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Asymmetric Carbonyl Addition and Asymmetric Polymerization Assisted by Axially Chiral Diamines Give Disparate Ligand/Product Configurational Correlations

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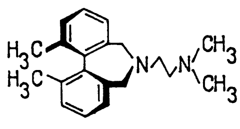
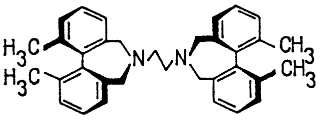
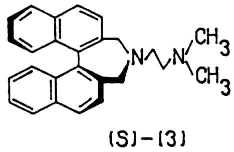
Synopsis. Organolithium reagents complexed with axially chiral biphenyl-substituted *N,N,N',N'*-tetramethylethylenediamines (**1** and **2**) add to aldehydes in good enantioface selectivity. The pattern of the stereoselection, however, disagrees with that of the helical choice observed for the asymmetric polymerization of triphenylmethyl methacrylate with the same complexes.

Recently, Cram and co-workers[1,2] have been reported that *N,N,N',N'*-tetramethylethylenediamine (TMEDA) derivatives having an atropisomeric 1,1'-binaphthyl unit (**3** and **4**) can be utilized as highly effective chirality-inducing ligands for organolithium compounds. They have successfully achieved the highly asymmetric alkylation of aldehydes by using the above complexes.[1] There is another interesting report, in which the asymmetric polymerization of methyl methacrylate (MMA) has been also studied with butyllithium (BuLi) complexed with **4**.[2] We almost concurrently presented reports that similar complexes between organolithiums and axially chiral biphenyl-substituted TMEDAs, such as **1** and **2**, serve as effective initiators in the asymmetric polymerization of related triphenylmethyl methacrylate (TrMA).[3,4] We directed our special attention to Cram's consideration:[2] a single stereoelectronic feature can explain consistently a variety of the ligand/product configurational correlations in the above two asymmetric reactions.

Herein, we report the asymmetric carbonyl addition of organolithium reagents to aldehydes assisted by **1** or **2**, and discuss the stereochemistry in connection with the mechanistic consideration on our asymmetric polymerization.


(S)-(1)


(S,S)-(2)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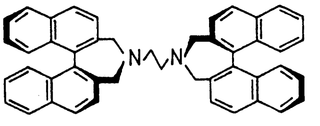
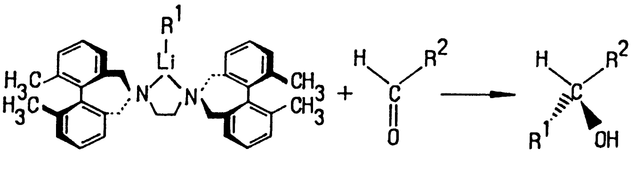

(S,S)-(4)

Experimental



Materials. Optically pure diamines, **1** and **2**, were prepared from the resolved 6,6'-dimethylbiphenyl-2,2'-dicarboxylic acid,[5] according to the method reported previously.[3] (*R*)-**1**: Bp 140 °C (0.05 Torr (1 Torr=133.322 Pa)) $[\alpha]_D^{25}$ +43.0° (*c* 1.0, tetrahydrofuran); (*S*)-**1**: $[\alpha]_D^{25}$ −42.9°. (*R,R*)-**2**: Mp 156.5—158 °C (from hexane), $[\alpha]_D^{25}$ +115.1° (*c* 1.0, ethanol); (*S,S*)-**2**, mp 155—157 °C, $[\alpha]_D^{25}$ −114.0°. These diamines gave satisfactory analytical data and the expected ^{1}H NMR and mass spectra.

