

releases oxygen gas when added to water solution, and  $p\text{-O}_2\text{NC}_6\text{H}_4\text{OH}$  is formed. The product is very unstable in moist air and forms new unidentified species rapidly. A unambiguous identification of the interesting new product(s) is in progress.

**Acknowledgment.**—The authors wish to express their appreciation to Dr. DeLos DeTar for his helpful comments during the course of this work and for his constructive ideas at the conclusion of this study.

[CONTRIBUTION FROM THE HOUSTON RESEARCH LABORATORY, SHELL OIL CO., DEER PARK, TEXAS]

## The Reactivity of Methylene from Photolysis of Diazomethane<sup>1</sup>

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RECEIVED SEPTEMBER 15, 1960

The evidence that methylene generated by solution photolysis of diazomethane reacts randomly with alkane carbon-hydrogen bonds has been considerably extended. Differences in reactivity of methylene produced by photolysis of diazomethane in the gas phase and in solution are ascribed to the reaction of methylene in two electronic states.

### Introduction

Recent research has demonstrated interesting differences concerning the reactivity of methylene toward alkane substrates. In the original study on this question, Doering, Buttery, Laughlin and Chaudhuri<sup>2</sup> reported that methylene produced by the solution photolysis of diazomethane reacted randomly with the carbon-hydrogen bonds of an alkane to give specific isomers of the next-higher homolog. In contrast, the methylene produced by gas-phase ketene photolysis<sup>3,4</sup> was found to react selectively with alkane carbon-hydrogen bonds, the products indicating 1.7 times the reaction with secondary bonds as with primary bonds. Frey<sup>5</sup> examined the gas-phase photolysis of diazomethane-alkane mixtures and found the methylene reacted selectively with carbon-hydrogen bonds in the approximate reactivity ratio  $k_{\text{tert}}/k_{\text{sec}}/k_{\text{prim}}$  of 1.5/1.2/1.0. This result showed the difference between the methylenes from the two precursors to be real, and indicated an unexplained difference in the reactivity of methylene produced by solution or gas-phase photolysis of diazomethane.

Subsequent to the original report<sup>2</sup> on methylene reactivity, computations were presented<sup>6</sup> which showed these results were not to be expected on the basis of transition state theory. These computations, as well as the selectivity of methylene produced by gas-phase photolysis of diazomethane, suggested an examination of the generality of the indiscriminate reaction of methylene produced by diazomethane photolysis in alkane solution. Accordingly, we have photolyzed diazomethane dissolved in a number of alkanes more complex than those studied previously. These results and their bearing on the general question of methylene reactivity are the subject of this report.

(1) Presented at the 16th Southwest Regional Meeting of the American Chemical Society, Oklahoma City, Okla., December 1-3, 1960.

(2) W. von E. Doering, R. G. Buttery, R. G. Laughlin and N. Chaudhuri, *J. Am. Chem. Soc.*, **78**, 3224 (1956).

(3) J. H. Knox and A. F. Trotman-Dickenson, *Chemistry & Industry*, 731 (1957).

(4) H. M. Frey and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **79**, 6373 (1957).

(5) H. M. Frey, *ibid.*, **80**, 5005 (1958).

(6) J. H. Knox and A. F. Trotman-Dickenson, *Chemistry & Industry*, 268 (1957).

### Experimental Details

The hydrocarbons used were either American Petroleum Institute standard samples (purity > 99.5%) or Phillips Petroleum Co. pure grade materials (purity > 99.0%). The hydrocarbon (1-2 ml.) and 1 ml. of 40% potassium hydroxide were cooled in an ice-bath, and the amount of N-nitrosomethylurea<sup>7</sup> calculated to generate 1-2 moles of diazomethane per 100 moles of hydrocarbon was added, with shaking. The yellow hydrocarbon layer was separated and dried over pellet potassium hydroxide. The dried solution was placed in a Pyrex flask cooled by running tap water and irradiated with a General Electric RS sunlamp until the color of diazomethane disappeared (1-2 hours).

