[Contribution from the Department of Chemistry of Purdue University]

Rates of Solvolysis of the Alkylphenyldimethylcarbinyl Chlorides. Evidence for the Importance of Carbon-to-Carbon Hyperconjugative Contributions in Alkyl Groups[1,2]

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Phenyldimethylcarbinol and its *o*-, *m*- and *p*-monoalkyl (methyl, ethyl, isopropyl and *t*-butyl) derivatives were synthesized. With one exception, these carbinols were converted readily to the corresponding tertiary chlorides by treatment with hydrogen chloride. The failure of *o*-*t*-butylphenyldimethylcarbinol to yield the expected tertiary chloride is attributed to the large strains to be expected in this molecule, a homomorph of the unknown *o*-di-*t*-butylbenzene. The rates of hydrolysis of the various tertiary chlorides in 90% aqueous acetone were measured at several temperatures. The small increase in rate (25°) observed in the *meta* alkyl derivatives (H, 1.00; *m*-Me, 2.00; *m*-Et, 1.94; *m*-*i*-Pr, 1.87; *m*-*t*-Bu, 1.85) is attributed primarily to the inductive effect of the substituent. The minor decrease in effect with increased branching is attributed to a small hyperconjugative contribution transmitted to the *ortho* position of the aromatic ring and relayed to the reaction center by induction. The much larger effect of the *para* alkyl groups (*p*-Me, 26.0; *p*-Et, 22.0; *p*-*i*-Pr, 18.8; *p*-*t*-Bu, 14.4) is attributed to hyperconjugation stabilization of the electron deficient center by the alkyl group. From the observation that both in the *meta* and *para* positions methyl and *t*-butyl groups have similar effects, it is concluded that carbon-to-carbon hyperconjugation must be nearly as important as carbon-to-hydrogen hyperconjugation. A methyl group in the *ortho* position (*o*-Me, 3.63) is far less important than a methyl group in the *p*-position (*p*-Me, 26.0). This is attributed to steric hindrance of resonance in the transition state. With increasing bulk of the *ortho* substituent, the effect increases (*o*-Et, 2.07; *o*-*i*-Pr, 0.847). The rate data obey the empirical relationship, $\log p_f = c \log (p_f/m_f)$, previously developed for the substitution reactions of toluene.

The available evidence indicates that the inductive effect of alkyl groups is quite small and increases moderately in the order Me < Et < *i*-Pr < *t*-Bu.[6] The steric requirements of these groups increase sharply in the same order. Consequently, in the study of steric effects it is frequently possible to assume, as a first approximation, that the polar effects of structural changes in the alkyl group are negligible and to attribute the observed reactivity changes to the altered steric requirements of the alkyl groups.[7]

Although the electronic effects of alkyl groups are quite small in neutral molecules, there is growing evidence of their major importance in electron deficient systems. Thus Norris and Banta observed that in the solvolysis of benzhydryl chloride a methyl group in the *meta* position increases the rate by a factor of 2.1, whereas in the *para* position the rate increases by a factor of 16.2.[8] Similarly, Hughes, Ingold and Taher demonstrated that in this system ethyl, isopropyl and *t*-butyl groups also exhibit a marked accelerating effect upon the rate, the effect decreasing in the order (25°): H (1.00) < Me (21.4) > Et (17.3) > *i*-Pr (13.8) > *t*-Bu (10.9).[9]

The minor increase in the solvolysis rate observed in *m*-methylbenzhydryl chloride[8] may be attributed to the inductive effect of the methyl group.[10] The much larger effect of the methyl substituent in the more distant *para* position[8] cannot be the result of this factor and must be attributed to hyperconjugative contributions of the methyl group rendered important by the demands of the electron deficient center in the transition state. The decreasing effect of the more branched alkyl groups[9] can then be attributed to the decreasing tendency for hyperconjugative contributions in the series, Me > Et > *i*-Pr > *t*-Bu.[11]

Two possible interpretations appear possible for the observed electronic effects of alkyl groups in electron deficient systems, Me > Et > *i*-Pr > *t*-Bu. In one interpretation, the observed order is attributed to an important hyperconjugative contribution of *alpha* carbon-to-hydrogen bonds (three in methyl, decreasing to none in *t*-butyl) accompanied by a significant increase in the inductive effect.[11] Alternatively, the observed order could be attributed to the sum of the hyperconjugative contributions of *alpha* hydrogen-to-carbon bonds and the slightly smaller hyperconjugative contributions of *alpha* carbon-to-carbon bonds. In terms of the first of these explanations, the large effect of the *t*-butyl group in *p*-*t*-butylbenzhydryl chloride would be attributed primarily to its inductive effect. In terms of the second interpretation the increase would be assigned to significant carbon-to-carbon hyperconjugative contributions with the inductive effect making only a minor contribution.

These questions are important in attaining an understanding of the effect of alkyl substituents on the stability of π- and σ-complexes,[12] on the rates of aromatic substitution[13] and on the orientation taken by entering substituents.[14] However, the available data do not permit a decision between these alternative interpretations. In order to answer this question, we decided to undertake a systematic study of the effect of both *para* (I) and

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(1) Directive Effects in Aromatic Substitution. X.

(2) Based upon theses submitted by James D. Brady (1949), Martin Grayson (1952) and W. Hallam Bonner (1952) in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Standard Oil Co. (Indiana) Fellow at Purdue University, 1947–1949.

(4) Standard Oil Co. (Indiana) Fellow at Purdue University, 1949–1950.

(5) Purdue Research Foundation Fellow, 1949–1951.

(6) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

(7) H. C. Brown, *J. Chem. Soc.*, 1248 (1956).

(8) J. F. Norris and C. Banta, This Journal, **50**, 1804 (1928).

(9) E. D. Hughes, C. K. Ingold and N. Taher, *J. Chem. Soc.*, 949 (1940).

(10) As will be pointed out later, in the Discussion, there is reason to believe that only a portion of this effect can be assigned to the simple +I effect of the methyl group.

(11) J. W. Baker, "Hyperconjugation," Oxford University Press, New York, N. Y., 1952.

(12) H. C. Brown and J. D. Brady, This Journal, **74**, 3570 (1952).

