The Stereochemistry and Mechanism of Cleavage of Alkylcobaloximes by Halogen

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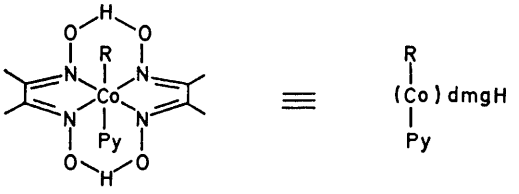
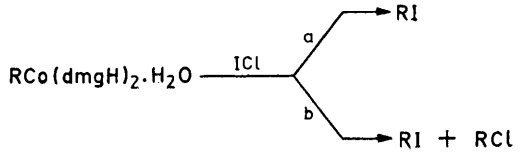
The cleavage of alkylcobaloximes by iodine monochloride was shown to occur with a partial net inversion at the α carbon atom. The products, iodides or chlorides, are explicable in terms of electron transfer from the alkylcobaloxime followed by heterolysis or homolysis of the alkyl–cobalt bond, dependent on the nature of the alkyl group.

ALTHOUGH the dealkylation of alkylcobaloximes (1) by halogen has been studied in some detail,[1-7] the mechanism of the reaction is uncertain. The organic products of dealkylation by iodine monochloride vary with the nature of the alkyl group [1,2] (Scheme 1). An electrophilic mechanism has been proposed [2] to account for the formation of iodoalkane (Scheme 1, route a) whereby the



(1; Py = *N*–pyridinato)

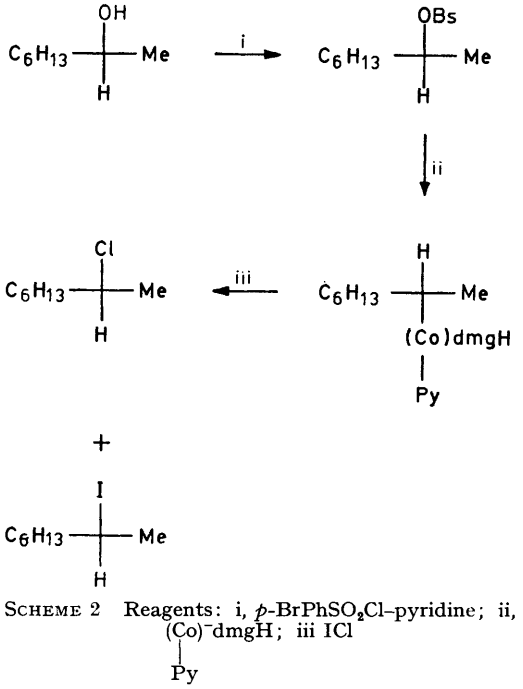
α carbon atom of the alkylcobaloxime is attacked by the more electrophilic end of the iodine monochloride molecule. The observation of mixed halogenoalkanes (Scheme 1, route b) from the dealkylation of benzyl and



SCHEME 1 a, R = Me, Pr^n; b, R = Pr^i, $PhCH_2$

certain secondary alkyl cobaloximes was suggested [2] to be the result of a secondary halogen exchange reaction [8] taking place on iodoalkane, the primary product. Knowledge of the stereochemistry of these dealkylations would be a valuable aid to the assignment of a reaction mechanism. We now present the results of a stereochemical study of halogenations with iodine chloride of a series of alkylcobaloximes.

