Friedel-Crafts Reaction of Aromatics with Epoxides. Stereochemistry and Selectivities

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The Friedel-Crafts reaction of toluene and anisole with 2-methyloxirane and 2,3-dimethyloxiranes was examined. The inter- and intramolecular selectivities of 2-methyloxirane were between those of conventional methylation and isopropylation. It was also found that all the positional isomers formed by the aluminum chloride-catalyzed reaction of toluene and anisole had almost completely inverted configurations of the epoxide carbons. These results are explained by a mechanism of the S_N2 type. Diminished stereospecificities were observed in aluminum bromide-catalyzed reactions.

The Friedel-Crafts reaction is one of the most intensively studied organic reactions.[1] Concerning the stereochemical aspect, it had been accepted until ten years ago that the alkylation proceeds with almost complete racemization. For example, Price and Lund reported that the alkylation of benzene with 2-butanol and boron trifluoride gave 2-phenylbutane with 1% net inversion.[2] Such other catalysts as aluminum chloride, hydrogen fluoride, sulfuric acid, and phosphoric acid also gave the product with less than 0.7% net inversion. Streitwieser and Stang reexamined the stereochemistry of the reaction by the use of 2-propanol-1-d_3[3] and found that the alkylation proceeded with at least 93% net racemization and very little net inversion in the presence of BF_3.[4] They concluded that the reaction is much like an S_N1 solvolysis and has little of the character of a direct (S_N2 type) displacement.

About ten years ago, Nakajima, Suga, and two of the present authors found a stereospecific Friedel-Crafts reaction of benzene with 2-methyloxirane (PO).[5] The reaction gave 2-phenyl-1-propanol with complete inversion, and the mechanism was concluded to be of the S_N2 type. At almost the same time, Brauman *et al.* reported that the alkylation of benzene with γ-valerolactone gave 4-phenylvaleric acid with 40% net inversion.[6] Thereafter, several reports have appeared concerning the stereospecific alkylations. The alkylating agents and stereospecificities are as follows: 2-methyltetrahydrofuran, 35% net inversion;[7] 3-chloro-1-butanol, 20% net inversion;[8] 3-chlorobutyric acid, 43% net inversion;[8] 2-chloro-1-phenylpropane, 82% net retention.[9,10] All of these stereochemical investigations, however, have been restricted to the reaction of benzene, and no attention has been paid to any aromatic substrate other than benzene. Thus, a problem remains unsolved: are the stereospecificities of the alkylation of toluene at each of the three possible positions really the same as that on benzene?

On the other hand, many papers have dealt with the intramolecular selectivity, *i.e.*, the isomer distribution in the alkylation of toluene, and with the intermolecular selectivity, *i.e.*, the relative rate of reaction, $k_{toluene}/k_{benzene}$.[11,12] The reaction mechanisms are most often discussed on the basis of the sets of these two selectivities. Although the stereochemical consequence of the reaction is also an essential component of any discussion of the mechanism, no report has appeared discussing the relationship between the stereochemical behaviour and the reactivity of the alkylating agent.

This paper will report on the Friedel-Crafts reaction of toluene and anisole with PO and with *cis*- and *trans*-2,3-dimethyloxiranes (*cis*- and *trans*-BO), and will discuss the stereochemistry and the intra- and intermolecular selectivities of the reaction.

Results and Discussion

Inter- and Intramolecular Selectivities of Friedel-Crafts Reaction with 2-Methyloxirane. The reaction of toluene with PO yielded three isomeric 2-tolyl-1-propanols (**1**). Nakajima *et al.* reported that an aromatic component attacked the methyl-substituted epoxide carbon in PO.[13] Although the product distributions in the reaction of xylenes with PO have already been discussed, those in the reaction of toluene with PO have not yet been examined because of the difficulties in the

