obviously one can retain the latter's mechanistic simplicity if the π-complex structure is substituted for the 1,2-diadsorbed alkane. However, our present stereochemical information does not demand such a distinction.

Our studies suggest that the stereochemistry which is observed at high hydrogen pressures is governed by a reaction which precedes the formation of the "half-hydrogenated" state. The organic moiety of the transition state for this reaction has a geometry similar to the reactants; however, the hybridization of the unsaturated carbon atoms has progressed from sp^2 to sp^3 to the extent that eclipsing effects between groups attached at C-2 and C-3, as in 2,3-dimethylcyclopentene, are observable. These geometrical requirements are met either by our formulation of the Horiuti–Polanyi mechanism or the π-complex concept. The groups attached to the π-bonded carbon atoms of the complex are apparently not in a plane which includes the latter.

π-Allyl complexes may be involved in the isomerization of alkenes as suggested by Smith and Burwell,[15] but our stereochemical data are adequately described without this additional postulate.

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Aromatic Substitution. XXI.[1a] Friedel–Crafts Acetylation of Benzene, Alkylbenzenes, and Halobenzenes with Acetyl Halides and Acetic Anhydride

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The Friedel–Crafts acetylation of benzene, alkylbenzenes, and halobenzenes has been investigated with acetyl halides (fluoride, chloride, and bromide) and acetic anhydride in the presence of a variety of Lewis and Brønsted acid catalysts. Relative reactivities compared with benzene and isomer distributions of homogeneous reactions in nitromethane solution were determined by a gas–liquid chromatographic analytical technique. Certain aspects of the mechanism and the nature of the acetylating agents are discussed on the basis of the experimental data, including n.m.r. investigations.

Introduction

The Friedel–Crafts acylation of aromatics with acid anhydrides and acyl halides in the presence of acidic halide catalysts has been the subject of a great many investigations during the 86 years since the discovery of the reaction. Extensive reviews have critically discussed the reaction mechanism, and we will therefore confine our discussion to work directly related to our own investigations.

Earlier investigations of the Friedel–Crafts acetylation reaction of aromatics have reported only small substrate reactivity differences between benzene and toluene. Ogata and Oda[2] have observed a relative rate $k_{toluene}:k_{benzene}$ of 8.35 and McDuffie and Dougherty[3] that of 13.3 in a competitive reaction using acetyl chloride and aluminum chloride in an excess of the hydrocarbons at 10°. McDuffie and Dougherty also have reported relatively low substrate selectivity for the acetylation of *m*-xylene and mesitylene.

TABLE I

RELATIVE RATES OF ACETYLATION OF BENZENE AND METHYLBENZENES (MCDUFFIE AND DOUGHERTY[3])

	$k_{Ar}:k_{benzene}$
Benzene	1.0
Toluene	13
m-Xylene	100
Mesitylene	27

These investigations, however, were carried out under heterogeneous reaction conditions and no homogeneous kinetic work was available until the investigations of Brown and his co-workers.

Relative rates and isomer distributions of the aluminum chloride-catalyzed acetylation of benzene and alkylbenzenes with acetyl chloride in ethylene dichloride solution at 25° were investigated by Brown, Marino, and Stock.[4,5] Their data are summarized in Table II.

TABLE II

ALUMINUM CHLORIDE-CATALYZED ACETYLATION OF BENZENE AND ALKYLBENZENES WITH ACETYL CHLORIDE IN ETHYLENE DICHLORIDE SOLUTION AT 25° (BROWN AND CO-WORKERS[4,5])

Aromatic hydrocarbon	$k_{Ar}:k_{benzene}$	Alkylacetophenone, %		
		ortho	*meta*	*para*
Benzene	1.0			
Toluene	128	1.2	1.2	97.6
Ethylbenzene	129	0.3	2.7	97.0
Isopropylbenzene	128		3.0	97
t-Butylbenzene	114		3.8	96.2

As seen from the investigations of Brown and his co-workers, toluene, ethylbenzene, isopropylbenzene, and *t*-butylbenzene all react with practically the same velocity, although the reactions were shown to be first order in aromatic substrates. The observed isomer distributions were also very similar. In the acetylation system investigated, using ethylene dichloride solvent (which has very poor solvent properties for aluminum halides, but dissolves to a certain degree the CH_3COCl–$AlCl_3$ complex in the form of the donor–acceptor complex and not as the oxocarbonium salt), the acylations show both high substrate and positional selectivity.

