

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

## Relative Rates of the Aluminum Chloride-Catalyzed Benzoylation of the Monoalkylbenzenes in Nitrobenzene Solution. Importance of Carbon-to-Carbon Hyperconjugation in Alkyl Substituents<sup>1,2</sup>

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A convenient procedure has been developed for following the rates of the aluminum chloride-catalyzed benzoylation of aromatics in nitrobenzene solution. Applied to the monoalkylbenzenes,  $\text{RC}_6\text{H}_5$ , this procedure gives the relative rates: R = Me, 1.00; Et, 0.89; *i*-Pr, 0.82; *t*-Bu, 0.69. In toluene 92% of the total reaction involves substitution in the *para* position. Consequently these results indicate that the rate of substitution *para* to the alkyl group decreases in the order, Me > Et > *i*-Pr > *t*-Bu. This order agrees with that predicted from the  $\sigma^+$  constants for these alkyl groups and indicates that carbon-to-carbon hyperconjugation in these alkyl groups must play a dominant role in controlling the rates of the benzoylation reaction in the *para* position.

Apparently conflicting results have recently appeared in the literature with regard to the relative influence of methyl and *t*-butyl groups in activating the *para* position of the aromatic ring toward electrophilic substitution. Thus, bromination in the *para* position occurs more readily in toluene than in *t*-butylbenzene.<sup>5,6</sup> This is the order which would be predicted on the basis of the  $\sigma^+$  constants which were recently proposed to correlate aromatic substitution.<sup>7</sup>

On the other hand, the rate of nitration in the *para* position has been reported to be greater for *t*-butylbenzene than for toluene.<sup>8</sup>

We recently examined the aluminum chloride-catalyzed benzoylation of toluene in nitrobenzene solution.<sup>9</sup> The reaction proceeds at a convenient rate and substitution involves the *para* position predominantly (92%). For this reason the reaction appeared eminently suitable for examining further the effect of alkyl substituents upon the rate of substitution in the *para* position. Accordingly, we undertook to determine the rates of benzoylation of methyl-, ethyl-, isopropyl- and *t*-butylbenzene.

**Results.** The original procedure<sup>9</sup> for following the benzoylation reaction involved hydrolyzing ali-

quots of the solution to convert unreacted benzoyl chloride to benzoic acid, followed by isolation and measurement of the benzoic acid. This procedure exhibited satisfactory precision, but proved to be very time-consuming.

Consequently, an alternative procedure was developed. In this method, aliquots of the reaction mixture were treated with water under carefully controlled conditions to remove aluminum chloride and hydrogen chloride without affecting the contained benzoyl chloride. The latter was then determined by utilizing a pyridine-catalyzed hydrolysis, followed by titration of the pyridine hydrochloride and benzoic acid formed in the hydrolysis.

Identical results were realized by both procedures. However, the latter procedure was far more convenient and it was adopted for the present rate determinations.

To test the reproducibility of the reaction, we redetermined the rates of benzoylation of benzene and toluene. With each reactant at 0.400 *M*, we obtained 3.5 order rate constants of 0.00620 l.<sup>2.5</sup> mole<sup>-2.5</sup> min.<sup>-1</sup> for benzene and 0.975 l.<sup>2.5</sup> mole<sup>-2.5</sup> min.<sup>-1</sup> for toluene, in excellent agreement with the values 0.00615 and 0.943 observed previously.<sup>9</sup> The ratio,  $k_{\text{toluene}}/k_{\text{benzene}}$  is 154, as compared with the rate ratio 151 based upon both the rate data and the observed half-lives of the reactions.<sup>9</sup>

Since the rate constants vary with the initial concentration of the aluminum chloride, the four monoalkylbenzenes were determined using a constant initial concentration of 0.200 *M* for each of the three reactants. The rate constants are summarized in Table I.

A series of measurements made with one particular preparation of aluminum chloride yielded values of the individual rate constants somewhat higher than those reported in Table I. However, the relative rates calculated from these rate constants (set B, Table I) were in satisfactory agreement with the other values (set A, Table I). These higher rate constants appeared to be due to the presence of traces of ferric chloride in the aluminum

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(4) Research assistant on a project supported by the Atomic Energy Commission, 1953-54; National Science Foundation Predoctoral Fellow, 1954-55.

