Bromination of Ketones by Palladium(II). An Asymmetric α-Bromoketones Catalytically Synthesized by a Mono Palladium(II) Catalyst

Arab K. El-Qisairi*, Hanan A. Qaseer

Department of Chemistry, Mu'tah University, P.O.Box 37, Mu'tah, Karak, Jordan

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Abstract

The oxidation of ketones by monometallic $[Pd(CH_3CN)_2(S)$-*Tol*-BINAP$](BF_4)_2$ **A** or $[Pd(CH_3CN)_2(S)$-METBOX$](BF_4)_2$ **B** in aqueous THF containing copper(II) bromide produced chiral α-bromoketones. The α-bromoketone products were obtained with moderate to high enantiomeric excess (68-89% ee) and good isolated yields (70-90%). The highest optical purities were 89% ee for cycloheptanone. Catalyst **B** gave slightly higher enantioselectivities than catalyst **A**. All symmetric ketones gives only one product whereas, oxidation of 2-butanone gives the 3-bromo-2-butanone and 1-bromo-2-butanone. The α-bromoketone products were characterized by FTIR, ^1H, ^{13}C-NMR and GC/MS.

Keywords: Palladium(II); Catalysis; Asymmetric; α-Bromoketone

Introduction

There has been considerable interest in the preparation of α-bromo carbonyl compounds due to their ability as useful organic intermediates,[1,2] introducing heteroatoms,[3] generating carbon radicals and/ or carbonions.[4-6] N-bromosuccinimide (NBS) and bromine in the presence of protic or Lewis acids are the most popular reagents used to synthesize α-bromo carbonyl compounds.[7-13] Recently, α-bromination of carbonyl compounds have been achieved using NBS either catalyzed by trimethylsilyl trifluoromethansulfonate (TMS.OTf) [14] or in the presence of silica supported sodium hydrogen sulfate.[7] A chiral α-bromo-β-alkyl ketone has been synthesized using chiral phosphoramidite in the presence of $Cu(OTf)_2$ as a catalyst.[15] These methods applying bromine or NBS reagents are suffering from the use of hazardous chemicals, long reaction time, or undesirable side products.[16]

In the present paper, we report a novel, direct, regioselective and enantioselective approaches for the synthesis of chiral α-bromo carbonyl compounds in moderate to high ee's and good yields. The chiral monometallic catalysts [17] used in this study are $[Pd(CH_3CN)_2(S)$-*Tol*-BINAP$](BF_4)_2$ **A**, and $[Pd(CH_3CN)_2(S)$-METBOX$](BF_4)_2$ **B** (figure 1). They are containing chiral bidentate ligands namely

* Corresponding author, Tel.: + (962-6) 4617890 ext 4610, fax: + (962-6) 4654061. E-mail address: aqaseer@yahoo.com & aqaseer@mutah.edu.jo

(S)-(-)-2,2`-bis(di-*p*-tolylphosphino)-1,1`-binaphthyl {(S)-*Tol*-BINAP} and *(S)*-(-)-2,2`-methylenebis-[(4S)-4-*tert*-butyl-2-oxazolone] {(S)-METBOX}.

