order rate constant was obtained by dividing the corrected first-order rate by the average aromatic concentration followed by multiplication with a thermal factor consisting of the ratio of the density of acetic acid at 25° to that of the reaction temperature.

Isomer Distribution Measurements.—The reaction mixtures utilized for the isomer distributions were identical in all respects to those employed in the kinetic measurements. To minimize possible complications arising from polymercuration, the aromatic was used in a 10-fold excess over the mercuric acetate present and the reaction was quenched after it had proceeded to approximately 30% completion.

In a typical experiment, 100 ml. of 3.00 *M* *t*-butylbenzene in glacial acetic acid and 200 ml. of 0.150 *M* mercuric acetate in the same solvent were allowed to come to thermal equilibrium with the bath at the desired temperature and then were quickly mixed. When the reaction had reached approximately 30% completion, calculated from the rate constants, the reaction mixture was quickly cooled and quenched in an equal volume of water. Excess unreacted *t*-butylbenzene was removed by aspiration under vacuum at room temperature and the soluble *t*-butylphenylmercuric acetates were converted into the insoluble bromide derivatives by addition of a 2- to 3-fold excess of bromide ion relative to the total mercuric concentration. The bromide derivatives were filtered, dried thoroughly under vacuum, and weighed. The yields of these derivatives were nearly quantitative.

The isomeric *t*-butylbenzenemercuric bromides were suspended in carbon disulfide and converted to the isomeric bromo-*t*-butylbenzenes by careful treatment with bromine. A slight excess of bromine was added, as evidenced by a slight red color in the carbon disulfide solution, and the mixture was then allowed to stand for several hours to ensure complete conversion of the mercuric derivatives. Excess bromine was removed by washing with sodium bisulfite solution followed by water. The carbon disulfide solution was thoroughly dried over calcium hydride and the proportions of the isomeric bromo-*t*-butylbenzenes were determined by infrared analysis. The conversions to the isomeric bromo-*t*-butylbenzenes, as based on the infrared analysis, were essentially quantitative.

Infrared analyses for the isomeric derivatives were generally carried out on solutions that were about 0.3 *M*. The wave lengths utilized for the *m*- and *p*-bromo-*t*-butylbenzenes were 12.8 and 12.2μ, respectively. *o*-Bromo-*t*-butylbenzene possesses a characteristic absorption band at 13.3 μ. Absorbancies at each of the above wave lengths were determined by means of the base line technique.

LAFAYETTE, IND.

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

Rate Data and Isomer Distributions in the Acetylation and Benzoylation of Ethyl-, Isopropyl- and *t*-Butylbenzene. Partial Rate Factors for the Acylation Reaction[1]

BY HERBERT C. BROWN AND GIANLORENZO MARINO[2]

RECEIVED MARCH 21, 1959

Rate constants have been determined for the reaction at 25° of benzoyl chloride–aluminum chloride in ethylene chloride solution with ethylbenzene, isopropylbenzene and *t*-butylbenzene, yielding the relative rates: benzene, 1.00; toluene, 117; ethylbenzene, 101; isopropylbenzene, 93; *t*-butylbenzene, 70. In these reactions the isomer distributions are: ethylbenzene, 3.6% *o*-, 3.4% *m*- and 93.0% *p*-; isopropylbenzene, 3.1% *o*-, 4.0% *m*- and 92.9% *p*-; *t*-butylbenzene, 0% *o*-, 5.4% *m*- and 94.6% *p*-. In the series of four alkylbenzenes, the values of o_f decrease from 29.5 for toluene, to 10.9 for ethyl-, to 8.6 for isopropyl-, to 0 for *t*-butylbenzene. Similarly, p_f exhibits a decrease with increasing branching of the alkyl group: 633, 563, 519 and 398, respectively. On the other hand, m_f exhibits a marked increase from toluene to ethylbenzene, and then increases moderately: 4.9, 10.3, 11.1, 11.4. Under the same conditions, the relative rates of acetylation were determined competitively: benzene, 1.00; toluene, 128; ethylbenzene, 129; isopropylbenzene, 128; *t*-butylbenzene, 114. The isomer distributions were determined to be: ethylbenzene, 0.3% *o*-, 2.7% *m*- and 97.0% *p*-; isopropylbenzene, 0% *o*-, 3.0% *m*-, 97.0% *p*-; *t*-butylbenzene, 0% *o*-, 3.8% *m*- and 96.2% *p*-. The lack of significant substitution in the *ortho* position indicates a higher steric factor for the acetylation reaction than for the corresponding benzoylation reaction. The changes in m_f in the four alkylbenzenes, 4.8, 10.4, 11.5 and 13.0, respectively, paralleled these quantities in the benzoylation reaction. However, the values of p_f, 749, 753, 745, 658, are surprisingly constant, in contrast to the consistent decrease in p_f with branching of the alkyl group observed in the benzoylation and other substitution reactions. It appears that hyperconjugative contributions of the alkyl substituent must be less important in the acetylation reaction than in the related benzoylation reaction.

