Pergamon

Tetrahedron Letters, Vol. 37, No. 46, pp. 8435-8436, 1996
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0040-4039/96 $15.00 + 0.00

PII: S0040-4039(96)01911-9

$Cu(OTf)_2$ - DBN/DBU Complex as an Efficient Catalyst for Allylic Oxidation of Olefins with *tert*-Butyl Perbenzoate

Govindasamy Sekar, Arpita DattaGupta and Vinod K. Singh*

Department of Chemistry, Indian Institute of Technology Kanpur, India - 208 016

Abstract: Olefins, on treatment with *tert*-butyl perbenzoate in the presence of a catalytic amount of a complex of $Cu(OTf)_2$ and chelating ligands such as DBN and DBU gave allylic benzoates under milder conditions. A variety of olefins were tested in the reaction. Copyright © 1996 Elsevier Science Ltd

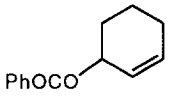
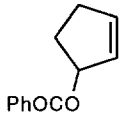
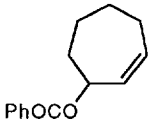
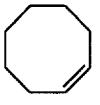
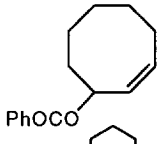
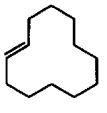
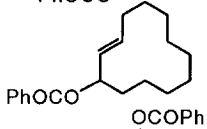
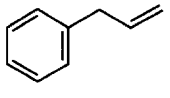
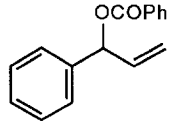
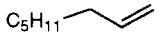
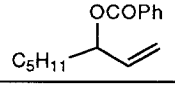
A substrate containing activated hydrogen reacts with an organic peroxyester in the presence of a catalytic amount of Cu (I) salt to give esters as indicated below. This reaction is popularly known as Kharasch reaction.[1,2]

$$\text{R-H} + \text{R}_1\text{COOOt-Bu} \xrightarrow{\text{Cu (I), 80 - 120 °C}} \text{R-OCOR}_1 + \text{t-BuOH}$$

Of particular theoretical and practical interests are the reactions of *tert*-butyl perbenzoate with allylic systems. Thus, the direct functionalization of olefins exploiting the special nature of the allylic C-H bond occurs to bring about allylic oxidation reaction. Allylic esters, thus obtained, can be converted into allylic alcohols by hydrolysis or reduction method. The whole transformation is very important from a synthetic organic chemist's view point. The main drawback with the method is that the reaction is very sluggish. In this communication, we report that the reaction can be performed at faster rate under milder conditions in the presence of a complex of copper (II) triflate and DBN or DBU.

Allylic oxidation of a variety of olefins was carried out with these ligands and results are summarized in the table. The general procedure is described as follows: A solution of DBN or DBU (0.12 mmol) and $Cu(OTf)_2$ (0.1 mmol) in 4 mL dry acetone was stirred at rt for 15 min. An olefin (10 mmol) was added followed by dropwise addition of *tert*-butyl perbenzoate (1 mmol). The reaction mixture was left till the disappearance of perbenzoate by tlc. Usual work up and purification gave allylic benzoate (Table) in good yield. In case of cyclohexene, cyclopentene, and cycloheptene the reaction was complete even at rt in few hours. However, in other cases, the reaction required reflux temperature. In the absence of DBN or DBU, the allylic oxidation reaction proceeded very poorly as negligible conversion took place in case of cyclohexene and a lot of decomposition was observed in other olefins. The results described here are very useful in view of its importance in asymmetric synthesis.[3] Further work is in progress in our laboratory towards aquisition of allylic alcohols using this methodology in complex systems. In view of the importance of enantiopure allylic alcohols in organic synthesis,[4] we are also in the process of developing new chiral nonracemic ligands for this purpose.[5]

Table: Catalytic Allylic Oxidation of Olefins with $Cu(OTf)_2$ - Ligand Complex in acetone.

Entry	Olefin[a]	Allylic benzoate	Ligand	Temp.	Time (h)	Yield (%)
1.			Nil	rt	90	5
2.			DBN	rt	24	65
3.			DBU	rt	32	80
4.			Nil	rt	11	decomp.
5.			DBN	rt	12	70
6.			DBU	rt	96	30
7.			Nil	rt	32	10
8.			DBN	rt	12	50
9.			DBU	rt	30	52
10.			Nil	60 °C	5	05
11.			DBN	60 °C	3	35
12.			DBU	60 °C	5	34
13.			DBN	60 °C	1	60
14.			Nil	60 °C	1	05
15.			DBN	60 °C	1	50
16.			DBU	60 °C	1	55
17.			DBN	60 °C	2.5	30
18.			DBU	60 °C	2	26

[a]In the cases of allylic benzene and 1-octene, the isomeric ratios of products are 93:7 and 91:9, respectively.

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5. We thank Department of Science and Technology (under SERC) for financial support.

(*Received in UK* 12 *August* 1996; *revised* 25 *September* 1996; *accepted* 27 *September* 1996)