Stirring was continued at reflux for 5 hr. and the bromide was then recovered in the usual way. The recovered bromide showed a slight increase in the amount of *trans* isomer, as evidenced by the diagnostic infrared bands of the latter, but was still very predominantly *cis*.

(c) The above experiment was repeated, expect that pure *cis*-bromide was used and the bromide was added to the silver acetate suspension one minute *before* bromine addition commenced. In this way, the *cis*-bromide was exposed to *both* bromine *and* silver bromide under the reaction conditions, rather than to silver bromide only. After 1 hr. boiling at reflux with stirring, the mixture was worked up as previously described. The product showed a marked ester band in the infrared at 5.77μ and very weak bands ascribable to the *trans* isomer, the one at 11.4μ being the most prominent (about six scale divisions). However, the recovered material was still very largely *cis*-bromide.

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NOTRE DAME, IND.

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The Substituent Constant of the 3,4-Benzo Group

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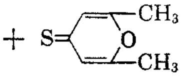
The effect of the 3,4-benzo substituent in different reactions has been examined by analyzing literature data, supplemented by further kinetic studies on the benzoylation of 2-naphthylamine, the alkaline hydrolysis of ethyl 2-naphthylacetate and of 2-naphthoic esters, and the acid-catalyzed esterification of 2-naphthoic acid. The substituent constant ($\sigma_{3,4\text{-benzo}}$) varies systematically with reaction type and it is possible to distinguish σ^-, σ and σ^+ values. The σ^- values display an unexpected anomaly, which is discernible also in the comparable data for the *p*-nitro substituent.

Hammett[1] calculated a value of 0.170 for the substituent constant of the 3,4-benzo substituent, using the dissociation constant of the 2-naphthylammonium ion. In testing this $\sigma_{3,4\text{-benzo}}$ value in nine other reactions he found a probable error of 0.102, one of the largest listed by him. Now for a number of reactions, plots of log k *vs.* σ show that the 3,4-benzo substituent is well removed from the best straight line and that a lower $\sigma_{3,4\text{-benzo}}$ value would provide a better fit. Examples of such reactions are (*a*) R-C_6H_4COOEt + OH^- in dioxane/water (Ref. 2, reaction 47L) (*b*) dissociation of R-$C_6H_4B(OH)_2$ in ethanol/water (Ref. 2, reaction 13) (*c*) R-$C_6H_4COCH_2Br$ +  in benzene (Ref. 2, reaction 105a) (*d*) dissociation of R-$C_5H_4NH^+$ in water (Ref. 14). For reaction (*a*) Jaffe[2] has already noted the marked deviation, from the linear plot, of this substituent.

Although a few independent determinations of $\sigma_{3,4\text{-benzo}}$ have been made, Hammett's value is still generally taken as the standard for reference. But if it be assumed that the benzo substituent has the ability to withdraw electrons by the conjugative mechanism (−T), then the substituent constant obtained by Hammett is likely to be a σ^- value. For reactions other than those of phenol or amine derivatives a normal σ value should apply although, with its weak conjugative withdrawal of electrons, this substituent is likely to have σ^- and σ values not greatly different in magnitude. However, it is clearly of interest to know whether such distinct values may be assigned to the 3,4-benzo group and also to learn whether, with its ability to donate electrons conjugatively (+T mechanism) in suitable circumstances, the group requires also a σ^+ value under these conditions. From the literature, data of sufficient accuracy have now been found for the calculation of over 20 sigma values for this substituent. In addition, in order to extend these values, and in one case to confirm a value derived from published data, further kinetic studies have been made.

EXPERIMENTAL

Benzoylation of naphthylamines. The reaction rates of many substituted anilines were measured at 25° by Stubbs and Hinshelwood,[3] and a smaller number of measurements were made by these workers at 40°. The data for 25° fit a Hammett plot exceptionally well in most cases but two amines, of which 2-naphthylamine is one, do not lie on the linear plot. Calculation gives the apparent $\sigma_{3,4\text{-benzo}}$ value as 0.06 (cf. Hammett's value of 0.17) and, to obtain confirmation of this value, the kinetics of reaction of 2-naphthylamine were re-examined using the same technique. Measurements were made over the temperature range 10–45°; the 1-naphthylamine reaction was similarly examined for general comparative purposes. Results are given in Tables I and II, and it will be seen that results at 25° agree well with those of the previous study.

