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Dilithium Tetrachloromanganate an Effective Reagent for Regioselective Ring Opening of Epoxides with Grignard Reagents

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The epoxides were obtained from substituted phenols and epichlorohydrin by reported methods. The regioselective ring opening of epoxides were studied in different solvents by reaction with Grignard's reagent in presence of dilithium tetrachloromanganate.

Keywords: Epoxide, Epichlorohydrin, Regioselective, Grignard, Transmetallation.

INTRODUCTION

The reactions of epoxides with Grignard reagents is an important reaction for the synthesis of alcohols by the formation of C-C bond [1] in organometallic chemistry. The regioselective ring opening of epoxides and substituted epoxides with organocopper and alkynyllithium reagents are routinely used for the synthesis of alcohols by attack at the less substituted carbon atom [2]. However, Grignard reagents [3] as an example RMgX, R_2Mg and MgX_2 reacts with epoxides and substituted epoxides that results in a very complicated side reactions and continuously forms a combination of products [4]. For instance aryl substituted epoxides like styrene oxide and disubstituted epoxides like isobutylene oxides results in a rearranged product before the formation of carbon-carbon bond. Tiffeneau and Fourneau [5] ascertained in their experiments that once styrene oxide reacts with Grignard reagents like alkyl magnesium bromides to yield 1-phenyl-2-alkanols. Presumably, the styrene oxide rearranged to a phenylacetaldehyde in presence of $MgBr_2$, finally that reacts with Grignard reagent. More recently, Deniau and co-workers [6] reported that when styrene oxide reacts with $MgBr_2$ provides a mixture of products like 2-phenyl-1-alkanol and 1-phenyl-2-alkanol. In asymmetric synthesis the Sharpless process of epoxidation is an important tool, which is highly enantioselective reaction and it has simple reaction protocol [7]. In the regioselective ring opening reactions of epoxy alcohols there are many efforts have been devoted so as to extend the scope and applications of this reaction. The nucleophilic attack of Grignard reagents occurs principally at less substituted carbon atom in Payne rearrangement [8]. The regioselective attack of nucleophiles like red-Al and dialkylcuprates ocuurs at less substituted position [9]. The regioselective ring opening reactions of epoxides with organoaluminium reagents has been reported by Oshima Nozaki and co-workers [10]. Sharpless and Caron [11] reported a regioselective attack at C3 position by completely different nucleophiles in presence of $Ti(OPr\text{-}i)_4$ as a catalyst. The synthesis of chiral secondary alcohols from the reduction of ketones by using chiral hydride [12] reagents is the highly successful reaction [13] in the presence of chiral ligands. However, the selective ring opening reactions of epoxides with various nucleophiles, which provides *o*-substituted alcohols and has two asymmetric centres that is still to be investigated [13]. In the presence of chiral ligands Grignard reagents and organocuprate reagents [14-16] readily cleave epoxide regioselectively and yields optically active alcohols having asymmetric carbon atom. Epoxides [17-22] are versatile intermediates in many reactions and natural products that reacts with numerous nucleophiles like organometallics and provides completely different products with different selectivity, it depends on the reagents and conditions used for the reaction. The attack of organometallics on carbonyl compounds gives products alcohols by nucleophilic ring opening of epoxides or by rearrangement reaction. In study of the organocuprate reagents a lot

of attention has been given on developing Gilman reagents, which are potentially valuable species obtained from organolithium reagents that remains to be investigated [23]. The reactivity of cuprate chemistry is sometimes sacrificed to some extent relative to its analogue homocuprates R_2CuLi [24-26], throughout the study of the course of reaction of the most strongest higher order cynocuprates. The aryl substituted cycloalkenes are formed from cycloalkanones by the nucleophilic addition of an aryl or alkyl Grignard reagents followed by removal of water molecule. The resulting alkenes formed by this strategies are important reactants for asymmetric epoxidation process [27-30]. For the preparation of the chiral secondary alcohols by the enantioselective and regioselective addition of organozinc reagents like alkylzinc to the aldehyde is convenient and most practical method [31-33] that is usually utilized in the organometallic chemistry. Moreover, the Grignard reagents acts a nucleophiles in ring opening of chiral epoxides and it is one of the most effective and economical protocol for the synthesis of optically active alcohols with high enantiomeric purity [34].

