demic Press, New York, N.Y., 1963, pp 192–237 and 572.
(12) L. J. Bellamy, "Advances in Infrared Group Frequencies", Methuen, Great Britain, 1968, pp 123–190.
(13) H. H. Freedman, *J. Am. Chem. Soc.*, **82**, 2454 (1960).
(14) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).
(15) L. A. Cohen and S. Takahashi, *J. Am. Chem. Soc.*, **95**, 443 (1973).
(16) C. D. Ritchie and W. F. Sager, *Prog. Phys. Org. Chem.*, **2**, 323 (1964).
(17) N. J. Leonard and F. H. Owens, *J. Am. Chem. Soc.*, **80**, 6039 (1958).
(18) K. J. Morgan and N. Unwin, *J. Chem. Soc. B*, 880 (1968).
(19) K. Bowden, N. B. Chapman, and J. Shorter, *Can. J. Chem.*, **41**, 2154 (1963).
(20) B. Nolin and J. R. Norman, *Can. J. Chem.*, **34**, 1382 (1956).

Aromatic Substitution. XXXVIII.[1a] Chloromethylation of Benzene and Alkylbenzenes with Bis(chloromethyl) Ether, 1,4-Bis(chloromethoxy)butane, 1-Chloro-4-chloromethoxybutane, and Formaldehyde Derivatives

George A. Olah,* David A. Beal,[1b] and Judith A. Olah

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

Received November 17, 1975

The chloromethylation of benzene and alkylbenzenes was studied with bis(chloromethyl) ether, 1,4-bis(chloromethoxy)butane, 1-chloro-4-chloromethoxybutane, and formaldehyde derivatives. Relative rate data of chloromethylations compared to benzene as well as isomer distributions were determined. The mechanisms of the reactions are considered in view of the experimental data. Preparative aspects of the novel chloromethylations with 1,4-bis(chloromethoxy)butane and 1-chloro-4-chloromethoxybutane are also discussed.

Since the discovery of the chloromethylation reaction by Grassi-Cristaldi and Maselli,[2] mechanistic studies have centered on establishing the role of formaldehyde in the reaction.[3] It is now generally accepted that the electrophilic reagent in chloromethylations in aqueous or polar solvents (such as glacial HOAc) is the hydroxycarbenium ion (protonated formaldehyde, $CH_2^+{=}OH$).[3,4] Interestingly, however, in our recent work[5] protonated chloromethyl alcohol, $ClCH_2O^+H_2$, was obtained as a stable species, thus indicating its possible significance in chloromethylations.

It was reported by Brown and Nelson[6] that chloromethylation shows high substrate and positional selectivity. The competitive rate between toluene and benzene in chloromethylation with paraformaldehyde, HCl gas, and $ZnCl_2$ in glacial acetic acid solution at 65 °C was found to be 112, with an ortho/para ratio of 0.54. At the same time they claimed that previously reported investigations of chloromethylation reactions,[7] showing low substrate selectivity, while maintaining high positional selectivity, were found to be unreproducible.

We have previously reported[8] that electrophilic aromatic substitution reactions generally can display variable substrate selectivity, not necessarily showing substantial loss of positional selectivity, as evidenced by generally low meta isomer contents observed in substitution of toluene.

We wish to report now related observations of the chloromethylation of benzene and alkylbenzenes with bis(chloromethyl) ether, 1,4-bis(chloromethoxy)butane, 1-chloro-4-chloromethoxybutane, and formaldehyde derivatives. The varied chloromethylations cannot be characterized by a single selected value of substrate and positional selectivity, which can vary widely depending on specific reaction systems and conditions used.

Results and Discussion

Chloromethylation with Bis(chloromethyl) Ether. Since reproducible kinetic data cannot be obtained in heterogeneous systems, it was decided to confine our studies to those chloromethylating agents which displayed good solubility in aromatic hydrocarbons or in a common solvent, thus allowing homogeneous reaction conditions. After preliminary experiments with paraformaldehyde in a number of solvent systems, it was discarded in favor of bis(chloromethyl) ether, which displays good solubility in aromatic hydrocarbons. Bis(chloromethyl) ether has found extensive use in the chloromethylation of aromatic compounds and was generally assumed to generate monomeric formaldehyde in situ, which then reacts analogously to paraformaldehyde or aqueous formaldehyde.[3] Our work shows, however (vide infra), that this is not the real reaction mechanism of chloromethylation with bis(chloromethyl) ether or other halomethyl ethers.

