Alkylation of Benzene with Optically Active 3-Chloro-1-butanol, 3-Chlorobutanoic Acid, and Their Esters

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The alkylations of benzene with optically active 3-chloro-1-butanol, 3-chlorobutanoic acid and their esters in the presence of aluminium chloride gave the corresponding 3-phenyl substituted derivatives in good optical yield. All these reactions were found to proceed with inversion of configuration at the attacking carbon atom. The products were not racemized under the conditions used, while the starting materials were racemized to a considerable extent during the reaction. Taking into account of the optical purity of the starting material recovered before the completion of reaction, net stereospecificity of each reaction was calculated to be about 90% except for the case of 3-chloro-1-butanol and its acetic ester. The high degree of stereospecificity of the reaction can be interpreted by the mechanism involving cyclic intermediate formed from the alkylating reagent and aluminium chloride.

Compared to extensive studies on the Friedel-Crafts alkylation of aromatic hydrocarbons with alkyl halide or alcohol, the stereochemistry of these reactions received relatively little attentions.[2] Generally, Friedel-Crafts type alkylation has long been pointed out to proceed with almost complete recemization when an optically active alkylating reagent was used.[3] Some examples of the stereospecific reaction were recently reported, *e.g.* the alkylation of benzene with (+)-γ-valerolactone and (+)-2-methyltetrahydrofuran in the presence of aluminium chloride proceeded with 47% and 35% net inversion of configuration at the attacking carbon, respectively.[4,5] We also observed complete inversion in the reaction of benzene with (+)-propylene oxide[6] and (+)-1,2-epoxybutane[7] by Lewis acid catalysts. The stereospecificity in these reactions has been explained on the basis of the cyclic nature of the alkylating reagents or the enforced proximity of ion pairs produced by the ring opening reaction. Furthermore, (−)-2-chloro-1-phenylpropane reacted with benzene in the presence of aluminium chloride or iron(III) chloride to give (−)-1,2-diphenylpropane with 70—95% retention of configuration.[8] This result was interpreted by the participation of the neighboring phenyl group to the reaction center.

In connection with these observations, it is interesting to investigate the stereochemistry of Friedel-Crafts reaction with acyclic alkylating reagents such as 3-chloro-1-butanol, 3-chlorobutanoic acid and their esters. Little is known about Friedel-Crafts reactions with halogenated alcohol, halogenated carboxylic acid and their ester.[9] In a communication we demonstrated that the alkylation of benzene with optically active 3-chloro-1-butanol (Ia) and 3-chlorobutanoic acid (Ib) by aluminium chloride catalyst proceeded with inversion of configuration to give 3-phenyl-1-butanol (IIa) and 3-phenylbutanoic acid (IIb), respectively.[10] In the present paper, we have extended our previous work on Ia and Ib to their esters, ethyl 3-chlorobutanoate (Ic), 3-chlorobutyl benzoate (Id), and 3-chlorobutyl acetate (Ie) with a view to obtaining more information on the stereochemistry of the Friedel-Crafts alkylation. Furthermore, the net stereospecificity of reaction was determined by taking into account of the remaining optical activity of the starting materials recovered.

Results and Discussion

At first, the reaction was run in usual manner in order to know a general tendency on the stereochemistry of the reaction. The alkylating reagent was gradually added to a stirred mixture of aromatic hydrocarbon and Lewis acid at such a rate that the temperature of the reaction mixture does not rise higher (see the method A in Experimental). Optically active Ia, Ib, Ic, Id, and Ie reacted with benzene in the presence of 1.2 equivalents of aluminium chloride at −5—50 °C to give the corresponding 3-phenyl substituted derivatives, 3-phenyl-1-butanol (IIa), 3-phenylbutanoic acid (IIb), ethyl 3-phenylbutanoate (IIc), 3-phenylbutyl benzoate (IId), and 3-phenylbutyl acetate (IIe), respectively, in optically active form. The results are described in Table 1.

In these reactions, by-products such as haloalkylated and haloacylated compounds and rearrengement products were not obtained under the conditions used. However, the esters (Ic, Id, and Ie), when treated under higher temperature (over 40 °C), gave considerable amounts of the hydrolyzed products (IIb from Ic, and IIa from Id or Ie) along with the normal products. Furthermore, diphenylbutane was also obtained in the case of Id and Ie. These by-products seem to arise from the primary products. This was confirmed by the experimental result that IIc and IId (or IIe) reacted with aluminium chloride in benzene to yield IIb and IIa, respectively.

