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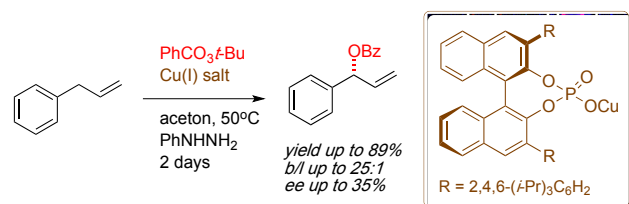
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Chiral Counterion Strategy in Cu-Catalyzed Asymmetric Allylic Oxidation of Linear Alkenes

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Abstract: Application of a chiral counter-ion strategy in the Kharasch-Sosnovsky reaction is reported. Copper(I) phosphates obtained from axially chiral, BINOL-derived phosphoric acids were investigated as catalysts in the enantioselective allylic oxidation of acyclic alkenes. Good yields and high regioselectivity towards branched allylic ester have been achieved. The chiral phosphates investigated exhibited modest enantioselectivities.



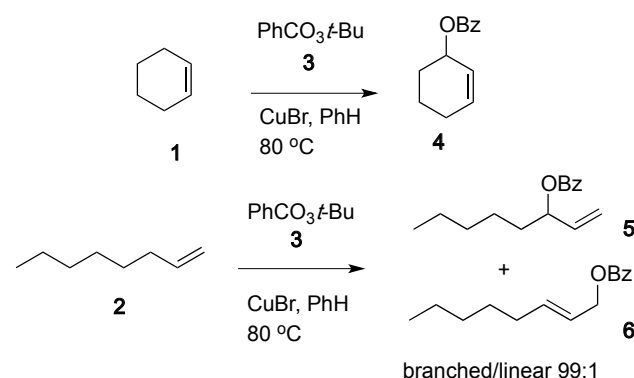
Keywords: allylic oxidation, allylic esters, asymmetric catalysis, chiral counterion, chiral phosphates, regioselectivity

Direct Cu-catalyzed oxidation of allylic C-H bonds discovered in 1958 by Kharasch and Sosnovsky [1-3] is an important synthetic transformation that enables a facile conversion of unsaturated hydrocarbon feedstock to valuable functionalized synthetic building blocks. The direct selective functionalization of an sp^3 C-H bond is a challenging problem due to the high bond dissociation energy (for methane, $\Delta H_{298} = 105$ kcal/mol), whereas an allylic C-H bond is weaker ($\Delta H_{298} = 89$ kcal/mol) due to the resonance stabilization of the allylic radical by the adjacent double bond [4], which is important for exercising control over the reaction.

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In the original work by Kharasch and Sosnovsky [2], oxidation of cyclohexene **1** and 1-octene **2** with *tert*-butyl peroxybenzoate **3** in the presence of catalytic amounts of CuBr (Scheme 1) was investigated. Cyclohexene afforded the corresponding allylic benzoate **4**, while in the case of terminal alkene **2**, selective formation of a branched isomer **5** was observed (**5/6** ratio 99:1). The mechanistic aspects of this reaction were later investigated by experimental and theoretical methods [5-12]. As compounds **4** and **5** feature a stereogenic centre, attempts at the asymmetric variant of this transformation soon followed, though these early efforts met with limited success [13,14]. Development of the enantioselective Kharasch-Sosnovsky reaction gained momentum three decades later with the introduction of chelating nitrogen ligands [15-25], that in some instances exhibited enantioselectivities up to 90% ee [26-29]. Considerable effort was also directed into optimization of the reaction conditions to make it appealing from a practical point of view [30-35].



Scheme 1

However, the success of the asymmetric methods is generally limited to cyclic alkenes, whereas enantioselectivity for linear terminal alkenes remains a challenging issue [16,25,27,36,37]. Herein, we report on the application of a chiral counter-ion strategy [38-40] to the Kharasch-Sosnovsky reaction. We reasoned that the close proximity of the chiral counterion to the catalytically active metal centre would confer sufficient

steric bias, leading to enantiodifferentiation in the product formation.

Chiral phosphoric acids and their conjugate bases perform excellently in chiral Brønsted acid catalysis [41,42]. Therefore, their copper salts were investigated as catalysts in a model Kharasch-Sosnovsky reaction, where allylbenzene served as the substrate and *tert*-butyl peroxybenzoate **3** was employed as the stoichiometric oxidant.