Early in our study it was realized that improved analytical methods were necessary for quantitative analysis of chloromethylated products formed in the reaction mixtures. Previous studies have relied on titrimetric methods, ir spectroscopy, or on analysis after isolating and subsequently converting the chloromethylated products by reduction with $LiAlH_4$ and uv analysis of the resultant methylarenes (utilized for example by Brown and Nelson[6]). We have developed a suitable GLC method to obtain unequivocal data of product compositions, which permits the reaction mixture to be analyzed directly for chloromethylated products (i.e., benzyl chloride and methylbenzyl chlorides). Product compositions could thus be directly determined with an accuracy of better than 1%.

With the choice of chloromethylating agent decided upon and using as solvent excess of neat aromatics, it was then necessary to select a suitable catalyst for the chloromethylation reactions to be studied. In our initial studies, zinc chloride was used because of the general utility it has enjoyed in chloromethylations. Its solubility in aromatic hydrocarbons, however, is poor, and we found that only after the chloromethyl ether was added to a slurry of aromatic hydrocarbon and zinc chloride did the zinc chloride go into solution. Consequently stannic chloride was chosen as a catalyst for the chloromethylation studies. It is a highly soluble catalyst, and generally not so active as to cause secondary reactions (i.e., condensation of chloromethylated products and excess aromatics to give diarylmethanes). Finally, our studies were carried out at 65 °C to allow comparison with the work of Brown and Nelson,[6] which was carried out at this temperature.

A summary of the results of chloromethylation of benzene and methylbenzenes with bis(chloromethyl) ether and stannic chloride catalyst is given in Table I.

Table I. Competitive Chloromethylation of Benzene and Methylbenzenes with Bis(chloromethyl) Ether (BCME)[a]

Registry no.	Substrate	Time, min	$k_{C_6H_5R}/k_{C_6H_6}$[b]	Isomer distribution
71-43-2	C_6H_6		1.0	
108-88-3	$C_6H_5CH_3$	100[c]	16.2	*o*-, 42%; *m*-, 3%; *p*-, 55%
		10[d]	15.5	*o*-, 44%; *m*-, 2%; *p*-, 54%
95-47-6	*o*-$(CH_3)_2$-C_6H_4	25	31.3	4-Chloromethyl-*o*-xylene 97% 3-Chloromethyl-*o*-xylene 3%
108-38-3	*m*-$(CH_3)_2$-C_6H_4	25	40.1	4-Chloromethyl-*o*-xylene 10
106-42-3	*p*-$(CH_3)_2$-C_6H_4	25	24.3	2-Chloromethyl-*p*-xylene 10

[a] All reactions run at 65 °C with ArH:PhH:BCME:$SnCl_4$ mole ratios of 10:10:1:0.75. [b] From direct GLC analysis (see text and Experimental Section). [c] Shorter reaction times did not yield sufficient product for reliable analysis. [d] Reaction run with $AgBF_5$ in place of $SnCl_4$; BCME/$AgBF_4$ = 1/0.1 (m/m).

The competitive method of kinetic evaluation of relative reaction rates was employed in our studies. The basis of this method lies in assuming that the substituting agent present competes for two aromatic substrates.

It is seen from Table I that the positional (regio-) selectivity is high in the chloromethylation of toluene, with only 2–3% of the meta isomer formed in the reaction. The substrate selectivity over benzene $k_{toluene}/k_{benzene}$ is 15.5–16.2. The ortho/para ratio of 0.77 (assuming no significant ortho steric hindrance) indicates that conjugative stabilization by the methyl group in the transition state is not excessive (vide infra).