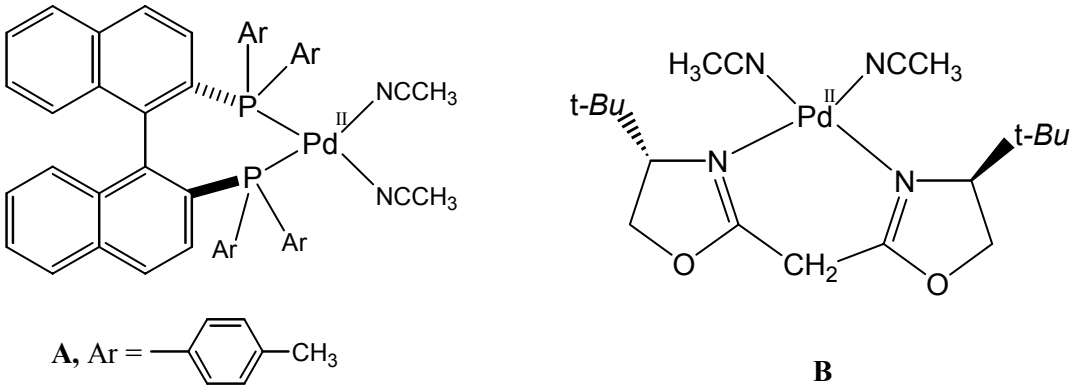


Figure 1. Structure of monometallic catalysts, **A** and **B**

Experimental

Materials

All solvents used were analytical grade reagents. Acetonitrile, dichloromethane, diethyl ether, and tetrahydrofuran were dried over calcium hydride (CaH_2) and distilled and stored under argon before use. Cyclopentanone, cyclohexanone, cycloheptanone, 4-dihydro-1(2 H)-naphthalenone (α-tetralone), 2-butanone, 3-pentanone, 4-heptanone, (S)-(-)-2,2`-bis(di-*p*-tolylphosphino)-1,1`-binaphthyl {(S)-*Tol*-BINAP}, (S)-(-)-2,2`-methylenebis-[(4S)-4-*tert*-butyl-2-oxazolone] {(S)-METBOX}, and tris[3-(heptafluoropropylhydroxy-methylene)-(+)-camphoratol], europium(III) derivatives ($Eu(hfc)_3$), were purchased from Aldrich Chemical Co. Tetrakis(acetonitrile) palladium(II) tetrafluoroborate $[Pd(MeCN)_4](BF_4)_2$ was purchased from Strem Chemicals. Chiral monometallic catalysts **A** and **B** were prepared in situ and used as described previously.[17]

Instrumentation

All ^{1}H-, and ^{13}C-NMR spectra were recorded on a 300 MHz Varian "INOVA-300" spectrometer in $CDCl_3$ using $(CH_3)_4Si$ as a reference. Measurements were performed at ambient probe temperature using 5 mm o.d. sample tubes. IR spectra were recorded on a NEXUS, Thermo Nicolet 470 FTIR spectrometer. The specific rotations were measured using Perkin Elmer polarimeter model 341 built with sodium and mercury source lamps. A Thermo Finnigan Trace GC/MS (San Jose, CA USA) was used for all analyses. The instrument was equipped with Rtx-5MS column, 15 m x 0.25 mm (Restek Corp., Bellefonte, PA USA). The GC was heated from 30 °C to 250 °C at a rate of 30 °C/ minute. The injector temperature was 50 °C. The source temperature was

200 °C. The instrument was operated in the positive ion mode for all analyses. The electron energy was 70 eV.

General procedure for the catalytic bromination of ketones.

In a typical experiment a 250-mL two-necked cone-shaped flask, with indented sides to increase the efficiency of stirring, was equipped with a magnetic stirring bar, sub seal septum and vacuum adapter. The flask was charged with 2 mL of H_2O, 23 mL of THF, (3.00 g, 13.4 mmol) of $CuBr_2$, (0.30 g, 3.5 mmol) of LiBr, (0.45 g, 4.7 mmol) of CH_3SO_3H, and 0.10 mmol of the catalyst **A** or **B**. The reaction was carried under room temperature and 1 atmospheric pressure of dioxygen using gas uptake apparatus.[18,19] Then 10.0 mmol of ketone was added to the reaction mixture by syringe. The reaction mixture was stirred overnight. The product was extracted with CH_2Cl_2 (3 x 50 mL), then washed with water (2 x 50 mL) and finally with saturated $NaHCO_3$ solution. The organic layer was dried over anhydrous $MgSO_4$. The excess methylene chloride was removed under vacuum and the residue was chromatographed on silica gel (60 – 270 mesh) using CH_2Cl_2/hexane (1:4) mixture to give the α-bromoketone in good yield (82 - 90%) based on the amount of dioxygen uptake for all runs. The structure of the α-bromoketone was elucidated by spectral analysis such as GC/MS, FTIR, and ^{1}H- and ^{13}C-NMR. In every reaction ~5% of the starting material was recovered. The enantiomeric excess (%ee) was determined by using ^{1}H-NMR in the presence of chiral shift reagent $Eu(hfc)_3$.

