TABLE IV

TYPICAL RATE DATA FOR THE REACTION OF BENZOYL CHLORIDE–ALUMINUM CHLORIDE WITH BENZENE AND WITH *p*-XYLENE IN ETHYLENE CHLORIDE AT 25.0°

Time, min.	NaOH, ml.	Reaction, %	$\frac{x}{a - x}$	Rate constant[c] $k_2 \times 10^3$, l. mole^{-1} sec.$^{-1}$
		A. Benzene[a]		
0	20.55[d]			
14.0	20.50	5.0		
1660	16.10	21.65	0.2763	0.00925
2922	13.80	32.85	.4892	.00930
3998	12.32	40.05	.6680	.00930
7194	9.28	54.84	1.214	.00937
11171	6.76	69.10	2.039	.01014
		B. *p*-Xylene[b]		
0	6.85[d]			
60	4.27	37.66	0.604	1.67
127	3.18	53.57	1.154	1.51
167	2.64	61.45	1.594	1.59
248	2.10	69.34	2.262	1.52

[a] Initial concentrations: [$C_6H_5COCl \cdot AlCl_3$], 0.300 *M*; [C_6H_6], 0.300 *M*. [b] Initial concentrations: [$C_6H_5COCl \cdot AlCl_3$], 0.100 *M*; [$1,4(CH_3)_2C_6H_4$], 0.100 *M*. [c] Graphical determination of the constant yields 0.00930 × 10^{-3} for benzene, 1.56 × 10^{-3} for *p*-xylene. [d] Calcd.

minum chloride were purified in the manner previously described.[5] The hydrocarbons were samples previously available[4] which had been demonstrated to possess purities of 99.5% or greater through cooling curve determinations.

Techniques.—The procedures followed were those described earlier.[5] In the case of benzene, the reaction was very slow and sealed ampules were used instead of the usual nitrogen-protected reaction flask.

To test our techniques for preparing and handling the solutions, a kinetic run was made with toluene (0.300 *M*) in large excess over the benzoyl chloride–aluminum chloride complex, and the reaction was followed to completion. As shown in Table III, the reaction proceeded to 99% utilization of benzoyl chloride, and this was considered to represent a confirmation of the adequacy of our methods.

Typical rate data are summarized in Table IV.

Benzoylation of *p*-Xylene.—*p*-Xylene (Phillips, 99%) was benzoylated on a 0.7-mole scale. The reaction product, 2,5-dimethylbenzophenone, m.p. of material recrystallized from methanol 36.0–36.5°, was obtained in a yield of 79%.[12]

A reaction mixture in ethylene chloride, 1.00 *M* in complex and *p*-xylene, was allowed to stand for 105 minutes. An aliquot of the reaction mixture was removed for the usual titration, indicating 50.4% reaction, and the remainder was poured into sodium hydroxide and crushed ice. There was isolated 2.33 g. of crude 2,5-dimethylbenzophenone, a yield of 94%. Infrared indicated a purity of at least 94%. From the alkaline phase, 1.30 g. of benzoic acid was isolated, 92% of the calculated quantity.

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(12) K. Elbs and E. Larson, *Ber.*, **17**, 2847 (1884), report m.p. 36°.

LAFAYETTE, IND.

[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY]

The Relative Rate and Isomer Distribution in the Acetylation of Benzene and Toluene in Ethylene Dichloride under the Influence of Aluminum Chloride[1,2]

BY HERBERT C. BROWN, GIANLORENZO MARINO[3] AND LEON M. STOCK[4,5]