The crude reaction mixture was analyzed directly with a capillary gas chromatograph<sup>8</sup> similar to that described by Lipsky, Landowne and Lovelock.<sup>9</sup> The 250-ft. capillary column was made of type-321 stainless steel (0.01 inch i.d.  $\times$  0.06 inch o.d.) and coated with squalane. The column was operated at room temperature with an argon flow rate of 1 ml. per minute. The argon ionization detector was maintained at 150° and the inlet system was heated to 250-300°. Because of the low concentration of product isomers, the column and detector were necessarily overloaded with the parent hydrocarbon, but this condition did not affect the resolution or relative retention times of the products.<sup>9</sup>

The identity of the products was established by comparison of the retention time of each component to that of an authentic sample insofar as these were available. In the absence of suitable reference samples, the identity of a particular product was established by comparison of its retention time to that of the same product prepared from alternate precursors. Compounds identified in this manner are designated in Table I. The identity of products not established by the above methods was assumed; these compounds are also indicated in Table I. Products are listed in Table I in the order of emergence from the squalane column. With the exception of one pair, 3-methyl-3-ethylhexane and 3-methyl-4-ethylhexane, this order is that of increasing boiling point, as is to be expected from the general property of the squalane-coated column to effect boiling-point separations. Four pairs of compounds indicated in Table I were not separated under the conditions of the operation of the column. These compounds were available or were prepared from other precursors, and it was shown that the pairs concerned should emerge from the column unresolved.

The areas of the product peaks were measured with a planimeter, and normalization of the peak areas led to the

(7) F. Arndt, "Organic Syntheses," Coll. Vol. II, Edited by A. H. Blatt, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 461.

(8) M. C. Simmons, D. B. Richardson and I. Dvoretzky, Preprints, "Third Symposium on Gas Chromatography, Edinburgh," Butterworths, London, 1960.

(9) J. R. Lipsky, R. A. Landowne and J. E. Lovelock, *Anal. Chem.*, **31**, 852 (1959).

TABLE I  
METHYLENE INSERTION PRODUCTS FROM C<sub>7</sub>, C<sub>8</sub>- AND C<sub>9</sub>-  
ALKANES