The absolute configurations of the dextrorotatory chlorides (Ia, Ib, and Ic) and the levorotatory products (IIa, IIb, and IIc) have been established to be *S*[11] and *R*,[12–14] respectively, whereas those of Id, Ie, IId, and IIe are not known yet. The configurations of (+)-Id and (+)-Ie were correlated with that of (+)-Ia (see Experimental) and assigned to be *S*. In the same way, (−)-IId and (−)-IIe were correlated to *R*-(−)-IIa. Consequently, it is apparent that all these reactions proceeded with inversion of configuration at the attacking carbon atom. The optical yield of each reaction was calculated by the use of maximum rotations in Table 2.

TABLE 1. ALKYLATION OF BENZENE WITH OPTICALLY ACTIVE $CH_3CH(Cl)CH_2Y$ BY ALUMINIUM CHLORIDE CATALYST (BY METHOD A)[a]

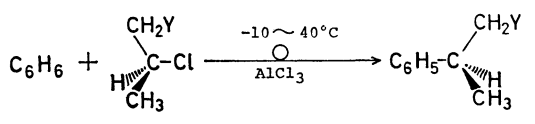
Compd	$CH_3CH(Cl)CH_2Y$ Y=	$[\alpha]_D$[b] °	Temp °C	Time h	Alkylated product $CH_3CH(Ph)CH_2Y$ Compd	Yield[c] %	$[\alpha]_D$[b] °	Optical yield[d] %
Ia	CH_2OH	−13.8	20	3.5	IIa	83	+1.97	14.1
		−13.8	10	3.5		88	+2.49	17.8
		+23.2	−10	4.5		77	−4.81	20.0
Ib	COOH[e]	+22.5[e]	30	4.0	IIb	81	−13.4	44.5
		−21.2[e]	20	4.0		84	+13.7	48.5
		+27.5[e]	5	4.0		46	−15.8	43.2
Ic	$COOC_2H_5$	+4.86	50	3.5	IIc	57	−0.8	19.7
					IIb	20	−1.5	16.5
		+3.66	40	3.5	IIc	48	−1.4	35.3
					IIb	35	−1.9	29.0
		+4.86	30	3.5	IIc	20	−3.0	53.7
Id	CH_2OCOPh	−41.2[f]	10	1.0	IId	75	+17.2[f]	28.2
		−41.2[f]	0	1.0		80	+18.8[f]	30.8
		−41.2[f]	−5	1.0		78	+20.1[f]	33.0
Ie	CH_2OCOCH_3	−38.4[f]	20	1.0	IIe	70	+11.0[f]	23.5
		−38.4[f]	10	1.0		77	+11.7[f]	23.9
		−38.4[f]	0	1.0		72	+10.2[f]	20.8

a) Molar ratio; $CH_3CH(Cl)CH_2Y$: $AlCl_3$: C_6H_6=1: 1.2: 30—50 CS_2 was added in the reaction below 5 °C. b) Rotations were measured in neat, unless otherwise noted. c) Based on the starting material used. d) Calculated from the maximum rotations of the starting material and the alkylating product as shown in Table 2. e) Measured in toluene (*c* 10.0). f) Measured in chloroform (*c* 5.0).

TABLE 2. MAXIMUM ROTATION OF STARTING MATERIALS AND PRODUCTS

Compd	$[\alpha]_D$/°	Compd	$[\alpha]_D$/°
S-Ia	+48.6 (neat)[a]	*R*-IIa	−45.3 (neat)[e]
S-Ib	−46.6 (toluene)[c]	*R*-IIb	−62.0 (neat)[f]
S-Ic	+31.2 (neat)[c]	*R*-IIc	−38.1 (neat)[g]
R-Id	−41.2 ($CHCl_3$)[d]	*S*-IId	+61.6 ($CHCl_3$)[h]
R-Ie	−38.4 ($CHCl_3$)[d]	*S*-IIe	+49.4 ($CHCl_3$)[i]

a) Calculated based on+23.5°of(+)-Ia obtained by reduction of (+)-Ib (optical purity 48.3%) with $LiAlH_4$. b) See Ref. 20. c) Calculated based on +8.84° of (+)-Ic obtained by esterification of (+)-Ib (optical purity 28.4%). d) This value seems to be of optically pure material because the precursor of this compound, ethyl 3-hydroxybutanoate, was obtained by biological method. See Ref. 21. e) See Ref. 13. f) See Ref. 13. g) See Ref. 22. h) Calculated based on +19.7° ($CHCl_3$) of IId obtained by esterification of(+)-IIa(optical purity 32%)with benzoyl chloride. i) Calculated based on +15.8° ($CHCl_3$) of IIe obtained by esterification of (+)-IIa (optical purity 32%) with acetyl chloride.