It is noted that the chloromethylation of the isomeric xylenes proceeds only modestly faster than that of toluene. Despite the diminishing substrate selectivity behavior of increasingly nucleophilic aromatics, the positional selectivity as shown in the case of *o*-xylene stays high (97% of 4-chloromethoxy- and 3% of 3-chloromethyl-*o*-xylene). Thus, no diffusion (or encounter) controlled reaction leading directly in a single step to isomeric products can be involved and it is suggested, as previously discussed,[8] that the reactions proceed through separate consecutive steps defining substrate and positional selectivity.[8] The substrate reactivity of the reactions thus can reach the encounter controlled limit, while regioselectivity stays high.

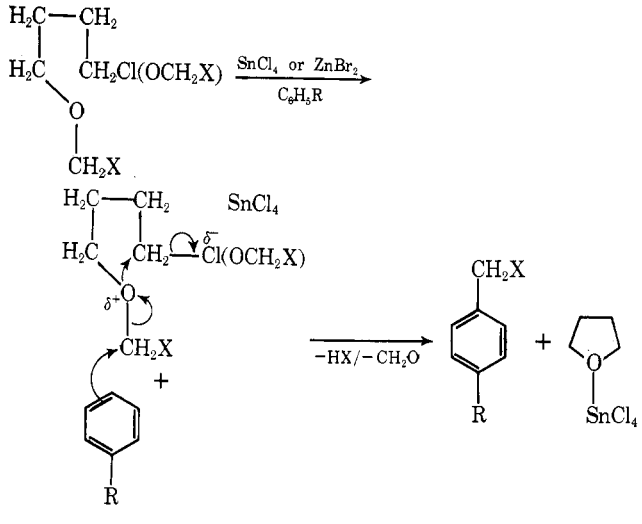
Chloromethylation with 1,4-Bis(chloromethoxy)butane and 1-Chloro-4-chloromethoxybutane. We reported recently preliminary findings to have found in 1-chloro-4-chloromethoxybutane and 1,4-bis(chloromethoxy)butane, respectively, extremely effective new chloromethylating agents of wide utility.[9] At the same time the substantially decreased volatility of these reagents decreases the danger associated with the use of more volatile chloromethyl ethers, which are powerful carcinogens.

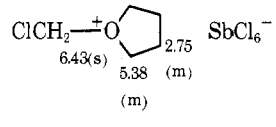
Preparative results of the tin(IV) chloride catalyzed chloromethylation of benzene and methylbenzenes are summarized in Table II (yields of isolated chloromethylarenes are given).

1-Chloro-4-halomethoxybutanes and 1,4-bis(halomethoxy)butanes in their Friedel–Crafts halomethylation reactions act, owing to strong oxygen participation in the developing carbocationic substituting agents, as incipient halomethyltetrahydrofuranonium ions, i.e., reactive Meerwein-type oxonium ions. Tetrahydrofuran formed as by-product of the reaction complexes the Lewis acid catalyst and greatly diminishes formation of diarylmethane by-products. The existence of the corresponding chloromethyltetrahydrofuranonium ion was proven by preparing the novel oxonium ion under stable ion conditions in sulfur dioxide solutions with antimony(V) chloride at −50 °C. The ^1H NMR parameters are as shown.

Table II. Preparative Chloromethylation of Benzene and Methylbenzenes

Arene	% yield of chloromethylarene: With 1,4-bis(chloromethoxy)butane	With 1-chloro-4-chloromethoxybutane
Benzene	43	50
Toluene	53	44
p-Xylene	41	41
m-Xylene	51	55
Mesitylene	60	70





1,4-Bis(chloromethoxy)- and 1-chloro-4-chloromethoxybutane are capable of chloromethylating aromatics under mild conditions, and are well suited for reaction mechanism studies.

The competitive chloromethylation of benzene and alkylbenzenes was carried out, giving results similar to those obtained for bis(chloromethyl) ether. The results obtained are shown in Table III. The most obvious conclusion from comparison of Tables I and III is that the reaction mechanism must be similar in both cases.

An interesting feature of these reactions is that their steric requirements are not as stringent as those of bis(chloromethyl) ether (compare for example yields of 2,3-dimethylbenzyl chloride in Table III vs. Table I).