The Selectivity Relationship[3] correlates with excellent precision the available data on the substitution reactions of toluene.[4] In order to test the applicability of this treatment to other aromatic derivatives, quantitative data on the rates and isomer distributions are required for a number of representative electrophilic substitution reactions.

We have adopted mercuration (k_T/k_B 6.4),[5] nitration (k_T/k_B 25),[6] acylation (k_T/k_B 120)[7] and halogenation (k_T/k_B 344 for chlorination, 605 for bromination)[8] as reactions of low, moderate and high selectivity to obtain the required data for this test. In the present study we undertook to obtain the relative rates of reaction of benzoyl chloride and acetyl chloride in ethylene chloride solution, under the influence of aluminum chloride, with ethyl-, isopropyl- and *t*-butylbenzene. The isomer distributions realized in the acylation reactions were also determined to permit calculation of the partial rate factors.

Results

Rates of Benzoylation.—A kinetic procedure had been developed previously to determine the second-order rate constants for the benzoylation of benzene and toluene.[7] This procedure was utilized without change to determine the rate con-

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[1] Directive Effects in Aromatic Substitution. XXXIX.

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

[3] H. C. Brown and K. L. Nelson, THIS JOURNAL, **75**, 6292 (1953).

[4] L. M. Stock and H. C. Brown, *ibid.*, **81**, 3323 (1959).

[5] H. C. Brown and C. W. McGary, Jr., *ibid.*, **77**, 2306, 2310 (1955).

[6] Fortunately, a considerable quantity of satisfactory nitration data is available through the efforts of C. K. Ingold and his co-workers. For a summary of the data and pertinent references, see C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter VI.

[7] F. R. Jensen, G. Marino and H. C. Brown, THIS JOURNAL, **81**, 3303 (1959); H. C. Brown and G. Marino, *ibid.*, **81**, 3308 (1959); H. C. Brown, G. Marino and L. M. Stock, *ibid.*, **81**, 3310 (1959).

[8] P. W. Robertson, P. B. D. de la Mare and W. T. G. Johnston, *J. Chem. Soc.*, 276 (1943); P. B. D. de la Mare and P. W. Robertson, *ibid.*, 279 (1943); H. C. Brown and L. M. Stock, THIS JOURNAL, **79**, 1421, 5175 (1957).

stants for the benzoylation of ethyl-, isopropyl- and *t*-butylbenzene.

The results are summarized in Table I.

TABLE I

RATE CONSTANTS FOR THE REACTION OF BENZOYL CHLORIDE–ALUMINUM CHLORIDE WITH THE MONOALKYLBENZENES IN ETHYLENE DICHLORIDE AT 25.0°

Aromatic	Complex concn., M	Rate constants $k_2 \times 10^3$, mole^{-1} sec.$^{-1}$	Rel. rate[a]
Toluene[b]	0.100	0.763	117
Ethylbenzene	.100	.660	101
Isopropylbenzene	.100	.606	93
t-Butylbenzene	.100	.462	70

[a] Benzene 1.00. [b] Ref. 7.