The halogenation of n-butyl- (1; R = Bu^n) and 1-methylheptyl- (1; R = 1-methylheptyl) pyridinatocobaloximes with iodine monochloride gave products analogous to those reported [2] for the dealkylation of primary and secondary alkylaquocobaloximes, as in Scheme 1. The stereochemistry of reaction in the secondary, 1-methylheptyl, case was determined using (*S*)-1-methylheptylpyridinatocobaloxime prepared by the treatment of optically active 1-methylheptyl *p*-bromobenzenesulphonate with pyridinatocobaloxime(I) nucleophile (Scheme 2). The mixed halides formed on dealkylation of (*S*)-methylheptylpyridinatocobaloxime were separated by preparative g.l.c. Both iodo- and chloro-octane were found to exhibit a negative rotation of −3.1 and −9.4° respectively, indicative of a low degree of net inversion in the formation of each (Scheme 2) {*cf.* (*R*)-2-iodo-octane $[\alpha]_D$ −56.6° and (*R*)-2-chloro-octane $[\alpha]_D$ −36.14°}. In the light of this result, the proposal [2] that the mixed halides arise *via* a secondary exchange of iodide for chloride is clearly incorrect since

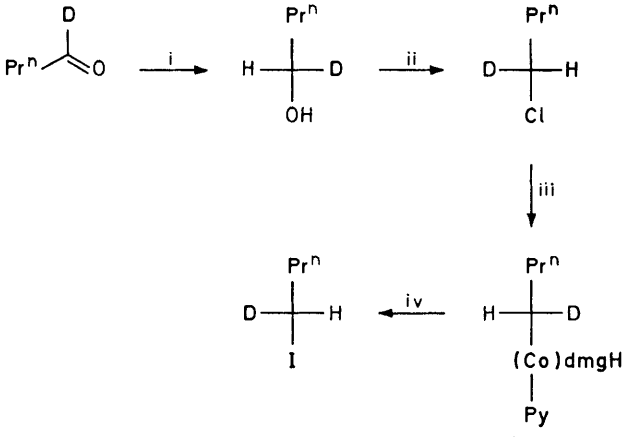


SCHEME 2 Reagents: i, *p*-$BrPhSO_2Cl$–pyridine; ii, (Co)⁻dmgH; iii ICl

the exchange reaction involves at least partial inversion, which would lead to chloro- and iodo-octane of opposite stereochemistries, the latter having undergone a double inversion process.

The stereochemistry of the n-butylpyridinatocobaloxime dealkylation was determined using asymmetrically deuteriated material (Scheme 3). 1-Deuteriobutanal was reduced with fermenting yeast to give (*S*)-1-deuteriobutan-1-ol [9] which was converted into chloride with inversion using chloromethylenedimethylammonium chloride.[10] (*S*)-1-Deuteriobutylpyridinatocobaloxime

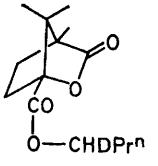
was prepared by reaction of (*R*)-1-deuterio-1-chlorobutane with pyridinatocobaloxime(I) nucleophile, a type of reaction known to occur stereospecifically with inversion.[11]



SCHEME 3 Reagents: i, fermenting yeast; ii, $Me_2\overset{+}{N}=CHCl\ Cl^-$; iii, $(Co)^-dmgH$; iv, ICl
Py

The (*S*)-1-deuteriobutylpyridinatocobaloxime was dealkylated with iodine monochloride to give 1-deuterio-1-iodobutane. The stereochemistry of this product was analysed using an n.m.r. technique [12] which utilises the fact that the prochiral α protons of primary alcohol camphanate esters are differentially shifted in the n.m.r. spectrum by the addition of a europium shift reagent.

The 1-deuterio-1-iodobutane was converted directly to a camphanate ester (2) by treatment with potassium



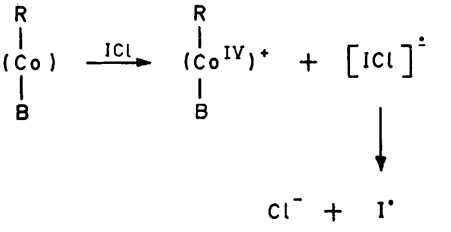
(2)

camphanate–18-crown-6. Such reactions are known to occur with inversion of configuration.[13] On addition of $Eu(thd)_3$ (30 molar %) to a solution of this 1-deuteriobutylcamphanate the *pro-R* and *pro-S* protons were shifted downfield in the n.m.r. spectrum by 1.0 and 2.4 p.p.m., respectively.[12] In the present study, the ratio of the integrals *pro R* : *pro S* is 1.5 : 1. Assuming 20% non-deuteriated material * this result indicates 33% net inversion during dealkylation of (*S*)-1-deuteriobutylpyridinatocobaloxime with iodine monochloride.

