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Retentive Friedel-Crafts Alkylation of Benzene with Optically Active 2-Chloro-1-phenylpropane and 1-Chloro-2-phenylpropane

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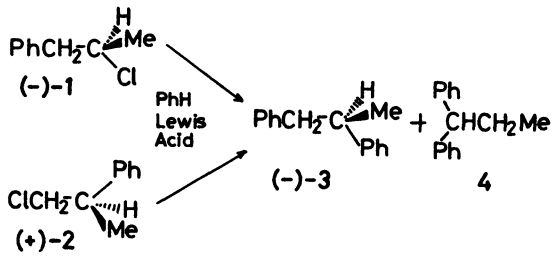
Alkylations of benzene with both (−)-2-chloro-1-phenylpropane (**1**) and (+)-1-chloro-2-phenylpropane (**2**) in the presence of Lewis acid gave the same products: (−)-1,2-diphenylpropane (**3**), 1,1-diphenylpropane, and polymeric materials. In these reactions, (−)-**3** was obtained in 45—100% optical yield and was not racemized under the conditions used. These results reveal that the reaction from **1** to **3** proceeds with retention of configuration and that from **2** to **3** with inversion. The stereochemistry of the alkylation with **1** is elucidated by the mechanism involving a neighboring phenyl π-assisted cation; benzene attacks only the β-carbon of **1** from the side on which the previously attached chloride anion is located. The result of the reaction with **2** can be explained by a process involving the 1,2-shift of phenyl group in the ionization step of **2**, followed by the formation of the same intermediate as in the reaction with **1**. The mechanism of the overall reaction is discussed.

Since the discovery of the Friedel-Crafts reaction with high stereospecific integrity,[1] many reports have been published during the past decade.[2] Most of these stereospecific reactions resulted in the inversion of configuration at the reaction center of the alkylating reagent. Although the Friedel-Crafts reactions have been expected to proceed through a free carbonium ion,[3] the stereospecific examples reported so far indicate that the intermediate cation exists as a tight ion pair with the counterion or as a complex with the Lewis acid used. The validity of such an assumption can be justified by recent stereochemical results on the alkylations of benzene with (+)-2-butanol[4] and (+)-2-chlrobutane;[5] both reactions proceeded with inversion of configuration to give 2-phenylbutane in 27—40% optical yield. Thus, it is expected that the stereospecificity in the Friedel-Crafts reaction using optically active alkylating reagent can be enhanced if the reaction condition was controlled so as not to cause the isomerization of the starting material or the product.

The reaction with inversion of configuration has often been studied. But there have been few studies on the Friedel-Crafts alkylation with retention of configuration. Sprung,[6] Hart,[7] and their co-workers reported that optically active *s*-butyl phenyl ether and α-phenylethyl *p*-tolyl ether rearranged intramolecularly in the presence of a Lewis acid to the corresponding *o*-alkylphenol with retention of configuration. These reactions are in a sence aromatic alkylations with retention. However, when the alkyl phenyl ether was conducted with phenol, the reaction proceeded intermolecularly to give a totally racemic product.[8] Thus, this stereochemical result (retention) of forcing the reaction to be intermolecular has not been reported so far.

In a preliminary account, we demonstrated that the alkylation of benzene with (−)-2-chloro-1-phenylpropane (**1**) by a Lewis acid catalyst proceeded with complete retention of configuration to give (−)-1,2-diphenylpropane (**3**) and that the reaction with (+)-1-chloro-2-phenylpropane (**2**) gave the same product with inversion, as shown in Scheme 1.[2e] The former reaction is the first example of a retentive Friedel-Crafts alkylation which proceeds intermolecularly. In the present paper, we have undertaken a broader investigation of stereochemistry in the Friedel-Crafts alkylation of benzene with (−)-**1** and (+)-**2**, and we discuss the reaction mechanism.



Scheme 1.

