

10 hr., until the rate of loss in weight became constant (approximately 0.5 mg. per 10 hr. period). Appropriate small corrections were applied to the data to correct for this loss of weight.

This procedure was thoroughly tested with blank experiments. Known samples of benzophenone of 0.1 to 0.3 g. in benzoyl chloride could be determined with an error of approximately 2 parts per 1000. The procedure also was tested by comparing the gravimetric results with an ultraviolet analysis utilizing the peak at 2540 Å. Close agreement was realized.

TABLE V

COMPARISON OF ANALYSES FOR BENZOPHENONE IN A KINETIC RUN BY GRAVIMETRIC AND SPECTROSCOPIC (ULTRAVIOLET) PROCEDURES

Time, min.	Benzophenone, g.		Deviation
	Gravimetric ^a	U.v. analysis	
35	0.0488	0.0487	-0.0001
100	.1087	.1092	+ .0005
215	.1677	.1678	+ .0001
310	.1998	.1984	- .0014
405 ^b	.2219	.2235	+ .0016

^a Adjusted, as described in text. ^b 55% reaction.

Kinetic Procedure.—The reactions were carried out in calibrated reaction vessels fitted with ground glass stoppers, with a side-arm just below the mouth. This side-arm was connected to a nitrogen supply with a pressure approxi-

mately 3 cm. above atmospheric, so that removal of the stopper immediately resulted in a flow of dry nitrogen out of the mouth of the flask.

The desired amount of the standard solution of aluminum chloride was transferred from the buret (Fig. 1) to the calibrated reaction vessel and diluted with pure benzoyl chloride to the desired concentration. The solution was brought to the desired temperature in a constant temperature bath ($\pm 0.01^\circ$) and the reaction initiated by adding the benzene from a special all-glass hypodermic syringe, followed by vigorous stirring. This item was constructed by drawing the end of a glass syringe into a long capillary. The amount of benzene was determined by weighing the syringe before and after adding the aromatic to the reaction mixture. In some cases relatively concentrated solutions were used and it was feared that the usual assumption of additive volumes of the various solutions might lead to significant errors. Therefore, the volume of the reaction solution was noted and the concentrations were calculated using this volume.

At appropriate intervals of time aliquots were removed with pipets and analyzed for benzophenone as described above. The tips were cut from these pipets to increase the rate of flow. The amount delivered by the pipet varied markedly with the temperature of the reaction solution and the rate of flow from the pipet. Consequently, the pipets were calibrated with benzoyl chloride at the appropriate temperature, with the pipet at room temperature. Fortunately, this procedure permitted the delivery of reproducible, constant aliquots of the reaction mixtures.

Data for a typical kinetic study are reported in Table I.

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

Relative Rates of the Aluminum Chloride-catalyzed Benzoylation of Representative Benzene Derivatives in Benzoyl Chloride Solution. Partial Rate Factors for the Benzoylation of Toluene^{1,2}

BY HERBERT C. BROWN AND FREDERICK R. JENSEN³

RECEIVED SEPTEMBER 26, 1957

Second-rate constants for the benzoylation reaction (aluminum chloride in benzoyl chloride) were determined for a number of representative benzene derivatives. The relative reactivities at 25° are: benzene, 1.00; toluene, 110; *t*-butylbenzene, 73; chlorobenzene, 0.0115; *o*-xylene, 1120; *p*-xylene, 140; *m*-xylene, 3940. The isomer distribution in the benzoylation of toluene under these conditions is 9.3% *ortho*, 1.45% *meta* and 89.3% *para*. From the relative rates and isomer distributions the partial rate factors for the benzoylation of toluene under these conditions are calculated to be: σ_o , 30.7; m_i , 4.8; p_i , 589. These partial rate factors are in excellent agreement with the Selectivity Relationship. The rates calculated from these factors for the benzoylation of the three xylenes are in fair agreement with the observed rates. Finally, the rates of benzoylation of the monosubstituted benzenes correlate well with the σ^+ constants.

