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Alkyl Metal Asymmetric Reduction. VII. Temperature Dependence of the Stereoselectivity of Alkyl Phenyl Ketone Reductions by Chiral Organoaluminum Compounds

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Abstract: The reduction of a series of alkyl phenyl ketones by optically active tris(2-methylbutyl)aluminum and its diethyl etherate has been investigated at temperatures ranging from 0 to −60°. The stereoselectivity of the process has been interpreted on the basis of enthalpic and entropic contributions. The suggestions previously proposed for the stereochemistry of this reaction are consistent with the results obtained. The stereochemical course of the reductions by the organoaluminum diethyl etherate confirms that the ligand to the aluminum atom partakes in the transition state of the reaction and controls the extent of stereoselectivity.

Reactions involving hydrogen transfer from chiral organometallic compounds to prochiral functional substrates have been widely investigated in recent years.[1] Stereochemical models which are commonly devised to rationalize such asymmetric reductions do not always imply an accurate knowledge of the mechanistic pathways of the reactions when the reacting species, for example Grignard reagents,[2] have a complex nature.

It is indeed to be considered that schemes of asymmetric induction based on steric requirements are usually oversimplified and that polar[3,4] and solvation effects[4] can assume a remarkable importance.

From this point of view, the use of organoaluminum compounds as chiral reducing agents has appeared suitable for investigating this kind of asymmetric reductions[4] taking into account that such compounds have a defined structure,[5] can be employed both in hydrocarbon and ethereal solvents, and reduce carbonyl substrates through well-established mechanisms.[6] In this connection, to check the picture previously proposed for the stereochemistry of reduction of alkyl phenyl ketones by optically active β-branched organoaluminum compounds,[4a] we have studied the effect of temperature on the stereoselectivity of reduction of alkyl phenyl ketones both by (+)-tris[(*S*)-2-methylbutyl]aluminum[7] (Al2MB) and (+)-tris[(*S*)-2-methylbutyl]aluminum diethyl etherate[8] (Al2MB·OEt$_2$).

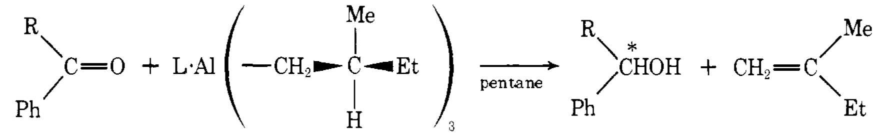
Experimental Section

General. (+)-Tris[(*S*)-2-methylbutyl]aluminum and (+)-tris[(*S*)-2-methylbutyl]aluminum diethyl etherate, prepared as previously reported,[10,3] were carefully redistilled under nitrogen and stored in sealed glass vials.

The ketones employed were obtained from the purification of commercial products; *tert*-butyl phenyl ketone was prepared according to the procedure already mentioned.[4a] Reductions were carried out at 0°, using ice-water baths, and in baths regulated at −30 and −60° (±3°). A Schmidt–Haensch polarimeter was used for all the determinations of the optical rotations. GLC analyses were performed on a C. Erba Fractovap Model GT instrument with flame ionization detectors, using 200 × 0.30 cm columns packed with 10% BDS on 60–80 mesh Chromosorb W at 150°.

Reactions. Reactions were carried out in a flame-dried, two-neck 100-ml flask, fitted with a reflux condenser, a dropping fun-