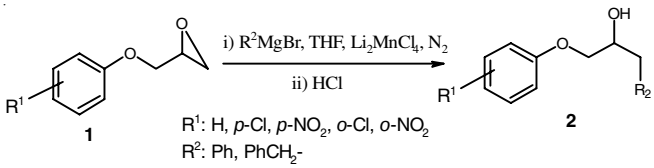
EXPERIMENTAL

The boiling points were determined are uncorrected. IR spectra were determined on a Shimadzu Miracle 10 ATR instrument. ^{1}H NMR spectra were recorded on a Bruker 500 MHz spectrometer with $CDCl_3$ as a solvent and TMS as the internal standard. ^{13}C NMR spectra were recorded on Brucker 125 MHz spectrometer with $CDCl_3$ as the solvent. Column chromatography was conducted on silica gel 60 (70-230 mesh). Thin layer chromatography (TLC) was carried out on aluminium sheets precoated with silica gel.

Preparation of Li_2MnCl_4 solution: In a 500 mL round bottom flask were added LiCl (1 M, 21.197 g) and $MnCl_2$ (1 M, 31.4610 g) and dried under vaccum at 250 °C for about 2 h and the mixture were allowed to cool at room temperature followed by addition of 250 mL dry THF. The resulting solution kept under stirring overnight at room temperature resulting homogeneous solution of Li_2MnCl_4.

Preparation of Grignard reagent: In a 500 mL three necked round bottom flask previously dried with heating gun and flushed with nitrogen gas were added magnesium turnings (6.07 g) and diethyl ether (250 mL), to which added iodine to initiate the reaction followed by addition of aryl bromide (39.2520 g) drop-wise through septum. After the complete addition of aryl halide the mixture were stirred at room temperature for about 1 h to get homogenious 1 M solution of Grignard reagent.

Addition of Grignard reagent to epoxide: In a 100 mL three necked round bottom flask were added epoxide (10 mmol) and charged dry THF (25 mL), Li_2MnCl_4 solution (10 mmol) followed by dropwise addition of Grinard reagent (11 mmol) at room temperature, after complete addition of Grignard reagent the progress of the reaction were studied by thin layer chromatography (TLC) and reaction were quenched with dil. HCl and stirred for 15 min. The product were extracted with diethylether (10 mL × 3) and dried over anhydrous sodium sulphate (**Scheme-I**).



Scheme-I: Addition of Grignard reagent to epoxides

1-Phenoxy-3-phenylpropan-2-ol (2a): Liquid, m.f.: $C_{15}H_{16}O_2$, IR (KBr, ν_{max}, cm^{-1}): 2970, 1600, 1110, 3600, ^{1}H NMR (500 MHz, $CDCl_3$), δ ppm, 6.90 (m, *J* = 8, 2.5 & 1 Hz, 2H), 7.2 (m, *J* = 8, 2.5 & 1 Hz, 2H), 6.93 (m, *J* = 8, 2.5 & 1 Hz, 1H), 7.15 (m, *J* = 7.5, 2.0 & 1 Hz, 2H), 7.22 (m, *J* = 7, 2 & 1 Hz, 2H), 7.1 (m, *J* = 7, 2 & 1 Hz, 1H), 4.1 (d, *J* = 7 Hz, 2H), 4.35 (m, *J* = 7 Hz, 1H), 2.8 (d, *J* = 7 Hz, 2H), 1.60 (s, 1H), ^{13}C NMR (125 MHz, $CDCl_3$), δ ppm, 158.5, 115, 129, 121.2, 72.9, 70.2, 42.5, 138.8, 130.1, 129.2, 127.