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The aluminum chloride-catalyzed acetylation of benzene and toluene has been examined in ethylene dichloride solution. The rate constants (× 10^3) in the acetylation of benzene have been determined at 0 and 25° as 0.339 ± 0.015 and 2.65 ± 0.13 l. mole^{-1} sec.$^{-1}$, respectively. The relative rate of acetylation of toluene to benzene is 128/1.00. The isomer distribution under these conditions is established as *o*- 1.17 ± 0.23, *m*- 1.25 ± 0.25 and *p*-methylacetophenone 97.6 ± 0.3 mole per cent. These data provide the partial rate factors for the acetylation reaction, o_f 4.5, m_f 4.8 and p_f 749. The relative rates are very similar to those established for the corresponding benzoylation reaction and adhere to the Selectivity Relationship governing electrophilic substitution in toluene. The steric requirements of the acetylation reagent appear to be larger than those of the benzoylation reagent as evidenced from the reduced rate in the *ortho* position in the former reaction. This fact is attributed to the non-coplanar conformation of the methyl group in the acetylating species.

The Friedel–Crafts acetylation reaction has been reported to provide only a small difference in reactivity between toluene and benzene. Ogata and Oda[6] observed a relative rate of 8.35, and McDuffie and Dougherty[7] reported this rate ratio to be 13.3 in a competitive reaction employing acetyl chloride, aluminum chloride and the hydrocarbons as solvent at 10°. On the basis of these observations and the Selectivity Relationship,[8-10] it would be predicted that significant concentrations of the *meta* isomeride would be produced in the acetylation. However, this isomer has not been detected in the products of the reaction,[11] although it has been reported that the reaction with *t*-butylbenzene yields 1.8% *m*-*t*-butylacetophenone.[12] These conflicting observations promoted a thorough examination of the acylation process utilizing the experimentally advantageous benzoylation reaction in nitrobenzene,[11] benzoyl chloride[13,14] and ethylene dichloride.[15,16] In each solvent the benzoylation reaction is highly selective, the relative rate, toluene to benzene, is large (110 to 151), and the amount of the *meta* isomer produced is small (1.1 to 1.45%).

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(1) Directive Effects in Aromatic Substitution. XXXIII.

(2) Based in part upon a thesis submitted by Leon M. Stock in partial fulfillment of the requirements for the Ph.D. degree.

(3) Post-doctorate research associate, 1957–1959, on project no. AT(11-1)-170 supported by the Atomic Energy Commission.

(4) Monsanto Chemical Co. Fellow at Purdue University, 1957–1958.

(5) This research supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society.

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

(7) H. F. McDuffie and G. Dougherty, THIS JOURNAL, **64**, 297 (1942).

(8) H. C. Brown and K. L. Nelson, *ibid.*, **75**, 6292 (1953).

(9) H. C. Brown and C. W. McGary, *ibid.*, **77**, 2300 (1955).

(10) H. C. Brown and C. R. Smoot, *ibid.*, **78**, 6255 (1956).

(11) For a discussion of this point and other pertinent references see H. C. Brown and H. L. Young, *J. Org. Chem.*, **22**, 719, 723 (1957).

(12) J. C. Butler, L. L. Ferstandig and R. D. Clark, THIS JOURNAL, **76**, 1906 (1954).

(13) H. C. Brown and F. R. Jensen, *ibid.*, **80**, 2291, 2296 (1958).

(14) F. R. Jensen and H. C. Brown, *ibid.*, **80**, 3039 (1958).

(15) F. R. Jensen, G. Marino and H. C. Brown, *ibid.*, **81**, 3303 (1959).

(16) H. C. Brown and G. Marino, *ibid.*, **81**, 3308 (1959).

In each case the results conform to the Selectivity Relationship.

These studies revealed, however, that the benzoylation reaction has several unusual features, for while the absolute reaction velocity depends on the metal halide employed as catalyst, the relative rate and isomer distribution are essentially unaltered.[14] An investigation of the analogous Friedel–Crafts sulfonylation reaction of toluene and benzene with benzenesulfonyl chloride indicated that this process was relatively non-selective and closely resembled the alkylation reaction in possessing a low relative rate and yielding 8.7% *meta* isomer.[17] This reaction was also demonstrated to fit the Selectivity Relationship.