The essential absence of *o*-isomers was attributed to the bulkiness of the acetylating agent: namely, the acetyl chloride–aluminum chloride complex.[4] Similar explanations had been advanced previously to account for the general absence of *o*-substitution in Friedel–Crafts acylation of alkylbenzenes.

(1) (a) Part XX: *J. Am. Chem. Soc.*, **86**, 1067 (1964); (b) correspondence should be addressed to Dow Chemical Company, Eastern Research Laboratory, Framingham, Mass.

(2) Y. Ogata and R. Oda, *Bull. Inst. Phys. Chem. Res.* (Tokyo), **21**, 728 (1942).

(3) H. F. McDuffie and G. Dougherty, *J. Am. Chem. Soc.*, **64**, 297 (1942).

(4) H. C. Brown, G. Marino, and L. M. Stock, *ibid.*, **81**, 3310 (1959).

(5) H. C. Brown and G. Marino, *ibid.*, **81**, 5611 (1959).

The acetylation of chlorobenzene, either in carbon disulfide[6–8] or chlorobenzene[9] as solvent, has been reported to give *p*-chloroacetophenone exclusively. Similarly, *p*-bromoacetophenone is reported to be the sole product of acetylation of bromobenzene[7,10–12] as was *p*-fluoroacetophenone in the case of acetylation of fluorobenzene.[13,14]

McDuffie and Dougherty determined the relative rates of acetylation of benzene, chlorobenzene, and bromobenzene[15] by the competitive method and found them to be: benzene 1.0, chlorobenzene 0.031, and bromobenzene 0.024. However the reaction conditions (excess aromatics as solvent, acetyl chloride, and aluminum chloride catalyst) were heterogeneous and consequently the results obtained are questionable.

Smeets and Verhulst[16] examined the kinetics of acetylation of benzene and a number of aromatic compounds, including chlorobenzene and bromobenzene. Their method was based on titration of the hydrogen chloride formed in the course of the reaction. The reaction of benzene, as compared with that of the halobenzenes investigated, was too fast for this technique to be useful.

Brown and Marino recently published results of their investigations relating relative rates and isomer distributions of the aluminum chloride-catalyzed acetylation of the halobenzenes in ethylene dichloride at 25°.[17]

Their results are summarized in Table III.

TABLE III

ALUMINUM CHLORIDE-CATALYZED ACETYLATION OF BENZENE AND HALOBENZENES WITH ACETYL CHLORIDE IN ETHYLENE CHLORIDE SOLUTION AT 25° (BROWN AND MARINO[17])

Aromatic	$k_{halobenzene}:k_{benzene}$	Haloacetophenones, % ortho	meta	para
Benzene	1.0			
Fluoro-	0.252			100
Chloro-	.0209		0.5	99.5
Bromo-	.0140			100

The results were explained as a high selectivity aromatic substitution, where *o*-substitution is suppressed by the inductive effect of the halogen substituent and the bulky substituting agent.

Results and Discussion

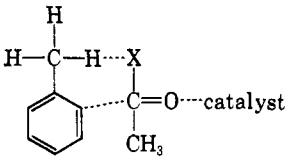
In continuation of our work on aromatic substitution, acetylations of benzene, alkylbenzenes, and halobenzenes were investigated in an attempt to correlate the reaction with the previously investigated nitration, halogenation, and alkylation systems. These investigations were carried out to obtain information on the effect of the (a) acylating agent, (b) catalyst, (c) solvent, and (d) complexes between acylating agents and catalysts.