Table I. Asymmetric Reduction of Phenyl Alkyl Ketones



Run	L	R	t, °C	(S) carbinol $[\alpha]^{25}$D (c, ether)	Optical purity,[a] %	Asymmetric reduction,[b] %	$\Delta\Delta G^{\ddagger}$,[c] cal/mol
1[d]		Me	0	−2.18 (neat)	5.0	5.9	−64
2[e]			−60	−2.71 (neat)	6.2	7.9	−67
3[d]		Et	0	−3.22 (neat)	11.2	13.2	−144
4[e]			−60	−3.32 (neat)	11.6	14.8	−123
5[f]		*i*-Pr	0	−15.56 (4.86)	32.6	44.3	−515
6[e]			−30	−14.48 (7.17)	30.4	38.9	−392
7[d]			−60	−13.17 (5.77)	27.6	32.4	−277
8[d]		*t*-Bu	0	−9.24 (5.02)	25.5	29.9	−335
9[e]			−30	−8.26 (12.76)	22.8	29.2	−290
10[d]			−60	−9.10 (3.53)	25.1	29.4	−250
11[d]		CF_3	0	+1.73 (5.94, benzene)	5.1	6.0	−65
12[e]			−60	+2.99 (neat)	9.4	12.0	−102
13[g]	Et_2O	Me	0	−2.55 (neat)	5.8	5.9	−64
14[g]	Et_2O		−60	−4.01 (neat)	9.2	9.4	−79
15[h]	Et_2O	Et	0	−2.89 (neat)	10.0	10.5	−109
16[i]	Et_2O		−60	−3.68 (neat)	12.8	13.8	−115
17[h]	Et_2O	*i*-Pr	0	−16.13 (4.82)	33.8	35.2	−398
18[h]	Et_2O		−30	−18.23 (5.23)	38.2	39.8	−408
19[h]	Et_2O		−60	−21.19 (5.82)	44.4	46.3	−414
20[h]	Et_2O	*t*-Bu	0	−11.40 (7.54)	31.5	32.8	−368
21[i]	Et_2O		−30	−12.77 (6.65)	35.3	38.0	−386
22[i]	Et_2O		−60	−15.55 (7.52)	43.0	46.3	−414
23[g,j]	Et_2O	CF_3	110	−0.56 (neat)	1.8	1.8	+27
24[h]	Et_2O		0	+1.49 (neat)	4.7	4.9	−49
25[i]	Et_2O		−60	+3.42 (neat)	10.7	11.6	−96

[a] See ref 4a. [b] Corrected for the minimum optical purity (o.p.) of the organoaluminum compound used. [c] Calculated from $\Delta\Delta G^{\ddagger} = -RT \ln k_S/k_r = -RT \ln [S]/[R] = -RT \ln (1 + a)/(1 - a)$, where a = asymmetric reduction. [d] Al2MB, o.p. 85.2%. [e] Al2MB, o.p. 78.1%. [f] Al2MB, o.p. 73.6%. [g] Al2MB·OEt_2, o.p. 98.0%. [h] Al2MB·OEt_2, o.p. 95.9%. [i] Al2MB·OEt_2, o.p. 92.8%. [j] Toluene as solvent.

nel, and a magnetic stirrer. In a typical run, a solution of 10.5 mmol of the ketone in 10 ml of anhydrous pentane was added rapidly, under nitrogen, to a solution of 11.7 mmol of the organoaluminum compound in 15 ml of pentane, cooled to the required temperature. When Al2MB was used, reaction was prolonged for 2 hr at 0 and −30°, and for 24 hr at −60°; in the case of Al2MB·OEt_2, reaction was complete within 2 hr at 0°, 24 hr at −30°, and 72 hr at −60°. After completion of the reduction, the mixture was cautiously hydrolyzed with dilute sulfuric acid (pH 5) and the organic products were extracted with purified ether and analyzed by GLC. The carbinols were recovered by accurate distillation.

Run 23 (Table I) was carried out at 110°, in boiling toluene, using the same procedure.

Results

The experiments were carried out at 0, −30, and −60°, in pentane solution, using a slight excess (about 10%) of the organoaluminum compounds with respect to the alkyl phenyl ketones. The results obtained are collected in Table I.

In the experimental conditions we have adopted neither addition nor significant enolization occur and the reaction affords the carbinols corresponding to reduction of the ketones in high conversions (>90%). The reduction rate is greater using Al2MB rather than Al2MB·OEt_2; in fact at −30°, whereas Al2MB reacts completely within 2 hr, the corresponding reduction by Al2MB·OEt_2 requires 12 hr for completion. By inspection of Table I, the following considerations can be made.

(1) All the alkylphenylcarbinols recovered have an absolute (S) configuration. The reduction of trifluoromethyl phenyl ketone by Al2MB·OEt_2 leads to the (R) carbinol at 110° in toluene (run 23) and to the enantiomer at 0 and −60° (runs 24 and 25).

(2) When the reaction temperature is lowered, the reductions by Al2MB·OEt_2 occur with higher stereoselectivity, this effect being more appreciable in the reduction of isopropyl and *tert*-butyl phenyl ketone.