1-(4-Chlorophenoxy)-3-phenylpropan-2-ol (2b): Yellow liquid, m.f.: $C_{15}H_{15}O_2Cl$, IR (KBr, ν_{max}, cm^{-1}): 2974, 1610, 1100, 3600, 650, ^{1}H NMR, (500 MHz, $CDCl_3$), δ ppm, 6.80 (d, *J* = 7.5 Hz, 2H), 7.25 (d, *J* = 7.5 Hz, 2H), 7.12 (m, *J* = 8, 2.5 & 1 Hz, 2 H), 7.22 (m, *J* = 8, 2.5 & 1 Hz, 2 H), 7.17 (m, *J* = 8, 2.5 & 1 Hz, 1H), 3.92 (d, *J* = 7 Hz, 2H), 4.35 (m, *J* = 7.0 Hz, 1H), 2.60 (d, *J* = 7 Hz, 2H), 1.63 (s, 1H), ^{13}C NMR (125 MHz, $CDCl_3$), δ ppm, 157, 115.7, 129.3, 126.5, 138.2, 131.4, 130, 127.6, 72.5, 70.10, 42.8.

1-(4-Nitrophenoxy)-3-phenylpropan-2-ol (2c): Liquid, m.f.: $C_{15}H_{15}NO_4$, IR (KBr, ν_{max}, cm^{-1}): 2978, 1596, 1110, 3650, 1350, ^{1}H NMR (500 MHz, $CDCl_3$), δ ppm, 7.10 (d, *J* = 8 Hz, 2H), 7.97 (d, *J* = 8 Hz, 2 H), 7.05 (m, *J* = 8, 2.5 & 1 Hz, 2H), 7.18 (m, *J* = 8, 2.5 & 1 Hz, 2H), 6.95 (m, *J* = 8, 2.5 & 1 Hz, 1H), 4.10 (d, *J* = 7 Hz, 2 H), 4.46 (m, *J* = 7 Hz, 1H), 2.85 (d, *J* = 7 Hz, 2 H), 1.20 (S, 1H). ^{13}C NMR (125 MHz, $CDCl_3$), δ ppm, 164.40, 114.9, 127.3, 142.1, 138, 130.2, 129.7, 127.5, 73, 71.3, 43.2.

1-(2-Chlorophenoxy)-3-phenylpropan-2-ol (2d): Pale yellow liquid, m.f.: $C_{15}H_{15}O_2Cl$, IR (KBr, ν_{max}, cm^{-1}): 2970, 1590, 1110, 3600, 640, ^{1}H NMR (500 MHz, $CDCl_3$), δ ppm, 7.22 (m, *J* = 8, 2.5 & 1.5 Hz, 1H), 6.80 (m, *J* = 8 & 2.5 Hz, 1H), 7.01 (m, *J* = 8 & 2.5 Hz, 1H), 6.65 (m, *J* = 8, 2.5 & 1.5 Hz, 1H), 7.17 (m, *J* = 8, 2.5 & 1 Hz, 2H), 7.24 (m, *J* = 8, 2.5 & 1 Hz, 2H), 7.16 (m, *J* = 8 & 2.5 Hz, 1H), 4.27 (d, *J* = 7 Hz, 2H), 4.46 (m, *J* = 7 Hz, 1H), 2.85 (d, *J* = 7.0 Hz, 2H), 1.47 (S, 1H), ^{13}C NMR (125 MHz, $CDCl_3$), δ ppm, 155.32, 124.8, 130.9, 123.7, 128.4, 116.7, 73.1, 70.3, 42.6, 138, 130.12, 129, 127.

1-(2-Nitrophenoxy)-3-phenylpropan-2-ol (2e): Yellow liquid, m.f.: $C_{15}H_{15}NO_4$, IR (KBr, ν_{max}, cm^{-1}): 2900, 1620, 1100, 3600, 1350, ^{1}H NMR (500 MHz, $CDCl_3$), 7.98 (m, *J* = 8, 2.5 & 1.5 Hz, 1 H), 7.16 (m, *J* = 8 & 2.5 Hz, 1H), 7.5 (m, *J* = 8 & 2.5 Hz, 1H), 7.08 (m, *J* = 8, 2.5 & 1.5 Hz, 1H), 7.14 (m, *J* = 8, 2.5 & 1.5 Hz, 2H), 7.21 (m, *J* = 8, 2.5 & 1.5 Hz, 2H), 7.11 (m, *J* = 8 & 2.5 Hz, 1H), 4.01 (d, *J* = 7 Hz, 2H), 4.43 (m, *J* = 7 Hz, 1H), 2.60 (d, *J* = 7 Hz, 2H), 1.52 (S, 1H), ^{13}C NMR (125 MHz, $CDCl_3$), δ ppm, 155.5, 137.3, 127.96, 121.7, 135, 118, 138.9, 130.6, 129.7, 127.3, 73.6, 70.4, 42.3