In the first stage of our investigations we attempted to ascertain whether the low degree of *o*-substitution previously observed is indeed a fundamental characteristic of Friedel–Crafts acetylation of alkylbenzenes and, if not, to establish the effect of acetylating agent and catalyst on the isomer distributions.

In order to gain information on these effects the Friedel–Crafts acetylation of toluene was compared using acetyl fluoride, chloride, and bromide, as well as acetic anhydride. The reactions were carried out under heterogeneous conditions in excess toluene at the reflux temperature. The isomer distribution of the formed methylacetophenones was determined by gas–liquid chromatography. The data obtained are summarized in Tables III and IV.

These data show that acetylation of toluene indeed gives isomer distributions different from those observed in other electrophilic aromatic substitutions, such as nitration, halogenation, and alkylations. Whereas the amount of *m*-isomer (1–8%) is generally in the order expected for a typical electrophilic substitution of toluene, the amount of *o*-isomer is generally very low. It is significant, however, to note that the nature of the catalyst affects the isomer ratio and whereas in previously reported work the amount of *o*-methylacetophenone was negligible, the present investigations provide evidence that with certain of the acetylating agents the *o*-isomer may be formed in amounts as large as 48%. It is interesting to observe that the highest *o*-isomer ratios were observed with acetyl bromide and the lowest with acetyl fluoride. This observation seems to be in contradiction to the steric requirement of the acyl halides. However, as discussed subsequently, the actual acetylating agent is the complex formed between acetyl halide and the acidic halide catalyst.

Coordination of the reagent–catalyst complex, as suggested by one of the referees of the paper, may also play



an important role in the isomer distribution. The ability of the halogen of the complexed RCOX to bond with the hydrogen of the methyl group will depend on several factors. One of these is orbital overlap of X with the carbonyl carbon. Fluorine might be expected to hydrogen bond less since orbital overlap is more favorable in comparison with other halogens. Another factor may be the fact that the stronger the bonding of the catalyst to the oxygen, the lower the electron density on the halogen. Therefore, hydrogen bonding should be less favorable with a very stable complex. The fluorides form the most and the bromides the least stable complexes.

The reactivity of the halogen of acetyl halides was qualitatively compared in acetylation of toluene with a number of Lewis acid halide catalysts. These comparisons were based on product yields obtained under otherwise identical conditions with acetyl fluoride, chloride, and bromide. Contrary to Calloway's reactivity order,[18] which recently has been questioned also by

(6) F. Straus and A. Ackermann, *Ber.*, **42**, 1804 (1909).
(7) W. L. Judefind and E. E. Reid, *J. Am. Chem. Soc.*, **42**, 1043 (1920).
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(10) A. Collet, *Compt. rend.*, **126**, 1577 (1898).
(11) M. Schopff, *Ber.*, **24**, 3766 (1891).
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(13) D. P. Evans, V. G. Morgan, and H. B. Watson, *J. Chem. Soc.*, 1167 (1935).
(14) N. P. Buu-Hoi, N. Hoan, and P. Jacquignon, *Rec. trav. chim.*, **68**, 781 (1949).
(15) H. F. McDuffie, Jr., and G. Dougherty, *J. Am. Chem. Soc.*, **64**, 297 (1942).
(16) F. Smeets and J. Verhulst, *Bull. soc. chim. Belges*, **63**, 439 (1954).
(17) H. C. Brown and G. Marino, *J. Am. Chem. Soc.*, **84**, 1658 (1962).
(18) N. O. Calloway, *ibid.*, **59**, 1474 (1937).

