over a least 2 half-lives of dication **2**. The hydride transfer rate measurement in $FHSO_3$–SbF_5 (5:1 molar ratio) with isopentane as hydride donor was performed by keeping the acid layer saturated with isopentane. This was effected by vigorous stirring between the pmr measurements. From the integration of the pmr peaks of isopentane and of the acid the concentration of isopentane was calculated to be 0.09 mol/l. *tert*-Pentyl cation was observed as a reaction product.

Aromatic Substitution. XXXVI.[1] Aluminum Trichloride and Antimony Pentafluoride Catalyzed Friedel–Crafts Alkylation of Benzene and Toluene with Esters and Haloesters

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Abstract: The $AlCl_3$ or SbF_5 catalyzed alkylation of benzene and toluene with alkyl chlorosulfites, arenesulfinates, chloro- and fluorosulfates, arenesulfonates, triflates, pentafluorobenzenesulfonates, and trifluoroacetates as alkylating agents was investigated in nitromethane, methylene chloride, carbon disulfide, 1,1,2-trichlorotrifluoromethane, or excess aromatics solution. The inter- and intramolecular selectivities of the alkylations was studied based on competitive toluene/benzene rate ratio and isomer distributions. The mechanism of the alkylation reaction is discussed.

The alkylation of aromatics with esters was known since Friedel and Crafts in 1877 observed the ethylation of benzene by ethyl chloroformate.[3] Esters since reported to effect the alkylation of aromatics include alkyl sulfates, sulfites, phosphates, orthosilicates, carbonates, borates, chloroformates, hypochlorites, halosulfates, chlorosulfites, arenesulfonates, and perchlorates.[4] In contrast to the vast literature of solvolysis of esters their alkylation reactions received but scarce attention.

In continuation of our studies on aromatic substitution[5] we therefore undertook a study of the Friedel–Crafts alkylation of benzene and toluene with alkyl chlorosulfites, arenesulfinates, tosylates, chloro- and fluorosulfates, trifluoromethanesulfonates (triflates), pentafluorobenzenesulfonates, and trifluoroacetates. The use of haloesters in aromatic alkylations has not yet been investigated and their comparison with arenesulfinates and tosylates also was of interest. Our studies were primarily directed toward an understanding of the mechanistic aspects of the reactions, particularly their selectivity and not to necessarily establish optimized preparative conditions. Consequently, our interest was directed to obtain relative reactivity data and isomer distributions reflecting the selectivity of the reactions.

In the alkylation of aromatic with esters, the acid formed as a by-product is generally nonvolatile and thus cannot escape from the reaction mixture, as do, for example, hydrogen halides formed in alkylation with alkyl halides. Since the continuously increasing acid concentration, which results as the reaction proceeds, may cause secondary reactions (*i.e.*, isomerization and disproportionation), there are few quantitative studies of alkylation with esters allowing evaluation of the mechanism, including selectivities of the reactions.

Results

(i) Alkyl Chlorosulfites. The alkylation of aromatics with alkyl chlorosulfites was little studied in the past. Barkenbus, *et al.*,[6] investigated butylation by *n*-butyl chlorosulfite, which took place without concurrent chlorination characteristic for related alkylations with alkyl chlorosulfates. We have now studied the alkylation of benzene and toluene with methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, and isobutyl chlorosulfites.

$$\mathrm{ROSOCl} + \mathrm{ArH} \xrightarrow{\mathrm{AlCl_3\text{–}CH_3NO_2\ or\ SbF_5}} \mathrm{ArR} + \mathrm{SO_2} + \mathrm{HCl} \quad (1)$$

$$\mathrm{R} = \mathrm{CH_3},\ \mathrm{CH_3CH_2},\ n\text{-Pr},\ i\text{-Pr},\ n\text{-Bu},\ i\text{-Bu}$$

$$\mathrm{Ar} = \mathrm{C_6H_5},\ \mathrm{C_6H_4CH_3}$$

Except for the reaction with methyl chlorosulfite, ready alkylation of benzene and toluene took place when using aluminum chloride–nitromethane as catalyst. Methyl chlorosulfite did not give methylated products under similar conditions even at 70°. Antimony pentafluoride, a much stronger Lewis acid catalyst than aluminum chloride, however, effects methylation of benzene and toluene with methyl chlorosulfite at 20°.

The reactions with *n*-propyl, *n*-butyl, and isobutyl chlorosulfite gave isopropylation, *sec*-butylation, and *tert*-butylation, accompanied by *n*-propylation, *n*-butylation, and isobutylation, respectively. In all cases, formation of skeletal rearranged products exceeded that of nonrearranged alkylates corresponding to the original alkylating agents. The ratio of skeletal re-

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(2) Postdoctoral Research Associate, 1971–1973.

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(6) C. Barkenbus, R. L. Hopkins, and J. F. Allen, *J. Amer. Chem. Soc.*, **61**, 2452 (1939).