(13) E. Berliner and F. Berliner, *ibid.*, **72**, 222, 3417 (1950); H. Cohn, E. D. Hughes, M. H. Jones and M. G. Peeling, *Nature*, **169**, 291 (1952).

(14) (a) K. L. Nelson and H. C. Brown, This Journal, **73**, 5605 (1951); (b) H. C. Brown and W. H. Bonner, *ibid.*, **76**, 605 (1954).

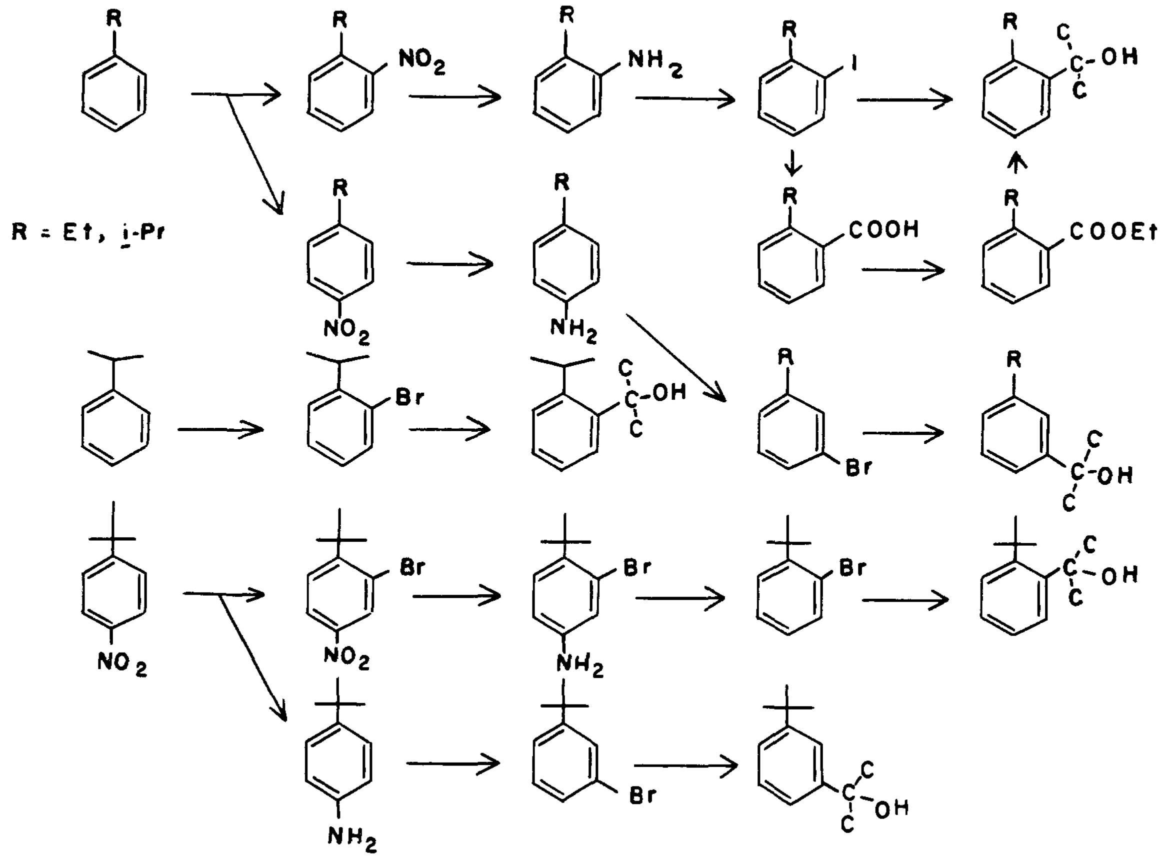
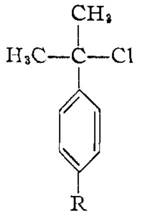
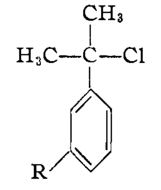


Fig. 1.—Synthetic routes to the *o*- and *m*-alkylphenyldimethylcarbinols.

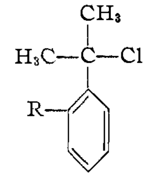
meta alkyl groups (II) (R = Me, Et, *i*-Pr and *t*-Bu) upon the rates of solvolysis of phenyldimethylcarbinyl chlorides. The *ortho* isomers III were included in order to provide information as to the effect of increasing steric strain upon the rate of the solvolysis reaction.



I



II



III

Results

Phenyl- and *o*-, *m*- and *p*-tolyldimethylcarbinols were synthesized by the reaction of the corresponding Grignard reagents upon acetone.

The *p*-alkylphenyldimethylcarbinols were synthesized by the action of the methyl Grignard reagent on the *p*-alkylacetophenones. Originally we attempted the synthesis of these intermediates by acetylating toluene following the procedure described for the preparation of *p*-bromo- and *p*-methylacetophenones.[15] However, the yields were low and the products were obviously impure. In view of the known sensitivity of the higher alkyl groups to isomerization and disproportionation under Friedel–Crafts conditions,[16,17] the procedure, was modified to permit the slow addition of aluminum chloride to a mixture of the alkyl benzene and acetyl chloride. Yields as high as 80–85% of pure product were readily realized.

The synthesis of the *o*- and *m*-alkyl (Et, *i*-Pr, *t*-Bu) phenyldimethylcarbinols proceeded for the most part through the *o*- and *m*-bromoalkylbenzenes prepared from the *o*- and *p*-nitroalkylbenzenes.[14] In some cases two alternative routes were utilized to a given end-product for confirmation of the structure. The synthetic routes are indicated in Fig. 1.

Since the route from diazonium derivative to *o*-haloalkylbenzene proceeded in much poorer yield for the bromide as compared to the iodide, we attempted to use the latter in the Grignard reaction with acetone. However, we observed that in the case of the iodide the yields in the Grignard reaction were considerably lower than with the corresponding bromide. These results are summarized in Table I.

In the case of the *t*-butyl derivative, none of the desired *o*-*t*-butylphenyldimethylcarbinol could be isolated from the Grignard reaction. The use of the corresponding organolithium derivative and acetone at −80° led to the formation of the desired product in yields of 1.1–1.3%.

