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

Relative Rates and Isomer Distributions in the Acetylation of the Methylbenzenes by Acetyl Chloride–Aluminum Chloride in Ethylene Dichloride Solution[1]

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RECEIVED MAY 1, 1959

The isomer distributions in the acetylation of the isomeric methylbenzenes by acetyl chloride–aluminum chloride in ethylene dichloride solution have been examined by gas chromatographic methods. The relative rates of acetylation of the various methylbenzenes have been determined in competitive reactions. The experimental data are compared with the relative rates and isomer distributions calculated from the partial rate factors for this reaction. The agreement between the calculated and observed rates is considerably better than that realized previously for the related study of the benzoylation of the methylbenzenes in nitrobenzene solution, although less satisfactory than for the mercuration and bromination reactions. Possible causes for the observed discrepancies are considered.

The kinetic requirements for simple additivity in the substitution of aromatic derivatives were considered many years ago by Scheffer.[4] However, it was Condon's attempt to calculate the rates of halogenation of the polymethylbenzenes from the partial rate factors derived from the substitution of benzene and toluene which suggested the possible general applicability and wide utility of this approach.[5]

Unfortunately, the data available to Condon in 1948 did not permit a rigorous test of his proposal. Accordingly, in the course of our studies of directive effects in aromatic substitution, we have attempted to obtain data to test the additivity of methyl substituents. Considerable success was achieved in the mercuration[6a] and bromination[6b] reactions between the calculated and observed rates of substitution. However, large discrepancies were observed in applying the treatment to the rates of benzoylation of the methylbenzenes in nitrobenzene solution.[7] It suggested that these discrepancies might arise from the formation of ternary complexes of aluminum chloride, the aromatic hydrocarbon and the solvent nitrobenzene.[7]

Recently, we utilized the aluminum chloride-catalyzed reactions of benzoyl chloride[8] and of acetyl chloride[9] in ethylene dichloride solution with benzene and toluene to test the applicability of the Selectivity Relationship. Partial rate factors for the benzoylation and acetylation reactions are available from these studies. Accordingly, it appeared desirable to apply these reactions to a study of the reactivities of the methylbenzenes.

The acylation reactions exhibit a high selectivity. Consequently, the range of reactivity from benzene to pentamethylbenzene encompasses an enormous range of reactivity. It proved impossible to cover this range by standard kinetic methods. Consequently, we were forced to use competitive reactions to establish the relative reactivities. Gas chromatography offered a convenient means for following these competitive reactions. Because of the greater volatility of the acetyl derivatives, we elected to utilize the acetylation reaction in this study.

Results

Isomer Distribution.—Each of the methylbenzenes was treated with acetyl chloride–aluminum chloride in ethylene dichloride solution at 25°. After hydrolysis to remove aluminum chloride, the reaction products were examined by gas chromatography, using as a stationary phase "RC polymeric BGA." This polyadipate substrate had been previously demonstrated to be very effective in resolving all of the isomeric monoalkylacetophenones into individual peaks.[10] It was established, by adding an internal standard to the reaction mixtures, that the reactions proceed to essential completion (90% or greater) in every case.

Either from the symmetry of the hydrocarbon, or from the calculation of the isomer distribution based on the partial rate factors, only a single major (~99%) acetylation product was anticipated for *o*-, *m*- and *p*-xylene, mesitylene, pseudocumene, the three tetramethylbenzenes and pentamethylbenzene. In actual fact, the chromatograms of the reaction products of these compounds exhibited only a single major peak and the structure of the reaction product is considered established by this agreement between the calculated and predicted behavior.

Calculation indicates that hemimellitene should yield two products in comparable amounts. Actually, two peaks were observed corresponding to yields of 79 and 21%. The two peaks were isolated and examined by means of infrared spectroscopy. On this basis, the isomer formed in larger amount is 3,4,5-trimethylacetophenone, and the minor component is 2,3,4-trimethylacetophenone. This identification was confirmed by preparing the semicarbazone of the larger fraction. Its m.p. of 215.5–216.5° agrees with the reported value of 217° for the semicarbazone of 2,4,5-trimethylacetophenone.[11]

In addition to the major product from *m*-xylene, 2,4-dimethylacetophenone, there was observed a minor component, 2.5%. This isomer has been identified as 3,5-dimethylacetophenone on the basis of its retention time.

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[1] Directive Effects in Aromatic Substitution. XXXVII.