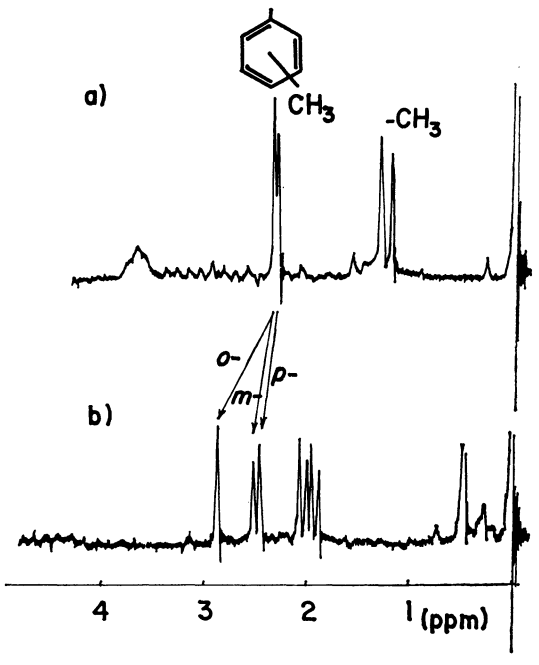
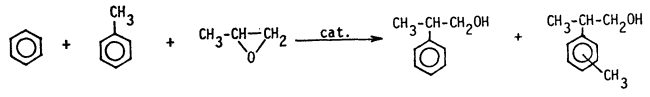


Fig. 1. NMR spectra of **1**; a) 7.0 mg of **1** in 581 mg of $CDCl_3$, b) sample a) plus 5.7 mg of tris(2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedionato)europium-(III).

Table 1. Inter- and intramolecular selectivities in the hydroxypropylation with methyloxirane at 0 °C



Catalyst	Yield[a] %	k_T/k_B	Isomer distribution/%			Stereospecificity[b] Inversion/%
			o-	*m*-	*p*-	
$AlCl_3$	60	3.5	38	35	27	100
$AlBr_3$	28	3.3	36	31	33	48
$TiCl_4$	38	2.9	46	21	33	100
$FeCl_3$	12	2.9	36	29	35	—

a) Yields of isolated products from the reaction of toluene with PO. b) Stereospecificities in hydroxypropylation with (+)-PO. Ref. 5b.

separation of the three isomeric products on GLC.

Efforts were made to separate the three isomers on GLC. It was found that a Bentone-34 column can separate three peaks, but the separation was insufficient. Therefore, we turned our attention to the determination of the product distribution by NMR. Although the NMR spectra of the isomeric mixture could not be resolved into the three components, we found that an europium shift reagent can separate the signals of the methyl protons on the aromatic ring into three peaks, as is shown in Fig. 1. The product distributions determined by this method are given in Table 1, together with the previously reported stereospecificities of the reaction of benzene and the intermolecular selectivities (*vide infra*).

The intermolecular selectivities of the reaction were determined by the usual competitive method, using benzene and toluene in a fifty-fold excess to PO. To discuss the relative rate ratio, k_T/k_B, two conditions should be satisfied: that the reaction is not diffusion-controlled, and that no subsequent reaction occurs. The latter condition seems to be satisfied, since the yields of the high-boiling materials were 5% at the highest, 1—2% usually, and negligible in the case of $TiCl_4$ catalysis. Whether or not the former condition is satisfied in the heterogeneous $AlCl_3$-catalyzed reaction is uncertain, but the fact that there is no remarkable discrepancy in the results between the heterogeneous reaction and the $TiCl_4$-catalyzed homogeneous one appears to show that the data can be used for the estimation of k_T/k_B.

Whereas aluminum bromide catalysis has been reported to result in a remarkable decrease in stereospecificity,[5] there seems to be no remarkable difference between aluminum bromide and the other catalysts as far as the selectivities are concerned. The reason for the diminished stereospecificity in $AlBr_3$ catalysis is uncertain; it is now under investigation.

Table 2 shows some typical results of the selectivities of hydroxypropylation, that is, the alkylation with PO, together with those of the usual Friedel-Crafts reactions summarized by Brown *et al.*[11] Both the intra- and intermolecular selectivities of hydroxypropylation are between those of isopropylation and methylation. Brown *et al.*[14] emphasized that a Friedel-Crafts reaction with primary and probably secondary halides involves an S_N2-type displacement reaction by the aromatics on a polarized alkyl halide-metal halide addition complex. The situation of hydroxypropylation seems to be similar to those mentioned by Brown *et al.*, because the hydroxypropylation of benzene resulted in complete inversion[5] and because the formation of fully developed carbonium ions was confirmed in only a few acid-catalyzed nucleophilic substitutions of epoxides, such as 2,2-diphenyloxirane[15] and some steroid epoxides.[16,17] In an epoxide-Lewis acid complex, the cleavage of the C–O bond of epoxide is made difficult by the presence of another C–O bond. A large nucleophilic contribution by the attacking aromatics is required, because a large covalent character remains in the C–O bond as compared with that in secondary halides and alcohols. Thus, the k_T/k_B of hydroxypropylation is larger than that of isopropylation, but smaller than that of methylation, which seems to show that a larger covalent character remains in the methyl–halogen bond than in the secondary carbon–oxygen bond of PO.

