The Substituent Effect. X. Solvolysis of 3- and 4-Substituted 1-(1-Naphthylethyl) Chlorides

Yuho Tsuno,* Masami Sawada, Takahiro Fujii, and Yasuhide Yukawa
The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka 565
(Received December 18, 1974)

The rates of the solvolysis of eleven 3- and 4-substituted 1-(1-naphthylethyl) chlorides were determined in 80% (v/v) aqueous acetone solution at 45 °C. The effect of substituents in 3- and 4-positions of the naphthalene can be correlated with the LArSR relationship ($\log k/k_0)_{3\alpha,4\alpha} = -5.12(\sigma^0 + 1.04\,\Delta\bar{\sigma}_R^+) - 0.12$ (correlation coefficient, 0.999; standard deviation, ± 0.12). The ρ value in the naphthalene is slightly larger and the r value is slightly smaller than values in the corresponding benzene system under the same condition ($\rho = -4.95$, $r = 1.15$). The difference is reasonably interpreted in terms of the steric effect for the *peri*-hydrogen relative to the reaction center at the α-position of the naphthalene. The effect of substituents can be correlated with the LSFE relationship for conjugatively electron releasing groups with high precision ($R > 0.999$) in the series, 3α and 4α; ($\log k/k_0 = \rho_i\sigma_i + \rho_\pi^+\sigma_\pi^+$). In this solvolysis, the 3α/4α inductive ratio, $\rho_{i,3\alpha}/\rho_{i,4\alpha}$, was 1.37, only slightly larger than the *meta*/*para* inductive ratio of 1.17 for the corresponding reaction in the benzene series. The applicability of these equations to 3- and 4-substituted α-naphthyl system is also shown for some other reactivities.

In our studies of the substituent effect on chemical reactivities, we established that the following Linear Aromatic Substituent Reactivity (LArSR) relationship[1-3] is, in general, applicable to electrophilic and nucleophilic reactions of *meta*- and *para*-substituted benzene derivatives:

$$\log k/k_0 = \rho(\sigma^0 + r^+\Delta\bar{\sigma}_R^+ + r^-\Delta\bar{\sigma}_R^-) \quad (1)$$

This holds on the assumption of additive description of the substituent effect in terms of the unexalted polar effect of substituted phenyl groups and the aryl resonance exaltation effect.

It has been generally assumed that the electronic effect of substituents consists, to a first approximation, of inductive and π-electronic effects.[4-7] We have shown that the substituent effect on benzene reactivities can be successfully correlated with the Linear Substituent Free Energy (LSFE) relationship[3a-3d,8] based on the σ_i—$\sigma_\pi^\pm$ combination in place of the σ^0—$\Delta\bar{\sigma}_R^\pm$ combination in Eq. (1):

$$\log k/k_0 = \rho(C_i\sigma_i + q_r^+\sigma_\pi^+ + q_r^-\sigma_\pi^-) \quad (2)$$

The first term, $C_i\sigma_i$, represents the contribution of inductive effect and the last two, $q_r^+\,\sigma_\pi^+$ and $q_r^-\,\sigma_\pi^-$, the contributions of π-electronic effects for conjugatively electron releasing ($-R$) and attracting ($+R$) substituents, respectively. σ_i is the inductive substituent constant characteristic of given substituents and independent of the resonance requirement of their reactions. σ_π^+ or σ_π^- is the π-electronic substituent constant characteristic of a given substituent describing the capability to donate or attract electron through π-electron delocalization. Both C_i and q_r^+ (q_r^-) are characteristic variables giving a measure of the inductive and π-electronic interactions with the reaction center, respectively.

From a statistical analysis of substituted benzene reactivities by means of Eq. (2), we arrived at two significant conclusions.[3a-3d,8] (i) The transmission coefficient of the inductive effect, C_i, depends only on the position of substituents and remains constant independent of reactions in the benzene system, that is, C_i is 1.00 for the *para* and 1.17 for the *meta* position. (ii) The contribution of the π-electronic effect, q_r^+ or q_r^-, effectively varies only for substituents that may conjugate with the reaction center and is a function of given reactions. Both q_r^+ and q_r^- are standardized to be unity in σ_p^0 scale and $q_r^\pm$ is 0.50 in *meta* position. These are summarized in the following generalized forms.

$$\log (k/k_0)_p = \rho(1.00\sigma_i + q_r^+\sigma_\pi^+ + q_r^-\sigma_\pi^-)$$
$$\log (k/k_0)_m = \rho(1.17\sigma_i + 0.50\sigma_\pi^\pm) \quad (3)$$

In naphthalene derivatives, there are ten positional combinations between substituents and reaction centers, excluding *ortho* and *peri* combinations. It is expected that contributions of both the inductive and the π-electronic effects may differ from each other, depending upon the relative position of substituents in any single reaction. Since the substituent constants, σ_i and $\sigma_\pi^\pm$, are believed to be characteristic of substituents independent of the parent hydrocarbon, the application of Eq. (2) to the substituent effect on the naphthalene system offers important information on the positional transmittance of the inductive and π-electronic effects in naphthalene reactivities.

Very few substituent effect data have been reported on naphthalene, as compared with those on benzene reactivities. Three electrophilic reactions have been reported in which the effects of a wide range of substituents at almost all of the positions in the naphthalene system are systematically investigated: (1) dissociation of naphthoic acids in 50% aq. EtOH,[6,9] (2) alkaline hydrolysis of naphthoic acid esters in aq. organic solvents,[10,11] (3) detritiation of tritionaphthalenes in CF_3COOH.[12,13] The first two reactions are representative σ-type reactivities in the benzene system, having no large contribution of the π-electronic effect. Since an acidic solvent was utilized in the last reaction, there were some problems, *e.g.*, the methoxy substituent was evidently modified by direct solvent-substituent interaction; only methyl and halogens could be treated as ordinary substituents. In order to get more information on the substituent effect for naphthalene reactivities in which electron requirement of the reaction center a great

* To whom inquiries should be addressed. Present address; Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Fukuoka 812

deal differs from the first two, we choose the solvolysis of substituted 1-(1-naphthylethyl) chlorides in an ordinary aqueous organic solvent. This reaction is representative of carbonium-ion type reactions and gives comparatively large π-electronic effects of $-R$ substituents at the conjugative positions in the naphthalene.