Benzoylation Isomer Distributions.—In earlier studies, we utilized infrared spectroscopy to determine the isomer distribution in the benzoylation of toluene.[9] However, in this reaction only minor amounts of the *meta* isomer are formed and an accurate analysis of this component required a tedious fractional crystallization procedure to remove much of the more abundant *para* isomer. Our success in utilizing vapor phase chromatography for the analysis of the product realized in the acetylation of toluene[7] led us to explore the possibility of applying this method for the analysis of the isomeric monoalkylbenzophenones formed in the benzoylation reactions.

Utilizing a polyadipate substrate at 246–248° it proved possible to resolve the reaction products into individual peaks corresponding to the individual isomers formed in the benzoylation reaction. (Only in the case of toluene was the resolution between the *m*-methyl and *p*-methylbenzophenone incomplete.) The individual peaks were trapped and the individual isomers were identified by means of their infrared spectra.

In order to test the procedure, we synthesized pure samples of *m*- and *p*-*t*-butylbenzophenones and prepared synthetic mixtures for analysis. The analytical results agreed closely with the known compositions of the mixtures. Moreover, the analysis of the methylbenzophenones by this method proved to be in satisfactory agreement with the earlier results from infrared analysis. The isomer distributions are summarized in Table II.

TABLE II

ISOMER DISTRIBUTIONS IN THE REACTION OF BENZOYL CHLORIDE–ALUMINUM CHLORIDE WITH THE MONOALKYLBENZENES IN ETHYLENE DICHLORIDE AT 25.0°

Aromatic	Alkylbenzophenones, % *o*-	*m*-	*p*-
Toluene[a,b]	8.4	1.4	90.2
Ethylbenzene	3.6	3.4	93.0
Isopropylbenzene	3.1	4.0	92.9
t-Butylbenzene	0	5.4	94.6

[a] Analysis by infrared, ignoring *meta* isomer: 9.7% *o*-, 90.3% *p*. [b] Reaction product in benzoyl chloride solution; infrared analysis: *o*- 9.3%, *m*- 1.4%, *p*- 89.3% (ref. 9).

Relative Rates of Acetylation.—The acetylation reaction is far faster than the related benzoylation reaction. It had proved possible earlier to measure the rate of acetylation of benzene in a typical kinetic study.[7] However, with a half-life of approximately 2 minutes under the same conditions, the corresponding reaction with toluene could not be handled by the same methods. Accordingly, the relative rate of reaction, k_T/k_B, was determined competitively, using vapor phase chromatography to analyze for the reaction products, acetophenone and the methylacetophenones.[7] Accordingly, the same procedure was adopted to determine the reactivity of ethyl-, isopropyl- and *t*-butylbenzene relative to toluene. The results are summarized in Table III.

TABLE III

RELATIVE RATES FOR THE REACTION OF ACETYL CHLORIDE–ALUMINUM CHLORIDE WITH THE MONOALKYLBENZENES IN ETHYLENE DICHLORIDE AT 25.0°

Aromatic	Relative rate[a]
Toluene[b]	128
Ethylbenzene	129
Isopropylbenzene	128
t-Butylbenzene	114

[a] Benzene 1.00. [b] Ref. 7.

In view of the decrease in reactivity with increasing branching of the alkyl group observed in benzoylation and in essentially all other substitution reactions,[10] this essential constancy in reactivity was unexpected. We tested the reliability of the method by running a competitive benzoylation of toluene and *t*-butylbenzene. The value obtained, $k_{t\text{-BuPh}}/k_T$ 0.62, was considered to be in satisfactory agreement with the value 0.60 established from the rate constants (Table I). We considered the possibility that the addition and diffusion of the acetylation reagent to the mixture of hydrocarbons might be the cause for these unusual reactivities. However, slow addition of a dilute solution of the acetyl chloride–aluminum chloride complex to a vigorously stirred solution of the two aromatics did not alter the relative reactivity. Finally, we carried out a competitive alkylation of benzene and *p*-xylene, and of *p*-xylene with *t*-butylbenzene. From these reactivity ratios, $k_{p\text{-Xy}}/k_B = 23.7$, $k_{t\text{-BuPh}}/k_{p\text{-Xy}}$ 4.69, the relative reactivity is calculated to be $k_{t\text{-BuPh}}/k_B$ 111, in excellent agreement with the previous value.