(*S*)-(+)-Ia—e (*R*)-(−)-IIa—e

Ia, IIa: Y=CH_2OH Id, IId: Y=$CH_2OCOC_6H_5$
Ib, IIb: Y=COOH Ie, IIe: Y=CH_2OCOCH_3
Ic, IIc: Y=$COOC_2H_5$

These reactions were so sensitive both to the moisture and to the activity of aluminium chloride used that it was diffcult to control the extent of the stereospecificity with sufficient reproducibility. The observed stereospecificity was found to be 20—30% for the reaction with alcohol (Ia) and its ester (Id and Ie), and 40—50% for that with chloroalkanoic acid (Ib) and its ethyl ester (Ic). The stereospecificity decreased slightly with an increase in reaction temperature. When these reactions were carried out in the presence of aluminium chloride equimolar to the alkylating reagent, the alkylation of benzene did not take place and the starting material was recovered without racemization.

In order to estimate the net stereospecificity of these reactions, one must know whether the starting chloride or the product is racemized in the course of reaction.

TABLE 3. TREATMENT OF THE ALKYLATED PRODUCT WITH ALUMINIUM CHLORIDE IN BENZENE[a]

Alkylated products	Temp °C	Time h	Specific rotation[b]/° Before reaction	After reaction
IIa	30	3	−4.80	−4.78
IIb	30	4	−15.8	−15.8
IIc	30	3	−2.22	−2.20
IId	10	1	+20.2[c]	+19.8[c]
IIe	10	1	+7.3[c]	+7.3[c]

a) Molar ratio; II: $AlCl_3$: C_6H_6=1: 1.2: 30.
b) Measured in neat liquid, unless otherwise noted.
c) Measured in chloroform (*c* 5.0).

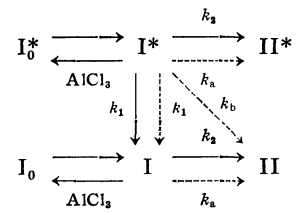
Table 4. The net stereospecificity in the alkylation of benzene with optically active $CH_3CH(Cl)CH_2Y$ by aluminium chloride catalyst (by method B)[a]

$CH_3CH(Cl)CH_2Y$		Temp	Time	Recovered $CH_3CH(Cl)CH_2Y$			Product				
Compd	$[\alpha]_D$[b] °	°C	min	Recovered %	$[\alpha]_D$[b] °	Remaining optical activity/%	Compd	$[\alpha]_D$[b] °	Optical yield %[c]	k_1/k_2[d]	Net stereospecificity %[e]
Ia	+19.8[f]	0	90	32	+4.88[f]	25	IIa	−6.36[f]	46	1.31	75
	+19.8[f]	10	90	7		9[i]		−2.29[f]	17	0.91	30
Ib	−11.9[g]	10	60	79	−10.23[g]	86	IIb	+12.7[f]	84	0.64	90
	−11.9[g]	10	90	76	−9.95[g]	84		+12.1[f]	80	0.64	87
Ic	−2.28[h]	30	60	66	−0.70[h]	31	IIc	+1.56[h]	59	2.82	97
	−2.28[h]	30	120	37	−0.17[h]	7		+1.10[h]	42	2.62	98
Id	−35.7	−5	10	61	−13.2	37	IId	+32.4	62	2.01	92
	−35.7	−5	20	34	−5.07	14		+28.5	47	1.82	91
Ie	−38.4	10	20	48	−8.0	21	IIe	+15.1	31	2.12	56
	−38.4	10	30	38	−7.3	19		+13.2	27	1.72	50

a) Molar ratio; $CH_3CH(Cl)CH_2Y$: $AlCl_3$: C_6H_6=1: 1.2: 30—40. CS_2 was added in the reaction below 5 °C. b) Rotation was measured in $CHCl_3$ (*c* 5.0), unless otherwise noted. c) See Table 1, footnote c. d) See the text. e) See the description in the text (Eq. 3). f) Measured in benzene (*c* 5.0). g) Measured in toluene (*c* 10). h) Neat liquid. i) By the ^1H NMR method using tris[trifluoroacetyl-(+)-camphorato]europium (III) as shift reagent.