The acylation of aromatics is a simple substitution reaction with desirable characteristics for our studies both of directive effects in aromatic substitution and of the role of Lewis acid catalysts on the rates of Friedel-Crafts reactions. Our first attempts to study the benzoylation of aromatics for this purpose utilized nitrobenzene as a solvent.⁴ Unfortunately, in this solvent the reaction exhibited complex kinetics with respect to the aluminum chloride. Moreover, in the case of the higher methylbenzenes deeply colored solutions were obtained which pointed to the formation of ternary complexes involving nitrobenzene, aluminum chloride and the aromatic.⁵

The observation that the benzoylation of benzene with aluminum chloride in benzoyl chloride solution exhibits simple second-order kinetics⁶ encouraged us to examine the utility of this reaction for our purposes. Accordingly a study was undertaken of the rates of benzoylation of toluene, *t*-butylbenzene, chlorobenzene, *o*-, *m*- and *p*-xylene, and of the isomer distribution in the benzoylation of toluene. A related study of the effect of various Friedel-Crafts catalysts on the reaction rate will be reported in a later publication.

Results

The benzoylation of toluene was carried out in the identical manner previously utilized for benzene.⁶ The reaction proceeded smoothly to the formation of methylbenzophenones in essentially quantitative yield. Since the rates were much greater than in the corresponding reaction of benzene, a lower range of temperatures was utilized to obtain the enthalpy and entropy of activation.

(1) Directive Effects in Aromatic Substitution. XXII.

(2) Based in part upon a thesis submitted by F. R. Jensen in partial fulfillment of the requirements for the Ph.D. degree.

(3) Research assistant on a project supported by the Atomic Energy Commission, 1953-1954; National Science Foundation Predoctoral Fellow, 1954-1955.

(4) H. C. Brown and H. L. Young, *J. Org. Chem.*, **22**, 719, 724 (1957).

(5) H. C. Brown, B. A. Bolto and F. R. Jensen, *ibid.*, **23**, 414 (1958).

(6) H. C. Brown and F. R. Jensen, *THIS JOURNAL*, **80**, 2219 (1958).

The rate constants are reported in Table I and the derived data are summarized in Table II.

TABLE I
RATE CONSTANTS AND RELATIVE RATES FOR THE BENZOYLATION OF REPRESENTATIVE AROMATICS IN BENZOYL CHLORIDE SOLUTION

Compound	0.0°	Rate constants, k_2 , l. mole ⁻¹ min. ⁻¹		Relative rates, 25°
		15.00°	25.00°	
Benzene			0.00297	1.00
Toluene	0.0430	0.143	0.326	110
<i>t</i> -Butylbenzene			0.215	73
Chlorobenzene			$(3.4 \times 10^{-5})^{a,b}$	0.0115
<i>o</i> -Xylene			3.33	1120
<i>m</i> -Xylene			11.7	3940
<i>p</i> -Xylene			0.415	140

^a Calculated from the rate constant at 70°, assuming that $\Delta S^\ddagger = -27$ e.u. ^b 0.00185 at 70.0°.

TABLE II
DERIVED DATA FOR THE BENZOYLATION OF BENZENE AND TOLUENE IN BENZOYL CHLORIDE SOLUTION

Compound	Energy of activation ^a		Enthalpy of activation ^b		Entropy of activation, ^b ΔS^\ddagger , e.u.
	E_{act} , kcal./mole	og A^a	ΔH^\ddagger , kcal./mole		
Benzene	15.8	7.28	15.1	-27.2	
Toluene	13.3	7.49	12.6	-26.7	

^a Arrhenius' parameters. ^b Calculated from the equation, $\ln k = (-\Delta H^\ddagger + T\Delta S^\ddagger)/RT + \ln(k_0T/h)$.

The reaction with *t*-butylbenzene proceeded at a slightly slower rate than that of toluene. In the case of the xylenes, the *ortho* and *meta* isomers reacted so rapidly that kinetic data could only be obtained for the latter portion of the reaction and the rate constants were calculated from these data. In view of the fact that all reactions yielded excellent second-order plots to better than 90% reaction, it is believed that this procedure has not introduced any significant error.

The reaction of chlorobenzene was quite slow, even at 70°. To operate at higher temperatures would have required modification of our kinetic procedure with extensive testing to ensure that the modification was not introducing any new uncertainties in the results. In order to avoid this difficulty, we decided to utilize the similarity in the entropies of activation for benzene and toluene and to extrapolate the rate constant for chlorobenzene at 70° down to 25° by assuming that the entropy of activation for this reaction is -27 e.u.