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

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[4] F. E. C. Scheffer and W. F. Brandsma, *Rec. trav. chim.*, **45**, 522 (1926), and earlier papers.

[5] F. E. Condon, THIS JOURNAL, **70**, 1963 (1948).

[6a] H. C. Brown and C. W. McGary, Jr., *ibid.*, **77**, 2310 (1955);

[6b] H. C. Brown and L. M. Stock, *ibid.*, **79**, 1421 (1957).

[7] H. C. Brown, B. A. Bolto and F. R. Jensen, *J. Org. Chem.*, **23**, 417 (1958).

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

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

[10] H. C. Brown and G. Marino, *ibid.*, **81**, in press 0000 (1959).

[11] G. Baddeley and A. G. Pendleton, *J. Chem. Soc.*, 807 (1952).

The retention times of the various methylacetophenones under identical conditions are summarized in Table I.

TABLE I

RETENTION TIMES OF THE METHYLACETOPHENONES[a]

Compound, acetophenone	Retention time, min.	Compound, acetophenone	Retention time, min.
2-Methyl-	5.7	2,4,6-Trimethyl-	10.5
3-Methyl-	7.3	2,3,4-Trimethyl-	17.8
4-Methyl-	8.0	2,4,5-Trimethyl-	15.3
		3,4,5-Trimethyl-	24.0
2,5-Dimethyl-	8.2		
2,4-Dimethyl-	8.8	2,3,5,6-Tetramethyl-	20.0
3,5-Dimethyl-	10.3	2,3,4,6-Tetramethyl-	21.6
3,4-Dimethyl-	13.8	2,3,4,5-Tetramethyl-	31.6
		2,3,4,5,6-Pentamethyl-	44.5

[a] RC polymeric BGA, 2 m., 184°, 80 cc. of helium per min.

In examining this list, it is apparent that a methyl group *ortho* to the acetyl grouping decreases the retention time below those observed for isomeric derivatives. A second *ortho* substituent results in a further decrease (compare the trimethylacetophenones). Presumably, the decrease in retention time is due to the effect of the *ortho* methyl substituents in hindering the polar acetyl group and thereby reducing its adsorption on the stationary substrate.

On the basis of this regularity, the minor component (2.5%) observed in the acetylation of *m*-xylene is assigned the structure 3,5-dimethylacetophenone, rather than the structure 2,6-dimethylacetophenone, for which a shorter retention time would have been anticipated.

Relative Rates.—The rate constant for the acetylation of benzene in ethylene dichloride solution under the influence of aluminum chloride was determined previously.[9] The relative rate, toluene/benzene 128, previously was established by a competitive procedure, using gas chromatography to analyze the product ratio.[9] The same technique was utilized in the present study to determine the relative reactivities of all of the methylbenzenes.

Suitable mixtures of two or more hydrocarbons were mixed with a deficient amount of the acetyl chloride–aluminum chloride complex in the same solvent. An inert internal standard was added to the reaction mixtures to permit the estimation of the actual concentration of each of the reaction products.

In each competitive experiment, methylbenzenes were selected with comparable reactivities and yielding ketones as reaction products with sufficiently different retention times as to make resolution of individual components possible. The relative rates then were calculated, using the formula[12]

$$\frac{k_1}{k_2} = \frac{\log [(C_1^0 - X_1)/C_1^0]}{\log [(C_2^0 - X_2)/C_2^0]}$$

where C_1^0 and C_2^0 refer to the initial concentration of the hydrocarbons and X_1 and X_2 refer to the final concentration of the products. The results are summarized in Table II.

The average deviations appear to be quite large in some cases, notably *p*-xylene, hemimellitene, prehnitene and pentamethylbenzene. It is probable that these large deviations arise from the relatively low accuracy of the method of competitive reactions when the relative rates differ by factors of 10 or greater.[13]

The range in reactivity covered is quite large, $>10^5$. In view of this large range in reactivity, the large average deviations do not introduce any major difficulty in the consideration of the results.

Discussion

The partial rate factors for the acetylation reaction have been established from the relative reactivity of benzene and toluene and the isomer distribution in toluene to be o_f 4.5, m_f 4.8, p_f 749.[9] Utilizing these partial rate factors, the relative rates and isomer distributions to be anticipated for the methylbenzenes may be calculated readily. The calculated isomer distributions are summarized in Table III.