Alkaline hydrolysis of ethyl naphthylacetates (in 87.83% ethanol/water). The only previous work is recorded by

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[1] L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill Book Co., New York, 1940, Ch. 7.

[2] H. H. Jaffé, *Chem. Revs.*, **53**, 237 (1953).

[3] F. J. Stubbs and C. N. Hinshelwood, *J. Chem. Soc.*, 152, S.71 (1949).

TABLE I

BENZOYLATION OF AMINES

Amine	Rate Constants k × 10^2 (l. mole^{-1} sec.$^{-1}$) 10°	25°[a]	35°	45°	Arrhenius Data E(kcal. mole^{-1})	Log$_{10}$A
1-Naphthylamine	0.430	1.02	1.71	2.71	9.50 ± 0.05	4.96 ± 0.03
	0.437	0.978	1.70	2.73		
	0.438	0.967	1.66	2.79		
		0.986	1.69	2.75		
		1.02	1.76	2.72		
		1.01	1.76			
		0.974	1.75			
			1.72			
2-Naphthylamine	2.31	4.57	7.48	11.4	7.96 ± 0.05	4.51 ± 0.04
	2.46	4.58	7.44	11.2		
	2.50	4.73	7.38	11.1		
	2.30	4.61	7.54	11.3		
	2.34	4.46	7.44	11.7		
	2.44	4.74	7.48	10.9		
	2.33	4.61	7.38	11.3		
	2.41	4.78		10.8		

[a] *cf.* Stubbs and Hinshelwood[3] $k \times 10^2$ = 1.04 (1-naphthylamine)
= 5.12 (2-naphthylamine)

TABLE II

DERIVED DATA FOR BENZOYLATION REACTIONS

Amine	$k_{25°} \times 10^2$ (l. mole^{-1} sec.$^{-1}$)	E (kcal. mole^{-1})	Log$_{10}$A	$\Delta\Delta H^\ddagger$ (kcal. mole^{-1})	$T\Delta\Delta S^\ddagger_{25°}$ (kcal. mole^{-1})
Aniline[a]	7.40	7.60	4.44	(0.00)	(0.00)
1-Naphthylamine	1.01	9.50	4.96	2.09	0.90
2-Naphthylamine	4.78	7.96	4.51	0.54	0.27

[a] Stubbs and Hinshelwood.[3]

TABLE III

ALKALINE HYDROLYSIS OF SUBSTITUTED ETHYL ACETATES

Ethyl Ester	Rate Constants k × 10^3 (l. mole^{-1} sec.$^{-1}$) 20°	30°	35°	40°	50°	E (kcal. mole^{-1})	Log$_{10}$A
Phenylacetate	5.50	12.3[a]	19.4		55.4	14.67 ± 0.12	8.66 ± 0.09
	5.33	12.1[a]	19.3		55.3		
	5.37		17.4[b]				
	5.26		17.7[b]				
1-Naphthylacetate	2.22[b]	5.56		12.4	25.4	15.43 ± 0.09	8.85 ± 0.07
	2.23[b]	5.64		12.5	25.8		
	2.23[b]	5.71			27.4		
	2.17[b]	5.55			26.2		
		5.58					
2-Naphthylacetate	6.98	14.9	23.2	32.0	69.2	14.58 ± 0.11	8.69 ± 0.08
	6.90	14.7	23.3	32.7	70.7		
		15.0	22.4[b]	34.6			
		15.1	22.5[b]	33.9			

[a] *Cf.* Kindler's value of 10.6. [b] Obtained with reactants in unequal concentrations.

Kindler,[4] who examined several substituted phenylacetic esters at 30°. The ethyl naphthylacetates were not included. These have now been studied, over the temperature range 20°–50°, and under similar conditions to those of Kindler. Ethyl phenylacetate was also included in our work and checked with the previous study. Hence a value for $\sigma_{3,4\text{-benzo}}$ may be derived from our results used in conjunction with those of Kindler. Results are given in Tables III and IV.