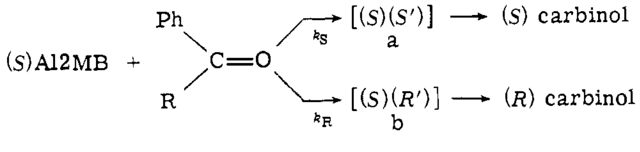
(3) By lowering the reaction temperature, the stereoselectivity of reduction by Al2MB increases when the R alkyl group in the ketone is Me, Et, and CF_3 and decreases when R is *i*-Pr. The extent of asymmetric reduction of *tert*-butyl phenyl ketone appears to be temperature independent at least in the range investigated (0 to −60°).

(4) It is noteworthy that the activation free energy differences ($\Delta\Delta G^{\ddagger}$) are generally small; however, values of 400–500 cal/mol are involved in the reductions of isopropyl phenyl ketone by Al2MB at 0° (run 5) and by Al2MB·OEt_2 (runs 17–19), and in the reduction of *tert*-butyl phenyl ketone by the organoaluminum etherate (runs 20–22).

Discussion

According to what is generally accepted for kinetically controlled asymmetric transformations,[2,9] the asymmetric reduction of a prochiral ketone by optically active organoaluminum compounds is assumed to proceed via competing diastereomeric transition states as depicted in Scheme I.

Scheme I



Since the reactants have obviously the same ground state free energy, the extent of asymmetric reduction only de-

Table II. Activation Parameter Differences[a] at −30° between the Competing States of the Reductions of Alkyl Phenyl Ketones by (+)(*S*)Al2MB in Pentane

R	$\Delta\Delta G^{\ddagger}$, cal/mol	$\Delta\Delta H^{\ddagger}$, cal/mol	$\Delta\Delta S^{\ddagger}$, eu
Me	−66	−66	~0
Et	−134	−85	+0.2
i-Pr	−392	+556	+3.9
t-Bu	−290	+50	+1.4
CF_3	−84	−229	−0.6

[a] $\Delta\Delta X^{\ddagger} = \Delta X_a^{\ddagger} - \Delta X_b^{\ddagger}$.

pends on the free energy difference between the two competing diastereomeric transition states

$$\Delta\Delta G^{\ddagger} = \Delta G_a^{\ddagger} - \Delta G_b^{\ddagger} = -RT \ln k_S/k_R \qquad (1)$$

where k_S and k_R are the rate constants for the processes leading to (*S*) and (*R*) carbinols, respectively. The study of the temperature dependence of the reduction stereoselectivity should allow an evaluation of the enthalpy and entropy term contributions and hence the factors determining a preferential diastereomeric transition state.

Asymmetric Reductions by (+)(*S*)Al2MB. The results reported in Table I show that, as the reaction temperature is lowered, the free energy difference ($\Delta\Delta G^{\ddagger}$) between the diastereomeric transition states decreases in the absolute value, when the alkyl group in the ketone is changed, in the order of Et < *i*-Pr < *t*-Bu and increases when R = CF_3. On the contrary, the stereochemical data of the asymmetric reduction of methyl phenyl ketone show that $\Delta\Delta G^{\ddagger}$ is temperature independent and therefore the entropy factor is zero ($\Delta\Delta G^{\ddagger} = \Delta\Delta H^{\ddagger}$).

The differences in the values of the activation parameters (at −30°) for the asymmetric reductions of alkyl phenyl ketones by (+)(*S*)Al2MB are listed in Table II.

The data reported indicate that enthalpy favors the formation of the (*S*) carbinol when R is Me, Et, and CF_3, whereas the "wrong" enantiomer is preferred when R is *i*-Pr and, to a lower extent, *t*-Bu. On the other hand, the sign of the entropy factors shows that, apart from the case of the reductions of methyl phenyl ketone and trifluoromethyl phenyl ketone, the reactants have lost a greater number of degrees of freedom in the transition states leading to (*R*) carbinol than in those leading to the other enantiomer. Therefore in the reduction of isopropyl and *tert*-butyl phenyl ketone the relatively large entropy term overcomes the $\Delta\Delta H^{\ddagger}$ value; thus, (*S*) carbinol is formed in all the cases investigated.

