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BORON FLUORIDE PROMOTED OPENING OF EPOXIDES BY ORGANOCOPPER AND CUPRATE REAGENTS

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Abstract - In the presence of BF_3 the reaction rate of organocopper and cuprate reagents with poorly reactive epoxides is dramatically enhanced. Lithium organocuprates are the best choice among the various organocopper and cuprate reagents tested. Even the dimesityl cyanocuprate is able to react with cyclohexene oxide in excellent yield. No products of cationic rearrangements are observed. The reaction with various epoxides shows a complete stereochemical (pure anti opening) and regiochemical control (attack on the less hindered side of the epoxide).

INTRODUCTION -

Nucleophilic opening of epoxides is an important reaction in synthetic organic chemistry[1]. And among the organometallic reagents used in this reaction, the organocopper ones are known as the most efficient to accomplish this transformation in a highly chemo- stereoselective manner[1,2]. Although very reactive towards epoxides, the main inconvenience in the use of organocopper derivatives lies in their thermal instability which necessitates an excess of reagent per epoxide (whenever it is a poorly reactive one). This inconvenience was partly overcome by organocopper reagents of greater thermal stability[3] or of enhanced reactivity[2c]. Dealing with the latter approach, we briefly described in a preliminary note the exceedingly higher reactivity of $RCu.BF_3$ and $R_2CuLi.BF_3$ reagents[4] and we report herein our full results.

Y. Yamamoto et al were first to demonstrate the enhanced reactivity of organocopper reagents, associated with a strong Lewis acid, towards conjugated enones[5] and their selective S_N2' attack on allylic halides[6]. Our contribution in this field concerned their reactivity towards the ether linkage of epoxides, acetals and orthoesters[7].

Since our preliminary note[4], Ganem et al published analogous results on epoxides with RLi/BF_3[8] whereas Lipschutz et al confirmed ours with $(thienyl)RCuCNLi_2/BF_3$[9].

CHOICE OF REAGENTS

The term "organocopper derivatives" covers a plethora of reagents[10] according to :
- the ratio of RM to CuX
- the nature of the main group organometallics (Mg, Li)

- the nature of the copper salt (CuI, CuBr, CuCN, CuSPh, Cu-C≡C-R, etc...)
- the presence or absence of main group metal salt.

Their reactivity towards epoxides has already been scrutinely examined, particularly towards cyclohexene oxide, a striking example of a poorly reactive one[10-16]. We also chose this epoxide to test the influence of added $BF_3.Et_2O$ under two experimental conditions :

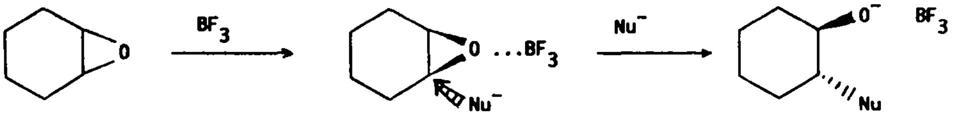
- *Procedure A* :

According to Yamamoto's procedure[6,7], we added, at -78°C, one equivalent of $BF_3.Et_2O$ to one equivalent of Bu_2CuLi (prepared from 2 BuLi, LiBr and $CuBr.Me_2S$, in Et_2O). After 5min, the epoxide (1eq.) is introduced into this mixture.

- *Procedure B* :

The epoxide (1eq.) is mixed with the Bu_2CuLi solution, in Et_2O, at -78°C, temperature at which no reaction takes place. After 5min, 1eq. of $BF_3.Et_2O$ is added to this mixture.

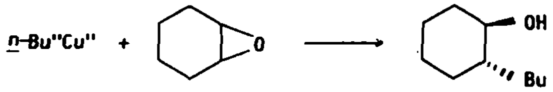
Both procedures gave exactly the same result which is compared in table I with the previous ones obtained without BF_3 added. It clearly appears that a dramatic enhancement of the reaction rate occurs in the presence of BF_3. The exact role of BF_3 cannot be actually ascertained, but two hypothetical pathways may be envisioned. According to Y. Yamamoto[6], a copper borate is formed when RCu or R_2CuLi and BF_3 are mixed together. This new reagent would be, then, highly reactive towards epoxides. A similar pathway was also favored by M. Yamaguchi[17] in the reaction of $RC{\equiv}CLi/BF_3$ with epoxides. On the other hand, the role of BF_3 could be restricted to a simple electrophilic assistance to the opening of the epoxide, the cuprate acting therafter as a simple nucleophile. This pathway is also favored by B. Ganem[8] in the reaction of RLi/BF_3 with epoxides. This latter process would be compatible with the fact that procedure B, in which no copper borate is preformed, is as efficient as procedure A.