At first, to examine the possibility of racemization of the product during the reaction, optically active IIa, IIb, IIc, IId, and IIe were treated with aluminium chloride in benzene under the same conditions as those of the alkylation. The specific rotation of these compounds remained almost unchanged before and after the treatment (Table 3). Thus, it turns out that the lesser stereospecificity in alkylation is not attributed to the successive racemization of the product. Next, we examined the possibility of simultaneous racemization of the starting chloride by observing the optical activity of that recovered before the completion of reaction; the reaction was quenched at about 30—70% conversion of the starting material after all reactants were mixed rapidely at lower temperature (see the method B in Experimental). The results are tabulated in Table 4. The starting chloride was racemized to a considerable extent as the reaction proceeds, and the optical yield of product decreased with the progress of reaction. Thus, these alkylation were found to be accompanied with simultaneous racemization of the starting material.

We have attempted to evaluate the extent of stereospecificity in the alkylation. The net stereospecificity of each reaction can be estimated from the extent of alkylation and the remaining optical activity of the starting material both observed at the same reaction time, by considering a kinetic model as shown in Scheme 1. I_0, I, and II indicate the starting material, the complex with aluminium chloride, and the alkylated product, respectively, and the asterisk indicates optically pure species. For convenience in the analysis we



Scheme 1. (course a: →, course b: ⇢)

assumed this reaction model in terms of optically pure and racemic species, although use of the enantiomers would be correct. The concentration of the complex (I* or I) would be equal to that of the starting material (I_0* or I_0) since the reaction from I_0* (or I_0) to I* (or I) is considered to be very rapid. In the conversion of I* into II* and II, two reaction courses are considered as shown in Scheme 1. The course a involves the reaction of I* to II* and the consecutive reaction of I* to II through I. The course b involves the direct conversion of I* into II in addition to the course a. Assuming that the racemization and disappearance of the starting material are pseudo-first-order in I* (or I), the reaction rates, k_1 and k_2, can be deduced from the fraction of the remaining optical activity in the starting material and that of the remaining starting material observed at the same time.[15] Thus, the optical yield of the product in the course a should be represented by Eq. 1.[16]

$$\left(\frac{[II^*]}{[II]+[II^*]}\right)_{\text{course a}} = \frac{k_2}{k_1+k_2}\,\frac{(1-e^{-(k_1+k_2)t})}{(1-e^{-k_2t})} \qquad (1)$$

In the course b, k_a and k_b represent the psendo-first-order rate constants for the formation of II* from I* (or of II from I) and that for the direct conversion of I* into II, respectively. Here,

$$k_a + k_b = k_2.$$

Thus, the optical yield of the product in the course b can be represented by Eq. 2, and corresponds to the observed optical yield.

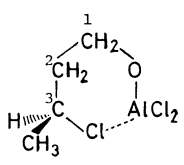
$$\left(\frac{[II^*]}{[II]+[II^*]}\right)_{\text{course b}} = \frac{k_a}{k_1+k_2}\,\frac{(1-e^{-(k_1+k_2)t})}{(1-e^{-k_2t})} \qquad (2)$$

Consequently, the net stereospecificity $(k_a/(k_a+k_b))$ should be given by Eq. 3.[17]

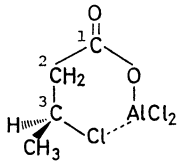
$$\left(\frac{[II^*]}{[II]+[II^*]}\right)_{\text{course b}} \Big/ \left(\frac{[II^*]}{[II]+[II^*]}\right)_{\text{course a}} = \frac{k_1+k_2}{k_2}\,\frac{(1-e^{-k_2t})}{(1-e^{-(k_1+k_2)t})} \times (\text{observed optical yield \%}) \qquad (3)$$

For example, in the alkylation with (−)-Ib at 10 °C (90 min), (+)-IIb was obtained in 24% yield and in 80% optical yield, and the optical activity of the starting material was depressed to 84% of the initial value. The k_1 and k_2 values were calculated to be $1.94\times10^{-3}\,min^{-1}$ and $3.05\times10^{-3}\,min^{-1}$ based on ln[fraction of remaining optical activity (0.84)] and ln[fraction of remaining chloride (0.76)], respectively. Therefore, the "true stereochemical consequence (net stereospecificity)" of this reaction was calculated to be 87%. Furthermore, the k_1/k_2 value (0.64) suggests that the rate of the alkylation is appreciably faster than that of the racemization of the starting material. The calculated values of the net stereospecificity and k_1/k_2 are given in the 11th and 12th column of Table 4, respectively.