Table I. $AlCl_3$ or SbF_5 Catalyzed Alkylation of Benzene and Toluene with Alkyl Chlorosulfites (ROSOCl)

R	Solvent	Temp, °C	Time, hr	Isomeric product[b]	Rate ratio k_T/k_B	Rearrangement ratio $k_{sec\ or\ tert}/k_{pri}$	% isomer ratio Ortho	Meta	Para
CH_3	Freon 113[a]	20	0.25				35.9	28.3	35.9
	CH_3NO_2	30	0.25[c]						
	CH_2Cl_2	30	0.25[c]						
	SO_2	−30	0.25[c]						
	CS_2	30	0.25[c]						
CH_3CH_2	Freon 113[a]	20	0.25		1.2		28.2	42.7	29.1
	CH_3NO_2	25	0.5		2.5		40.9	32.5	26.7
	CH_2Cl_2	30	0.25		1.1		33.7	32.1	34.2
	CS_2	30	0.25		2.4		41.8	30.7	27.5
$CH_3CH_2CH_2$	CH_3NO_2	30	0.25	n-	2.6		29.0	35.0	36.0
				iso	2.2	6.9	42.8	21.1	36.1
	CH_3NO_2	10	0.25	n-	3.2	4.6	34.3	31.7	34.0
				iso	2.4		41.8	20.4	37.8
	CH_3NO_2	−20	0.25	n-	2.2	2.6	34.5	30.5	35.0
				iso	2.3		39.9	17.7	42.4
$(CH_3)_2CH$	Freon 113[a]	20	0.25		1.3		39.3	24.6	36.1
	CH_3NO_2	30	0.25		2.4		42.3	20.3	37.4
	CH_3NO_2	10	0.25		2.1		44.4	19.6	36.0
	CH_3NO_2	−20	0.25		2.0		42.8	14.4	42.8
$CH_3(CH_2)_3$	CH_3NO_2	30	0.25	n-	3.1	9.3	41.0	20.1	38.9
				sec	2.1		36.5	27.6	35.9
	CH_3NO_2	10	0.25	n-	2.2	5.3	35.6	25.0	39.4
				sec	3.5		44.3	18.4	37.3
	CH_3NO_2	−20	0.25	n-	2.0	1.5	30.6	28.1	41.3
				sec	3.7		44.7	19.3	36.0
$(CH_3)_2CHCH_2$	CH_3NO_2	30	0.25	iso	4.1	4.6	33.3	27.2	39.5
				t-	6.6			20.7	79.3
	CH_3NO_2	10	0.25	iso	3.1	13.6	30.6	27.4	42.0
				t-	22.3			6.3	93.7
	CH_3NO_2	−20	0.25	iso	8.4	16.0	37.5	17.5	45.0
				t-	33.0			4.3	95.7

[a] Antimony pentafluoride was used as a catalyst. [b] The symbols, n-, iso, sec, and t-, mean that products are *n*-, iso-, sec-, and *tert*-alkylaromatics, respectively. [c] Alkylation did not occur under the reaction conditions.

arranged products over nonrearranged straight-chain alkylated products is characteristic and the results, obtained in nitromethane solution in the temperature range from −20 to +30°, are listed in Table I. The degree of skeletal rearrangement showed increase at higher temperature for the reactions with *n*-alkyl chlorosulfites. However, a reverse trend was observed for isobutyl chlorosulfite.

(ii) Alkyl Arenesulfinates. Alkyl arenesulfinates are more stable and therefore easier to handle than alkyl chlorosulfites (especially the *tert*-butyl derivative). Therefore, a wider scope study of alkylation with alkyl arenesulfinates was possible. Isopropyl, *tert*-butyl, benzyl, *p*-methoxybenzyl, *m*-methoxybenzyl, and *p*-methylbenzyl arenesulfinates gave alkylation of benzene and toluene using aluminum chloride–nitromethane as catalyst. Ethyl and *p*-nitrobenzyl arenesulfinates reacted in the presence of neat aluminum chloride catalyst. Methyl benzenesulfinate, however, did not give methylation in the presence of aluminum chloride.

$$ArSO_2R + ArH \xrightarrow{AlCl_3-CH_3NO_2} RAr + ArSO_2H \qquad (2)$$

Ar = C_6H_5, $CH_3C_6H_4$

R = C_3H_5, *i*-C_3H_7, *t*-C_4H_9, *p*-$CH_3OC_6H_4CH_2$, *m*-$CH_3OC_6H_4CH_2$, *p*-$CH_3C_6H_4CH_2$, $C_6H_5CH_2$, *p*-$O_2NC_6H_4CH_2$

In reaction 2 the conditions affect remarkably the substrate and positional selectivity. Solvent can change the selectivities significantly. In excess aromatics as a solvent, the k_T/k_B rate ratio is 1.8–0.5 at 60° and at the same time high meta isomer ratios (65–70%) are obtained. In carbon disulfide, as in excess aromatics as a solvent, similar results were obtained, even at lower temperature. When nitromethane was used as solvent, isomerization (disproportionation) of alkylbenzenes hardly occurred. Higher k_T/k_B ratios were obtained and at the same time lower meta isomer ratios. It is suggested that secondary reactions caused by aluminum chloride and arenesulfinic acid (formed as by-product) can be substantially reduced or avoided in nitromethane. The results obtained are summarized in Table II.