TABLE IV

ACETYLATION OF TOLUENE WITH ACETYL HALIDES (HETEROGENEOUS REACTION CONDITIONS, EXCESS TOLUENE AS SOLVENT)

Acetyl halide	Catalyst	Methylacetophenone, % ortho	meta	para	Acetyl halide	Catalyst	Methylacetophenone, % ortho	meta	para
Fluoride	$AlBr_3$	2.1	4.2	93.7	Bromide	$BiCl_3$	11.8	3.7	84.5
	$AlCl_3$	5.9	5.3	88.8		$FeBr_3$	4.0	2.5	93.5
	BF_3	1.8	1.4	96.8		$FeCl_3$	2.1	2.6	95.3
	$FeCl_3$	1.7	1.2	97.1		$GaCl_3$	2.4	2.1	95.5
	$SnCl_4$	2.4	1.2	96.4		I_2	48.0	0.7	51.3
	Polyphosphoric acid (PPA)	2.3	1.0	96.7		$InBr_3$	13.6	1.4	85.0
						$InCl_3$	9.4	0.9	89.7
Chloride	$AlBr_3$	2.9	3.1	94.0		$MoCl_5$	23.1	0.7	76.2
	$AlCl_3$	3.0	3.1	93.9		$SbBr_3$	3.4	1.5	95.1
	$AuCl_3$	8.2	9.7	82.1		$SbCl_5$	17.1	6.9	76.0
	$FeCl_3$	2.7	1.6	95.7		$SnBr_4$	14.2	1.2	84.6
	I_2	35.3	2.3	62.9		$SnCl_4$	9.8	1.4	88.8
	$MoCl_5$	8.0	1.3	90.7		$TiBr_4$	7.3	0.3	92.4
	$NbCl_5$	5.9	3.4	90.7		$TiCl_3$	9.4	0.9	89.7
	$SbCl_5$	9.3	3.0	87.7		$TiCl_4$	5.3	0.4	94.3
	$SnCl_4$	15.0	3.8	81.2		TiF_4	1.7	2.6	95.7
	$TaCl_5$	3.6	1.2	95.2		TiI_4	9.5	3.3	87.2
	$TiCl_4$	8.2	2.3	89.5		$TlCl_3$	13.7	1.4	84.9
	$ZnCl_2$	17.0	4.7	78.3		VCl_4	5.4	1.6	93.0
Bromide	$AlBr_3$	4.0	3.7	92.3		$ZnBr_2$	13.0	2.2	84.8
	$AlCl_3$	2.3	4.7	93.0		$ZnCl_2$	9.9	1.7	88.4
	AsF_3	2.9	6.6	90.5		ZnI_2	20.7	2.3	77.0
						H_2SO_4	18.3	1.2	80.5

Yamase and Goto,[19] we observed that acetyl fluoride frequently was the most, and not the least, reactive of the halides (for example, with boron trifluoride as catalyst). Acetyl bromide on the other hand was frequently, but not always, more reactive than acetyl chloride, giving an apparent reactivity sequence of the acetyl halides, F > Br > Cl. It must be stressed, however, that any comparison at this stage of the investigations is highly qualitative. If acetyl halides are treated with acidic halide catalysts containing other halogens, the reactions proceed with substantial halogen exchange. Acetyl fluoride exchanges readily with chlorides and bromides and acetyl chloride and bromide also exchange fairly easily. Thus a comparison of reactivities based only on product yields can be misleading, since, because of the possibility of halide exchange, the nature of the acetylating agent is not well defined.

TABLE V

ACETYLATION OF TOLUENE WITH ACETIC ANHYDRIDE (HETEROGENEOUS REACTION CONDITIONS, EXCESS TOLUENE AS SOLVENT)

Catalyst	Methylacetophenone, % ortho	meta	para
$AlCl_3$	6.2	5.2	88.6
BF_3	5.0	0.9	94.1
$BF_3 \cdot H_3PO_4$	10.2	1.9	87.9
H_2SO_4	15.3	2.6	82.1
I_2	29.1	3.2	67.7
Polyphosphoric acid	12.0	3.2	84.8
$ZnBr_2$	11.9	2.8	85.3
$ZnCl_2$	13.6	3.1	83.3
ZnI_2	17.2	2.9	79.9

The relatively high amount of *o*-isomer formed in acetylations with acetic anhydride reflects the relative instability of the acetic anhydride–Lewis acid halide complexes. In cases where these complexes are more stable, as with boron trifluoride, the amount of the *o*-isomer sharply decreases.