It may be seen from Table III that the chloromethylation of toluene with bis(chloromethoxy)butane at 65 °C gives an isomer distribution identical with that found at 35 °C, indicating no temperature dependence of the isomeric products, i.e., no isomerization (which would, however, not prevent some

Table III. Competitive Chloromethylation of Benzene and Alkylbenzenes with 1,4-Bis(chloromethoxy)butane

Substrate	Time, min	$k_{C_6H_5R}/k_{C_6H_6}$[b]	Isomer distribution, %[b]
C_6H_6		1.0	
$C_6H_5CH_3$	25	21.0	*o*-, 45; *m*-, 4; *p*-, 51
	100[c]	22.2	*o*-, 43; *m*-, 3; *p*-, 54
o-$(CH_3)_2C_6H_4$	12.5	23.6	4-Chloromethyl-*o*-xylene 94 3-Chloromethyl-*o*-xylene 6
m-$(CH_3)_2C_6H_4$	12.5	34.5	4-Chloromethyl-*m*-xylene 100
p-$(CH_3)_2C_6H_4$	12.5	21.5	2-Chloromethyl-*p*-xylene 100

[a] All reactions run at 65 °C with ArH:PhH:BCMB:$SnCl_4$ = 10:10:1:0.1 (m/m). [b] Determined by GLC. [c] This reaction run at 35 °C.

Table IV. Relative Rate of the Chloromethylation of Benzene and Toluene as a Function of Their Varying Ratios in Competition Experiments

Mole ratio $C_6H_5CH_3/C_6H_6$	Observed product ratios of toluene/benzene	k_T/k_B
1/1	21.0	21.0
1/5	4.1	20.5
1/10	2.4	24.0

isomerization within the arenium ion type intermediates prior to their deprotonation).

A small kinetic hydrogen isotope effect was found in the reaction of bis(chloromethoxy)butane with hexadeuteriobenzene compared to benzene at 35 °C.

$$k_{C_6H_6}/k_{C_6D_6} = 1.4$$

This observation is in line with the absence of primary isotope effects in studied Friedel–Crafts type alkylations.

Competition experiments were also carried out with various toluene/benzene mole ratios. The dependence of the relative rate upon aromatic hydrocarbon concentration is shown in Table IV. These values compare well with each other and indicate first-order dependence in aromatic hydrocarbons.

In the study of the chloromethylations it was observed that change in catalyst concentration has a marked effect on the selectivities of the reactions. Higher catalyst concentrations favor a more reactive reaction system, whereas increasingly smaller amounts of catalyst have the opposite effect. To study this effect a series of reactions were run with benzene and toluene in competition in which the amount of catalyst ($SnCl_4$) used in the reactions was systematically varied. The reactions were sampled at varying intervals, and the relative rate constants, $k_{toluene}/k_{benzene}$, were obtained by extrapolating these measurements to zero time. The data are shown in Table V.

It is apparent from these data that a significant change occurs with changes in catalyst concentration. What was initially a rather low substrate selectivity reaction has become extremely substrate selective. At the same time the ortho/para isomer ratios also show a continuous decrease. This again suggests, as had related work from this laboratory, that the position of the transition state of highest energy in aromatic substitutions is *not* a fixed one, and depending upon reaction conditions it can either lie early (π-complex-like) or late (σ-complex- or arenium-ion-like) on the reaction coordinate. Further, these results suggest that there is a continuum of substrate and positional selectivity and mean that no single selected set of substrate and positional selectivity values can be used to characterize chloromethylation reactions.

Table V. Variation of the Selectivity of Chloromethylation of Toluene and Benzene with Catalyst Concentration

		Chloromethyltoluenes			
10^{-5} M $SnCl_4$	$k_{toluene}/k_{benzene}$	% ortho	% meta	% para	*o*-/*p*-
100	21	45	4	55	0.83
68.6	41	37	3	60	0.61
34.3	56	36	2	62	0.58
7.68	317	32.5	1.5	66	0.49

Table VI. Relative Reactivities of Methylbenzenes and Benzene in Chloromethylations at Low (3.84×10^{-5} M) $SnCl_4$ Concentration

Substrate	k^0_{ArH}/k^0_{PhH}
C_6H_6	1
$C_6H_4CH_3$	370
p-$(CH_3)_2C_6H_4$	1 200
o-$(CH_3)_2C_6H_4$	2 700
m-$(CH_3)_2C_6H_4$	27 000

On obtaining these results the question of substrate selectivity in reactive hydrocarbons such as xylenes was also further studied. In view of the seemingly significant substrate discrimination for toluene displayed under low catalyst concentration, these substrates should also show a much enhanced reactivity over benzene. Indeed, in these chloromethylation reactions xylenes could only be compared with benzene via the indirect comparison with toluene, owing to the greatly enhanced reactivity of the xylenes. The results are summarized in Table VI.