In addition to the dealkylation of 1-methylheptyl- and n-butyl-cobaloximes we have studied the halogenation by iodine monochloride of a number of substituted alkylcobaloximes (Table). These were chosen as examples for which the desired carbonium ions would be destabilised. Such cobaloximes would be unlikely to fragment by a pathway involving these ions. In no case was any organochloride detected although fragmentation and disproportionation was competitive with halogenation in certain cases (Table, runs 2, 4). Dealkylation of alkylcobaloximes by bromine is known to involve inversion of configuration at the α-carbon atom.[3-6] A mechanism involving oxidation of the cobalt centre followed by S_N2 attack of halide ion on the α-carbon atom has been put forward to explain this inversion.[3] Such a mechanism, however, would lead to the formation of chloroalkane and iodocobaloxime when the halogen used was iodine monochloride, whereas the converse has been observed [2] when R is a primary alkyl group.

Electrophilic attack of halogen on the α-carbon atom with inversion of configuration *via* an 'S_E2 open' type intermediate has also been proposed for alkylcobaloxime halogenation.[2,5,6] This would account for the formation of iodoalkane in the iodine monochloride dealkylation but does not readily explain the formation of mixed halides when secondary alkylcobaloximes are used. Furthermore the feasibility of an 'S_E2 open' intermediate generally has been criticised on grounds of insufficient molecular orbital overlap.[14]

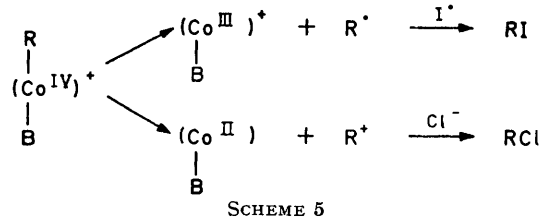
A mechanism which reasonably accounts for the chemical and stereochemical observations of dealkylation by iodine monochloride involves an initial one-electron oxidation of the alkylcobaloxime to give an alkylcobalt(IV) cationic complex,[3] chloride ion, and an iodine radical (Scheme 4). Subsequent homolysis of the carbon–cobalt bond could be followed by coupling of the alkyl radical so formed, with the iodine radical, leading to racemised iodoalkane (*e.g.* Table, run 5). The partial net inversion observed in the n-butylpyridinatocobaloxime dealkylation may arise from some degree of bimolecular attack of iodine radical on the α-carbon atom of the oxidised alkylcobaloxime. S_H2



SCHEME 4

Substitution with inversion of this kind has recently been observed.[15] The dealkylation reactions of iodine monochloride which produce mixtures of iodoalkane and chloroalkane may be the result of competing heterolysis of the carbon–cobalt bond of the oxidised complex (Scheme 5). It is of particular note that the alkyl

* 1-Deuteriobutylcamphanate prepared by reaction of camphanic acid chloride with the original (*S*)-1-deuteriobutan-1-ol showed a ratio of *pro-R* : *pro-S* of 5 : 1. Reduction of the yeast is 100% stereospecific [9] and the *pro-S*-proton resonance is due to contamination derived from ethanol formed during the fermentation and not separated from 1-deuteriobutanol during purification.



SCHEME 5

cobaloximes which give chloroalkane as well as iodoalkane are those for which carbonium ion formation would be more favourable (1-methylheptyl, isopropyl, benzyl). This mechanism would also account for the observed low degree of inversion of configuration in the formation of chloroalkane since a competitive S_N2 attack of chloride ion might be expected.