The isomer distribution in the benzylation of toluene was determined by infrared analysis of the product. Preliminary experiments indicated that the *ortho* was present to the extent of 9%, with the *para* isomer constituting almost all of the remainder of the product. The product from a small scale benzylation reaction (0.04 mole) was therefore analyzed by maintaining the *ortho* isomer at 9.00%, while the *meta* to *para* composition was systematically varied in order to fix the *meta* content. This procedure indicated the presence of 1.38% of *m*-methylbenzophenone in the product.

The second determination was carried out on a much larger scale (2.66 moles) and a large fraction of the *para* isomer present (63.8%) was removed by fractional crystallization prior to the infrared

analysis. The *ortho* and *para* isomers were determined in carbon disulfide solution. Because of the low intensity of the usual *meta* peaks and the low concentration of this isomer, the analyses for *meta* were carried out at very high ketone concentrations using solutions of the *ortho* and *para* isomers in the reference beam.

The isomer distributions obtained in this way are summarized in Table III.

TABLE III
DISTRIBUTION OF ISOMERS IN THE REACTION OF BENZOYL CHLORIDE-ALUMINUM CHLORIDE WITH TOLUENE IN BENZOYL CHLORIDE AS SOLVENT AT 25°

Reagents, M $AlCl_3$	$CH_3C_6H_5$	Product G.	Yield, %	Isomer distribution, %		
				<i>ortho</i>	<i>meta</i>	<i>para</i>
0.40	0.70	7.8	99		1.38	
.76	.77	511.5	97.9	9.3	1.52	89.2
Adopted values				9.3	1.45	89.3

From the relative rates of benzylation of toluene and benzene of 110 (Table I) and the isomer distribution (Table III), the partial rate factors are calculated to be o_t 30.7, m_t 4.8 and p_t 589.

Discussion

Some time ago, in attempting to account for the high yields of *meta* isomer in the Friedel-Crafts alkylation of toluene, it was suggested that the isomer distribution realized in electrophilic substitutions will be markedly influenced by the "activity" of the attacking reagent.⁷ A highly active reagent will not differentiate significantly between the *meta* and *para* positions of toluene; a reagent of low activity will exhibit considerable selectivity between these positions.

Development of this concept led to a proposed quantitative relationship for the substitution reactions of toluene^{7,8}

$$\log p_i = c \log (p_i/m_i)$$

Considerable success has now been realized in correlating the substitution reactions of toluene by means of this Selectivity Relationship.⁹

The benzylation reaction in benzoyl chloride solution yields a relatively high toluene/benzene rate ratio with relatively low *meta* substitution. In terms of the above interpretation, it would be considered a reaction of low "activity" and high "selectivity." It is apparent from Fig. 1 that the agreement with the Selectivity Relationship is good.

Previously, partial rate factors for the benzylation reaction in nitrobenzene as solvent were determined (Table IV).⁴ In this solvent the kinetics were not simple, as they are in benzoyl chloride. As a result there is necessarily some uncertainty in interpreting the rate data and in reducing the measurements to a precise rate ratio. However, it appears that the difference in the two k_T/k_B values, 151 in nitrobenzene and 110 in benzoyl chloride, is greater than can be attributed to this factor and probably represents a real difference in the two reactions. Nevertheless, benzylation under both conditions obeys the Selectivity Relationship (Fig.

(7) H. C. Brown and K. L. Nelson, *THIS JOURNAL*, **75**, 6242 (1953).

(8) H. C. Brown and C. W. McGary, Jr., *ibid.*, **77**, 2300, 2306, 2310 (1955).

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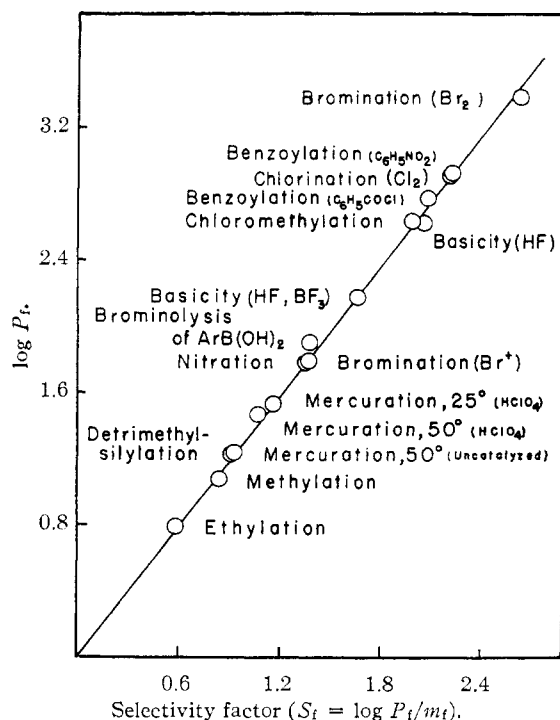


Fig. 1.—The benzoylation reaction in the selectivity relationship for toluene.