The present paper is mainly concerned with the treatment based on Eqs. (1) and (2) on the substituent effect of the solvolysis of 3- and 4-substituted 1-(1-naphthylethyl) chlorides in 80% aqueous acetone at 45 °C. These effects can be directly compared with those of *meta*- and *para*-substituted 1-phenylethyl chlorides which have been studied extensively under the same conditions.[3e]

Experimental

Materials. 3- and 4-Substituted 1-Acetylnaphthalenes: Commercial 1-acetylnaphthalene was purified by recrystallization of the picrate (mp 119—120 °C),[14] followed by fractional distillation of the regenerated ketone. No impurities were detected by vpc. 4-Methyl-, 4-chloro-, 4-bromo-, and 4-methoxy-1-acetylnaphthalenes were prepared by the Friedel-Crafts acetylation of the corresponding 1-substituted naphthalenes and fractionated or recrystallized.[15-17] 1-Acetyl-4-cyanonaphthalene was synthesized from 1-acetyl-4-bromonaphthalene by the method of Friedmann and Shechter[18] (45% yield), using CuCN in DMF.

1-Acetyl-4-ethylnaphthalene: 1-Ethylnaphthalene was obtained by the Wolff-Kishner reduction[19] of 1-acetylnaphthalene in 84% yield. Friedel-Crafts acetylation of 1-ethylnaphthalene (32 g) with AcCl (19 g) and $AlCl_3$ (33 g) in CS_2 gave 1-acetyl-4-ethylnaphthalene in 63% yield; bp 159—159.5 °C/2.5 mmHg.[20]

1-Acetyl-3-chloronaphthalene: 1-Bromo-3-chloronaphthalene was prepared according to the prescription of Fischer *et al.*[21] Chlorination of *N*-acetyl-4-bromo-1-naphthylamine (mp 195—196 °C from MeOH or 95% aq. EtOH)[21,22] gave *N*-acetyl-4-bromo-2-chloro-1-naphthylamine; mp 233—233.5 °C from MeOH or 95% EtOH.[21] 1-Bromo-3-chloronaphthalene distilled at 141—145 °C/5 mmHg,[21,23] solidified on being left to stand (mp 45—50 °C), was obtained by deamination of crude 4-bromo-2-chloro-1-naphthylamine (mp 108—110 °C)[21] prepared by hydrolysis of the above naphthalide in EtOH–aq. H_2SO_4 solution.

A mixture of the bromochloronaphthalene and CuCN in DMF solution was refluxed for 4 hr.[18] The crude 3-chloro-1-naphthonitrile obtained (mp 88—94 °C) was hydrolyzed in AcOH–aq. H_2SO_4 solution. The resulting 3-chloro-1-naphthoic acid was purified by recrystallization from aq. EtOH and aq. AcOH; mp 229—232 °C.[21]

The acid was successfully converted into the 1-acetyl-3-chloronaphthalene by application of Browman's procedure[24] in 75% yield; *via* 3-chloro-1-naphthoyl chloride (mp 77—83 °C from hexane). The fractionated product was recrystallized from hexane.

1-Acetyl-3-bromonaphthalene: 3-Bromo-1-naphthoic acid (mp 234—237 °C from EtOH)[25] was prepared by a similar synthetic route by Dewar and Grisdale;[25] mercuration[26,27] of 3-bromonaphthalic acid anhydride (mp 243.5—244.5 °C)[25,28] and subsequent decomposition of the mercurated product.[26] The acid was converted into 3-bromo-1-naphthoyl chloride and subsequently to 1-acetyl-3-bromonaphthalene by the method described for the 3-chloro derivative.

1-Acetyl-3-cyanonaphthalene: This ketone (7 g) was obtained from 1-acetyl-3-bromonaphthalene (10 g) and purified by recrystallization from benzene–hexane.

1-Acetyl-3-methoxynaphthalene: 4-Bromo-2-naphthylamine (mp 71 °C)[29,30] was obtained, according to the prescription of Bergman,[29] from 1-bromo-3-nitronaphthalene (mp 128—130 °C)[29] derived from the deamination of the diazonium solution of 4-bromo-2-nitro-1-naphthylamine (mp 198—201 °C).[29] The 4-bromo-2-naphthylamine obtained was converted into 4-bromo-2-naphthol (bp 130—132 °C/1.5 mmHg, mp 117—120 °C)[31] by the usual diazonium method; the diazonium sulfate was decomposed by the dropwise addition to *ca.* 40% aq. H_2SO_4 solution at about 80 °C. Methylation of the 2-naphthol with Me_2SO_4 in an alkaline solution gave 1-bromo-3-methoxynaphthalene (mp 112—114 °C).

Reaction of the bromide and CuCN in DMF and working up by Friedmann's procedure[18] gave crude 3-methoxy-1-naphthonitrile (mp 102—104 °C). Direct hydrolysis of the

Table 1. Physical constants and analytical data of 3- and 4-substituted (X) 1-acetylnaphthalenes

X	Bp or Mp*	Carbon		Hydrogen		Other	
		Found	Calcd	Found	Calcd	Found	Calcd
4-MeO-α	147°C/1.5mmHg, 71—72°C[a]	77.74	77.98	5.94	6.04		
4-Me-α	136°C/1.5mmHg[b]	84.57	84.75	5.82	6.57		
4-Et-α	159—159.5°C/2.5mmHg[c]	84.87	84.82	7.06	7.11		
H-α	133—135.5°C/4mmHg[d]	84.92	84.64	5.76	5.92		
4-Cl-α	142°C/1mmHg[e]	70.31	70.43	3.80	4.43	17.60	17.32(Cl)
4-Br-α	141—143°C/0.7mmHg[f]	58.26	57.86	3.00	3.64	31.87	32.08(Br)
4-CN-α	134—135°C	79.54	79.98	4.36	4.65	7.19	7.17(N)
3-MeO-α	140—143°C/1mmHg	78.10	77.98	5.96	6.04		
3-Cl-α	169—171°C/8mmHg,37—37.5°C	70.50	70.43	4.26	4.43	17.06	17.32(Cl)
3-Br-α	137—138°C/1mmHg	57.85	57.86	3.63	3.64	32.04	32.08(Br)
3-CN-α	154—156°C	80.31	79.98	4.38	4.65	7.32	7.17(N)

