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ASYMMETRIC ALKYLATION OF CARBONYL COMPOUNDS WITH LITHIUM OR SODIUM TETRAALKYLALUMINATES MODIFIED BY CHIRAL AMINOALCOHOLS

GÉRARD BOIREAU,* DAVID ABENHAÏM and ERICA HENRY-BASCH
Laboratoire de Chimie Organométallique Bât. 411, Université Paris-Sud, 91405 Orsay, France

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Abstract—Asymmetric alkylation of benzaldehyde and acetophenone by modified aluminium "ate" complexes are reported. $LiAlMe_4$, $NaAlEt_4$, $LiAln\text{-}Bu_4$, $NaAln\text{-}Bu_4$ modified by either (−)-N-methylphedrin or (+)cinchonine or (−)quinine were used.

Using hydrocarbon solvents and sometimes under nickel catalysis the treatment of carbonyl compounds by modified "ate" complexes produced chiral alcohols with both chemical and optical good yields. $NaAlEt_4$ modified by (−)-N-methylephedrin reacted with benzaldehyde to give S(−)1-phenyl-1 propanol in 20% enantiomeric excess. The same reagent reacted with acetophenone to give S(−)2-phenyl-2 butanol in 33% e.e. $NaAln\text{-}Bu_4$ modified by (−)-N-methylephedrin reacted with benzaldehyde to give S(−)1-phenyl-1-pentanol in 27% e.e. or with acetophenone to give (−)2-phenyl-2-hexanol in 44% e.e.

Since a wide range of new asymmetric alkylating reagents has been obtained from aluminium "ate" complexes and chiral compounds, it can be assumed that the method described could be useful to synthetise chiral alcohols with high optical yield.

Although, many papers have dealt with asymmetric reduction of prochiral carbonyl compounds,[1-3] asymmetric alkylation of these compounds has not been studied as much. Such asymmetric alkylation reactions, expected to yield chiral tertiary alcohols were attempted with organometallic compounds in chiral solvents,[1,4] or with organomagnesium compounds modified by optically active compounds.[5,6,7] However low enantiomeric ratios were usually obtained.

On the other hand, it is well known that reagents obtained from lithium aluminium hydride and chiral alcohols, amines or aminoalcohols provided high enantiomeric ratios by asymmetric reductions of prochiral carbonyl compounds.[8-10]

Recently, it was observed that aluminium "ate" complexes were able to alkylate carbonyl compounds and epoxides.[11,12] Our experiments have shown that the reactivity of aluminium "ate" complexes increased when the solvent was hydrocarbon and when catalytic amount of nickel chloride was added.[13,14] We concluded that aluminium "ate" complexes modified by chiral aminoalcohol when sufficiently reactive, could be useful in asymmetric alkylation reactions and the present study began after the observation that lithium tetrabutylaluminate modified by (−)-N-methylephedrin could alkylate carbonyl compounds with asymmetric induction.[15] In this paper we describe asymmetric alkylation of benzaldehyde and acetophenone with various aluminium "ate" complexes, modified by various aminoalcohols in diethylether or hydrocarbon solvents.

RESULTS AND DISCUSSION

Modified aluminium "ate" complexes were prepared by reacting equimolar amounts of an "ate" complex and chiral aminoalcohol according to Scheme 1.

Such modified "ate" complexes reacted with carbonyl compounds according to Scheme 2. Results are reported in Tables 1–4.

Several investigators[16-21] have presented spectroscopical evidences that the structure of aluminium "ate" complexes was solvent dependent. In hydrocarbon solvents "ate" complexes existed mainly as contact ion pairs whereas an equilibrium occured between solvated ion pairs and separated ions in coordinating solvents (Et_2O, THF, DMF, DMSO—).

$$MAlR_4 + R^*OH \xrightarrow[\text{solvent}]{20^\circ} MAlR_3OR^* + RH$$

$$M = Li \begin{cases} R = Me \\ n\text{-}Bu \end{cases} \qquad Me = Na \begin{cases} R = Et \\ n\text{-}Bu \end{cases}$$

R^*OH = (−)-N-methylephedrin
(−)quinine
(+)cinchonine

Scheme 1.

$$MAlR_3OR^* + C_6H_5COR_1 \xrightarrow{H_3O^\oplus} C_6H_5R_1RCOH$$

R_1 = H, Me, Et

Scheme 2.