We originally undertook to prepare analytically pure samples of the tertiary chlorides. However,

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[15] A. H. Blatt, ed., "Organic Syntheses," Coll. Vol. 1, 2nd Ed., John Wiley and Sons, Inc., 1941, p. 109.

[16] D. V. Nightingale, *Chem. Revs.*, **25**, 329 (1939).

[17] A. P. Lien and D. A. McCaulay, THIS JOURNAL, **75**, 2407 (1953).

TABLE I

YIELDS OF CARBINOL IN THE REACTION OF *o*-ALKYLPHENYLMAGNESIUM HALIDE WITH ACETONE

Arylhalide	Yield, % Bromo	Iodo
o-Halotoluene	75	40
o-Haloethylbenzene		25
o-Haloisopropylbenzene	60	22
o-Halo-*t*-butylbenzene	0	

these compounds proved to be quite unstable and lost hydrogen chloride upon attempted distillation, even at pressures as low as 0.1 mm. Experiment revealed that identical rate constants were realized from the crude product obtained by treating the carbinol with hydrogen chloride at 0° and the distilled material. Accordingly, we were content to prepare pure samples of the carbinols and to utilize the tertiary chlorides prepared from these carbinols without further treatment.

With one exception, the tertiary alcohols all reacted readily with hydrogen chloride to yield the corresponding chlorides. However, in the case of *o*-*t*-butylphenyldimethylcarbinol no tertiary chloride was formed, only olefin. Since the tertiary chloride would be a homomorph of *o*-di-*t*-butylbenzene,[18] this result is not surprising.

We undertook to examine the effect of the steric requirements of the *o*-alkyl groups on this reaction by following the absorption of hydrogen chloride by solutions of the carbinols in an inert solvent within a modified micro Zerewitinoff apparatus.[19] The results are summarized in Table II.

TABLE II

ABSORPTION OF HYDROGEN CHLORIDE BY SOLUTIONS OF ALKYLPHENYLDIMETHYLCARBINOLS IN 1-BROMODECANE SOLUTION AT 25°

Alkyl substituent	Wt., g.	Hydrogen chloride absorbed[a] Calcd. for chloride	Calcd. for olefin[b]	Obsd.	Product, % Chloride	Olefin
m-*t*-Butyl	0.0153	2.36	0.58	2.33	98	2
o-Methyl[c]	.0103	2.03	.50	1.80	84	16
o-Ethyl	.0158	2.85	.70	2.57	86	14
o-Isopropyl	.0146	2.44	.60	1.97	74	26
o-*t*-Butyl	.0069	1.07	.26	0.22	0	100

[a] Ml. (S.T.P.). [b] To produce saturated solution of hydrogen chloride in water from carbinol. [c] Duplicate determination: 86% chloride, 14% olefin.

Many of the carbinols prepared in this study are new compounds. Their physical properties and analyses are summarized in Table III.

The rates were run in a solvent prepared by mixing 9 parts of acetone and 1 part of water. In any given solvent the rate constants were easily reproducible to 2–3%. However, the rates are highly sensitive to minor changes in the water content. Since the studies were carried out by three different workers over a period of years, it proved impractical to use the same solvent for all of the measurements. New batches of solvent were adjusted to give the original rate constant for phenyldimethylcarbinyl chloride. However, because of this additional uncertainty, the rate constants in different solvents can be compared only with a larger degree of uncertainty, estimated as ±5%. Since the structural effects in the present study are relatively large, this uncertainty introduces no serious difficulty.

The experimental results are summarized in Table IV.

Discussion

The introduction of a methyl group into the *meta* position of phenyldimethylcarbinyl chloride increases the rate of solvolysis by a factor of 2.00. This small increase is reasonably attributed to the inductive effect of the methyl substituent, which by increasing the electron density at the reaction center of the incipient carbonium ion should serve to stabilize the transition state.

Changes in the alkyl group from methyl to ethyl, isopropyl and *t*-butyl have little further effect upon the rate (Fig. 2). It is somewhat surprising that a small decrease is observed rather than the small increase which would have been expected to result from the increasing inductive effect of these substituents. This suggests that hyperconjugative contributions which decrease from methyl to *t*-butyl may also be significant here. Such hyperconjugation would increase the electron density in the *ortho* positions, whence it could be relayed to the reaction center by induction (IV).[20]

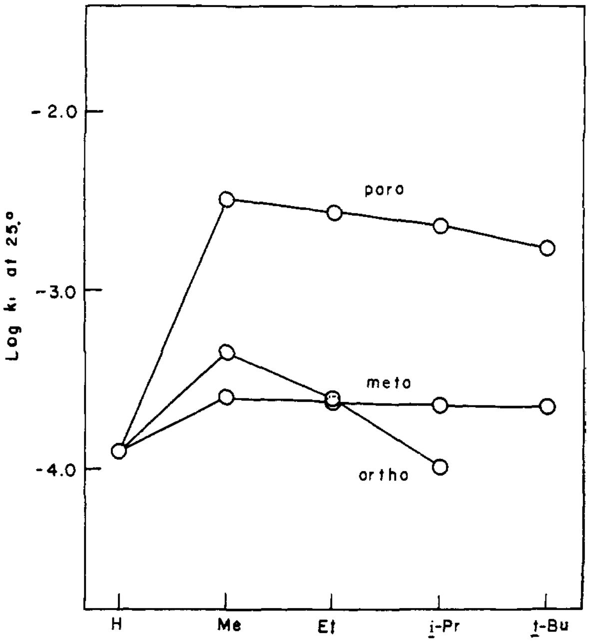

Fig. 2.—Effect of alkyl substituents upon the rates of solvolysis of the alkylphenyldimethylcarbinyl chlorides in 90% aqueous acetone at 25°.

In the *para* position a methyl group has a much larger effect—it increases the solvolysis rate by a factor of 26.0. Since the effect is so much larger in the more distant *para* position than in the nearer *meta*

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[18] H. C. Brown and K. L. Nelson, THIS JOURNAL, **75**, 24 (1953).

[19] H. C. Brown and O. Hafliger, *Anal. Chem.*, **26**, 757 (1954).