With the exception of hemimellitene, the calculations indicate that only a single major acetylation product (99–100%) is to be anticipated. This was actually observed. In the case of *m*-xylene, where the calculation predicts 0.30% of 2,6- and 0.34% of 3,5-dimethylacetophenone, the gas chromatogram indicated only a single minor component in the reaction product, 2.5%, to which the 3,5-dimethylacetophenone structure is assigned on the basis of the retention time.

In the mercuration reaction, it was observed that substitution between two methyl groups is somewhat slower than the calculated rate.[5] This decrease in rate was attributed to an enhanced steric effect resulting from the combined effect of two "*ortho*" substituents. The acetylation reaction is one of unusually high steric requirements.[9] Consequently, the failure to observe the formation of the small quantity of 2,6-dimethylacetophenone (0.30%) predicted by the calculations may be the result of such a "double *ortho*" effect.

A more serious discrepancy is exhibited by hemimellitene. Here the calculations predict 65.2% 2,3,4- and 34.8% 3,4,5-trimethylacetophenone, whereas the experimental observation is 21% 2,3,4- and 79% 3,4,5-. Here also there is observed a decreased tendency to substitute *ortho* to the strongly buttressed assembly of three methyl groups.

In view of the observation that with the sole exception of hemimellitene only a single major acetylation product is realized (>97%), the acetylation reaction should be highly useful synthetically. It should be especially useful for the synthesis of 2,4-dimethyl-, 3,4-dimethyl- and 2,4,5-trimethylacetophenones.

In Table IV the observed relative rates are summarized together with the relative rates calculated from the partial rate factors.

The extent of the agreement is indicated by Fig. 1. The agreement between experimental and calculated values is far better than that observed for the benzoylation reaction in nitrobenzene, but is

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[12] C. K. Ingold and M. S. Smith, *J. Chem. Soc.*, 905 (1938).

[13] See discussion by T. S. Lee, in "Technique of Organic Chemistry," Vol. VIII, Interscience Publishers, Inc., New York, N. Y., 1953, p. 110.

TABLE II

RELATIVE RATES[a] OF ACETYLATION OF THE METHYLBENZENES AT 25°

Expt.	Benzene	Toluene	*o*-Xylene	*m*-Xylene	*p*-Xylene	Mesitylene	Hemimellitene	Pseudocumene	Durene	Isodurene	Prehnitene	Pentamethyl
A		(128)	1930						114			
B		(128)	2100									
C		(128)	2180									
D		(128)	2330									
E		(128)				2750						
F		(128)				3130						
G			(2130)			2890						
H	(1.00)				20.0				90.2			
I	(1.00)				27.1							
J		(128)									9650	
K			(2130)	377			8610					
L			(2130)	330			8650					
M			(2130)	332								
N			(2130)				9690					13170
O			(2130)							7540	5690	
P			(2130)					1670				
Q						(2920)	6080				6170	
R						(2920)		1720		7320		9850
S						(2920)		1900				
T						(2920)						14330
U									(102)		7720	
Av.	1.00	128	2130 ±110	347 ±20	23.5 ±3.5	2920 ±140	8260 ±1050	1760 ±90	102 ±12	7430 ±110	7300 ±1400	13200 ±2100
Dev., %			5.2	5.8	15.0	4.8	13.0	5.2	12	1.5	19.0	16.0

[a] Values in parentheses refer to relative reactivities utilized for the reference compounds.

TABLE III

PREDICTED ISOMER DISTRIBUTIONS IN THE ACETYLATION OF THE METHYLBENZENES

Compound	Acetylation position, % 2-	3-	4-	5-	6-
o-Xylene		0.60	99.40		
m-Xylene	0.30		99.36	0.34	
p-Xylene	100				
Hemimellitene			65.2	34.8	
Pseudocumene		0.59		98.77	0.63
Mesitylene	100				
Prehnitene	100				
Isodurene	100				
Durene	100				

less satisfactory than that noted for the mercuration[5] and bromination[6] reactions.[14]

These observations support the suggestion that the formation of ternary complexes between aluminum chloride, nitrobenzene and the aromatic must be at least partially responsible for the large deviations observed in that system. However, the observation that moderate deviations persist in the present system indicates that the above factor is not entirely responsible for the observed discrepancies. For some reason the acylation reaction gives less satisfactory agreement between the observed and calculated rates.

The acylation reaction differs from the mercuration and bromination reaction in possessing a much larger steric factor. Thus, the mercuration of toluene produces 29.4% *ortho*, bromination produces 32.9% *ortho*, whereas acetylation produces only 1.2% *ortho* substitution product.