We have shown, in previous papers, that the reactivity of "ate" complexes with epoxides and carbonyl compounds was solvent dependent[13,14] and much higher in a hydrocarbon solvent than in diethylether. Moreover when the "ate" complex was dissolved in THF, no reaction took place with epoxides or ketones. This dependancy of the reactivity with regard to the solvent, underlines the important role of the cation. This solvated by coordinating solvents was no longer able to intervene through the electrophilic assistance which was essential for the alkylation of epoxides and ketone.

The reactivity of aluminium "ate" complexes modified by chiral aminoalcohols was found also solvent dependant. In diethylether, the various modified "ate" complexes studied, reacted very slowly with ketones (Tables 1, 3 and 4) whereas using hydrocarbon solvents, the reactivity increased strikingly (Table 4). Nevertheless in diethylether, benzaldehyde was still alkylated, but an inversion in stereoselectivity occured: $LiAln\text{-}Bu_4$

Table 1. Reaction of $LiAlMe_4$ modified by (−)-N-methylephedrin[a]

carbonyl compound	addition alcohol yield %	$(\alpha)_D^{21}$	optical purity %	Configu.
C_6H_5CHO	42[b]	+ 1,9[d]	4,4[e]	R[f]
C_6H_5COEt	8[c]	-	-	-

[a]Solvent: Et_2O; reaction time at 20°; [b]24 hr; [c]48 hr.
[c]No attempt to isolate alcohol (too poor yield). About 90% of the ketone was recovered.
[d]Liquid l = 1.
[e]R. MacLeod, F. J. Welch and H. S. Mosher, *J. Am. Chem. Soc.* 82, 876 (1960).
[f]A. Schoofs and A. Horeau, *Tetrahedron Letters* 3259 (1977).

Table 2. Reaction of $NaAlEt_4$ modified by (−)-N-methylephedrin[a]

carbonyl compound	addition alcohol yield %	$(\alpha)_D^t$ deg, measd	optical purity %	configu.
C_6H_5 - CHO	80[b]	-5,60[d]	20[e]	S[h]
C_6H_5 - $COCH_3$	65[c]	-5,78[f]	33[g]	S[g]

[a]Solvent: cyclohexane. Reaction time at 20°: [b]20 hr; [c]48 hr.
[b]2-3% of reduction product $C_6H_5CH_2OH$.
[d]Liquid l = 1; t = 22°.
[e]R. MacLeod, F. J. Welch and H. S. Mosher, *J. Am. Chem. Soc.* 82, 876 (1960).
[f]Liquid l = 1; t = 20°.
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[h]A. Schoops and A. Horeau, *Tetrahedron Letters* 3259 (1977).

Table 3. Reaction of $NaAln\text{-}Bu_4$ modified by (−)-N-methylephedrin[a]

carbonyl compounds	addition alcohol yield %	$(\alpha)_D^{20}$ deg, measd	optical purity %	Configu.
C_6H_5 - CHO	45[h]	-5,4[f]	27[g]	S[h]
C_6H_5 - $COCH_3$	14[c, d]			
C_6H_5 - $COCH_3$	40[c, e]	-4,84[i]	44[j]	

[a]Solvent: cyclohexane. Reaction time at 20°.
[b]24 hr 1-2% of reduction product.
[c]50 hr.
[d]The other product was the unreactive carbonyl compound.
[e]With catalytic amounts of $NiCl_2$ introduced before (−)-N-methylephedrin. Reaction gave 1-2% of reduction product $C_6H_5CHOHCH_3$.
[f]Liquid l = 1.
[g]A. Horeau, J. P. Guette and R. Weidman, *Bull. Soc. Chim. Fr.* 3513 (1966).
[h]A. Schoffs and A. Horeau, *Tetrahedron Letters* 3259 (1977).
[i]Ethanol C = 12.1; t = 22°.
[j]Evaluated by NMR with the aid of chiral shift reagent Eu(t.fac.Cam)$_3$.

modified by (−)-N-methylephedrin gave R-1-phenyl-1-pentanol with 2.5% e.e. in diethylether whereas S-1-phenyl-1-pentanol was obtained with 8% e.e. in cyclohexane (Table 4).

On the other hand, the reactivity of modified "ate" complexes reacting in a hydrocarbon solvent was found closely dependent on the cation $M^{\oplus}$ itself (Tables 3 and 4). Using benzaldehyde or acetophenone as substrate and cyclohexane as solvent, $Li^{\oplus}$ was found more potent than $Na^{\oplus}$ in yielding addition alcohols. $NaAln\text{-}Bu_4$ modified by (−)-N-methylephedrin on acetophenone gave 10% of 2-phenyl-2-hexanol in 50 h while $LiAln\text{-}Bu_4$ in the same reaction yielded 56% of the same alcohol in 24 hr.