It has been reported that sulfinic acid esters produce sulfones upon acid hydrolysis (or pyrolysis).[7] The mechanism of this reaction was suggested as recombination of the alkyl cation and sulfonyl anion formed upon fission of the C–O bond. Methyl and benzyl *p*-tolylsulfinate, however, do not give the rearrangement. Therefore the possibility of a sulfone intermediate in the alkylation with alkyl arenesulfinate is remote. We have found, however, that alkylation of aromatics with certain alkyl, aryl sulfones takes place under more severe conditions than alkylation with alkyl arenesulfinates (to be reported separately).[8]

(iii) Alkyl Halosulfates. Alkyl chlorosulfates are known to alkylate aromatics using aluminum chloride as catalyst.[6] However, in these alkylations benzene is found to be simultaneously ring chlorinated, whereas toluene is also chlorinated in the side chain. Methylsulfonylation of reactive aromatic rings was also re-

(7) A. H. Wragg, J. S. McFadyen, and T. S. Stevens, *J. Chem. Soc.*, 3603 (1958).
(8) G. A. Olah and J. Nishimura, *J. Org. Chem.*, in press.

Table II. $AlCl_3$ Catalyzed Alkylation of Benzene and Toluene with Alkyl Arenesulfinates ($ArSO_2R$)

R	Ar	Solvent	Temp, °C	Time, hr	k_T/k_B	% isomer ratio		
						Ortho	Meta	Para
Et	Ph		60	0.5	1.8	8.4	66.1	25.6
Et	Ph	CS_2	30	0.25	2.6	18.6	65.8	15.6
i-Pr	Ph		60	1.0	0.6	2.0	64.8	33.2
i-Pr	Ph	CH_3NO_2	30	0.25	2.6	45.2	21.5	33.2
i-Pr	Ph	CS_2	30	0.25	1.0	0	82.3	17.7
t-Bu	Ph		60	1.0	0.5	0	69.9	30.1
t-Bu	Ph	CH_3NO_2	30	0.25	16.5	0	6.9	93.2
p-CH_3OBz	*p*-Tol	CH_3NO_2	30	0.25	30.3	30.1	9.5	60.4
m-CH_3OBz	*p*-Tol	CH_3NO_2	30	0.25	3.5	50.4	0	49.6
p-CH_3Bz	*p*-Tol	CH_3NO_2	30	0.25	15.9	27.9	2.9	69.2
Bz	*p*-Tol	CH_3NO_2	30	0.25	3.0	59.9	3.4	36.7
Bz	*p*-Tol		60	0.5	1.1	21.2	51.5	27.3
p-O_2NBz	*p*-Tol		60	2.0	1.8	*a*		

[a] Isomer distribution was not determined in this case as no glc conditions suitable to separate isomers were found.

Table III. $AlCl_3$ Catalyzed Alkylation of Benzene and Toluene with Alkyl Chlorosulfates ($ROSO_2Cl$)

R	Solvent	Temp, °C	Isomeric product	Rate ratio k_T/k_B	Rearrangement ratio $k_{sec\ or\ tert}/k_{pri}$	% isomer ratio		
						Ortho	Meta	Para
CH_3	CH_3NO_2	30[a]						
	CH_2Cl_2	30				43.1	9.9	47.1
	CS_2	30				42.7	16.4	40.9
CH_3CH_2	CH_2NO_2	30		3.4		45.5	29.7	24.8
	CH_2Cl_2	30		1.1		45.0	35.8	19.2
	CS_2	30		1.3		11.5	65.5	23.0
$CH_3(CH_2)_2$	CH_3NO_2	30	n-	2.7	6.9	35.0	22.0	43.0
			iso	2.5		43.3	20.6	36.1
	SO_2	−30	n-	2.1	1.3	39.5	15.6	44.9
			iso	1.4		47.9	17.7	34.4
	CH_2Cl_2	30	n-	1.2	1.9	31.0	37.1	31.9
			iso	0.7		1.5	55.8	42.7
	CS_2	30	n-	1.2	1.5	34.6	29.9	35.5
			iso	0.7		1.9	67.3	30.8
$CH_3(CH_2)_3$	CH_3NO_2	30	n-	3.7	7.5	35.5	24.5	40.0
			sec	3.3		39.0	21.0	40.0
	SO_2	−30	n-	2.4	1.3	34.8	29.0	36.2
			sec	1.6		41.0	21.5	37.5
	CH_2Cl_2	30	n-	1.5	2.1	28.6	35.1	36.3
			sec	0.6			76.9	23.1
	CS_2	30	n-	1.4	2.1	32.6	30.2	37.2
			sec	0.5			69.9	30.1
$(CH_3)_2CHCH_2$	CH_3NO_2	30	iso	3.0	7.3	46.5	18.1	35.4
			t-	3.4			31.4	68.6
	SO_2	−30	iso	1.5	15.9	32.0	24.8	43.2
			t-	7.0			21.7	78.3
	CH_2Cl_2	30	iso					
			t-	1.0			67.7	32.3
	CS_2	30	iso					
			t-	0.5			68.4	31.6

[a] No alkylation occurred.

ported in the case of methyl halosulfates,[9] although other investigators found no evidence for this sulfonylation.[6,10]

We studied the aluminum chloride catalyzed alkylation of benzene and toluene with alkyl chlorosulfates in nitromethane, carbon disulfide, and methylene chloride solutions. Results are summarized in Table III. In nitromethane at 30°, no chlorination of benzene and toluene was observed, but substantial chlorination occurred in carbon disulfide and methylene chloride solution.