Benzoylation was previously selected as a model for the acylation reaction since it possessed major experimental advantages over the corresponding acetylation reaction. However, in view of the unique character of the benzoylation process when contrasted with alkylation and sulfonylation reactions, it appeared necessary to overcome the experimental difficulties and to examine the acetylation of toluene and benzene. In order to provide a direct comparison of the two acylations, the acetylation has been studied under the same conditions employed in one of the benzoylation studies. Since benzoyl chloride[13,14] could not be employed as the solvent for this reaction and since it appeared desirable to avoid the kinetic difficulties associated with nitrobenzene,[11] ethylene dichloride[14] was selected and the acetylation reaction was examined in this reaction medium.

Results

It is well known that aluminum chloride is insoluble in non-polar solvents such as ethylene dichloride. However, the addition of acetyl chloride to the heterogeneous mixture of the metal halide and solvent provided a homogeneous solution. These homogeneous solutions were prepared at 0° over a 3-hour interval and freshly prepared before each kinetic experiment.

The kinetics of the benzoylation reaction have been studied both through the actual isolation of the products[13] and the employment of volumetric techniques based on the titration of residual benzoyl halide.[11,15] The product isolation procedure was denied to us due to the greater volatility of the acetophenones as compared to the benzophenones. The instability of acetyl chloride in aqueous solutions prevented the application of the convenient extraction and titration procedure previously utilized for benzoylation. Techniques based on the measurement of hydrogen chloride produced in the reaction were not considered since they had proved ineffective in earlier attempts.[13] Gas–liquid partition chromatography[18] appeared to provide a simple solution to these problems. This technique was employed successfully not only for the kinetic measurements, but also provided the relative rate data and the isomer distribution.

The rate of acetylation of benzene was followed by the application of 1,2,4-trichlorobenzene as an internal standard in the solvent. Each aliquot was treated to provide a sample for chromatographic analysis, which indicated the increase in concentration of acetophenone with respect to the unchanged chlorocarbon concentration. The results of the kinetic study are presented in Table I, and the reaction parameters in Table II.

TABLE I

SPECIFIC SECOND-ORDER RATE CONSTANTS FOR THE ALUMINUM CHLORIDE-CATALYZED ACETYLATION OF BENZENE IN ETHYLENE DICHLORIDE AT 25°

Reagents, *M*				Rate constant $k_2 \times 10^3$, l. mole^{-1} sec.$^{-1}$
[C_6H_6]	[$CH_3COCl \cdot AlCl_3$]	[CH_3COCl]	[1,2,4-$C_6H_3Cl_3$]	
0.120	0.200	0.020	0.060	2.47
.200	.200	.020	.100	2.60
.200	.200	.020	.100	2.50
.400	.200	.020	.200	2.54
.200	.200	.040	.100	3.31[a]
.200	.200	.100	.100	2.84
.200	.200	.200	.100	2.68
.200	.200	.200	.100	2.91
.200	.200	.020	.100	0.399[b]
			Mean value	2.65 ± 0.13

[a] Discounted due to slight decomposition of complex. [b] At 0°.

TABLE II

RATE CONSTANTS AND DERIVED DATA FOR THE ALUMINUM CHLORIDE-CATALYZED ACETYLATION OF BENZENE IN ETHYLENE DICHLORIDE

Temp., °C.	0.0	25.0
Rate constant, $10^3 k_2$, l. mole^{-1} sec.$^{-1}$	0.339 ± 0.015	2.65 ± 0.13
No. of observations	1	7
Energy of activation, E_a	13.3 kcal. mole^{-1}	
Log *A*	7.33	
Enthalpy of activation, $\Delta H^{\ddagger}$	12.7 kcal. mole^{-1}	
Entropy of activation, $\Delta S^{\ddagger}$	−27.6 cal. deg.$^{-}$	

The rate constants obtained indicate that the reaction obeys simple second-order kinetics, first order in benzene and first order in the acetyl chloride–aluminum chloride complex, through any single experiment. This rate constant is independent of the initial concentration of the aromatic and any added excess acetyl chloride. The kinetic form indicated by these results is quite similar to that observed for the benzoylation reaction in the same solvent.[15] Indeed, the entropy of activation for the acetylation of benzene is the same as that observed for benzoylation in either ethylene dichloride[15] or benzoyl chloride.[13] The only significant difference in the reactions is that acetylation is some 500-fold more rapid.