Bromination of cyclopentanone

Oxidation of cyclopentanone by the procedure described above was afforded only one product with 84% yield. The product was identified as 2-bromo cyclopentanone using GC/MS, ^{1}H- and ^{13}C-NMR spectra. The ions at m/z = 162/164 are consistent with the molecular formula C_5H_7OBr and the presence of a single Br atom (one is ^{79}Br and the other is ^{81}Br amu). Data for 2-bromo cyclopentanone: MS m/z (%RI) = [M^+, 164.0 (80)], [M^+, 162.0 (85)], [(M^+ – CO), 134.0 (24)], [(M^+ – C_3H_4O), 108.0 (80)], [(M^+ – Br), 83.1 (100)], [(M^+ – C_2H_3Br), 55.2 (95)]. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.92 - 2.03 (m, 1H), 2.10 - 2.22 (m, 3H), 2.33 - 2.40 (m, 2H), 4.20 (t, 1H, *J* = 4.90 Hz) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 20.1, 33.8, 34.9, 48.1, 211.3 ppm. FTIR (neat): ν = 2945, 2867, 1732, 1442, 1410, 1314, 1293, 1175, 1121, 922, 816, 691, 651, 530, 511 cm^{-1}. The %ee of 2-bromo cyclopentanone was determined to be 82%. Optical rotation $[\alpha]_D^{20}$ = -2.04° (*c* = 2.70, CH_3OH).

Bromination of cyclohexanone

This oxidation was afforded only one product in 86% yield. The product was identified as 2-bromocyclohexanone using GC/MS, ^{1}H- and ^{13}C-NMR spectra. The 176/178 ratios obtained are consistent with the presence of one Br atom (one is ^{79}Br

and the other is ^{81}Br amu) with the molecular formula C_6H_9OBr. Data of 2-bromocyclohexanone: MS m/z (%RI) = [M^+, 178.1 (70)], [M^+, 176.1 (76)], [(M^+ – C_2H_2O), 132.0 (48)], [(M^+ – Br), 97.1 (100)], [(M^+ – C_6H_9O), 79.1 (32)], [(M^+ – C_2H_3Br), 69.2 (83)]. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.73 – 1.83 (m, 2H), 1.88 - 2.06 (m, 2H), 2.18 - 2.27 (m, 2H), 2.30 – 2.34 (m, 1H), 2.95 (2dd, 1H, *J* = 6.00, 9.50 Hz), 4.42 (dt, 1H, *J* = 1.10, 5.45 Hz) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 22.1, 26.7, 36.7, 37.9, 53.4, 203.5 ppm. FTIR (neat): ν=2944, 2865, 1716, 1448, 1430, 1314, 1296, 1178, 1120, 1056, 916, 816, 691, 651, 528, 509 cm^{-1}. The %ee of 2-bromo cyclohexanone was determined to be 85%. Optical rotation $[\alpha]_D^{20}$ = -1.75^o (*c* = 2.15, CH_3OH).