Nitromethane showed again a characteristic solvent effect and gave high substrate selectivity and lower meta isomer ratio. The reactions with *n*-propyl, *n*-butyl, and isobutyl chlorosulfates afforded mainly products of isopropylation, *sec*-butylation, and *tert*-butylation. On the other hand, in carbon disulfide and methylene chloride solution, lower substrate selectivity and higher meta isomer ratio were obtained. At the same time in the reactions with *n*-propyl and *n*-butyl chlorosulfate, more secondary alkyl products were obtained in CH_3NO_2 than in CH_2Cl_2 or CS_2 solution, where *n*-propylation and *n*-butylation are also significant. The reaction with isobutyl chlorosulfate gave exclusively *tert*-butylated products with low selectivity. Thus, in these solvents, the active alkylating species is less solvated and reacts with aromatics with lower selectivity, accompanied by intramolecular isomerization, and disproportionation.

Alkyl fluorosulfates gained recently much interest for

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(10) G. A. Olah, S. Kobayashi, and J. Nishimura, *J. Amer. Chem. Soc.*, **95**, 564 (1973).

Table IV. Alkylation of Benzene and Toluene with Alkyl Fluorosulfates ($ROSO_2F$)

R	Solvent	Cat.	Temp, °C	Time, hr	Isomeric product	Rate ratio k_T/k_B	Rearrangement ratio $k_{sec\ or\ tert}/k_{pri}$	% isomer ratio Ortho	Meta	Para
CH_3		$AlCl_3$	40	0.5				42.3	30.5	27.2
	Freon 113	SbF_5	20	0.25				34.5	28.0	37.5
CH_3CH_2	CH_3NO_2	$AlCl_3$	25	0.5		3.1		43.6	30.2	26.2
$CH_3(CH_2)_2$	CH_3NO_2	$AlCl_3$	30	0.25	n-	2.8	7.1	37.9	23.2	38.9
					iso	2.5		42.4	19.6	38.6
	SO_2	$AlCl_3$	−30	0.25	n-	2.1	1.5	28.5	26.8	44.7
					iso	1.4		40.8	18.7	40.5
	CH_2Cl_2	$AlCl_3$	30	0.25	n-	1.7	1.9	28.6	45.3	26.1
					iso	1.0		0.9	70.2	28.9
	CS_2	$AlCl_3$	30	0.25	n-	1.7	1.8	12.5	58.0	29.5
					iso	1.0		2.1	57.0	40.9
$(CH_3)_2CH$	SO_2	$AlCl_3$	−78	0.25		1.1		43.3	23.4	33.3

Table V. $AlCl_3$ Catalyzed Alkylation of Benzene and Toluene with Alkyl Arenesulfonates ($ROSO_2Ar$)

R	Ar	Solvent	Temp, °C	Time, hr	k_T/k_B	% isomer ratio Ortho	Meta	Para
CH_3	Ph		40	0.5		46.7	27.5	25.8
CH_3CH_2	*p*-Tol		10	0.5	3.3	24.6	45.2	30.2
		CH_3NO_2	30	0.25	2.4	50.2	29.8	20.0
		CS_2	30	0.25	2.1	0.6	98	1
$(CH_3)_2CH$	*p*-Tol		10	0.5	1.3	1.4	74.1	24.5
		CH_3NO_2	30	0.25	2.5	46.4	21.8	31.8
		CS_2	30	0.25	1.1	0	81.6	18.4

heteroatom alkylations,[11] but no study of aromatic alkylation was yet reported. We therefore investigated the alkylation of benzene and toluene with alkyl fluorosulfates.

Methyl fluorosulfate in nitromethane solution with aluminum chloride as catalyst did not alkylate aromatics. Methylation could be achieved, however, when using antimony pentafluoride as catalyst in 1,1,2-trichlorotrifluoroethane solution. Ethylation of benzene and toluene took place readily with ethyl fluorosulfate and aluminum chloride–nitromethane. Alkylation with *n*-propyl fluorosulfate showed results similar to those obtained with *n*-propyl chlorosulfate (Table IV). Isopropyl fluorosulfate was found to be so reactive that it readily alkylated benzene and toluene in excess aromatic or SO_2 solution even without the use of added catalyst (see subsequent discussion).