Results and Discussion

Both (−)-2-chloro-1-phenylpropane (**1**) and (+)-1-chloro-2-phenylpropane (**2**) reacted with benzene in the presence of 0.1 equivalent of $AlCl_3$ or $FeCl_3$ at −20—40 °C to give the same products: (−)-1,2-diphenylpropane (**3**), 1,1-diphenylpropane (**4**), and polymeric materials. The results under various conditions are summarized in Tables 1 and 2. The structures of **3** and **4** were identified by IR and NMR spectroscopies, and by comparing the retention time of their gas chromatograms with those of authentic samples. The isomer ratio of **3**/**4** was determined by NMR analysis. The optical rotations were taken on the mixture of **3** and **4**, since the two isomers could not be isolated in pure form.[9] The optical yields of the reactions were calculated from the optical purities of the starting materials, the reported rotation of **3**,[4] and the isomer ratio of **3**/**4** in the mixture obtained. The maximum rotation ($[\alpha]_D$) of optically active **1** was evaluated to be +23.9° on the basis of the rotation power of (+)-**1** derived by a series of reaction from optically pure (+)-propylene oxide, as mentioned in the experimental section.[10]

The absolute configurations of (−)-**1**, (+)-**2**, and (−)-**3** have been established to be R,[10] R,[11] and R,[12] respectively. Thus, it is apparent that the reaction from **1** to **3** proceeded with retention of configuration and

Table 1. Alkylation of benzene with (−)-2-chloro-1-phenylpropane (**1**) in the presence of Lewis acid[a)]

1 $[\alpha]_D^{25}$[b)] °	Lewis acid	Temp °C	Time h	Alkylated product: Yield[b)] %	Isomer (%)[d)] **3**	**4**	$[\alpha]_D^{25}$[e)] °	Optical yield of **3**[f)] %
−18.4	$AlCl_3$	20	0.3	74	81	19	−27.7	69
−18.4	$AlCl_3$	0	1.0	62	76	24	−37.8	100
−20.0	$AlCl_3$	−20	2.0	71	80	20	−41.7	96
−20.0	$FeCl_3$	40	0.3	62	46	54	−12.5	50
−20.0	$FeCl_3$	20	1.0	67	53	47	−20.2	70
−20.0	$FeCl_3$	0	3.0	61	61	35	−30.1	86
0.0	$FeCl_3$	−20	8.0	51	73	27	—	—

a) Molar ratio; **1**: Lewis acid: C_6H_6=1 : 0.1 : 30—40. Carbon disulfide was added in the reaction below 5 °C. b) Measured in $CHCl_3$ (*c* 5). Maximum rotation of (−)-**1**: $[\alpha]_D^{25}$−23.9° (*c* 5, $CHCl_3$). c) Based on **1** used. d) Determined by NMR analysis. e) Rotations were taken on the mixture of **3** and **4**, (*c* 5, $CHCl_3$). f) Calculated from the optical purity of **1** used, the reported rotation of **3** ($[\alpha]_D^{25}$+63.5° (*c* 2.34, $CHCl_3$)[4)]), and the isomer ratio of **3**/**4**.[9)]

Table 2. Alkylation of benzene with (+)-1-chloro-2-phenylpropane (**2**) in the presence of Lewis acid[a)]

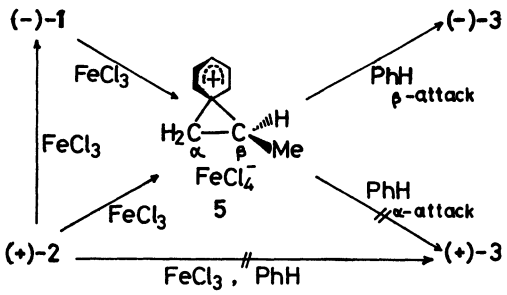
2 $[\alpha]_D^{25}$[b)] °	Lewis acid	Temp °C	Time h	Alkylated product: Yield[c)] %	Isomer (%)[d)] **3**	**4**	$[\alpha]_D^{25}$[e)] °	Optical yield of **3**[f)] %
14.0	$AlCl_3$	20	0.5	70	86	14	−26.3	51
14.0	$AlCl_3$	0	1.0	60	75	25	−45.0	100
14.0	$AlCl_3$	−20	1.5	65	76	24	−40.3	88
13.5	$FeCl_3$	40	0.2	55	46	54	−14.5	55
14.0	$FeCl_3$	20	1.0	64	52	48	−21.9	71
14.0	$FeCl_3$	0	3.0	60	65	35	−32.0	83
13.5	$FeCl_3$	−20	8.0	61	75	25	−40.2	97