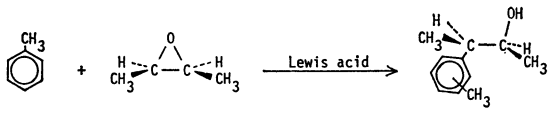
*Stereospecificities of the Formation of Isomeric (*o-, m-, *and* p-*) Products from Toluene.* To explore the specificities of the reaction of toluene, we first examined the reaction with optically active PO. An isomeric mixture of the product was optically active, but, unfortunately, they could not be separated either by column chromatography or by preparative gas chromatography. Therefore, the reaction of toluene with BO was examined. This reaction afforded a mixture of 3-chloro-2-butanols and 3-tolyl-2-butanols (**2**). The stereochemistry of the formation of the former compounds was reported previously.[18] The yields and stereochemistry of **2** are given in Table 3.

Table 2. Summary of inter- and intramolecular selectivities in electrophilic substitution of benzene and toluene

Reaction	Reaction conditions	k_T/k_B	Isomer distribution/%			Ref.
			o-	*m*-	*p*-	
Methylation	MeBr, $GaBr_3$, 25 °C	5.70	55.7	9.9	34.4	a)
Hydroxypropylation	CH_3CH-CH_2, $TiCl_4$, 0 °C (O)	2.9	46	21	33	b)
Ethylation	EtBr, $GaBr_3$, 25 °C	2.47	38.4	21.0	40.6	a)
Isopropylation	*i*-PrBr, $GaBr_3$, 25 °C	1.82	26.2	26.6	47.2	a)

a) Ref. 11. b) This work.

Table 3. Stereochemistry of alkylation of toluene with 2,3-dimethyloxirane



Epoxide	Catalyst	Yield %	Isomer distribution/%			Stereochemistry Inversion/%
			o-	*m*-	*p*-	
cis	$AlCl_3$	14.7	—	—	—	100
cis	$AlBr_3$	6.7	—	—	—	98
trans	$AlCl_3$	29.8	35.4	23.6	41.0	100
trans	$AlBr_3$	8.3	41.7	26.5	31.8	90

The yields of **2** in the reaction with BO were lower than those of **1** in the reaction with PO. The reaction of BO can be expected to proceed by the same S_N2 mechanism as in the case of PO. Since S_N2 reactions are sensitive to the steric factors, methyl substitution at the carbon which is in the β-position to the reacting carbon resulted in a decrease in the yield of the alkylation reaction. The fact that 2,2-dimethyloxirane gave only small amounts of a Friedel-Crafts reaction product under conditions similar to those in this paper[19] can be explained by the steric factors.

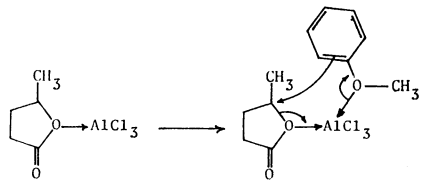
Although the retention times of the three isomers (*o*-, *m*-, and *p*-) of *erythro*-**2** on GLC were different from one another and were much larger than those of *threo*-isomers, the three isomers of *threo*-**2** could not be separated on GLC. As is shown in Table 3, only *threo*-**2** from *cis*-BO and only *erythro*-**2** from *trans*-BO were obtained in an aluminum chloride-catalyzed reaction. Therefore, all the three positional isomers of **2** were formed with complete inversion of configuration of the carbon attacked by toluene, showing that the reaction is of the S_N2 type. Aluminum bromide catalysis was found to decrease the stereospecificities, as in the reaction of benzene with PO.