Cleavage by iodine chloride of alkylcobaloximes R(Co)-dmgHB

	R	B	Product(s) (%)	Ratio
(1)	$CH_3\underset{\vert}{C}HCOCH_3$	C_5H_5N [a]	$CH_3CHICOCH_3$ (11)	
(2)	$CH_3\underset{\vert}{C}HCO_2CH_3$	C_5H_5N	$CH_2{=}CH{\cdot}CO_2Me$	1 [b,c]
			$CH_3CH_2CO_2Me$	1
(3)	$\underset{\vert}{C}H_2CH_2CO_2Me$	C_5H_5N	$ICH_2CH_2CO_2Me$ (32)	
(4)	$CH_3\underset{\vert}{C}HCN$	C_5H_5N	CH_3CHICN	2 [b]
			CH_3CH_2CN	2
			$CH_2{=}CHCN$	1
(5)	$CH_3\underset{\vert}{C}HCO_2Me$	Bu^n_3P	$CHICO_2Me$(30)	
(6)	$CH_3\underset{\vert}{C}HCN$	Bu^n_3P	CH_3CHICN (27)	

[a] Pyridine. [b] Determined by n.m.r. spectroscopy. [c] No methyl 1-iodopropionate was detected by g.l.c.

EXPERIMENTAL

Unless otherwise stated, all reactions were performed under anhydrous conditions. Solutions of alkylcobaloxime were handled under nitrogen in subdued daylight using degassed solvents. Solvents were purified and dried by standard methods.[16]

Characterisation of Products.—^{1}H N.m.r. spectra were recorded on a Varian T60 spectrometer in deuteriochloroform with tetramethylsilane as internal standard (unless indicated otherwise). Mass spectra were measured on an A.E.I. MS9 instrument operating at 70 eV. Melting points were determined using a Kofler hot-stage apparatus. Gas–liquid chromatographs were recorded on a Perkin-Elmer F11 instrument using flame-ionisation detection. A Carbowax 20M column was employed at 30—150 °C. Optical rotations were recorded for solutions in chloroform on a Perkin-Elmer 141 polarimeter.

Merck Kieselgel GF_{254} was used for analytical and preparative t.l.c. Chromatograms of mixtures containing alkylcobaloxime were developed using chloroform–ethyl acetate–methanol (2 : 2 : 1).

Dealkylation of 2-Methoxycarbonylethylpyridinatocobaloxime.—2-Methoxycarbonylethylpyridinatocobaloxime (3 g, 6.6 mmol) in dichloromethane (40 ml) was treated at 0 °C with iodine monochloride (1.07 g, 6.6 mmol). The solution was allowed to reach room temperature. After 30 min the solvent was slowly evaporated off. The remaining volatile material was collected by vacuum transfer (10^{-4} mmHg) to a liquid nitrogen trap. The product was identified as methyl 3-iodopropionate, τ 6.2 (3 H, s, OMe) and 6.5—7.4 4 H, m, CH_2CH_2), *m/e* 214 (M^+) and 87 (100%).

All alkylcobaloxime dealkylation reactions (Table) with halogen were carried out using analogous procedures to the above. Yields and methods of identification are given in the Table.

(R)- *and* (S)-1-*Methylheptylpyridinatocobaloximes.*—(i) The general procedure [17] was followed for the reaction of (−)-1-methylheptyl *p*-bromobenzenesulphonate (17 g, 49 mmol) with pyridinatocobaloxime(I) (13.6 g, 37 mmol) affording (*S*)-1-methylheptylpyridinatocobaloxime (9 g, 67%).

(ii) (−)-Octan-2-ol (6 g, 46 mmol) was treated with chloromethylenedimethylammonium chloride (7 g, 55 mmol), as previously described [10] to give (+)-2-chloro-octane (5.7 g, 83%), $[\alpha]_D^{21}$ +29.8° (lit.,[18] $[\alpha]_D^{20}$ −36.14°).