In contrast the stereoselectivity was found more im-

Table 4. Reaction of LiAln-Bu_4 modified by (−)-N-methylephedrin[a,b]

Carbonyl compound	addition alcohol yield %	$(\alpha)_D^t$ deg, measd	optical purity	Config.
C_6H_5 - CHO[a]	51[c]	+0,50[e]	2,5	R
C_6H_5 - CHO[b]	79[d]	-1,60	8	S
C_6H_5 - $COCH_3$[a]	13[f, g]	-	-	-
C_6H_5 - $COCH_3$[a]	22[f, g, h]	-	-	-
C_6H_5 - $COCH_3$[b]	56[f]	-3,40[i]	31[j]	

[a]Solvent: Et_2O. Reaction time at 20°.
[b]Cyclohexane.
[c]72 hr; 6% of reduction product.
[d]4 hr; 4–5% of reduc. product.
[e]Liquid l = 1, t = 20°.
[f]24 hr; 3–4% of reduc. product.
[g]No attempt to isolate additional alcohol.
[h]With catalytic amounts of $NiCl_2$ (≃ 2%).
[i]Ethanol, C = 11.8, t = 22°.
[j]Evaluated by NMR.

Table 5. Reaction of LiAln-Bu_4 modified by (−)quinine[a,c] or (+)cinchonine[b,c]

Carbonyl compounds	addition alcohol yield %	$(\alpha)_D^t$ deg, measd	optical purity %	Configu.
C_6H_5 - CHO[a]	74[d]	+0,60[g]	3	R
C_6H_5 - CHO[b]	72[d]	-3,80[g]	19	S
C_6H_5 - $COCH_3$[a]	38[e]	+2,62[h]	24	
C_6H_5 - $COCH_3$[b]	37[f]	-2,40[i]	22	

Chiral amino alcohol: [a](−)quinine; [b](+)cinchonine.
[c]Solvent: 50% cyclohexane + 50% toluène; reaction time at 20°.
[d]6 hr. 4–6% of reduction product $C_6H_5CH_2OH$.
[e]5 days.
[f]4 days.
[g]Liquid l = 1, t = 22°.
[h]Ethanol C = 13, t = 22°.
[i]Ethanol C = 10.5, t = 22°.

portant with $Na^{\oplus}$ than with $Li^{\oplus}$; the chiral alcohol was obtained with 44% e.e. using $Na^{\oplus}$ and with 31% e.e. when the cation was $Li^{\oplus}$.

We have shown previously that nickel chloride catalysed the alkylation of carbonyl compounds by aluminium "ate" complex.[14] As the sodium salt of modified "ate" complex gave a poor yield of the chiral alcohol when reacted with acetophenone, similar catalysis of reaction by $NiCl_2$ was attempted.

We have found that the alkylating reaction was catalysed only if nickel chloride was introduced in the mixture before the chiral amino-alcohol. In the present case, upon addition of the nickel chloride a black suspension appeared probably due to Ni^0 formation. Although the mechanism of nickel catalysis has not been yet clearly elucidated, our results were closely related to those obtained by reacting trimethylaluminium with ketones,[22] nitriles[23] or α, β unsatured ketones,[24,25] under Ni catalysis. It should be noted that the stereoselectivity of alkylation increased with seric hindrance of alkyl group: sodium tetraethylaluminate modified by (−)-N-methylephedrin reacted with acetophenone giving chiral

Table 6. Effect on the reactivity with acetophenone of the age and the manner of preparing lithium alcoxy tri-n-butylaluminate[a]

exp	Organometallic compounds	addition alcohol yield %
1	Li Al nBu_3OR^* [b,e]	56
2	Li Al nBu_3OR^* [c,e]	28
3	Li Al nBu_3OR^* [d,e]	15
4	Al nBu_3 + $R\ddot{O}^{\ominus}$ $Li^{\oplus}$ [f]	traces
5	Al nBu_3 + $C_6H_5CH(Et)O^{\ominus}Li^{\oplus}$ [f]	6
6	Li Al $nBu_3OCH(Et)C_6H_5$ [e]	57

R*OH: (−)-N-methylephedrin.
[a]Solvent: cyclohexane, reaction time at 20°: 24 hr.
[b]Modified aluminium "ate" complex freshly prepared.
[c]Modified aluminium "ate" complex was let one week before the ketone was added.
[d]Allowed to stand for 15 days before the ketone was added.
[e]Obtained by mixing equimolar amount of "ate" complex and alcohol.
[f]Obtained by mixing equimolar amount of alcohol and n-butyllithium at 0°, then adding tri-n-butylaluminium.

tertiary alcohol with 33% e.e., whereas using sodium tetrabutylaluminates in the same reactions, 44% e.e. of chiral tertiary alcohol were obtained.