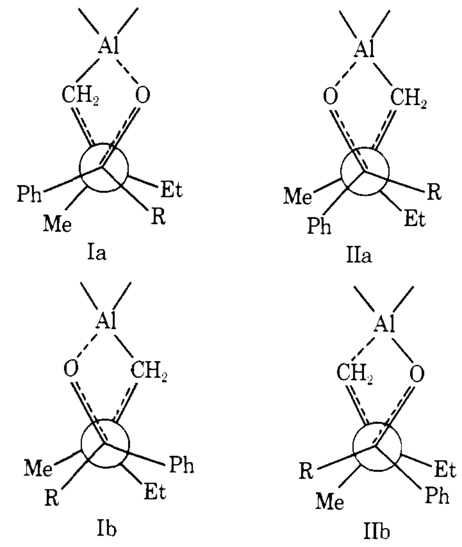
On the basis of our previous suggestions,[4a] the mechanism of the hydrogen transfer should involve a cyclic transition state in which the coordinative bond between aluminum and oxygen atoms has to be relatively loose to minimize the steric compressions among the groups. Thus steric interactions might be estimated from Newman type projections of four reacting conformations, viewed along the C··· H-C* axis (Scheme II), the transition states Ia and IIa leading to (*S*) carbinol, the others to the enantiomer. Under the hypothesis that electronic factors play the main role,[3,4] the conformations IIa and IIb should have the highest energies; so, in relation to the different ability of the groups to minimize their mutual steric interactions, the stereoselectivity of reduction should depend essentially on the balance between the conformation Ia and the relatively more hindered conformation Ib. According to this picture[4a] and from inspection of molecular models, the steric hindrance of the alkyl group in the ketone should prevent the conformational mobility of all the groups being compressed in the transition states more in Ib than in Ia.[10] For this reason a decrease of temperature will contribute to reduce the conformational mobility both in Ia and Ib, this effect being more remarkable in Ia. So the difference of the activation free energies between the diastereomeric transition states will decrease by lowering the temperature.

Table III. Activation Parameter Differences[a] at −30° between the Competing States of the Reductions of Alkyl Phenyl Ketones by (+)(*S*)Al2MB·OEt_2 in Pentane

R	$\Delta\Delta G^{\ddagger}$, cal/mol	$\Delta\Delta H^{\ddagger}$, cal/mol	$\Delta\Delta S^{\ddagger}$, eu
Me	−71	−120	−0.2
Et	−112	−161	−0.2
i-Pr	−408	−505	−0.4
t-Bu	−386	−580	−0.8
CF_3	−72	−266	−0.8

[a] $\Delta\Delta X^{\ddagger} = \Delta X_a^{\ddagger} - \Delta X_b^{\ddagger}$.

Scheme II



Asymmetric Reductions by (+)(*S*)Al2MB·OEt_2. When the reducing agent is Al2MB·OEt_2, a decrease in the reaction temperature results in an increase of both the stereoselectivity and the absolute values of the free energy differences between the competing transition states (Table I).

On the basis of steric requirements, the reduction of trifluoromethyl phenyl ketone should lead to (*R*)-trifluoromethylphenylcarbinol.[4a] Actually at 110° the (*R*) enantiomer is formed while at temperatures below 70° the carbinol recovered has an absolute (*S*) configuration.

This reversal in stereochemistry is not, however, a result of a change in the reaction mechanism but is due to the negative entropy factor ($|\Delta\Delta S^{\ddagger}| \simeq 0.8$ eu) which favors the conformation leading to (*S*) carbinol.

The data of Table III show that the enthalpy promotes the formation of (*S*) carbinol in all cases and that the activation entropy differences are always very low (≤0.8 eu) indicating that the rotational conformation restrictions in the competing diastereomeric states do not differ greatly although the transition states leading to (*S*) carbinol seem to have a more restricted mobility.

The absolute value of $\Delta\Delta H^{\ddagger}$ increases in the order of Me < Et < CF_3 < *i*-Pr < *t*-Bu and appears to be related in some way to the formal bulk of the alkyl group in the ketone. This regularity is however apparent, since the increasing bulk of the alkyl substituent to the carbonyl carbon atom should in principle contribute to decreasing the free energy differences between the transition states.[4b]

The data of Table III are substantially different from those of Table II and indicate that the reduction of alkyl phenyl ketones by (+) tris[(*S*)-2-methylbutyl]aluminum diethyl etherate proceeds through mechanistic pathways different from those invoked for the reduction by (+) tris[(*S*)-2-methylbutyl]aluminum.

Our previous findings have shown that, in the reductions by organoaluminum etherate, the ether ligand takes part in the transition state of the reaction.[4a] The electronegativity of the aluminum atom in $\mathrm{Al2MB{\cdot}OEt_2}$ should operate to make the cyclic transition state looser. The increased distance between the aluminum atom and the carbonyl oxygen atom should imply that the interactions among the groups are relatively weaker.[4a] So the restrictions to the conformational mobility and consequently the activation entropy should be similar in both diastereomeric states. On the other hand, the ligand, by itself exerting a certain compression on the groups, should modify the steric requirements of the transition states with respect to those involved in the reduction of ketones by Al2MB.