Consequently, it appears that these relative reactivities (Table III) are real and not the result of any difficulty in the experimental procedure.

Acetylation Isomer Distributions.—The reaction products from the acetylation of ethyl-, isopropyl- and *t*-butylbenzene were analyzed by vapor phase chromatography, utilizing a polyadipate substrate and temperatures in the range 175–195°. In contrast to the difficulty encountered with the methylacetophenones,[7] the individual peaks corresponding to the individual isomers were all readily resolved, with only a minor overlap in the case of *m*- and *p*-ethylacetophenone. These peaks were individually collected and identified by infrared examination.

Pure samples of *m*- and *p*-ethylacetophenones and of *m*- and *p*-*t*-butylacetophenones were prepared

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[9] H. C. Brown and H. L. Young, *J. Org. Chem.*, **22**, 719 (1957); H. C. Brown and F. R. Jensen, THIS JOURNAL, **80**, 2296 (1958).

[10] For a summary of the data and literature references see L. M. Stock and H. C. Brown, THIS JOURNAL, **81**, 5621 (1959).

and used to check both the analyses and the identifications.

The vapor phase chromatogram of the product from the acetylation of *t*-butylbenzene exhibited several major by-products. The two most important were identified as *m*- and *p*-di-*t*-butylbenzene. Fortunately, it proved possible largely to eliminate these undesired side-reactions by carrying out the acetylation with a 100% excess of acetyl chloride, simultaneously removing the hydrogen chloride formed in the reaction with slight suction. The isomer distributions are summarized in Table IV.

TABLE IV

ISOMER DISTRIBUTIONS IN THE REACTION OF ACETYL CHLORIDE–ALUMINUM CHLORIDE WITH THE MONOALKYLBENZENES IN ETHYLENE DICHLORIDE AT 25.0°

Aromatic	Alkylacetophenones, % *o*-	*m*-	*p*-
Toluene[7]	1.17	1.25	97.7
Ethylbenzene	0.3	2.7	97.0
Isopropylbenzene	0	3.0	97.0
t-Butylbenzene	0	3.8	96.2

The acetylation of *t*-butylbenzene under somewhat different conditions previously was reported to yield 0% *o*-, 1.8% *m*- and 98.2% *p*-*t*-butylacetophenone.[11] The major discrepancy in the amount of the *meta* isomer does not appear to be explicable in terms of the modest difference in experimental conditions. The authors distilled their reaction product and examined the individual fractions of mixed isomers by infrared. They did not have available an authentic sample of *m*-*t*-butylacetophenone. It is possible that the discrepancy arises from the consequent analytical difficulties.

Discussion

The relative rate data and the isomer distributions permit the calculation of the various partial rate factors. These values are summarized in Table V.

TABLE V

PARTIAL RATE FACTORS FOR THE BENZOYLATION AND ACETYLATION OF THE MONOALKYLBENZENES IN ETHYLENE DICHLORIDE AT 25.0°

	Benzoylation			Acetylation		
Aromatic	o_f	m_f	p_f	o_f	m_f	p_f
Toluene	29.5	4.9	633	4.5	4.8	749
Ethylbenzene	10.9	10.3	563	1.0	10.4	753
Isopropylbenzene	8.6	11.1	519	0	11.5	745
t-Butylbenzene	0	11.4	398	0	13.0	658

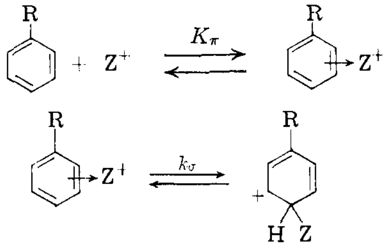
In accordance with the increasing bulk of the alkyl substituent, o_f exhibits a decrease from toluene to *t*-butylbenzene. As was pointed out earlier,[7] acetylation appears to exhibit a larger steric requirement than does benzoylation. This marked difference in the steric requirements of the two reactions is currently under investigation[12] and further discussion therefore will be deferred.