[20] The importance of resonance which modifies reactivity indirectly through its effect on the positions *ortho* to the functional group has been pointed out by C. C. Price and D. C. Lincoln, THIS JOURNAL, **73**, 5841 (1951), and by P. B. D. de la Mare and C. A. Vernon, *J. Chem. Soc.*, 1764 (1951).

TABLE III

PHYSICAL PROPERTIES AND ANALYSES OF THE ALKYLPHENYLDIMETHYLCARBINOLS

Compound dimethylcarbinol	Observed constants: B.p. °C.	Observed constants: B.p. Mm.	Observed constants: M.p., °C.	Observed constants: $n^{20}D$	Analyses, %: Calcd. C	Analyses, %: Calcd. H	Analyses, %: Found C	Analyses, %: Found H
Phenyl[a]	93	11	30–31					
o-Methylphenyl[b]	117	17	38–39					
o-Ethylphenyl	90	1.5		1.5251	80.43	9.83	80.61	9.91
o-Isopropylphenyl			68.5–69		80.84	10.18	80.49	9.99
o-*t*-Butylphenyl			127.5–128		81.19	10.49	80.41	10.11
m-Methylphenyl[c]	73	3	9–9.5	1.5182				
m-Ethylphenyl	103	4		1.5152	80.43	9.83	80.28	9.98
m-Isopropylphenyl	98	1	36.5	1.5098	80.84	10.18	80.42	10.00
m-*t*-Butylphenyl			88.5–89		81.19	10.49	80.80	10.02
p-Methylphenyl[d]	101	10	5	1.5180				
p-Ethylphenyl	114	10		1.5140	80.43	9.83	79.90	9.79
p-Isopropylphenyl	120	10	44		80.84	10.18	80.81	10.04
p-*t*-Butylphenyl[e]			79					

[a] A. Klages, *Ber.*, **35**, 2637 (1902), reports b.p. 94° (13 mm.), $n^{20}D$ 1.5314. [b] M. Tiffeneau, *Ann. chim.*, [8] **10**, 194 (1907), reports b.p. 116° (22 mm.), m.p. 41°. [c] W. H. Perkin and G. Tattersall, *J. Chem. Soc.*, **87**, 1106 (1905), report b.p. 115–116° (16 mm.), m.p. 4–5°. [d] W. H. Perkin and S. S. Pickles, *ibid.*, **87**, 652 (1905), report b.p. 111–112° (16 mm.), m.p. 5°. [e] M. Walther, *J. Pharm. Chem.*, **27**, 416 (1938), reports m.p. 79°.

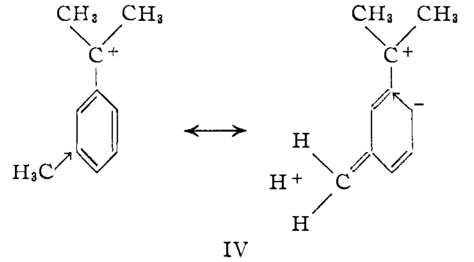
TABLE IV

RATE CONSTANTS AND DERIVED DATA FOR THE SOLVOLYSIS OF THE ALKYLPHENYLDIMETHYLCARBINYL CHLORIDES IN 90% AQUEOUS ACETONE[d]

Alkyl group	Rate constant, k_1 (sec.$^{-1}$ × 10^5) 0°	15°	25°	35°	R k_1/k_{1H} (25°)	$E_{act.}$	log A	$\Delta H\ddagger$	$\Delta S\ddagger$	$\Delta F\ddagger - \Delta F_0\ddagger$
Hydrogen[a]	0.600		12.4	36.1	1.00	19.5	10.4	18.8	−12.4	0
o-Methyl[a]	2.21	14.4	45.0		3.63	19.6	11.0	19.0	−10.4	−0.76
o-Ethyl[c]	1.05	8.08	25.7		2.07	20.8	11.7	20.3	−6.9	− .43
o-Isopropyl[c]	0.400	2.97	10.5		0.847	21.2	11.6	20.7	−7.5	.097
o-*t*-Butyl[c,e]										
m-Methyl[a]	1.26	8.39	24.8		2.00	19.4	10.6	18.6	−11.8	− .41
m-Ethyl[c]	1.14	7.50	24.1		1.94	19.8	10.9	19.2	−10.6	− .39
m-Isopropyl[c]	1.05	6.94	23.2		1.87	19.4	11.0	19.4	−10.2	− .37
m-*t*-Butyl[c]	1.09	7.25	23.0		1.85	19.8	10.9	19.3	−10.6	−0.36
p-Methyl[a]	20.6	111	322		26.0	17.8	10.6	17.3	−12.0	−1.92
p-Ethyl[b]	16.9	95.6	273		22.0	18.1	10.7	17.5	−11.5	−1.82
p-Isopropyl[b]	13.9	75.3	233		18.8	18.0	10.5	17.4	−12.2	−1.71
t-Butyl[b]	11.0	61.9	178		14.4	17.9	10.3	17.3	−13.3	−1.56

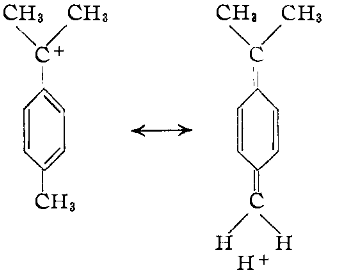
[a] Observations of J. D. Brady. [b] Observations of M. Grayson. [c] Observations of W. H. Bonner. [d] Each set of observations used an individual batch of solvent adjusted to give 12.4 ± 0.3 × 10^{-5} sec.$^{-1}$ for k_1^{25} with phenyldimethylcarbinyl chloride. [e] *o*-*t*-Butylphenyldimethylcarbinyl chloride does not form.

position, it cannot be attributed to the inductive effect[21] and must be attributed to hyperconjugative stabilization of the incipient carbonium ion (V).[22]



IV

The decrease in effect observed with increasing branching in the alkyl group (Me, 26.0; Et, 22.0; *i*-Pr, 18.8; *t*-Bu, 14.4) is consistent with the decreased possibilities for hyperconjugation as the



V

alpha hydrogen atoms are replaced by methyl groups.[11] However, even in the case of *p*-*t*-butyl, a group with no *alpha* hydrogen atoms, the observed rate is far larger than in the case of the corresponding *m*-*t*-butyl derivative (Fig. 2).