(iv) Alkyl Arenesulfonates. Since Földi's discovery[12] of the benzylation of aromatics by benzyl benzenesulfonate, several alkylations of aromatics with alkyl arenesulfonates have been reported.[4] It is also known that when the alkylation is catalyzed by aluminum chloride, the catalyst can induce isomerization and disproportionation of products.[13] We studied alkylation of aromatics with alkyl arenesulfonates in order to determine the selectivity of the reaction. As shown in Table V, both ethylation and isopropylation with alkyl tosylates could be effected in nitromethane solution, observing higher k_T/k_B values and lower meta isomer ratios than in carbon disulfide or excess aromatics solutions. Thus alkylations with alkyl arenesulfonates in nitromethane are also more selective and isomerization and disproportionation are reduced.

(v) Alkyl Triflates and Pentafluorobenzenesulfonates. We also investigated the alkylation of benzene and toluene with methyl, ethyl, and isopropyl triflates, esters of the very strong monobasic trifluoromethanesulfonic acid. Methyl triflate gave no alkylated products with benzene and toluene when using aluminum chloride as catalyst in nitromethane solution, although methylation occurred at 40° when using excess aromatics as a solvent and at 20° in 1,1,2-trichlorotrifluoromethane using antimony pentafluoride as a catalyst. Ethyl triflate ethylates benzene and toluene in nitromethane solution with aluminum chloride catalyst. Isopropyl triflate is as reactive as isopropyl fluorosulfate and reacts with benzene and toluene without any catalyst.

We also carried out alkylation of benzene and toluene with methyl and ethyl pentafluorobenzenesulfonate, to compare these esters of pentafluorobenzoic acid with trifluoromethanesulfonates. Results are summarized in Table VI.

(vi) Alkyl Trifluoroacetates. Carboxylic acid esters RCOOR′ can undergo Friedel–Crafts reactions with aromatics to give besides alkylated aromatics also arylalkyl ketones. The proportions of ketone and hydrocarbon formed vary with the reaction conditions employed.[4] Studying alkylations with trifluoroacetates, however, we have found no competing acylations to occur.

Methyl trifluoroacetate gave with toluene xylenes in the presence of aluminum chloride at 60°. Ethyl trifluoroacetate readily gave ethylated products even under milder conditions. Isopropyl trifluoroacetate was found the most reactive trifluoroacetate studied (Table VII). In alkylations with alkyl trifluoroacetates,

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(12) Z. Földi, *Ber.*, **61**, 1609 (1928); U. S. Patent 1,897,795 (1930).

(13) F. Drahowzal, D. Klamann, and F. Haas, *Justus Liebigs Ann. Chem.*, 580, 210 (1953).

Table VI. Alkylation of Benzene and Toluene with Alkyl Triflates ($ROSO_2CF_3$) and Alkyl Pentafluorosulfonates ($ROSO_2C_6F_5$)

R	C_nF_m	Solvent	Cat.	Temp, °C	Time, hr	k_T/k_B	% isomer ratio		
							Ortho	Meta	Para
CH_3	CF_3	Freon 113	SbF_5	20	0.25		44.5	31.8	23.8
CH_3CH_2			$AlCl_3$	40	0.5		30.6	55.0	14.4
CH_3CH_2	CF_3	CH_3NO_2	$AlCl_3$	25	0.5	2.6	41.7	34.4	23.9
$(CH_3)_2CH$	CF_3	SO_2	$AlCl_3$	−78	0.25	1.6	43.8	21.8	34.4
				25	0.5	2.9	46.5	19.1	34.4
CH_3	C_6F_5		$AlCl_3$	40	0.5		28.0	39.8	32.2
CH_3CH_2	C_6F_5	CH_3NO_2	$AlCl_3$	30	0.25	3.6	35.0	36.3	28.7

Table VII. $AlCl_3$ Catalyzed Alkylation of Benzene and Toluene with Alkyl Trifluoroacetates (CF_3COOR)

R	Solvent	Temp, °C	Time, hr	k_T/k_B	% isomer ratio		
					Ortho	Meta	Para
CH_3	CH_3NO_2[a]						
CH_3		60	16		26.5	54.3	19.2
CH_3CH_2		60	0.5	1.0	2.9	77.0	20.0
CH_3CH_2	CH_3NO_2	30	2.0	2.4	46.4	28.9	24.7
$(CH_3)_2CH$		60	1.0	0.8	1.1	64.0	34.9
$(CH_3)_2CH$	CH_3NO_2	30	0.25	2.6	45.1	22.0	33.0
$(CH_3)_2CH$	CS_2	30	0.25	1.0	0.7	83.6	15.7

[a] No alkylation occurred.

the same solvent effects were observed as in the reactions with arenesulfinates and sulfonates. Nitromethane was able to reduce isomerization and disproportionation of products.

Discussion

According to solvolysis data,[14] the decreasing order of effective leaving groups is as follows: $CF_3SO_3^-$, $FSO_3^- > ClSO_3^- > CF_3CO_2^-$. The nature of the leaving group did not seem to affect significantly substrate and positional selectivity, if the alkylation reactions were carried out in nitromethane solution, using aluminum chloride as catalyst. However, the selectivities remarkably depend on the solvent. In excess aromatics, methylene chloride, and carbon disulfide solutions, the aluminum chloride catalyzed reactions gave low substrate selectivity and high meta isomer ratio, which would indicate low substrate and positional selectivity or substantial degree of isomerization (of alkylation products either in an intra- or intermolecular fashion of the benzenium ion intermediate prior to deprotonation).