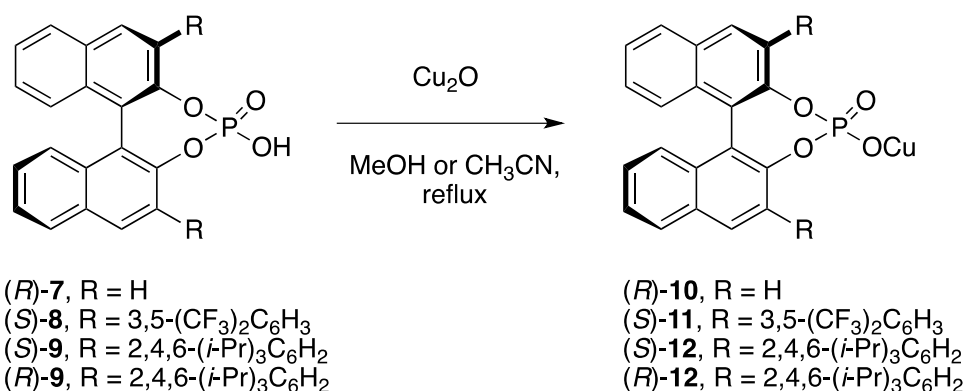
A series of chiral Cu(I) phosphates **10–12** were prepared by heating at reflux Cu_2O with excess of the appropriate BINOL-derived phosphoric acids **7–9** (acid: Cu_2O 3:1) in an appropriate anhydrous solvent (Scheme 2). Synthesis of **11** and **12** was carried out in acetonitrile, Cu_2O fully dissolved in under 3 h to afford, after removal of solvent, the respective copper salts as pure white solids. Thus prepared salts were stored under inert atmosphere as on exposure to air, they rapidly turned light blue in colour due to oxidation of Cu(I) to Cu(II). Phosphoric acid **7** derived from the parent (*R*)-BINOL proved virtually insoluble in acetonitrile, therefore the reaction was carried out in methanol. It was difficult to monitor the end point of the reaction (disappearance of the red Cu_2O) as the soluble product formed a deep red solution. Nonetheless, a complete conversion was achieved after 7 days and the resulting salt was obtained after filtration of the reaction mixture and removal of solvent under vacuum.

Initial screening of the reaction conditions was carried out at 0.5 mmol scale in acetone (1 mL) using *tert*-butyl peroxybenzoate **3** as the oxidant and a 5-fold excess of allylbenzene **13** (Table 1). To facilitate analysis of the reaction mixtures including determination of the enantiomeric composition of the products by chiral chromatography, authentic racemic samples of **14** and **15** were synthesized by literature methods (see Experimental for details).

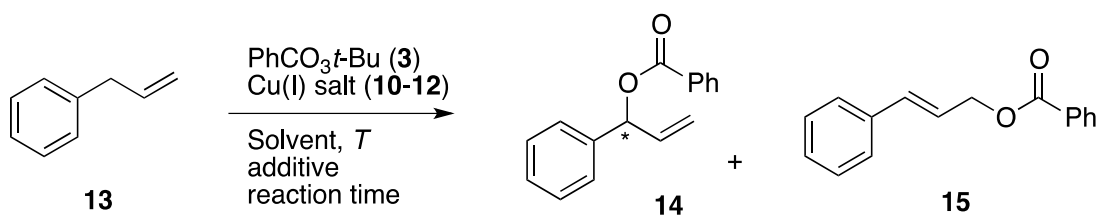
First, phosphate (*R*)-**10** derived from the parent (*R*)-BINOL was examined as a catalyst. At room temperature there was no sign of any product formation after 4 days. At 50°C, some conversion was achieved and the branched isomer **14** was isolated in 18% yield, but in racemic form. Only traces of the linear isomer **15** were detected by ^1H NMR spectroscopy (entry 1).

A bulkier catalyst (*S*)-**11** under the same conditions demonstrated essentially the same results: low reactivity, high regioselectivity towards the branched isomer **14** but negligible enantioselectivity (entry 2). The low reactivity of the catalyst could be affected by oxidation of Cu(I) species to the inactive Cu(II) counterparts. To accelerate the reaction, phenylhydrazine was added to reduce Cu(II) to Cu(I) *in situ* [23,25]. In the presence of phenylhydrazine, the reaction was complete at room temperature in just 2 days to afford **14** as the major isomer in 71% yield, albeit in racemic form (entry 3).