The relative rate, toluene to benzene, was established by a competitive procedure employing gas chromatography for the determination of the product ratio, Table III. These observations reveal that the relative rate is very reproducible as measured by this technique. A minor change in the relative rate was observed when the concentration of benzene was increased to 2 *M*. Since the isomer distribution was determined in the absence of benzene, the measurement was not utilized in the calculation of the mean relative rate value. The resultant relative rate, toluene to

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[17] F. R. Jensen and H. C. Brown, THIS JOURNAL, **80**, 4046 (1958).

[18] A. T. James and A. J. P. Martin, *Analyst*, **77**, 915 (1952).

benzene, is 128 ± 4. This result is within experimental error of the value observed in the corresponding benzoylation,[16] 117 ± 3. These relative rate data are vastly different from the observations of earlier studies,[6,7] 8.35 and 13.3. Although these experiments were carried out under different conditions, such a great difference in rate would not be anticipated. However, this rate ratio, 13.3, was quite reproducible.[7] Since the conditions employed by these workers would lead to a heterogeneous system, the low relative rate data suggest that the reaction may have taken place in the highly polar catalyst phase.

TABLE III

RELATIVE RATE OF THE ALUMINUM CHLORIDE-CATALYZED ACETYLATION OF TOLUENE AND BENZENE IN ETHYLENE DICHLORIDE AT 25°

Reactants, *M*			
[$C_6H_5CH_3$]	[C_6H_6]	[$CH_3COCl.AlCl_3$]	Relative rate[a]
0.100	0.300	0.050	125
.100	.600	.050	128
.200	.900	.050	131
.200	2.00	.100	144[b]

[a] Benzene taken as 1.00. [b] Excluded from mean because of high concentration of aromatic.

The isomer distribution, as noted above, was also established by vapor phase chromatography. This technique presented some experimental difficulties (described in the Experimental Part). The composition of the product, methylacetophenones, was determined by the chromatographic procedure utilizing two different stationary liquid phases employed independently. These observations obtained in each examination are presented in Table IV. The isomer distribution is in accord with the previous observations concerning high yields and predominant substitution in the *para*-position.[19,20] The low concentrations of the *ortho* and *meta* isomers and the fact that their boiling points are nearly the same as that of the *para* isomer provides the explanation for the absence of reports concerning the detection of these isomers in the acetylation of toluene.

TABLE IV

ISOMER DISTRIBUTION IN THE ALUMINUM CHLORIDE-CATALYZED ACETYLATION OF TOLUENE IN ETHYLENE DICHLORIDE AT 25°

	Methylacetophenones, mole %		
Experiment	*o*-	*m*-	*p*-
A		1.21[a]	
B	1.10[b]	1.30[a]	97.6
C	0.89[b]	1.22[c]	97.9
D	1.52[b]	1.28[c]	97.2
Normalized value[e]	1.17 ± 0.23	1.25 ± 0.25[d]	97.6

[a] Liquid phase for analysis: tricresyl phosphate. [b] Liquid phase for analysis: dioctyl phthalate. [c] Liquid phase for analysis: polymeric BGA (polyadipate), from Rubber Corporation of America. [d] Error assigned on the basis of uncertainty in evaluation of area; see Experimental Part. [e] These values have been confirmed using the so-called bracketing technique.