1-Phenoxy-4-phenylbutan-2-ol (2f): Liquid, m.f.: $C_{16}H_{18}O_2$ IR (KBr, ν_{max}, cm^{-1}): 2972, 1600, 1110, 3650, 1H NMR (500 MHz, $CDCl_3$), δ ppm, 6.8 (m, *J* = 8, 2.5 & 1 Hz,

2H), 7.22 (m, *J* = 8, 2.5 & 1 Hz, 2H), 6.9 (m, *J* = 8 & 2.5 Hz, 1H), 7.1 (m, *J* = 8, 2.5 & 1 Hz, 2H), 7.25 (m, *J* = 8, 2.5 & 1 Hz, 2H), 7.17 (m, *J* = 8 & 2.5 Hz, 1H), 3.73 (d, *J* = 7 Hz, 2H), 4.0 (m, *J* = 7 Hz, 2H), 1.8 (q, *J* = 7 Hz, 2H), 2.6 (t, *J* = 7 Hz, 2H), 1.09 (S, 1H), 13C NMR (125 MHz, $CDCl_3$), δ ppm, 158.9, 115.6, 129.6, 121.2, 141.7, 128.7, 128.9, 126.3, 74.2, 69, 34.8, 34.4.

1-(4-Chlorophenoxy)-4-phenylbutan-2-ol (2g): Yellow liquid, m.f.: $C_{16}H_{17}O_2Cl$, IR (KBr, ν_{max}, cm^{-1}): 2900, 1610, 1100, 3600, 650, ^1H NMR (500 MHz, $CDCl_3$), δ ppm, 6.77 (dd, *J* = 8 Hz, 2H), 7.24 (dd, *J* = 8 Hz, 2H), 7.19 (m, *J* = 8, 2.5 & 1.5 Hz, 2H), 7.27 (m, *J* = 8, 2.5 & 1.5 Hz, 2H), 7.14 (m, *J* = 8 & 2.5 Hz, 1H), 3.95 (d, *J* = 7 Hz, 2H), 4.05 (m, *J* = 7 Hz, 1H), 1.86 (q, *J* = 7 Hz, 2H), 2.56 (t, *J* = 7 Hz, 2H), 1.06 (S, 1H), ^{13}C NMR (125 MHz, $CDCl_3$), δ ppm, 157, 115, 129.2, 126.4, 141.7, 128.6, 128, 126.5, 74.1, 69.3, 34.2, 34.6.

1-(4-Nitrophenoxy)-4-phenylbutan-2-ol (2h): Yellow Liquid, m.f.: $C_{16}H_{17}NO_4$, IR (KBr, ν_{max}, cm^{-1}): 2974, 1600, 1100, 3600, 1350, ^1H NMR (500 MHz, $CDCl_3$), δ ppm, 7.11 (dd, *J* = 8 Hz, 2H), 8.01 (dd, *J* = 8 Hz, 2H), 6.9 (m, *J* = 8, 2.5 & 1.5 Hz, 2H), 7.06 (m, *J* = 8, 2.5 & 1.5 Hz, 2H), 7.18 (m, *J* = 8 & 2.5 Hz, 1H), 4.2 (d, *J* = 7 Hz, 2H), 3.26 (m, *J* = 7 Hz, 1H), 1.9 (q, *J* = 7 Hz, 2H), 2.65 (t, *J* = 7 Hz, 2H), 1.40 (S, 1H), ^{13}C NMR (125 MHz, $CDCl_3$), δ ppm, 164.4, 115, 128.7, 142, 141.6, 128.4, 129, 127, 75, 72, 34.6, 34.1.