In the present results, the observed rates of substitution are smaller than the observed values for all cases involving substitution *ortho* to a methyl group, with one exception, *p*-xylene. It is significant that substitution in positions not involving one or more methyl groups in an *ortho* location, such as in the formation of 3,4- and 3,5-dimethyl and 3,4,5-trimethylacetophenones, the relative rates are actually higher than the calculated values (Fig. 1).

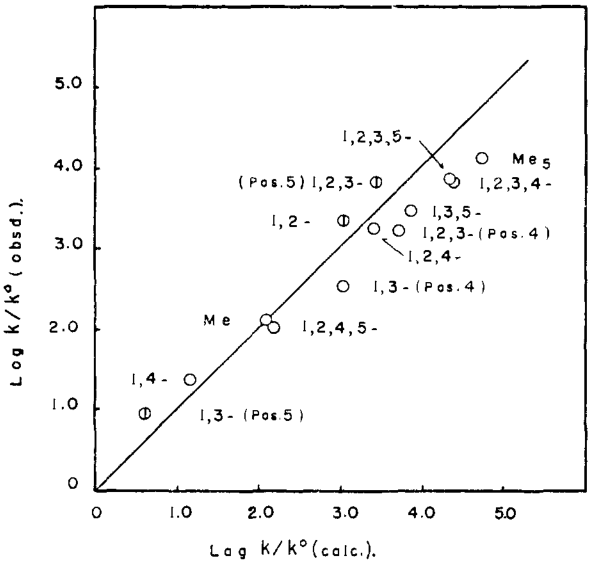

Fig. 1.—Observed and calculated relative rates of acetylation of the methylbenzenes. The barred points ⦶ indicate relative rates of substitution at positions not adjacent to a methyl group.

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(14) Compare Fig. 1 with the related diagrams for the mercuration and bromination reactions: H. C. Brown and L. M. Stock, THIS JOURNAL, **79**, 5175 (1957).

TABLE IV

OBSERVED AND CALCULATED RELATIVE RATES OF ACETYLATION OF THE METHYLBENZENES IN ETHYLENE DICHLORIDE AT 25°

Compound	Observed relative rates	Calculated relative rates^a	Calculated/ Observed
Benzene	1.00	1.00	1
Toluene	128	128	1
o-Xylene	2130	1200	0.56
m-Xylene	347	1130	3.2
position 4	338	1120	3.3
position 5	8.67	3.83	0.44
p-Xylene	23.5	14.4	0.61
Mesitylene	2920	7580	2.6
Hemimellitene	8260	8240	1.00
position 4	1740	5370	3.1
position 5	6530	2860	0.44
Pseudocumene	1760	2720	1.5
Durene	102	156	1.5
Isodurene	7430	24200	3.3
Prehnitene	7300	25800	3.5
Pentamethylbenzene	13200	58000	4.4

^{a} From the partial rate factors for toluene: o_f 4.5, m_f 4.8, p_f 749.

TABLE V

COMPETITION EXPERIMENTS IN THE ACETYLATION OF THE METHYLBENZENES

Expt.	Reactants, M^a		Acetophenone product, M^b
A	Toluene	0.300	0.00700
	o-Xylene	.100	.03003
	Durene	.600	.01256
B	Toluene	.300	.00844
	o-Xylene	.100	.03736
C	Toluene	.300	.00858
	o-Xylene	.100	.03895
D^c	Toluene	.100	.00350
	o-Xylene	.100	.0477
E	Toluene	.300	.01004
	Mesitylene	.100	.05202
F	Toluene	.300	.00643
	Mesitylene	.100	.04117
G	*o*-Xylene	.100	.03010
	Mesitylene	.100	.01990
H	Benzene	.600	.00120
	p-Xylene	.100	.00375
	Durene	.300	.04750
I	Benzene	.500	.00947
	p-Xylene	.100	.04053
J^d	Toluene	.300	.00407
	Prehnitene	.100	.06440
K	*o*-Xylene	.100	.01014
	m-Xylene	.100	.00198
	Hemimellitene	.100	.03508
L	*o*-Xylene	0.100	0.01002
	m-Xylene	.100	.00162
	Hemimellitene	.100	.03489
M	*o*-Xylene	.100	.04132
	m-Xylene	.100	.00800
N	*o*-Xylene	.150	.00722
	Hemimellitene	.100	.01542
	Pentamethylbenzene	.100	.02304
O^e	*o*-Xylene	.200	.00703
	Isodurene	.025	.00297
	Prehnitene	.100	.00919
P	*o*-Xylene	.100	.02359
	Pseudocumene	.100	.02295
Q^f	Mesitylene	.100	.00823
	Hemimellitene	.100	.01639
	Prehnitene	.100	.01659
R^f	Mesitylene	.100	.00551
	Pseudocumene	.100	.00328
	Isodurene	.075	.00992
	Pentamethylbenzene	.100	.01739
S	Mesitylene	.100	.02853
	Pseudocumene	.100	.01962
T	Mesitylene	.100	.01002
	Pentamethylbenzene	.100	.04050
U	Durene	.300	.00236
	Prehnitene	.100	.04508