a) Molar ratio; **2**; Lewis acid: C_6H_6=1 : 0.1 : 30—40. Carbon disulfide was added in the reaction below 5 °C. b) Measured in $CHCl_3$ (*c* 5). Maximum rotation of (+)-**2**: $[\alpha]_D^{25}$+14.9° (neat), see Experimental section. c) Based on **2** used. d) Determined by NMR analysis. e) Rotations were taken on the mixture of **3** and **4**, (*c* 5, $CHCl_3$). f) Calculated from the optical purity of **2** used, the reported rotation of **3** (see footnote f in the table 1), and the isomer ratio of **3**/**4**.[9)]

that from **2** to **3** with inversion of configuration at the asymmetric carbon. The $AlCl_3$ catalyzed reaction at 0 °C revealed the highest (complete) stereospecificity. When the reaction was carried out in the presence of $FeCl_3$ or at elevated temperature, considerable racemization of **3** was observed. On the whole, increasing temperature tends to decrease the magnitude of the optical yield of **3** and the isomer ratio of **3**/**4**.

Thus, the stereochemistry (retention) of the alkylation using **1** may be interpreted by a mechanism involving an intermediate (**5**) of the phenonium ion type, in which benzene attacks only β-carbon of the two bridged carbon atoms from the opposite side of the bulky phenyl ring (the side on which the previously attached chloride anion is located); (Scheme 2).

On the other hand, the stereochemistry of the reaction using **2** indicates that the migration of the phenyl group on C_α to the adjacent carbon takes place simultaneously with the departure of the chlorine atom and then the same phenonium ion (**5**) as mentioned above was formed prior to the attack of benzene. In connection with this observation, we had found previously that (+)-**2** was converted stereospecifically into (−)-**1** by trace amounts of Lewis acid.[2e)] If the chlorine atom of **2** was directly replaced with a phenyl group, as suggested by Brown *et al.*,[13)] the alkylation of benzene with (+)-**2** should give (+)-**3**; this does not accord with the result obtained here.



Scheme 2.

The existence of a phenonium ion has recently been recognized on the basis of studies on the rates and products of acetolysis of *threo*-2-aryl-1-methylpropyl brosylate with a number of different substituents,[14)] and has been confirmed spectroscopically to be a stable symmetrically bridged ion in superacid medium,[15)] although there were many controversies over the past two decades.[16)] McMahon *et al.*[17)] also have concluded that the Friedel-Crafts alkylation of toluene with 2-

Table 3. Alkylation of *p*-xylene with **1** and **2** the presence of $FeCl_3$[a]

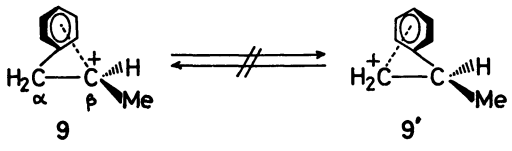
Starting chloride	Temp °C	Time h	Alkylated product Yield[b] %	Isomer (%)[c] **6**	**7**
1	40	0.2	83	54	46
1	20	1.0	88	67	33
1	0	3.0	81	74	26
2	30	0.5	85	61	39
2	0	3.0	87	76	24

a) Molar ratio; **1** (or **2**): $FeCl_3$: *p*-xylene=1 : 0.1 : 35 b) Based on starting chloride. c) Determined by NMR analysis.

phenylethyl-1-^{14}C chloride proceeded *via* a symmetric phenyl bridged intermediate. In our experiment, if the phenyl ring in the intermediate is equally bonded to both the α and β carbons and if the benzene attacks equally both these carbons, the product (**3**) would not be optically active; such an intermediate must yield a racemic product.