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TABLE I  
RATE CONSTANTS FOR THE ALUMINUM CHLORIDE-CATALYZED BENZOYLATION OF THE  
MONOALKYLBENZENES IN NITROBENZENE SOLUTION AT 25°

Aromatic	Rate Constants <sup>a</sup> $k_{3,5}$ ( $l.^{2.5}$ mole <sup>-2.5</sup> min. <sup>-1</sup> )			A	Relative Rates	
	Duplicate	Values	Mean		B <sup>c</sup>	C <sup>d</sup>
Benzene	0.0144 <sup>b</sup>			1/154		1/151 <sup>e</sup>
Toluene	2.23	2.18	2.20	1.00	1.00	1.00
Ethylbenzene	1.86	1.84	1.85	0.84	0.93	0.89
Isopropylbenzene	1.80	1.78	1.79	0.81	0.83	0.82
<i>t</i> -Butylbenzene	1.58	1.53	1.55	0.71	0.67	0.69

<sup>a</sup> Concentrations:  $[ArH] = [C_6H_5COCl] = [AlCl_3] = 0.200M$ . <sup>b</sup> Calculated from the toluene rate at  $0.200M$  and the  $k_{toluene}/k_{benzene}$  ratio obtained with each component  $0.400M$ . <sup>c</sup> Relative rates obtained with aluminum chloride containing traces of ferric chloride. <sup>d</sup> Average relative rates. <sup>e</sup> Ref. (9).

chloride used as catalyst. It has been noted that minor amounts of ferric chloride in the aluminum chloride can have a marked accelerating effect upon the rate of the acylation reaction.<sup>10</sup>

Average values for the relative rates are summarized as set C in Table I.

*Discussion.* The benzylation of toluene results in the formation of 7.2% *ortho*, 1.1% *meta* and 91.7% *para* substitution. Unfortunately, similar data for the isomer distribution in the benzylation of the other monoalkylbenzenes are not now available. However, it is well known that the extent of *ortho* substitution decreases with the increasing steric requirements of the alkyl group. Thus the per cent of the *ortho* isomer decreases in nitration from 58.5% for toluene, to 45.0% for ethylbenzene, to 30.0% for isopropylbenzene, to 15.8% for *t*-butylbenzene.<sup>11</sup>

Fortunately, the benzylation reaction is one of large steric requirements with but 7% substitution in the *ortho* position of toluene and no significant error would be introduced by ignoring the extent of substitution in the *ortho* (and *meta*) positions. However, it probably involves a smaller uncertainty to estimate that the extent of *ortho* substitution decreases linearly with the degree of branching of the alkyl group. On this basis, the *ortho* substitution has been estimated as 5% for ethyl-, 2.5% for isopropyl- and 0% for *t*-butylbenzene.<sup>12</sup>

In this way the *para* partial rate factors have been calculated for the benzylation reactions. The results are summarized in Table II with related values for other reactions.

The marked difference in the  $\sigma^+$  values for *m*-

TABLE II

*Para* PARTIAL RATE FACTORS FOR THE MONOALKYLBENZENE

Reaction	Alkylbenzene, $RC_6H_5$			
	R = Me	Et	<i>i</i> -Pr	<i>t</i> -Bu
$\sigma^+$ Constants <sup>a</sup>	-0.306	-0.291	-0.276	-0.250
Benzylation <sup>b</sup>	830	755	715	615
Bromination (Br <sub>2</sub> )	2420 <sup>c</sup>			775 <sup>d</sup>
Bromination (Br <sup>+</sup> )	59 <sup>e</sup>			38.5 <sup>f</sup>
Nitration <sup>g</sup>	58			75

<sup>a</sup> Ref. 7. <sup>b</sup> Present study. <sup>c</sup> H. C. Brown and L. M. Stock, *J. Am. Chem. Soc.*, **79**, 1421 (1957). <sup>d</sup> Ref. 6. <sup>e</sup> P. B. D. de la Mare and J. T. Harvey, *J. Chem. Soc.*, 36 (1956). <sup>f</sup> P. B. D. de la Mare and J. T. Harvey, *J. Chem. Soc.*, 131 (1957). <sup>g</sup> Ref. 8.