Alkaline hydrolysis of ethyl and methyl 2-naphthoates (in 60% acetone/water). The experimental procedure was that of Tommila and Hinshelwood.[5] We included kinetic results on 1-naphthoates in an earlier communication[6] in which compatibility between our conditions and those of Tommila and Hinshelwood was demonstrated by agreement on ethyl benzoate. Present results are given in Table V.

Acid-catalyzed esterification, in methanol, of 2-naphthoic acid. This also is an extension of work reported earlier,[6]

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(4) K. Kindler, *Ann.*, **452**, 90 (1927).

(5) E. Tommila and C. N. Hinshelwood, *J. Chem. Soc.*, 1801 (1938).

(6) J. Packer, J. Vaughan, and E. Wong, *J. Org. Chem.*, **23**, 1373 (1958).

TABLE IV

DERIVED DATA FOR REACTIONS IN TABLE III

Ethyl Ester	$k_{30°} \times 10^3$ (l. mole^{-1} sec.$^{-1}$)	E (kcal. mole^{-1})	$\text{Log}_{10}A$	$\Delta\Delta H^\ddagger$ (kcal. mole^{-1})	$T\Delta\Delta S_{30°}{}^\ddagger$ (kcal. mole^{-1})
Phenylacetate	12.3	14.7	8.66	(0.00)	(0.00)
1-Naphthylacetate	5.44	15.4	8.85	0.76	0.27
2-Naphthylacetate	18.1	14.6	8.69	−0.09	0.03

TABLE V

HYDROLYSIS AND FORMATION OF 2-NAPHTHOIC ESTERS

Ester Hydrolyzed or Acid Esterified	Rate Constant k × 10^4 (l. mole^{-1} sec.$^{-1}$)					Arrhenius Data	
	15°	25°	40°	50°	60°	E (kcal. mole^{-1})	$\text{Log}_{10}A$
Ethyl 2-naphthoate	15.66	36.0	119.2	247.1		14.62 ± 0.03	8.29 ± 0.02
	15.69	36.3	120.9	248.5			
Methyl 2-naphthoate	51.4	121.2	387	767		14.34 ± 0.05	8.59 ± 0.03
	51.7	121.3	390	783			
2-Naphthoic acid		2.05	6.85	14.52	28.94	14.95 ± 0.03	7.27 ± 0.02
				14.39	29.28		

in which a method similar to that of Hartman and Borders[7] was used, and in which compatibility of results between the two sets of workers was demonstrated. Results are included in Table V. Unfortunately, the σ values from this reaction prove subject to large errors. Using reaction constant (ρ) values from Jaffé,[2] σ values for the 3,4-benzo substituent are $\sigma_{25°} = 0.054$; $\sigma_{40°} = 0.066$; $\sigma_{50°} = 0.075$; $\sigma_{60°} = 0.079$. But the values for the correlation coefficients ($r \approx 0.4$) and the standard deviations ($s \approx 0.14$) calculated by Jaffé for these reaction series indicate that they fit the Hammett equation very poorly. Thus substituent constants obtained from these esterification experiments were not used in compiling Table VI.