In order to confirm the reaction site in the intermediate, both **1** and **2** were allowed to react with *p*-xylene in the presence of $FeCl_3$. These two reactions gave the same products: 1-phenyl-2-(2,5-dimethylphenyl)propane (**6**) and 1-phenyl-1-(2,5-dimethylphenyl)-propane (**7**), in 80—90% yield. However, no amount of 1-(2,5-dimethylphenyl)-2-phenylpropane (**8**) was detected at all, as shown in Table 3. The process from **2** to **6** involves the 1,2-shift of phenyl group on C_β of **2** to the adjacent carbon, accompanied by the attack of *p*-xylene to the β-carbon. Thus, it is evident that both reactions using **1** and **2** proceed through the same intermediate, in which the β-carbon is attacked exclusively by aromatics.

Accordingly, much of the positive charge in the intermediate resides on the β-carbon, and the participation of phenyl group to that carbon seems to be of the π-bridged type (**9**)[18] (or unsymmetrically bridged type)[19] rather than of symmetrically σ-bridged type (**5**) mentioned above, as shown in Scheme 3. Furthermore, the above result excludes the rapid equilibration between the secondary cation (**9**) and the primary one (**9'**) although such an interconversion between the above two cations is still controversial.[18,19]



Scheme 3.

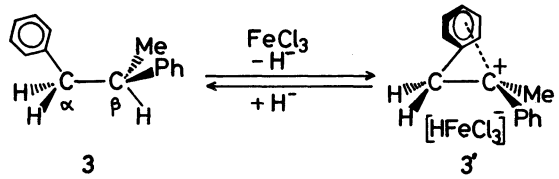
The stereospecificity of both reactions using **1** and **2** decreased remarkably with a rise in the reaction temperature, as mentioned above (Tables 1 and 2). In order to estimate the net stereospecificity of these reactions, one must know whether the starting chloride or the product is racemized in the course of reaction. Optically

Table 4. Treatment of (−)-**3** with $FeCl_3$ in benzene at 30 °C[a]

Time h	Specific rotation[b]/° Before reaction	After reaction
0.5	−24.7	−24.7
1.5	−24.7	−24.6
2.5	−24.7	−24.5
5.0	−24.7	−24.1

a) Molar ratio; (−)-**3**: $FeCl_3$: C_6H_6=1 : 0. 1 : 35. b) Measured in $CHCl_3$ (*c* 5) at 25 °C.

active alkylbenzenes having the asymmetric carbon atom attached to a benzene ring undergo rapid racemization under Friedel-Crafts conditions.[20] The racemization process has been considered to be due to a hydride transfer reaction through a free carbonium ion. In order to ascertain the possibility of such a process, (−)-**3** was treated with $FeCl_3$ in benzene at 30 °C. The result in Table 4 shows that the specific rotation of (−)-**3** remained unchanged before and after the reaction. Furthermore, no rearrangement of **3** to **4** was observed in this treatment. Thus, it turns out that the lesser stereospecificity in the reaction at elevated temperature can not be attributed to the successive racemization of the product. The greater optical stability of **3** than of alkylbenzenes such as 2-phenylbutane[20b] may be interpreted as the following considerations. The first is on the basis of a steric factor for the abstraction of hydrogen of the β-carbon of **3**. If the α-phenyl group of **3** assists the departure of the β-hydrogen as a hydride ion anchimerically, **3** should have the conformation in which two bulky phenyl and methyl groups are next to each other, in the transition state of reaction, as presented in Scheme 4. Such a conformation,



Scheme 4.

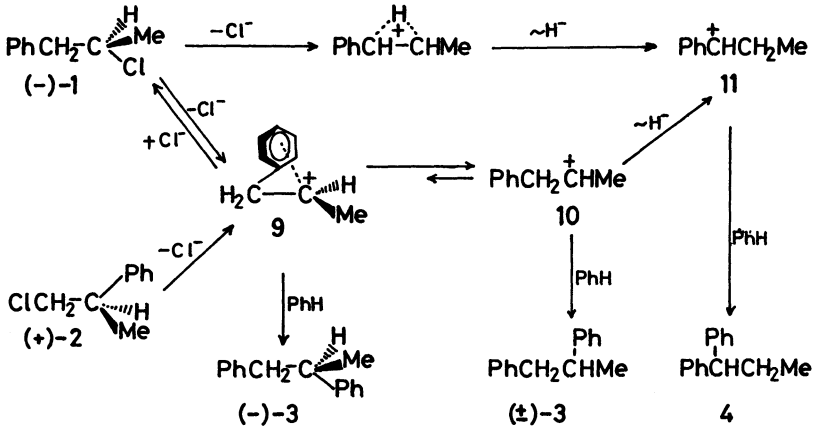
however, is unfavorable due to the steric hindrance, and thus the β-hydrogen may not be removed under the condition used. The second involves the formation of π-bridged cation such as **3'** yielded by the removal of the β-hydrogen of **3**. If the hydrogen was abstracted with the aid of $FeCl_3$ or a positive ion (R^+), the phenyl group on C_α would participate with β-carbon to form the π-bridged cation (**3'**), and a reverse attack of hydride ion would take place on the β-carbon from the opposite side of the assisting phenyl group to give (−)-**3** again. Thus, the configuration of (−)-**3** would remains unchanged during the reaction. In this stage, however, it is not clear which explanation is more reasonable.