Discussion

The 1:1 complex between acetyl chloride and aluminum chloride has been known for a considerable time.[21,22] This complex has not been investigated in ethylene dichloride. It is apparent that acetyl chloride and aluminum chloride interact in this solvent, since the metal halide is insoluble and the system slowly becomes homogeneous after the addition of acetyl chloride. This solubility behavior may be most reasonably attributed to the formation of a 1:1 complex.

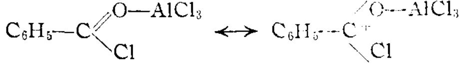
The kinetic results reveal that the acetylation reaction is second order

$$\text{rate} = k_2[\text{ArH}][\text{CH}_3\text{COCl}\cdot\text{AlCl}_3]$$

It is well established that one mole of the metal halide catalyst is consumed for each mole of ketone produced in accordance with the equation.

$$\text{ArH} + \text{CH}_3\text{COCl}\cdot\text{AlCl}_3 \longrightarrow \text{ArCOCH}_3\cdot\text{AlCl}_3 + \text{HCl}$$

Much of the physical evidence for the benzoyl chloride complex favors a structure wherein the aluminum chloride is complexed with oxygen,[23] I. However, recently it has been reported that



I

the corresponding acetyl chloride derivative has the ionized structure[24] II

$$[\text{CH}_3\text{—}\overset{+}{\text{C}}\text{=O} \longleftrightarrow \text{CH}_3\text{—C}\equiv\overset{+}{\text{O}}]\text{AlCl}_4^-$$

II

Furthermore, the acetylonium ion has been detected in sulfuric acid and nitromethane.[25,26] These solutions both reveal Friedel–Crafts activity.

The kinetic evidence obtained in this study does not distinguish between possible mechanisms involving the oxonium structure, separated acylonium ions or acylonium ion pairs.[13,27] The relative rate, toluene to benzene, the entropy of activation, isomer distribution and partial rate factors for the aluminum chloride-catalyzed benzoylation and acetylation, Table V, do establish that the reactions are very similar. The only kinetic difference in these reactions is that the acetylation is 500-fold more rapid than benzoylation. Such a change in absolute rate with unchanging partial rate factors has been noted previously in the benzoylation reaction under the influence of gallium chloride.[14] This observation has been interpreted in terms of the similar character of the intermediate in the reaction.[14] On this basis, the acetylonium and benzylonium ion-pairs or oxonium complexes, which serve as intermediates, must

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(19) C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1941, p. 214.

(20) E. Berliner in R. Adams, "Organic Reactions," Vol. 5, John Wiley and Sons, Inc., New York, N. Y., 1945, Chapter V.

(21) G. Perrier, *Ber.*, **33**, 815 (1900).

(22) M. J. Boeseken, *Rec. trav. chim.*, **20**, 102 (1901).

(23) See ref. 13 for a summary of the information regarding the structure of the complex.

(24) B. P. Susz and J. J. Wuhrmann, *Helv. Chim. Acta*, **40**, 971 (1957).

(25) R. J. Gillespie, *J. Chem. Soc.*, 2997 (1950).

(26) H. Burton and P. F. G. Praill, *ibid.*, 2034 (1950); 529 (1951).

(27) For a critical discussion of possible mechanisms for the acylation reaction, see P. H. Gore, *Chemistry & Industry*, 1385 (1951); *Chem. Revs.*, **55**, 229 (1955).

TABLE V

KINETIC AND RELATIVE RATE DATA FOR ALUMINUM CHLORIDE ACYLATION IN SEVERAL SOLVENTS

	Benzoylation			Acetylation
	In $C_6H_5NO_2$[11]	In C_6H_5COCl[13]	In $C_2H_4Cl_2$[15,18]	In $C_2H_4Cl_2$
Rate constant for benzene at 25° $k_2 \times 10^5$, l. mole^{-1} sec.$^{-1}$		4.95	0.928[a] 0.619[b]	265[c]
$\Delta S^{\ddagger}$, cal. deg.$^{-1}$		−27.2[d]	−28.1[e]	−27.6[d]
Relative rate, k_T/k_B	151	110	117	128
Isomer distribution				
% *ortho*	7.2	9.3	8.9	1.17
% *meta*-	1.1	1.45	1.4[f]	1.26
% *para*	91.7	89.3	89.7[g]	97.6
o_f	32.6	30.7	32.6[g]	4.5
m_f	5.0	4.8	4.9[g]	4.8
p_f	831	589	626	749