a) Lit, bp 224—225 °C/15 mmHg,[17] mp 72—74 °C; G. G. Joshi and N. M. Shah, *J. Indian Chem.* **29**, 225 (1952): *Chem Abstr.*, **47**, 5924 (1953), mp 69—71 °C; N. J. Leonard and A. M. Hyson, *J. Amer. Chem. Soc.*, **71**, 1392 (1949). b) Lit, bp 172—174 °C/12 mm Hg, mp 38 °C,[15] bp 174—175 °C/15 mmHg; R. D. Haworth and C. R. Mavin, *J. Chem. Soc.*, **1932**, 2720. c) Lit, bp 182 °C/10 mmHg.[20] d) Lit, bp 127 °C/1 mmHg.[1] e) Lit, bp 140—142 °C/1.5 mmHg,[16] mp 35—37 °C; F. H. Bassilios, Y. A. Salem, M. Shawky, and M. Zaki, *Ann. Chim.* (Rome), **1968**, 1139: *Chem. Abstr.* **70**, 67979q (1969).f) Lit, 165—175 °C/2—4 mmHg,[16] bp 141—143 °C/0.6 mmHg, mp 45—46 °C; S. Berkovic, *Israel J. Chem.*, **1**, 1 (1963): *Chem. Abstr.*, **60**. 1667a (1964). *) All boiling and melting points were uncorrected.

Table 2. Physical constants and analytical data of 3- and 4-substituted (X) 1-(1-naphthylethanols)

X	Mp or Bp*	Carbon		Hydrogen		Other	
		Found	Calcd	Found	Calcd	Found	Calcd
4-Me-α	79—80.5°C	83.73	83.83	7.48	7.58		
4-Et-α	162—168°C/4—5mmHg	83.72	83.96	8.04	8.05		
H-α	65.5—66.5°C[a]	84.00	83.69	6.90	7.02		
4-Cl-α	78—78.5°C[b]	70.07	69.74	5.22	5.37	17.19	17.15(Cl)
4-Br-α	70—72°C[c]	57.92	57.39	4.02	4.42	31.68	31.84(Br)
4-CN-α	79°C	78.94	79.17	5.33	5.62	6.99	7.10(N)
3-Cl-α	102—103°C	69.66	69.74	5.22	5.37	16.87	17.15(Cl)
3-Br-α	71—72°C	57.54	57.39	4.22	4.42		
3-CN-α	82—84°C	79.34	79.17	5.59	5.62	7.41	7.10(N)

a) Lit, mp 62.5—63.5 °C,[34] mp 62—64 °C; Y. Okamoto and H. C. Brown, *J. Amer. Chem. Soc.*, **79**, 1903 (1957). b) Lit, mp 75.5—76 °C; C. C. Price and Sing-Tuh Voong, *J. Org. Chem.*, **14**, 111 (1949). c) Lit, mp 72—73 °C; S. Berkovic, *Israel J. Chem.*, **1**, 1 (1963); *Chem. Abstr.*, **60**, 1667a (1964). *) All melting and boiling points were uncorrected.

nitrile in AcOH–aq. H_2SO_4 gave 3-methoxy-1-naphthoic acid. This material was purified by recrystallization from MeOH; mp 220—223 °C. 1-Acetyl-3-methoxynaphthalene was prepared by the same method as described before.

3- and 4-Substituted 1-(1-Naphthylethanols). Alcohols were prepared by the $LiAlH_4$ reduction of the corresponding ketones in the ethereal solution,[3e,32] unless otherwise stated. The mixture was gently refluxed for about 1 hr and allowed to stand overnight at room temperature, and treated in the usual manner. The crude alcohols were purified by fractionation or recrystallization from appropriate solvents.

$NaBH_4$ in MeOH[33] was utilized for the reduction of bromo-, chloro-, and cyano-ketones. Gentle refluxing of the reaction mixture was continued until the ketone was consumed, which was confirmed by the disappearance of the 2,4-dinitrophenylhydrazone of the corresponding ketone. The methanol solution was decomposed by dil. HCl, neutralized, concentrated, and extracted with benzene.

The physical properties and the elemental analytical data for ketones and alcohols are listed in Tables 1 and 2, respectively.

3- and 4-Substituted 1-(1-Naphthylethyl) Chlorides. All the chlorides except for 3-chloro, and 3- and 4-cyano derivatives were obtained by passing a stream of dry HCl gas into the ethereal solution of purified alcohols at room temperature in the presence of $CaCl_2$.[3c,34] After prompt filtration, the ether was evaporated under reduced pressure. The crude product, dissolved in petroleum ether, was treated with excess K_2CO_3, filtered and evaporated. The same treatment was repeated twice. After final evaporation, the chloride was purified by fractionation or recrystallization from appropriate solvents (*e.g.*, petroleum ether). In the case of methoxy derivatives, the chlorinated products were directly employed for the rate measurements without further purification.

For 3- and 4-cyano- and 3-chloro-1-(1-naphthylethanols), chlorination with excess $SOCl_2$ in benzene was utilized. The solution was gently refluxed until the peaks of O–H vibration in IR spectra disappeared, and refluxing was further continued for 1 hr. Excess $SOCl_2$ was removed by azeotropic distillation, dry benzene being added twice. The chlorides obtained were purified by recrystallization from benzene–hexane or fractionation (Table 3).

Solvent. Acetone which had been refluxed with $KMnO_4$ for over 6 hr was distilled, dried over K_2CO_3 for several days. and fractionated. The stock solutions of 80% and 95% aqueous acetone were prepared by mixing the nominal volumes of acetone and freshly-boiled deionized water, both components being measured at 25 °C.