Among the various aminoalcohols tested the best stereoselectivity was usually observed using (−)-N-methylephedrin. But lithiumtetrabutylaluminate modified by (+)cinchonine gave 19% e.e. with benzaldehyde, while (−)-N-methylephedrin and (−)quinine gave 8% and 3% e.e. respectively.

Mosher *et al.*[26,27] have shown the important effect of age of the asymmetric reducing agent obtained by reaction of $LiAlH_4$ with a chiral aminoalcohol. They observed a reversal in stereoselectivity and a decrease in reactivity as a function of the age of chiral reducing agent.

In the present work it was found that when lithiumtetrabutylaluminate modified by (−)-N-methylephedrin was allowed to stand for 15 days at room temperature before the introduction of acetophenone, the yield of 2-phenyl-2-hexanol was very low (Table 6). This decrease of reactivity could be related to a modification of the structure of the reagent.

Attempts to prepare the chiral alkylating reagent by mixing equimolar ratio of tri-n-butylaluminium and lithium aminoalcoholate were ineffective and the reagent obtained did not give any reaction with acetophenone (Table 6, experiment 4). We could suppose that, when the reagent was prepared in this way, tri-n-butylaluminium gave a complex with the amino-group, such a complex being unable to alkylate the ketone.

However, the experiments shown in the present study (Table 6, experiment 6) do not indicate that this interpretation is completely valid. When alkylating reagent was prepared by mixing equimolar amounts of tri-n-butylaluminium and lithium alcoholate instead of lithium aminoalcoholate, we still observed the lack of reactivity. Such lack of reactivity was also observed very recently with alkylating reagents prepared by mixing equimolecular amounts of triethylaluminium and lithium salt of chiral aminoalcohol in diethylether, whereas a similar reagent, prepared by using organolithium or organomagnesium, gives, by reaction with aldehydes, chiral secondary alcohols with good chemical and optical yields.[28,29]

At the present time, we cannot propose models that could account for both the reversal of stereoselectivity as a function of the solvent used, the variation of the reactivity of the alkylating reagent as a function of its age and the way of its preparation.

The complexity of the reaction described is probably due to the presence of different reactive species formed by mixing equimolar amounts of "ate" complex and chiralaminoalcohol; i.e. $(MAlR_3OR)_n$ or $(MAlR_4, MAlR_2(OR)_2)_n$. As the state of aggregation or the structure of such alkylating reagents has not been established, it seems unwise to attempt an interpretation of the present results in terms of transition state models.

EXPERIMENTAL

Solvents. Diethylether and toluene were distilled from $LiAlH_4$. Cyclohexane, n-heptane and n-pentane were distilled from sodium. All solvents were stored in a dry box under N_2 atm.

Organometallic compounds. Manipulation of organometallic compounds was performed whenever possible in a dry box under pure N_2. $LiAl(Me)_4$ etheral solns of $LiAl(Me)_4$ were prepared by mixing slowly at 0° under stirring, equimolar amounts of MeLi (low halogenure 3.4% Alfa) and pure $(Me)_3Al$ (purity 99% K & K). $LiAl(n\text{-}Bu)_4$ was prepared by mixing equimolar amounts of n-BuLi dissolved in hexane (Aldrich) and pure tri-n-butylaluminium (K & K). The white powder formed was filtered off, washed three times with pentane and dried under vacuum (3 hr, 50°, 0.1 mm Hg). The salt was then used without further purification. $NaAl(Et)_4$ was prepared by the method of Frey, Jr. *et al.*[30] by heating at 110° during 2 hr dispersed sodium and triethylaluminium (K & K) in toluene. After the solid has settled, the hot upper layer was transferred into an evacuated flask. Needles obtained after cooling were washed three times with pentane and dried under vacuum (3 hr, 50°, 0.1 mm Hg). $NaAl(n\text{-}Bu)_4$ was prepared by the method of Schaschel and Day.[31] Na dispersed in n-heptane was obtained by washing with n-heptane a 50% Na dispersion in paraffin. A mixture of tri-n-butylaluminium

(K & K) with an excess of Na dispersion in n-heptane was refluxed for 4 hr. The mixture was filtered through a fine porosity sintered glass funnel (4–6 μ) to separate "ate" complexe from Al and excess Na, n-heptane was evaporated under vacuum and the salt was crystallized from n-pentane at dry ice temp., filtered off and dried under vacuum.