In this context the different values of $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$, calculated for the asymmetric reduction of isopropyl phenyl ketone by (+)(*S*)Al2MB and by (+)(*S*)$\mathrm{Al2MB{\cdot}OEt_2}$, really appear very significant.

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(10) Since the most important contributions to $\Delta S^{\ddagger}$ come from losses in internal motions, the positive difference of the activation entropies, when the alkyl group in the ketone is *i*-Pr and *t*-Bu, should reasonably fit this hypothesis. On this basis, the high symmetry of the *t*-Bu group could explain why $\Delta\Delta S^{\ddagger}$ is lower in this case rather than in that of the asymmetric reduction of isopropyl phenyl ketone[4a] (Table II).

Anodic Cleavages of Secondary and Tertiary Alkylphenylcarbinols

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Abstract: The oxidation of secondary alkylphenylcarbinols $\mathrm{PhC(R_1)(R_2)OH}$ (R_1 = H; R_2 = methyl, ethyl, isopropyl or *tert*-butyl) in acetonitrile-tetra-*n*-butylammonium fluoroborate at platinum led to the formation of carbonyl compounds. When R_2 = methyl or ethyl, acetophenone or propiophenone were respectively formed. For R_2 = isopropyl or *tert*-butyl, benzaldehyde and either *N*-isopropyl- or *tert*-butylacetamide were isolated. Tertiary alkylphenylcarbinols (R_1, R_2 = methyl, ethyl, isopropyl, or *tert*-butyl) were found to cleave to yield ketones and either gases or *N*-alkylacetamides from the corresponding alkyl fragments. The relative leaving group abilities were methyl < ethyl < isopropyl < *tert*-butyl. An ECE mechanism is proposed in which the initial step is oxidation of the aromatic ring (E) to form a cation radical, then followed by loss of a proton or an alkyl radical (C) by the cation radical, and finally oxidation of the alkyl or alkylphenylcarbinol radical (E). Of the alkyl radicals, only the methyl radical failed to undergo further oxidation.

The chemical oxidation of *tert*-alkylphenylcarbinols has been reported,[1] but there has been only one previous study on its electrochemical oxidation. Maruyama and Murakami[2] investigated the electrochemical oxidation of various *tert*-alkylphenylcarbinols in water-dioxane-sodium hydroxide, utilizing a platinum electrode and constant current. With this alkaline solvent system, the *tert*-alkylphenylalkoxide was proposed as the species undergoing oxidation, yielding the *tert*-alkylphenylalkoxy radical which cleaved to produce alkyl phenyl ketones and alkyl radicals. The relative leaving group abilities were then measured by determining the ratio of the two possible alkyl phenyl ketones. The relative leaving group abilities were allyl > *sec*-butyl > isopropyl > ethyl > *n*-propyl > *n*-butyl > *n*-pentyl > isobutyl > methyl, implying the hyperconjugative effect of the β hydrogen was the most important factor in determining which group was cleaved. Hydrocarbons, C_2 to C_5, derived from the alkyl fragment, were also detected. The determination of the mechanism is, however, complicated by the oxidation of the solvent since a large quantity of oxygen was detected, and therefore a chemical reaction, i.e., radical abstraction, between an electrochemically generated species and the *tert*-alkylphenylcarbinol cannot be eliminated.

Benzylic ethers, esters, alcohols, and phenyl epoxides have been previously reported to yield carbonyl compounds upon anodic oxidation in acetonitrile at a platinum electrode.[3] It, therefore, became of interest to examine the electrochemical behavior of such carbinols in acetonitrile since it would be the carbinol and not the alkoxide which would be oxidized, and solvent decomposition could be eliminated.

Results

All the oxidations were controlled potential electrolyses and conducted with platinum electrodes in a divided cell. The electrolyte was 0.2 *M* tetra-*n*-butylammonium fluoroborate in acetonitrile, and cyclic voltammetry indicated no substantial oxidation up to +3.0 V vs. $\mathrm{Ag^+|Ag}$ (Figure 1). Generally 1.0–0.5 g of substrate and 2.0 g of anhydrous sodium carbonate were added. The potential was pulsed to