Next, we examined the possibility of simultaneous racemization of the starting chloride (**1**) by observing

Table 5. The net stereospecificity in the alkylation of benene with (+)-**1** in the presence of Lewis acid

(+)-**1** $[\alpha]_D^{25b)}$ °	Lewis acid	Temp °C	Time min	Conversion[c] %	Recovered **1** $[\alpha]_D^{25b)}$ °	Recovered **1** Remaining optical activity/%	Alkylated products Isomer (%)[d] **3**	Alkylated products Isomer (%)[d] **4**	Alkylated products $[\alpha]_D^{25e)}$ °	Net stereo-[f] specificity %
21.2	$AlCl_3$	5	4	65	21.0	99	80	20	43.8	100
21.2	$FeCl_3$	30	25	80	16.5	78	50	50	17.9	70
21.2	$FeCl_3$	5	120	45	19.6	92	61	39	31.0	94

a) Molar ratio; (+)-**1**: Lewis acid: C_6H_6=1 : 0.15 : 35. b, c, d, and e) See footnotes b, c, d, and e in Table 1, respectively. f) Calculated by the reported method.[2d)]



Scheme 5. Lewis acid and its conjugated base are abbreviated for conciseness.

the optical activity of that recovered before the completion of reaction. As can be seen from Table 5, the racemization of (−)-**1** is evident in the reaction catalyzed by $FeCl_3$, especially at elevated temperature. Thus, the lesser stereospecificity at these conditions depends on the simultaneous racemization of the starting chloride. This may be explained in terms of the formation of an open carbonium ion such as 2-phenyl-1-methylethyl-cation (**10**)[21)] followed by an internal return as shown in Scheme 5. Then, the net stereospecificity of reaction was estimated on the basis of the remaining optical activity of **1** and the extent of alkylation observed at the same reaction time according to the method described previously.[2d)] The net stereospecificity of the reaction catalyzed by $FeCl_3$ decreased from 94 to 70% with the rise of temperature from 5 to 30 °C. This result suggests that the alkylation of benzene with **1** involves both intermediates, **9** and **10**, and that the latter plays a rather important role at elevated temperatures.

Consequently, the overall reaction can be illustrated as in Scheme 5. The precursor of 1,1-diarylpropane (**4** or **7**) seems to be 1-phenylpropyl cation (**11**) formed through two distinct pathways; the first path involves the hydride participation in minor competition with the phenyl participation accompanied by ionization of **1**, and the second involves the carbonium ion rearrangement of **10** to **11** (1,2-hydride shift). At the lower reaction temperature, the rate of the reaction (**9**→**10**) is so much slower than those of reactions (**9**→**3**, and **1**→**11**) that the total reaction from **1** to **3** proceeds with high stereospecificity, and the formation of **4** is suppressed. On the contrary, the reversible reaction from **9** to **10** is accelerated by increasing the reaction temperature so that the racemization of **9** takes place easily, which leads to the formation of (±)-**3**. Thus, the stereospecificity in the reaction from **1** to **3** decreases under the high temperature conditions. Furthermore, the formation of **4** is enhanced because of the easy rearrangement of **9** to **10**. The isomer ratio of **6**/**7** in the reaction of *p*-xylene with **1** (or **2**) is lower than that of **3**/**4**. This depends on the higher reactivity (higher basicity) of *p*-xylene toward the intermediate cations than that of benzene.

