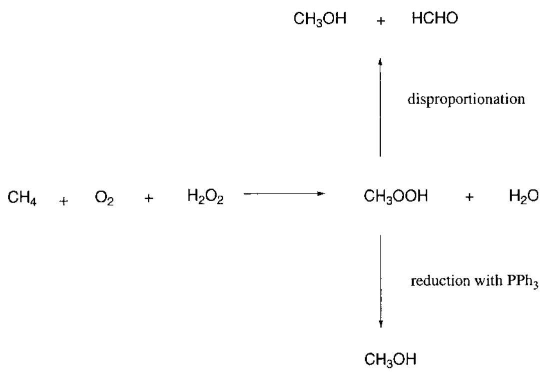
1 INTRODUCTION

Methane, the major component of natural gas, is one of the most important feedstocks for the chemical industry, although it is the least reactive organic compound.[1,2] It is extremely inert, even in comparison with other aliphatic hydrocarbons.[3–6] Almost all transformations of methane require high temperatures above 500 °C, and only in recent years have new methods of C–H activation been reported for it.[7–26] The partial oxidation of methane into valuable oxygenates (methanol, formaldehyde, formic acid) at temperatures below 100 °C remains a challenging task for homogeneous catalysis.

Recently, we have shown that a catalytic system composed of vanadate ($[VO_3]^-$) and pyrazine-2-carboxylic acid (pcaH) efficiently catalyses the oxidative functionalization of methane with air and hydrogen peroxide to give, as consecutive products, mainly methanol and formaldehyde.[27–30] We have also demonstrated that the catalyst precursor and the co-catalyst react, under catalytic conditions, to give the anionic complexes $[VO_2(pca)_2]^-$ (**1**) and $[VO(O_2)(pca)_2]^-$ (**3**).[31] In this paper we report the catalytic implications of these complexes in the catalytic functionalization of methane and other hydrocarbons.

2 RESULTS AND DISCUSSION

The oxidative functionalization of methane with air and hydrogen peroxide is catalysed by a combination of metavanadate ($[VO_3]^-$) with pyrazine-2-carboxylic acid (pcaH). The primary oxidation product is methyl hydroperoxide, which slowly decomposes to give methanol and formaldehyde



Scheme 1 Transformation of methane with molecular oxygen and hydrogen peroxide in the presence of the VO_3^-/4 pcaH catalytic system.

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(Scheme 1). After prolonged reaction, especially at higher temperature, formic and acetic acid are also formed. Methyl hydroperoxide reacts quantitatively with triphenylphosphine in acetonitrile to give triphenylphosphine oxide and methanol, which allows the GC detection of CH_3OOH.[27,30] After 24 h, the yield of CH_3OOH had attained 24% (based on H_2O_2), the catalytic turnover number being 480.[29]

The incorporation of molecular oxygen from air into the oxygenated products has been demonstrated using the analogous reaction with cyclohexane (which is liquid and allows a better dosage): in the absence of air (N_2 atmosphere, CH_3CN, $[NBu_4][VO_3]$ 10^{-4} M, pcaH 4×10^{-4} M, 40 °C, 2 h) no reaction takes place between cyclohexane and H_2O_2. However, if the reaction vessel is opened to air, the reaction starts immediately with the same rate as observed in the presence of air. Moreover, the cyclohexane oxidation under an $^{18}O_2$ atmosphere unambiguously leads to a high degree of ^{18}O incorporation into the oxygenated products.[27]

The catalytic reaction does not work with the vanadate alone, but requires a co-catalyst. Pyrazine-2-carboxylic acid is one of the best co-catalysts, pyrazine-2,3-dicarboxylic acid and picolinic acid having a comparable activity. These compounds have in common a six-membered aromatic cycle containing at least one nitrogen ring atom and one carboxylato substituent in the α-position with respect to the nitrogen atom.[31] The highest catalytic activity is observed for a catalyst/co-catalyst ratio of 1:4.[29]