Analyses. Lithium and sodium tetraalkylaluminates were analysed for Li and Na by flame spectrometry and for Al by EDTA–zinc acetate titration at pH 4 using dithizone as indicator.

Other compounds. Benzaldehyde, acetophenone 1-phenyl-1-propanone and 1-phenyl-1-propanol were commercial products purified by vacuum distillation. (−)-N-methylephedrin $[\alpha]_D^{20} = -29.5°$ (MeOH *c* 4.5) was prepared by the method of Eschweiler–Clarke[32] from (−)ephedrin $[\alpha]_D^{20} = -41°$ N HCl (*c* 5) EGA; (−)quinine $[\alpha]_{546}^{20} = -154°$ $CHCl_3$ (*c* 1.5) commercial product (Fluka); (+)cinchonine $[\alpha]_{546}^{20} = +265°$ ethanol (*c* 0.5) commercial product (Fluka).

Reaction of $LiAl(Me)_4$ *modified by* (−)-N-*methylephedrin with benzaldehyde and* 1-*phenyl*-1-*propanone.* 21.6 mmol of (−)-N-methylephedrin dissolved in 200 ml of Et_2O were added slowly under N_2 to a stirred ethereal soln 20 ml of $LiAl(Me)_4$ (1.083 M) at 28°. Gas was evolved during the introduction of the amino alcohol. Subsequently, 21.6 mmol benzaldehyde in 20 ml Et_2O were added. 24 hr later, the mixture was hydrolysed by 20 ml water. The organic layer was washed three times with 20 ml 2 N HCl to separate the amino alcohol. The analysis was performed by GC (Carbowax 20 M, 150°) with tetradecane as internal standard. 1-Phenyl-1-ethanol was purified by preparative GC (Carbowax 20 M) for the determination of the $(\alpha)_D$.

The aqueous layers were made basic with NaOH. (−)-N-Methylephedrin was almost quantitatively recovered by extraction with Et_2O.

Similar procedures were used for the reaction with 1-pheayl-1-propanone. Analysis was performed by GC (Carbowax 20 M, 160°) with hexadecane as internal standard.

Reaction of $NaAl(Et_4)$ *modified by* (−)-N-*methylephedrin with benzaldehyde and acetophenone.* Reactions were carried out in cyclohexane by a similar procedure to that used for $LiAl(Me)_4$ from weighed portions of $NaAl(Et)_4$. With acetophenone, the reaction needed catalysis. About 2% of $NiCl_2$ were introduced before the addition of (−)-N-methylephedrin to the "ate" complex.

After hydrolysis, analysis was performed by GC (Carbowax 20 M, 160°) with tetradecane as internal standard.

Addition alcohols were purified by preparative GC (Carbowax 20 M) for determination of $(\alpha)_D$.

Reaction of $NaAl(n\text{-}Bu)_4$ *modified* (−)-N-*methylephedrin with benzaldehyde and acetophenone.* Reactions were carried out in cyclohexane by a similar procedure to that for $NaAl(Et)_4$. With acetophenone, the reaction needed $NiCl_2$ catalysis.

Analyses was performed by GC (Carbowax 20 M, 170°) with hexadecane as internal standard. Addition alcohols were purified by preparative GC (Carbowax 20 M) for determination of $(\alpha)_D$.

With 2-pheayl-2-hexanol the optical yield was evaluated by NMR by means of chiral shift reagent Eu (t.fac. cam)$_3$[33] using the protons of -2-methyl group.

Reaction of $LiAl(n\text{-}Bu)_4$ *modified by* (−)-N-*methylephedrin*(−)*quinine or* (+)*cinchonine with benzaldehyde and acetophenone.* With (−)-N-methylephedrin the reaction was carried out by a similar procedure to that for $NaAl(Et)_4$ or $NaAl(n\text{-}Bu)_4$.

Due to the low solubility in hydrocarbures solid (−)quinine or (+)cinchonine were added in small portions under argon flow to the "ate" complex recovered by a 50% toluène + 50% cyclohexan soln. In this case and using acetophenone, the reaction was very slow. Attempt to increase the yield of the reaction by means of $NiCl_2$ catalysis was ineffective.

Analysis of the products of the reaction was carried out by a similar procedure to that for $NaAl(n\text{-}Bu)_4$.

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