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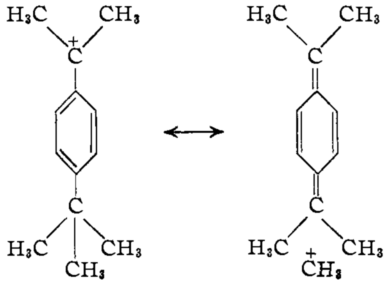
[21] Evidence that the inductive effect is nearly the same in the *meta* and *para* positions is reported by J. D. Roberts, R. A. Clement and J. J. Drysdale, THIS JOURNAL, **73**, 2181 (1951). Moreover, R. W. Taft, Jr., has demonstrated that this is generally true, including *meta* and *para* alkyl groups: M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 594–597.

[22] For convenience, the diagrams (IV, V, VI) show the effect of hyperconjugation upon the carbonium ion. Strictly speaking the ion is an intermediate, and the transition state will not contain a fully formed carbonium ion. However, the available evidence indicates that the transition state is well on the way to the carbonium ion [G. S. Hammond, THIS JOURNAL, **77**, 334 (1955)] so that no significant difference should be anticipated between the effects of structural changes upon the stability of the carbonium ion and the stability of the transition state.

In all respects the phenomenon is quite similar to that observed for the methyl substituent. If hyperconjugation constitutes a satisfactory explanation for the difference in behavior of *m*- and *p*-methyl, it appears reasonable also to ascribe to hyperconjugation the related difference in the behavior of *m*- and *p*-*t*-butyl (VI).



VI

The effect in the case of *t*-butyl ($k^{p\text{-}t\text{-Bu}}/k^{m\text{-}t\text{-Bu}} = 7.8$) is slightly smaller than that in methyl ($k^{p\text{-Me}}/k^{m\text{-Me}} = 13.0$). The *meta* results suggest that in this system the inductive effects of these alkyl groups must be relatively small and not greatly different.[23] Consequently it appears that the hyperconjugative contributions of carbon-to-hydrogen and carbon-to-carbon bonds must be quite similar, with the former being moderately more favorable in order to account for the observed decrease in rate in the series, *p*-Me > *p*-Et > *p*-*i*-Pr > *p*-*t*-Bu.

It is possible to make a rough quantitative estimate of the relative importance of the hyperconjugative contributions of the two bonds from the available rate data (Table IV).

Within the limits of experimental error the entropies of ionization of phenyldimethylcarbinyl chloride and the *meta* and *para* monoalkyl derivatives appear to be constant. Consequently, we may take differences in the free energies of the reaction (Table IV) as a measure of the relative stabilities of the transition states.[24,25]

An alkyl group in the *meta* position increases the stability of the transition state by 0.36–0.41 kcal./mole. In the *para* position, an alkyl group increases the stability by 1.56–1.92 kcal./mole. The difference in the stability produced by a given group in the *meta* and *para* positions may be taken as a measure of the hyperconjugative contribution of the group in the *para* position. On this basis, it can be estimated that each *alpha* carbon-to-hydrogen bond of a *para* alkyl group contributes 0.50 kcal./mole to the stability of the transition state, whereas each α-carbon-to-carbon bond contributes 0.40 kcal./mole (Table V). Thus the hyperconjugative effect of carbon-to-carbon bonds in this system can be estimated to be approximately 80% of the corresponding effect of carbon-to-hydrogen bonds.

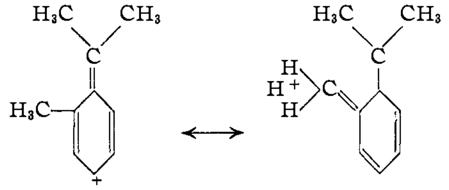
TABLE V

ESTIMATED HYPERCONJUGATIVE CONTRIBUTION OF EACH *alpha* CARBON-TO-HYDROGEN AND CARBON-TO-CARBON BOND OF *para* ALKYL GROUPS

Group	$\Delta F^{\ddagger}_{m\text{-}R} - \Delta F^{\ddagger}_{p\text{-}R}$ kcal./mole	Calcd. hyperconjugative contribution,[a] kcal./mole
Methyl	1.51	1.51
Ethyl	1.43	1.41
Isopropyl	1.34	1.30
t-Butyl	1.20	1.20

[a] Assuming each α-C–H bond contributes 1.51/3 and each α-C–C bond contributes 1.20/3 to the total hyperconjugative effect of the *p*-alkyl group.

An *o*-methyl group is considerably less effective (3.63) than a *p*-methyl group (26.0). It is reasonable to attribute this diminished effect of an *o*-methyl group to steric inhibition of resonance (VII).[26]



VII

The increasing effect of *o*-ethyl (2.07) and *o*-isopropyl (0.847) is consistent with this observation. In the case of the latter derivative, the effect is sufficient to overcome the combined inductive and hyperconjugative effects of the alkyl substituent and to reduce the rate of solvolysis below that for the parent compound.

With increasing bulk of the *ortho*-substituent it appears possible that the effect of the resonance inhibition could be swamped by the increasing steric strain.[27] However, we were unable to synthesize the *o*-*t*-butyl isomer and could not test this prediction.

The hyperconjugative contributions of *p*-methyl in these solvolyses studies resemble closely the hyperconjugative stabilization of the σ-complexes used to account for the directive effects observed in toluene substitution. Accordingly, we examined the data in order to see whether they would fit the empirical relationship previously established for toluene substitutions.[28]

A moderately good fit was realized (Fig. 3). This observation suggested that the solvolysis reaction could serve as the basis for substituent constants suitable for aromatic substitutions[29] and other electrophilic reactions.[30] This possibility is explored in the following papers of this group.

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[23] Estimates of the relatively small and nearly equal inductive effects of *meta* alkyl groups is presented by Taft (ref. 21).

[24] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 118.