In order to understand the role of the co-catalyst in the oxidative functionalization of alkanes catalysed by vanadate, we studied the reaction of various co-catalysts with $[NBu_4][VO_3]$ in acetonitrile solution. The reaction with pcaH and anthranilic acid (anaH) (Eqns [1] and [2]) leads to the disubstituted vanadate derivatives $[VO_2(pca)_2]^-$ (**1**) and $[VO_2(ana)_2]^-$ (**2**), which can be isolated as the tetrabutylammonium salts.

$$[VO_3]^- + 2pcaH \longrightarrow \underset{(\mathbf{1})}{[VO_2(pca)_2]^-} + H_2O \qquad [1]$$

$$[VO_3]^- + 2anaH \longrightarrow \underset{(\mathbf{2})}{[VO_2(ana)_2]^-} + H_2O \qquad [2]$$

The single-crystal X-ray structure analyses of these compounds show both anions to be pseudo-octahedral with the two oxo ligands in a *cis*-position. There is, however, an important difference in the coordination of the two chelating ligands which might explain the different activities of the two co-catalysts: whereas the two pca ligands (derived from the efficient co-catalyst pcaH) are coordinated through a nitrogen atom of the aromatic cycle and an oxygen atom of the α-carboxylato function (*N*,*O*-coordination), the two ana ligands (derived from the less efficient co-catalyst anaH) are coordinated through the two oxygen atoms of the carboxylato function (*O*,*O*-coordination) (Fig. 1).[31]

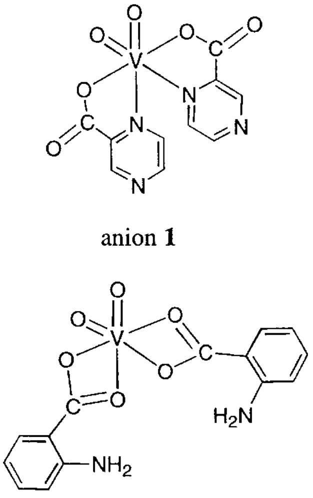


Figure 1 Molecular structures of anions **1** and **2**.

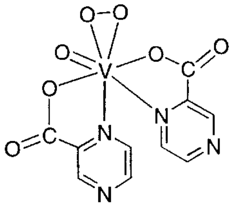
As hydrogen peroxide is present in the reaction solution of the oxidative methane functionalization catalysed by $[VO_3^-]$/pcaH, we studied the reaction of complex **1** with H_2O_2 which gives rise to the formation of the peroxo derivative $[VO(O_2)(pca)_2]^-$ (**3**) (Eqn [3]).

$$\underset{(\mathbf{1})}{[VO_2(pca)_2]^-} + H_2O_2 \longrightarrow \underset{(\mathbf{3})}{[VO(O_2)(pca)_2]^-} + H_2O \qquad [3]$$

With the tetrabutylammonium cation, the double salt $[NBu_4][VO_2(pca)_2][VO_2(pca)_2]$ crystallizes from acetonitrile. The ^{51}V NMR spectrum of this salt in CD_3CN shows signals at $\delta = -537$ ppm (anion **1**) and -558 ppm (anion **3**). They are identical with the two ^{51}V NMR signals observed in the reaction mixture of the oxidative functionalization of cyclohexane with air and hydrogen peroxide catalysed by $[NBu_4][VO_3]$/pcaH (1:4) in CH_3CN after a catalytic run.

In order to characterize the peroxo complex $[VO(O_2)(pca)_2]^-$ (**3**) unambiguously, and to separate it from anion **1**, with which it tends to crystallize as the tetrabutylammonium double salt, we decided to synthesize **3** in aqueous solution and to crystallize it as the ammonium salt. NH_4VO_3 was found to react in H_2O with pcaH and H_2O_2 to give $[NH_4][VO(O_2)(pca)_2]$, which crystallizes directly from water upon addition of ethanol. The single-crystal X-ray structure analysis of $[NH_4][VO(O_2)(pca)_2]$ revealed the presence of two water molecules of crystallization per molecule of complex. As found for complex **1**, the vanadium atom is at the centre of an irregular octahedron, and both pca ligands are *N,O*-coordinated. Surprisingly, the orientation of the two *N,O*-pca ligands is different from that in **1** and also from that found for the same anion **3** in the double salt $[NBu_4]_2[VO_2(pca)_2][VO(O_2)(pca)_2]$. Whereas for anion **3** in the double salt both pca ligands (as in **1**) are found to be *N,O*-coordinated with the two nitrogen atoms *cis* with respect to each other (isomer **3a**), anion **3** in the salt $[NH_4][VO(O_2)(pca)_2]$ contains the two pca ligands *N,O*-coordinated with the nitrogen atoms trans with respect to each other (isomer **3b**), as was also found by X-ray crystallography[32] for the picolinato analogue $[VO(O_2)(pic)_2]^-$ (picH = picolinic acid) (Fig. 2).[31,33]