Recent mechanistic works on Friedel-Crafts reactions have suggested that the transition state of the reaction of a reactive substrate resembles the nature of the π-complex[12] or the oriented π-complex,[20] which determines the substrate selectivity, the k_T/k_B value.[22] The second transition state, from the π-complex to the σ-complex, determines the positional (intramolecular) selectivity. However, the details of the structural change of the alkylating species accompanying π- and σ-complex formation have not been discussed.[21] The results reported in this paper show that the partial bond between the reacting carbon and the leaving group remains in the transition state, and that the reaction is of the S_N2 type. However, the above discussion does not answer the question whether the transition state of S_N2 alkylation involves a π-complex nature or a σ-complex one.[23]

Olah *et al.* examined the Friedel-Crafts benzylation and found that the reaction had high positional and low substrate selectivities.[28] They also found that aluminum chloride-catalyzed benzylation afforded a larger amount of the *meta* product than the other mild catalysis, they attributed this fact to the inter- and intramolecular rearrangement of the primary product. As the present hydroxypropylation has low substrate and low positional selectivities, the results might be explained by the subsequent isomerization processes, which are generally accepted as resulting in a substantial increase in the amount of the *meta* isomer. However, such an intramolecular-rearrangement mechanism that involves the cleavage of the bond between an aryl ring and an alkyl group, *e.g.*, ionization and subsequent internal return, cannot be applied to the hydroxyalkylation with epoxide, and intermolecular rearrangement or transalkylation can be excluded on the basis of the stereochemical results.

Reaction of Anisole with 2-Methyloxirane and 2,3-Dimethyloxiranes. A previous paper has described that the Friedel-Crafts reaction of anisole with epoxides proceeds by two different paths, *i.e.*, direct alkylation and the rearrangement of epoxides to carbonyl compounds, followed by condensation with anisole.[29] The products formed *via* the latter process in the reaction of anisole with PO were 1,1-bis(methoxyphenyl)propanes; the mechanisms of the reaction were discussed in some detail in the previous paper. The *o*-/*p*- isomer ratio of the 2-(methoxyphenyl)-1-propanols formed *via* direct alkylation of anisole with PO was 1.35. The reported *o*-/*p*- isomer ratio for the isopropylation of anisole with 2-propanol is 1.00—1.04, while that for methylation with methyl chloride is 1.75—1.91.[30] Thus, the present hydroxypropylation follows the general tendency of the usual primary and secondary alkylations.

The reaction of anisole with BO afforded a mixture composed of chlorohydrins,[18] 3-(methoxyphenyl)-2-butanols, and 1,1-bis(methoxyphenyl)-2-methylpropanes. The last-named compounds are formed *via* rearrangement, followed by condensation. The stereochemistries of the direct hydroxybutylation products are summarized in Table 4. As is the case of the reaction of toluene, the two isomers produced have a configuration with substantially complete inversion.

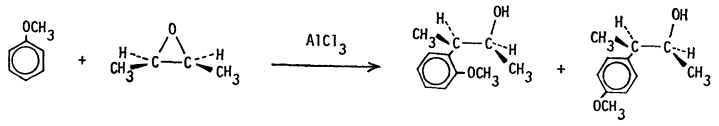


Scheme 1.

Kretchmer *et al.* proposed the mechanism depicted in Scheme 1 for the reaction of anisole with γ-valerolactone and several other alkylating agents on the basis of their finding that the proportions of the *ortho* products obtained from these reactions are higher than those from ordinary reactions.[31] This mechanism, however, cannot be applied to the reaction reported here, because the reaction mechanism expects the formation of an *ortho* product with retention of configuration.

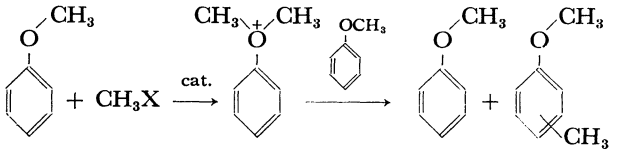
It was demonstrated that the methylation of anisole proceeds concurrently by two paths: the direct alkylation of the aromatic nucleus and the alkylation of oxygen to form an oxonium ion, followed by inter-

TABLE 4. STEREOCHEMISTRY OF ALKYLATION OF ANISOLE WITH 2,3-DIMETHYLOXIRANE



Epoxide	Isomer distribution	Stereochemistry	
		Inversion/%	Retention/%
cis	*o*- 47.8 %	100	0
	p- 52.2 %	99	1
trans	*o*- 25.7 %	92	8
	p- 74.3 %	100	0

molecular transalkylation.[32] If the latter path is assumed for the present hydroxyalkylation, the stereochemistry of the product should be retention (through double inversion) or racemization. Since the results given in Table 4 show almost complete inversion, the above oxonium ion-intermediate path would be only a minor one, even if it were to occur, in hydroxyalkylation with epoxides; the products seem to be formed by the direct alkylation of the aromatic nucleus of anisole.



Scheme 2.