Improvement in enantioselectivity was achieved with catalyst **12** derived from TRIP **9**. In contrast to phosphoric acid **8**, rotation about the C-C bond linking the aryl groups to the BINOL core is restricted in the TRIP **9**, thus creating an additional steric bias. At 50°C, in the absence of the reducing reagent the reaction required 4–7 days for completion to afford the branched isomer (**14**) in up to 18% ee (entries 4, 5). In the presence of phenylhydrazine, it took just 2 days to afford ester **14** in high yield (89%) and improved enantioselectivity (25%, entry 6). Next, we examined the possibility of preparing the catalyst *in situ* by mixing $\text{Cu}(\text{OTf})_2$ with (*R*)-TRIP (**9**) followed by reduction to Cu(I) with phenylhydrazine, however, this led to a complete loss of enantioselectivity (entry 7). Our attempt at improving enantioselectivity by lowering the reaction temperature was equally unsuccessful (entry 8).



Scheme 2

Table 1. Screening reaction conditions for allylic oxidation^a

Entry	Cu(I) Salt (mol%)	Solvent	Additive ^b	T, °C	Reaction time	Yield, %	Ee, % (config)	14:15
1	(<i>R</i>)-10 (5)	Me ₂ CO	-	50	4 d	18	<5	>25:1
2	(<i>S</i>)-11 (5)	Me ₂ CO	-	50	4 d	26	<5	>25:1
3	(<i>S</i>)-11 (5)	Me ₂ CO	PhNHNH ₂	r.t.	2 d	71	<5	20:1
4	(<i>S</i>)-12 (5)	Me ₂ CO	-	50	7 d	37	17(<i>S</i>)	>25:1
5	(<i>R</i>)-12 (5)	Me ₂ CO	-	50	4 d	60	18 (<i>R</i>)	20:1
6	(<i>R</i>)-12 (5)	Me ₂ CO	PhNHNH ₂	50	2 d	89	25 (<i>R</i>)	20:1
7	(<i>R</i>)-12 (5) ^c	Me ₂ CO	PhNHNH ₂	50	2 d	56	<5	20:1
8	(<i>S</i>)-12 (2)	Me ₂ CO	PhNHNH ₂	r.t.	3 d	10	10 (<i>S</i>)	20:1
9	(<i>R</i>)-12 (5)	DCE	PhNHNH ₂	50	4 d	97	<5	>25:1
10	(<i>R</i>)-12 (5)	<i>c</i> -C ₆ H ₁₂	PhNHNH ₂	50	4 d	87	6 (<i>R</i>)	>25:1
11	(<i>R</i>)-12 (5)	CH ₃ CN	-	50	7 d	91	<5	>25:1
12	(<i>R</i>)-12 (1)	CH ₃ CN	-	50	7 d	60	<5	>25:1

^aUnless stated otherwise, the reactions were carried out on a 5 mmol scale, in solvent (1.0 mL) using *tert*-butyl peroxybenzoate **3** as the oxidant and a 5-fold excess of allylbenzene **13**; ^b 5 mol%; ^c catalyst was made *in situ* by stirring a mixture of (Cu(OTf)₂ (5 mol%) and (*R*)-**9** in acetone for 5 min prior to addition of other reactants.

Influence of solvent on the outcome of the reaction was briefly investigated. In dichloroethane (entry 9) and in cyclohexane (entry 10), using phenylhydrazine as a reducing reagent, at 50°C the reaction reached completion in 4 days to afford pure branched isomer **14** in high yield (97 and 87%, respectively) but in almost completely racemic form. In acetonitrile, the allylic oxidation was investigated using 5 or 1 mol% catalyst loading (entries 11 and 12, respectively). In the absence of the reducing agent, the reaction was slower compared to the same experiment in acetone and, despite high regioselectivity in favour of the branched isomer **14**, the enantioselectivity remained negligible.

Mechanistic investigations [5] of the Kharasch-Sosnovsky reaction suggested that the reaction commences with the oxidation of peroxybenzoate

3 by Cu(I) to give Cu(II) benzoate **A** and *tert*-butoxy radical (Scheme 3). The latter then abstracts hydrogen from the alkene, e.g. **13**, and the resulting allylic radical **B** combines with benzoate **A** to give the Cu(III) intermediate **C**, which upon reductive elimination affords allylic benzoate **14**. An alternative non-radical route, in which hydrogen abstraction takes place in an intramolecular fashion converging to intermediate **C**, was also proposed based on computational data [7].