In both acetylation and benzoylation, m_f increases from toluene to *t*-butylbenzene. All of the available aromatic substitution data for *t*-butylbenzene[10] support the conclusion that substitution *meta* to a *t*-butyl group occurs faster than substitution *meta* to a methyl group. However, it is somewhat unexpected to observe the sharp increase from m_f^{Me} to m_f^{Et}, with a more moderate increase with the more branched groups. Unfortunately, with the exception of the present study, the available partial rate data are largely restricted to toluene and *t*-butylbenzene, so that it is not possible to say whether this is a general phenomenon.

It should be pointed out that the dipole moments of the alkyl benzenes exhibit a somewhat similar behavior: toluene, 0.37 D.; ethylbenzene, 0.58 D.; isopropylbenzene, 0.65 D.; *t*-butylbenzene, 0.70 D.[13] The magnitude of these dipole moments are believed to reflect the inductive contributions of the alkyl substituents. Consequently, it appears that the inductive effects of these alkyl groups must play a dominant role in influencing the relative rates of acylation in the positions *meta* to the alkyl groups.

The regular decrease in the values of p_f from toluene to *t*-butylbenzene in the benzoylation reaction is in accord with the usual effect of these alkyl groups in stabilizing electron deficient intermediates. However, the essential constancy in the value of p_f for these groups in the acetylation reaction is puzzling.

Aromatic substitution presumably involves an initial rapid equilibrium involving the formation of a π-complex, followed by a slower rate-determining conversion of the π-complex into the σ-complex.[14,15]



Consequently, the rate of substitution will involve the factor $K_\pi k_\sigma$. Fortunately, K_π does not appear to vary greatly with the nature of the substituent,[16] whereas the stability of the σ-complex is markedly dependent upon the substituent.[17] Consequently, the stability of the σ-complex appears to be the dominant factor and the moderate variations in the stability of the π-complex usually can be ignored.

In the alkylbenzenes, the stability of the π-complexes with hydrogen chloride increases in the order: toluene < ethylbenzene < isopropylbenzene < *t*-butylbenzene,[16] whereas the stability of the σ-complexes presumably decreases in this order. If the stability of the π-complex is a somewhat greater factor in the acetylation reaction than in the corresponding benzoylation reaction, a net

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

[12] Research in progress.

[13] J. W. Baker and L. G. Groves, *J. Chem. Soc.*, 1144 (1939).

[14] K. L. Nelson and H. C. Brown, Chapt. 56 in "The Chemistry of Petroleum Hydrocarbons," ed. by B. T. Brooks, *et al.*, Vol. III, Reinhold Publishing Corp., New York, N. Y., 1955.

[15] V. Gold and D. P. N. Satchell, *J. Chem. Soc.*, 3609, 3619, 3622 (1955).

[16] H. C. Brown and J. D. Brady, THIS JOURNAL, **74**, 3570 (1952).

[17] H. C. Brown and Y. Okamoto, *ibid.*, **79**, 1913 (1957).

TABLE VI

VALUES OF LOG p_f/LOG m_f FOR THE ACYLATION AND MERCURATION REACTIONS

Aromatic	Benzoylation	Acetylation	Mercuration
Toluene	4.06	4.22	4.12
Ethylbenzene	2.71	2.83	
Isopropylbenzene	2.60	2.71	
t-Butylbenzene	2.46	2.53	2.44

TABLE VII

COMPETITIVE ACETYLATIONS OF TOLUENE AND ALKYLBENZENES

Alkyl group	Initial concentrations				Final concentrations		Rel. rate
	[RC_6H_5]	[$CH_3C_6H_5$]	[Complex]	[CH_3COCl]	[$RC_6H_4COCH_3$]	[$CH_3C_6H_4COCH_3$]	k_{RPh}/k_T
Ethyl	0.100	0.100	0.075	0.075	0.0257	0.0255	1.01
	.100	.100	.075	.075	.0268	.0265	1.01
						Average	1.01
Isopropyl	.080	.080	.060	.060	.0231	0.0237	0.967
	.080	.080	.060	.060	.0262	.0250	1.05
						Average	1.00
t-Butyl	.100	.100	.075	.075	.0271	0.0301	0.882
	.100	.100	.075	.075	.0280	.0305	.902
	.150	.100	.075	.075	.0348	.0252	.908
						Average	0.897

cancelation might result and thereby bring about the observed essential constancy in the relative rates of substitution for the four alkylbenzenes.