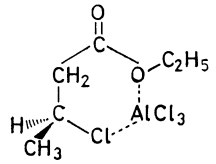
Such high stereospecificities have not been reported in the Friedel-Crafts alkylation with acyclic alkylating reagent. In this case, the polar group (OH, COOH, and COOR) being a part of the alkylating reagent would be responsible for the high stereospecificity of the reaction. The predominance of inversion in the alkylation is reasonably interpreted by considering the formation of cyclic intermediates as follows.



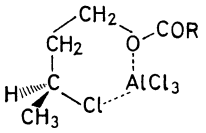
(Ia′)



(Ib′)



(Ic′)



(Id′: R=C_6H_5)
(Ie′: R=CH_3)

In the initial stage of the reaction with Ia and Ib, we observed the evolution of appreciable amounts of hydrogen chloride. This suggests that Ia (or Ib) reacted with aluminium chloride to form the salt evolving hydrogen chloride. The aluminium atom in the salt would coordinate with the chlorine atom at C_3 to form six-membered quasi-ring structure (Ia′ and Ib′), and the C_3–Cl bond would be polarized appreciably. Then, benzene would attack the C_3 atom from the back-side of the leaving chlorine atom. Even if the abstraction of the chlorine atom took place initially to give the carbonium ion (C_3^+), the interaction between the cation and the leaving chloride anion would prevent the rotation about the C_2–C_3 bond. Thus, the stereospecificity of the reaction may be interpreted in terms of the stability of the ring structure and the tightness of this ion pair. The increased tightness of the ion pair would increase the stability of the quasi-ring structure and thus the stereospecificity of the reaction. The higher stereospecificity of the reaction with Ib compared to Ia may be attributed to the enforced tightness of the ion pair by the electron withdrawing effect of the carbonyl group.

In the case of esters, Ic, Id, and Ie, the ether oxygen of ester group coordinates with aluminium chloride to form similar quasi-ring structures (Ic′, Id′, and Ie′). The high stereospecificity in the alkylation may also be interpreted in terms of the tightness of the ion pair as mentioned above. However, the large difference in the stereospecificity between the reaction with Id and Ie remained unexplainable.

The k_1/k_2 value for the reaction with Ia or Ib was found to be 0.6—1.3 while that for the reaction with esters was over 2. The lower value of k_1/k_2 in the former case may be attributed to lesser amounts of aluminium chloride remaining in the reaction mixture, because most of aluminium chloride were consumed for the salt-formation with Ia (or Ib).

Experimental

The optical rotations were taken on a JASCO DIP-SL polarimeter with use of 0.05 and 0.1 dm tubes at 25—30 °C. The NMR spectra were recorded on a JEOL JNM PS-100 spectrometer. Chemical shifts are given in ppm downfield from internal TMS. The IR spectra were determined on a JASCO DS-301 spectrometer. GLPC analyses were carried out on a 3 m column of 10% Carbowax 20 M on Diasolid L for IIa, IIb, and IIc, and on a 2 m column of 10% High Vacuum Silicon grease on Diasolid L for IId and IIe, with a Shimadzu GC-3A instrument.

Commercial grade aluminium chloride was purified by sublimation under nitrogen gas stream. Benzene was washed with concentrated sulfuric acid and water, and distilled after drying on sodium ribbon. Other solvents were dried by the most efficient ways reported in the literature[18] and distilled before use.

(+)-3-Chlorobutanoic Acid (Ib). Racemic Ib was prepared by addition of hydrogen chloride to crotonic acid[19] and resolved by the use of quinine[20] or (+)-ephedrine. When quinine was used as a resolving agent, (+)-Ib was obtained in about 50% optical purity, $[\alpha]_D$ +25.0° (*c* 10, $C_6H_5CH_3$), lit,[19] $[\alpha]_D$ +46.6° (*c* 10, $C_6H_5CH_3$). When (+)-ephedrine was used, (+)-Ib was obtained in lower optical purity, $[\alpha]_D$ +7.82° (neat). In both cases, (−)-Ib was recovered from the mother liquors.