According to the proposed reaction mechanism, oxidation of allylbenzene and β-methylstyrene should proceed either through the common allylic intermediate **B** [5] or involve the common η³-allylcopper complex resulting from the fast haptotropic rearrangement in **C** [7]. Therefore, we next examined allylic oxidation of both isomers of β-methylstyrene, (*E*)-**16** and (*Z*)-**16**

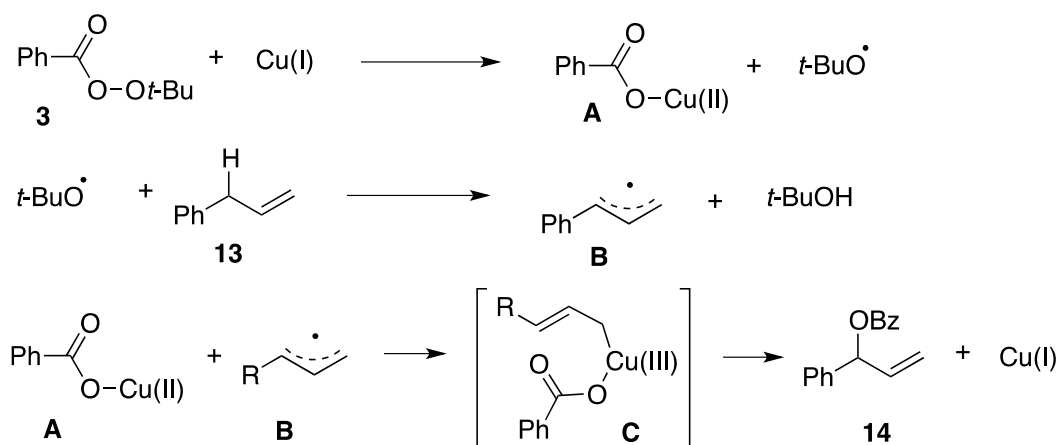
(Scheme 4). In acetone at 50°C, with catalyst (*R*)-**12** (5 mol% loading) and phenylhydrazine (5 mol%) as reducing reagent, the reactions went to completion in 5 days but, rather unexpectedly, furnished racemic *trans*-epoxide **17** as the major product (70% from (*E*)-**16** and 80% from (*Z*)-**16**). Allylic oxidation products were formed in minor quantities. Nonetheless, in both cases formation of only branched isomer **14** was observed. Furthermore, the ester (*R*)-**14** resulting from (*E*)-**16** showed the highest enantioselectivity obtained for the whole series (35% ee). This result is comparable with recent literature results reported for this reaction [37].

In conclusion, application of Cu(I) salts derived from axially chiral phosphoric acids in asymmetric Kharasch-Sosnovsky oxidation of acyclic alkenes has been investigated. Under the optimized conditions, the reaction proceeded in good yield and exhibited high regioselectivity towards the branched ester. Despite the low enantioselectivity obtained to-date, the chiral counterion strategy produced promising leads which warrant further investigation.

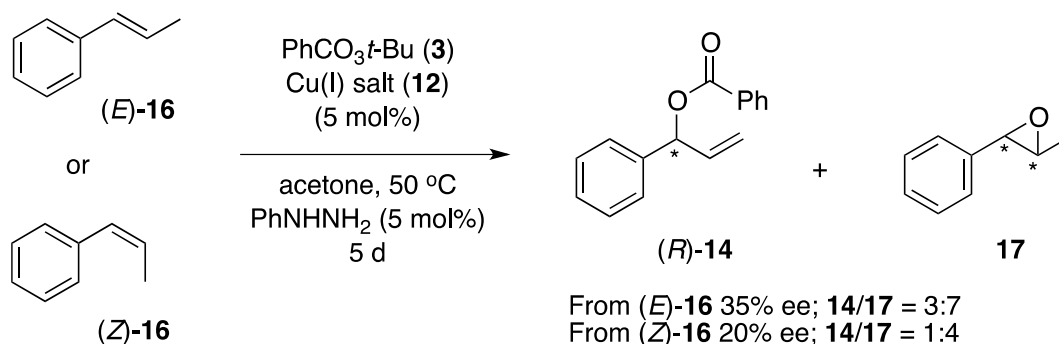
Experimental part

A typical procedure for allylic oxidation.

Copper (I) salt (20.3 mg, 0.025 mmol, 5 mol%) was weighed in a reaction tube and was evacuated and backfilled with N₂. The reaction vessel was charged with acetone (1 mL) that had been previously deoxygenated by purging with a stream of nitrogen for 20 min. This was followed by addition *via* syringe of phenylhydrazine (3 μL, 0.025 mmol, 5 mol%) and allylbenzene (0.33 mL, 2.5 mmol, 5 equiv.). The reaction mixture was stirred for 30 min, then *tert*-butyl peroxybenzoate (0.1 mL, 0.5 mmol, 1 equiv.) was added *via* syringe and the resulting mixture was stirred at the temperature specified in Table 1 until the oxidant was fully consumed, according to TLC. The solvent was evaporated and the residue was dissolved in dichloromethane (15 mL). The resulting solution was washed successively with saturated aqueous KHCO₃ (15 mL), brine (15 mL) and water (15 mL) and dried over MgSO₄. The solvent was removed under reduced pressure



Scheme 3



Scheme 4

and the residue was purified by column chromatography on silica gel (20 x 150 mm) eluting with a 98:2 mixture of light petroleum/ethyl acetate.