1). This suggests that the solvent can serve to modify both the "activity" and the "selectivity" of the attacking species. It was previously demonstrated that the catalyst, perchloric acid, could likewise influence both the relative rates and the isomer distributions in the mercuration of aromatics⁸ (Fig. 1).

TABLE IV

PARTIAL RATE DATA FOR THE BENZOYLATION OF BENZENE AND TOLUENE IN NITROBENZENE AND BENZOYL CHLORIDE

$k_{\text{Toluene}}/k_{\text{Benzene}}$	Nitrobenzene ^a	Benzoyl chloride ^b
Relative rates (25°),	151	110
Isomer distribution, %		
ortho	7.2	9.3
meta	1.1	1.45
para	91.7	89.3
Partial rate factors		
ρ_i	32.6	30.7
m_i	5.0	4.8
p_i	831	589

^a Ref. 4. ^b This study.

It was of interest to test the utility of the partial rate factors in calculating the relative rates of benzoylation of the higher methylbenzenes. Excellent results had been realized previously in calculations of this kind for mercuration,⁸ bromination¹⁰ and chlorination.¹¹ However, serious discrepancies were observed for the benzoylation reaction in nitrobenzene solution.⁵ These discrepancies were attributed to the formation of relatively stable ternary aluminum chloride-nitrobenzene-aromatic complexes.^{5,12}

(10) H. C. Brown and L. M. Stock, *THIS JOURNAL*, **79**, 1421 (1957).

(11) H. C. Brown and L. M. Stock, *ibid.*, **79**, 5175 (1957).

(12) H. C. Brown and M. Grayson, *ibid.*, **75**, 6285 (1953).

The calculated and observed relative rates are summarized in Table V. The agreement is an improvement over that realized in nitrobenzene, but less satisfactory than that observed for mercuration, chlorination and bromination. Unfortunately the reaction rate was already very great in the case of *o*- and *m*-xylene, so that it was impractical to extend this reaction to the higher, more reactive methylbenzenes.

TABLE V

OBSERVED AND CALCULATED RELATIVE RATES OF BENZOYLATION OF THE METHYLBENZENES

	Obsd. Relative rate	Calcd.	Ratio Obsd./calcd.
Benzene	1.00	1.00	
Toluene	110	110	
<i>o</i> -Xylene	1120	993	1.13
<i>m</i> -Xylene	3940	6190	0.64
<i>p</i> -Xylene	140	99	1.41

In toluene approximately 90% of the reaction involves substitution in the *para* position. In *t*-butylbenzene little or no substitution in the *ortho* position would be expected.¹³ Consequently, the observed relative rate may be attributed entirely to substitution in the *para* position. This leads to a partial rate factor for benzoylation in the position *para* to the *t*-butyl group of 430 as compared to 589 for the corresponding factor *para* to the methyl group. This decrease is consistent with the great majority of substitution data.¹⁴

The steric requirements of a chlorine atom and a methyl group are quite similar. Consequently, it may be assumed that the benzoylation of chlorobenzene likewise proceeds predominantly in the *para* position. This assumption leads to an estimated value for the *para* partial rate factor of 1/14.6.

It was suggested recently that the rates of aromatic substitution might be correlated by means of σ^+ constants derived from the solvolysis of substituted phenyldimethylcarbinyl chlorides.¹⁵ The available data on the benzoylation of the substituted benzenes does indeed yield a reasonably good linear plot, with a value of $\rho = -9.57$ (Fig. 2).

Recently Smeets and Verhulst¹⁶ determined the rates of benzoylation of benzene, toluene, bromobenzene and chlorobenzene and reported that a plot of their rate data *versus* the Hammett σ constants yielded a linear relationship. This was puzzling, in view of the evidence that it is the σ^+ rather than the σ values which apply to aromatic substitution. Accordingly, we examined this plot. These authors plot the logarithms of the total rates *versus* σ and such a plot does indeed give a satisfactory linear relationship. However, if the conclusion is accepted that the observed rate in toluene, chlorobenzene and bromobenzene ap-

(13) 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, *THIS JOURNAL*, **76**, 1906 (1954).