(19) Y. Yamase and R. Goto, *J. Chem. Soc. Japan*, **81**, 1906 (1960); *Chem. Abstr.*, **56**, 3397 (1962).

Aluminum chloride-catalyzed acetylation of toluene with ketene gave an isomer distribution of 1.4% *o*-, 1.9% *m*-, and 96.7% *p*-methylacetophenone. Thus complexing of the carbonyl oxygen atom must in this case provide also a bulky acetylating agent.

Concerning the isomer distributions obtained in acetylation of toluene, in excess under heterogeneous conditions, it is believed that the methylacetophenone isomer distributions were obtained under reaction conditions which practically exclude isomerization. This belief is based on observations[20] that isomeric methylacetophenones were not isomerized by aluminum chloride, even under forcing conditions (elevated reaction temperatures and excess of catalyst, under prolonged heating) where secondary condensations affecting the acetyl group already take place. As acetophenones first complex with aluminum chloride (or related acidic halides) on the carbonyl oxygen atom, there results a strongly deactivating, positively charged group on the aromatic ring, which makes ring protonation, necessary for any isomerization, highly improbable. It is, however, not entirely excluded that some isomerization might occur concurrently with acetylation, if the reaction proceeds through an activated state corresponding in nature to a σ-complex.

The relative reactivity of alkylbenzenes was investigated in competitive acetylations with benzene. Tables VI and VII show the results of the aluminum chloride-catalyzed competitive acetylation of benzene and alkylbenzenes with acetyl chloride and bromide in homogeneous nitromethane solutions at 25°.

The similarity of the results obtained with acetyl chloride and bromide indicate that the effect of the difference of halogen in the acyl halide is negligible both on relative rates and isomer distributions. The close similarity of results obtained in heterogeneous reactions with those obtained in homogeneous nitromethane solution further indicate that in all cases similar acetylating agents must be formed. The generally high

(20) G. A. Olah and M. W. Meyer, unpublished observations.

TABLE VI

COMPETITIVE ALUMINUM CHLORIDE-CATALYZED ACETYLATION OF BENZENE AND ALKYLBENZENES WITH ACETYL CHLORIDE IN NITROMETHANE SOLUTION AT 25°

Aromatic hydrocarbon	$k_{Ar}:k_{benzene}$	Alkylacetophenone, % ortho	meta	para
Benzene	1.0			
Toluene	134	1.2	1.3	97.5
Ethylbenzene	126	0.4	0.8	98.8
Isopropylbenzene	82.6		3.5	96.5
t-Butylbenzene	83.8		2.9	97.1
o-Xylene	1365	100% 3,4-dimethylacetophenone		
m-Xylene	887	100% 2,4-dimethylacetophenone		
p-Xylene	22	100% 2,5-dimethylacetophenone		
Mesitylene	2250	100% 2,4,6-trimethylacetophenone		

TABLE VII

COMPETITIVE ALUMINUM BROMIDE-CATALYZED ACETYLATION OF BENZENE AND METHYLBENZENES WITH ACETYL BROMIDE IN NITROMETHANE SOLUTION AT 25°

Aromatic	$k_{Ar}:k_{benzene}$	Isomer distribution, % ortho	meta	para
Benzene	1.0			
Toluene	136	0.8	1.5	97.7
o-Xylene	756	100% 3,4-dimethylacetophenone		
m-Xylene	436	100% 2,4-dimethylacetophenone		
p-Xylene	23.3	100% 2,5-dimethylacetophenone		
Mesitylene	1393	100% 2,4,6-trimethylacetophenone		

stability of the acetyl halide–catalyst complexes can account for this postulate. The common acetylating agent must be of substantial bulkiness, as shown by steric effects inhibiting substitution *ortho* to the methyl group in toluene. This is the case even in solutions, which indicates that the complex is either the donor–acceptor complex or the solvated ion-pair with very little, if any, ionization to the free CH_3CO^+ ion.