Bromination of cycloheptanone

Bromination of cycloheptanone gave 2-bromo cycloheptanone in 80% yield. The product was identified as 2-bromocycloheptanone using GC/MS, ^{1}H- and ^{13}C-NMR spectra. The ions at m/z = 190/192 are consistent with the molecular formula $C_7H_{11}OBr$ and the presence of one bromine atom. Data of 2-bromocycloheptanone: MS m/z (%RI) = [M^+, 192.1 (18)], [M^+, 190.1 (16)], [(M^+ – CO), 163.0 (5)], [(M^+ – Br), 111.0 (90)], [(M^+ – HBrO), 93.1 (76)], [(M^+ – C_2H_3Br), 84.1 (100)], [(M^+ – C_3H_5Br), 70.2 (73)]. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.28 - 1.42 (m, 1H), 1.49 - 1.57 (m, 2H), 1.68 – 1.78 (m, 1H), 1.86 – 2.03 (m, 3H), 2.28 – 2.38 (septet, 1H, *J* = 2.10, 5.25 Hz), 2.42 – 2.50 (2dd, 1H, *J* = 2.78, 7.88 Hz), 2.78 – 2.87 (2t, 1H, *J* = 3.30, 10.5 Hz), 4.32 – 4.37 (dd, 1H, *J* = 5.25, 9.45 Hz) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 25.0, 26.8, 29.5, 34.2, 39.4, 53.7, 206.3 ppm. FTIR (neat): ν=2933, 2858, 1710, 1454, 1323, 1295, 1240, 1186, 1160, 1116, 935, 810, 691, 651, 540, 507 cm^{-1}. The %ee of 2-bromocycloheptanone was determined to be 89%. Optical rotation $[\alpha]_D^{20}$ = -16.8^o (*c* = 1.95, CH_3OH).

Bromination of 3,4-dihydro-1(2H)-naphthalenone (α-tetralone)

Bromination of 3,4-dihydro-1(2H)-naphthalenone (α-tetralone) gave 2-bromo-α-tetralone in 85% yield. The product was identified as 2-bromo-α-tetralone using GC/MS, ^{1}H- and ^{13}C-NMR spectra. The ions at m/z = 224.1/226.1 are consistent with the molecular formula $C_{10}H_9OBr$ and the presence of one bromine atom. Data of 2-bromo-α-tetralone: MS m/z (%RI) = [M^+, 224.1 (21)], [M^+, 226.1 (18)], [(M^+ – CO), 196.1 (12)], [(M^+ – Br), 144.0 (92)], [(M^+ – HBrO), 127.1 (75)], [(M^+ – C_3H_5Br), 104.1 (100)]. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.24 - 2.27 (m, 2H), 2.28 - 2.30 (m, 1H), 2.34 – 2.36 (m, 1H), 4.07 (t, 1H, *J* = 6.0 Hz), 7.52 – 7.61 (m, 3H), 8.22 (dd, 1H, *J* = 2.1, 8.0 Hz) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 28.3, 34.1, 50.3, 128.1, 128.2, 129.9, 130.2, 135.8, 136.1, 195.3 ppm. FTIR (neat):ν= 1689, 1583, 1463, 1375, 1296, 1242, 1185, 1161, 1118, 935, 810, 690, 651, 540, 507 cm^{-1}. The NMR and IR data are similar to those reported recently.[7] The %ee of 2-bromo-α-tetralone was determined to be 83%. Optical rotation $[\alpha]_D^{20}$ = -1.80^o (*c* = 2.10, CH_3OH).

Bromination of 3-pentanone

Bromination of 3-pentanone was afforded only one product in 90% yield. The product was identified as 2-bromo-3-pentanone using GC/MS, ^{1}H- and ^{13}C-NMR spectra. The ions at m/z = 164/166 are consistent with the molecular formula C_5H_9OBr and the presence of one bromine atom. Data for 2-bromo-3-pentanone: MS m/z (%RI) = [M^+, 166.0 (58)], [M^+, 164.0 (60)], [($M^+ - C_2H_5$), 135.0 (12)], [($M^+ - C_3H_5O$), 107.1 (85)], [($M^+ - C_2H_4Br$), 57.1 (100)]. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.08 (t, 3H, *J* = 7.24 Hz), 1.71 (d, 3H, *J* = 6.88 Hz), 2.54 – 2.64 (2d, 1H, *J* = 7.32 Hz), 2.77 – 2.88 (2d, 1H, *J* = 7.32 Hz), 4.40 (q, 1H, *J* = 6.81 Hz), ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 8.1, 20.1, 31.9, 47.2, 205.1 ppm. FTIR (neat): ν = 2962, 1719, 1380, 1183, 1095 cm^{-1}. The %ee of 2-bromo-3-pentanone was determined to be 80%. Optical rotation $[\alpha]_D^{20}$ = -0.56^{o} (*c* = 2.40, CH_3OH).