It can be seen from these data that the chloromethylation reactions show increasing substrate selectivity with lower catalyst concentration (note *m*-xylene is 27 000 times more reactive than benzene) with simultaneous decrease of the ortho/para isomer ratio. There is also a decrease of meta substitution (from 4 to 1.5%).

Having observed chloromethylations with chloromethyl ethers which do not always display the high substrate, high positional selectivity characteristics reported by Brown and Nelson,[6] it was also felt necessary to extend our studies to formaldehyde systems to clarify any discrepancies which might exist, and to see if modification of the reaction conditions would vary the substrate selectivity. With regard to the latter point, the work of Ogata and Okano[4] suggested that increasing the acidity of the reaction mixture might accomplish this, since they found a strong dependence of the rate of chloromethylation of mesitylene with aqueous formaldehyde on the Hammett acidity function.

In order to use a source of formaldehyde which is soluble in aromatic solvents and which would not be prone to secondary reactions with chloromethylated products, paraformaldehyde and dialkyl formals were considered unsuitable. The reactions were accordingly carried out with *s*-trioxane as a source of formaldehyde. Since it was necessary to have a highly soluble proton acid catalyst, a solution of $SnCl_4$ saturated with HCl was used. In some experiments the use of *s*-tetraoxane was also attempted. This highly soluble cyclic tetramer of formaldehyde has recently become available.[10] However, *s*-tetraoxane was found to be rapidly depolymerized in the presence of acid and gives via repolymerization insoluble paraformaldehyde.

The repetition of the work of Brown and Nelson[6] was also considered necessary, because it was felt possible that in their pre-gas–liquid chromatography analytical method used they may have encountered difficulties in the analysis of reaction

Table VII. Competitive Chloromethylation of Benzene and Toluene with Formaldehyde Derivatives

Reagent/catalyst (mole ratio)	k_{PhMe}/k_{PhH}[a]	Isomer distribution, %		
		Ortho	Meta	Para
Trioxane/$SnCl_4$[b] (5/1)	63	37	2	61
Trioxane/$SnCl_4$[b] (0.9/1)	7.8	55	5	40
Paraform/$ZnCl_2$[c,d] (6/1)	28.2	43	4	53
Paraform/$ZnCl_2$[d] (6/1)	40.3	40	3	57
Paraform/$ZnCl_2$[e] (6/1)	112	35	2	64

[a] Analysis by GLC. [b] Mole ratio PhMe:PhH:*s*-trioxane = 12:12:1 at 65 °C (excess aromatic used as solvent). [c] Paraform = paraformaldehyde. [d] From the same reaction; fourth entry subjected to more extensive workup (both run at 65 °C in glacial acetic acid solvent; see text and note *e*). [e] Data of H. C. Brown and K. L. Nelson, *J. Am. Chem. Soc.*, **75**, 6292 (1953).

products, particularly when considering the necessity of indirect uv spectroscopic analysis, after first converting the chloromethylated products to methylarenes by reduction with $LiAlH_4$. To this end their procedure for the competitive chloromethylation of benzene and toluene was repeated. For convenience the quantities of materials and the reaction time were reduced by a factor of 20 (while keeping molar ratios identical) and gaseous HCl was used from a lecture bottle (Matheson). The reaction mixture was divided into two parts for analysis. One part was washed with ice water, dried over $CaSO_4$, and analyzed by the direct GLC analytical method developed in our work for benzyl chlorides and methylbenzyl chlorides (see Experimental Section). The other portion was carried through the identical workup reported by Brown and Nelson: washings with ice water and with 10% aqueous potassium carbonate, extraction of washings with petroleum ether, drying of organic materials over calcium chloride–potassium carbonate, and removal of the petroleum ether and excess hydrocarbon by distillation at atmospheric pressure and at 95 mm. This portion was then analyzed by the same GLC method as used throughout in our work in contrast to Brown and Nelson's method of reducing the benzyl chlorides with $LiAlH_4$ to the corresponding methylbenzenes followed by uv spectroscopic analysis. It was necessary to dilute samples with carbon tetrachloride prior to GLC analysis, but this in no way affected the product composition.

