

of the added diazonium ion was used as a criterion for the acceptance of the measurements of the rate and equilibrium constants.

Buffers.—Eastman Kodak Co. trichloroacetic acid was used without further purification. Dichloroacetic acid was distilled at atmospheric pressure through a 50-cm. Vigreux column. The fraction boiling between 193.5 and 194.5° was collected and used for the preparation of buffers.

The buffer solutions were prepared by adding weighed amounts of the acid to a known volume of 2.0×10^{-3} molar sodium hydroxide in methanol, which had been standardized by titration with standard hydrochloric acid.

Rate and Equilibrium Measurements.—The sulfinate or sulfinic acid and the diazonium salts were prepared in separate *ca.* 10^{-2} molar stock solutions; the diazonium salt solutions were stabilized by the addition of 10^{-3} molar HCl. On further dilution, this amount of acid was neglected. Measured samples of each of the stock solutions were diluted with the buffer solution, mixed, and placed in the absorption cell. The reaction was followed by the change in absorbance of the solutions near 320μ . When no further change with time was noted, the entire spectrum from 220μ

to 360μ was recorded. This spectrum was used for the analysis of the reaction mixture for the components.

Another sample of the same buffer, and another sample of sulfinate solution were mixed alone to determine the fraction, *f*, in the ionized form.

The spectrum of the diazosulfone was determined from the absorbance of *ca.* 10^{-2} molar solutions of the reactants in thin cells, so that dissociation would be small. Measurements were made rapidly after mixing in order to eliminate as much as possible the decomposition of the diazosulfone as a factor in the measurement. Although some error could have been introduced from this decomposition, it was possible to obtain reproducible spectra. The minor corrections for dissociation in these solutions were calculated after first tentative association constants were calculated, then the new extinction coefficients were used to calculate refined association constants. Further cycles were not necessary.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO, CHICAGO 37, ILL.]

Rates, Relative Rates and Product Distributions for the Non-catalytic Chlorination of Benzene, Toluene and *t*-Butylbenzene in Certain Non-aqueous Non-hydroxylic Solvents. The Influence of Solvent on the Reaction and the Baker-Nathan Effect

BY LEON M. STOCK AND ALBERT HIMOE¹

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The non-catalytic chlorination of benzene, toluene, *t*-butylbenzene and *p*-xylene has been examined in several solvents with particular reference to the influence of the reaction medium on the relative rate: k_{p-Me}/k_{p-t-Bu} . Certain results for the absolute rates of reaction, competitive measurements of relative rates and product distributions for the chlorination of the aromatics in nitromethane, nitrobenzene, acetonitrile, acetic anhydride and chlorobenzene are presented in this manuscript. In summary, the absolute rate of chlorination of toluene in nitromethane was approximately 10^4 greater than the rate in chlorobenzene. Product distributions were observed to be dependent on the reaction solvent. Moreover, the selectivity of the reagent chlorine was found to be appreciably modified by the solvent. However, the relative rate, k_{p-Me}/k_{p-t-Bu} , was not altered significantly beyond the variation expected for the observed reagent selectivity and was measured to be somewhat larger in these solvents than in aqueous acetic acid media.

Introduction

Considerable interest in the Baker-Nathan effect has led to a number of different views concerning its origin.² Of the alternative explanations for the apparent greater electron donor ability of a methyl substituent compared to a *t*-butyl substituent in certain electron-deficient reactions, two ideas have become familiar. The concept of hyperconjugation³ as an electrical influence and the suggested steric inhibition of solvation by the *t*-butyl group have been presented in detail.^{2,4} In a recent study, these alternatives have been examined through an investigation of the influence of solvent on reactivity and relative reactivity in a typical electrophilic substitution reaction.⁵