[25] Ideally we should utilize the differences in the energies or enthalpies of activation for this purpose. However, the free energies are directly related to the rate constants and the uncertainties in these quantities are considerably smaller than in the derived energies and enthalpies of activation.

[26] For a recent study of the role of steric inhibition of resonance on the rate of ethanolysis of a number of phenyldialkylcarbinyl chlorides, see G. Baddeley, J. Chadwick and H. T. Taylor, *J. Chem. Soc.*, 448 (1956).

[27] The strain in homomorphs of *o*-di-*t*-butylbenzene is estimated to be 25 kcal./mole; H. C. Brown, D. Gintis and L. Domash, THIS JOURNAL, **78**, 5387 (1956).

[28] H. C. Brown and K. L. Nelson, *ibid.*, **75**, 6292 (1953); H. C. Brown and C. W. McGary, Jr., *ibid.*, **77**, 2300 (1955); H. C. Brown and C. R. Smoot, *ibid.*, **78**, 6255 (1956).

[29] C. W. McGary, Y. Okamoto and H. C. Brown, *ibid.*, **77**, 3037 (1955).

[30] D. W. Pearson, J. F. Baxter and J. C. Martin, *J. Org. Chem.*, **17**, 1511 (1952).

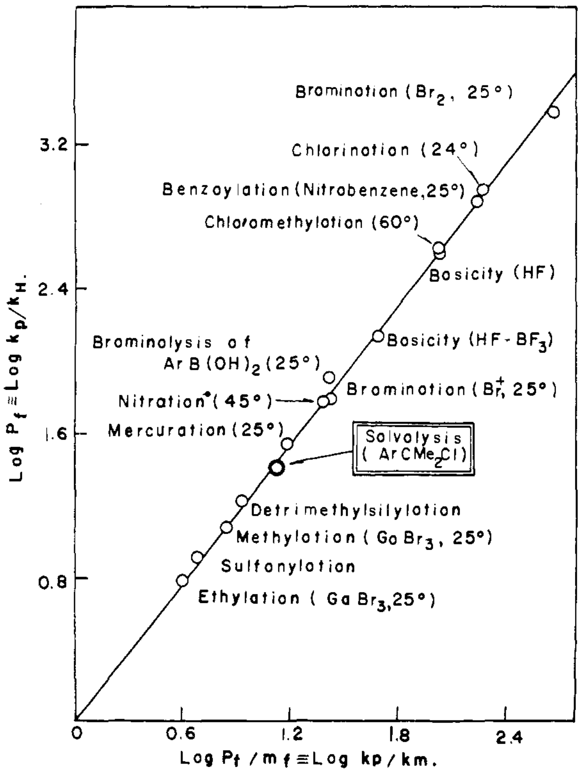

Fig. 3.—Correlation between the solvolysis data for the *m*- and *p*-tolyldimethylcarbinyl chlorides and the substitution data for toluene.

Experimental Part

Phenyl- and Tolyldimethylcarbinols.—Bromobenzene and the three isomeric bromotoluenes were carefully fractionated, converted to the Grignard reagents and treated with acetone. After hydrolysis of the reaction mixtures with a cold saturated solution of ammonium chloride, the tertiary alcohols were isolated by distillation at reduced pressure. Yields were in the range of 65–70%. The physical properties of the materials are given in Table III.

***p*-Alkylphenyldimethylcarbinols.**—The monoalkylbenzenes were acetylated in accordance with the following procedure described for *p*-*t*-butylacetophenone.

In a 1-liter 3-necked flask fitted with stirrer, reflux condenser and thermometer were placed 109 g. (1.0 mole) of *t*-butylbenzene, 200 ml. of dry carbon disulfide and 117 g. (1.5 moles) of acetyl chloride. The flask was cooled in an ice-bath and 146 g. (1.1 moles) of anhydrous aluminum chloride was added through the third neck of the flask over a period of 1 hr., the temperature being maintained at 0 to 5°. (The aluminum chloride was contained in a wide-mouth flask attached to the reaction vessel by a short length of wide bore Tygon tubing. In this way the solid could be added in controlled portions without exposure to the air.) The mixture was permitted to stand overnight at room temperature. After hydrolysis the carbon disulfide layer was separated, dried and distilled. An 83% yield of *p*-*t*-butylacetophenone was obtained. The following constants were observed: *p*-*t*-butylacetophenone, b.p. 144° (20 mm.), $n^{20}\mathrm{D}$ 1.5205; *p*-isopropylacetophenone, b.p. 133° (20 mm.), $n^{20}\mathrm{D}$ 1.5227; *p*-ethylacetophenone, b.p. 125° (20 mm.), $n^{20}\mathrm{D}$ 1.5289.

The *p*-alkylacetophenones were converted into the tertiary alcohols by reaction with the methyl Grignard reagent in yields of 80%. The products are described in Table III.

***m*-Ethylphenyldimethylcarbinol.**—*p*-Nitroethylbenzene[14b] was reduced catalytically by the method of Biel[31] to *p*-ethylaniline in 89% yield, b.p. 49–51° at 0.41 mm., $n^{20}\mathrm{D}$ 1.5548.[32] The amine was converted to *m*-bromoethylbenzene by successive acetylation, bromination, hydrolysis and deamination by hypophosphorous acid in an over-all yield of 59% of a colorless liquid, b.p. 74–77° (7 mm.), $n^{20}\mathrm{D}$ 1.5454.[33] The bromide was converted into the Grignard reagent and treated with acetone to form the carbinol in a yield of 59% (Table III).

***m*-Isopropylphenyldimethylcarbinol.**—*p*-Nitrocumene[14b] was reduced catalytically[31] to *p*-cumidine in 94% yield of a light yellow liquid, b.p. 55–60° (0.32 mm.), $n^{20}\mathrm{D}$ 1.5429.[34] This amine was converted to *m*-bromocumene by the sequence of reactions mentioned above. The product was obtained as a colorless liquid in 60% yield, b.p. 71–74° (2.5 mm.), $n^{20}\mathrm{D}$ 1.5370.[35] The carbinol was obtained *via* the Grignard reagent in a yield of 60% (Table III).