Bromination of 4-heptanone

Bromination of 4-heptanone afforded only one product in an 86% yield. A pure sample was isolated by column chromatography and identified as 3-bromo-4-heptanone. The ions at m/z = 192.2/194.2 are consistent with the molecular formula $C_7H_{13}OBr$ and the presence of one bromine atom. Data for 3-bromo-4-heptanone: MS m/z (%RI) = [M^+, 194.2 (56)], [M^+, 192.2 (62)], [($M^+ - C_3H_7$), 149.1 (18)], [($M^+ - C_3H_5O$), 121.1 (82)], [($M^+ - C_3H_6Br$), 70.1 (100)]. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.91 (t, 3H, *J* = 7.40 Hz), 1.00 (t, 3H, *J* = 7.35 Hz), 1.63 (m, 2H), 1.80 – 2.05 (m, 2H), 2.61 (t, 2H, *J* = 7.29 Hz), 4.24 (dd, 1H, *J* = 5.60, 8.12 Hz) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 10.6, 13.6, 17.1, 27.2, 40.6, 50.2, 205.4 ppm. FTIR (neat): ν= 2965, 1716, 1383, 1186, 1096 cm^{-1}. The %ee of 3-bromo-4-heptanone was determined to be 76%. Optical rotation $[\alpha]_D^{20}$ = -1.38^{o} (*c* = 1.50, CH_3OH).

Bromination of 2-butanone

Bromination of 2-butanone gave 3-bromo-2-butanone (**4a**) and 1-bromo-2-butanone (**4b**), (scheme 2) in 80% and 20%, relative yield respectively and 88% over all reaction yield. Data of 3-bromo-2-butanone: MS m/z (%RI) = [M^+, 152.0 (55)], [M^+, 150.0 (58)], [($M^+ - CH_3$), 135.0 (15)], [($M^+ - C_2H_3O$), 107.0 (80)], [($M^+ - C_2H_4Br$), 43.1 (100). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.68 (d, 3H, *J* = 6.84 Hz), 2.34 (s, 3H), 4.42 (q, 1H, *J* = 6.72 Hz), ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 20.3, 33.1, 47.0, 204.8 ppm. FTIR (neat): ν= 2960, 1720, 1382, 1185, 1095 cm^{-1}. The %ee of 3-bromo-2-butanone was determined to be 72%. Data of 1-bromo-2-butanone: MS m/z (%RI) = [M^+, 152.0 (58)], [M^+, 150.0 (62)], [($M^+ - C_2H_5$), 120.9 (20)], [($M^+ - C_3H_5O$), 93.0 (76)], [($M^+ - CH_2Br$), 57.1 (100)]. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.12 (t, 3H, *J* = 7.20 Hz), 2.64 (q, 2H, *J* = 6.70 Hz), 4.36 (s, 2H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 8.8, 28.9, 48.4, 204.8 ppm. FTIR (neat): ν= 2961, 1716, 1380, 1179, 1095 cm^{-1}.