DISCUSSION

In Table VI are listed the substituent constant values for the 3,4-benzo substituent, calculated from reactions for which rate or equilibrium data for 2-naphthyl derivatives are available. For many of the reactions Jaffé[2] has already calculated the reaction constant ρ. Where rate data for 2-naphthyl derivatives were available, Jaffé used appropriate log k values together with Hammett's $\sigma_{3,4\text{-benzo}}$ value of 0.170 in determining the corresponding ρ values. In such cases, therefore, ρ values have now been recalculated without using the rate data for this substituent. Application of the log $k_{3,4\text{-benzo}}$ values to these newly calculated figures for ρ then gave $\sigma_{3,4\text{-benzo}}$ values. Also listed in the table are values for ρ, the correlation coefficient r, and standard deviation s of the best straight line through the points, and n, the number of substituents for which data were available. In the last column, where references are given to sources of rate data for 2-naphthyl derivatives, the absence of a reference number indicates that such rate data were obtained from direct references given in Jaffé's review.[2] Principles guiding selection of material for Table VI were: (i) in calculating ρ values, only σ constants given by Jaffé were included, the restriction being imposed because many σ values reported more recently have yet to be tested in other reactions. (ii) Only those reaction series with a correlation coefficient >0.95 were listed. This restriction follows Jaffé, but in the present calculations it resulted in the elimination of only one or two possible sources of $\sigma_{3,4\text{-benzo}}$ values. (iii) In certain reactions $\sigma_{3,4\text{-benzo}}$ values could be calculated for more than one temperature. In order that no particular reaction should be overweighted in the calculation of mean σ values (see later), σ in such a reaction was calculated only for the temperature at which data for the greatest number of substituents were available. This restriction also is far from severe, because σ shows little change with temperature. On the other hand, solvent variation appears to have an appreciable effect and $\sigma_{3,4\text{-benzo}}$ values, determined for the same reaction in different solvents, have been included. Reactions 1–9 are reactions of anilines, phenols, or their derivatives; reactions 10–13 cover carbinyl chloride solvolyses; reactions not entering either of the first two categories are those numbered 14–26. It is clear that reactions 14–26 are those which should require normal σ values; reactions 10–13 presumably demand σ^+ values, and to reactions 1–9 σ^- values should apply. The calculated σ values do indeed group themselves accordingly, although the substituent constants for phenol and amine reactions (1–9) are less internally consistent (see later, however).

Reactions other than aniline, phenol and solvolysis reactions. The mean value of σ from reactions 14–26 is 0.042 ± 0.030. Two comments may be made concerning the small error on this mean value. First, no reaction with a negative ρ value is included in this set of reactions and it appears that such data are neither available nor readily obtainable. However, the range of positive ρ values

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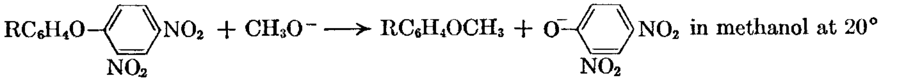
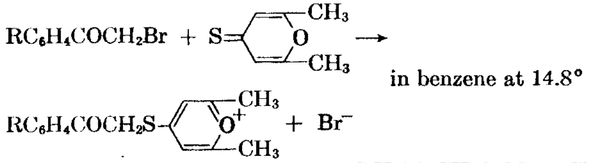
[7] R. J. Hartman and A. M. Borders, *J. Am. Chem. Soc.*, **59**, 2107 (1937).