The results of the chloromethylation reactions with formaldehyde derivatives are summarized in Table VII.

Turning first to the reactions with *s*-trioxane, it can be seen that the chloromethylations are indeed highly dependent on acidity (catalyst concentration) of the reaction systems. The fact that increased acidity has decreased the relative rate of reactions (cf. $k_{toluene}k_{benzene}$ = 63 vs. 7.8, with a 5.5-fold decrease in acid concentration) and also causes significant changes in the isomer distribution clearly indicates that at high acidity the reactivity of the system is higher than that observed at low acidity. This is compatible with an equilibrium-controlled increase in the concentration of the hydroxycarbenium or chloromethyloxonium ion, which would be expected to react more rapidly than a formaldehyde–proton acid complex. There is further evidence of this in the ortho/para ratios of the two reactions. In the low acidity reaction the methyl group plays a greater role in stabilizing the arenium-ion- (or σ-complex) -like transition state by conjugation, and the para isomer predominates (*o*-/*p*- = 0.63). This conjugative stabilization is less important in the high-acidity case where in the earlier transition state of aronium ion (or π-complex) nature the electrophile requires less contribution of the aromatic π electrons. As a consequence inductive stabilization predominates and the ortho/para ratio is high (1.38).

While the determination of the isomer distribution in the chloromethylation reactions was accurate (they are considered to be accurate to 1%), it is not possible to exclude some intramolecular isomerization in the arenium type transition states prior to deprotonation. This can be of significance, particularly in reactions with high catalyst concentrations, and affect the results through thermodynamically controlled factors.

Returning to the repetition of the Brown–Nelson experiments, it may be seen that there is less significant difference in the distribution of methylbenzyl chloride isomers from either the simple workup and direct GLC analysis (third entry, Table VII) or the original more elaborate workup (fourth entry, Table VII) or from the results Brown and Nelson reported (fifth entry, Table VII). These differences lie probably within experimental error of the methods used. Clearly, however, the same cannot be said of the relative rates determined from product compositions obtained from the two different workup procedures. The most probable explanation lies in the difficulty of separating chloromethylated products from excess aromatics by distillation without losses of the former, a factor obviously seriously affecting the data of Brown and Nelson. Judging from the difference in $k_{toluene}/k_{benzene}$ between these experiments, the removal of solvent causes some loss of the more volatile benzyl chloride. In fact, when the aromatic hydrocarbon forerun obtained from the Brown–Nelson workup procedure was subjected to GLC analysis, a significant amount of benzyl chloride was found in it. The more benzyl chloride lost, the higher the apparent value of $k_{arene}/k_{benzene}$.

Conclusions

The paucity of mechanistic information about the chloromethylation reaction led previously to somewhat contradictory results. In our studies we have been able to show that a wide range of selectivity exists for chloromethylations with varying reaction conditions and, therefore, no single set of data can characterize all electrophilic chloromethylation reactions. It is clear from our studies that toluene remains predominantly ortho/para directing in all chloromethylations with the change in meta substitution ranging from 1.5 to 5%, with simultaneous substrate selectivity, i.e., k_T/k_B ratio changes ranging from 15 to 320.

Experimental Section

Reagents. Aromatic hydrocarbons were of the highest purity available and were dried over molecular sieves prior to use. Benzene, toluene, alkylbenzenes, and all solvents used were spectral or highest purity grade, dried over molecular sieves. Stannic chloride was ACS reagent quality. Bis(chloromethyl) ether (Eastman Kodak) was obtained in sealed glass ampules (100 g). These ampules were open in a drybox, and the reagent was stored in and dispensed from Teflon bottles. 1,4-Bis(chloromethoxy)butane and 1-chloro-4-chloromethoxybutane were prepared as reported.[9]

Warning! Bis(chloromethyl) ether[11] and 1,4-bis(chloromethoxy)butane are toxic even in small quantities. In addition, bis(chloromethyl) ether has been shown to be a powerful carcinogen.[12] Because of its higher boiling point at atmosphere pressure, 1,4-bis(chloromethoxy)butane is considered a lesser inhalation hazard than bis(chloromethyl) ether, but all chloromethyl ethers (as well as other haloalkyl ethers and difunctional haloalkyl compounds such as haloalkyl tosylates, alcohols, etc) should be stored and dispensed in a fume hood, using rubber gloves and eye protection. Concentrated aqueous NaOH solution was used to hydrolyze material before disposal.