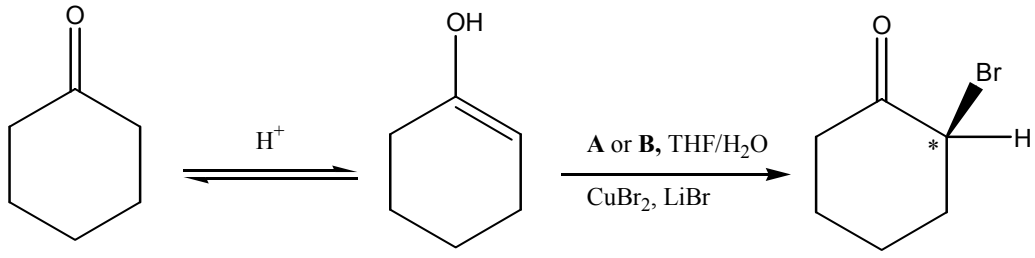
Control experiments

To confirm that the mono-palladium(II) is the actual catalyst, two control experiments were carried out. The first experiment was the oxidation of cyclohexanone using all reactants except the mono-palladium(II) catalyst. Our results indicated that there was no oxygen uptake and no α-bromoketone product was detected as shown by GC/MS. In the second experiment, the reaction was resumed until the usual amounts of product were accumulated, then the catalyst was isolated from the reaction mixture. This has been proved to be the mono-palladium(II) catalyst as tested by ^{1}H and ^{13}C NMR analyses.

Results and Discussion

In our previous work, we have described a palladium(II)-catalyzed hydroxylation of ketones.[20] The α-hydroxy ketone formed from the oxidation of ketone encouraged us to further investigate the bromination of ketone using chiral palladium(II) catalyst in the presence of $CuBr_2$. Chiral monometallic catalyst (**A** or **B**, figure 1) is employed in this bromination reaction to give chiral α-bromoketones (scheme 1).

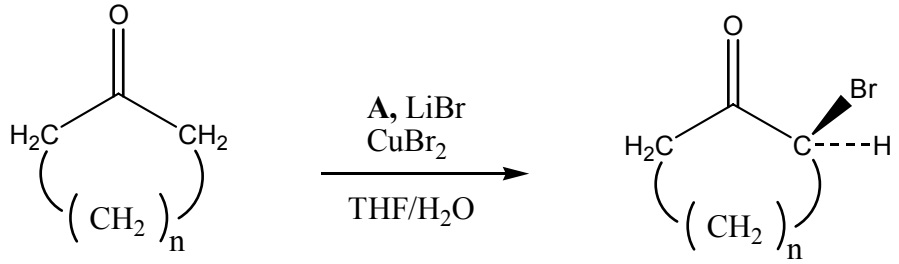
Scheme 1.



1 **2**

The characterization of the α-bromoketone products was achieved by using spectroscopic techniques such as ^{1}H-, ^{13}C-NMR, FTIR, and GC/MS. The α-bromoketone products, namely, 2-bromocyclopentanone, 2-bromo-cyclohexanone, 2-bromo-α-tetralone, 2-bromocycloheptanone, 2-bromo-3-pentanone, 3-bromo-4-heptanone and 3-bromo-2-butanone were all obtained in ~80-90% yield. Using either catalyst **A** or **B** there is no dramatic changes in the yield or in the enantioselectivities of the α-bromoketone products (table 1) was observed. This might suggest that the size of the chiral ligand in the coordination sphere of the catalyst does not play a significant role in the enantioselectivity. The percent yields, the %ee and the catalytic turnovers of the products are summarized in (table 1).

Table 1. Enantioselective synthesis of cyclic ketones **2a-g** by chiral monometallic **A** catalysts.[a]



1 **2**

1a: n = 2**; 1b**: n = 3; **1c** :n = 4;
1d: 3-pentanone; **1e**: 4-heptanone;
1f: 1--tetralone; **1g**: 2-butanone

2a: n = 2**; 2b**: n = 3; **2c** :n = 4;
2d: 2-bromo-3-pentanone; **2e**: 3-bromo-4-heptanone;
2f: 2-bromo-1--tetralone; **2g**: 3-bromo-2--butanone