TABLE VI

SUBSTITUENT CONSTANT VALUES FOR THE 3,4-BENZO GROUP

Reaction	$\sigma_{3\,4\text{-benzo}}$	ρ	r	s	n	Reference	Description
1	0.120	2.798	0.999	0.046	13		$RC_6H_4NH_3^+ \rightleftharpoons RC_6H_4NH_2 + H^+$ in water at 25°
2	0.153	−0.947	0.993	0.062	9		$RC_6H_4O^- + \overline{CH_2CH_2O} \longrightarrow RC_6H_4OCH_2CH_2O^-$ in 98% ethanol/water at 70.4°
3	0.184	−0.770	0.987	0.068	9		$RC_6H_4O^- + CH_3\,\overline{CHCH_2O} \longrightarrow RC_6H_4OCH(CH_3)CH_2O^-$ in 98% ethanol/water at 70.4°
4	0.219	0.598	0.987	0.053	14		$RC_6H_4OSO_2OH + H^+ \longrightarrow RC_6H_4OH + SO_2OH^+$ in water at 48.7°
5	0.154	1.450	0.999	0.020	4		 in methanol at 20°
6	0.046	2.099	0.991	0.077	17	8	$RC_6H_4OH \rightleftharpoons RC_6H_4O^- + H^+$ in water at 25°
7	0.070	−1.245	0.997	0.026	8		$RC_6H_4OH + HCOOH \longrightarrow RC_6H_4NHCHO + H_2O$ in 67% pyridine/water at 100°
8	0.066	−3.220	0.999	0.051	10	Present work	$RC_6H_4NH_2 + C_6H_5COCl \longrightarrow RC_6H_4NHCOC_6H_5 + HCl$ in benzene at 25°
9	0.053	−1.545	0.983	0.104	18		(*trans*) $R'C_6H_4N{=}NC_6H_4R'' + C_6H_5COOOH \longrightarrow$ (*trans*) $R'C_6H_4N(O){=}NC_6H_4R'' + C_6H_5COOH$ in benzene at 15°
10	−0.132	−4.639	1.000	0.07	18	9	$RC_6H_4C(CH_3)_2Cl + H_2O \longrightarrow RC_6H_4C(CH_3)_2OH + HCl$ in 90% acetone/water at 25°
11	−0.188	−4.376	0.997	0.14	12	10	$RC_6H_4CH(C_6H_5)Cl + C_2H_5OH \longrightarrow RC_6H_4CH(C_6H_5)OC_2H_5 + HCl$ in ethanol at 25°
12	−0.147	−2.606	0.994	0.11	7	11	$RC_6H_4C(C_6H_5)_2Cl + C_2H_5OH \longrightarrow RC_6H_4C(C_6H_5)_2OC_2H_5 + HCl$ in ethanol/ether (40/60) at 0°
13	−0.113	−4.669	0.993	0.06	5		$RC_6H_4CH(C_6H_5)Cl + (CH_3)_2CHOH \longrightarrow RC_6H_4CH(C_6H_5)OCH(CH_3)_2 + HCl$ in isopropyl alcohol at 25°
14	0.042	1.000				12	$RC_6H_4COOH \rightleftharpoons RC_6H_4COO^- + H^+$ in water at 25°
15	0.084	0.483	0.981	0.033	14	13	$RC_6H_4CH_2COOH \rightleftharpoons RC_6H_4CH_2COO^- + H^+$ in water at 25°
16	0.045	2.137	0.996	0.062	13		$RC_6H_4B(OH)_2 \rightleftharpoons RC_6H_4B(OH)O^- + H^+$ in 25% ethanol/water at 25°
17	0.032	0.879	0.956	0.104	11		$RC_6H_4AsO_2OH^- \rightleftharpoons RC_6H_4AsO_2O^{2-} + H^+$ in water at 22°
18	0.084	0.961	0.970	0.077	14		$RC_6H_4SeOOH \rightleftharpoons RC_6H_4SeOO^- + H^+$ in water at 25°
19	0.022	5.685	0.995	0.147	10	14	$RC_5H_4NH^+ \rightleftharpoons RC_5H_4N + H^+$ in water at 23°–25°
20	0.079	2.537	0.998	0.067	12	15	$RC_6H_4COOC_2H_5 + OH^- \longrightarrow RC_6H_4COO^- + C_2H_5OH$ in 85% ethanol water at 25°
21	0.031	2.310	0.999	0.026	3		$RC_6H_4COOC_2H_5 + OH^- \longrightarrow RC_6H_4COO^- + C_2H_5OH$ in 70% dioxan/water at 25°
22	0.036	2.265	0.984	0.141	25	Present work	$RC_6H_4COOC_2H_5 + OH^- \longrightarrow RC_6H_4COO^- + C_2H_5OH$ in 60% acetone/water at 25°
23	0.042	2.229	0.995	0.106	11	Present work	$RC_6H_4COOCH_3 + OH^- \longrightarrow RC_6H_4COO^- + CH_3OH$ in 60% acetone/water at 25°
24	0.000	0.824	0.974	0.105	6	Present work	$RC_6H_4CH_2COOC_2H_5 + OH^- \longrightarrow RC_6H_4CH_2COO^- + C_2H_5OH$ in 87.83% ethanol/water at 30°
25	−0.005	0.862	0.982	0.064	9		 in benzene at 14.8°
26	0.060	0.618	0.980	0.050	4		$RC_6H_4SO_2CH_2CH_2Cl + I^- \longrightarrow RC_6H_4SO_2CH_2CH_2I + Cl^-$ in acetone at 75°

covered is from 0.483 to 5.685. Within this range no trend in σ is observed and there seems to be no reason to expect a variation if the range were extended to negative reaction constants. Second, in certain of the reactions (i.e. reactions 14, 16–18, 20–23) weak resonance interaction between a $-$T side-chain and a $+$T *para* substituent should be possible. In each case, however, there is cross-conjugation in the side-chain itself and it is evident that in these cases any side-chain-substituent resonance has a negligible effect on the substituent constant.