^{a} Concentration of $CH_3COCl \cdot AlCl_3$ 0.050 M except where otherwise indicated. 100% excess of acetyl chloride was used. ^{b} Determined by comparison with the area of the peak of the internal standard (1,2,4-trichlorobenzene) which was added to the reaction mixtures in 0.020 M concentration. ^{c} 0.0625 M $CH_3COCl \cdot AlCl_3$. ^{d} 0.075 M $CH_3COCl \cdot AlCl_3$. ^{e} 0.020 M $CH_3COCl \cdot AlCl_3$. ^{f} 0.040 M $CH_3COCl \cdot AlCl_3$.

This large *ortho* effect cannot be the only factor. Thus the deviation is smaller for the highly hindered molecule durene than for the less hindered derivative prehnitene. The postulate of additivity ignores the possible role of π-complex formation on the reaction rate[15,16] and the complete theory will doubtless have to include this factor.

Although this discussion has emphasized the discrepancies between the calculated and observed rates, it may be desirable to point out that the agreement is really moderately satisfactory. The relative reactivities vary by a factor of 10^5. Yet the calculated and observed rates agree within an average factor of approximately 2, with a maximum discrepancy of 4. It is a real advantage to be able to predict rates within a range of 10^5 within a factor of 2 to 4.

Experimental Part

Materials.—Ethylene dichloride, aluminum chloride and acetyl chloride were purified by the procedures previously described.[8,9] *o*-, *m*- and *p*-xylenes were Phillips Petroleum Co. products, pure grade. The other polymethylbenzenes were available from previous studies.[5] All of the hydrocarbons were examined by gas chromatography and demonstrated to be at least 99% pure by this analytical technique.

Competition Experiments.—The procedure utilized for the competitive reactions was identical with that utilized previously for establishing the toluene/benzene reactivity ratio.[9] The initial concentrations of the aromatic hydrocarbons were 0.100 to 0.600 M, according to the reactivity anticipated. The concentration of the acetyl chloride–

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(15) K. M. 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.

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

aluminum chloride complex was usually 0.040 to 0.050 *M*. An excess (100%) of acetyl chloride was used. Data for individual experiments are summarized in Table V.

The acetyl chloride–aluminum chloride solution in ethylene dichloride was added with vigorous stirring over a period of 10 minutes to the solution of hydrocarbons in ethylene dichloride. This solution was 0.0200 *M* in 1,2,4-trichlorobenzene, used as an internal standard to determine the concentrations of the products. The reaction mixture was allowed to stand for 10 minutes, and then quenched with an ice–sodium hydroxide mixture. The organic layer was washed twice with water and the greater portion of the solvent removed by careful distillation. The acetylation products were analyzed using a 2-m. column with a polyadipate substrate (Rubber Corporation polymeric BGA on Celite) at 185° and 80 cc. of helium per min.

Identification of the Isomeric Hemimellitene Acetylation Products.—The two peaks were individually collected in cyclohexane solution and examined with a Perkin–Elmer Infracord spectrophotometer. The isomer having retention time 17.8 min. exhibited a band at $12.30\ \mu$, characteristic of 1,2,3,4-tetrasubstituted benzenes,[17] and it was therefore assigned the structure 2,3,4-trimethylacetophenone. The isomer with a retention time of 24.0 min., exhibited a band at $11.30\ \mu$, characteristic of 1,3,4,5-tetra-substituted benzenes.[17] It was assigned the structure 3,4,5-trimethylacetophenone. For additional confirmation, collection of this peak was repeated several times until a sample was collected sufficiently large for conversion to the semicarbazone. Recrystallized from 95% ethanol, it melted at 215.5–216.5°, in satisfactory agreement with the m.p. reported for this derivative.[11]