The electrochemical characteristics of the vanadate complexes used for catalytic methane functionalization are not easy to understand: Whereas the cyclovoltammogram of $[NBu_4][VO_3]$ in acetonitrile solution shows no signal in the area of -0.5 to -1.5 V (with respect to a saturated silver electrode), three reduction and oxidation peaks are observed for $[NBu_4][VO_2(pca)_2]$ (anion **1**) ($E_{1/2} = -1.11$ V, cathodic $E_{pc} = -1.22$ V, $I_{pc} = 1.80$ μA and anodic $E_{pa} = -0.99$ V, $I_{pa} = 0.30$ μA; $E_{1/2} = -1.30$ V, cathodic $E_{pc} = -1.36$ V, $I_{pc} = 0.28$ μA and anodic $E_{pa} = -1.24$ V, $I_{pa} = 0.20$ μA; $E_{1/2} = -1.43$ V, cathodic $E_{pc} = -1.48$ V, $I_{pc} = 0.48$ μA and anodic $E_{pa} = -1.38$ V, $I_{pa} = 0.20$ μA for 2.6×10^{-2} M). In the case of anion **3**, employed as double salt $[NBu_4]_2[VO(O_2)(pca)_2][VO_2(pca_2]$ (anion **3a**) in acetonitrile solution, only one wave is observed ($E_{1/2} = -0.61$ V, cathodic $E_{pc} = -0.67$ V, $I_{pc} = 0.05$ μA and anodic $E_{pa} = -0.55$ V, $I_{pa} = 0.044$ μA for 1.74×10^{-2} M), quasi-reversible for a scanning rate of 50 mV s^{-1}; these peaks are tentatively assigned to the vanadium(V)/vanadium(IV) transitions. In addition, complex **3a** shows an oxidation wave at 1.15 V ($I_{pa} = 0.33$ μA) which is supposed to represent the oxidation of the peroxo ligand to the O_2 molecule, while no signal is found in the positive domain for anion **1**.


isomer **3a**

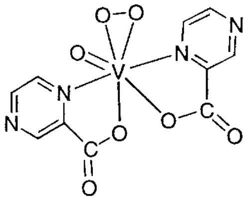

isomer **3b**

Figure 2 Molecular structure of anion **3** (isomers **a** and **b**).

Both complexes **1** and **3** can be used as catalysts in the oxidative functionalization of cyclohexane and, even if they are less active than the precursor system $[VO_3]^-$/pcaH (1:4), activity and selectivity become comparable with that of the precursor system, when 2 equiv. of pcaH are added (Table 1). These observations suggest the dioxo complex **1** and the oxoperoxo complex **3** to be catalytic species in the oxidative functionalization process.

On the basis of these experiments we believe that our vanadium system intervenes in the catalytic functionalization of methane as a catalytic pump of hydroxyl radicals implying neutral vanadium(V) and vanadium(IV) complexes (Scheme 2). The additional 2 equiv. of pcaH (which can be replaced by 2 equiv. of perchloric acid) required for efficient catalysis are presumably used to protonate anion **3** at the peroxo ligand to give the neutral vanadium(V) complex **4** containing a hydroperoxyl ligand. An OOH ligand has been discussed in the case of iron complexes.[34] Complex **4** could split off an OH radical to give the vanadium(IV) complex **5** which could react with hydrogen peroxide to give **4** and another OH radical. In such a way, the reversible interconversion of **4** and **5** would catalytically transform hydrogen peroxide into two OH radicals.