Whatever the exact mechanism, no purely electrophilic pathway can be envisioned since the reaction is totally stereoselective, the epoxide being opened by a purely anti process[18] (only the trans 2-alkyl cyclohexanol is obtained). The electrophilic role of BF_3 should, therefore, be concerted with the action of the nucleophile which undergoes a normal SN_2 displacement. The combination of R"Cu" and BF_3 may be viewed as an "amphophilic" reagent in the same manner as R_3Al, which is a Lewis acid as well as a nucleophile[19].

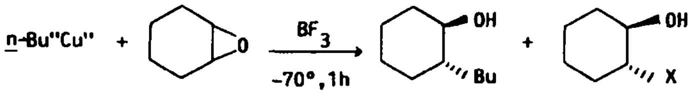
As indicated in table II, the association of BF_3 to various organocopper derivatives enhances dramaticaly their reactivity towards cyclohexene oxide. Carefull examination of this table shows that cyanocuprates (entries 10, 11 and 12) are the most suitable reagents for the most efficient transfer of a nBu group. Another point of interest is shown in entries 6, 7, 8, 9, 10 and 15 with the presence of halohydrins as side products (no 2-cyano-cyclohexanol was observed in any experiment). Indeed, the competitive action of halide ion was noted as the primary source of side reactions. A more striking example of this fact is illustrated by the different behaviour of organocuprate (entry 7) and organocopper (entry 6) reagents where the halohydrin is largely the predominent product (in the latter case).

Table I -



Entry	Reagent	Stoichiometry BuM/ CuX/ Epoxide			Solvent	Temp. °C	Time h	Isolated Yield %	Ref
1	Bu_2CuLi,BF_3	2	1	1	Et_2O	-78°	0.5	83	this work
2	Bu_2CuLi	10	5	1	Et_2O	+25°	4	60	Johnson[11]
3	BuCuCNLi	2	2	1	Et_2O	0°	5	66	Acker[12]
4	$Pr(2\text{-}Th)Cu(CN)Li_2$	2.2	1.1	1	THF/Et_2O	0°	1	55	Lipshutz[13c]
5	BuMgCl/ CuI	1.5	0.15	1	THF	0°	2	58	Linstrumelle[14]

Table II -



Entry	Organocopper reagent	Solvent	Salt present	Yield[a] %	Side Products (halohydrins)	
6	BuCu[b]	Et_2O	2 LiBr	5	X=Br	82%
7	Bu_2CuLi[c]	Et_2O	2 LiBr, 1 LiI	80	X=I X=Br	12% 2%
8	Bu_2CuLi[d]	Et_2O	3 LiBr	83	X=Br	4.5%
9	Bu_2CuLi[e]	THF	3 LiBr, 1 LiCl	78	X=Br	20%
10	$Bu_2CuCNLi_2$[f]	Et_2O	2 LiBr	79	X=Br	1%
11	$Bu_2CuCNLi_2$	Et_2O	none	88	-	
12	$Bu_2CuCNLi_2$	THF	none	87	-	
13	BuCuCNLi	Et_2O	none	52	-	
14	BuCuCNLi	THF	none	40	-	
15	$Bu_2CuCNMg$[g]	THF	1 LiCl, 1 $MgCl_2$	54	X=Cl	28%

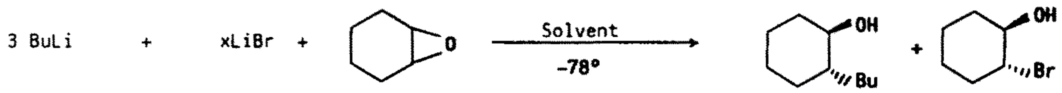
a : Yield of isolated 2-butyl cyclohexanol ; b : BuLi,LiBr + $CuBr.Me_2S$; c : 2 BuLi,LiBr + CuI
d : 2 BuLi,LiBr + $CuBr.Me_2S$; e : 2 BuLi, LiBr + CuBr,LiCl ; f : 2 BuLi,LiBr + CuCN
g : 2 BuMgCl + CuCN,LiCl

The main conclusion of these experiments is that the amount of halide ion should be minimized as much as possible. This result may be attained by acting on the two partners which generate the organocopper derivative.

1/ The copper source. CuCN is the most suitable to this purpose and is prefered to other salts, such as Cu-C≡C-R[20], due to its easy availability and low cost. CuSR, CuOR, $CuNR_2$ and $CuPR_2$ were not suitable candidates due to their known nucleophilicity or their difficult accessibility[3].

2/ The lithium reagent. This reagent is devoided of lithium salt when prepared in hexane or in Et_2O from Li metal and R-Cl ; the formed LiCl precipitates out of solution.