The non-catalytic chlorination reaction of benzene and the alkylbenzenes was selected as the model reaction for the evaluation of substituent effects on the basis of its high selectivity, $\rho = -10$, the relatively simple kinetics and mechanism, the highly electron-deficient transition state and the

dependence of the reaction rate on the composition of the solvent.⁶ This reaction was examined in six acetic acid solvents varying in water content from 0.0 to 27.6 *M*. The absolute rate of chlorination of benzene changed by 6.3×10^3 from the anhydrous to highly aqueous media. However, the relative rates for the alkylbenzenes compared to benzene exhibited only minor changes. Indeed, the quantity $\log p_{t-Me}/\log p_{t-Bu}$ was 1.10 ± 0.02 among the six solvents. On the basis of these observations, it was concluded that the Baker-Nathan effect did not have its origin in solvation phenomena.⁵ It is clear that the results are not decisive as the relative importance of solvation of the electron-deficient aromatic residue and the departing chloride ion has not been assessed. In an attempt to evaluate the importance of solvation as a stabilizing factor on the two fragments of the transition state, it appeared desirable to examine a group of structurally different solvents. In the different reaction media, the degree of solvation of the component parts of the activated complex could be expected to vary according to the properties of the polar and non-polar fragments of the solvent. This approach appeared to offer an opportunity to assess the influence of major structural variations

(1) Research Corporation Fellow, 1959-1961.

(2) For a partial review see, *Tetrahedron*, **5**, 107 (1959).

(3) R. S. Mulliken, C. A. Rieke and W. G. Brown, *J. Am. Chem. Soc.*, **63**, 41 (1941).

(4) W. M. Schubert, J. M. Craven, R. G. Minton and R. B. Murphy, *Tetrahedron*, **5**, 194 (1959); W. M. Schubert and R. G. Minton, *J. Am. Chem. Soc.*, **82**, 6188 (1960).

(5) L. M. Stock and A. Himoe, *ibid.*, **83**, 1937 (1961).

(6) See ref. 5 for literature citations and a more detailed discussion.

in the solvent on the electrical influences of the alkyl groups.

The experimental problem was greatly assisted by the recent report by Andrews and Keefer concerning the chlorination reaction in several non-aqueous solvents.⁷ Surprisingly, the relative rate of chlorination of toluene compared to benzene was reported as 1530/1.00 in acetonitrile⁷ contrasted to the value of 300/1.00 found for the reaction in acetic acid.⁵ This observation indicated a major change in the selectivity of the reagent halogen in the different solvents. The kinetic results were further substantiated through an examination of the solvent effect on the products of chlorination of toluene.⁸ For example, the more selective reaction in acetonitrile was found to yield 62% *p*-chlorotoluene in contrast to only 40% *p*-product for chlorination in acetic acid solvents.^{5,8} Preliminary results for non-aqueous acids, *e.g.*, for chlorination in pivalic acid and trifluoroacetic acid,⁸ revealed the same product ratio as obtained in acetic acid media. The invariant isomer distributions presumably reflected the unchanged selectivity of the reaction conditions. Inasmuch as it had already been demonstrated that large variations in rate did not lead to alteration of the Baker-Nathan order in acidic solvents,⁵ we turned our attention to the reaction in non-aqueous non-acidic conditions. These more selective solvents offered an excellent method for the evaluation of variations in the selectivity of the reagent halogen and the structural characteristic of the solvent on the Baker-Nathan effect. Of the several solvents available, acetonitrile, acetic anhydride, nitromethane, nitrobenzene and chlorobenzene were selected as typical of a variety of structural and dielectric properties.

Results

Kinetic Observations.—The rates of chlorination of the aromatics were followed by iodometric and spectrophotometric procedures as described.^{7,9} In those instances where the kinetic observations are comparable, the results of this investigation are in excellent agreement with the data of the earlier study.⁷ Kinetic experiments were customarily followed to 50–75% completion. An attempt was made to employ the convenient competitive procedure to evaluate the relative rate for toluene and *t*-butylbenzene in three solvents. Unfortunately, the analytical difficulties involved prevented the successful application of the technique for the reaction in nitrobenzene and chlorobenzene. The method provided excellent results, however, for the chlorination of the alkylbenzenes in acetic anhydride. The kinetic rate data are summarized in Table I and the competitive studies presented in Table II.