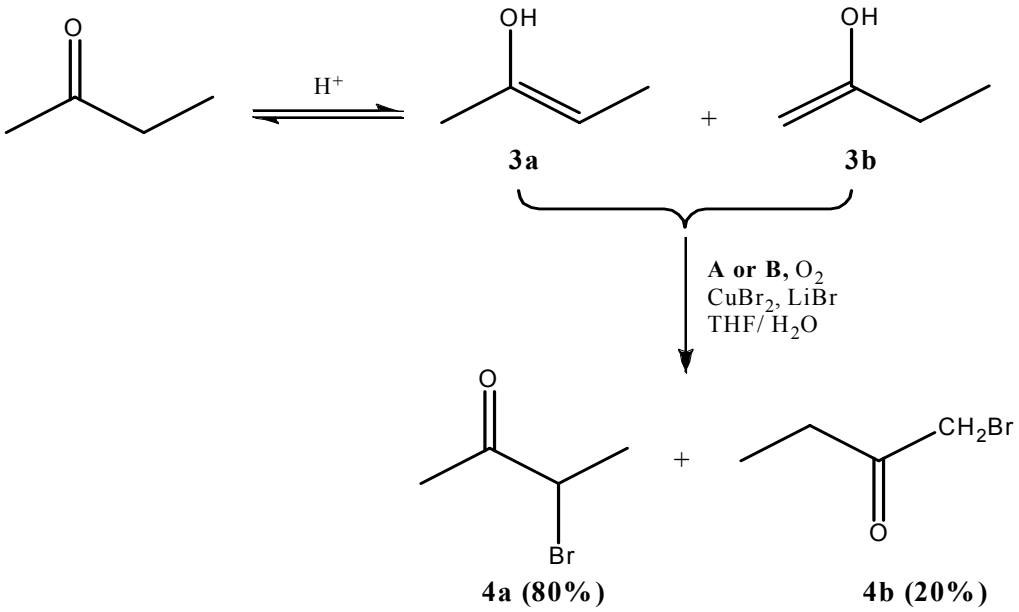
Entry	Substrate	Catalyst	Yield of **2** (%)[b]	ee of **2** (%)[c]	Turnovers[d]
1	**1a**	**A**	75	78	92
		B	84	82	136
2	**1b**	**A**	78	76	106
		B	86	85	158
3	**1c**	**A**	70	80	94
		B	80	89	152
4	**1d**	**A**	80	78	88
		B	90	80	122
5	**1e**	**A**	71	70	76
		B	86	76	108
6	**1f**	**A**	75	72	80
		B	78	83	110
7	**1g**	**A**	80[e]	68	95
		B	88[e]	72	105

[a] Reactions are run with 0.05-0.1 mmole of chiral catalyst in 25-30 ml of solvent and 0.6-1.4 M of $CuBr_2$. Temperature = 25 °C. LiBr = 0.06-0.2 M. The solvent was H_2O-THF mixture containing 83% THF by volume. Completion of the reaction is monitored by O_2 uptake using gas buret considering. [b] Isolated yield of the product after column chromatography. Yields are calculated assuming dioxygen is a 4-electron oxidant. [c] Determined by using ^{1}H-NMR in the presence of chiral Eu(hfc)$_3$. [d] Turnovers measured by O_2 uptake using gas burets. [e] The ratio of 3-bromo-2-butanone and 1-bromo-2-butanone was 4:1 respectively.

We started this work by the bromination of symmetrical ketones. The symmetrical ketones are rather interesting because they are expected to give only one enol form (scheme 1). The unsymmetrical acyclic ketone also afforded two products derived from the two possible enols (**3a**, **3b**). This is shown in (scheme 2) which illustrates the reaction using 2-butanone as a substrate. Compound 4**a** (80%) is found to be the major product rather than compound 4**b** (20%). This result could be explained by the formation of the most stable enol form (**3a**). Since the reaction is enolization, it is expected to be acid catalyzed. Methanesulfonic acid was used in all