This halide ion problem may be dramatically illustrated in Ganem's procedure[8] (RLi/BF_3 + epoxide), where we carried out the reaction purposely in the presence of lithium bromide :



x = 0	Et_2O	65% isolated	-
0	THF	97% ref. 8	
3	Et_2O	2%	98%
3	THF	5%	78%

In the absence of LiBr (BuLi in hexane) the reported yield is 97% (in THF), whereas in the presence of LiBr (as we did) almost the exclusive formation of halohydrin is observed.
The synthetic potential of such a preparation of halohydrins (under anhydrous conditions) is currently under study.

In this context it is evident that organocuprate reagents are less sensitive to the presence or absence of halide ion. In entry 8 (table II) a 83% yield of 2-butyl cyclohexanol is obtained with only one equivalent of organocuprate (2eq. of organolithium reagent) and in the presence of 3eq. of lithium bromide.

SCOPE AND LIMITATIONS -

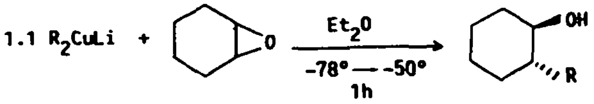
1/ Organocopper reagent

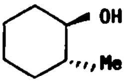
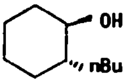
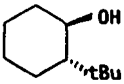
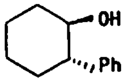
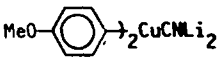
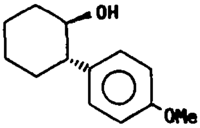
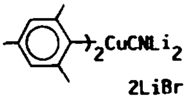
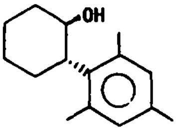
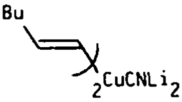
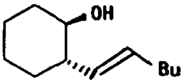
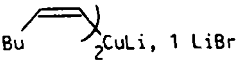
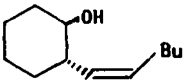
Having stated the experimental conditions for the best transfer of a butyl cuprate derivative to cyclohexene oxide, we turned our attention to the transferability of various organic groups to the same epoxide. The poor reactivity of this epoxide is again an excellent model system for such a study. These results are shown in table III.

Dimethyl cyanocuprate (entry 16) reacts as well as dibutyl cyanocuprate, affording in high yield (85%) trans -2 methyl-1-cyclohexanol (80% yield with $Me_2CuLi,3LiBr/BF_3$). This same product was obtained, in the absence of BF_3, in modest yield after 2-15h reaction time at room temperature[15].

Diphenyl cyanocuprate (entry 19) is also very reactive (92% isolated yield). Surprisingly, in this case, competition from LiBr does not take place, since the bromohydrin in totally absent, although the PhLi used contained one eq. of LiBr. It should be noted that aryl copper or cuprate reagents were considered as the least reactive organic groups, toward epoxides[13b]. Functionalized aryl cuprates, such as p-anisyl (entry 20), behave similarly (92% yield). The

Table III -



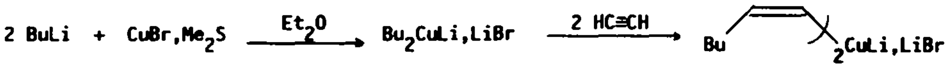
Entry	Cuprate	Product [a]	Isolated yield	Side Product (by g.l.c.)
16	$Me_2CuCNLi_2$		85%	-
17	$nBu_2CUCNLi_2$		88%	-
18	$tBuCuCNLi$ [b]		78%	Cyclohexanol (1%)
19	$Ph_2CuCNLi_2$, 2 LiBr		92%	-
20			92%	-
21	 2LiBr		87%	2-bromocyclohexanol(4%)
22			81%	-
23			59%	2-Bromocyclohexanol(15%)

a : Procedure B was used in all cases

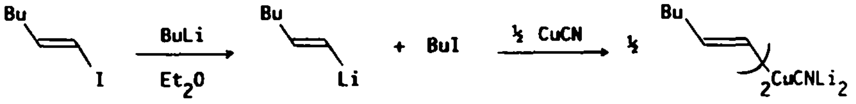
b : The reaction is run with the cyanocopper reagent

generation of the p-anisyl lithium reagent from p-iodo anisole, by metal-halogen exchange, was performed with one eq. of nBuLi (which generates one eq. of nBuI) rather than 2 eq. of tBuLi (which generates one eq. of LiI). Competition from halide ion (4% halohydrin) appears in the case of dimesityl cyanocuprate (entry 21), one of the most sterically demanding aryl groups. Nevertheless, an excellent yield of mesityl cyclohexanol is again obtained. It should be recalled that the mesityl group was considered so inert that it was recommended as a non-transferable ligand [21].