and *p*-*t*-butyl was considered to require a large, hyperconjugative contribution from the *p*-*t*-butyl group.<sup>13-15</sup> The small increase in the values of the  $\sigma^+$  constants with increasing branching of the alkyl groups was considered to mean that each carbon-to-carbon bond was slightly less effective in hyperconjugation (a factor of 0.8 was indicated) than a corresponding carbon-to-hydrogen bond.<sup>14</sup> The satisfactory linear agreement between the log of the *para* partial rate factors and the  $\sigma^+$  constants (Fig. 1) indicates that hyperconjugation must also be playing a dominant role in determining the relative reactivity of the *para* positions in the benzylation reaction.

The  $\sigma^+$  constants clearly predict that the partial rate factors for substitution in the *para* position should decrease more or less regularly with increasing branching of the alkyl group. Such a decrease is observed for benzylation, for the uncatalyzed bromination in acetic acid (Br<sub>2</sub>), and the perchloric acid-catalyzed bromination with hypo-

(10) L. F. Martin, P. Pizzolato, and L. S. McWaters, *J. Am. Chem. Soc.*, **57**, 2584 (1935).

(11) K. L. Nelson and H. C. Brown, *J. Am. Chem. Soc.*, **73**, 5605 (1951); H. C. Brown and W. H. Bonner, *J. Am. Chem. Soc.*, **76**, 605 (1954).

(12) Acetylation of *t*-butylbenzene has been reported to yield 0% *ortho*, 1.8% *meta* and 98.2% *para*. J. C. Butler, L. L. Ferstandig, and R. D. Clark, *J. Am. Chem. Soc.*, **76**, 1906 (1954).

(13) N. N. Lichtin and P. D. Bartlett, *J. Am. Chem. Soc.*, **73**, 5530 (1951).

(14) H. C. Brown, J. D. Brady, M. Grayson, and W. H. Bonner, *J. Am. Chem. Soc.*, **79**, 1897 (1957).

(15) For an alternative interpretation, see W. M. Schubert, et al., *J. Org. Chem.*, **21**, 119 (1956), and *J. Am. Chem. Soc.*, **79**, 910 (1957).

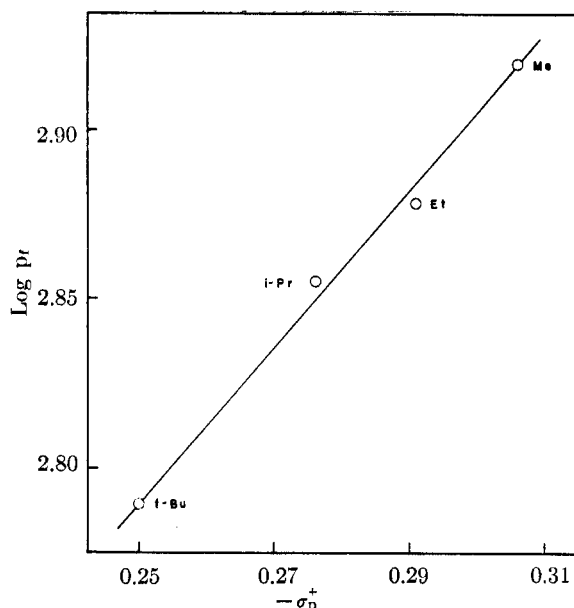


Fig. 1. Relationship between the *para* partial rate factors for the benzoylation reaction and the  $\sigma_p^+$  constants

bromous acid ( $\text{Br}^+$ ).<sup>16</sup> However, the nitration results of Hughes and his coworkers<sup>8</sup> constitute a serious exception to this correlation between the  $\sigma^+$  constants and the partial rate factors. This exception appears deserving of a renewed scrutiny.

#### EXPERIMENTAL

**Materials.** The nitrobenzene, benzoyl chloride, and aluminum chloride were carefully purified by the procedures previously described.<sup>9</sup> Benzene, toluene, ethyl-, isopropyl- and *t*-butylbenzene were carefully purified commercial samples. Purities, as established by cooling curves, were 99.5% or better.