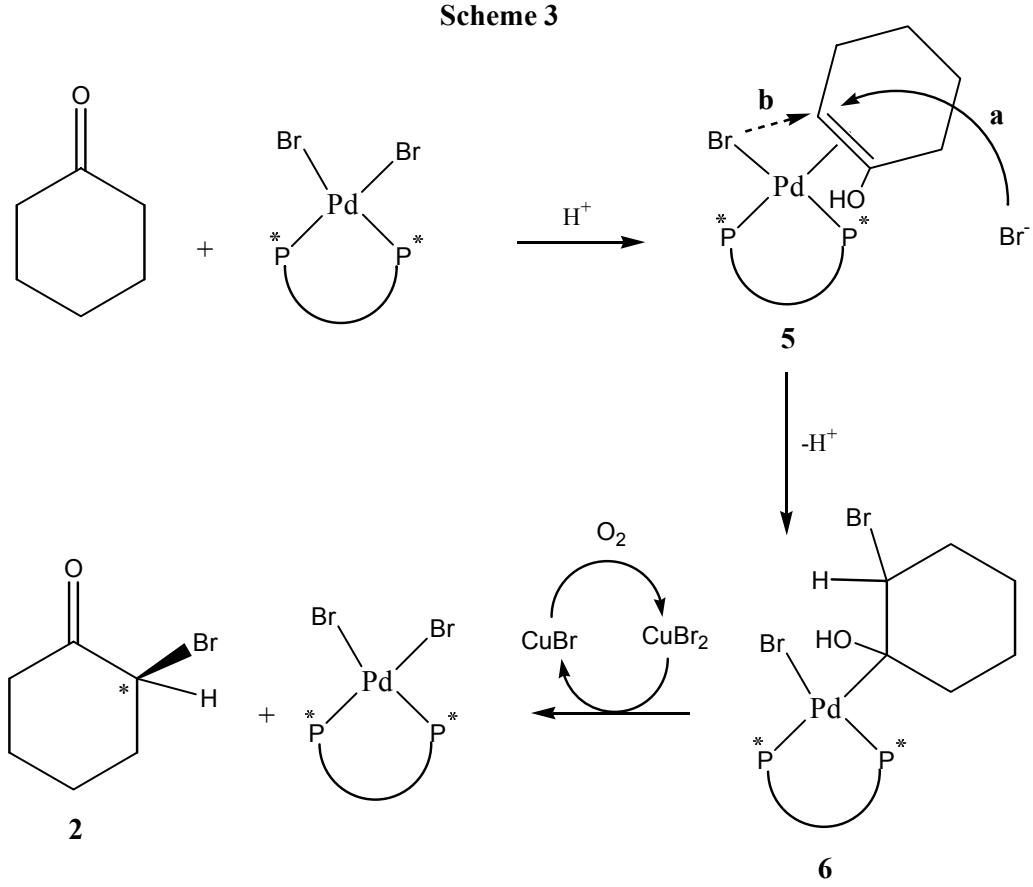
reactions to accelerate the enolization of ketone. The oxidation becomes faster and gave almost quantitative yields.

Scheme 2



The bromination of ketone by chiral palladium(II) is a new method used to prepare chiral α-bromoketone. The present synthetic method is a one-step catalytic air oxidation since the CuBr formed during the reaction readily reacts with dioxygen to give $CuBr_2$. The reaction sequence is shown in (scheme 3) using cyclohexanone as substrate. The bromide ion attacks the π-complex **5**, either from the outside (path **a**) or from the coordination sphere (path **b**) to produce compound **6**. Oxidative decomposition of **6** produces the final product creating a chiral carbon at α-position. More than 100 turnovers have been achieved without any loss of activity of the catalyst (table 1). The rate of oxidation did not decrease during the course of the reaction. This raises the possibility that the catalyst turnovers could be further improved. Even though, more investigation is required to demonstrate this experimentally.

Scheme 3



In conclusion, we have developed a novel method for asymmetric bromination of ketones since it does not involve an olefin and it is unique in transition metal catalysis. It is simple and convenient approach for preparing chiral α-bromo ketone compounds without using hazardous chemicals.

Acknowledgments

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