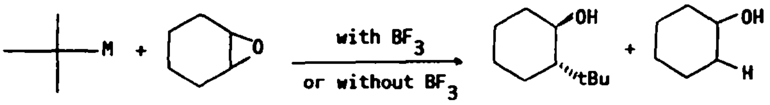
On the other hand, Z-alkenyl cuprates, compete less efficiently with bromide ion, and a 85/15 mixture of Z-hexenyl-cyclohexanol and bromo-cyclohexanol is produced (entry 23). These Z-dialkenyl cuprates are directly prepared by carbocupration of acetylene[22] :



A better yield of alkenyl cyclohexanol may be obtained if halide ion is totally absent, as examplified with E-hexenyl cyanocuprate (entry 22) :

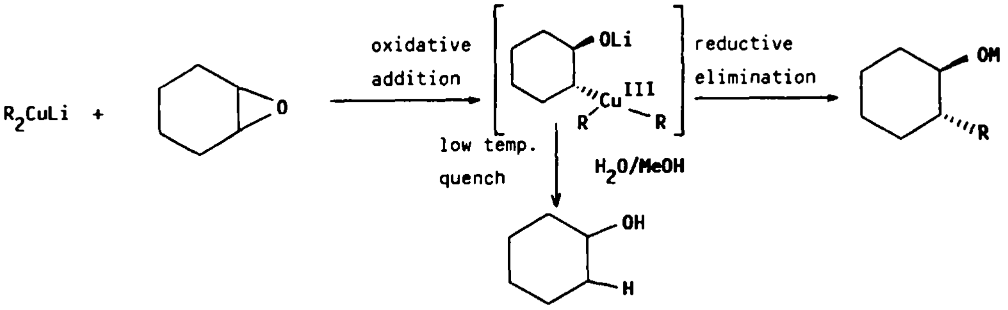


Finally, the transfer of a t-butyl group was best performed with t-butyl cyano copper reagent (78% yield), instead of a cuprate reagent. Indeed, with this last reagent, an important side reaction takes place, *viz* the reduction of cyclohexene oxide to cyclohexanol. This side reaction was therefore studied in more details.



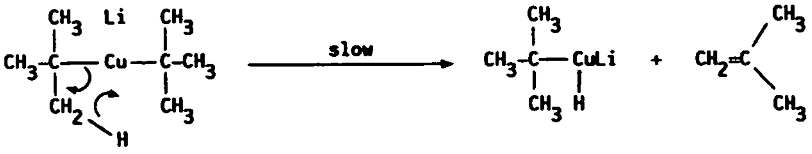
As seen in table IV, when the reaction was performed in Et$_2$O with di-t-butyl cyanocuprate at low temperature (with BF$_3$) and quenched at low temperature (entry 26), a high yield of reduction product was obtained. On the other hand, when BF$_3$ is added at higher temperature (-30°) (entry 27) a much lower proportion of the reduction product, cyclohexanol, is produced. t-Butyl cyclohexanol is isolated in 65% yield. This behaviour is not due to the type of cuprate used, since cyanocuprates and more classical cuprates behave similarly (entry 29). Nor is it due, at first sight, to the presence of BF$_3$, since cyano cuprates, without BF$_3$, also afford mainly this reduction product (entry 30), though the reaction is very slow.

A plausible rationalization of these results may be found in the postulated mechanism of organocopper reagents opening of epoxides[11] :



After the oxidative addition, the copper^{III} intermediate collapses by reductive elimination to the desired product. However, if the copper^{III} intermediate does not collapse fast enough, it should be possible to quench it at low temperature. Unfortunately this hypothesis is not withstanding with the fact that attempted deuterolysis (AcCl/D$_2$O) did not afford any of deuterated cyclohexanol. The reductive elimination is too fast a process.

It is more likely that di-t-butyl cuprate , decomposes slowly, even at low temperature, to a hydride species which is responsible for the reduction product[2a,10].



At low temperature, the bulkiness of the t-butyl group, does not allow an easy nucleophilic attack by the copper atom, and the slow process of decomposition to a hydrido-copper species takes place. This last species is able, even at low temperature, to react with the epoxide, with preferential transfer of the hydride moiety instead of the t-butyl group.

This hypothesis is corroborated by the following facts.

It is known that when t-butyl lithium is added, at -78°C, to a THF solution of trialkyl borane, a lithium trialkyl borate is obtained, indicating a decomposition of the t-butyl group to isobutylene and a hydride moiety[23-25].