Parent	Product	Precursor bond		Dist., %	
		Type	Number	Calcd.	Obsd.
Heptane	2-MeC <sub>7</sub>	2	4	25.0	25
	4-MeC <sub>7</sub>	2	2	12.5	13
	3-MeC <sub>7</sub>	2	4	25.0	24
	C <sub>8</sub>	1	6	37.5	38
2-Methylheptane	2,2-Me <sub>2</sub> C <sub>7</sub>	3	1	5.6	6
	2,4-Me <sub>2</sub> C <sub>7</sub> <sup>a</sup>	2	2	11.1	9
	2,6-Me <sub>2</sub> C <sub>7</sub> <sup>b</sup>	2	2	11.1	13
	2,5-Me <sub>2</sub> C <sub>7</sub> <sup>a</sup>	2	2	11.1	12
	2,3-Me <sub>2</sub> C <sub>7</sub> <sup>a</sup>	2	2	11.1	11
	2-MeC <sub>8</sub> <sup>b</sup>	1	3	16.7	17
	3-MeC <sub>8</sub> <sup>a</sup>	1	6	33.3	32
3-Methylheptane	[3,5-Me <sub>2</sub> C <sub>7</sub> <sup>a</sup>	2	2] <sup>c</sup>	22.2	24
	[2,5-Me <sub>2</sub> C <sub>7</sub> <sup>a</sup>	2	2]		
	3,3-Me <sub>2</sub> C <sub>7</sub> <sup>b</sup>	3	1	5.6	6
	2,3-Me <sub>2</sub> C <sub>7</sub> <sup>a</sup>	2	2	11.1	12
	3,4-Me <sub>2</sub> C <sub>7</sub> <sup>a</sup>	2	2	11.1	10
	4-MeC <sub>8</sub> <sup>a</sup>	1	3	16.7	17
	3-EtC <sub>7</sub> <sup>a</sup>	1	3	16.7	14
	3-MeC <sub>8</sub> <sup>a</sup>	1	3	16.7	17
4-Methylheptane	2,4-Me <sub>2</sub> C <sub>7</sub> <sup>a</sup>	2	4	22.2	25
	4,4-Me <sub>2</sub> C <sub>7</sub> <sup>b</sup>	3	1	5.6	4
	[3,4-Me <sub>2</sub> C <sub>7</sub> <sup>a</sup>	2	4] <sup>c</sup>	38.9	38
	[4-EtC <sub>7</sub> <sup>a</sup>	1	3]		
	4-MeC <sub>8</sub> <sup>a</sup>	1	6	33.3	33
2,4-Dimethylhexane	2,2,4-Me <sub>3</sub> C <sub>6</sub>	3	1	5.6	5
	2,4,4-Me <sub>3</sub> C <sub>6</sub>	3	1	5.6	4
	2,3,5-Me <sub>3</sub> C <sub>6</sub>	2	2	11.1	12
	2,4-Me <sub>2</sub> C <sub>7</sub> <sup>a</sup>	1	3	16.7	19
	2-Me-4-EtC <sub>6</sub> <sup>a</sup>	1	3	16.7	16
	3,5-Me <sub>2</sub> C <sub>7</sub> <sup>a</sup>	1	6	33.3	35
	2,3,4-Me <sub>3</sub> C <sub>6</sub> <sup>a</sup>	2	2	11.1	10
3,4-Dimethylhexane	2,3,4-Me <sub>3</sub> C <sub>6</sub> <sup>a</sup>	2	4	22.2	22
	3-Me-4-EtC <sub>6</sub> <sup>a</sup>	1	6	33.3	35
	[3,3,4-Me <sub>3</sub> C <sub>6</sub>	3	2] <sup>c</sup>	44.4	43
	[3,4-Me <sub>2</sub> C <sub>7</sub> <sup>a</sup>	1	6]		
3-Ethylhexane	2-Me-4-EtC <sub>6</sub> <sup>a</sup>	2	2	11.1	11
	2-Me-3-EtC <sub>6</sub> <sup>b</sup>	2	4	22.2	22
	3-Me-3-EtC <sub>6</sub> <sup>b</sup>	3	1	5.6	5
	3-Me-4-EtC <sub>6</sub> <sup>a</sup>	2	2	11.1	11
	4-EtC <sub>7</sub> <sup>a</sup>	1	6	33.3	33
	3-EtC <sub>7</sub> <sup>a</sup>	1	3	16.7	18
2,2,4-Trimethylpentane	2,4,4-Me <sub>3</sub> C <sub>5</sub>	1	9	50.0	51
	2,2,3,4-Me <sub>4</sub> C <sub>5</sub>	2	2	11.1	10
	2,2,4,4-Me <sub>4</sub> C <sub>5</sub>	3	1	5.6	4
	2,2,4-Me <sub>3</sub> C <sub>6</sub>	1	6	33.3	35
2,2,3-Trimethylpentane	2,2,3,4-Me <sub>4</sub> C <sub>5</sub>	2	2	11.1	9
	[2,2,3-Me <sub>3</sub> C <sub>6</sub>	1	3] <sup>c</sup>	33.3	35
	[2,2-Me <sub>2</sub> -3-EtC <sub>5</sub>	1	3]		
	2,2,3,3-Me <sub>4</sub> C <sub>5</sub>	3	1	5.6	4
	3,3,4-Me <sub>3</sub> C <sub>6</sub>	1	9	50.0	52
2,3,3-Trimethylpentane	2,3,3-Me <sub>3</sub> C <sub>5</sub>	1	3	16.7	18
	2,2,3,3-Me <sub>4</sub> C <sub>5</sub>	3	1	5.6	5
	3,3,4-Me <sub>3</sub> C <sub>6</sub>	1	6	33.3	34
	2,3,3,4-Me <sub>4</sub> C <sub>5</sub>	2	2	11.1	11
	2,3-Me <sub>2</sub> -3-EtC <sub>5</sub> <sup>b</sup>	1	6	33.3	32
2,3,4-Trimethylpentane	2,2,3,4-Me <sub>4</sub> C <sub>5</sub>	3	2	11.1	10
	2,4-Me <sub>2</sub> -3-EtC <sub>5</sub>	1	3	16.7	16
	2,3,4-Me <sub>3</sub> C <sub>6</sub> <sup>a</sup>	1	12	66.7	69
	2,3,3,4-Me <sub>4</sub> C <sub>5</sub>	3	1	5.6	5