Pyridinatocobaloxime(I) (14.7 g, 40 mmol) was treated with (+)-2-chloro-octane (5.5 g, 42 mmol) according to the general procedure [17] to give (*R*)-1-methylheptylpyridinatocobaloxime (6 g, 32%).

Dealkylation of (S)-1-*Methylheptylpyridinatocobaloxime with Iodine Monochloride.*—(*S*)-1-Methylheptylpyridinatocobaloxime (3.94 g, 8.2 mmol) was treated with iodine monochloride (1.34 g, 8.2 mmol) in the manner described for butylcobaloxime (see below). The volatile products were shown (g.l.c.) to consist principally of 2-iodo- and 2-chloro-octane in the ratio 1.4 : 1. These two components were separated by preparative g.l.c. to yield 2-chloro-octane (76 mg), $[\alpha]_D^{22}$ −9.4° (lit.,[18] $[\alpha]_D^{20}$ −36.14°), and 2-iodo-octane (98 mg), $[\alpha]_D^{22}$ −3.1° (lit.,[19] $[\alpha]_D^{18}$ −56.8°).

(S)-[1-^{2}H]*Butylpyridinatocobaloxime.*— [1-^{2}H]*Butanal.* (i) Via 2-*propyl*-1,3-*dithian.* Propane-1,3-dithiol (4 g, 0.037 mol) was added to butanal (2.68 g, 0.037 mol) in chloroform (38 ml). The solution was set aside for 1 h before cooling to 120 °C. A stream of dry hydrogen chloride was passed into the solution for 3 min. The reaction mixture was allowed to reach room temperature and left for 15 h. The chloroform solution was washed with water (3 × 25 ml), 10% aqueous potassium hydroxide (3 × 25 ml), water (3 × 25 ml), and dried over anhydrous potassium carbonate. The solution was distilled to yield 2-propyl-1,3-dithian [20] (3.9 g, 65%), b.p. 60° at 0.5 mmHg, τ 6.3 (1 H, t), 6.9—7.3 (4 H, m), and 7.5—9.2 (9 H, m).

Butyl-lithium (10 ml, 2.5M in hexane, 25 mmol) was added to a solution of 2-propyl-1,3-dithian (3.8 g, 23.3 mmol) in dry tetrahydrofuran (60 ml) at −15 °C. To this was added deuterium oxide (0.5 ml). The solution was warmed to room temperature and shaken with a mixture of chloroform (50 ml) and water (50 ml). The organic layer was separated and washed with water (3 × 50 ml), 5% hydrochloric acid (2 × 50 ml), and water (3 × 50 ml). The solvent was distilled off to leave 2-[2-^{2}H]propyl-1,3-dithian (3.24 g, 85%), τ 6.9—7.3 (4 H, m) and 7.5—9.2 (9 H, m). 2-[2-^{2}H]Propyl-1,2-dithian (1.6 g, 10 mmol) was added to a solution of methyl fluorosulphonate (1.7 g, 12 mmol) in refluxing sulphur dioxide (15 ml). After 10 min water (0.4 ml) was added. The solvent was allowed to evaporate off and the residue was distilled to yield [1-^{2}H]-butanal [21] (130 mg, 19%); integration of the small peak at τ 1.6 showed *ca.* 1.5% of non-deuteriated material.

(ii) Via [1,1-$^2H_2$]*butan*-1-*ol.* Methyl-lithium (93 ml, 1.7M solution in ether, 158 mmol) was added slowly to a cooled solution of butanoic acid (14 g, 159 mmol) in dry ether (30 ml). To this solution lithium aluminium deuteride (3 g, 79 mmol) in dry ether (250 ml) was added at a rate sufficient to maintain gentle reflux. On complete addition the solution was boiled under reflux for 2 h. Water (3 ml)

followed by 15% aqueous sodium hydroxide (3 ml) and then water (9 ml) was added to the solution. The white precipitate was filtered off through Celite. The filtrate was evaporated and distilled to yield [1,1-$^2H_2$]butan-1-ol [21] (7.7 g, 71%), τ 5.1 (1 H, s) and 8.5—9.6 (7 H, m), $\nu_{max.}$ 3 350, 2 920, 2 200, 2 100, 1 470, 1 160, and 960 cm^{-1}.