That the bulkiness of the acetylating agent causing steric hindrance *ortho* to a methyl group is by no means the only factor influencing acetylations in these positions is clearly demonstrated by comparing the data for acetylation of xylenes and mesitylene. *p*-Xylene generally shows only a moderately increased reactivity over benzene (19–23), which could be explained on steric grounds. *o*-Xylene shows much higher substrate selectivity since acetylation takes place predominantly in the nonhindered 4-position. However, this concept is difficult to apply to *m*-xylene and mesitylene, where acetylation must take place *ortho* to one or two methyl groups, respectively. In spite of the expected substantial steric effect prohibiting acetylation, *m*-xylene and mesitylene are acetylated with great ease and high substrate selectivity, owing to the combined effect of the methyl groups.

The competitive aluminum chloride-catalyzed acetylation of benzene and alkylbenzenes with acetic anhydride in nitromethane solution at 25° was investigated under conditions similar to those used in acetylations with acetyl halides. The data obtained are summarized in Table VIII.

TABLE VIII

COMPETITIVE $AlCl_3 \cdot CH_3NO_2$-CATALYZED ACETYLATION OF BENZENE AND METHYLBENZENES WITH ACETIC ANHYDRIDE IN NITROMETHANE SOLUTION AT 25°

Aromatic	$k_{Ar}:k_{benzene}$	Methylacetophenone, % ortho	meta	para
Benzene	1.0			
Toluene	128	1.3	1.0	97.6
o-Xylene	1464	100% 3,4-dimethylacetophenone		
m-Xylene	556	100% 2,4-dimethylacetophenone		
p-Xylene	25	100% 2,5-dimethylacetophenone		
Mesitylene	1012	100% 2,4,6-trimethylacetophenone		

Results of the competitive acetylation of benzene and halobenzenes by the aluminum chloride-catalyzed acetylation with acetyl chloride and acetic anhydride in nitromethane solution are shown in Table IX.

TABLE IX

ALUMINUM CHLORIDE-CATALYZED ACETYLATION OF BENZENE AND HALOBENZENES WITH ACETYL CHLORIDE AND ACETIC ANHYDRIDE IN NITROMETHANE SOLUTION AT 25°

Aromatic	Acetyl chloride $k_{Ar}:k_{benzene}$	Acetic anhydride $k_{Ar}:k_{benzene}$
Benzene	1.0	1.0
Fluoro-	0.46	0.48
Chloro-	.03	.03
Bromo-	.01	.02
Iodo-	.02	.03

Whereas chlorobenzene and bromobenzene gave relative reactivities similar to those reported by Brown and Marino, fluorobenzene gave substantially higher reactivity. The only detectable isomers with the gas–liquid chromatographic method used (for details see Experimental part) were the *p*-isomers; thus, even if minor amounts of *m*- or *o*-haloacetophenones could not entirely be excluded, their amount must have been less than 0.5%.

All the investigated competitive acetylations were found to be first order in aromatics, based on concentration variation of the competing aromatics.

In homogeneous nitromethane solutions acetylation with acetic anhydride and acetyl chloride, bromide or fluoride gave practically identical results. Thus these results suggest that in solution there is little difference in the nature of the acetylating agent starting either from acetyl halides or acetic anhydride. This suggestion was substantiated by high resolution nuclear magnetic resonance investigations of the acetyl chloride–aluminum chloride and acetic anhydride–aluminum chloride systems in nitromethane solution. In both cases, as shown schematically in Fig. 1 (in p.p.m. from TMS as internal reference), there is evidence only of the donor–acceptor complexes I′ causing a moderate shift of the proton peaks to less shielding, and not of the methyloxocarbonium ion (CH_3CO^+) known from our previous investigations.[21] The chemical shift of the oxocarbonium ion is at least twice that of the donor–acceptor complexes.