In nitromethane solution, other side reactions were also reduced. For example, chlorination generally accompanying alkylation with alkyl chlorosulfates were not observed in this solvent.

Methyl chlorosulfate alkylated benzene and toluene in methylene chloride and carbon disulfide using aluminum chloride as catalyst. Methyl benzenesulfonate, triflate, fluorosulfate, pentafluorobenzenesulfonate, and trifluoroacetate gave aluminum chloride catalyzed methylation in excess aromatics. In these methylations, the nature of leaving groups only slightly affected the reactivity of the reagent.

All ethylations with the esters used occurred readily in nitromethane solution using aluminum chloride as catalyst. k_T/k_B ratios found were 2.4–3.4 and meta isomer ratios 36.3–28.9%, indicating again low selectivity and/or contribution of isomerization (disproportionation). This might be due to the effect of strong acids formed in the systems.

Isopropylation showed k_T/k_B values of 2.5–2.0 and meta isomer ratios of 21.5–14.4%. It is noteworthy that the meta isomer ratio depends on the temperature, indicating that isomerization (and disproportionation) is becoming more important with increasing temperature in the systems.

Isopropylations with isopropyl fluorosulfate and triflate (trifluoromethanesulfonate) are interesting, because alkylation of benzene and toluene can take place without the need of any added catalyst. Isopropyl fluorosulfate when reacted with toluene at 25° for 2 hr gave 47.4% *o*-, 9.7% *m*-, and 42.9% *p*-cymene. This interesting isomer distribution is, however, somewhat fortuitous, as it is affected by the fluorosulfuric acid formed in the reaction as by-product. It seemingly selectively reacts with the most reactive *m*-cymene, reducing its apparent amount in the product. This was proven when carrying out the reaction under identical conditions, but in the presence of a bulky Hünig base, such as *N*,*N*-diisobutyl-3-amino-2,4-dimethylpentane,[15] which itself is not alkylated, but will bind the acid formed in the reaction. The isomer distribution found in this case is 44.3% *o*-, 17.7% *m*-, and 38% *p*-cymene. A similar isomer distribution was also obtained in SO_2 solution at −40° without added base (the secondary reaction being obviously of lesser importance): 47.4% ortho, 19.7% meta, and 32.9% para. That the reaction at room temperature is indeed affected by selective removal of part of the *m*-cymene formed is also shown by time dependence studies. After only 5 min of reaction time at 25° the isomer distribution was 45.7% *o*-, 17.9% *m*-, and 36.4% *p*-cymene. After 15 min it changed to 48.3% ortho, 11.1% meta, and 41.3% para isomer and after 60 min to 46.2% ortho, 9% meta, and 44.8% para. The isopropylation with isopropyl triflate showed no similar changes as trifluoromethanesulfonic acid formed in the reaction does not cause secondary reactions.

tert-Butylation with *tert*-butyl benzenesulfinate in nitromethane solution showed a low meta isomer ratio and high k_T/k_B value, which would indicate a kinetically controlled system and that there is not significant effect of the formed relatively weak acid.

Comparison of benzylation with *p*-methoxy, *m*-methoxy, *p*-methyl, and *p*-nitrobenzyl toluenesulfinates with the parent benzyl benzenesulfinate using aluminum chloride as catalyst in nitromethane solution showed that electron-donating substituents para to the benzylic

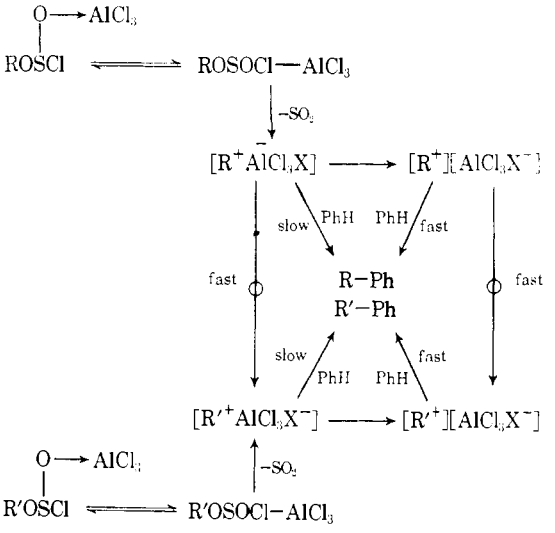
(14) (a) A. Streitwieser, Jr., C. C. Wilkins, and E. Kiehlmann, *J. Amer. Chem. Soc.*, **90**, 1598 (1968); (b) T. M. Su, W. F. Sliwinski, and P. v. R. Schleyer, *ibid.*, **91**, 5386 (1969); (c) E. Buncel and J. P. Millington, *Can. J. Chem.*, **43**, 556 (1965); (d) G. Gorin, O. R. Pierce, and E. T. McBee, *J. Amer. Chem. Soc.*, **75**, 5622 (1953).