For the oxidative functionalization of methane (and other alkanes) we propose the general scheme

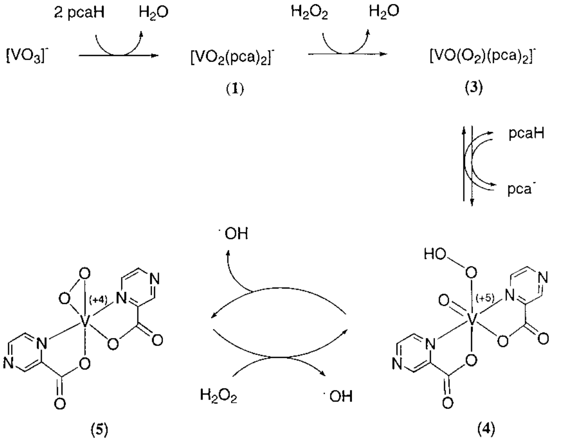
Table 1 Oxidative functionalization of cyclohexane[a]

Catalyst (10^{-4} M)	Co-catalyst	Total TON[b]
$[NBu_4][VO_3]$	pcaH (4×10^{-4} M)	1100
$[NBu_4][VO_3]$	pcaH (2×10^{-4} M)	330
$[NBu_4][VO_3]$	None	0
$[NBu_4][VO_2(pca)_2]$ (anion **1**)	None	215
$[NBu_4][VO_2(pca)_2]$ (anion **1**)	pcaH (2×10^{-4} M)	924
$[NBu_4][VO_2(pca)_2]$ (anion **1**)	$HClO_4$ (2×10^{-4} M)	892
$[NH_4][VO(O_2)(pca)_2]$ (anion **3b**)	pcaH (2×10^{-4} M)	1120

[a] Reaction conditions: CH_3CN; catalyst, 1×10^{-4} M; cyclohexane, 0.464 M; H_2O_2, 0.5 M; 40 °C; 24 h.
[b] Total turnover number: (mol cyclohexanol + mol cyclohexanone)/(mol catalyst).

accepted for radical reactions (Scheme 3). The reaction is initiated by the attack of the OH radical on the methane molecule to give water and a methyl radical. The radical chain is propagated by the reaction of the methyl radical with the diradical O_2 to give the CH_3OO radical, which can attack a CH_4 molecule to give the product CH_3OOH and another methyl radical. The radical chain can be terminated by combination of two radicals. The implication of OH radicals in the oxidative functionalization of methane is supported by the fact that the reaction with methane works best in aqueous solution, water being known to be an excellent solvent for OH radicals.[35]

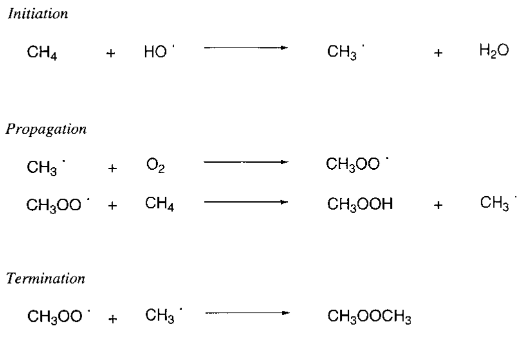
The oxidative functionalization of methane, catalysed by a vanadium system in aqueous solution, takes place under milder conditions (25–75 °C) than those used in the methane functionalization catalysed by mercury salts[36] or by platinum complexes (Catalytica process),[37] both requiring fuming sulfuric acid (100%) as reaction medium and temperatures between 160 and 220 °C.[36,37]



Scheme 2 Suggested role of the vanadium complexes functioning as a catalytic pump for the generation of hydroxyl radicals.

3 EXPERIMENTAL

All reactions were carried out in air. Acetonitrile for synthesis reactions (Fluka) was distilled over CaH_2, all other solvents (puriss) were used without any purification. Tetrabutylammonium vanadate was prepared according to the literature method.[38] All organic acids (Fluka) were used without purification. Hydrogen peroxide (30%) in water (Fluka) was stored in the refrigerator (maximum 4 °C) after each use. NMR spectra were recorded with a Varian Gemini 200 BB instrument or a Bruker AMX 400 spectrometer with tetramethylsilane (TMS) for ^1H and $VOCl_3$ for ^{51}V as external references. IR spectra were recorded with a Perkin-Elmer 1720x FT-IR spectrometer. Mass spectra (electrospray) were measured using a LCQ Finnigan instrument. Microanalyses were carried out by the Mikroelementaranalytisches Laboratorium of the ETH



Scheme 3 Radical mechanism proposed for the functionalization of methane catalyzed by the VO_3^-/4 pcaH system.