Preliminary experiments were carried out to justify the adoption of the solvents and kinetic measurements as reported in Tables I and II. In particular, the dark reaction between chlorine

(7) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **81**, 1063 (1959).

(8) L. M. Stock and A. Himoe, *Tetrahedron Letters*, No. 13, 9 (1960).

(9) H. C. Brown and L. M. Stock, *J. Am. Chem. Soc.*, **79**, 5175 (1957).

TABLE I

SECOND-ORDER RATE CONSTANTS FOR THE CHLORINATION OF BENZENE, TOLUENE, *t*-BUTYLBENZENE AND *p*-XYLENE IN NON-HYDROXYLIC SOLVENTS AT 25°

| Compound | Reactants, <i>M</i> | | 10 ⁴ <i>k</i> _s , l. mole ⁻¹ sec. ⁻¹ |
|------------------------|---------------------|--------------------|---|
| | [ArH] | [Cl ₂] | |
| In nitromethane | | | |
| Benzene | 0.223 | 0.0887 | 0.054 ^a |
| Toluene | .202 | .0224 | 132 ^b |
| | .202 | .0516 | 130 ^b |
| <i>t</i> -Butylbenzene | .200 | .0428 | 30.9 |
| | .200 | .0408 | 30.5 |
| <i>p</i> -Xylene | .183 | .0209 | 765 |
| | .200 | .0358 | 682 |
| In nitrobenzene | | | |
| Toluene | 0.467 | 0.0260 | 46 ^c |
| | .467 | .0240 | 44 ^c |
| | .467 | .0175 | 0.55 ^d |
| <i>t</i> -Butylbenzene | .321 | .0242 | 9.55 ^e |
| | .321 | .0254 | 9.61 ^e |
| In acetonitrile | | | |
| Toluene | 0.467 | 0.0197 | 15 ^f |
| <i>t</i> -Butylbenzene | .321 | .0150 | 5.8 |
| <i>p</i> -Xylene | .201 | .0354 | 110 ^g |
| In acetic anhydride | | | |
| Toluene | 0.369 | 0.0500 | 2.44 ^h |
| In chlorobenzene | | | |
| Toluene | 0.595 | 0.0132 | 0.013 |
| <i>t</i> -Butylbenzene | 0.557 | 0.0130 | 0.0036 |

^a Initial rate, see text. ^b For similar conditions the rate is reported as 124×10^{-4} l. mole⁻¹ sec.⁻¹, ref. 7. ^c In the presence of 0.122 *M* hydrochloric acid, see text. ^d Initial in the absence of added hydrogen chloride. ^e For similar conditions the rate is reported as $15.8, 14.9 \times 10^{-4}$ l. mole⁻¹ sec.⁻¹. ^f Observations of F. A. Leaver and J. Budin. ^g For similar conditions, the rate is reported as 3.5×10^{-4} l. mole⁻¹ sec.⁻¹, ref. 7.

TABLE II

COMPETITIVE DETERMINATION OF THE RELATIVE RATE OF CHLORINATION OF TOLUENE AND *t*-BUTYLBENZENE IN ACETIC ANHYDRIDE AT 25°

| Compound | Concentration, <i>M</i> | | Relative rate ^a <i>k</i> _{toluene} / <i>k</i> _{tbutylbenzene} |
|------------------------|-------------------------|-------|---|
| | Initial | Final | |
| Toluene | 0.445 | 0.418 | 4.70, 4.55 |
| <i>t</i> -Butylbenzene | .465 | .459 | |
| Chlorine | .044 | .000 | |
| Toluene | .242 | .223 | 4.28 |
| <i>t</i> -Butylbenzene | .220 | .216 | |
| Chlorine | .044 | .000 | |

^a Based on expression of derived by C. K. Ingold and F. R. Shaw, *J. Chem. Soc.*, 2918 (1927).

and the solvent was investigated. The reported catalysis of aromatic chlorination in ethylene dichloride by hydrogen chloride⁷ also led us to examine the importance of this route. The observations bearing on these questions and other points are summarized in the following notes.