The Friedel-Crafts alkylation of benzene with **1** in the presence of Lewis acid resembles the solvolysis of 2-phenyl-1-methylethyl tosylate in trifluoroacetic acid with complete retention of configuration.[19)] The solvolysis of all primary and most secondary 2-arylalkyl system has been suggested to proceed through discrete aryl-assisted (retention) and solvent-assisted (inversion) pathways.[14)] However, our Friededl-Crafts alkylation does not involve the latter path in the solvolysis reaction.

Experimental

The optical rotations were taken on a JASCO DIP-SL polarimeter with use of 0.05 and 0.1 dm cells at 25 °C. The NMR spectra were recorded on a JEOL PS-100 spectrometer. The chemical shifts are given in ppm downfield from internal TMS. The IR spectra were determined on a JASCO DS-301 spectrometer. Gas chromatograph analyses (GC) were carried out on a 3 m column of 10% Carbowax 20 M on Diasolid L with Shimadzu DC-6A and GC-3A instruments. All the boiling points are uncorrected.

Benzene was washed with concentrated sulfuric acid and then water, distilled after drying on calcium chloride, and stored over sodium wire. *p*-Xylene was purified by fractional distillation and stored over sodium wire. Other solvents were dried and distilled before use.

Preparation of Optically Active Chlorophenylpropanes. *(+)-2-Chloro-1-phenylpropane (1)*: A solution of (+)-propylene oxide (11.6 g, 0.2 mol, $[\alpha]_D^{25}$ +7.96° (c 5, $CHCl_3$))[2b] in ether (50 ml) was added dropwise into an etheral solution of phenyllithium (0.25 mol). The resulting mixture was stirred at room temperature for 4 h, and then quenched by the slow addition of water. After the organic layer was separated, the aqueous layer was extracted with ether. The combined organic solution was dried over sodium sulfate and concentrated. The resulting yellow oil was distilled under reduced pressure to give a distillate (20.3 g), bp 103—108 °C/17 Torr.* The distillate was subjected to column chromatography on silica gel. Elution with hexane afforded biphenyl (0.7 g) and then that with chloroform gave (−)-1-phenyl-2-propanol in 66% yield (18 g), bp 102—105 °C/19 Torr, $[\alpha]_D^{25}$ −37.57° (*c* 5, $CHCl_3$), [lit,[19] $[\alpha]_D$ +38.69° (*c* 13.4, $CHCl_3$)].

To a stirred solution of the above optically active alcohol (10 g, 74 mmol) in pyridine (10 ml) was added thionyl chloride (9.6 g, 81 mmol) at such a rate that the temperature did not exceed 5 °C. After the addition was complete, the mixture was heated at 65 °C for 6 h, and poured into water. The organic layer was separated and the water layer was extracted with three portions of ether. The combined organic mixture was washed with water, dilute hydrochloric acid, saturated sodium chloride, 6% sodium hydrogencarbonate and water, successively. After drying over sodium sulfate, ether was removed. The residual liquid was distilled under reduced pressure to give (+)-**1** in 68% yield (7.8 g), bp 91 °C/17 Torr, $[\alpha]_D^{25}$ +21.85° (neat), $[\alpha]_D^{25}$ +23.19° (*c* 5, $CHCl_3$). Provided that this chlorination step proceeded with complete inversion, the optical purity of (+)-**1** obtained is evaluated to be 97.1%. Thus the maximum rotation was calculated to be $[\alpha]_D^{25}$ +23.88° [lit,[10] $[\alpha]_{25}^{D}$ −24.9° (neat)]. IR (neat): 1605 (skeltal vibration of phenyl ring), 760 and 700 (δ CH, monosubstituted phenyl), and 610 cm^{-1} (νC–Cl, secondary chloride). NMR ($CDCl_3$, 10%): δ=1.41 (d, *J*=7.6 Hz, 3H, $-CH_3$), 2.92 (m, 2H, $-CH_2-$), 4.10 (m, 1H, –CH=), 7.10 (m, 5H, phenyl).