Kinetic Measurements. The rates of the solvolysis of 3- and 4-substituted chlorides were determined in 80% (v/v) or 95% (v/v) aqueous acetone solutions at appropriate temperatures by means of the usual titration method. The procedure employed for these measurements was essentially the same as that given in the literature.[3e,34] The bath temperature was controlled to ±0.02 °C. For reactions studied at below 0 °C, the runs were carried out in a thermo-

Table 3. Physical constant and analytical data of 3- and 4-substituted (X) 1-(1-naphthylethyl) chlorides

X[a]	Bp or Mp*	Carbon		Hydrogen		Chlorine	
		Found	Calcd	Found	Calcd	Found	Calcd
4-Me-α	103—104°C/1mmHg,41—41.5°C	76.19	76.28	6.22	6.40	17.50	17.32
4-Et-α	31.5—32°C	76.75	76.88	6.79	6.91	16.23	16.21
H-α	116—118°C/2mmHg[b]	75.85	75.79	5.77	5.82	18.87	18.59
4-Cl-α	59—60°C	64.08	64.03	4.22	4.48	31.73	31.50
4-CN-α	76—78°C	72.94	72.39	4.57	4.67	16.21	16.44
3-Cl-α	116.5—118°C/1mmHg	63.89	64.03	4.38	4.48	31.68	31.50
3-Br-α	137—138°C/1mmHg	53.56	53.47	3.63	3.74	13.02	13.15
3-CN-α	78—79.5°C	72.30	72.39	4.58	4.67	16.28	16.44

a) 4-Br-α derivative, bp 137—139 °C/1 mmHg; mp 58—60 °C. b) Lit, bp 128—129 °C/4 mmHg,[34] bp 125—126 °C/2 mmHg; Y. Okamoto and H. C. Brown, *J. Amer. Chem. Soc.*, **76**, 1903 (1957). *) All boiling and melting points were uncorrected.

stated bath maintained at ±0.05 °C or better with cooling by an external bath containing a dry ice–acetone solution.

All the runs at 45 °C and above were carried out at the initial concentration of the chloride, *ca.* 0.02 mol/l in aqueous acetone, in sealed tubes. After the ampoules (more than 10) had been brought to bath temperature, each ampoule was withdrawn at appropriate intervals and quickly immersed into an ice–water bath with vigorous shaking to stop the reaction. A 10 ml aliquot was pipetted, poured into *ca.* 50 ml ice-cooled distilled acetone, and titrated with standardized NaOH aqueous solution. Bromocresol purple or bromothymol blue was employed as an indicator. The two ampoules were allowed to react for at least 10 half-lives in a water bath at *ca.* 90 °C in order to get the infinity reading.

Kinetic runs below 45 °C were conducted in a stoppered Erlenmeyer flask. Ten ml sample solutions were pipetted out, at appropriate intervals, quenched with ice-cooled acetone (*ca.* 50 ml) except for 4-MeO-α derivative, and titrated immediately. For the 4-MeO-α one, about 100 ml acetone which had been cooled about −60 °C with dry ice–acetone was used to stop the reaction.

All the runs involving more than 10 measurements were covered up to 70—85% reaction. In the case of 4-CN-α derivative, calculated values of infinity titers were employed and runs were covered up to *ca.* 50% reaction. Rate constants were determined from the integrated form of the first-order rate equation by means of least squares calculation. The experimental uncertainty of a run was estimated to be less than ±1% and the rate constants from duplicated runs agreed within ±2%.

Table 4. Rate constants of 3- and 4-X-1-(1-naphthylethyl) chlorides in 80 and 95% aq. acetone

X	Solvent %(V/V)	Temp (°C)	$k_1 \times 10^5$ (s^{-1})
H-α	80	45	12.7[a]
4-Me-α	80	25	44.1
		15	13.5
4-Et-α	80	25	33.6
		15	9.83
4-Cl-α	80	45	2.79
4-Br-α	80	45	2.09
4-CN-α	80	95	0.64
		75	0.099
3-MeO-α	80	45	3.42
3-Cl-α	80	85	5.79
		75	2.14
3-Br-α	80	85	5.54
		65	0.746
3-CN-α	80	93	2.61
		85	1.19
		75	0.475
4-MeO-α	95	−10	25.6
		−20	9.71
		−30	2.97
4-Me-α	95	45	2.36
5-MeO-α[b]	95	85	8.98
		75	3.55
6-MeO-β[b]	95	45	6.85
6-MeS-β[b]	95	45	1.36

a) Lit,[34] 12.3×10^{-5}. b) Data taken from Part XI; Y. Tsuno *et al.*, This Bulletin, **48**, 3356 (1975).

Results and Discussion

The rate constants of the solvolysis of 3- and 4-substituted 1-(1-naphthylethyl) chlorides (denoted by 3α and 4α, respectively) in 80% (v/v) aq. acetone at various temperatures are listed in Table 4. The solvolysis of 4-MeO-α derivative was too fast to follow by our method in 80% aq. acetone even at −35 °C, and an extrapolation from the rates in 95% (v/v) aq. acetone solution was employed. The reaction was retarded about 100-fold in the latter solvent, and could then be followed by titration in the temperature range from −10 °C to −30 °C. The rates of four derivatives, 4-Me-α, 5-MeO-α, 6-MeO-β, and 6-MeS-β derivatives in both 80% and 95% aq. acetone (Table 5) are correlated by

$$\log k_{80\%} = 0.847 \log k_{95\%} + 1.462 \quad (4)$$

with a correlation coefficient of 0.9991 and a standard deviation of ±0.031 (Fig. 1). From Eq. (4), the rate constant of the 4-MeO-α derivative in 80% aq. acetone can be estimated to be 1.22 s^{-1} at 45 °C. The extrapolation is supported by the substituent effect for substituted 1-phenylethyl chlorides;[3f] the solvent change from 80% to 90% aq. acetone mainly brings about a change in the ρ value but not in the *r* value of the LArSR Eq. (1). The relative rates in 80% aq. acetone at 45 °C, together with the activation parameters, are summarized in Table 5.

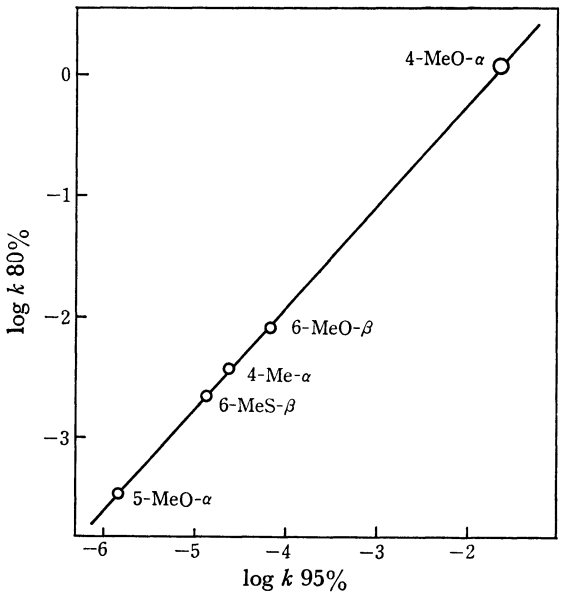

Fig. 1. Logarithmic plot of the present solvolysis rates between 80% and 95% aq. acetone at 45°C.