Equipment Used. Flasks and pipets used to contain and dispense the reagents were cleaned with H_2SO_4–$K_2Cr_2O_7$ solution, rinsed with distilled water, and dried in an oven. Kinetic measurements were carried out in thermostated solutions using a Haake F4291 circulating bath fitted with immersion heater and thermoregulator. This bath was capable of maintaining temperature with a precision of better than ±0.1 °C.

Chloromethylation Reactions. Reaction mixtures were prepared in clean glassware in a fume hood. In competitive studies, 0.05 mol of each aromatic was weighed into a flask and to it was added (calibrated Pasteur pipet) 0.005 mol of the reagent under study. The desired volume of a 0.5 M solution of $SnCl_4$ in cyclohexane (1.00 ml = 0.0005 mol of $SnCl_4$) was added and the flask transferred to the constant-temperature bath. After a predetermined heating period to allow the reactants to come to the bath temperature, the similarly prepared and thermostated solution of the chloromethylating agent was than added with good stirring. The mixtures were either quenched after a specified time or periodically sampled, as described previously.

GLC analysis of products (Aerograph 1200 with flame ionization detector) was carried out using the following columns: 15 ft × 0.125 in. in 5% bentone-34 + 1% DC-200, 60/80 mesh Chromosorb W, acid-washed (for separation of benzyl chloride and isomeric methylbenzyl chlorides) and 5 ft × 0.125 in. 5% SE-30, 80/120 mesh silanized acid-washed Chromosorb W (for separating dimethylbenzyl chlorides). Both columns gave good baseline separation allowing quantitative determination of isomers.

Calculation of product concentration was by the relative response method, and competitive rate ratios were determined from product ratios.

Acknowledgment. Support of our work by the National Institutes of Health is gratefully acknowledged.

Registry No.—BCME, 542-88-1; $SnCl_4$, 7646-78-8; bis-1,4-(chloromethoxy)butane, 13483-19-7; 1-chloro-4-chloromethoxybutane, 3970-17-0; mesitylene, 108-67-8; *s*-trioxane, 110-88-3; paraformaldehyde, 30525-89-4.

References and Notes

(1) (a) Part XXXVII: G. A. Olah and J. Nishimura, *J. Am. Chem. Soc.*, **96**, 2214 (1974). (b) Taken in part from the Ph.D. Thesis of D. A. Beal, Case Western Reserve University, 1973.
(2) G. Grassi-Cristaldi and M. Maselli, *Gazz. Chim. Ital.*, **20**, 477 (1898).
(3) For reviews see G. A. Olah and W. S. Tolgyesi in "Friedel-Crafts and Related Reactions", Vol. II, G. A. Olah, Ed., Wiley-Interscience, New York, N.Y., 1964, pp 659–784; R. C. Fuson and C. H. McKeever, *Org. React.*, **1**, 64 (1942).
(4) M. Ogata and Y. Okano, *J. Am. Chem. Soc.*, **78**, 5423 (1956).
(5) G. A. Olah and S. H. Yu, *J. Am. Chem. Soc.*, **97**, 2293 (1975).
(6) H. C. Brown and K. L. Nelson, *J. Am. Chem. Soc.*, **75**, 6292 (1953).
(7) (a) H. H. Szmant and J. Dudek, *J. Am. Chem. Soc.*, **71**, 3763 (1949); (b) G. Vavon, J. Bolle, and J. Calin, *Bull. Soc. Chim. Fr.*, **6**, 1025 (1939).
(8) For a review see G. A. Olah, *Acc. Chem. Res.*, **4**, 240 (1971), and references cited therein.
(9) G. A. Olah, D. A. Beal, S. H. Yu, and J. A. Olah, *Synthesis*, 560 (1974).
(10) We gratefully acknowledge the gift of a sample of *s*-tetraoxane by Mitsui Toatsu Chemicals, Ltd.
(11) N. I. Sax, Ed., "Dangerous Properties of Industrial Materials", Reinhold, New York, N.Y., 1963, p 696.
(12) B. L. Van Duren et al., *J. Natl. Cancer Inst.*, **43**, 481 (1969); L. Collier, *Environ. Sci. Technol.*, **6**, 930 (1972).