Asymmetric Carbonyl Additions. According to the procedure of Mazaleyrat and Cram,[1] a typical chiral organolithium (R^1Li) complex was prepared by mixing 4.6 cm^3 (3.0 mmol) of BuLi (0.65 mol l^{-1}) in hexane with a solution of (*S,S*)-**2** (1.56 g, 3.3 mmol) in 50 cm^3 of dry Et_2O under a nitrogen atmosphere at −50 °C. The solution was cooled to −78 °C, and a solution (1.0 cm^3; 1.2 mol l^{-1}) of benzaldehyde (1.2 mmol) in Et_2O was added. The homogeneous mixture was stirred for 3 h at −78 °C, and then rapidly quenched with 1 mol l^{-1} HCl. Extractive work-up gave an oil, which was purified by preparative TLC (silica gel, benzene) followed by bulb-to-bulb distillation to give (*S*)-(−)-1-phenyl-1-pentanol (0.17 g, 87%) pure by GLPC and ^{1}H NMR. Similarly, routine runs were carried out in various combinations among aldehydes, R^1Li, and the chiral diamines under different reaction conditions. The dominant configurations and enantiomeric excesses (ee's) of the produced alcohols were determined from their optical rotations based on the reported maximum values. The used bases were recovered in more than 90% yields without any noticeable loss in optical purity.

Results and Discussion

The results are summarized in Table 1. As can be seen from the ee's of produced alcohols, the both-side substituted TMEDA (**2**) exhibited a more preferable enantioface selectivity than **1** did. Both the temperature and the solvent of the reaction were important in order to achieve high optical yields. The highest ee. value of 99% was recorded in the reaction by using **2** in Et_2O at −120 °C. An addition way that R^2CHO was treated with an R^1Li reagent having a more bulky R^1 than R^2 resulted in a substantial decrease of the optical yield compared with that of the same product obtained in the reversed way. These results were quite analogous to those observed previously with similar chiral ligands of a 1,1'-binaphthyl analogue, **3** and **4** by Mazaleyrat and Cram.[1] Under the same reaction con-

Table 1. Asymmetric Carbonyl Addition of Organolithium Complexes of **1** or **2** to Aldehydes.[a]

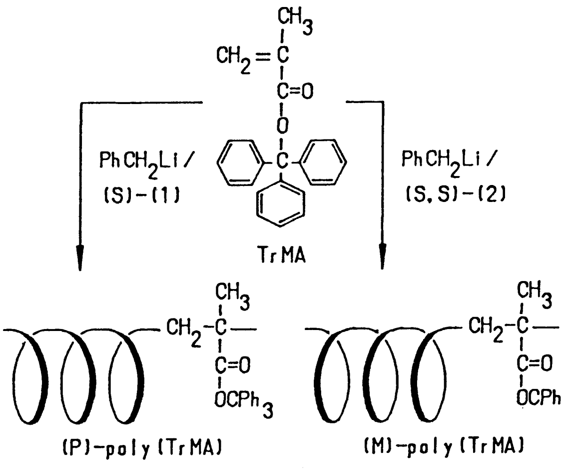
Chiral reagent		R^2 in		Alcohol produced		
Diamine	R^1	R^2CHO	Solvent	Isolated yield/%	$[\alpha]_D^{25}$[b] /°	%Ee.[c] (configuration)
(*S*)-**1**	Bu	Ph	Et_2O	95	−20.1	53 (*S*)
(*S*)-**1**	Bu	Ph	PhMe	93	−12.4	33 (*S*)
(*S*,*S*)-**2**	Bu	Ph	Et_2O	88	−32.2	86 (*S*)
(*R*,*R*)-**2**	Bu	Ph	Et_2O	75	+32.2	86 (*R*)
(*R*,*R*)-**2**	Bu	Ph	Et_2O[d]	62	+37.1	99 (*R*)
(*S*,*S*)-**2**	Bu	Ph	PhMe	74	−10.2	27 (*S*)
(*R*)-**1**	Ph	Bu	Et_2O	59	−6.7	18 (*S*)
(*S*,*S*)-**2**	Ph	Bu	Et_2O	53	+6.8	18 (*R*)
(*S*)-**1**	$PhCH_2$[e]	Ph	PhMe	64	0[f]	0
(*S*,*S*)-**2**	$PhCH_2$[e]	Ph	PhMe	48	0[f]	0