Comparison between Naphthalene and Benzene Systems. In 3- and 4-substituted 1-(1-naphthylethyl) chlorides, the reaction center and substituent groups are in the same relative positions as in *m*- and *p*- substituted 1-phenylethyl chlorides, respectively. Figure 2 shows the logarithmic plot of relative rates between the naphthalene and the benzene systems under the same conditions; in 80% aq. acetone at 45 °C. The correlation line suggests that the degree of the π-electronic effect of substituents is slightly less effective in the naphthalene system than in the corresponding benzene one.

Table 5. RATE CONSTANTS AND log k/k_0 VALUES IN 80% (v/v) AQ. ACETONE AT 45 °C

X	$k_1 \times 10^5$ [c] s^{-1}	$\log(k/k_0)_{naph}$ [a]	E_a kcal/mol	log A	$\log(k/k_0)_{benz}$ [b]
H-α	12.7	0.000			0.000
4-MeO-α	1.22×10^5** (2.38×10^3*)	3.98**			4.76
4-Me-α	379* (2.36)	1.475	20.3	11.5	1.628
4-Et-α	313*	1.391	21.0	11.9	1.534
4-Cl-α	2.79	−0.658			−0.480
4-Br-α	2.09	−0.784			−0.684
4-CN-α	0.0039*	−3.51*	23.8	8.9	
3-MeO-α	3.42	−0.570			−0.234
3-Cl-α	0.0730*	−2.241*	24.8	10.9	−1.876
3-Br-α	0.0778*	−2.213*	24.2	10.5	−1.947
3-CN-α	0.0179	−2.852*	24.0	9.7	
5-MeO-α	33.0[d] (0.150*)				
6-MeO-β	813*[d] (6.85)				
6-MeS-β	223*[d] (1.36)				

a) Values of the present solvolysis of substituted 1-(1-naphthylethyl) chlorides. b) Values of the solvolysis of the corresponding *meta*- and *para*- substituted 1-phenylethyl chlorides in 80% (v/v) aq. acetone at 45 °C; data taken from Ref. 3e. c) Rate constants in 95% (v/v) aq. acetone at 45 °C are listed in parenthesis. d) Ref. 38. * Values were obtained by extrapolation from rates at other temperatures. ** See text.

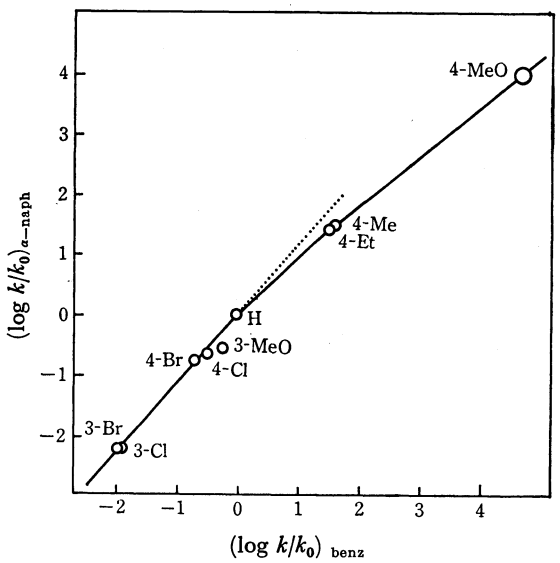

Fig. 2. Log-log plot of the solvolysis rates between α-naphthyl and benzene systems in 80% aq. acetone at 45 °C.

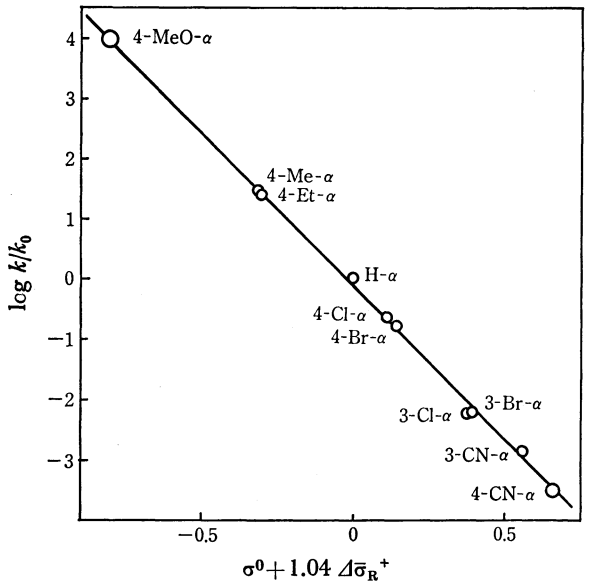

Fig. 3. LArSR plot for the solvolysis of 3- and 4-X-α-naphthylmethylcarbinyl chlorides in 80% aq. acetone at 45 °C.

Equation (1) is applied to the solvolysis rates in the naphthalene derivatives using the σ^0 parameters derived from benzene reactivities to give a correlation

$$\log(k/k_0)_{3\alpha,4\alpha} = -5.12(\sigma^0+1.04\Delta\bar{\sigma}_R^+)-0.12$$

with a correlation coefficient of 0.9990 and a standard deviation of ±0.116 (n=10) (Fig. 3). The corresponding solvolysis rates in the benzene system under the same conditions satisfy Eq. (1) with high precision (R= 0.9997).[3e,35]

$$\log(k/k_0)_{m,p} = -4.95(\sigma^0+1.15\Delta\bar{\sigma}_R^+)-0.023$$

The ρ value in the present naphthalene system is slightly larger but the r value is slightly smaller than that in the benzene system. The difference in the r value of the two systems results in the curvature in Fig. 2.