Metathesis Catalysts. V. Competitive Character of Metathesis and Alkylation Reactions Catalyzed by Tungsten Hexachloride–Ethylaluminum Dichloride

Léonard Hocks,* Alfred Noels, André Hubert, and Philippe Teyssie

Laboratoire de Chimie Macromoléculaire et de Catalyse Organique, Université de Liège, Sart Tilman par 4000 Liège, Belgium

Received May 27, 1975

The olefin metathesis catalytic system WCl_6–$EtAlCl_2$ in an aromatic solvent promotes both olefin metathesis and solvent alkylation reactions. The yields of these two competitive reactions strongly depend on the relative concentration of the three compounds of the system (olefin, solvent, catalyst), with a marked dependence on the π donor ability of the aromatic solvent; moreover, our catalytic conditions can promote exclusive formation of monosubstituted benzenes at the thermodynamic equilibrium. The mechanism proposed involves competitive coordination equilibria of the solvent and of the olefin as the key step.

The use of WCl_6–$EtAlCl_2$ as a catalytic system for olefin metathesis reactions has been described by several groups.[1] This catalyst, which is also a strong Lewis acid, can consequently promote a variety of cationic reactions such as prototropic isomerizations,[2] oligomerization of olefins,[3] and alkylation of aromatic solvents.[4]

However, neither the specificity nor the optimal conditions for the competition between metathesis and cationic-like reactions have been thoroughly investigated; it is the goal of this paper to study the parameters which govern this competition between metathesis and alkylation processes.

Experimental Section

All solvent and olefins (*trans*-2-pentene, *trans*-4-octene, 1-octene, and 1-dodecene) were dried over $LiAlH_4$ or CaH_2 before distillation and the operations were conducted under an inert atmosphere (argon).

Ethylaluminum dichloride (Fluka), obtained as a 50% solution in hexane, was diluted (after titration) with the appropriate amount of hexane to obtain 0.2 M solutions.

Tungsten hexachloride (Fluka) was purified by sublimation of the volatile impurities ($WOCl_4$, WO_2Cl_2) before dissolution in the aromatic solvents, respectively benzene; *o*-, *m*-, *p*-xylenes; 1,2,4 and 1,3,5-trimethylbenzenes; and finally *o*-dichlorobenzene. The solutions obtained (0.05 M) are intensively colored: benzene, violet blue; toluene, blue; xylenes, green blue; trimethylbenzenes, green; dichlorobenzene, brown.

The different components were injected into the reaction vessel through a septum, together with an internal VPC standard (cyclooctane or undecane).

The solution of olefin in the suitable aromatic solvent was cooled to 5 °C and the appropriate amount of the aromatic solution of WCl_6 was added, immediately followed by the solution of $EtAlCl_2$ in hexane with a molar ratio Al to W kept equal to 4. After 1 min of reaction time, the system was quenched with water.

Quantitative VPC analysis was performed using a silicone column (20% SE-30 on Chromosorb 80/100) (flame ionization detector) and the yields calculated by comparison with the internal standard.

The different olefins and alkylated products have been identified by comparison with standard products which have been obtained from Fluka or by the following classical reaction sequence: addition of the suitable Grignard reagent on the corresponding α-ketoalkylbenzene gives a tertiary alcohol which is dehydrated on *p*-toluenesulfonic acid to a phenylalkene. Subsequent hydrogenation of the olefin on Raney nickel gives the required phenylalkane.

Moreover, some of the alkylated products have been isolated by preparative GLC and analyzed by mass spectrometry which shows a fragmentation pattern characteristic of alkylbenzenes; for in-