Table IV -

Entry	$+$M		Solvent	Experimental Procedure	Reac. Conditions		Yield[a] Substitution	Reduction
24	—Li	BF_3	Et_2O	A	-80°	30min	18%	60%
25	—Li	BF_3	THF	A	-80°	1h	2%	98%
26	$+_2CuCNLi_2$	BF_3	Et_2O	B	-78°	1h	6%	85%
27	$+_2CuCNLi_2$	BF_3	Et_2O	B	-30°	15min	76%(65%)	22%
28	$+_2CuCNLi_2$	BF_3	THF	B	-30°	15min	72%	28%
29	$+_2$CuLi,LiCl	BF_3	Et_2O	B	-60°	1h	24%	54%
30	$+_2CuCNLi_2$	-	Et_2O	-	-78° to +20°	12h	10%	50%
31	—CuCNLi	BF_3	Et_2O	B	-78° to -60°	30mn	89%(78%)	1%

a : Yield determined by glpc (Carbowax 20M) using n-hexadecane as internal standard. Yields in parentheses are isolated ones

This process seems to occur also with BF_3 at a low enough temperature, so that the usual disproportionation :

$$4\ HLiBF_3 \longrightarrow LiBH_4 + 3\ LiBF_4$$

does not take place. Indeed, mixing of t-butyl lithium and BF_3, at -110°C, in THF followed by addition of cyclohexene oxide afforded almost exclusively ($>$98%) cyclohexanol (entry 25).

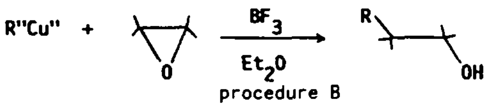
A similar but less pronounced result is obtained in Et_2O solvent (entry 24). With diterbutyl cyanocuprate the same trend is observed, at low temperature (entry 26), as well as with the "classical" cuprate reagent (entry 29). At higher temperature, in Et_2O or THF, the transfer of the terbutyl group becomes a competitive process and both alkylated (terbutyl cyclohexanol) and reduced products (cyclohexanol) are present (entries 27 and 28). Finally t-butyl cyano copper (entry 31) in Et_2O is completely insensitive to this decomposition process and a high yield of t-butyl cyclohexanol is obtained. This last reagent does not seem to form ate complexes fast enough with BF_3, the promoter of this decomposition process.

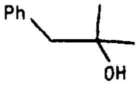
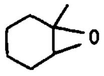
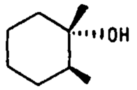
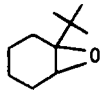
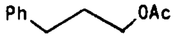
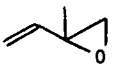
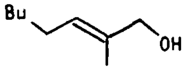
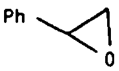
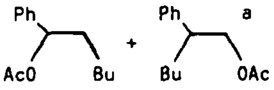
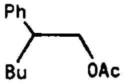
It should be noted that the combination $tBuLi/BF_3$ results in a highly reactive reagent for the reduction of epoxides to alcohols. This method of reduction appears particularly competitive with presently known methods[26], and is currently under study.

2 - Epoxide

The BF_3 promoted opening of epoxides by organocopper reagents was also examined towards a variety of epoxides (see table V). And each epoxide was chosen to test a specific goal. We have seen with cyclohexene oxide that the reaction was totally stereoselective, with an anti opening of the epoxide, the one which is always observed with organocopper reagents. Isobutene oxide (entry 32) was chosen to test the regioselectivity of the reaction knowing

Table V -



Entry	R"Cu"	Epoxide	Reac.cond.	Product	Isolated yield
32	$Ph_2CuCNLi_2,2LiBr$		-78° to -65° 30mn		93%
33	$Me_2CuCNLi_2$		-78° to -70° 30mn		55%
34	$Bu_2CuCNLi_2$		-78° to +20° 24h	-	0%
35	$Ph_2CuCNLi_2,2LiBr$		-78° to -50° 1h	 a	87%
36	$Bu_2CuCNLi_2$	 b	-78° to -70° 30mn		100%[c]
37	$Bu_2CuCNLi_2$	 b	-78° to -60° 30mn	 a	17%/50%
38	BuCuCNLi(THF)	" b	-78° to -20° 30mn	 a	69%

a : The crude product is acetylated (AcCl, pyridine) before being distilled
b : Reaction run according to procedure A
c : G.C. yield on the crude product

