Table I. Reaction of Photoactivated Alkylcobaloxime and Ethyl Mercaptoacetate[a]

run	cobaloxime	temp, °C	time, h	yield, % 3	yield, % 4	conversion, %
1	**1a**	35	24	3	27	79
2	**1b**	35	24	52	15	100
3		35	48	61	6	100
4		-20	24	55	18	100
5[b]		-20	24	0	76	76

[a] Conditions: alkylcobaloxime, 1.5 mmol; thiol, 1.0 mmol; CH_2Cl_2, 15 mL; tungsten lamp (400 *W*), distance from lamp to reaction vessel 20 cm, under an argon atmosphere. [b] Dark reaction.

In every case, both ethyl 2-(alkylthio)acetate (**3**) and bis[(ethoxycarbonyl)methyl] disulfide (**4**) were obtained (runs 1-4). Methylcobaloximine (**1a**) showed a lower reactivity than benzylcobaloxime (**1b**) (run 2) because of its higher dissociation energy[1b] of the Co-C bond and instability of methyl radical formed. The yield of sulfide **3** increased by extending the reaction (run 3). The reaction proceeded similarly even at a low temperature under irradiation (run 4), but in the dark, the reaction at low temperature failed to give the sulfide **3** and the only product was disulfide **4** (run 5). Besides **3** and **4**, a considerable amount of [[(ethoxycarbonyl)methyl]thio]bis(dimethylglyoxymato)pyridinecobalt(III) **5** was detected in the reaction mixture by the ^1H NMR measurement. Similarly, benzyl-transfer reaction occurred when **1b** was treated with other thiols such as benzenethiol, α-toluenethiol, and 2-mercaptoethanol.[7]

The reaction course was assumed as in Scheme I by considering below additional results and discussions.

In the first step of this reaction (path a), the abstraction of hydrogen by an alkyl radical formed from thermal- or photoactivated alkylcobaloxime gives alkane and (alkylthio)cobaloxime **5**. In the case of the reaction of benzylcobaloxime (**1b**) and thiol **2**, a slight amount of toluene was detected by gas chromatography.[8] The bimolecular homolytic substitution reaction between **1** and **2**, which is an assumed path of direct alkyl sulfide formation, will not occur for high dissociation energy of RS-H bond.[9]

(Alkylthio)cobaloxime **5** prepared from sodium thiolate and chloro(pyridine)cobaloxime[5] worked as a catalyst for the formation of disulfide **4** from **2**,[10] where **5** worked catalytically just as (phenylthio)cobaloxime has been reported[11] to catalyze the hydrogen evolution and diphenyl disulfide formation from benzenethiol under irradiation. The result of the disulfide formation in Table I would be ascribed this catalytic reaction. In the second step, the cobaloxime **5** reacts with **2** (path b) to give **4** and hydridocobaloxime, of which further reaction with **2** gives **5** and hydrogen (path c).

Disulfide **4** reacted with 1.5 M benzylcobaloxime (**1b**) at -20 °C under the irradiation condition to give sulfide **3** in 106% yield. Sulfide **3** would be formed by the bimolecular homolytic displacement reaction[12] of **1** and **4** (path d). Photoactivation is responsible for the decreased yield of disulfide by extending the reaction time (Table I, runs 2 and 3). In addition, the above result suggests the (alkylthio)cobaloxime **5** formed in the reaction is also reacted with benzylcobaloxime (**1b**) to give sulfide **3**. The equimolar reaction of **1b** and (alkylthio)cobaloxime **5** gave sulfide **3** in 14% yield under the same reaction condition. In parallel to the main path (d) for disulfide formation, path e is presumed to exist.

(7) Yield of benzyl sulfides; benzyl phenyl sulfide (51%), dibenzyl sulfide (38%), 2-benzylthioethanol (34%).

(8) Yield of toluene was determined to be 7% by GLC with *m*-xylene as an internal standard.

(9) The dissociation energy of RS-H (about 90 kcal/mol) is considerably higher than that of substrates (CCl_3Br, PhSSPh, RSO_2Cl, etc.) which can take place in homolytic displacement with alkylcobaloxime.

(10) The mixture of thiol **2** (1 mmol) and cobaloxime **5** (0.02 mmol) in CH_2Cl_2 (2 mL) were irradiated with W lamp to give disulfide **4** in 60% yield.