It was pointed out in earlier papers of this series that log p_f/log m_f = σ_p^+/σ_m^+ provides a quantity which should be essentially independent of the reaction constant, ρ. Comparison of this quantity for the benzoylation, acetylation and mercuration[18] reactions does indeed reveal a satisfactory constancy (Table VI).

A detailed examination of the applicability of the Selectivity Relationship to these data is deferred to the final paper of this group.[10]

Experimental Part

Materials.—The aromatic hydrocarbons utilized in these experiments were Phillips research grade hydrocarbons having purities greater than 99.5%. Acetyl chloride, benzoyl chloride, aluminum chloride and ethylene dichloride were purified as described previously.[7]

A number of ketones were required as standards for the infrared and vapor phase chromatographic examinations.

Crude *p*-ethylacetophenone was prepared by the acetylation of ethylbenzene, converted into the semicarbazone, which was recrystallized three times from 50% acetic acid. (Recrystallization from ethanol failed to remove the *meta* isomer.) The pure semicarbazone, b.p. 193–194°,[19] was transformed with 5 *N* hydrochloric acid into the ketone, *p*-ethylacetophenone, b.p. 85–86° at 3 mm., n^{20}D 1.5298.[20]

m-Ethylacetophenone was prepared by the reaction of *m*-ethylphenylcadmium chloride with acetyl chloride in a yield of 61%. The semicarbazone was prepared, purified by crystallization from ethanol, m.p. 171–173°,[21] and converted into the ketone, *m*-ethylacetophenone, b.p. 80–81° at 3 mm., n^{20}D 1.5261.[22]

Crude *p*-*t*-butylacetophenone was transformed into the semicarbazone. After three recrystallizations from ethanol, the semicarbazone, m.p. 219–220°, was transformed into *p*-*t*-butylacetophenone, b.p. 107–108° at 5 mm., n^{20}D 1.5215.[23]

m-*t*-Butylacetophenone was synthesized from *m*-bromo-*t*-butylbenzene, converted to the Grignard reagent, then to the cadmium derivative, and finally treated with acetyl chloride. The reaction product was isolated by distillation under vacuum. However, gas chromatographic examination of the fractions revealed major quantities of impurities. Accordingly, the fractions were combined and treated with semicarbazide hydrochloride and potassium acetate to convert the ketone to the semicarbazone. There was obtained 10.8 g. of semicarbazone, a yield of 41%. After several recrystallizations from ethanol, 8.0 g. of crystals, m.p. 188–189°, was obtained.

TABLE VIII

INFRARED ABSORPTION OF ALKYLACETOPHENONES IN THE 11–15 μ REGION

Substituent	Wave length of characteristic band,[a] μ		
m-Methyl	12.70	12.85	14.50
m-Ethyl	12.48	12.60	14.40
m-Isopropyl	12.45	12.60	14.40
m-*t*-Butyl	12.42	12.60	14.32
p-Methyl			12.30
p-Ethyl		11.88	12.08
p-Isopropyl		11.85	12.05
p-*t*-Butyl		11.82	12.02

[a] Cyclohexane was used as solvent.

Anal. Calcd. for $C_{13}H_{19}N_3O$: C, 66.95; H, 8.15; N, 18.02. Found: C, 66.60; H, 8.28; N, 18.08.

The semicarbazone was treated with 5 *N* hydrochloric acid at 100° for 3 hours, and the *m*-*t*-butylacetophenone was distilled, b.p. 102–103° at 5 mm., n^{20}D 1.5175

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.77; H, 9.14. Found: C, 81.75; H, 8.94.

p-*t*-Butylbenzophenone from the Friedel–Crafts reaction was purified through the semicarbazone, m.p. 157–159°, after recrystallization from 98% petroleum ether (b.p. 65–70°) and 2% ethanol.