a) Reaction conditions: R^2CHO/R^1Li/diamine=1.2/3.0/3.3 mmol; solvent, 50 cm^3; reaction temperature, −78 °C; reaction time, 3 h. b) The optical rotations were taken in benzene solutions. c) Based on $[\alpha]_D$ 37.6° (*c* 3, benzene) (Refs. 1 and 5). d) Temperature, −120 °C, at which the reaction system became heterogeneous. e) When the BuLi complexes were prepared in toluene at room temperature, the anion was smoothly replaced by $PhCH_2Li$ (Ref. 6). f) In ethanol (Ref. 7).

ditions, **1** and **2** were found to provide almost equal levels of enantioface selection to those of **3** and **4**, respectively, as expected from the structural similarity of each couple of the ligands. The stereochemical consequences gained or reported in various combinations among the four axially chiral ligands, R^1Li, and R^2CHO can be predicted consistently in terms of the axial chirality of the biaryl substituents; that is, when the ligands have (*R*)-configuration, the chiral R^1Li complexes always prefer the *re*-facial approach onto aldehydes.

Previously, we reported that **1** and **2** recognized the helicity in high levels in the asymmetric polymerization of TrMA by using several organolithium complexes of these diamines in toluene at −78 °C.[3,4] The chiral catalysts generated successively asymmetric carbons of a single configuration through the polymerization in an isotactic manner, though after growing up, the polymer became pseudoasymmetric as the whole polymer chain. Okamoto et al. have reported that when poly(TrMA) is composed of the (*S*)-configurated monomer units in the initiating side, the polymer adopts (*P*)-helical conformation because of the isotactic sequence (more than 9-mer) of the bulky ester groups.[8] Accordingly, it was obvious that the chiral consequences of both the present carbonyl addition and the previous polymerization were dominated by carbon-carbon bond-forming processes.

Thus, we compared the ligand/product correlations in the two reactions. One of the most suitable anionic initiators was the benzyllithium (BzLi) complex of **1**.[4] On the contrary, no asymmetric induction occurred in the addition of this complex to benzaldehyde in toluene, which was the same solvent as that used for the polymerization. The result suggested that the initiation reaction between TrMA and the chiral complex took place with no or a very poor stereoselectivity. The stereoselection in the following addition steps might be considered to be primarily important to form the monomer sequence of single configuration, as pointed out by Okamoto et al.[8]



Most interestingly, even if **1** and **2** had the same configuration their BzLi complexes showed the opposed helical preferences in the asymmetric polymerization,[4] as shown in the scheme. The polymerization with (*S*)-**1** gave the (*P*)-helical polymer composed of the (*R*)-configurated monomeric units, while (*S*,*S*)-**2** induced (*S*)-configuration to the monomeric units leading to (*M*)-helicity. This pattern of the ligand/product stereochemical outcomes was contrary to that observed for the above asymmetric addition. It has been found that the BuLi complexes are not suitable initiators for the asymmetric polymerization.[9] This however does not mean a poor stereoselectivity toward the helical conformation, but does a problem on the poor solubility of the produced polymer in organic solvents because of its high molecular weight.[4] In the polymerization of TrMA by using the various complexes of **1** or **2**,[4] the pattern of the helical choice was not altered at all by changing organolithium compounds including BuLi. The disagreement in the stereoselection between the asymmetric carbonyl addition and the asymmetric polymerization of TrMA strongly suggests that different stereoelectronic interactions operate in the chiral discrimination of the two reactions by using **1** or **2**.

On the other hand, Cram et al. have proposed an explanation that the stereochemistry of the asymmetric carbonyl addition of the BuLi/**4** complex may be applicable to that of the asymmetric polymerization of MMA with the same complex.[2] However this is contrary to our present results, although the monomers differ in the bulkiness of their ester groups. We may conclude at least that a transition state for the asymmetric polymerization of TrMA can't be compatibly depicted by Cram's model.

The asymmetric polymerization of less bulky MMA is very interesting for us and now under studying.

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