1-(2-Chlorophenoxy)-4-phenylbutan-2-ol (2i): Liquid, m.f.: $C_{16}H_{17}O_2Cl$, IR (KBr, ν_{max}, cm^{-1}): 2970, 1594, 1050, 3600, 620, 1H NMR (500 MHz, $CDCl_3$), δ ppm, 7.3 (m, *J* = 8, 2.5 & 1 Hz, 1H), 6.95 (m, *J* = 8 & 2.5 Hz, 1H), 7.2 (m, *J* = 8 & 2.5 Hz, 1H), 6.85 (m, *J* = 8, 2.5 & 1 Hz, 1H), 7.17 (m, *J* = 8, 2.5 & 1.5 Hz, 2H), 7.2 (m, *J* = 8, 2.5 & 1.5 Hz, 2H), 7.15 (m, *J* = 8 & 2.5 Hz, 1H), 4.3 (d, *J* = 7 Hz, 2H), 4.12 (m, *J* = 7 Hz, 1H), 1.7 (q, *J* = 7 Hz, 2H), 2.5 (t, *J* = 7 Hz, 2H), 1.46 (S, 1H), ^{13}C NMR (125 MHz, $CDCl_3$), δ ppm, 155, 124.6, 130.9, 123.7, 128.4, 116.2, 142, 129, 18.9, 126.6, 74.7, 69, 34.7, 34.5.

1-(2-Nitrophenoxy)-4-phenylbutan-2-ol (2j): Yellow liquid, m.f.: $C_{16}H_{17}NO_4$, IR (KBr, ν_{max}, cm^{-1}): 2970, 1604, 1100, 3650, 1350, ^1H NMR (500 MHz, $CDCl_3$), δ ppm, 7.98 (m, *J* = 7.5, 2 & 1.5 Hz, 1H), 7.17 (m, *J* = 7.5 & 2 Hz, 1H), 7.57 (m, *J* = 7.5 & 2 Hz, 1H), 7.08 (m, *J* = 7.5, 2 & 1.5 Hz, 1H), 7.18 (m, *J* = 8, 2.5 & 1.5 HZ, 2H), 7.26 (m, *J* = 8, 2.5 & 1.5 Hz, 2H), 7.14 (m, *J* = 8 & 2.5 Hz, 1H), 3.92 (d, *J* = 7 Hz, 2H), 4.17 (m, *J* = 7 Hz, 1H), 1.75 (q, *J* = 7 Hz, 2H), 2.55 (t, *J* = 7 Hz, 2H), 1.59 (S, 1H), ^{13}C NMR (125 MHz, $CDCl_3$), δ ppm, 155.2, 137.6, 127.9, 121.7, 135, 118, 142, 128.6, 129, 126.3, 76, 71.5, 35.1, 34.9.

RESULTS AND DISCUSSION

In order to justify the importance of solvent in this method, the reaction were performed in the absence of Li_2MnCl_4 wherever within the reaction it needs longer time and poor yields (Table-1). The reactions were performed in the presence of Li_2MnCl_4 and various solvents like diethylether, THF and 1,4-dioxane where in the reaction it results totally different yields and good regioselectivity. It has been found that substituted epoxides gives different results with different Grignard reagents in the presence of homogenious solution of Li_2MnCl_4 (Table-1). The ratio of the reactants to the Grignard reagents used were 1:1.1. The nucleophilic attack of Grignard reagent were occured at less substituted side of epoxides to give alcohols as the final products (Table-2). It has also been observed that the different regioselectivity obtained in absence of Li_2MnCl_4 reagent and mixture of products were formed.