[a] Concentration of complex: 0.300 *M*; [b] 0.100 *M*; [c] 0.200 *M*. [d] Benzene. [e] Toluene. [f] Assumed. [g] Based on k_T/K_B 117; *o*-, 9.3%; *m*-, 1.4%; *p*-, 89.3%.

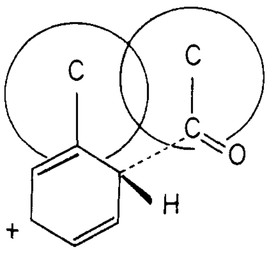
also be quite similar in their electronic demand on the aromatic nucleus and its substituents.

The most striking difference in the two reactions is the relative reactivity at the *ortho* position. The electrophile in the acetylation reaction appears to possess somewhat greater steric requirements than those of the benzoylation intermediate, as indicated by the o_f/p_f ratios, 0.0060 and 0.052, respectively.

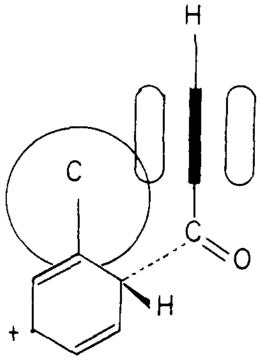
The preferred concept of the transition state for electrophilic substitution in the benzene nucleus involves the approach of the electrophile from above (or below) the plane of the benzene molecule[28,29] (III, IV). The increased steric requirements of the acetylonium species may reasonably be attributed to the change from the fully coplanar phenyl substituent with van der Waals radius of 1.7 Å.,[30] to the tetrahedral methyl group, with van der Waals radius of 2.0 Å.[30]

The isomer distribution and the relative rate, toluene to benzene, provide the partial rate factors for the acetylation reaction. These values, Table V, reveal that acetylation, like benzoylation, is a highly selective reaction. Furthermore, an excellent fit to the Selectivity Relationship[9] is obtained as log p_f/log m_f is 4.22, while for 47 other electrophilic reactions this same ratio is 4.04 ± 0.55.[31]

In the original proposal of the Selectivity Relationship,[8] three reactions (chlorination, nitration and isopropylation) conformed to the proposed correlation, and three other reactions (chloromethylation, mercuration and acetylation) did not.[8] These constituted all the substitution reactions of toluene for which relative rate and isomer distribution data were available. Reinvestigation of chloromethylation[8] and mercuration[9] had pre-



III



IV

viously eliminated the discrepancies in the data which were responsible for these apparent deviations from the correlation. With the present study of the acetylation reaction, the last of the original discrepancies has now been eliminated.

Experimental Part

Materials.—The aromatic hydrocarbons utilized in these experiments were Phillips Research Grade hydrocarbons, having purities greater than 99.5 mole %. Acetyl chloride was purified by two rectifications under nitrogen; b.p. 51.5° at 740 mm. Initial experiments revealed that identical results were obtained when the acid chloride was first purified by treatment with aluminum chloride and toluene and subsequently distilled. Aluminum chloride, which had been purified by sublimation, was available from a previous study.[15] Ethylene dichloride was first washed with sulfuric acid, water and then allowed to remain over sodium hydroxide for two days.[32] It was subsequently filtered and fractionated from calcium hydride; b.p. 83.7° at 750 mm., n^{20}D 1.4446. The materials employed as standards for the vapor phase chromatographic experiments were highly purified ketones which were free of contamination. The *o*- and *m*-methylacetophenones were samples generously provided by the E. I. du Pont de Nemours Co. The *para* isomer was obtained in a pure state by the preparation, recrystallization twice from ethanol and subsequent acid hydrolysis[33] of the semicarbazone. Earlier attempts to remove the *meta* ketone from the commercial material by rectification through an efficient column failed.