[1,1-$^2H_2$]Butan-1-ol (7 g, 92 mmol) was stirred very rapidly (mechanically) in a three-necked flask. The flask was fitted with a reflux condenser at the top of which was a condenser set for downward distillation. Cold water was circulated through the downward condenser and water at 83 °C through the reflux condenser. The alcohol was heated to boiling and a solution of potassium dichromate (8.8 g, 30 mmol) in 10% sulphuric acid (61 ml) was added over a period of 1 h. After complete addition, the contents of the flask were boiled for a further 30 min. The distillate from the downward condenser was collected and the organic layer separated to yield [1-^{2}H]butanal [1] (3.9 g, 53%); integration of the resonance at τ 1.6 indicated less than 1% undeuteriated material.

Yeast culture. *Saccharomyces cerevisiae* (strain NCYC 1236) was grown aerobically in 1 l flasks containing sterile culture medium [22] of water (500 ml), D-glucose (25 g), dried yeast extract (2.5 g), hydrolysed casein (2.5 g), mycological peptone (1.5 g), potassium dihydrogenphosphate (5.42 g), and dipotassium hydrogenphosphate (0.52 g). The flasks were agitated on an orbital shaker at 30 °C for 48 h. The yeast was harvested by centrifugation.

(S)-[1-^{2}H]*Butan-1-ol*. Freshly grown yeast (228 g) was added to a solution of D-glucose (230 g) in water (950 ml) at 30 °C and agitated on an orbital shaker. When rapid fermentation commenced (5 min), a solution of [1-^{2}H]-butanal (4 g) in ethanol (3 ml) was added. After 48 h the mixture was steam-distilled until 400 ml of distillate had been collected. The distillate was saturated with sodium sulphate and continuously extracted with ether (40 ml) for 24 h. The ether extract was fractionally distilled using a 10 cm column packed with Fenske helices. The fraction distilling at 85—95° was collected and cooled to 4 °C. An aqueous phase separated and was discarded. The organic layer was dried over 4 Å molecular sieve to yield (*S*)-[1-^{2}H]butan-1-ol [9] (2.2 g, 54%), τ 5.4 (1 H, s), 6.3—6.8 (1 H, m), and 8.4—9.5 (7 H, m).

(R)-[1-^{2}H]*Chlorobutane*. (*S*)-[1-^{2}H]Butan-1-ol (1 g, 13.3 mmol) was added dropwise to a stirred suspension of chloromethylenedimethylammonium chloride (2.24 g, 17.5 mmol) in dioxan (6 ml) cooled in ice.[10] When the addition was complete, the solution was refluxed for 1 h. Water (20 ml) was added to the solution, whereupon a clear oil separated out as an upper layer which was collected and distilled to yield (*R*)-1-chloro-[1-^{2}H]butane [23] (0.91 g, 74%), b.p. 79°.

(S)-[1-^{2}H]*Butylpyridinatocobaloxime*. (*R*)-1-Chloro[1-^{2}H]-butane (0.7 g, 7.5 mmol) was added to a stirred solution of pyridinatocobaloxime(I) (2.6 g, 7.1 mmol) at −10 °C, prepared as previously described.[17] The solution was stirred overnight and reduced in volume by 50% (without heating). Water (50 ml) was added and the orange crystals collected by centrifugation and decantation of the liquid. The product was washed with water (2 × 50 ml) and collected and dried *in vacuo* to yield (*S*)-[1-^{2}H]-butylpyridinatocobaloxime (1.5 g, 49%), τ 1.4—2.8 (5 H, m), 7.9 (12 H, m), and 8.1—9.5 (8 H, m).