Even if the inductive effect of the substituents may be transmitted through space or carbon-carbon bond or both, it is reasonably assumed from the geometrical similarity that the contributions of the inductive effect from 3α and 4α positions are approximately equal to those from *meta* and *para* positions, respectively. If there are any differences, they would be the slight differences in bond length and/or bond order between the parent naphthalene and the benzene.

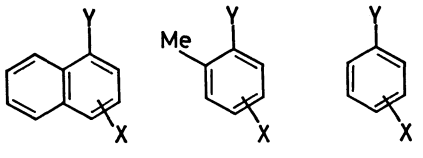

Chart 1

One model in which the steric requirement at the reaction center is analogous to the α-naphthyl derivative (I) is the benzene derivative with a methyl group *ortho* to the reaction site (II). In the dissociation of benzoic acids in 50% aq. EtOH, the ρ value is 1.77 with (II),[36a] and 1.51 without an *ortho* methyl group (III).[36b] In the substituent chemical shifts of the hydroxyl proton of substituted phenols in DMSO, ρ is 1.60 in (II)[3b] and 1.53 in (III),[3a] both values having high precision. The results indicate that, when a group is introduced into the proximity of the reaction site, the ρ value is not necessarily identical with that in the simple benzene system, possibly because of the difference in the solvation around the reaction center. In the analysis of the substituent effect on naphthalene reactivities, it was assumed that the ρ value in the α-naphthyl system (I) is identical with that in the benzene system (III).[6,9,10b] However, we consider that the assumption may not always be the case.

The *r* value for naphthalene solvolysis, 1.04, is smaller than 1.15 for the corresponding benzene solvolysis. In α-naphthyl derivatives, the *peri*-hydrogen prevents maximum overlap of the vacant orbital of the reaction site developed in the transition state with the ring π-orbitals. The *peri*-hydrogen steric effect causes a decrease in the bond order between the reacting carbon and the ring α-carbon. In the absence of the steric effect, it is suggested by the MO reactivity indices that the π-electronic effect in the conjugated 4α position in the naphthalene is more effective than in the *para* position in the benzene system.[6,12,13,37] Thus we may reasonably conclude that the increased contribution of the π-electronic effect in the 4α position is over-compensated by the decreased bond order due to the effective *peri*-hydrogen steric effect, resulting in a smaller *r* value in the present solvolysis.

The same type of approach is applicable to the data of alkaline hydrolysis of ethyl 3- and 4-substituted 1-naphthoates in 85% aq. EtOH at 50 °C.[10] Figure 4 shows the log-log plot of the relative rates between the naphthalene and the corresponding benzene systems. An excellent linear free energy correlation is obtained for all the substituents except 4-NO_2 and 4-NMe_2. The deviations are reasonably interpreted in terms of the non-coplanarity of these substituents with the ring due to the *peri*-hydrogen steric effect.[3b] The application of Eq. (1) to the hydrolysis of ethyl 1-naphthoates, except for the above two substituents, leads to an excellent linear correlation. The standard deviation from the regression line is ±0.03 and the correlation coefficient, 0.999(n= 10).

$$\log (k/k_0)_{3\alpha,4\alpha} = 2.19(\sigma^0+0.27\Delta\bar{\sigma}_R^+) + 0.02$$

On the other hand, the hydrolysis of ethyl benzoates (85% aq. EtOH, 25 °C)[38,39] is correlated by

$$\log (k/k_0)_{m,p} = 2.54(\sigma^0+0.27\Delta\bar{\sigma}_R^+) + 0.04$$
$$(R=0.997,\ s=\pm 0.08)$$

Nearly the same *r* value for both the naphthalene and benzene systems is evident.

In this hydrolysis, the increased contribution of the π-electronic effect in the 4α in the naphthalene is perhaps compensated by the decreased bond order between the ring α-carbon and the ethoxycarbonyl carbon, and consequently the overall contribution of the π-electronic effect becomes close to that in the *para* in the benzene system.

The present solvolysis is a typical carbonium-ion reaction and is known to show an exalted contribution of resonance (π-electronic) effect from the substituents at the conjugated position, whereas the ester hydrolysis is a typical σ-fit reaction having a small contribution of π-electronic effect. Thus it appears from the results in both reactions that the substituent effect on 3- and 4-substituted naphthalene α-reactivities can be treated successfully by means of Eq. (1) in the same way as on *m*-

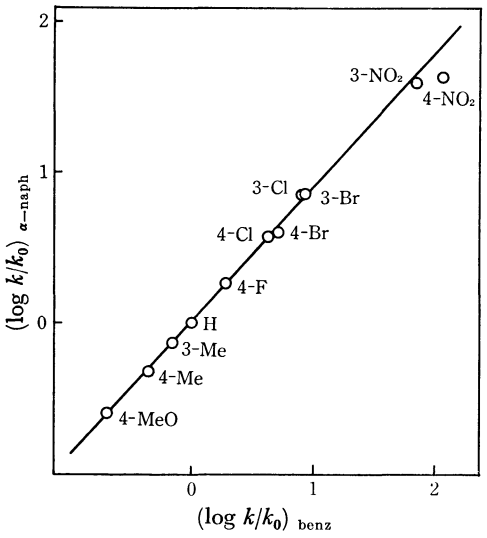

Fig. 4. Log-log plot of the alkaline hydrolysis rates between ethyl α-naphthoates (50 °C) and ethyl benzoates (25 °C).