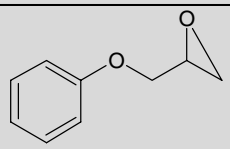
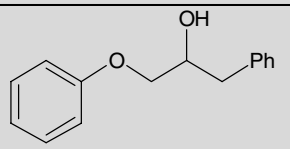
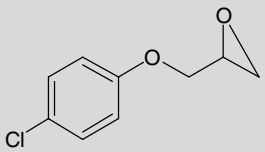
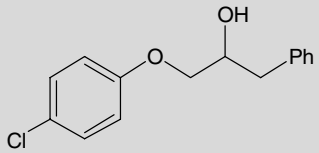
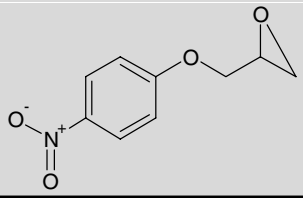
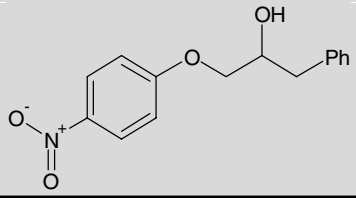
TABLE-1
EFFECTS OF SOLVENTS IN THE SYNTHESIS OF COMPOUNDS **2a** AND **2f**

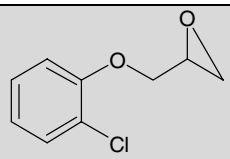
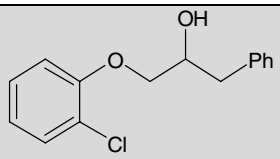
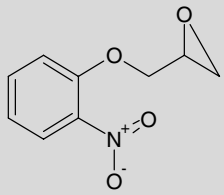
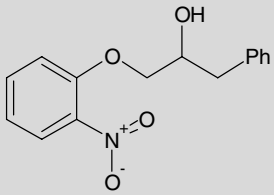
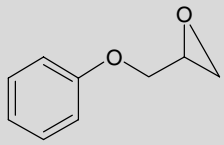
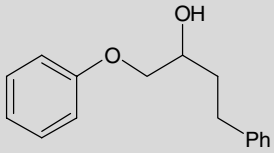
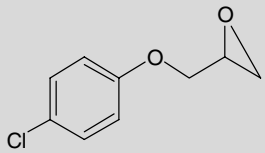
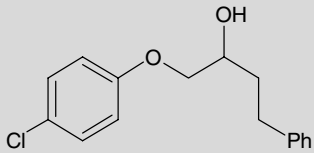
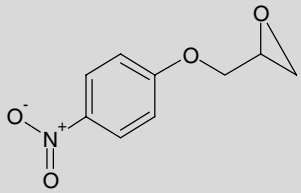
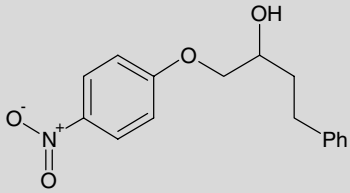
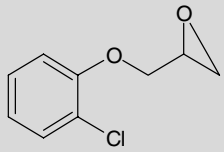
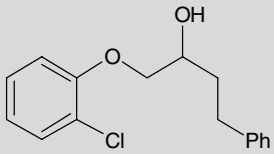
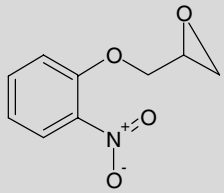
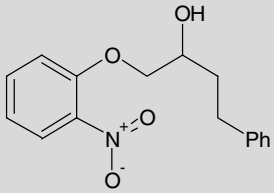
Entry	Reagent	Solvent	Time (min)		Yield (%)	
			2a	**2f**	**2a**	**2f**
1	Li_2MnCl_4	THF	30	25	72	70
2	Li_2MnCl_4	Diethyl ether	30	28	70	75
3	Li_2MnCl_4	1,4-Dioxane	35	30	65	67
4	–	THF	45	40	52	45
5	–	Diethyl ether	48	35	48	50
6	–	1,4-Dioxane	60	35	40	42

Conclusion

It is found that addition of Grignard reagents to the varied substituted epoxides in presence of dilithium tetrachloro-

TABLE-2
SYNTHESIS OF COMPOUNDS **2a-j**

Entry	Reactant	Product	Time (min)	Yield (%)
2a			30	72
2b			35	69
2c			40	65

2d			42	60
2e			48	58
2f			25	70
2g			30	67
2g			35	64
2i			45	65
2j			60	61

manganate reagent for transmetallation under nitrogen atmosphere that results in excellent yields. The easy work up of reaction, high yields and short time for reaction makes this reagent a more convenient alternative to the reported methods.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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