Carbinyl chloride solvolyses. The mean $\sigma^{+}{}_{3,4\text{-benzo}}$ value from reactions 10–13 is -0.145 ± 0.028. It is true that the four reactions listed are similar in type and that it would be desirable to obtain data for the 3,4-benzo substituent on reactions of different types which still require σ^{+} values. However, Okamoto and Brown[9] have shown that σ^{+} for other $+$T substituents (*e.g.* *p*-OCH_3) have a remarkably wide applicability.

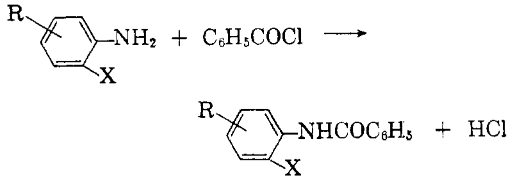
Reactions of anilines, phenols and their derivatives. Reactions 1–9 are those which appear to require σ^{-} values. Of the listed reactions the highest substituent constants are those for reactions 1–5. These are presumably uncomplicated $\sigma^{-}{}_{3,4\text{-benzo}}$ values, the mean of which is 0.166 ± 0.033. In support of this assumption, other $-$T substituents such as the well studied *p*-nitro group also require their accepted σ^{-} values in these reactions. For reactions 6–9, however, the substituent constants are significantly lower and distinction between the two sets appears to be real. In only one earlier investigation have unexpectedly low σ^{-} values been particularly noted and that was by Bordwell and his coworkers,[16,17] who measured pK_a values for certain phenols and thiophenols. The substituents concerned were the *p*-NO_2 and *p*-CH_3SO_2 groups. This work, and Bordwell's suggested explanation, indicate that large differences in the abilities of side-chains to enter into conjugation with a given substituent result in a variation in the σ^{-} value. In the present case, however, we cannot even suggest a single explanation, of low σ^{-} figures, which would cover the three "amine" reactions 7–9. As far as these reactions are concerned, the results appear reliable and for reaction 8, for example, the substituent constant obtained in the present work confirms that derived from the study of Stubbs and Hinshelwood.[3] Furthermore, these "low σ^{-}" values for the 3,4-benzo substituent run parallel to similar low σ^{-} values for the *p*-nitro group (the only other $-$T substituent for which satisfactory rate data are available) in these and other amine reactions. This is demonstrated in Table VII. The comparative substituent constants given by Hammett are: $\sigma^{-}{}_{3,4\text{-benzo}} = 0.170$; $\sigma^{-}{}_{p\text{-nitro}} = 1.270$, and data are drawn from references in Jaffé's review with the exception of reactions 8 and 8a (present work).

TABLE VII

SUBSTITUENT CONSTANTS IN AMINE REACTIONS

Reaction	Apparent $\sigma^{-}{}_{3,4\text{-benzo}}$	Apparent $\sigma^{-}{}_{p\text{-nitro}}$	ρ	r	s	n
7	0.070	...	-1.245	0.997	0.03	8
8	0.066	1.022	-3.220	0.999	0.05	10
8a[a]	0.064	0.975	-3.167	0.995	0.03	3
9	0.053	1.043	-1.545	0.983	0.10	18
9a[b]	0.054	1.056	-1.488	0.982	0.10	18
27[c]	...	1.022	-3.192	0.997	0.09	6
28[c]	...	0.980	-3.398	1.000	0.01	4

[a] Reaction 8a is reaction 8 at 40°. [b] Reaction 9a is reaction 9 at 15°. [c] Reactions 27 and 28:



in benzene at 25°.

For reaction 27, X = CH_3.
For reaction 28, X = OCH_3.

The differences between the apparent σ^{-} figures and the normally accepted figures originally derived by Hammett appear to be appreciable and, for example, when Hammett plots are made for reactions 7, 8, and 28 there are significant and striking deviations of these two substituents from otherwise accurately linear plots when the Hammett σ^{-} values are used.

It is evident that further information is desirable about the "accepted" σ^{-} values for $-$T substituents in amine reactions (reaction 1 is the sole example) and about "low σ^{-}" values for such substituents in phenol reactions (reaction 6 is the sole example). Without such information it can only be stated that in reactions 1–5 the difference in resonance interaction (involving substituent and side-chain) between reactant and product (or transition state) appears to be markedly greater than this difference for reactions 6–9.

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