(15) We thank Chemische Werke Hüls for a sample.

group increase the k_T/k_B ratio and at the same time decrease the ortho:para isomer ratio of the methyldiphenylmethanes formed (*e.g.*, para substitution is becoming predominant). On the other hand, electron-withdrawing substituents decrease the value of k_T/k_B. This trend is consistent with the results of the reported comprehensive investigation of benzylation with ring-substituted benzyl chlorides using titanium tetrachloride as a catalyst.[16]

Alkylations with *n*-propyl, *n*-butyl, and isobutyl chlorosulfite or chlorosulfate using aluminum chloride catalyst showed effects of substantial isomerization. For these isomerizations, several mechanisms are possible (a) intramolecular rearrangement of alkyl chlorosulfite (chlorosulfate) in SNi type reactions. This is in accordance with the finding that alkylation accompanied by isomerization generally had a 5–10-fold preference over alkylation without rearrangement. On the other hand, if alkylation is carried out in less polar solvents, such as methylene chloride or carbon disulfide, only twice as much alkylation accompanied by rearrangement was observed as alkylation corresponding to the original alkylating agent (*i.e.*, without skeletal rearrangement of the alkylating agent). In these solvents, the alkylating agents are considered to be less solvated and could react with benzene and toluene as easily as undergo intramolecular rearrangement (Scheme I).

Scheme I

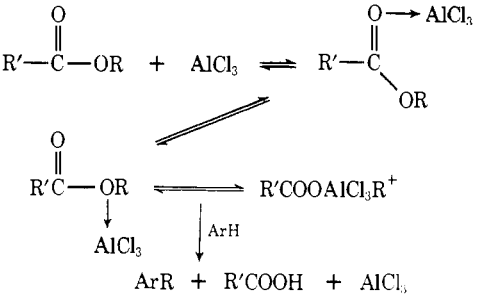


(b) isomerization of products; and (c) rearrangement of intermediate alkyl cation (or ion pair). SNi rearrangement of alkyl chlorosulfites (chlorosulfates) does not seem to make significant contribution, considering their obvious coordination with aluminum chloride, which will make the nonbonded oxygen electron pair unavailable for the rearrangement. The experimental results also show no evidence of isomerization of products.[17] Thus, the probable mechanism is competition between the SN2 type reaction path giving nonrearranged products and the SN1 type path with rearrangement in the alkyl cation (ion pair).

The following general reaction scheme can be suggested for reactions of halosulfites (halosulfates). O-coordinated (with aluminum chloride or antimony pentafluoride) sulfite (sulfate) is in equilibrium with the halogen coordinated species or with the corresponding alkyl cation ion pair. Nakane has suggested that the alkylating agent in Friedel–Crafts systems in suitable nucleophilic solvents (such as nitromethane) is a tight ion pair, which then undergoes SN2 type reaction with the aromatic compound.[18] On the other hand, in less polar solvents, the alkylating agent was suggested to be a "freer" alkyl cation which reacts in a more SN1 like fashion with the aromatic compound. Since varying degrees of skeletal rearrangement of the alkylating agent was directly observed in the present work even in nitromethane solution, the alkyl cation ion pair can undergo rearrangement as well as SN2 type alkylation of aromatic compounds. The well-solvated ion pair could more easily undergo intramolecular rearrangement than intermolecular SN2 type alkylation.

The nature of complex formation, isomerization, and fragmentative formation of alkyl cations from alkyl halosulfites and related haloesters was studied in detail and is reported in the accompanying paper.[19] Results are in accordance with suggested mechanism.

Considering the mechanism of alkylation with esters, the site of coordination with the acid catalyst (Lewis or related conjugate Brönsted acid) is on the carbonyl oxygen atom. Subsequent rearrangement to the ether oxygen coordinated complex followed the alkyl–oxygen cleavage, either in the SN1 fashion with subsequent fast reaction with aromatics, or in the SN2 fashion gives the alkylated aromatics.



Competing acyl–oxygen cleavage would give acylation products. These are much decreased or absent if R is a tertiary alkyl group and/or R′ an increasingly lower nucleophilic leaving group.

Concerning the observed positional selectivities experimental data show that in alkylation systems it is practically impossible to exclude concurrent isomerizations. Any discussions of quantitative relationship of selectivities is therefore questionable.

Experimental Section

Materials. Benzene, toluene, nitromethane, methylene chloride, and carbon disulfide used were commercial products of Spectrograde and dried over molecular sieves. Aluminum chloride (sub-

(16) G. A. Olah, S. Kobayashi, and M. Tashiro, *J. Amer. Chem. Soc.*, **94**, 7448 (1972).

(17) In the reaction mixture of *n*-butylbenzene (0.0025 mol) and aluminum chloride (0.01 mol) in benzene (10 g) and carbon disulfide (10 ml) at 30° for 15 min, no trace of isomerized *n*-butylbenzene could be observed. It is considered that in used dilution and under mild reaction conditions no alkylbenzene rearrangement takes place. (For a discussion of alkylbenzene rearrangements, see R. M. Roberts, *Intra-Sci. Chem. Rep.*, **6**, 89 (1972)).