2,2,4,4-Tetra-	2,2,4,4-Me <sub>4</sub> C <sub>6</sub> <sup>b</sup>	1	18	90.0	93
methyl-	2,2,3,4,4-Me <sub>5</sub> C <sub>6</sub> <sup>b</sup>	2	2	10.0	7
pentane					

<sup>a</sup> Compound was identified by comparison of its column retention time to that obtained by its synthesis from other parent hydrocarbons. <sup>b</sup> Identity of compound was assumed. <sup>c</sup> These compounds emerged from the column unresolved.

product composition. Corrections for variation in detector sensitivity of the C<sub>9</sub>-and-higher products were not applied. A check of the sensitivity of available nonanes showed the variation to be about 5%. Consideration of this variation and the errors in area measurement lead to an estimated uncertainty of about 2% (absolute) in the normalized product composition.

## Results

The compositions of the product mixtures obtained from the various alkanes used as solvents in the photolysis of diazomethane are shown in Table I. The product compositions calculated for random reaction are listed for comparison. Differences between the observed and calculated values are within the estimated experimental error, and statistical analysis by means of the  $\chi^2$  test<sup>10</sup> shows these data are not inconsistent with random reaction.

In addition to extending the number and molecular-weight range of alkanes used as solvents in diazomethane photolysis, Table I includes the first examples which have primary, secondary and tertiary carbon-hydrogen bonds in the same molecule. The range of parent hydrocarbons in Table I represents a considerable difference in the steric environment of the various carbon-hydrogen bonds, and a steric effect on reactivity might have been expected. However, it is clear from Table I that a steric effect, if any, is small and is of the order of experimental error.

The intramolecular random reactivity of this methylene being further established by the data in Table I, the question of intermolecular reactivity was briefly examined by photolysis of diazomethane dissolved in a mixture of the four trimethylpentanes. Each trimethylpentane gave two unique C<sub>9</sub>-products. After correction for the relative number of carbon-hydrogen bonds leading to the unique products, the observed ratio was used to calculate the composition of the original C<sub>8</sub>-mixture. This result is compared with the measured composition of the C<sub>8</sub>-mixture in Table II and, within experimental error, the values are the same. This not unexpected agreement shows both the intramolecular and intermolecular methylene-alkane reactions are random.

In summary, the above data provide strong support for the description of this methylene by Doering, *et al.*,<sup>2</sup> as "the most indiscriminate reagent known in organic chemistry."

Demonstrating the efficacy of the capillary column, an interesting side result occurred with those substrates leading to 2,3,4-trimethylhexane as a product. In each of these three cases, the peak for the 2,3,4-trimethylhexane appeared in the chromatogram as an equally-split doublet. This doublet is undoubtedly a consequence of the

(10) P. G. Hoel, "Introduction to Mathematical Statistics," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1954, p. 164.

separation of the compound into its diastereomeric pairs and is the first such alkane separation known to us.<sup>11</sup> None of the other alkanes containing two asymmetric carbons could be similarly resolved.