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Catalytic Asymmetric Induction in Enantioselective Conjugate Addition of Dialkylzincs to Enones[†]

Summary: Chiral complex derived in situ from nickel acetylacetonate and *N,N*-dibutylnorephedrine catalyzed the asymmetric addition of dialkylzinc reagents to enones to afford optically active β-substituted ketones in moderate enantiomeric excesses.

Sir: Increasing interest has been centered on *catalytic* asymmetric carbon-carbon bond forming reaction.[1] Although many methods have been reported on the asymmetric conjugate addition of organometallic reagents to α,β-unsaturated carbonyl compounds,[2] all methods require at least a stoichiometric amount of chiral auxiliary. No attempts have been made in the area of *catalytic* asymmetric conjugate addition of organometallic reagents to α,β-unsaturated carbonyl compounds.

During our continuing study on asymmetric 1,2-addition of dialkylzincs to aldehydes,[3] we found the first catalytic asymmetric conjugate addition of dialkylzincs to enones catalyzed by a chiral nickel complex. Chiral nickel catalyst **2** was prepared by stirring a mixture of nickel acetylacetonate [$Ni(acac)_2$] (1 equiv)[4] and either (1*S*,2*R*)-(-)- or (1*R*,2*S*)-(+)-2-(*N,N*-dibutylamino)-1-phenylpropan-1-ol (**1**) (*N,N*-dibutylnorephedrine) (1.2 equiv)[3c] in toluene (eq 1). Although we have not yet managed to prepare a characterizable chiral *N,N*-dibutylnorephedrinato complex of nickel, asymmetric conjugate additions with in situ generated chiral nickel complexes **2** have been encouraging (eq 2). As shown in Table I, conjugate addition of diethylzinc (**4b**) to chalcone (**3a**) using **2** [prepared from (1*S*,2*R*)-(-)-**1**] as catalyst [0.50 mol equiv to **3a**] afforded optically active (*R*)-(-)-1,3-diphenylpentan-1-one (**5b**) in 75% isolated yield and in 45% enantiomeric excess (ee) as determined by HPLC analysis using chiral column (Daicel Chiralcel OD) (Table I, entry 2). Without **2**, no

[†] A preliminary account of these results has been reported at the 56th National Meeting of the Chemical Society of Japan, Tokyo, 1988; Paper 1XII B37.

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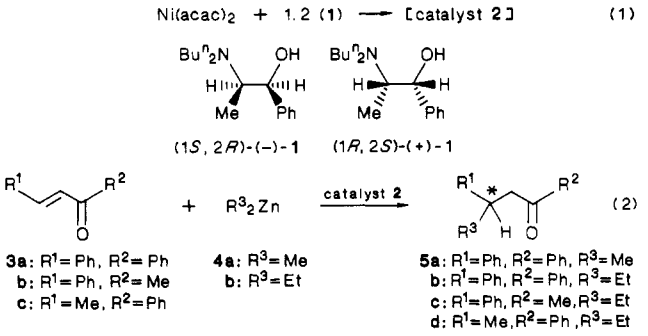
Table I. Catalytic Asymmetric Addition of Dialkylzincs to Enones 3 Using 2

entry	3	4, R^3	molar ratio 2:3	5	[α] (c, solvent)	yield, %	% ee[a]	config[b]
1	a	Me	0.60[c]	a	$[\alpha]^{24}_{546}$ −6.78° (1.80, CCl_4)	72	40	R
2	a	Et	0.50[c]	b	$[\alpha]^{22}_{365}$ −58.09° (2.50, EtOH)	75	45	R
3	a	Et	0.06[c]	b	$[\alpha]^{22}_{D}$ −1.92° (2.50, EtOH)	94	20	R
4	a	Et	0.06[d]	b	$[\alpha]^{25}_{D}$ +1.32° (2.50, EtOH)	89	22	S
5	b	Et	0.60[c]	c	$[\alpha]^{23}_{D}$ −3.48° (2.30, EtOH)	63	12	R
6	c	Et	0.50[c]	d	$[\alpha]^{22}_{D}$ −4.26° (1.01, Et_2O)	78	44	R