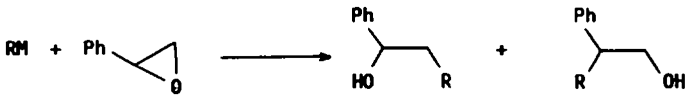
that organocopper reagents prefer to attack the sterically less hindered side of the epoxide[10]. This general trend is followed here again and the expected alcohol is produced in high yield to the exclusion of its isomer, the one which would be obtained through the most stable cation, as is the case with trialkylalanes[27], a typical amphophilic reagent. Methyl cyclohexene oxide (entry 33) illustrates again a regiochemistry problem, but it is also a more sterically demanding case. The reaction with dimethyl cyanocuprate proceeds smoothly and affords 1,2-dimethyl-1-cyclohexanol in 55% yield. However the difference of the steric hindrance of the two epoxidic carbons is more subtile and 10% of isomeric 2,2-dimethyl-1-cyclohexanol are also formed. Thus, the balance between the Lewis acid promoted formation of the most stable cation and the preference of the organocopper reagent for the less hindered site lies largely in favor of the latter. The cationic character of this reaction is seen only with particularly hindered cases.

Even more sterically hindered is t-butyl-cyclohexene oxide (entry 34), which, however, did not react in our hands. Under forcing conditions (-70° to room temperature for 12h) the only obtained products are the ones arising from cationic rearrangement of this epoxide.

Oxetanes are also opened by organocopper reagents[28], and in the presence of BF_3 the reaction rate is again strongly enhanced. A high yield is obtained with only one equivalent of the diphenyl cyanocuprate (entry 35). Increasing now the ring size of the cyclic ether to tetrahydrofuran shows a sharp decrease in the reactivity and a low yield ($<$10%) of ring opened product is isolated, under a variety of conditions. In these reactions, run at higher temperature than usual, we had some trouble during the distillation of the crude product, due to boron impurities (eventually borates). In such cases, and in others when the reaction was run at higher temperature ($>$ -50°C), the crude product was acetylated (AcCl, pyridine) and then distilled without any subsequent problem.

Unsaturated epoxides, such as isoprene oxide or styrene oxide are much more reactive epoxides and they usually react with any kind of organocopper reagent without the assistance of a Lewis acid. However, its presence may alter the regioselectivity of the reaction. For example isoprene oxide may be attacked at the less hindered position or at one of the two allylic positions by an S_N2 or S_N2' process. The latter mode is the one observed without BF_3[29]. The same result is obtained with BF_3 present, before the addition of the epoxide (procedure A) as shown in entry 36 Table V. The stereochemistry of the newly created double bond is also E 95%.

With styrene oxide, where the benzylic position is also the more hindered, a less clearcut result is obtained with the various organocopper and cuprate reagents (without BF_3).



I II

		I	II	
BuCuCNLi	Et_2O	21%	74%	réf. 12
$Bu_2CuCNLi_2$	THF	85%	8%	13
$BuLi,BF_3$	THF	64%	36%	8
Bu_2Mg	Et_2O	-	70%	30

Under our standard conditions (entry 37, Table V), we also obtain a mixture of both alcohols

I and II. The ratio I/II (25/75) indicates a high affinity of our reagent for the softer carbon, the benzylic one despite its greater steric hindrance. The increase of this tendency is attained by using a "softer" reagent *viz* BuCuCNLi[31] and switching to THF as solvent[32]. It is thus possible to obtain only the desired alcohol II (entry 38, Table V), a remarkable result as compared to other combinations of organocopper reagents.

CONCLUSION -

The results presented along these lines widely show the dramatic enhancement of reactivity due to the Lewis acid : BF_3. This increase of reactivity is not obtained at the expense of the stereo- or regioselectivity. Indeed, despite the presence of BF_3, no products of cationic origin are noted. The general applicability of this reaction makes it a useful tool for various syntheses which need a smooth and selective opening of an epoxide.

Acknowlegments - *We thank the C.N.R.S. (UA 473) for financial support.*

EXPERIMENTAL -

^1H NMR spectra were recorded on a Jeol MH100 apparatus ($CDCl_3$; ppm from TMS).
^{13}C NMR on a Jeol FX90Q ($CDCl_3$; ppm from TMS).
IR spectra were obtained on a Perkin Elmer model 457 spectrometer.
GLPC analyses were performed on a Carlo Erba chromatograph model G1 and 2150 using a 3m glass column (10% SE30 on silanized chromosorb G 80/100 mesh or Carbowax 20M) and 25m capillary glass column (OV 101).
The gas chromatograph was coupled to an integrator LTT9400.
All reactions are performed under a nitrogen atmosphere in a 250ml flask equipped with a low temperature thermometer, a mechanical stirrer and a pressure equalized addition funnel.

Et_2O and THF are freshly distilled from sodium benzophenone. Organolithium reagents were prepared in Et_2O or commercially obtained ("salt free" nBuLi or tBuLi solutions in hexane).

$CuBr.Me_2S$ complex was prepared according to ref. 33.