Nitromethane.—The dark reaction of chlorine with nitromethane presented no difficulty in the rapid chlorination of the alkylbenzenes. No evidence for autocatalysis was obtained. On the other hand, benzene under the same conditions exhibited a small autocatalytic effect identifiable with the formation of hydrogen chloride. In order

to test the merit of this suggestion,⁷ hydrogen chloride was added to the reaction mixture. The rate of disappearance of chlorine was accelerated, but the kinetic behavior was erratic. Presumably the added hydrogen chloride also catalyzed the chlorination of the solvent, a reaction kinetically competitive with the reaction of benzene with chlorine.¹⁰ The initial rate constant evaluated for the chlorination of benzene was 0.054×10^{-4} l. mole⁻¹ sec.⁻¹. This result compares very favorably with the observation of Andrews and Keefer.⁷

As our intention was to examine the potential consequences of differential solvation of the electron deficient transition state it appeared desirable to study the influence of the steric requirements of the alkyl residues in a group of nitroparaffins. Accordingly, nitroethane and 2-nitropropane were examined. The kinetic behavior observed for aromatic chlorination in these media was not satisfactory even for the alkylbenzenes. Chlorine was consumed in a dark reaction with the solvent in the presence of hydrogen chloride. Kinetic behavior was autocatalytic. In another side-reaction nitroethane, in the presence of hydrogen chloride, yielded hydroxylamine hydrochloride. The hydrochloride was precipitated from solution in the course of the reaction; it was identified analytically and spectroscopically. Extensive purification of these solvents did not prevent the consumption of chlorine in side-reactions. These difficulties forced us to abandon this approach.

Nitrobenzene.—The kinetic difficulties attendant to the reaction in nitroparaffins were easily identified with the presence of an acidic hydrogen. Nitrobenzene was selected to avoid this problem. In this medium the first kinetic experiments employing chlorine and toluene proved to be sharply autocatalytic. The addition of excess hydrogen chloride provided simple second-order kinetic behavior. As indicated in Table I, the rate of the catalyzed reaction was increased by a factor of approximately 100 over the initial rate for the apparently uncatalyzed reaction. Since the kinetic behavior in nitrobenzene differed greatly from nitromethane, direct comparison of the results in the two solvents was not possible.

Acetonitrile.—The reaction of the alkylbenzenes with chlorine in acetonitrile was conveniently followed iodometrically. In first experiments the precision of the kinetic data did not allow a firm test of possible autocatalysis.¹¹ Spectrophotometric examination of the reaction with toluene indicated a measurable, but small, catalytic influence of the hydrogen chloride produced. The catalysis by the product acid was not sufficiently large to be significant in the measurement of relative rate. The necessary rate data for benzene were taken from the previous study.⁷

Acetic Anhydride.—The dark reaction of chlorine with acetic anhydride proved to be significant even after extensive attempts to purify the solvent. In this case, an estimate of the rate with

toluene was obtained by kinetic measurement and the relative rate, toluene to *t*-butylbenzene, obtained by competitive procedures. The competitive relative rate values were calculated by taking into account the consumption of chlorine by the solvent. The relative rate determined exclusively on the basis of product ratios is smaller, but not significantly different from the reported values.

Chlorobenzene.—Carefully dried chlorobenzene was employed to represent the non-polar medium.¹² The reaction between toluene and the halogen did not exhibit autocatalysis under the conditions reported in Table I. However, the iodometric method failed to provide satisfactory results.¹³ The reaction was conveniently followed by the spectrophotometric procedure.

Product Distributions.—The necessary product ratios were obtained by infrared spectroscopy and vapor phase chromatography.^{5,8} In these experiments, the concentration of the aromatic exceeded that of the halogen by a factor of 5–10 to avoid disubstitution. Side-chain substitution was not an important reaction. An attempt was made to study this side-reaction through hydrolysis of the reaction mixture and measurement of the benzyl alcohol produced. The results obtained by this approach indicated this pathway consumed less than 5% of the available chlorine.