Experimental

Materials. *cis*- and *trans*-2,3-dimethyloxiranes (*cis*- and *trans*-BO's) were prepared by the method of Pasto and Cumbo.[34] Optically active 2-methyloxirane (PO), $[\alpha]_D^{26}$ 13.10 (neat) [lit,[37] $[\alpha]_D^{16}$ 12.72 (neat)], was prepared from chloroacetone.[35] Inactive PO was a commercially available material, and each epoxide was distilled over calcium hydride before use. Benzene and toluene were washed with sulfuric acid and were distilled before use. Anisole was dried over sodium hydroxide and distilled over calcium hydride before use. Aluminum chloride was purified by sublimation.

Authentic Samples. 2-(*m*-Tolyl)-1-propanol, bp 128—129 °C/18 mmHg, was prepared by the hydroboration-oxidation[38] of 2-(*m*-tolyl)propene, which has been prepared by the Grignard reaction of *m*-tolylmagnesium bromide with acetone, followed by dehydration with $KHSO_4$. 2-(*o*-Tolyl)-1-propanol was prepared in a similar fashion, bp 119—121 °C/13 mmHg. (*Z*)- and (*E*)-2-(*o*-, *m*-, and *p*-tolyl)-2-butenes were prepared by methods similar to those used for preparing all the isomers of 2-(methoxyphenyl)-2-butenes described by Sneeden and Zeiss.[39] The hydroboration-oxidation of (*E*)-2-(*o*-methoxyphenyl)-2-butene yielded *threo*-3-(*o*-methoxyphenyl)-2-butanol (54% yield), bp 122—123 °C/6 mmHg. *erythro*-3-(*o*-Methoxyphenyl)-2-butanol was obtained in a similar fashion from (*Z*)-2-(*o*-methoxyphenyl)-2-butene (55% yield), bp 122—123 °C/6 mmHg. Similarly, other analogs were synthesized from suitable 2-butenes except for the cases of *erythro*-3-(*o*- and *m*-tolyl)-2-butanols. In these cases, (*E*)-2-(*o*- and *m*-tolyl)-2-butenes could not be obtained in the desired purity.[40] *erythro*-3-(*m*-Tolyl)-2-butanol was prepared by the reaction of lithium bis(*m*-tolyl)cuprate with *trans*-BO (18% yield),[41] bp 126—130 °C/29 mmHg; ^{13}C NMR ($CDCl_3$), 16.1, 21.0, 21.4, 47.1, 72.4, 124.8, 127.1, 128.2, 128.5, 137.9, and 144.1 ppm from TMS. The ^{13}C NMR spectrum of the *threo*-isomer was 17.6, 20.4, 21.4, 47.8, 72.1, 124.9, 127.3, 128.3, 128.7, 137.9, and 143.6. *erythro*-*o*-Methyl and *p*-methoxyl substituted analogs were also prepared in a similar fashion. The NMR spectra of the authentic samples are given in Table 5.

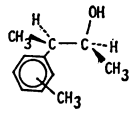
Isomer Distribution. A Typical Procedure of Aluminum Chloride-catalyzed Reaction. To a stirred mixture of toluene (30 ml) and aluminum chloride (12 mmol), cooled in an ice bath, a solution of PO (10 mmol) in 20 ml of toluene was slowly added over a period of 2 h. The resulting mixture was stirred for an additional 30 min and then poured into ice water, extracted with diethyl ether, dried over $MgSO_4$, and concentrated; the crude product was distilled *in vacuo* to give a mixture of 2-tolyl-1-propanols, bp 117—129 °C/20 mmHg (60 % yield). The isomer distribution of this fraction was determined by NMR using an europium shift reagent; it is shown in Fig. 1.

Competitive Hydroxypropylation. A Typical Procedure of Aluminum Chloride-catalyzed Reaction. To a mixture of benzene (0.5 mol), toluene (0.5 mol), and aluminum chloride (12 mmol), cooled in an ice bath, a solution of PO (10 mmol) in 50 ml of 1,2-dichloroethane was added, drop by drop with vigorous stirring over a period of 2.5 h. The vigorous stirring was essential to prevent the formation of undesired oligomers of PO. After the reaction has been allowed to proceed further for 30 min, the reaction mixture was poured into ice water. After the usual work-up, the crude product was analyzed by GLC.