TABLE II

INTERMOLECULAR REACTION OF METHYLENE WITH THE TRIMETHYLPENTANES

Trimethylpentane	Compn. of C <sub>5</sub> -mixture, mole %	
	Observed	Calcd. from C <sub>9</sub> -products
2,2,4-	26	27
2,2,3-	29	29
2,3,4-	22	23
2,3,3-	23	21

### Discussion

The data of Table I on comparison with the published results of gaseous diazomethane photolysis confirm a difference in the reactivity of the methylenes produced under the different experimental conditions. This difference is further indicated by the results of Doering and Prinzbach<sup>12</sup> in their demonstration that methylene reacts with carbon-hydrogen bonds primarily by direct insertion. The reaction of methylene from diazomethane photolysis with 2-methylpropene-1-C<sup>14</sup> in the liquid phase produced 2-methylbutene-1 having 1% C<sup>14</sup> mixing while the 2-methylbutene-1 formed in the gas phase had 8% C<sup>14</sup> mixing.

This variation in reactivity with experimental conditions has been ascribed<sup>4,12</sup> to cage effects present in solution but absent in the gas phase. However, a more satisfactory interpretation is found by considering the problem in terms of methylene reacting in two electronic states. The interpretation on this basis is indicated by recent spectroscopic evidence of Herzberg,<sup>13,14</sup> who has obtained spectra of methylene produced by gas-phase photolysis of diazomethane showing both singlet and triplet states, the singlet state being the shorter lived. Theoretical considerations<sup>14</sup> indicate the methylene produced by diazomethane photolysis is first formed in an excited singlet state and the triplet state arises from a later transition.

Skell and Woodworth<sup>15</sup> have ascribed the stereospecific reaction of methylene with olefins to methylene in the singlet state (paired non-bonding electrons). We suggest that the random reaction of methylene with alkane carbon-hydrogen bonds observed in solution arises from the excited singlet, and further, that this reaction occurs at a much higher rate than the transition of the singlet to the triplet state (unpaired non-bonding electrons). Thus, there is little or no radical component to the reaction in solution. In the gas phase, we suggest the frequency of reactive collision is sufficiently less that the singlet-triplet transition occurs at a rate of the same order of magnitude as the random

singlet insertion. Methylene in the triplet state would be expected to react selectively with carbon-hydrogen bonds as do other radicals. Therefore, methylene in the gas phase reacts with carbon-hydrogen bonds by two paths: a random singlet insertion and a selective triplet abstraction. The abstraction leads to methyl and alkyl radicals which can combine to give apparently selective insertion, attack diazomethane or react in other ways typical of free radicals to produce secondary products. The extent of insertion selectivity and of secondary product formation will thus depend on the ratio of singlet-triplet transition to singlet carbon-hydrogen insertion.

The interpretation of the variation in methylene reactivity with experimental procedure in this manner is particularly indicated by observations of Frey.<sup>16</sup> In the photolysis of gaseous diazomethane-alkane mixtures, secondary products were found which indicated a radical component to the reaction. The presence of oxygen during the photolysis eliminated the formation of these secondary products and altered the ratio of the primary products toward that expected for random reaction. These results are readily rationalized by the above interpretation. Oxygen would be expected to react selectively with methylene in the triplet state or with radicals arising from the reaction of triplet methylene with the alkane. The formation of secondary products and insertion selectivity should thereby be decreased and the reaction should show more singlet or random character.

The above explanation for the variation in methylene reactivity suggests there should be pressures above which the gas-phase photolysis gives the same product mixture as solution photolysis. Further, the triplet character of the gas-phase reaction should increase as the pressure is lowered. The data from the photolysis of diazomethane-*trans*-butene-2 mixtures<sup>4,17</sup> are in accord with these effects. "Very similar" product compositions are reported for the liquid phase (-70°) and the gas phase (25°) at pressures greater than 1200 mm. As the pressure was lowered the yield of *trans*-1,2-dimethylcyclopropane decreased and the formation of *cis*-pentene-2,2-methylbutene-1 and *cis*-1,2-dimethylcyclopropane was observed.<sup>13</sup> These C<sub>5</sub>-products formed at the lower pressures are those to be expected from the reaction of methylene in the triplet state with the olefin as indicated by the work of Skell and co-workers.<sup>19,20</sup> Methylene in the triplet state should add to the olefin to form a biradical which can close in a non-stereospecific manner to form the *cis*-cyclopropane. The olefins are most likely formed by hydrogen migration in the biradical or through abstraction reactions followed by recombination. The observed formation of ethane and other secondary products with decreasing pressure also indicates