A direct determination of the extent of *m*-substitution was not attempted. An estimate of the *m*-chlorotoluene produced in nitromethane is 0.15% based on the Selectivity relationship as discussed below.¹⁵ *m*-Chloro-*t*-butylbenzene would be produced to a somewhat greater extent but probably not more than the analytical uncertainty in the concentration of the *p*-isomer. The results for the predominant isomers are summarized in Table III.

TABLE III
ISOMER DISTRIBUTION IN THE CHLORINATION OF TOLUENE AND *t*-BUTYLBENZENE^a

| Solvent | Chlorotoluene ^b | | Chloro- <i>t</i> -butylbenzene ^c | |
|------------------|----------------------------|------------|---|------------|
| | <i>o</i> - | <i>p</i> - | <i>o</i> - | <i>p</i> - |
| Nitromethane | 33.6 ± 1.9 | 66.4 ± 1.9 | 13.0 ± 1.0 | 87.0 ± 1.0 |
| Nitrobenzene | 61.6 ± 1.1 | 38.4 ± 1.1 | 16.2 ± 1.1 | 83.8 ± 1.1 |
| Acetonitrile | 37.6 ± 0.4 | 62.4 ± 0.4 | 18.0 ± 0.6 | 82.0 ± 0.6 |
| Acetic anhydride | 49.0 ± 0.3 | 51.0 ± 0.3 | 10.6 ± .3 | 89.4 ± .3 |
| Chlorobenzene | 53.6 ± 1.3 | 46.4 ± 1.3 | 6.8 ± .3 | 93.2 ± .3 |

^a Based on two or more experiments. ^b Analyzed by vapor phase chromatography. ^c Analyzed by infrared spectroscopy.

Discussion

The rate data reported in summary in Table I are in quite good agreement with the values determined by Andrews and Keefer.⁷ Kinetic and competitive measurements of the relative rate of chlorination of the alkylbenzenes have previously

(12) Several curious results obtained for the reaction in slightly wet chlorobenzene are recorded in the Experimental section.

(13) The spurious measurements were the consequence of the heterogeneous quenching mixture. The thiosulfate titer depended on the rate of mixing of the chlorobenzene and potassium iodide solutions. At the same time, the water in chlorobenzene greatly accelerated the reaction between halogen and the aromatic.¹⁴

(14) The accelerating influence of water in carbon tetrachloride has been observed for the bromination of mesitylene; R. M. Keefer, J. H. Blake and L. J. Andrews, *J. Am. Chem. Soc.*, **76**, 3062 (1954).

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

(10) R. G. Pearson and R. L. Dillon, *J. Am. Chem. Soc.*, **75**, 2439 (1953).

(11) Autocatalytic behavior appeared to be significant on the basis of observed isomer distributions for the chlorination of toluene in acetonitrile and in the same solvent with added hydrogen chloride, ref. 8.

been shown to give comparable results.⁵ In view of the very slow reaction of benzene with chlorine in certain of the solvents under consideration and the consumption of chlorine in side-reactions, benzene was examined in only two solvents. As discussed in our earlier report, the relative rate measurements obtained by kinetic or competitive methods are presumably accurate to $\pm 10\%$.

The chlorination of toluene in nitromethane, acetic anhydride or chlorobenzene was free of the complexity of auto-catalysis. Product acid had a detectable but negligibly small influence on the chlorination of toluene in acetonitrile and an important effect in nitrobenzene solution. The role of the reaction solvent as a factor in the determination of the importance of the uncatalyzed and acid-catalyzed halogenation pathways is not yet defined.¹⁴ The acid itself apparently serves as an electrophilic catalyst in assisting the rupture of the chlorine-chlorine bond in the transition state.^{5,16}

The isomer distributions presented for toluene in certain of the solvents have been reported in a previous communication.⁸ The remarkable dependence of the *ortho* to *para* ratio on the reaction solvent has been noted there. A minor uncertainty is introduced in the isomer ratio because the catalyzed and uncatalyzed reactions yield different *ortho* to *para* ratios. The isomer ratio for the chlorination of toluene is altered from 62% *p*- in pure acetonitrile to 43% *p*-isomer with 0.6 *M* hydrogen chloride added.¹⁷ In the absence of large concentrations of added acid the variation in the product distribution is sufficiently small to be disregarded.