(14) For a detailed discussion of this question with pertinent references, see H. C. Brown, B. A. Bolto and F. R. Jensen, *J. Org. Chem.*, **23**, 417 (1958).

(15) H. C. Brown and Y. Okamoto, *THIS JOURNAL*, **79**, 1913 (1957).

(16) F. Smeets and J. Verhulst, *Bull. soc. chim. Belg.*, **63**, 439 (1954).

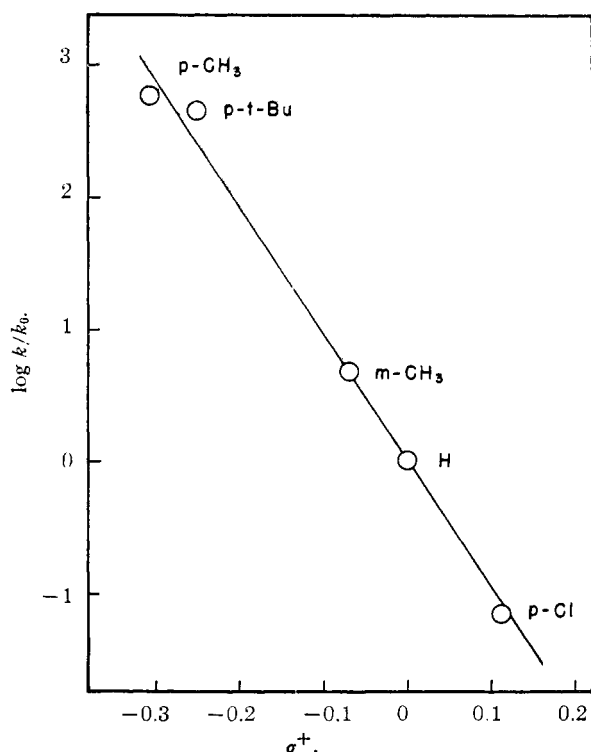


Fig. 2.—Correlation of the partial rate factors for the benzoylation reaction in benzoyl chloride with the σ^+ constants.

plies largely to substitution in the *para* position ($\sim 90\%$), whereas benzene possesses six equivalent positions, the observed rate must be corrected for the statistical factor of 6 to obtain the partial rate factors. With this correction the data no longer give a satisfactory linear plot *versus* σ , but they are correlated reasonably well by the σ^+ constants (Fig. 3).

Experimental Part

Materials.—The aromatic derivatives were carefully purified and exhibited purities of at least 99.5% by cooling curve analysis. The isomeric methylbenzophenones used for the infrared analyses were pure samples synthesized by H. L. Young.⁴ Carbon disulfide used in these analyses was distilled from mercuric chloride and stored over calcium hydride. The benzoyl chloride and aluminum chloride were purified and handled in the manner described previously.⁶

Kinetic Measurements.—The procedure was identical to that used in the kinetic study of the benzoylation of benzene.⁶ The lower volatility of the substituted benzophenone as compared to the parent compound simplified the isolation and weighing of the product. Whereas benzophenone exhibited a weight loss of approximately 0.5 mg. per 10 hr. period in the desiccator,⁶ the substituted benzophenones showed no significant loss and readily could be brought to constant weight.

Determination of the Isomer Distribution in the Benzoylation of Toluene. Procedure A.—Aluminum chloride, 0.0400 mole in 93 ml. of benzoyl chloride at 25.0°, was treated with 6.35 g. of toluene (0.070 mole) over a period of 5 min. The flask was maintained in the bath for 60 min. The solution was then poured into a 20% excess of 4 *M* sodium hydroxide and hydrolysis accomplished by shaking the solution vigorously while heating on the steam-bath. (This operation should be performed cautiously since the reaction can become violent. However, it can be performed satisfactorily provided the mixture is agitated vigorously as the temperature is raised.) At the conclusion of the reaction, a clear aqueous layer is obtained, surmounted by a clear ketone layer.

The solution was extracted three times with 100 ml. of chloroform. Each extract was washed with 500 ml. of distilled water and the wash solution was returned to the alkaline solution after each extraction. The solvent was removed under reduced pressure. The product was obtained as an oily solid, m.p. 45–56°, 7.8 g., a yield of 99% based on the aluminum chloride used.