Zürich, Switzerland. Gas chromatographic analyses were recorded with a Dani 86.10 Doppler instrument (with CH_3NO_2 as internal reference) using a capillary Cp-wax 52-CB (25 m × 0.32 mm) column from Chrompack, and a Chrom Jet integrator (Spectra-Physics). Cyclic voltammetry was performed with a Metrohm VA-Scanner E612 and a Metrohm Polarecord E506 using a Hewlett-Packard 7040A *X–Y* recorder. A three-electrode system was employed with a platinum disc as the working electrode, an Ag/AgCl reference electrode and a platinum sheet auxiliary electrode, CH_3CN as solvent and NBu_4PF_6 (0.1 M) as supporting electrolyte. Under the conditions used, the one-electron oxidation of ferrocene occurs at +0.52 V in acetonitrile solution.

3.1 Synthesis of $[NBu_4][VO_2(pca)_2]$ (anion 1)

NBu_4VO_3 (681 mg, 2 mmol) was dissolved in 20 ml of CH_3CN. After complete dissolution, pyrazine-2-carboxylic acid (492 mg, 4 mmol) was added, and the solution was stirred under reflux for 5 h. After filtration of the green solution, evaporation of the solvent gave a yellow–green powder, which was dissolved in a minimum quantity of CH_2Cl_2. Addition of the same volume of cyclohexane led, after a few days, to the formation of light yellow crystals. Yield 61%. Found: C, 54.64; H, 7.32; N, 12.33. $C_{26}H_{42}N_5O_6V$ requires C, 54.63; H, 7.41; N, 12.25%. IR (cm^{-1}): 862s, 873s, 1668vs. ^1H NMR (acetone-d_6): $\delta = 0.9406$ (12H, t, $J = 7.5$ Hz CH_3), 1.4227 (8H, m, $J = 7.3$ Hz, CH_2), 1.8298 (8H, m, $J = 7.5$ Hz, CH_2), 3.4976 (8H, m, $J = 8.1$ Hz, CH_2) NBu_4^+; 8.521 (2H, dd, J(H5–H3) = 1.46 Hz and J(H5–H6) = 2.64 Hz, H5), 8.8547 (2H, d, J(H6–H5) = 2.68 Hz, H6), 9.1828 (2H, d, J(H3–H5) = 1.48 Hz, H3) pca ligand. ^{51}V NMR (acetone-d_6): $\delta = -525$. MS (electrospray, negative): $m/z = 329$.

3.2 Synthesis of $[NBu_4][VO_2(ana)_2]$ (anion 2)

NBu_4VO_3 (681 mg, 2 mmol) was dissolved in 20 ml of CH_3CN. After complete dissolution, anthranilic acid (547 mg, 4 mmol) was added, and the solution was stirred under reflux for 4 h. After filtration, evaporation of the solvent gave a yellow–green powder, which was dissolved in a minimum quantity of CH_2Cl_2. Addition of the same volume of cyclohexane led, after a few days, to the formation of light violet crystals. Yield 78%. Found: C, 60.17; H, 8.06; N, 7.08. $C_{30}H_{48}N_3O_6V$ requires C, 60.29; H, 8.09; N, 7.03%. IR (cm^{-1}): 825s, 875s, 1623vs. ^1H NMR (acetone-d_6): $\delta = 0.9410$ (12H, t, $J = 7$ Hz, CH_3), 1.4045 (8H, m, $J = 6.6$ Hz, CH_2), 1.774 (8H, m, CH_2), 3.421 (8H, m, CH_2) NBu_4^+; 6.507 (2H, ddd, J(H4–H3) = 8 Hz, J(H4–H5) = 6.8 Hz and J(H4–H6) = 1 Hz, H4), 6.7065 (2H, dd, J(H3–H4) = 8 Hz and J(H3–H5) = 0.6 Hz, H3), 7.154 (2H, ddd, J(H5–H6) = 8.4 Hz, J(H5–H4) = 7 Hz and J(H5–H3) = 1.8 Hz, H5), 7.867 (2H, dd, J(H6–H5) = 7.2 Hz and J(H6–H4) = 1 Hz, H6) ana ligand. ^{51}V NMR (acetone-d_6): $\delta = -503$. MS (electrospray, negative): $m/z = 354.7$.