1-Phenylallyl benzoate (14)

¹H NMR (400 MHz, CDCl₃) δ: 5.20 (dt, *J* = 10.4, 1.2 Hz, 1H), 5.31 (dt, *J* = 17.2, 1.2 Hz, 1H), 6.04 (m, 1H), 6.43 (d, *J* = 6 Hz, 1H), 7.20–7.47 (m, 8H), 8.02 (d, *J* = 8 Hz, 2H). **¹³C NMR (100 MHz, CDCl₃)** δ: 76.7 (d), 117.1 (t), 127.2 (d), 128.2 (d), 128.4 (d), 128.6 (d), 129.7 (d), 129.9 (s), 130.3 (s), 133.1 (d), 136.3 (d), 139.0 (s), 165.5 (s). **IR:** *ν* 3066, 30332, 1719, 1451, 1266, 1107, 1069, 1025, 711, 699 cm⁻¹; in agreement with literature data [43].

HPLC: Chiralpak IA-3; 99.5:0.5 hexane:*i*PrOH: 8.81 min., major (*R*)-enantiomer; 12.67 min., minor (*S*)-enantiomer.

1-Phenylallyl benzoate (racemic)

Benzaldehyde (2 mmol, 0.2 mL, 1 eq.) and freshly distilled THF (5 mL) were placed in a 25 mL oven-dried RBF under N₂ atmosphere. The solution was cooled to 0°C. A solution of vinyl magnesium bromide 1M in THF (2 mmol, 2 mL) was added dropwise and the resulting mixture was stirred at that temperature for 1.5 hours. After that time, pyridine (4 mmol, 0.32 mL, 2 equiv.) and benzoyl chloride (2.6 mmol, 0.30 mL, 1.3 equiv.) were added dropwise *via* syringe and the mixture was allowed to warm up to room temperature and the reaction was stirred overnight. The suspension was quenched with 5 mL HCl 1M. The resulting solution was washed with saturated aqueous NaHCO₃. Organic phase was dried over MgSO₄ and volatiles were removed under reduced pressure. The residue mixture was purified by column chromatography (20 x 150 mm) eluting with 98:2 light petroleum/ethyl acetate to afford the title compound as a colorless oil.

Cinnamyl benzoate (15)

25 mL RBF was evacuated and backfilled with N₂ and charged with cinnamyl alcohol (3 mmol, 402.5 mg, 1 equiv.) and freshly distilled THF (5 mL). Pyridine (6 mmol, 0.485 mL, 2 equiv.) was added dropwise followed by benzoyl chloride (4 mmol, 0.46 mL, 1.3 equiv.) at room temperature. The reaction mixture was allowed to stir for 1.5 hours. After that time, the mixture was quenched with 5 mL HCl 1M and washed with 5 mL of a saturated aqueous NaHCO₃. The organic phase was dried over MgSO₄ and solvent was removed under reduced pressure. The residue was purified by column chromatography (35 x 120 mm) eluting with a 95:5 mixture of light petroleum/ethyl acetate, to afford the title compound as a colorless oil (548 mg, 77%).

¹H NMR (400 MHz, CDCl₃) δ: 5.03 (dd, *J* = 6.4, 1.2 Hz, 2H), 6.45 (dt, *J* = 16, 6.4 Hz, 1H), 6.78 (d, *J* = 16 Hz, 1H), 7.28–7.32 (m, 1H), 7.36 (t, *J* = 5.2 Hz, 2H), 7.45–7.51 (m, 4H), 7.60 (t, *J* = 6.8 Hz, 1H), 8.13 (d, *J* = 8.2 Hz, 2H). **¹³C NMR (100 MHz, CDCl₃)** δ: 65.7 (t), 1233 (d), 126.7 (d), 128.1 (d), 128.4 (d), 128.6 (d), 129.7 (d), 130.2 (s), 133.0 (d), 134.3 (d), 136.2 (s), 166.4 (s). **IR:** *ν* 3060, 3027, 2941, 1718, 1601, 1495, 1450, 1208, 1175, 1116, 965, 746, 710, 691 cm⁻¹; in agreement with literature data [44].

HPLC: Chiralpak IA-3; 99.5:0.5 hexane:*i*PrOH: 15.51 min.

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Supplemental Material: The online version of this article (DOI: 10.1515/asorg-2015-0005) offers supplementary material.