For the quantitative analysis, the absorption peaks used were 8.3 μ for *meta*, 12.8 μ for *para* and 13.2 μ for *ortho*. Preliminary experiments established the concentration of the *ortho* derivative to be 9%. A number of standard solutions were prepared containing 9.00% by weight of the *ortho* isomer, and 0.75, 1.50, 2.25 and 3.00% by weight of the *meta*, with the *para* making up the difference. These known mixtures were placed in the reference cell and compared directly with the product in the other cell, using a concentration of 2.6 g. of ketone in 5 ml. of carbon disulfide solution. These measurements led to an estimate of 1.38% of *m*-methylbenzophenone in the product.

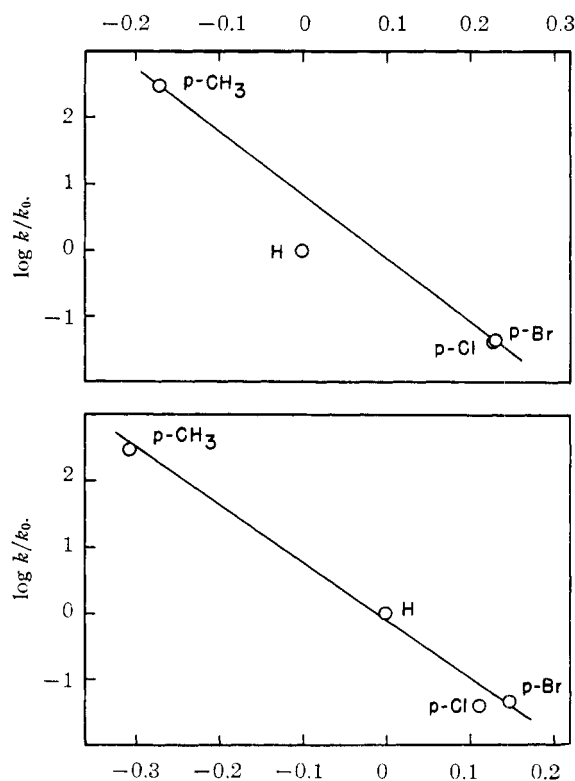


Fig. 3.—Correlation of the partial rate factors calculated from the benzoylation data of Smeets and Verhulst with the σ (upper) and σ^+ (lower) constants.

Procedure B.—The aluminum chloride (355 g., 2.66 moles) was dissolved in 3.1 l. of purified benzoyl chloride in a 5-l. flask. The flask was placed in a constant temperature bath at 25.0°, and when it had reached bath temperature, 250 g. of toluene (2.71 moles) was added over a period of 15 min. After 55 min. additional, the contents were poured into 19 l. of 4 *M* sodium hydroxide (10% excess of the calculated amount) and hydrolyzed using the precautions mentioned in Procedure A.

The ketone product was obtained by four extractions with petroleum ether, followed by an extraction with chloroform. The chloroform was evaporated and the residual solid (trace) added to the ether. The ether was distilled, no attempt being made at this time to remove the last traces. A portion of the *para* isomer was removed by consecutive recrystallizations using a procedure similar to that developed by H. L. Young,⁴ but utilizing petroleum ether to facilitate separation of the pure *para* isomer. In this way the product, 511.5 g., 97.9% yield, was separated into 326.3 g. of the pure *p*-methylbenzophenone and a liquid fraction of 185.2 g. containing all three isomers.

The *o*- and *p*-methylbenzophenone content of this liquid

fraction was determined at a total concentration of 0.2 g./5 ml. of carbon disulfide solution, with pure solvent in the reference cell. The concentration of the *meta* isomer was determined in concentrated solution by the method utilized in Procedure A. Summing up the results for the liquid

fraction and the amount of the pure *para* isomer separated resulted in an analysis of 9.3% *ortho*, 1.52% *meta* and 89.2% *para*.

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[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Shifts in Nuclear Magnetic Resonance Absorption Due to Steric Effects. I. 2-Halobiphenyls

By S. BROWNSTEIN

RECEIVED SEPTEMBER 20, 1957

A shift in proton resonance absorption toward higher field is observed for some of the protons in 2-halobiphenyls and is attributed to steric effects of the halogen upon the *ortho* protons of the unsubstituted ring.

