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Letter

Copper(II)-catalyzed aerobic oxidation of indane in the presence of aldehydes: intermediate formation of hydroperoxides

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Abstract

Indane reacts with oxygen, at room temperature, in the presence of isobutyraldehyde, and a copper(II) derivative ($Cu(OH)_2$, $CuCl_2$, $Cu(TPIP)_2$) to give a mixture of indan-1-yl hydroperoxide and indanone, together with small amounts of indanol. In the presence of Tempo or diphenylamine, as radical scavengers, no reaction takes place. Thus, no direct formation of indanol, as precursor of indanone, via metal-oxo derivatives is likely to occur. The ratio hydroperoxide/indanone is highly dependent on the nature of the transition metal in TPIP-derived complexes.

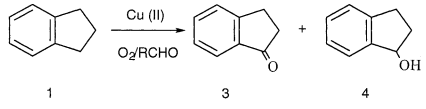
Keywords: Copper(II); Indane; Hydroperoxides

1. Introduction

During our investigations [1] on the use of the very soluble tetraphenylimidodiphosphinate (TPIP) derived metal complexes for the oxidation of alkenes and alkanes under aerobic conditions, we were led to examine the behavior of $Cu(TPIP)_2$ in these reactions and especially in the oxidation of alkanes such as indane and adamantane, in the presence of aldehydes. [1]

The choice of $Cu(TPIP)_2$ was linked to the observation by Murahashi et al. that Cu(II) salts cleanly and very efficiently converted alkanes, e.g., indane **1**, in the absence and in the presence of external ligands such as crown ethers, into indanone **3** together with smaller amounts of indanol **4** [6–8] (Scheme 1).

Under the same conditions, and according to the same authors, adamantane yielded a mixture of secondary and tertiary adamantanols. These



Scheme 1.

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[1] For recent contributions to the aerobic oxidation of alkanes in the presence of aldehydes, see for example: Refs. [2–5].

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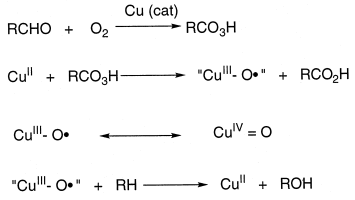


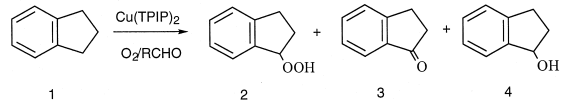
Scheme 2.

transformations were conducted either at room temperature or at 70°C in chlorinated solvents and the analytical data were mainly obtained from GC/MS. In the light of their results, these authors concluded thus on the formation of an alcohol via the direct insertion of a metal-oxo species into the benzylic carbon-hydrogen bond as depicted in Scheme 2, a reaction which would mimic the cytochrome *P*-450 oxidation of alkanes. Further on, oxidation of indanol to indanone **3** was assumed to take place under these reaction conditions.

The purpose of this Letter is to demonstrate that the reaction is in fact radicalar in nature, and that the alcohols are not the primary products of these reactions but that instead hydroperoxides are formed, the temperature-induced decomposition of which leads to ketones.

2. Results and discussion

When a solution of indane in dichloroethane ($0.9\ ml^{-1}$) was stirred at room temperature in the presence of oxygen, isobutyraldehyde ($5.5\ ml^{-1}$) and a catalytic amount ($3 \times 10^{-3}\ ml^{-1}$) of the new $Cu(TPIP)_2$ complex[2] for 4 h, a complete transformation of the aldehyde into isobutyric acid was observed. Analysis by GC indicated the presence of a main product the retention time of which agreed with that of indanone. However, in the ^1H NMR spectrum, a signal at δ 5.5 ppm for a major compound, besides a small signal at δ 5.2 ppm for the benzilic proton of indanol **4**, was also observed: the presence of indan-1-yl hydroperoxide **2** was thus suspected (Scheme 3).



Scheme 3.

According to the literature [9], this hydroperoxide can easily be extracted with aqueous sodium hydroxide, so its isolation by careful acid–base work up of the reaction mixture was attempted. Indeed, separation of the reaction residue into two fractions, which were characterized by their physical data, was achieved. Their GC retention times as well as their R_f values on TLC were surprisingly identical. However, the compound which was soluble in sodium hydroxide had the following ^1H and ^{13}C NMR data:[3] a broad signal for one proton at δ 7.84 ppm (OO**H**), a triplet for one proton at δ 5.51 ppm (C**H**OOH), two multiplets for one proton each at δ 3.09 and 2.80 ppm, and a multiplet for two protons at δ 2.30 ppm. The ^{13}C NMR spectrum indicated a signal at δ 89.33 for the carbon bearing the hydroperoxyl group whereas no signal for a carbonyl group could be detected. All these data together with the elemental analysis and a positive peroxide test, agreed with a structure such as **2**, the hydroperoxide derived from indane **1**. The spectroscopic data of the second product were in accordance with those of indanone **3**. Thus, a 49% conversion of indane into a mixture of indanyl 1-hydroperoxide (31%), indanone (12%) and indanol (6%) was observed in contrast to a 27% conversion of this same substrate into a mixture of indanone (75%) and indanol (22%)

[2] The X-ray structure of this complex has been established and the data are given as supplementary material.