The nuclear magnetic proton resonance investigations, however, show only that there is no methyloxocarbonium ion in the investigated systems in concen-

(21) G. A. Olah, S. J. Kuhn, W. S. Tolgyesi, and E. B. Baker, *J. Am. Chem. Soc.*, **84**, 2733 (1962).

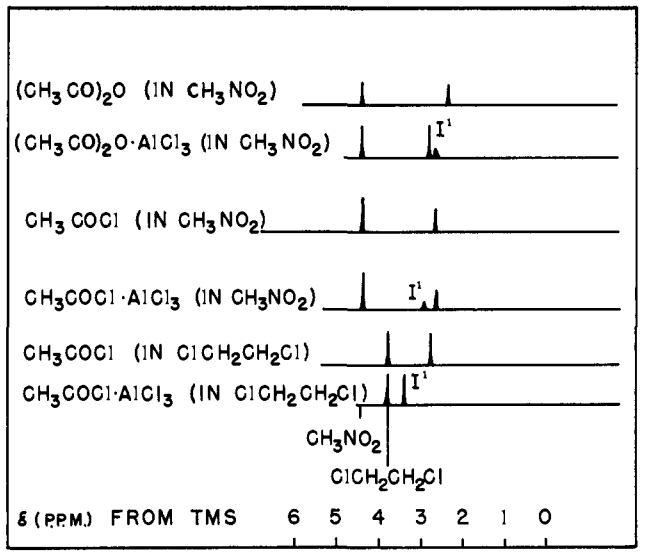

Fig. 1.—H^1 magnetic resonance spectra of the acetyl chloride–aluminum chloride and acetic anhydride–aluminum chloride systems in nitromethane and ethylene chloride solutions at 60 Mc.

trations needed to be detected by the method (thus concentrations larger than 2%). This does not exclude the possibility of a small, subspectroscopic amount of the oxocarbonium ion being present in equilibrium in the solutions and consequently contributing to the acetylations.

Attempts to investigate the acetyl chloride–aluminum chloride and acetic anhydride–aluminum chloride systems in nitromethane solutions by infrared spectroscopy were hindered by solvent interference and the relatively low solubility of the complexes.

Experimental

Benzene and alkylbenzenes were used in purities comparable to those reported in previous papers of this series. Nitromethane was purified as described.[22] Acetyl chloride, bromide, and acetic anhydride were commercially available chemicals of highest purity, redistilled before used. Acetyl fluoride was prepared as reported.[23] Acid catalysts used were comparable in purity to those used previously.[24]

Substituted acetophenone isomers were all known from the literature and were available in this laboratory either from commercial sources or preparation by standard methods. Their purity was checked by g.l.c. analysis and infrared spectroscopy. When necessary, they were purified by preparative scale gas chromatography using a Wilkens Aerograph Autoprep Model A-700 instrument with polypropylene glycol column.

Acetylation of Toluene with Acetyl Halides (Excess Toluene as Solvent). (a) **Reactions with Acetyl Fluoride.**—To 0.2 mole of toluene in a small three-necked reaction flask, kept with ice–water at around 0°, and equipped with reflux condenser (connected through a drying tube to a hydrogen halide absorber), thermometer, and dropping funnel (jacketed and cooled at 0°) 0.04 mole of the appropriate catalyst was added. While the reaction flask was kept with an ice bath at around 0–5°, 0.04 mole of acetyl fluoride was added to the stirred reaction mixture (magnetic stirrer). The ice bath was then removed, the reaction mixture was allowed to warm up to room temperature, and was stirred in a constant temperature bath at 25° for 5 hr. After washing with cold water, the organic layer was separated, dried ($MgSO_4$), and analyzed for the isomer distribution of methylacetophenones by gas chromatography (see following section). In experiments where volatile catalysts were used (BF_3) the acetyl fluoride was first dissolved in toluene and the gaseous catalysts then introduced.