Anal. Calcd. for $C_{18}H_{21}N_3O$: C, 73.17; H, 7.17; N, 14.23. Found: C, 73.13; H, 7.65; N, 14.26.

The semicarbazone was transformed into the ketone by the usual procedure, b.p. 167° at 3 mm., n^{20}D 1.5786.[24]

m-*t*-Butylbenzophenone was synthesized from *m*-bromo-*t*-butylbenzene and benzoyl chloride through the cadmium intermediate. The crude product, 54% yield, was purified by recrystallization of the semicarbazone from 95% petroleum ether–5% ethanol, m.p. 179–180°.

Anal. Calcd. for $C_{18}H_{21}N_3O$: C, 73.17; H, 7.17; N, 14.23. Found: C, 72.92; H, 7.23; N, 14.06.

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(18) H. C. Brown and M. Dubeck, THIS JOURNAL, **81**, 5608 (1959).

(19) G. Baddeley, *J. Chem. Soc.*, 232 (1944), reports m.p. 191°.

(20) D. T. Mowry, M. Renoll and W. F. Huber, THIS JOURNAL, **68**, 1105 (1946), report b.p. 116–117° at 13 mm., n^{25}D 1.5275.

(21) G. Baddeley, ref. 19, reports m.p. 175°.

(22) D. T. Mowry, THIS JOURNAL, **67**, 1050 (1945), reports b.p. 113–116° at 14 mm., n^{25}D 1.5232.

(23) G. F. Hennion and S. F. deC. McLeese, *ibid.*, **64**, 2421 (1942), report b.p. 133–134° at 11 mm., n^{20}D 1.5199, m.p. of semicarbazone 220–221°.

(24) I. R. Kaplan, H. N. Parton and J. Vaughan, *ibid.*, **75**, 4341 (1953), report b.p. 198° at 13 mm., n^{19}D 1.5762.

The semicarbazone was transformed into the ketone, b.p. 156° at 3 mm., $n^{20}D$ 1.5748.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.66; H, 7.62. Found: C, 85.39; H, 7.29.

Each of the ketones was established to be of high purity by vapor phase chromatographic examination.

Rates of Benzoylation.—The rates of benzoylation were measured by the technique previously utilized for determining the rates of benzoylation of benzene and toluene.[7] The reactions were run in duplicate. The rate constants reported in Table I are averages of these duplicate measurements with an average deviation no greater than ±2%.

Relative Rates of Acetylation.—A solution of acetyl chloride–aluminum chloride complex in ethylene dichloride with excess acetyl chloride was added quickly to a vigorously stirred solution containing an excess of toluene and the second hydrocarbon. It was established that the temperature did not increase by more than 0.5°. An inert internal standard, 1,2,4-trichlorobenzene, was added to facilitate the determination of the actual concentrations of the products.

After 4 to 6 minutes, the reaction mixture was quenched in an ice–sodium hydroxide mixture. The organic layer was washed twice with water. The greater portion of the solvent was removed by distillation and the product concentrations determined by vapor phase chromatographic examination. The extent of reaction ranged from 80 to 90%. The relative rates were determined using the formula

$$\frac{k_A}{k_T} = \frac{\log A/A_0}{\log T/T_0}$$

The experimental results are summarized in Table VII.

Isomer Distributions.—The composition of the products was determined utilizing a polyadipate substrate (Rubber Corporation of America polymeric BGA). In the acetylation products of isopropylbenzene and *t*-butylbenzene only two major peaks were observed, corresponding to the *meta* and *para* acetylation products. In the case of ethylbenzene, a minor peak at the position anticipated for the *ortho* isomer was observed. This peak was estimated from the area to be 0.3%, but no great precision is claimed for this analysis.