Dealkylation of (S)-[1-^{2}H]*Butylpyridinatocobaloxime with Iodine Monochloride*.—(*S*)-[1-^{2}H]Butylpyridinatocobaloxime (850 mg, 2.0 mmol) was dissolved in dichloromethane (6 ml) and cooled to 0 °C. A cooled solution of iodine monochloride (324 mg, 1.99 mmol) in dichloromethane was added with stirring in the dark. After 5 min at room temperature the solvent was evaporated off under reduced pressure and the remaining 1-iodo[1-^{2}H]butane (40 mg, 11%) was collected by vacuum transfer at 10^{-4} mmHg to a liquid nitrogen trap.

Butyl Camphanate.—(a) *From* (S)-[1-^{2}H]*butan-1-ol*. Camphanoyl chloride [24] (120 mg, 0.56 mmol) was added to a solution of (*S*)-[1-^{2}H]butan-1-ol (41 mg, 0.56 mmol) in pyridine (2 ml). The solvent was evaporated off to leave an oil, which was sublimed (80° at 5 × 10^{-4} mmHg) to yield (*S*)-[1-^{2}H]butyl camphanate [12] (98 mg, 61%), m.p. 71°, τ (CCl_4) 5.5—5.9 (1 H, m, $-CO_2-CHDC_3H_7$), 7.2—8.7 (11 H, m), 8.8 (3 H, s), 8.83 (3 H, s), and 9.0 (3 H, s).

(b) *From potassium camphanate and iodobutane*. Potassium camphanate (65 mg, 0.28 mmol), dried *in vacuo* at 120 °C, was added to a solution of 1-iodobutane (50 mg, 0.27 mmol) and 18-crown-6 (70 mg, 0.27 mmol) in acetone (8 ml). The solution was left at room temperature for 48 h. The product was isolated by preparative t.l.c. (silica) to give butyl camphanate (39 mg, 55%), τ 5.75 (2 H, t, OCH_2CH_2), 7.2—8.7 (11 H, m), 8.80 (3 H, s), 8.83 (3 H, s), and 9.0 (3 H, s).

(S)-*Ethyl 2-Bromopropionate*.—Phosphorus tribromide (62.5 g, 0.23 mol) was added dropwise to a stirred flask containing (*R*)-ethyl lactate [25] (77 g, 0.65 mol) maintained at −15 °C. After complete addition the reaction mixture was washed with water (3 × 100 ml), saturated aqueous sodium hydrogencarbonate (3 × 50 ml), and water (3 × 100 ml), and distilled (67° at 10 cmHg) to give (*S*)-ethyl 2-bromopropionate (89 g, 76%), $[\alpha]_D^{21}$ +14.2° (lit.,[26] $[\alpha]_D^{20}$ +35.5°), τ 5.7 (1 H, q, CH_3CHBr), 5.8 (2 H, q, $CH_3CH_2O_2C$), 8.25 (3 H, d, CH_3CHBr), and 8.75 (3 H, t, $CH_3CH_2O_2C$).

(R)-1-*Ethoxycarbonylethyltributylphosphinatocobaloxime*.—Tributylphosphinatocobaloxime(I) (19.1 g, 0.039 mol) was alkylated with (*S*)-ethyl 2-bromopropionate (8.2 g, 0.045 mol), according to the general procedure described before,[17] to yield (*R*)-1-ethoxycarbonylethyltributylphosphinatocobaloxime [27] (6 g, 26%), τ 5.8 (2 H, q, CH_3CH_2OCO), 7.7 (12 H, d, *J* 4 Hz, $H_3CC{=}N$), and 8.3—9.6 (24 H, m).

Dealkylation of (R)-1-*Ethoxycarbonylethyltributylphosphinatocobaloxime*.— (*R*)-1-Ethoxycarbonylethyltributylphosphinatocobaloxime (2 g, 3.6 mmol) was treated with iodine monochloride (0.585 g, 3.6 mmol) as before. The product, ethyl 2-iodopropionate (130 mg, 16%), exhibited no optical activity.

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