(11) The racemic and *meso* forms of 2,3-dichlorobutane have been separated by packed-column gas chromatography; P. S. Fredricks and J. M. Tedder, *Proc. Chem. Soc.*, 9 (1959).

(12) W. von E. Doering and H. Prinzbach, *Tetrahedron*, 6, 24 (1959).

(13) G. Herzberg and J. Shoosmith, *Nature*, 183, 1801 (1959).

(14) G. Herzberg, "Report of Welch Foundation Conference on Molecular Structure," Houston, Tex., November 16-18, 1959, in press.

(15) P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, 78, 4496, 6247 (1956); 81, 3383 (1959).

(16) H. M. Frey, *Proc. Chem. Soc.*, 318 (1959).

(17) H. M. Frey, *Proc. Roy. Soc. (London)*, A251, 575 (1959).

(18) These results have been interpreted on the basis of hot-molecule isomerization. While such an interpretation may be necessary in some cases, the importance of such reactions appears difficult to assess in view of the demonstrated<sup>13</sup> radical component of the reaction.

(19) R. M. Etter, H. S. Skovronek and P. S. Skell, *J. Am. Chem. Soc.*, 81, 1008 (1959).

(20) P. S. Skell and J. Klebe, *ibid.*, 82, 247 (1960).

the growing importance of the triplet reaction as the pressure is lowered.

The present rationalization of methylene reactivity in terms of the two electronic states implies the presence of an inert gas should increase the triplet character of the reaction by increasing the ratio of singlet-triplet transition to singlet-hydrocarbon reaction. This implication is supported by the formation of *cis*-1,2-dimethylcyclopropane in the photolysis of diazomethane-*trans*-butene-2 mixtures in the presence of 1-2 atmospheres of nitrogen or argon.<sup>17,21</sup> The formation of radicals,

most reasonably triplet methylene, under somewhat similar conditions was clearly demonstrated by Doering and Prinzbach.<sup>12</sup>

**Acknowledgment.**—We gratefully acknowledge the experimental assistance of Mr. L. M. Taylor. We are indebted to Dr. H. W. Anderson and Dr. S. H. Levin of this Laboratory and to Prof. E. S. Lewis of Rice University for helpful comments.

(21) Anet, *et al.* [F. A. L. Anet, R. F. W. Bader and A. M. van der Auwera, *J. Am. Chem. Soc.*, **82**, 3217 (1960)], have extended these observations of Frey and concluded from the results that the ground state of methylene is triplet.

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

## Rates and Isomer Distributions in the Chlorination of Benzene, Toluene and *t*-Butylbenzene in Aqueous Acetic Acid Solvents. The Influence of Solvent on the Reaction and the Baker-Nathan Effect

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RECEIVED DECEMBER 2, 1960

The rates, relative rates and isomer distributions for the non-catalytic chlorination of benzene, toluene and *t*-butylbenzene have been obtained in five aqueous acetic acid solvents. The addition of water to acetic acid provided a large rate acceleration in the chlorination of these hydrocarbons. However, the relative rates and partial rate factors,  $o_i^{Me}$ ,  $p_i^{Me}$  and  $p_i^{t-Bu}$ , for chlorination are quite insensitive to the variation in absolute rate. The  $o_i^{t-Bu}$  value exhibits a major change. The activation parameters determined for two aqueous acetic acid solvents revealed the rate variations were a consequence of changes in the enthalpy of activation. The large increase in the rate is attributed to the modification of the dielectric and increased solvation of the electron-deficient transition state. The ratio  $\log p_i^{Me}/\log p_i^{t-Bu}$  obtained for six solvent compositions is  $1.11 \pm 0.02$ . Under the conditions of these experiments the absolute rate of chlorination of benzene is altered by a factor of  $6.5 \times 10^3$ . The large influence of solvent on the rate and its negligible influence on relative reactivity suggests the Baker-Nathan effect does not have its origin in solvation phenomena.