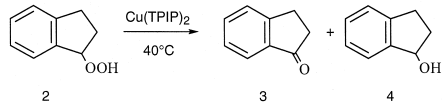
[3] Data for **2** : ^1H NMR ($CDCl_3$) δ 7.84 (s, b, 1H), 7.59–7.26 (m, 4H), 5.51 (t, 1H), 3.15–3.03 (m, 1H), 2.92–2.68 (m, 1H), 2.30 (m, 2H); ^{13}C NMR ($CDCl_3$) δ145.60, 139.90, 129.41, 126.50, 126.16, 125.12 (Ar), 89.33 (COOH), 30.42, 30.14 (2 CH_2). Analysis. Calc.: C, 71.98; H, 6.71. Found: C, 71.88; H, 6.75.

as indicated by Murahashi et al. in the presence of $CuCl_2$ or $Cu(OH)_2$ [7].

In order to find out the reasons for this unexpected discrepancy between $Cu(TPIP)_2$ and $CuCl_2$ or $Cu(OH)_2$, we repeated the oxidation reactions of indane in the presence of the two latter catalysts, in the absence and in the presence of a crown ether, at room temperature and at 70°C. In all the cases examined, the presence of the hydroperoxide was established, this compound being the main product of the reaction at room temperature. The best conversions were obtained in the presence of a crown ether, as described in the literature [7]. Work up of the reaction mixtures as above allowed the separation of the different products and especially the identification of the hydroperoxide **2**.

The temperature dependence of the amount of hydroperoxide in the presence of the catalysts could be established by ^1H NMR: when a solution of indanyl 1-hydroperoxide in chloroform was heated even at 40°C for a few hours in the presence of a Cu(II) complex, progressive disappearance of the signals due to the starting product was observed with the concomitant formation of indanone and small amounts of indanol. This result explains the low yields of hydroperoxide for the reactions carried out at 70°C. Similarly, by using $Cr(TPIP)_3$ instead of $Cu(TPIP)_2$, no hydroperoxide could be detected: only indanone was formed in 40% yield. This latter result is easily understood since hydroperoxide **2** is unstable in the presence of the chromium complex, even at 40°C, leading quantitatively to indanone (Scheme 4).

It appears therefore that in all the reactions examined, hydroperoxides are formed as the



2 3 4

Scheme 4.

main products at room temperature, as the minor products at higher temperature. Moreover, the best technique to monitor such reactions is to use ^1H or ^{13}C NMR spectroscopies since results by GC are misleading, the hydroperoxides being easily decomposed during their analysis by this method into mixtures of ketones and alcohols. Inhibition of the oxidation reaction was complete in the presence of Tempo or diphenylamine, two radical scavengers. It is thus clear that, even if a copper(III) oxy radical is formed, it rather abstracts an hydrogen atom from the alkane to lead, after reaction with oxygen, to a peroxyl radical which then promotes the free-radical chain reaction.

References

[1] H. Rudler, B. Denise, J. Ribeiro Gregorio, J. Vaissermann, J. Chem. Soc. Chem. Commun. (1997) 2299.
[2] C. Einhorn, J. Einhorn, C. Marcadal, J.L. Pierre, J. Chem. Soc. Chem. Commun. (1997) 447.
[3] T. Punniyamurthy, B. Bhatia, M. Madhava Reddy, G.C. Maikap, J. Iqbal, Tetrahedron 53 (1997) 7649.
[4] V. Kesavan, S. Chandrasekaran, J. Chem. Soc. Perkin Trans. 1 (1997) 3115.
[5] A.K. Mandal, J. Iqbal, Tetrahedron 53 (1997) 7641.
[6] S.I. Murahashi, Y. Oda, T. Naota, N. Komiya, J. Chem. Soc., Chem. .Commun. (1993) 139.
[7] N. Komiya, T. Naota, Y. Oda, S.I. Murahashi, J. Mol. Cat. A Chem. 117 (1997) 21.
[8] N. Komiya, S.I. Murahashi, T. Naota, in: Communication at 10th IUPAC Symposium OMCOS 10, Versailles, France, July 18–22, 1999.
[9] H. Hock, S. Lang, Chem. Ber. 75 (1942) 1051.