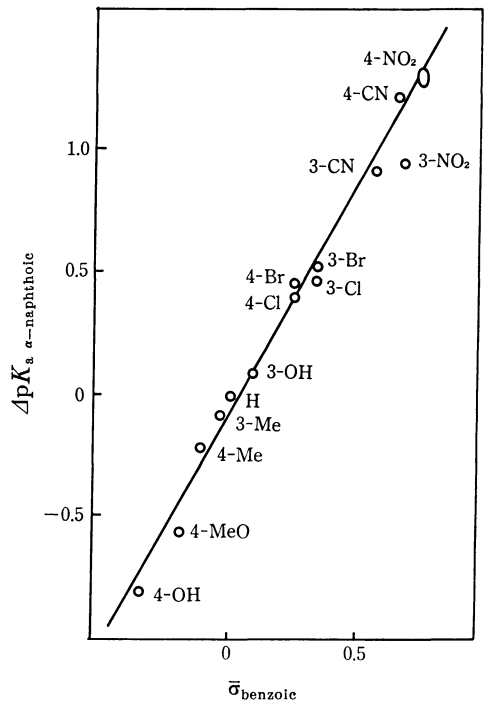

Fig. 5. The plot of ΔpK_a of α-naphthoic acids *vs.* the apparent $\bar{\sigma}$ values from ΔpK_a of benzoic acids in 50% aq. EtOH.

and *p*-substituted benzene reactivities, at least as far as electrophilic reactions are concerned.[40] Figure 5 shows the plot of ΔpK_a values of substituted 1-naphthoic acids in 50% aq. EtOH[6,9] against the apparent $\bar{\sigma}$ values calculated from the dissociation of benzoic acids in the same solvent.[36] In this case, however, considerable scattering is observed in the correlation.

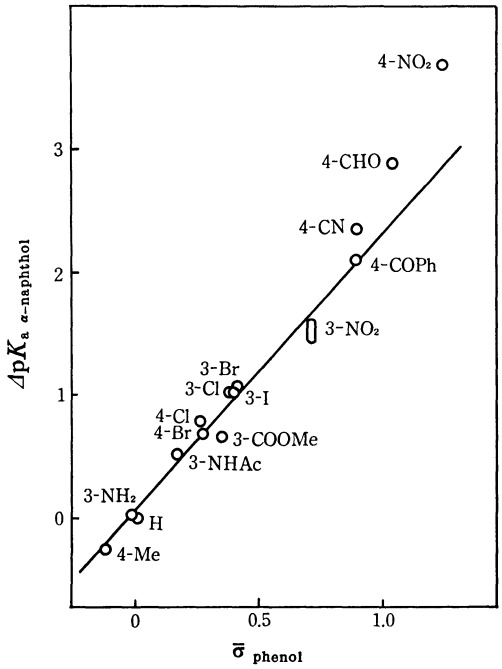

Fig. 6. Relation between ΔpK_a in α-naphthols and the apparent $\bar{\sigma}$ derived from ΔpK_a in phenols in H_2O.

The above argument may be consistent with the results of the application of Eq. (1) to nucleophilic reactivities of α-naphthyl system. An example is found in the substituent effect for dissociation of 3- and 4-substituted 1-naphthols in water at 25 °C.[41] Figure 6 shows the correlation of ΔpK_a in the 1-naphthols with the apparent $\bar{\sigma}$ derived from ΔpK_a in *m*- and *p*-substituted phenols in water. NO_2, CHO, and COC_6H_5 substituents in the 4-position may be forced out of coplanarity with the parent naphthalene ring by *peri*-hydrogen steric effect. Nevertheless the correlation line appears to be curved upward. The vertical deviations for these $+R$ substituents in 4-position from the line determined by 3α substituents and $-R$ 4α ones suggest a larger contribution of electron attracting π-electronic effect in the naphthols than that in the phenols. These findings of the direction of the change of *r* in both the naphthalene and the benzene systems are the same as the prediction based on the simple MO theory, presumably because of the less effective *peri*-hydrogen steric effect around the reaction site in this dissociation.

Application of LSFE Eq. (2) to α-Naphthyl Reactivities. According to Eq. (3), the contribution of inductive effect from substituents in *meta* position is transmitted 1.17 times more effectively to a reaction center than in *para* position. In the case of naphthalenes, the extent of the inductive contribution is also expected reasonably to depend upon the relative position of substituents to a reaction center, such as 4α, 5α, 6α, and so on. When substituents are attached to another ring of the naphthalene, *i.e.*, 5, 6, and 7-positions, the actual substituent effects may, in general, not be described successfully by any single set of substituent constants derived from the benzene system. The π-electronic contributions relative to inductive contributions from substituents at any positions of naphthalene system may differ from the relative π-electronic contributions in the benzene system.

In the pioneering studies of the substituent effect for dissociation of 1-naphthoic acids, Dewar and Grisdale proposed the *FM* equation[6]

$$\sigma_{ij} = 1/r_{ij}F + q_{ij}M$$

They considered simply that the field effect which corresponds to inductive effect in our sense was assumed to be transmitted with reciprocal of the simple distance between the ring carbons at which both substituents and COOH group were attached. Later, similar or revised treatments were employed by several authors in order to interpret other electrophilic reactivities in the naphthalene system.[42-46] However, these treatments are heavily based on the assumption of the transmission coefficients ($1/r_{ij}$ and q_{ij}) in the parent naphthalene ring.

On the other hand, Taft *et al.* adopted an alternative approach,[47] not based on any presumption of the transmission coefficients. They utilized the substituent parameters, σ_I and σ_R^0, derived from the benzene system, and analysed the substituent effect in the naphthalene system empirically; the transmission coefficients were determined by

$$\log k/k_0 = \rho_I\sigma_I + \rho_R\sigma_R^0 \qquad (5)$$

By means of statistical analysis, they examined the relative abilities of transmissions of both the inductive effect (ratio of ρ_I) and π-electronic effect (ratio of ρ_R) for a series of relative substituent positions. However, this treatment based on the substituent constant pair, σ_I and σ_R^0, must not be applied to general electrophilic reactivities such as the present solvolysis.

We have attempted a similar statistical approach by means of Eq. (2), where unique substituent constants, σ_i and $\sigma_\pi^\pm$, were employed instead of σ_I and σ_R^0. It would be expected that the relative transmission coefficients of inductive effect, C_i, can be derived from a given reaction. The expectation had been justified by the statistical analysis for both electrophilic and nucleophilic reactivities in the benzene system; C_i for *meta* relative to C_i for *para* is 1.17.

Conjugatively electron releasing ($-R$) substituents and conjugatively electron attracting ($+R$) substituents should be treated independently by Eq. (2)[1-3,8]; q_r^+ and q_r^- are substantially independent in any single reaction except for a σ^0-type reaction. Then, the present solvolysis rates for only $-R$ substituents were analysed by the least squares application of the equation

$$\log k/k_0 = \rho_i\sigma_i + \rho_\pi^+\sigma_\pi^+ \qquad (6)$$

The obtained statistical values are listed in Table 6, together with the results for other electrophilic reactivities available in 3α and 4α series. The substituent parameters utilized in this analysis are listed in Table 7.