***m*-*t*-Butylphenyldimethylcarbinol.**—Catalytic reduction[31] of *p*-nitro-*t*-butylbenzene[14a] to *p*-*t*-butylaniline was carried out in 84% yield, b.p. 89–90° (1 mm.), $n^{20}\mathrm{D}$ 1.5381.[36] The amine was converted by the usual route to *m*-bromo-*t*-butylbenzene in a yield of 42%, b.p. 89° (4 mm.), $n^{20}\mathrm{D}$ 1.5356.[37] The bromide was converted into the carbinol in a yield of 60% (Table III).

***o*-Ethylphenyldimethylcarbinol.**—*o*-Nitroethylbenzene[14b] was reduced catalytically[31] to *o*-ethylaniline in 95% yield: light yellow liquid, b.p. 39° (0.2 mm.), $n^{20}\mathrm{D}$ 1.5599.[38] Pilot experiments on *o*-toluidine revealed that under a variety of conditions the replacement of the amino group by bromine could not be realized in yields of over 42%, although *m*- and *p*-toluidines gave good yields. However, diazotization of *o*-toluidine and treatment with potassium iodide yielded the *o*-iodotoluene in yields of 65% and higher. Accordingly, *o*-ethylaniline was converted into *o*-iodoethylbenzene in yields of 69–77%, b.p. 95–96° (8 mm.), $n^{20}\mathrm{D}$ 1.5952.[39]

o-Iodoethylbenzene was converted into the Grignard reagent and treated with acetone. The reaction product proved to be complex, containing ethylbenzene and mesityl oxide in addition to a 25% yield of the desired carbinol. It appears to be a general phenomenon that *o*-iodoalkylbenzenes give poor yields in this reaction (Table I). Accordingly, we adopted an alternative route.

o-Iodoethylbenzene was converted into the Grignard reagent and treated with carbon dioxide gas at −10 to −20°. A 69% yield of *o*-ethylbenzoic acid, m.p. 64–66° was obtained.[40] The acid was converted into the ethyl ester, b.p. 92–94° (1 mm.), $n^{20}\mathrm{D}$ 1.5050.[41] The ester was treated with methylmagnesium iodide. A 44% yield of the desired carbinol was obtained (Table III). Identical rate constants were obtained from chlorides obtained from the two samples of the carbinol synthesized by these different procedures.

***o*-Isopropylphenyldimethylcarbinol.**—*o*-Nitrocumene[14b] was reduced catalytically in 90% yield to *o*-cumidine, a yellow liquid with a pleasant odor, b.p. 64° (0.4 mm.), $n^{20}\mathrm{D}$ 1.5480–1.5490.[42] The amine was converted to the iodide, b.p. 84–85° (2 mm.), $n^{20}\mathrm{D}$ 1.5830–1.5838.

Anal. Calcd. for $C_9H_{11}I$: C, 43.92; H, 4.51. Found: C, 44.10; H, 4.52.

o-Iodocumene was converted into the Grignard reagent and treated with acetone. A 22% yield of the carbinol was realized. *o*-Iodocumene was converted to the Grignard reagent and treated with carbon dioxide. A 40% yield of *o*-isopropylbenzoic acid, m.p. 63–64°, was realized.[43] The acid was transformed into the ethyl ester in 60% yield, b.p. 95° (3 mm.), $n^{20}\mathrm{D}$ 1.5010.

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 75.00; H, 8.33. Found: C, 74.43; H, 8.00.

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[31] J. H. Biel, THIS JOURNAL, **71**, 1308 (1949).

[32] S. F. Birch, R. A. Dean, F. A. Fidler and R. A. Lowry, *ibid.*, **71**, 1362 (1949), report $n^{20}\mathrm{D}$ 1.5550.

[33] J. H. Brown and C. S. Marvel, *ibid.*, **59**, 1176 (1937), report $n^{20}\mathrm{D}$ 1.5465.

[34] A. Newton, *ibid.*, **65**, 2437 (1943), reports $n^{20}\mathrm{D}$ 1.5415.

[35] E. C. Sterling and M. T. Bogert, *J. Org. Chem.*, **4**, 20 (1939), report b.p. 208–210°.

[36] J. H. Boyd, U. S. Patent 2,507,755; *C. A.*, **44**, 8369 (1950), reports $n^{20}\mathrm{D}$ 1.5380.

[37] C. C. Price and D. C. Lincoln, THIS JOURNAL, **73**, 5836 (1951), report b.p. 116.5° (27 mm.), $n^{20}\mathrm{D}$ 1.5343–1.5351.

[38] Literature values (ref. 32): b. p. 108° (30 mm.), $n^{20}\mathrm{D}$ 1.5588.

[39] E. Schreiner, *J. prakt. Chem.*, [2] **81**, 559 (1910), reports $n^{20}\mathrm{D}$ 1.5941.

[40] T. Zincke and C. Frölich, *Ber.*, **20**, 2895 (1887), report m.p. 68°.

[41] G. Giebe, *ibid.*, **29**, 2534 (1896), reports b.p. 231° (763 mm.).

[42] J. V. Braun, O. Bayer and G. Blessing, *ibid.*, **57**, 397 (1924), report b.p. 95° (13 mm.).

[43] R. Kothe, *Ann.*, **248**, 64 (1888), reports m.p. 51°.

The ester was treated with the methyl Grignard reagent to give the desired carbinol in 50% yield. Because of the low yields in the various stages of this synthesis, an alternative synthetic route was examined.

Cumene was treated with bromine in the presence of finely divided iron at −5° to 0°.[44] From 500 g. of the mixed monobromocumenes prepared in this manner, fractionation produced 29 g. of *o*-bromocumene, b.p. 71–72° (3 mm.), $n^{20}\text{D}$ 1.5411.[45] This product was converted into the Grignard reagent and treated with acetone. A 60% yield of the carbinol was obtained (Table III). No depression in m.p. was observed in a comparison of the products from the three different routes.

***o*-*t*-Butylphenyldimethylcarbinol.**—Bromination of *p*-nitro-*t*-butylbenzene[14a] gave 45–62% yields of 2-bromo-4-nitro-*t*-butylbenzene, m.p. 93–94°.[46] This product was reduced catalytically (74% yield) to 2-bromo-4-amino-*t*-butylbenzene, b.p. 125° (1 mm.), $n^{20}\text{D}$ 1.5828, which was deaminated with hypophosphorus acid to give *o*-bromo-*t*-butylbenzene, b.p. 93° (8 mm.), $n^{20}\text{D}$ 1.5442.