(−)-**1**; The solution of (+)-1-chloro-2-phenylgropane (**2**) (5.0 g, 32 mmol, $[\alpha]_D^{25}$ +14.0°) in dichloroethane (20 ml) was added dropwise to a stirred mixture of anhydrous iron(III) chloride (50 mg, 0.3 mmol) and 1,2-dichloroethane (20 ml) at room temperature. The resulting mixture was stirred at 65 °C for 2 h, and then poured onto a mixture of crushed ice (15 g) and concentrated hydrochloric acid (15 g). The organic layer was separated and the aqueous layer was extracted with two 15 ml portions of 1,2-dichloroethane. The combined organic solution was washed with water, 6% sodium hydrogencarbonate and water, successively, and then dried over sodium sulfate. After removal of the solvent, the residue was distilled under reduced pressure to give (−)-**1** in 70% yield, $[\alpha]_D^{25}$ −20.0° (*c* 5, $CHCl_3$). IR and NMR spectra of (−)-**1** were identical to those of (+)-**1** obtained above.

(+)-1-Chloro-2-phenylpropane (2): The reaction of (+)-2-phenyl-1-propanol (13.6 g, 0.1 mol, $[\alpha]_D^{25}$ +15.7° (neat), 94% optically pure)[2b] with thionyl chloride (9.6 g, 0.1 mol) in pyridine gave (+)-**2** in 80% yield (7.8 g). Bp 94 °C/18 Torr, $[\alpha]_D^{25}$ +14.0° (neat). Thus, the maximum rotation was evaluated to be $[\alpha]_D^{25}$ +14.9° (neat). IR (neat): 1605 (skeltal vibration of phenyl ring), 700 and (δCH, monosubstituted phenyl), and 645 cm^{-1} (νC–Cl, primary chloride). NMR: δ=1.38 (d, *J*=7.4 Hz, 3H, $-CH_3$), 3.20 (m, 1H, –CH=), 3.50 (m, 2H, $-CH_2-$), 7.14 (m, 5H, phenyl).

Reaction Procedures. *Method A*: A slurry of pulverized anhydrous aluminium chloride (60 mg, 0.45 mmol) in dry benzene (12 ml) and carbon disulfide (4 ml) was cooled to 0 °C in a three-necked 100 ml flask equiped with a thermometer, an additional funnel, and a drying tube. To this stirred mixture was added a solution of (−)-**1** or (+)-**2** (0.7 g, 45 mmol) in benzene (3 ml) carefully over a period of 2 min at 0 °C. The reaction mixture was stirred at 0±0.5 °C for 1 h and then poured onto a mixture of crushed ice (5 g) and concentrated hydrochloric acid (5 ml). The benzene layer was separated and the aqueous layer was extracted with two 10 ml portions of benzene. The combined organic solution was washed with dilute hydrochloric acid, water, 6% sodium hydrogencarbonate solution and water, successively, and then dried over anhydrous sodium sulfate. After removal of the solvent, the residue was distilled under reduced pressure to give a distillate (bp 150—155 °C/20 Torr.) and high boiling materials. The distillate was shown to be a mixture of **3** and **4** by NMR analysis. The structure of these products was confirmed by the spectroscopic comparison with their authentic samples (see below). The optical rotations and the isomer ratio of **3**/**4** were determined on this distillate.[9]

The alkylation of *p*-xylene with **1** and **2** were also carried out in the same way as those of benzene and gave a mixture of **6** and **7** in 80—90% yield, bp 158—163 °C/15 Torr.

Details of reaction conditions and results are given in Tables 1, 2, and 3.

Method B: In order to estimate the net stereospecificity of the reaction, the experiment was carried out as follows. To a cooled suspension (below 0 °C) of $FeCl_3$ (0.45 mmol) in benzene (15 ml) was added, all at once, a solution of (+)-**1** (45 mmol) in benzene (3 ml), and the reaction mixture was stirred at the prescribed temperature for the prescribed period (see Table 5). After the reaction was quenched by an addition of water, the resulting benzene solution was subjected to gas chromatography to determine the conversion percent, and then worked up as mentioned above. The unreacted starting chloride and the product were separated by fractional distillation. The results are summarized in Table 5.