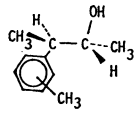
Hydroxypropylation of Toluene with Optically Active PO. Optically active PO (10 mmol) in toluene (20 ml) was added to toluene (30 ml) in the presence of aluminum chloride (12 mmol) at an ice-bath temperature over a period of 2 h, after which the reaction was continued for an additional 30 min. After the usual work-up, the distillation of the crude product gave a mixture of 2-tolyl-1-propanols (60% yield) which was optically active, $[\alpha]_D^{18}$ 8.02 (*c* 3.08, $CHCl_3$). Chromatography on neither silica gel nor alumina could spearate the mixture into three components.

Aluminum Chloride-catalyzed Reaction of Toluene with BO. Into a mixture of toluene (150 ml) and aluminum chloride (60 mmol), a mixture of *cis*-BO (50 mmol) and toluene (50 ml) was added over a period of 3 h with vigorous stirring in an ice bath. The stirring was then continued for an additional 30 min. After the usual work-up, the crude product was distilled giving 1.21 g (15%) of *threo*-3-tolyl-2-butanols, bp 91—94 °C/4 mmHg. GLC analysis showed that the product was not contaminated with the *erythro*-isomers.

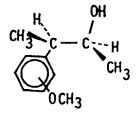
Table 5. NMR spectra of 3-tolyl-2-butanols (**2**) and 3-(methoxyphenyl)-2-butanols (**3**)



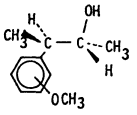
threo-**2**



erythro-**2**



threo-**3**



erythro-**3**

Compd	Chemical shifts/ppm							Coupling constants/Hz[a]		
	H(1)	H(2)	H(3)	H(4)	OH	CH_3	Phenyl	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$
threo-**2**-*o*	1.24	3.77	3.00	1.18	1.7	2.34	7.1	6.7	7.9	5.9
threo-**2**-*m*	1.14	3.77	2.60	1.20	2.0	2.31	7.0	6.0	7.0	7.0
threo-**2**-*p*	1.20	3.81	2.63	1.24	1.6	2.33	7.1	6.1	7.2	7.1
erythro-**2**-*o*	1.10	3.89	3.30	1.28	1.7	2.31	7.1	6.8	6.6	6.8
erythro-**2**-*m*	1.07	3.86	2.68	1.30	1.7	2.33	7.0	6.3	6.2	7.0
erythro-**2**-*p*	1.05	3.83	2.68	1.29	1.9	2.32	7.0	6.3	6.4	6.9
threo-**3**-*o*	1.16	3.93	3.21	1.21	1.9	3.79	7.0	6.0	6.9	6.9
threo-**3**-*p*	1.18	3.77	2.61	1.22	1.6	3.78	7.0	6.0	7.2	7.0
erythro-**3**-*o*	1.07	3.94	3.26	1.26	2.1	3.80	7.0	6.1	5.5	7.1
erythro-**3**-*p*	1.06	3.81	2.67	1.28	2.0	3.77	6.9	6.2	5.9	7.0

a) Limits of error: ± 0.2 for $J_{1,2}$ and $J_{3,4}$, ± 0.5 for $J_{2,3}$.

Reaction of Anisole with BO in the Presence of Aluminum Chloride. The reaction was carried out in a procedure similar to that described in a previous paper.[29] After the usual work-up, the crude product was chromatographed on silica gel. Benzene eluted a mixture of 1,1-bis(methoxyphenyl)-2-methylpropanes. Recrystallization from hexane gave a pure bis-*para* isomer; mp 62—63 °C; NMR ($CDCl_3$) $\delta = 1.8^6$ (d, 7.8 Hz, 6H), 2.37 (m, 1H), 3.30 (d, 10.9 Hz, 1H), 3.73 (s, 6H), 6.9 (phenyl, AA'BB' type coupling, 8H); Found: C, 79.76, H, 8.42%. Further elution with 5% ethyl acetate–benzene gave a mixture of the two isomers of 3-(methoxyphenyl)-2-butanols. The isomer distribution of this fraction was determined by GLC.

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21) Olah *et al.* found that the *o*-/*p*- isomer ratio of the ethylation of toluene with diethylhalonium ions (0.60—0.92) was significantly lower than those obtained in the ethylation of toluene with all the other conventional Friedel-Crafts ethylating agents (1.09—1.84); they explained the observation in terms of steric hindrance in an S_N2-like transition state.[22] As they mentioned that the positional selectivity was determined by the transition state from the π-complex to the σ-complex, their complex must involve a partial bond or some interaction between the alkyl cation and the leaving group, which is consistent with the finding reported in this paper.

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