(+)-3-Chloro-1-butanol (Ia). (+)-Ib ($[\alpha]_D$ +22.5°) was reduced with lithium aluminium hydride according to the procedure of Searles[22] to give (+)-Ia, bp 68 °C/20 mmHg, $[\alpha]_D$ +23.5° (neat), optical purity 48.3%.

(+)-Ethyl 3-Chlorobutanoate (Ic). (+)-Ib was esterificated with anhydrous ethanol in the presence of boron trifluoride to give (+)-Ic, bp 62—63 °C/20 mmHg, $[\alpha]_D$ +4.80° (neat). Optically pure (+)-Ic was prepared from thionyl chloride and (+)-ethyl 3-hydroxybutanoate obtained by the yeast reduction of ethyl acetoacetate as follows:[21] ethyl acetoacetate (100 g, 0.77 mol) was treated with baking yeast (1 kg) and sugar (1 kg) in water (10 liter) at 35 °C. After 24 h, (+)-ethyl 3-hydroxybutanoate was isolated by the repeated extraction with ether, bp 75—77 °C/15 mmHg, $[\alpha]_D$ +28.3° (*c* 5.0, $CHCl_3$), yield 56%. The hydroxybutanoate was converted with thionyl chloride in pyridine to (+)-Ic, yield 67%, $[\alpha]_D$ +18.8° (*c* 5.0, $CHCl_3$).

(−)-3-Chlorobutyl Benzoate (Id) was prepared by the esterification of (−)-Ia ($[\alpha]_D$ −46.6° (*c* 5.0, $CHCl_3$) with benzoyl chloride in pyridine at 100 °C, bp 101—102 °C/0.7 mmHg, $[\alpha]_D$ −41.2° (*c* 5.0, $CHCl_3$), yield 81%.

(−)-3-Chlorobutyl Acetate (Ie) was prepared from (−)-Ia ($[\alpha]_D$ −46.6°) and acetyl chloride in pyridine, bp 76—77 °C/17 mmHg, $[\alpha]_D$ −38.4° (*c* 5.0, $CHCl_3$), yield 60%.

Reaction Procedures and Product Identification. *Method A*: To a stirred mixture of dry benzene (20 ml) and aluminium chloride (9.8 mmol) was added a solution of the starting chloride (Ia, Ib, Ic, Id, or Ie) (8.3 mmol) in benzene (20 ml) at a rate sufficient to maintain the temperature shown in Table 1. The reaction mixture was stirred at that temperature until the starting chloride was almost consumed, and then was poured onto a mixture of crashed ice and 20 ml of concentrated hydrochloric acid. In the case of the reaction with Ia, Id, and Ie, the resulting mixture was treated as follows. The benzene layer was separated and the aqueous layer was extracted three times with 30 ml portions of ether. The combined organic layers were washed with water and dried over anhydrous sodium sulfate. After the removal of solvent, the residue was distilled *in vacuo* to give the corresponding 3-phenyl derivatives (IIa, IId or IIe). The results were summarized in Table 1.

In the case of the reaction with Ib and Ic, the reaction mixture was treated as follows. The benzene layer was separated and extracted five times with 30 ml portions of 5% sodium hydrogencarbonate solution and dried over anhydrous sodium sulfate. After the removal of benzene, the residue was distilled *in vacuo* to give IIc. The hydrogencarbonate solution was acidified with 6 M hydrochloric acid and extracted five times with 30 ml portions of ether and dried over anhydrous sodium sulfate. After the removal of the ether, the residue was distilled *in vacuo* to give IIb.

Method B: In order to estimate the net stereospecificity of the reaction, the experiment was carried out as follows.

To a cooled (−10 °C) suspension of aluminium chloride (5.6 mmol) in dry benzene (6 ml) was added, all at once, a solution of the chloride (4.7 mmol) in benzene (6 ml), and the reaction mixture was stirred at the prescribed temperature for the prescribed period (see Table 4). The resulting mixture was worked up as mentioned above. The unreacted starting material and the product were separated by fractionated distillation *in vacuo*. The results were summarized in Table 4.