Partial Rate Factors and Selectivity Relationship.—The results obtained in the course of this investigation provide data for the determination of partial rate factors for chlorination in two solvents. The partial rate factors for acetonitrile and nitromethane are compared with the values for the reaction in acetic acid and for the acid-catalyzed hypochlorous acid chlorination of toluene in Table IV.

TABLE IV
PARTIAL RATE FACTORS AND ASSOCIATED QUANTITIES FOR THE CHLORINATION OF TOLUENE

| Conditions | Partial rate factors ^a | | | S_f | $-\rho$ |
|---|-----------------------------------|------------------|------------|-------|---------|
| | σ_f^{Me} | m_f^{Me} | p_f^{Me} | | |
| Cl ₂ , CH ₃ NO ₂ , 25° ^a | 2420 | 8.3 ^b | 9500 | 3.06 | -13.8 |
| Cl ₂ , CH ₃ CN, 25° ^a | 1830 | 9.1 ^b | 6250 | 2.84 | -13.6 |
| Cl ₂ , CH ₃ CO ₂ H, 25° ^c | 617 | 5.0 | 820 | 2.22 | -10.0 |
| HOCl, HClO ₄ , H ₂ O, 25° ^d | 134 | 4.0 | 82 | 1.31 | -7.7 |

^a This study. ^b Calculated from relative rate, *p*-xylene to benzene and σ_f^{Me} , see text. ^c Ref. 9. ^d P. B. D. de la Mare, J. T. Harvey, M. Hassan and S. Varma, *J. Chem. Soc.*, 2756 (1958).

The *meta* partial rate factors for chlorination in nitromethane and acetonitrile are not directly available from the observations for toluene. These partial rate factors, Table IV, were calculated from the expression

$$\frac{k_{p\text{-Xylene}}}{k_B} = \frac{4\sigma_f^{Me} m_f^{Me}}{6}$$

(16) Experimental results on this aspect of the mechanism are incomplete.

(17) L. M. Stock and A. Himoe, Abstracts 138th Meeting American Chemical Society, New York, N. Y., September, 1960, p. P1.

employing the determined values for the relative rate, $k_{p\text{-xylene}}/k_B$, and σ_f^{Me} . The m_f^{Me} results, Table IV, predict the formation of 0.15% *m*-chlorotoluene in direct chlorination.¹⁸ Clearly, this concentration of *m*-isomer will not lead to discrepancies in the product ratio for toluene. The error in the % *p*-chloro-*t*-butylbenzene is somewhat larger but still not significant to the following discussion.

The solvent introduces a remarkable variation in the selectivity of the chlorine molecule. Chlorination in nitromethane represents the most selective aromatic substitution reaction thus far found. Pertinent to this inquiry is the fit of these data to the Selectivity relationship.¹⁵ A test of the adherence of the results is provided by the ratio

$$\frac{\log p_f^{Me}}{\log m_f^{Me}} = \frac{\sigma_{p\text{-Me}}^+}{\sigma_{m\text{-Me}}^+} = \text{constant}$$

For chlorination in nitromethane, the ratio is 4.32; for acetonitrile solvent it is 3.96; while for 47 other electrophilic substitution reactions of toluene it has been assessed as 4.04 ± 0.55 .

Influence of Solvent on Relative Reactivity.—The results pertaining to the influence of the solvent on the Baker-Nathan effect are summarized in Table V.