Di n-Butyl cuprate was prepared either from CuI,CuBr or $CuBr.Me_2S$ in Et_2O or THF at -40°C.

Organo cyano cuprate reagents were prepared according to ref. 34.

Di-alkyl cyano cuprate reagents were prepared according to ref. 13a,b.

Di(Z-hexen-1-yl) cuprate was prepared as described in ref. 35 from n-BuLi (hexane solution), $CuBr.Me_2S$ and acetylene.

Commercial $BF_3.Et_2O$ is distilled (E=126°C) and kept under nitrogen.

The following epoxides : cyclohexene oxide, styrene oxide, isobutylene oxide and oxetane are commercially available.

1-t-Butyl cyclohexene oxide[36], 1-methyl cyclohexene oxide[37] and isoprene oxide[38] were prepared according to litterature procedures.

General procedure

To a solution of organocopper or cuprate reagent (31mmol) in 150ml Et_2O (or THF) at -80°C, are slowly added 30mmol of epoxide dissolved in 10ml Et_2O (or THF). Immediately after, a solution of $BF_3.Et_2O$ (4,2ml : 33mmol) in 10ml Et_2O (or THF) is dropwise added (procedure B).

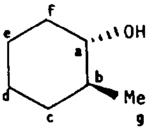
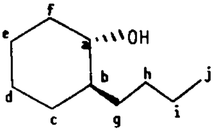
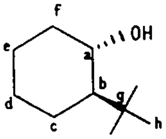
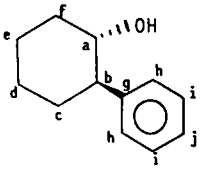
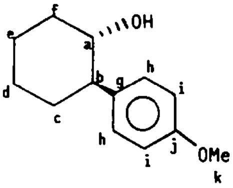
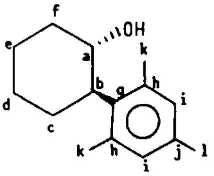
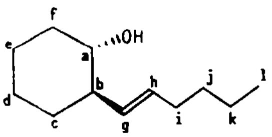
The mixture is usually kept below -70°C for 30min, then the cooling bath is removed. The course of the reaction is followed by GLPC and after completion it is quenched by NH_4Cl/NH_3 aqueous solution and allowed to warm for 30min. Standard extractive workup, and distillation or column chromatography afford pure alcohol.

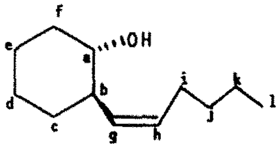
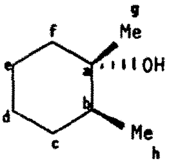
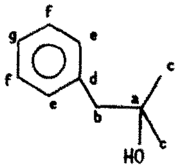
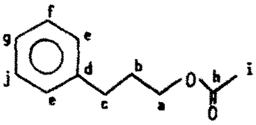
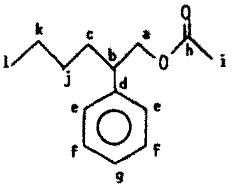
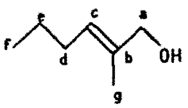
Procedure A (addition of $BF_3.Et_2O$ before addition of epoxide) is used in the case of reactive epoxides (e.g. styrene oxide) which could react with the organocopper reagent in the absence of BF_3.

When acetates are preferred to alcohols, the crude product is dissolved in 50ml pyridine, 5,7ml (60mmol) acetic anhydride are added and the solution is stirred at room temperature overnight. The solution is diluted with 150ml Et_2O, washed with aqueous $NaHCO_3$, then with HCl 1N, dried over $MgSO_4$ and concentrated. Distillation affords pure acetate.

In the case of organolithium reagent (with or without salts, in Et_2O or THF) instead of the organocopper one, the procedure used is exactly the one described in ref. 8.