3.3 Synthesis of $[NH_4][VO(O_2)(pca)_2]$ (anion 3b)

NH_4VO_3 (100 mg, 0.855 mmol) was dissolved in 20 ml of water and pyrazine-2-carboxylic acid (212 mg, 1.7 mmol) in 20 ml of water. Both solutions were mixed, and H_2O_2 (30%) (87 μl, 0.9 mmol) was added. The resulting solution was stirred at room temperature for 1 h. Slow evaporation of the solvent at room temperature to *ca* 2/3 of its volume and addition of the same volume of ethanol led after a few days at −18 °C to the formation of light red crystals. Yield 64%. Found: C, 33.14; H, 2.71; N, 19.03; O, 30.96. $C_{10}H_{10}N_5O_7V$ requires C, 33.07.; H, 2.78; N, 19.28; O, 30.84%. IR (cm^{-1}): 533s, 553s, 939s, 1668vs. ^1H NMR (CD_3OD): $\delta = 9.2275$ (1H, d, $J = 3$ Hz), 9.3815 (2H, d, $J = 3$ Hz), 9.410 (1H, d, $J = 1.2$ Hz), 9.4925 (1H, d, $J = 1$ Hz), 9.922 (1H, m) pca ligand. ^{51}V NMR (D_2O): $\delta = -600$. MS (electrospray, negative): $m/z = 344.9$.

3.4 $[NBu_4]_2[VO_2(pca)_2][VO(O_2)(pca)_2]$ (double salt containing anions 1 and 3a)

The salt $[NBu_4][VO_2(pca)_2]$ (500 mg, 0.875 mmol) was dissolved in 5 ml of CH_3CN and, after complete dissolution, H_2O_2 (30%) (90 μl, 0.88 mmol) was added. The solution was stirred at 0 °C for 4 h. After filtration of the red solution, evaporation of the solvent gave a red powder, which was dissolved in a minimum amount of acetone. Addition of the same volume of diethyl ether led, after a few days at room temperature, to crystallization of light red crystals. Yield 56%.

3.5 Catalytic runs

The oxidation of methane was carried out in cylindrical glass vessels placed in stainless steel autoclaves with intensive stirring at 50 °C (volume of the reaction solution, 30 ml; total volume of the autoclave, 100 ml). Gaseous air and methane were introduced in the autoclave (10 and 75 bar, respectively) containing the solution of H_2O_2 (0.193 M) and the catalyst ($NaVO_3$ in water or NBu_4VO_3 in acetonitrile, 10^{-4} M; pcaH, 4×10^{-4} M). **CAUTION: mixtures of air and H_2O_2 with organic compounds are potentially explosive at elevated temperatures and pressures!** The reactions were stopped by cooling the autoclave with ice, the concentration of methanol was analysed by GLC, and methyl hydroperoxide was determined in the form of methanol after reduction of the reaction solution with $NaBH_4$ in water[29] or PPh_3 in acetonitrile.[27,30] Formaldehyde was determined spectrophotometrically after its conversion into 3,5-diacetyl-2,6-dimethyl-1,4-dihydropyridine.[39]

The oxidation of cyclohexane was carried out in thermostated cylindrical glass vessels equipped with reflux condensers, with intensive stirring in air. The reagents (catalyst, co-catalyst and CH_3NO_2 as internal standard) were dissolved separately in acetonitrile, and these solutions were added to cyclohexane. After addition of H_2O_2 (30% aqueous solution), the reaction solution (total volume 10 ml) was stirred at 40 °C for 24 hours. The reaction was monitored by withdrawing aliquots (0.5 ml) and, after addition of triphenylphosphine to saturation, the samples were analysed by GLC.

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