TABLE V
RELATIVE RATES FOR CHLORINATION *para* TO METHYL AND *t*-BUTYL GROUPS

| Solvent | Dielectric constant | 10 ⁴ k_T , b l. mole ⁻¹ sec. ⁻¹ | $\frac{\log p_f^{Me}}{\log p_{p\text{-}t\text{-Bu}}^{Me}}$ | $\frac{k_{p\text{-}t\text{-Bu}}}{k_{p\text{-}Me}}$ |
|------------------------------|---------------------|--|--|--|
| Aq. acetic acid ^e | 45 | 27,000 | 1.06 | 1.6 |
| Nitromethane | 37.5 | 131 | 1.15 | 3.2 |
| Nitrobenzene | 35.7 | 45 ^d | | 2.1 |
| | | (0.55) ^f | | |
| Acetonitrile | 37.5 | 15 | 1.08 | 2.0 |
| Acetic acid ^f | 6.15 | 5.3 | 1.10 | 2.1 |
| Acetic anhydride | 20 | 2.5 | | 2.6 |
| Chlorobenzene | 5.71 | 0.013 | | 1.8 |

^a Value for aqueous acetic acid estimated; others are taken from J. Hine, "Physical-Organic Chemistry," McGraw-Hill Book Co., Inc., New York, 1956, p. 43. ^b Second-order rate, see Table I. ^c Aqueous acetic acid, 27.6 *M* water, 1.2 *M* HCl, ref. 5. ^d Hydrogen chloride catalyzed. ^e Uncatalyzed. ^f Ref. 9.

The intent of this investigation was the evaluation of the influence of variations in reagent selectivity and solvation phenomena on the Baker-Nathan effect. These two interdependent influences provide a complex problem for analysis. However, it is possible to unravel the selectivity dependence of the Baker-Nathan effect from the solvent influence through the elimination of ρ from the Hammett expressions

$$\frac{\log p_f^{Me}}{\log p_{f\text{-}t\text{-Bu}}^{Me}} = \frac{\sigma_{p\text{-}t\text{-Bu}}^+}{\sigma_{p\text{-}Me}^+} = \text{constant}$$

The quantitative data necessary for the evaluation of this ratio are available for two new solvents. The modification of p_f^{Me} from 9500 in nitromethane ($\rho = -13.8$) to 820 to anhydrous acetic acid ($\rho = -10.0$) serves to indicate the variation in selectivity. The observed ratio of the logarithms for

(18) The validity of this approach to the evaluation of m_f has been demonstrated, ref. 9.

the halogenation reaction in eight solvent systems are in excellent agreement, Table V. Thus, the Baker-Nathan order is maintained quantitatively in these eight media covering a span of absolute reactivity of 10^4 with major variation in reagent selectivity and large structural modifications in the solvent.

Unfortunately, side-reactions have prevented the evaluation of the partial rate factors for the non-catalytic chlorination reaction in nitrobenzene, acetic anhydride and chlorobenzene. In these solvents, the relative rate, k_{p-Me}/k_{p-t-Bu} is approximately 2 in accord with the observations for the other media. These results are qualitative in the sense that ρ cannot be eliminated from consideration. Nevertheless, the conclusion appears clear that the alkyl groups are responding to the electron-deficiency in the same fashion in all these solvents.

In summary, the relative rate for the chlorination of toluene extends over a range of more than 10^5 from dry chlorobenzene to highly aqueous acetic acid. This large variation in rate does not give rise to significant alteration of the Baker-Nathan order for *p*-substitution in toluene and *t*-butylbenzene. The quantitative evaluation of the greatly modified partial rate factors for reaction in non-aqueous nonhydroxylic solvents provides evidence for the independence of the influence of the alkyl groups from the selectivity of the reagent. Further, the structural, dielectric and solvation properties of the reaction media have been varied over a wide range without apparent modification of the contributions of the electric influences of the *p*-methyl and *p*-*t*-butyl groups. The results of this study and our earlier report support the view that the Baker-Nathan effect is to be identified with a polar influence.