(+)-3-Phenyl-1-butanol (IIa): IR(neat); 3340 (νOH), 1600 (skeletal vibration of phenyl ring), 1050 (νC–OH), 760, and 700 cm^{-1} (δCH, monosubstituted phenyl). NMR ($CDCl_3$, 7%); δ 1.26 (d, J=7.0 Hz, 3H, $-CH_3$), 1.70 (s, 1H, –OH), 1.72—1.96 (m, 2H, $-CH_2-$), 2.68—3.07 (m, 1H, –CH=), 3.54 (t, J=6.9 Hz, 2H, $-CH_2O-$), and 7.09—7.39 ppm (m, 5H, phenyl). The GLPC retention time was identical with that of the authentic sample.

(+)-3-Phenylbutanoic Acid (IIb): Bp 106 °C/2.0 mmHg, $[\alpha]_D$ +15.8° (neat), IR(neat); 3000 (νOH, dimeric carboxylic acid), 1710 (νC=O), 1605 (skeletal vibration of phenyl ring), 1300 (νC–O), 760, and 700 cm^{-1} (δCH, monosubstituted phenyl). NMR($CDCl_3$, 7%); δ 1.30 (d, J=7.2 Hz, 3H, $-CH_3$), 2.46—2.63 (m, 2H, $-CH_2-$), 3.03—3.42 (m, 1H, –CH=), 7.21 (s, 5H, phenyl), and 10.30 ppm (s, 1H, –COOH).

(−)-Ethyl 3-Phenylbutanoate (IIc): Bp 118—119 °C/17 mmHg, $[\alpha]_D$ −3.04° (neat). IR (neat); 1740 (νC=O), 1604 (skeletal vibration of phenyl ring), 1170 (νC–O–C), 760, and 700 cm^{-1} (δCH, monosubstituted phenyl). NMR ($CDCl_3$, 7%); δ 0.89 (t, J=7.5 Hz, 3H, $-CH_2C\underline{H}_3$), 1.18 (d, J=6.9 Hz, $=CHC\underline{H}_3$), 2.10—2.77 (m, 2H, $-OC\underline{H}_2CH=$), 3.11—3.48 (m, 1H –CH=), 3.91 (q, J=7.5 Hz, 2H, $-C\underline{H}_2CH_3$), and 7.04—7.38 ppm (m, 5H, phenyl).

(+)-3-Phenylbutyl Benzoate (IId): Bp 140—141 °C/0.5 mmHg, $[\alpha]_D$ +18.8° (*c* 5.0, $CHCl_3$). IR (neat); 1724 (νC=O), 1604 (skeletal vibration of phenyl ring), 1280 (νC–O–C), 758, and 710 cm^{-1} (δ CH, monosubstituted phenyl). NMR ($CDCl_3$, 5%); δ 1.36 (d, J=7.3 Hz, 3H, $-CH_3$), 1.96—2.20 (m, 2H, $-CH_2-$) 2.76—3.15 (m, 1H, –CH=), 4.00—4.42 (m, 2H $-CH_2O-$), 7.24 (s, 5H, $=CH-C_6\underline{H}_5$), 7.14—8.20 ppm (m, 5H, $-OC-C_6H_5$).

(+)-3-Phenyl Butyl Acetate (IIe): Bp 130 °C/14 mmHg, $[\alpha]_D$+15.8° (*c* 5.0, $CHCl_3$). IR (neat); 1745 (νC=O), 1604 (sketetal vibration of phenyl ring), 1245 (νC–O–C), 765, and 700 cm^{-1} (δCH, monosubstituted phenyl). NMR ($CDCl_3$, 7%); δ 1.26 (d, J=7.2 Hz, 3H, $-CH_3$), 1.73—2.05 (m, 2H, $=CHC\underline{H}_2-$), 1.96 (s, 3H, $-COCH_3$), 2.64—3.00 (m, 1H, =CH–), 3.96 (t, J=6.9 Hz, 2H, $-OCH_2O-$), and 7.18—7.37 (m, 5H, phenyl).

The GLPC retention time of the recovered chloride (Ia, Ib, Ic, Id, and Ie) was identical with that of the corresponding starting material, respectively.

Reaction of Optically Active IIa, IIb, IIc, IId, and IIe with Aluminium Chloride. To a stirred mixture of benzene (20 ml) containing aluminium chloride (5.6 mmol) was added a solution of optically active IIa IIb, IIc, IId, or IIe (4.7 mmol) in benzene (5 ml) at the prescribed temperature for 2—3 h. The reaction mixture was worked up as mentioned above. The data of specific rotation of II before and after the reaction were presented in Table 3.

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