[a] Determined by HPLC analysis using a chiral column (Daicel Chiralcel OD, 250 mm). Flow rate, 0.5 mL/min; eluant, 0.25% 2-propanol in hexane; UV detector (254 nm). Retention time for **5a**, *S* isomer (minor), 33.8 min, *R* isomer (major), 37.3 min. For **5b**, *S* isomer (minor), 28.9 min, *R* isomer (major), 32.7 min. For **5d**, eluant, 0.20% 2-propanol in hexane, *S* isomer (minor), 36.8 min, *R* isomer (major), 40.2 min. [b] Based on the reported values of optical rotations. For (*R*)-(−)-**5a**, $[\alpha]^{25}_{546}$ −18.9° (*c* 1.8, CCl_4): Leitereg, T. J.; Cram, D. J. *J. Am. Chem. Soc.* **1968**, *90*, 4011. For (*S*)-(+)-**5b**, $[\alpha]^{23}_{D}$ +10.5° (*c* 2.5, EtOH), cf. $[\alpha]^{23}_{364}$ +75° (*c* 2.5, EtOH): Brienne, M. J.; Ouannes, C.; Jacques, J. *Bull. Soc. Chim. Fr.* **1967**, 613. For (*S*)-(+)-**5c**, $[\alpha]^{22}_{D}$ +30° (*c* 2.3, EtOH), see the literature for **5b**. For (*S*)-(+)-**5d**, $[\alpha]_{D}$ +19.6° (*c* 5, Et_2O): Seebach, D.; Steinmuller, D. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 619. [c] (1*S*, 2*R*)-(−)-1 was used. [d] (1*R*, 2*S*)-(+)-1 was used.



5b was formed.[5] Conjugate addition of dimethylzinc (**4a**) to **3a** also afforded (*R*)-**5a** in 40% ee (entry 1). The both enantiomers of norephedrine are readily available. Thus either enantiomers of **5b** were synthesized by employing an appropriate enantiomer of **1** (entries 3 and 4). Conjugate addition of **4b** to 1-phenyl-2-buten-1-one (**3c**) (without a phenyl substituent in the olefinic part) afforded (*R*)-**5d** in 44% ee (entry 6).

Ee's of **5** were depend upon the molar ratio of **2** to **3**. Ee's increased according to the increase of the molar ratio. Although further investigation should be necessary, we tentatively assume two possibilities to account for the above result. One is that catalyst **2** is unstable under the reaction conditions and decomposes to yield some other nickel species which will also catalyze the reaction. The other is that the aggregation(s) of the complex between catalyst **2** and dialkylzinc may be reactive species. In this case, the concentration of the catalyst may affect ee's.

In a typical experiment (Table I, entry 2), a mixture of $Ni(acac)_2$ (0.50 mmol) and (1*S*,2*R*)-(−)-**1** (0.60 mmol) in toluene (1 mL) was stirred at 80 °C for 1 h and then cooled to room temperature.[6] Chalcone (**3a**) (1.00 mmol) in toluene (2 mL) was added, and the mixture was stirred for 20 min and then cooled to −30 °C. Diethylzinc (**4b**) (1 M solution in hexane, 2.20 mmol) was added dropwise, and then the resulting mixture was stirred at −30 °C for 2 h. The reaction was quenched with 1 M hydrochloric acid (7 mL), the organic layer was separated, and the aqueous layer was extracted with dichloromethane (8 mL × 4). The combined organic layer was dried (Na_2SO_4) and then evaporated under reduced pressure. The residue was purified by preparative TLC over silica gel (eluent, hexane/chloroform, 1:1, v/v) to afford (*R*)-(−)-**5b** (0.75 mmol) in 75% (45% ee).

Although the degrees of the asymmetric induction are moderate, the present results may open the way to the catalytic enantioselective conjugate addition of organometallic reagents to enones.

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(5) In addition, no reaction occurred between **3a** and **4b** in the presence of (−)-**1**.

(6) When the eliminated acac was evaporated in vacuo at this stage, catalyst **2** afforded (*R*)-(−)-**5b** of 37% ee in 80% yield.

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Intramolecular Arylations of Soft Enolates Catalyzed by Zerovalent Palladium

Summary: A new method of ring formation involving palladium-catalyzed displacement of halide from aromatic substrates by stabilized enolates is described. The new reaction permits creation of benzo-fused, five- or six-membered rings, in the homocyclic or in the heterocyclic mode.

Sir: The direct arylation of carbonyl enolates is an unusual mode of C–C connectivity. Such transformation normally requires activation of the aromatic component, as a result of the reluctance of ordinary aromatic substrates to function as electrophiles.[1] Several methods for arylation

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