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(17) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed., Methuen and Co., Ltd., London, 1958, pp. 78–79.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CONNECTICUT]

Friedel–Crafts Isopropylation of Acetophenone, Methyl Benzoate and Benzoic Acid[1]

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RECEIVED MARCH 30, 1959

The isopropylation of acetophenone, methyl benzoate and benzoic acid was studied to determine the composition of the resulting monoalkylated products. Although generally the yields were low, it was noted that with all the experimental conditions used the products were largely or entirely composed of the meta isomers. In most cases these isomers constituted 95% or more of the products. This is a far greater selectivity than has been observed in the nitration of these compounds, and can best be explained as resulting from complexing of the catalyst with the carbonyl oxygen to increase greatly the electron-withdrawing character of the substituent groups.

This paper describes the investigation of the isomeric composition of the products of Friedel–Crafts isopropylation of negatively substituted benzenes, in particular, acetophenone, methyl benzoate and benzoic acid. There are only three reports in the literature of the successful Friedel–Crafts alkylation of benzene compounds containing electron-withdrawing substituents. Baddeley[3] reports the alkylation of acetophenone and benzonitrile with methyl and ethyl ether. Benzaldehyde was alkylated with isopropyl and *t*-butyl chloride by Gilman and Burtner.[4] Aluminum chloride was the catalyst in both cases. Hydrogen fluoride and isopropyl ether was used by Calcott, Tinker and Weinmayr[5] to alkylate benzoic acid. In these three reports there was no clear evidence for the presence or absence of the *o*- or *p*-isomers. Further, the present authors desired to compare the results of the alkylation of acetophenone to those previously obtained in this Laboratory with 2-acetylthiophene[6] since the two compounds have in common the same electron-withdrawing substituent. In the latter case[6] it was found that neither the usual relative magnitudes of the directional influences of the acetyl group or the sulfur atom nor the influence of the incoming group could explain the preponderance of 4-isopropyl-2-acetylthiophene in the product.

The isopropylations of acetophenone, methyl benzoate and benzoic acid could each produce three monoisopropylated isomers. The first step in the quantitative investigation of these reactions was the preparation of these nine compounds by unequivocal syntheses which do not use the Friedel–Crafts reaction or depend on isomer separation. The nine are: from acetophenone, *o*-isopropylacetophenone (I), *m*-isopropylacetophenone (II) and *p*-isopropylacetophenone (III); from methyl benzoate, methyl *o*-isopropylbenzoate (IV), methyl *m*-isopropylbenzoate (V) and methyl *p*-isopropylbenzoate (VI); and from benzoic acid, *o*-isopropylbenzoic acid (VII), *m*-isopropylbenzoic acid (VIII) and *p*-isopropylbenzoic acid (IX). The infrared spectra of acetophenone, I, II and III, and mixtures of them were recorded and used to establish a scheme for the analysis of these four compounds in the products of the isopropylation of acetophenone. Similarly, an infrared analysis scheme was set up for the esters. The solid product acids from the isopropylation of benzoic acid were converted with diazomethane to the methyl esters for analysis The three substrate compounds were then isopropylated under a variety of conditions, and the products were analyzed by fractional distillation and infrared spectrophotometry.

Experimental[7]

***o*-Isopropylacetophenone (I).**—The starting material from which all the standard compounds with *ortho* configuration were derived was methyl anthranilate, Eastman Kodak Co.,

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(1) Based on part of the 1958 Ph.D. thesis of Bruce N. Campbell, Jr.

(2) To whom inquiries should be sent: Department of Chemistry, MacMurray College, Jacksonville, Ill.

(3) G. Baddeley, *J. Chem. Soc.*, S229 (1949).

(4) H. Gilman and R. R. Burtner, THIS JOURNAL, **57**, 909 (1935).

(5) W. S. Calcott, J. M. Tinker and V. Weinmayr, *ibid.*, **61**, 1010 (1939).

(6) E. C. Spaeth and C. B. Germain, *ibid.*, **77**, 4066 (1955).

(7) Melting points were taken with calibrated, completely immersed, short-range thermometers. Careful fractionation was done with a Wheeler, all-glass, vacuum, semi-micro fractionating column with a modified Sargent hollow-tube design, model number GV-130-2 of the Precision Distillation Apparatus Co. Microanalyses were performed by The Laboratory of Microchemistry, Teaneck, N. J. Each analytical value for carbon or hydrogen is the average of the values from two analyses.