The Grignard reagent from *o*-bromo-*t*-butylbenzene was treated with acetone. There was isolated from the reaction product *t*-butylbenzene, mesityl oxide and triacetone alcohol, m.p. 57–58°.[47]

The alcohol was finally synthesized by the following procedure. Under a nitrogen atmosphere 100 ml. of ether and 0.69 g. (0.10 g. at.) of lithium wire was placed in the usual Grignard-type apparatus and a solution of 11 g. (0.05 mole) of *o*-bromo-*t*-butylbenzene in 50 ml. of ether was added over a period of 1 hr. Reflux was maintained for 3 hr., until all the metal had gone into solution. The solution was cooled to −75° and a solution of 3.0 g. (0.05 mole) of acetone in 20 ml. of ether was added. The reaction mixture was permitted to warm to room temperature, hydrolyzed with ice and worked up in the usual manner. The product was distilled at 1 mm. until no more material distilled with a flask temperature of 100°. The residue in the flask was dissolved in pentane and cooled. A crop of white crystals was obtained, m.p. 123–128°. A second crop was obtained. The yield was 125 mg., 1.3% of theory. The product could be readily purified (m.p. 127.5–128.0°) by sublimation at 100° at 1 mm. A second preparation gave the product in a yield of 1.1%.

Conversion of Carbinols into Tertiary Chlorides.—In a small round bottom flask, 2–5 g. of the carbinol was placed and hydrogen chloride passed over the material until the mixture separated into two layers. The lower layer of aqueous hydrochloric acid was removed with a fine capillary, the chloride was treated with a crystal of calcium chloride, and dissolved hydrogen chloride removed by pumping for a few minutes. The product was utilized for the rate measurements without further purification. In the case of phenyldimethylcarbinyl chloride, which could be purified by distillation at low pressures, it was observed that identical rate constants were obtained with material distilled in this way as with the crude reaction product prior to distillation.

Kinetic Measurements.—Temperatures were controlled to ±0.02°. The solvent, 100 ml., was placed in a long necked flask and brought to reaction temperature. Approximately 1 ml. of the tertiary chloride was added, mixed thoroughly and 5-ml. aliquots removed at appropriate intervals of time. The aliquots are run into 100 ml. of cold (0°) dry acetone to stop the reaction and free hydrogen chloride titrated with 0.03 *N* sodium hydroxide using methyl red as the indicator. The reaction mixture was usually permitted to stand overnight (at least ten times the calculated half-life) to obtain the aliquot for the "infinity" titer. Some of the reactions were quite fast and considerable attention to detail was required to obtain reproducible results.

LAFAYETTE, INDIANA

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[44] R. R. Dreisbach and R. A. Martin, *Ind. Eng. Chem.*, **41**, 2876 (1949).

[45] Literature[44] value $n^{20}\text{D}$ 1.54084.

[46] J. B. Shoesmith and A. Mackie, *J. Chem. Soc.*, 2334 (1928).

[47] E. E. Connolly, *ibid.*, 338 (1944).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Rates of Solvolysis of α- and β-Naphthyldimethyl- and -monomethylcarbinyl Chlorides. Steric and Electronic Effects of the Naphthalene System[1,2,3]

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α- and β-naphthyldimethylcarbinyl chlorides and α- and β-naphthylmonomethylcarbinyl chlorides were synthesized and their rates of solvolysis in 80% and 90% aqueous acetone were determined. The rate of solvolysis of β-naphthyldimethylcarbinyl chloride in 90% acetone at 25° is faster than that of phenyldimethylcarbinyl chloride by a factor of 4.0. The increase is attributed to the greater capacity of the naphthyl system to accommodate an electron deficiency. The same effect is observed in β-naphthylmonomethylcarbinyl chloride which undergoes solvolysis in 80% acetone at a rate 9.0 times greater than that of the corresponding phenyl derivative. No significant difference in rates is observed in the solvolysis of α- and β-naphthyldimethylcarbinyl chlorides. It is concluded that steric inhibition of resonance due to the *peri* position must be reducing the expected greater capacity of the α-naphthyl system to stabilize the electron deficient transition state. In the case of the secondary derivatives, α- and β-naphthylmonomethylcarbinyl chlorides, the steric effect is less and the expected enhancement in rate of the α-naphthyl over the β-naphthyl derivative ($k^{\alpha}/k^{\beta} = 2.5$) is observed.

The substitution chemistry of the naphthalene system offers many points of both theoretical and practical interest.[4] Unfortunately, the available data are essentially qualitative in nature. In contrast to benzene derivatives no measurements are now available on the partial rate factors for electrophilic substitution in the naphthalene molecule.

In the previous paper[5] it was pointed out that the solvolysis data for *m*- and *p*-tolyldimethylcarbinyl chlorides agree with the empirical relationship previously proposed for the partial rate factors governing electrophilic substitution in the toluene system.[6] It appeared possible, therefore, to attain some quantitative information as to the relative reactivities of the α- and β-positions of naphthalene in electrophilic reactions by studying the solvolysis of α- and β-naphthyldimethylcar-

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[1] Directive Effects in Aromatic Substitution. XI.

[2] Supported by the Petroleum Research Fund of the American Chemical Society.

[3] Based upon a thesis submitted by Y. Okamoto, in 1956, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[4] L. F. Fieser, "Theory of the Structure and Reactions of Aromatic Compounds," Chapter 3 in "Organic Chemistry," Vol. I, edited by H. Gilman, John Wiley and Sons, Inc., New York, N. Y., 1943.

[5] H. C. Brown, J. D. Brady, M. Grayson and W. H. Bonner, THIS JOURNAL, **79**, 1897 (1957).

[6] H. C. Brown and K. L. Nelson, *ibid.*, **75**, 6292 (1953); H. C. Brown and C. W. McGary, Jr., *ibid.*, **77**, 2300 (1955); H. C. Brown and C. R. Smoot, *ibid.*, **78**, 6255 (1956).