**Analytical procedure.** Considerable time was devoted to the development of a convenient analytical procedure which would permit accurate determination of the unreacted benzoyl chloride. Since careful attention to detail is required for accurate results, the procedure will be fully described.

A 5-ml. sample was pipetted from the reaction vessel into a 125-ml. separatory funnel which contained 15 ml. of distilled water and 20 ml. of ice chips. The pipet was a fast delivery pipet and its delivery volume with nitrobenzene had been accurately determined. The separatory funnel

(16) The mercuration reaction also appears to exhibit the hyperconjugative order. H. C. Brown and C. W. McGary, Jr., *J. Am. Chem. Soc.*, **77**, 2310 (1955). Unfortunately, isomer distributions other than for toluene are not presently known. Moreover, reliable estimate of the *para* partial rate factors could not be made in the manner utilized for the benzoylation reaction, since mercuration results in relatively large amounts of substitution in both the *ortho* and *meta* positions. Consequently, the mercuration reaction was not included in Table II. We hope to obtain accurate experimental data on the isomer distribution for this reaction shortly.

was vigorously shaken for 20 seconds in order to stop the reaction and to bring the hydrogen chloride and aluminum chloride into the water layer. After allowing the solution to settle, the nitrobenzene was drained off and the aqueous layer extracted twice with 2 ml. portions of chloroform. Ten milliliters of ice water was added to the combined extracts, the mixture was shaken, 2 drops of phenolphthalein in acetone was added to the water layer, and then the water layer was neutralized with 0.03M sodium hydroxide.

Sufficient 85% pyridine-15% water mixture (neutralized to the phenolphthalein end point) was added to make the solution homogeneous. The solution was covered and allowed to stand for a definite time interval, 10 min. being sufficient to hydrolyze the acid chloride completely. The pyridine hydrochloride and benzoic acid formed were titrated with standard base to the phenolphthalein end point. During the titration, sufficient neutralized 95% ethanol was added to maintain the homogeneity of the solution.<sup>17</sup>

The results obtained in one experiment were checked by a procedure which has been previously reported.<sup>9</sup> In this procedure the sample from the reaction solution was hydrolyzed in base, the solution acidified, the benzoic acid extracted with ether, the ether evaporated, ethanol and water were added, and then the benzoic acid was titrated with standard base.

The results obtained by the two analytical procedures are given in Table III.

TABLE III

COMPARISON OF THE RESULTS OBTAINED USING DIFFERING ANALYTICAL PROCEDURES

Time, <sup>b</sup> min.	Unreacted Benzoyl Chloride <sup>a</sup>		Differ- ence
	Method A <sup>c</sup>	Method B <sup>d</sup>	
3.6	0.2263	0.2398	0.0035
10.0	.1916	.1961	.0045
19.2	.1571	.1604	.0033
28.8	.1372	.1413	.0041
38.7	.1230	.1258	.0028
47.7	.1139	.1183	.0044
57.4	.1051	.1097	.0046

<sup>a</sup> Reaction mixture:  $[\text{C}_6\text{H}_5\text{CH}_3] = [\text{C}_6\text{H}_5\text{COCl}] = [\text{AlCl}_3] = 0.309 \text{ M}$ , in nitrobenzene solution. <sup>b</sup> The samples were removed from the same reaction mixture at the times indicated. <sup>c</sup> Method A: pyridine-catalyzed hydrolysis. <sup>d</sup> Method B: isolation of benzoic acid, ref. (9).

The values given for Method B (isolation of benzoic acid) were not corrected for the usual small blank measurements. Such corrections would largely eliminate the present small differences in the two sets of data. The accuracy of the two methods is seen by comparing the differences which are always in the same direction. The samples were taken simultaneously using two pipets which were alternated from sample to sample. Since the pipets did not deliver exactly the same volume the differences are alternately low and high. The analytical data reported in Table III by method B were obtained by Dr. H. L. Young.

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(17) Pyridine has been used previously in analytical procedures to assist in the hydrolysis of acid halides. D. Klamann, *Monatsh. Chem.*, **83**, 719 (1952) and references cited therein.