Introduction

In 2-substituted biphenyls the benzene rings may be twisted out of a common plane if the 2-substituent is large enough. For the 2,2'-halobiphenyls this effect has been measured by electron diffraction experiments, and has been studied in terms of ultraviolet spectra and dipole moment data.¹⁻³ The angle between the benzene rings also has been determined for biphenyl and 2-fluorobiphenyl, and found to be the same within experimental error; but this angle has not been determined for the other 2-halobiphenyls.¹ This twisting of the benzene rings is required so that the *ortho* groups on the two rings do not overlap.

A proton resonance shift attributed to steric effects has been observed for the 4- and 5-protons in phenanthrene.⁴ The aromatic rings are bent out of a common plane in order to avoid overlap of the 4- and 5-hydrogens. Since this situation is similar to that of the 2-substituted biphenyls, a proton resonance shift might also be expected in these compounds.

The proton magnetic resonance spectra of the 2-halobiphenyls and of the 4-halobiphenyls were obtained. It was hoped that any structure of the proton absorption signal due to electronic effects would be similar in both cases. Thus the change in the spectrum due to steric effects in the 2-substituted cases could be isolated.

Experimental

The nuclear magnetic resonance spectra were obtained with a Varian model V 4300B spectrometer equipped with an auxiliary stabilizer model VK 3506 and using a 12" Varian magnet. The samples were contained in cylindrical glass tubes having an inside diameter of 3 mm. The sample tubes were filled with about 0.4 cc. of sample and sealed, but the actual volume contained within the receiver coil was only 0.01 cc. The samples were rotated at a speed of 500-1500 r.p.m. to effectively improve the uniformity of the magnetic field. The spectrometer was operated at a frequency of 40 Mc. and a magnetic field of approximately 9400 gauss.

Measurements of the frequency shifts were obtained by superimposing an audio-frequency signal, from a Hewlett Packard model 200CD audio oscillator, upon the sawtooth sweep voltage applied to modulate the magnetic field.⁵

This produced sidebands about the proton resonances with a separation corresponding to the frequency of the audio-oscillator. The spectra were recorded on a strip chart recorder and the separation of the sidebands used to calibrate the trace obtained. By this procedure the accuracy is thought to be about 1 cycle per second.

Relative intensities were obtained by cutting out and weighing the chart paper enclosed by the trace. It was found that different results were obtained from the Sanborn recorder supplied with the spectrometer (2" chart) and from a Leeds-Northrup Speedomax recorder (10" chart), although the results were reproducible for a given recorder. The intensities presented were obtained from the 10" chart.

Changing the bulk diamagnetism of a sample, and dilution in the case of aromatic compounds, may alter the position of the proton resonance absorption with respect to an absolute standard.⁶ However, the measurements of interest in this study are the separation of closely adjacent peaks. Since they would be affected in a similar manner the separation between them would change very little. Therefore it is unnecessary to consider any changes due to differences in bulk diamagnetism or in concentration of the solutions. The spectra of 2-bromo- and 2-iodobiphenyl were obtained from the pure liquids, and that of 4-iodobiphenyl in a saturated dioxane solution. In the latter case the signal due to the solvent is sufficiently removed from the one due to 4-iodobiphenyl so that it is beyond the region shown in Fig. 2. The spectra of the other compounds were obtained in saturated carbon tetrachloride solutions. The magnetic field decreases from left to right in all spectra except 4-iodobiphenyl. In this case the field is increased to the right in order to avoid ringing from the very intense absorption due to the solvent.

Except for 2-fluorobiphenyl all the compounds studied were purchased from various chemical supply houses and used without further purification. There would be little effect due to small amounts of impurities since it is primarily the separation between the principal peaks which is of interest in this discussion.

2-Fluorobiphenyl was prepared by the Schieman reaction and had a m.p. 71-72°.⁷

Results

The significant features of the N.M.R. spectra are summarized in Table I. Δ is the difference in parts per million of the applied field between the observed peaks.

The fluorine resonance absorption of 2-fluorobiphenyl and 4-fluorobiphenyl are envelopes of width 24 cycles each or 0.60 Δ unit.

For 2-chloro-, 2-bromo- and 2-iodobiphenyl, the intensity ratios of the peaks are 2:4.7, 2:5.3 and 2:8.2, respectively, compared to a theoretical ratio of 2:7.

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(4) C. Ried, *J. Molec. Spectros.*, **1**, 18 (1957).
(5) J. T. Arnold and M. E. Packard, *J. Chem. Phys.*, **19**, 1608 (1951).