Preparation of Authentic Samples. *1,2-Diphenylpropane (3)* was prepared by a series of reactions as follows: 2-Phenylpropionic acid, prepared from 2-phenylpropanol[22] by the silver nitrate oxidation, was converted into 2-phenylpropionyl chloride by the reaction with phosphoryl chloride. The acylation of benzene with the acid chloride obtained above yielded 1,2-diphenyl-1-propanone. The above ketone was reduced according to the method[23] of Clemmensen to give 1,2-diphenylpropane (**3**). Bp 155 °C/20 Torr. IR (neat): 1325 (δCH, $-CH_3$), 700 and 755 cm^{-1} (δCH, monosubstituted phenyl). NMR: δ=1.17 (d, *J*=6.4 Hz, 3H, $-CH_3$), 2.80 (m, 2H, $-CH_2-$), 2.86 (m, 1H, –CH=), 7.10 (m, 10H, 2 phenyl).

1,1-Diphenylpropane (4) was prepared by the alkylation of benzene with 3-phenyl-1-propene in the presence of aluminium chloride at 5 °C, bp 160 °C/18 Torr. IR (neat): 700 and 740 cm^{-1} (δCH, monosubstituted phenyl). NMR: δ=0.88 (t, *J*=8.0 Hz, 3H, $-CH_3$), 2.20 (q, *J*=8.0 Hz, 2H, $-CH_2-$), 3.72 (t, *J*=8.0 Hz, –CH=), 7.11 (s, 10H, 2 phenyl).

1-Phenyl-2-(2,5-dimethylphenyl)propane (6) was prepared by the alkylation of *p*-xylene with **1** in the presence of aluminium chloride at −20 °C. Although the reaction gave a trace amount of **7** as a by-product, the fractional distillation of the mixture gave **6**, bp 169 °C/14 Torr. IR: 810 and 880 (δCH, 1,2,5-trisubstituted phenyl), 700 and 750 cm^{-1} (δCH, monosubstituted phenyl). NMR: δ=1.18 (d, *J*=7.8 Hz, 3H, $-CH_3$), 2.26 (s, 3H, *ortho*-CH_3), 2.37 (s 3H, *meta*-CH_3), 2.86

* 1 Torr≈133.322 Pa

(d, J=7.8 Hz, 2H, $-CH_2-$), 3.20 (m, 1H, -CH=), 7.00 (m, 3H, 1,2,5-trisubstituted phenyl), 7.18 (s, 5H, phenyl).

1-Phenyl-1-(2,5-dimethylphenyl)propane (7) was prepared by the alkylation of *p*-xylene with 3-phenyl-1-propene in the presence of aluminium chloride at 5 °C. Bp 174 °C/15 Torr. IR (neat): 880 and 810 (δCH, 1,2,5-trisubstituted phenyl), 760 and 700 cm^{-1} (δCH, monosubstituted phenyl). NMR: δ= 0.88 (t, J=8.0 Hz, 3H, $-CH_3$), 2.25 (s, 3H, *meta*-CH_3), 3.82 (t, J=8.0 Hz, 1H, -CH=), 6.90 (m, 3H, 1,2,5-trisubstituted phenyl), 7.05 (s, 5H, phenyl).

1-(2,5-Dimethylphenyl)-2-phenylpropane (8) was prepared by the Clemmensen reduction of 1-(2,5-dimethylphenyl)-2-phenyl-1-propanone obtained from the reaction of *p*-xylene with 2-phenyl propionyl chloride. **8**: Bp 182 °C/15 Torr. IR: 880 and 810 (δCH, 1,2,5-trisubstituted phenyl), 760 and 700 cm^{-1} (δCH, monosubstituted phenyl). NMR: δ=1.20 (d, J=7.4 Hz, 3H, $-CH_3$), 2.13 (s, 3H, *ortho*-CH_3), 2.18 (s, 3H, *meta*-CH_3), 2.78 (m, 2H, $-CH_2-$), 2.86 (m, H, -CH=). 7.00 (m, 3H, 1,2,5-trisubstituted phenyl), 7.18 (s, 5H, phenyl).

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