### Introduction

In recent years considerable effort has been directed toward a fuller understanding of the origin of the Baker-Nathan effect.<sup>2</sup> Many of the early experimental studies and the more recent contributions have been reviewed.<sup>3</sup> In brief, three alternative ideas have been presented to account for the Baker-Nathan sequence. The concept of hyperconjugation was introduced several years ago and has been amplified in recent discussions.<sup>4</sup> Two other recently expressed viewpoints contend that hyperconjugation is not significant, and suggest the predominant mode of electron release from alkyl groups is through an inductive mechanism. These interpretations differ, however, with respect to the factor responsible for the inverted sequence. Schubert and his co-workers have argued for the importance of a differential energy of solvation. According to this view, the steric requirements of the bulky *t*-butyl group hinder solvation and are responsible for the inversion.<sup>5</sup> Burawoy postulated that the Baker-Nathan sequence resulted from the repulsive energy

attendant to the contraction of an alkyl carbon-aryl carbon bond under the stress of inductive electron demand.<sup>6</sup>

Much chemical evidence suggesting the reality of the effect has been provided through studies of substituted benzenes. Both typical Hammett side-chain reactions and reactions yielding highly electron deficient transition states have been examined. Unfortunately, the Hammett side-chain reactions exhibit only minor differences in reactivity between the alkyl substituted and parent compounds.<sup>7</sup> The electron deficient side-chain reactions have provided the best experimental evidence for the effect.<sup>8</sup> However, these reactions also exhibit small values for the reaction constant. Selective electrophilic substitution reactions, *e.g.*, halogenation or Friedel-Crafts acylation, have large reaction constants, but a detailed study of the influence of solvent has not been attempted. Accordingly, it appeared desirable to weigh the alternative interpretations for the Baker-Nathan order through an experimental investigation of the influence of solvent on a highly selective substitution process.

(1) Research Corporation Fellow, 1959-1961.

(2) For clarity, the Baker-Nathan effect is identified with the experimental observation: Me > *t*-Bu. Interpretations for this observation are distinguished by other terminology.

(3) See *Tetrahedron*, **5**, 107 (1959).

(4) R. S. Mulliken, C. A. Rieke and W. G. Brown, *J. Am. Chem. Soc.*, **63**, 41 (1941); R. S. Mulliken, *Tetrahedron*, **5**, 253 (1959); R. S. Mulliken, *ibid.*, **6**, 68 (1959).

(5) W. M. Schubert, J. M. Craven, R. G. Minton and R. B. Murphy, *ibid.*, **5**, 194 (1959); W. M. Schubert, J. Robins and J. L. Haun, *J. Am. Chem. Soc.*, **79**, 910 (1957); W. M. Schubert and W. A. Sweeney, *J. Org. Chem.*, **21**, 119 (1956).

(6) A. Burawoy and E. Spinner, *J. Chem. Soc.*, 3752 (1954); 2557 (1955); E. Spinner, *ibid.*, 1590 (1956).

(7) Indeed, the major portion of Baker's monograph is devoted to the discussion of typical Hammett side-chain reactions.  $\rho$ , the reaction constant, for these reactions rarely exceeds  $\pm 3$ . See J. W. Baker, "Hyperconjugation," Oxford University Press, 1952.

(8) Solvolytic reactions of benzhydryl- and phenyldimethylcarbinyl chloride are in the order: *p*-Me > *p*-*t*-Bu  $\gg$  H. The inductive order has never been observed for these substituents in solvolytic reactions. For a summary of the available data see E. Berliner, *Tetrahedron*, **5**, 202 (1959).