(18) R. Nakane, O. Kurihara, and A. Natsubori, *J. Amer. Chem. Soc.*, **91**, 4528 (1969).

(19) G. A. Olah, P. Shilling, J. M. Bollinger, and J. Nishimura, *J. Amer. Chem. Soc.*, **96**, 2221 (1974).

limed reagent grade, Fluka) was used without further purification. Antimony pentafluoride was distilled before use.

Methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, and isobutyl chlorosulfite were prepared by literature methods.[20]

Sulfinic esters were synthesized from the sulfinyl chloride and appropriate alcohol.[21] Methyl [bp 78–82° (0.4 mm) (lit. 67–68° (0.04 mm))], ethyl (bp 102–106° (0.5 mm)), and isopropyl benzenesulfinate (bp 92–94° (0.2 mm)) were purified by distillation. *p*-Methoxybenzyl (mp 102–104°) and *p*-nitrobenzyl toluenesulfinate (mp 70°) were recrystallized from ethanol. The other esters were purified by the methods reported for the purification of sulfonates.[22]

Methyl, ethyl, *n*-propyl, *n*-butyl, and isobutyl chlorosulfate were prepared by the reaction of sulfuryl chloride and appropriate alcohol.[23]

Ethyl and isopropyl tosylate were prepared as reported.[22]

Ethyl (bp 51° (81 mm) (lit.[24] 112–113°)), isopropyl (bp *ca.* 20° (6 mm)), and *n*-propyl fluorosulfate [bp 68° (80 mm) (lit.[24] 49° (35 mm))] were prepared from ethylene, propylene, cyclopropane, and fluorosulfuric acid at 0 to −78°, respectively, as reported.[12] These fluorosulfates were stored over potassium carbonate at −90° to avoid any decomposition.

Methyl triflate (bp 98° (lit.[25] 99°)) was prepared from trifluoromethanesulfonic acid and dimethyl sulfate. Ethyl (bp 54° (92 mm) (lit.[25] 115°)) and isopropyl triflate (bp ~20° (15 mm))[26] were made from ethylene and propylene with trifluoromethanesulfonic acid, respectively, using the same procedure as alkyl fluorosulfate.[12]

Methyl and ethyl pentafluorobenzenesulfonate were synthesized by the reaction of pentafluorobenzenesulfonic acid and the appropriate diazoalkane.

All other reagents used were commercially available.

Competitive Alkylation of Aromatics. Data reported are those of at least two parallel determinations. Preparative yields were generally not determined for individual runs, but were 30–50% with no apparent by-products. Dialkylation products were generally less than 5% of monoalkylates.

(a) With Aluminum Chloride as Catalyst. Into a 50-ml three-necked flask equipped with a reflux condenser, a thermometer, and a stirring bar, 7.5 g of 1:1 mol/mol benzene–toluene mixture and 0.01 mol of aluminum chloride were placed. When a solvent (10 ml of nitromethane, methylene chloride, or carbon disulfide) was used, it was added at this stage. The mixture was stirred vigorously in a temperature-controlled oil bath. The 0.005 mol of alkylating agent desolved in 2.5 g of 1:1 benzene–toluene mixture was slowly added to the reaction mixture with vigorous stirring. After stirring for the specified time, the mixture was poured into 25 ml of ice–water. The organic layer was separated, and the aqueous phase was washed with water, 5% of alkaline solution, and water and dried over anhydrous magnesium sulfate. Analysis was carried out by gas–liquid chromatography.

(b) With Antimony Pentafluoride as a Catalyst. Into the same type of a reaction flask as above, 10 g of a 1:1 mol/mol benzene–toluene mixture, 5 ml of 1,1,2-trichlorotrifluoroethane (Freon 113), and 0.02 mol of alkylating agent were placed; 20 mmol of antimony pentafluoride in 5 ml of Freon 113 was slowly added with vigorous stirring. The reactions were carried out as previously.

Gas–Liquid Chromatographic Analysis. The analysis of the alkylation mixture was carried out on a Perkin-Elmer Model 226 gas chromatograph, using a hydrogen flame ionization detector equipped with an electronic printing integrator.

A MBMA (*m*-bis(*m*-phenoxyphenoxy)benzene and Apiezon L) or MBMS (*m*-phenoxyphenoxy)benzene and squalane) coated 150 ft × 0.01 in. open tubular stainless steel column was used for the analyses of the alkylation mixtures (methylation, ethylation, propylation, and butylation), a purified Apiezon-L coated column for benzylation mixtures (except *p*-nitro derivative), and a butanediol succinate coated column for *p*-nitrobenzylation mixtures, respectively.

The products of alkylation were identified by comparison with authentic samples. Details of analysis and observed retention times of benzylation products have been described previously.[16]

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(25) T. Gramstad and R. N. Haszeldine, *J. Chem. Soc.*, 173 (1956).

(26) This compound is very easily decomposed on attempting the distillation at higher temperature.