Kinetic Measurements.—A solution of the complex between aluminum chloride and acetyl chloride in ethylene dichloride was prepared by dissolving aluminum chloride in a solution of acetyl chloride in ethylene dichloride containing a known quantity of 1,2,4-trichlorobenzene. The solution was effected by magnetic stirring at 0° over a 3-hour interval. Another solution containing a known concentration of benzene in ethylene dichloride was prepared. Appropriate volumes of these two solutions were mixed and the reaction initiated at 25°. The reaction was followed by the withdrawal of 40-ml. aliquots which were quenched in ice-water; the layers were then separated. The organic layer was washed with water and dried over sodium sulfate. The solution was filtered and the excess ethylene dichloride removed by distillation. The residue was analyzed by vapor phase chromatography employing a Perkin–Elmer model 154B Vapor Fractometer operated with a 2-m. column packed with dioctyl phthalate on Celite using a flow rate of 50 ml. of helium per minute at 170°. The peaks were easily resolved. The areas were measured with a planimeter and the percentage weight of 1,2,4-trichlorobenzene and acetophenone determined from an equilibration curve based on the analysis of known mixtures. The data for a typical reaction are presented in Table VI and the results of the kinetic investigations presented in Table I.

Competitive Relative Rate Determination.—The reagent solutions containing the acetylating reagent and toluene and

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(28) For a discussion of this view and its basis, together with pertinent literature references, see K. L. Nelson and H. C. Brown, Chapter 56 in "The Chemistry of Petroleum Hydrocarbons," ed. by B. T. Brooks, *et al.*, Vol. III, Reinhold Publishing Corp., New York, N. Y., 1955.

(29) E. J. Corey and C. K. Sauers, THIS JOURNAL, **79**, 249 (1957).

(30) J. M. Robertson, "Determination of Organic Structures by Physical Methods," ed., E. A. Braude and F. C. Nachod, Academic Press, Inc., New York, N. Y., 1955, p. 494.

(31) See Fig. 1, ref. 16. For a survey of the electrophilic substitution reactions of toluene, see L. M. Stock and H. C. Brown, THIS JOURNAL, **81**, 3323 (1959).

(32) F. R. Jensen, *ibid.*, **79**, 1226 (1957).

(33) L. I. Smith and J. Nichols, *J. Org. Chem.*, **6**, 489 (1941).

TABLE VI

RATE DATA FOR ALUMINUM CHLORIDE-CATALYZED ACETYLATION OF BENZENE IN ETHYLENE DICHLORIDE AT 0°

Time, min.	Reaction, %	Rate constant, $k_2 \times 10^3$, l. mole^{-1} sec.$^{-1}$
47	15.25	0.319
91	28.28	.370
191	44.35	.347
254	50.80	.339
379	59.35	.321

$[C_6H_6] = [CH_3COCl \cdot AlCl_3] = 0.200\ M$; $[CH_3COCl] = 0.020\ M$; $[1,2,4\text{-}C_6H_3Cl_3] = 0.100\ M$.

benzene were prepared as previously described; 1,2,4-trichlorobenzene was omitted. The reaction was initiated by mixing the solutions and the reaction was allowed to proceed to completion over a 20-hour interval. The kinetic experiments with benzene at 25° revealed that this reaction was essentially complete in three hours. The products were isolated and analyzed as indicated above. The chromatographic analysis was accomplished by application of the expression[34]

$$\frac{m_i}{W} = \frac{A_i M_i^{1/2}}{\Sigma A_i M_i^{1/2}}$$

(m_i/W) is the weight per cent. of the ith component, A_i is the observed chromatographic area and M_i the molecular weight. This procedure was tested by the analysis of known mixtures containing acetophenone, *o*- and *p*-methylacetophenone (under the conditions of the analysis the *meta* and *para* isomers were not resolved), Table VII. These data were employed to calculate the necessary concentration terms in the expression[35]

$$\frac{\log T/T_0}{\log B/B_0} = \frac{k_T}{k_B}$$

The results are summarized in Table II.