(b) **Reaction with Acetyl Chloride and Bromide.**—Reactions were carried out similarly to those described in (a), but the reaction mixtures were, after mixing, refluxed for 2 hr. The work-up and analyses of the mixture were similar to that described above. Reactions with I_2 as catalysts were slow and needed to be refluxed for 12 hr.

Acetylation of Toluene with Acetic Anhydride (Excess Toluene as Solvent).—To 0.02 mole of toluene in a three-necked reaction flask equipped with reflux condenser, thermometer, and dropping funnel 0.04 mole of the appropriate catalyst was added. While the reaction flask was cooled, 0.04 mole of acetic anhydride was dropped into the reaction mixture, which was then allowed to warm up and refluxed for 2 hr. The work-up of the mixture and the analyses were similar to that previously employed. Again the I_2-catalyzed reaction was slow and it was necessary in this case to reflux the mixture for 12 hr.

Competitive Acetylation of Benzene and Alkylbenzenes in CH_3NO_2 Solution.—To a solution of 0.05 mole of $AlCl_3$ ($AlBr_3$) dissolved in 50 g. of CH_3NO_2 was added 0.25 mole each of benzene and alkylbenzene in a three-necked reaction flask equipped with a thermometer, dropping funnel, and reflux condenser connected through a drying tube to a hydrogen halide absorber. The reaction flask was placed in a constant temperature bath at 25 ± 0.5°. With vigorous stirring (magnetic stirrer), 0.05 mole of acetyl chloride (acetyl bromide) or acetic anhydride dissolved in 30 g. of CH_3NO_2 was added dropwise over a period of 10 min. The reaction was allowed to proceed an additional 10 min. The solution was then washed with water, three times with approximately 200 ml. of a 5% sodium hydroxide solution (to remove CH_3NO_2), and again with water. The organic layer was separated, dried over $CaCl_2$, and analyzed by gas–liquid chromatography. The data obtained are summarized in Tables VI–VIII.

Gas–Liquid Chromatographic Analyses.—The analyses of all acetylations were carried out by gas-liquid chromatography on a Perkin–Elmer Model 154-C vapor fractometer equipped with a thermistor thermal conductivity cell detector. The 4-m. long, 0.25-in. stainless steel column was packed with polypropylene glycol (Ucon LB 550-X) on diatomaceous earth (30% w./w.). The column temperature was 180°, with dry hydrogen carrier gas flow rate at approximately 60 ml. per minute. Peak areas were obtained by the use of the electronic printing integrator.

Relative response data were obtained by running known quantities of acetophenone and alkylacetophenones in benzene in the approximate amounts in which they appeared in the experimental samples. Characteristic retention times of acetophenone and alkylacetophenones are shown in Table X.

TABLE X

RETENTION TIMES OF ACETOPHENONE AND ALKYLACETOPHENONES AT 180°

Compound	Time, min.	Compound	Time, min.
Acetophenone	12.5	Acetophenone	
o-Methyl-	15.4	*o*-Isopropyl-	18
m-Methyl-	19.2	*m*-Isopropyl-	19.5
p-Methyl-	20.5	*p*-Isopropyl-	32.5
3,4-Dimethyl-	37	*m*-*t*-Butyl-	34
2,4-Dimethyl-	25	*p*-*t*-Butyl-	43
2,5-Dimethyl-	23.5	*p*-Fluoro-	12
2,4,6-Trimethyl-	31	*p*-Chloro-	29
o-Ethyl-	16.5	*p*-Bromo-	35
m-Ethyl-	21		
p-Ethyl-	23		

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