TABLE IX

RETENTION TIMES OF ALKYLACETO-[a,b] AND -BENZOPHENONES[a,c]

Compound	Temp., °C.	Retention time, min. *o*-	*m*-	*p*-	Separation, min. *o–m*	*m–p*
Methylacetophenone	165	8.0	10.4	11.7	2.4	1.3
Ethylacetophenone	175	7.1	10.1	12.1	3.0	2.0
Isopropylacetophenone	185		8.9	11.2		2.3
t-Butylacetophenone	195		8.1	11.0		2.9
Methylacetophenone	185	4.9	6.0	6.6	1.1	0.6
Ethylacetophenone	185	6.3	7.9	9.2	1.6	1.3
Isopropylacetophenone	185		8.9	11.2		2.3
t-Butylacetophenone	185		10.5	13.9		3.4
Methylbenzophenone	247	9.4	11.9	13.9	2.5	2.0
Ethylbenzophenone	247	10.9	15.4	19.4	4.5	4.5
Isopropylbenzophenone	247	10.9	16.2	22.0	5.8	5.3
t-Butylbenzophenone	247		17.0	24.8		7.4

[a] Column: 2 m. RCA polymeric BGA on Celite. [b] Flow rate 125 cc. of helium per min. [c] Flow rate 350 cc. of helium per min.

The major peaks ascribed to the *meta* and *para* isomers were isolated and identified as these isomers by infrared examination. The characteristic absorption bands for *ortho* disubstituted benzenes (13–13.5 μ) were definitely absent in all the spectra.

The comparative examination of the infrared spectra of *m*- and *p*-alkyl-acetophenones exhibits an interesting shift of the absorption bands toward shorter wave lengths with increasing size of the alkyl groups (Table VIII).

Retention times of all the alkylacetophenones and benzophenones are summarized in Table IX. The retention times exhibit a consistent regularity and the separations improve with increasing size of the alkyl substituent.

LAFAYETTE, IND.

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

Relative Rates and Isomer Distributions in the Halogenation of *t*-Butylbenzene and Some of Its Derivatives. Partial Rate Factors for Non-catalytic Bromination and Chlorination in Acetic Acid[1—3]

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The non-catalytic bromination of *t*-butylbenzene in 85% acetic acid at 25° yields 1.20% *o*-, 1.47% *m*- and 97.3% *p*-bromo-*t*-butylbenzene. Under these conditions the relative rate of bromination of benzene to *t*-butylbenzene is 1.00/138. These data provide the partial rate factors o_f 4.7, m_f 6.1 and p_f 806. Greater than 99% 2- and 3-bromo-4-*t*-butyltoluene are formed in the bromination of *p*-*t*-butyltoluene. The isomer distribution for the non-catalytic chlorination of *t*-butylbenzene in 99.9% acetic acid at 25° is 21.5% *o*-, 2.29% *m*- and 76.2% *p*-chloro-*t*-butylbenzene. Under these conditions the relative rate of chlorination of benzene to *t*-butylbenzene is 1.00/87.7. The partial rate factors for this reaction are o_f 56.6, m_f 6.02 and p_f 401. The chlorination of *p*-di-*t*-butylbenzene produces 28.6% *p*-chloro-*t*-butylbenzene and 71.4% 2 -chloro-1,4-di-*t*-butylbenzene. The chlorination of *p*-*t*-butyltoluene yields 5.0% *p*-chlorotoluene and 95% 2- and 3-chloro-4-*t*-butyltoluene. The observed relative rates of chlorination of these *p*-alkyl-*t*-butylbenzenes, after correction for the chloro-de-*t*-butylation side-reaction, are in good agreement with the relative rates calculated on the basis of the partial rate factors.

That the electrophilic substitution reactions of toluene are correlated by the proposed simple linear relationship[6–8] has been adequately confirmed.[9] It has been suggested that the substitution reactions of other monosubstituted benzenes obey a similar relationship.[6,7] Unfortunately, the number of quantitative experimental observations for compounds other than toluene is quite limited.

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(1) Directive Effects in Aromatic Substitution. XL.

(2) This research supported in part by the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of the Petroleum Research Fund.

(3) Based upon a thesis submitted by Leon M. Stock in partial fulfillment for the degree Doctor of Philosophy.

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