TABLE VII

ANALYSIS OF SYNTHETIC MIXTURES OF KNOWN COMPOSITION

Wt. % known			Wt. % found		
Acetophenone	Methylacetophenone *o*-	Methylacetophenone *p*-	Acetophenone	Methylacetophenone *o*-	Methylacetophenone *p*-
	4.74	95.26		4.20	95.80
	5.48	94.52		6.10	93.90
3.55	4.57	91.88	3.75	4.10	92.15
2.05	4.64	93.31	2.32	4.14	93.54
4.16	4.54	91.30	4.75	4.32	90.34

Isomer Distribution.—The isomer distribution was established for reactions carried out and treated in the manner that has already been described. The isolated materials were subjected to chromatographic analysis. The determination of the *ortho* isomer relative to the *meta* and *para* products was accomplished with relative ease as the peak for the former isomer was readily resolved under the conditions described above. The separation of the *meta* and *para* ketones presented a considerably more difficult problem in that these materials were eluded from the absorption column in similar times. A variety of column packings were investigated in order to obtain more satisfactory resolution. In Table VIII are presented the observed retention times for the *o*-, *m*- and *p*-methylacetophenones under identical operating conditions for which only the liquid phase[36] on Celite has been altered. The maximum resolution was achieved with either tricresyl phosphate or Rubber Corporation of America BGA (a polyadipate). The resolution was improved by a reduction in the sample size, to approximately 0.003 ml., but the large excess of the *para* isomer still slightly overlapped the area for the *meta* ketone. This difficulty was circumvented by the measurement of the rear half area for the *para* ketone and the front half area for the *meta* isomer. The symmetrical nature of the peaks precludes any serious error by this technique. In testing the quantitative determination of the *m*-methylacetophenone, it was observed that known mixtures gave results that were slightly higher than the known *meta* concentration. These results were then utilized for the establishment of an analytical relationship between the known and found concentration of the *meta* isomer. These analyses were carried out employing both tricresyl phosphate and, independently, the polyadipate. The results of the analyses of the products from the acetylation of toluene are identical. The observations obtained with known mixtures and the precise measurement of the small areas evolved leads to an uncertainty of approximately 20%. Accordingly, the error in this determination must be somewhat larger than that indicated by the experimental results and is estimated to be ±0.25 mole per cent.

TABLE VIII

RESOLUTION OBTAINED FOR SYNTHETIC MIXTURES OF METHYLACETOPHENONES

Liquid phase on Celite	Retention time, min. at 170° and 50 ml. min.$^{-1}$ He *o*-	*m*-	*p*-
Silicone grease	7.2	..[a]	9.2
Dow-Corning 6590 silicone fluid	17.4	21.8[b]	24.0
Dow-Corning 703 silicone fluid	9.8	11.7[b]	12.6
Dow-Corning 550 silicone fluid	8.7	10.4[b]	11.2
Dow-Corning F60 silicone fluid	5.6	..[a]	7.2
Propylene glycol adipate polymer	10.5	13.5[b]	15.0
Reoplex 400	11.6	14.8[b]	16.9
RCA BGA (polyadipate)	12.8	16.4	18.2
Tricresyl phosphate[c]	13.9	17.8	20.0

[a] *Meta* and *para* isomers unresolved. [b] *Meta* isomer observed as shoulder on *para* elution peak. [c] At 171° and 55 ml. min.$^{-1}$ He.

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