PHYSICAL AND SPECTROSCOPIC DATA OF THE OBTAINED PRODUCTS

Product	B.p. °C mmHg (Litt.)	n_D^{20} (Litt.)	I.R. cm^{-1}	^{1}H NMR ppm	^{13}C NMR	
	67°/16 (66,7°/12)[39]	1,4612 (1,4616)[39]	3380	3,15(m,1H,Ha) 1,06(s,3H,Hg)	76,4(a) 40,2(b) 35,5(f) 33,7(c)	25,7(d) 25,2(e) 18,6(g)
	59°/0,2 (111-112°/16) ref.40	1,4640 (n_D^{17}=1,4654) ref.40	3370	3,25(m,1H,Ha) 0,92(t,3H,Hj)	74,7(a) 45,1(b) 35,7(f) 31,9(c) 30,2(g)	28,9(h) 25,6(d) 25,0(e) 23,2(i) 14,2(j)
	m.p.=84,5°C (84,4-85°)[41]	-	3340	3,55(m,1H,Ha) 1,02(s,9H,Hh)	73,6(a) 53,8(b) 38,0(f) 33,1(g)	29,3(h) 26,9 (c,d) 26,3 (c,d) 25,3(e)
	m.p.=57,5°C (56-57°)[42]	-	3340 755 700	7,33(s,5H,Hh, Hi,Hj) 3,60(m,1H,Ha) 2,38(m,1H,Hb)	145,5(g) 128,5(i) 127,9(h) 126,5(j) 74,1(a)	53,1(b) 34,5(f) 33,4(c) 26,0(d) 25,1(e)
	m.p.=74° (71-72°)[43]	-	3390 2835 1607	7,22(d,2H,Hh) 6,0(d,2H,Hi) 3,80(s,3H,Hk)	158,5(j) 135,2(g) 128,8(h) 114,2(i) 74,6(a)	55,2(k) 52,4(b) 34,5(f) 29,8(c) 26,2(d) 25,1(e)
	m.p.= 76.5°	-	3400 1610 854	6,84(s,2H,Hi) 4,1(m,1H,Ha) 2,9(m,1H,Hb)) 2,40(s,3H,Hk) 2,31(s,3H,Hk) 2,21(s,3H,Hl)	138,5 (h) 136,1 (h) 135,8(g) 135,0(j) 131,5 (i) 129,7 (i) 71,5(a) 49,3(b)	36,3(f) 29,9(c) 26,8(d) 25,2(e) 21,9 (k) 21,7 (k) 20,6(l)
	a	1,4725	3330 970	5,67(dt,1H,Hh) 5,34(dd,1H,Hg) 3,22(m,1H,Ha) 0,91(t,3H,He) ^{3}Jgh=16Hz ^{3}Jgb=7Hz ^{3}Jhi=8Hz	133,1(g) 132,3(h) 73,1(a) 50,1(b) 33,9(c) 32,4(i)	31,7(j) 25,4(d) 24,9(e) 22,3(k) 13,9(l)

Product	B.p. °C mmHg	n_D^{20}	I.R. cm^{-1}	^{1}H NMR ppm	^{13}C NMR	
	58°C/10^{-2}	1,4755	3390 2990	5,63(dt,1H,Hh) 5,21(dd,1H,Hg) 3,22(m,1H,Ha) 0,91(t,3H,Hl) ^{3}Jgh=11Hz ^{3}Jgb=10Hz ^{3}Jhi=7,5Hz	133,0(g) 131,9(h) 73,8(a) 44,9(b) 33,7(c) 32,9(f)	31,6(j,f) 27,6(i) 25,3(d) 24,9(e) 22,4(k) 14,0(l)
	a	1,4648	3380 1115	1,10(s,3H,Hg) 0,93(d,3H,Hh) ^{3}Jhb=7Hz	72,9(a) 42,2(b) 41,5(f) 32,2(c)	25,5(d) 24,2(e) 20,7(g) 15,5(h)
	48-50°/0,01 (110,1°/21,5)[4]	1,5166 (1,5152)[4]	3390 728 702	7,27(s,5H,He, Hf,Hg) 2,72(s,2H,Hb) 1,17(s,6H,Hc)	137,8(d) 130,4(f) 128,0(e) 127,3(g)	70,7(a) 49,8(b) 29,0(c)
	74°/0,05 (245°/760)[46]	1,4990 (1,4975)[46]	1740 748 701	7,28(m,5H,He, Hf,Hg) 4,12(t,2H,Ha) 2,70(t,2H,Hc) 2,01(s,3H,Hi)	170,8(h) 141,2(d) 128,4(e,f) 126,0(g)	63,7(a) 32,2(c) 30,2(b) 20,8(i)
	93°/0,12	1,4878	1740 1240 762 703	7,29(s,5H,He, Hj,Hg) 4,24(d,2H,Ha) 2,90(m,1H,Hb) 1,93(s,3H,Hi) 0,84(t,3H,He)	170,7(h) 142,1(d) 128,4(f) 127,8(e) 126,6(g) 68,5(a)	45,0(b) 32,2(c) 29,4(j) 22,7(k) 20,8(i) 13,9(l)
	b	b	3340 1660 1060	5,25(t,1H,Hc) 4,02(s,2H,Ha) 2,04(dt,2H,Hd) 1,67(s,3H,Hg) 1,35(m,2H,He) 0,91(t,3H,Hf)	134,8(b) 126,0(c) 68,6(a)	29,8(d) 22,8(e) 13,9(f,g)

a : Purified by column chromatography on silica gel

b : Crude product

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