Experimental Part

Materials.—The source of the aromatic materials have been presented previously.⁵ The solvents under examination here were obtained in the highest state of purity available commercially and further purified by treatment with chlorine and other conventional methods prior to fractionation. The boiling point and other physical properties were in agreement with literature values. The dark rate of reaction with chlorine was adopted as the principal criterion of purity. As discussed in the Results, acetic anhydride exhibited a significant rate of consumption of chlorine, $k_1 = 2.6 \times 10^{-5} \text{ sec.}^{-1}$. For the other solvents this reaction was not important in the absence of added hydrogen chloride.

Kinetic Observations.—The kinetic results were obtained as described.^{5,7}

Product Distributions.—The methods employed for the analysis of the products have been described.⁵ All reactions were carried out in the dark to avoid initiation of radical reactions. Large aromatic to chlorine ratios, 10 to 1.0 or greater, avoided disubstitution as checked by vapor phase chromatography. A curious result was obtained for chlorination in chlorobenzene in preliminary experiments. It was observed that the mixing of two homogeneous solutions of aromatic and chlorine in chlorobenzene led to another homogeneous solution which became opaque after a brief interval. The products of chlorination of a large excess of *t*-butylbenzene in such a solution were about 50% monochloro- and 50% dichloro-*t*-butylbenzene. The principal product was identified as 3,4-dichloro-*t*-butylbenzene by the infrared spectrum¹⁹ of material trapped from the chromatography column. The opaque solution was shown to be the result of hydrogen chloride in moist chlorobenzene. Careful drying of the solvent obviated the problem. The product acid apparently caused a phase separation of traces of water yielding the opaque mixture. The chlorination occurred rapidly in the aqueous phase and the reaction presumably was controlled by the slow rate of transfer across the phase boundary with disubstituted material resulting from the chlorination of the trapped monochloro compound.

Acknowledgment.—It is a pleasure to acknowledge the support of the Research Corporation.

(19) M. Lerer, C. Fabre and G. Hugel, *Bull. soc. chim.*, 177 (1957).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY, STANFORD, CALIF.]

Optical Rotatory Dispersion Studies. LIX.¹ The Octant Rule and Deuterium. Synthesis of 3-Deuteriocyclopentanone²

BY CARL DJERASSI AND B. TURSCH

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In order to examine the rotational contribution of a deuterium atom β to a carbonyl group, a stereospecific synthesis of 3-deuteriocyclopentanone (XI) was developed starting with (+)- α -pinene (IV).

A substantial amount of work has been done in recent years³ on optically active substances of type R_1R_2CHD , the deuterium atom representing one of the substituents attached directly to the asymmetric carbon atom. Such compounds have proved to possess very low rotations and it seemed to us of interest to determine whether a situation could be found where "asymmetric deuterium"

(1) Paper LVIII, C. Djerassi, P. Quitt, E. Mosettig, R. C. Cambie, P. S. Rutledge and L. H. Briggs, *J. Am. Chem. Soc.*, **83**, 3720 (1961).

(2) Supported by grant No. CRTY-5061 from the National Cancer Institute of the National Institutes of Health, U. S. Public Health Service.

(3) For pertinent references see A. Streitwieser, Jr., J. R. Wolfe and W. D. Schaeffer, *Tetrahedron*, **6**, 338 (1959).

might produce a large rotational contribution. A valuable test case would be an optically active cyclic ketone, where the rotational effect of a suitably placed deuterium substituent could be examined in the ultraviolet near the extremum of the Cotton effect associated with the carbonyl group.⁴ In terms of the tenets of the octant rule,⁵ what we would be attempting to measure is the interaction between the electrons in the excited-state orbitals of the carbonyl's $n \rightarrow \pi^*$ -transition

(4) See C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Book Co., Inc., New York, N. Y., 1960.

(5) W. Moffitt, R. B. Woodward, A. Moscowitz, W. Klyne and C. Djerassi, *J. Am. Chem. Soc.*, **83**, 4013 (1961).