It is evident from the results that all of the four reactivities are successfully described by Eq. (6) with high

Table 6. Statistical analysis of α-naphthyl reactivities for $-R$ substituents

$$\log k/k_0 = \rho_i\sigma_i + \rho_\pi^+\sigma_\pi^+ + \delta$$

Reaction	Series	ρ_i	ρ_π^+	δ	R[a]	$\pm s$[b]	n[c]
Solvolysis[d]	3α	−6.96	−2.56	−0.00	0.999	0.01	4(MeO, Cl, Br, H)
	4α	−5.09	−17.6	−0.06	0.999	0.07	5(MeO, Et, Me, Cl, Br, H)
Detritiation[e]	3α	−7.81	−1.13				3(Me, Cl, H)
	4α	−5.87	−23.4	−0.09	0.996	0.14	5(Me, F, Cl, Br, H)
Ester Hydrolysis[f]	3α	2.52	0.27	0.00	0.999	0.02	4(Me, Cl, Br, H)
	4α	2.13	3.71	0.04	0.993	0.08	6(MeO, Me, F, Cl, Br, H)
Acid Dissociation[g]	3α	1.48	0.61	0.02	0.995	0.04	5(OH, Me, Cl, Br, H)
		1.90[h]	0.88[h]	0.04[h]	0.997	0.04[h]	5(OH, Me, Cl,[h] Br,[h] H)
	4α	1.38	3.08	0.06	0.991	0.09	8(NH_2,OH, MeO, Me, F, Cl, Br, H)

a) Correlation coefficient. b) Standard deviation. c) Number of substituents. d) Present study. e) Data taken from Ref. 13. f) Data taken from Ref. 10. g) Data taken from Refs. 6 and 9. h) Corrected ΔpK_a for Br and Cl were employed; Ref. 38.

Table 7. Substituent parameters, σ_i and σ_π^+[a]

Substituent	σ_i	σ_π^+
NH_2	0.06	−0.42
OH	0.19	−0.34
CH_3O	0.185	−0.281
CH_3	−0.045	−0.078
C_2H_5	−0.045	−0.069
H	0.000	0.000
F	0.363	−0.118
Cl	0.348	−0.070
Br	0.337	−0.054

a) Parameters taken from Ref. 8.

precision (R>0.99). The reliability of both ρ_i and ρ_π^+ values obtained in this approach is strongly dependent upon both the number of the substituents involved in the calculation and a wide variety of the electronic nature of the substituents. Although the numbers of substituents involved here are not sufficient in respective series of reactivities given in Table 6, typical $-R$ substituents such as alkoxy, alkyl, halogen, and hydrogen, are involved in the present solvolysis and in almost all of the remainder.

Since rate data for 3α series are limited in number by comparison with the *meta* series of the benzene system, the precision with which the parameters ρ_i and ρ_π^+ are determined is inevitably restricted, nevertheless the inductive contribution ratio, $\rho_{i,3\alpha}/\rho_{i,4\alpha}$, 1.37, appears to be slightly large as compared with 1.17 for the corresponding series in benzene systems. Similar ratios, 1.33, 1.19, and 1.38[48] are found in the detritiation, the ester hydrolysis, and the acid dissociation, respectively. The significance of these results might not be clear, but it is suggested that the transmission coefficient for 3α series relative to 4α in the naphthalene ring may differ slightly from that in the benzene ring. This might indicate that σ_p^0 and σ_m^0 are not exactly applicable to 4α and 3α series in the naphthalene reactivity. The LArSR treatment might be restricted for the application especially to the effects of substituents in another ring positions in the naphthalene. The LSFE treatment should be promising for these cases.

References

1) Y. Yukawa, Y. Tsuno, and M. Sawada, This Bulletin, **39**, 2274 (1966); *ibid.*, **45**, 1198 (1972); *ibid.*, 1206 (1972); *ibid.*, 1210 (1972).

2) Y. Yukawa and Y. Tsuno, *ibid.*, **32**, 971 (1959); Y. Tsuno, *Memoir, ISIR, Osaka Univ.*, **16**, 197 (1959).

3) a) Y. Tsuno, M. Fujio, Y. Takai, and Y. Yukawa, This Bulletin, **45**, 1519 (1972); b) M. Fujio, M. Mishima, Y. Tsuno, Y. Yukawa, and Y. Takai, *ibid.*, **48**, 2127 (1975); c) Y. Tsuno, M. Fujio, and Y. Yukawa, *ibid.*, **48**, 3324 (1975). d) M. Fujio, Y. Tsuno, Y. Yukawa, and Y. Takai, *ibid.*, **48**, 3330 (1975). e) Y. Tsuno, Y. Kusuyama, M. Sawada, T. Fujii, and Y. Yukawa, *ibid.*, in press. f) Y. Tsuno *et al.*, unpublished.

4) R. W. Taft and I. C. Lewis, *J. Amer. Chem. Soc.*, **80**, 2436 (1958); *ibid.*, **81**, 5343 (1959); R. W. Taft, S. Ehrenson, I. C. Lewis, and R. E. Glick, *ibid.*, **81**, 5354 (1959).

5) S. Ehrenson, "Progress in Physical Organic Chemistry," Vol. 2, John Wiley and Sons (1964), p. 195; C. D. Ritchie and W. F. Sager, *ibid.*, Vol. 2, p. 323; P. R. Wells, S. Ehrenson, and R. W. Taft, *ibid.*, Vol. 6, p. 147 (1968); S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, *ibid.*, Vol. 10 (1973), p. 1.

6) M. J. S. Dewar and P. J. Grisdale, *J. Amer. Chem. Soc.*, **84**, 3539, 3546, 3548 (1962). ΔpK_a values of 3-Me-α, 4-Cl-α 4-F-α, 3-NO_2-α, and 4-NO_2-α were taken from Ref. 9.

7) C. G. Swain and E. C. Lupton, *ibid.*, **90**, 4328 (1968).

8) Y. Yukawa and Y. Tsuno, *Nippon Kagaku Zasshi*, **86**, 863 (1965); Y. Yukawa and Y. Tsuno, *Memoir, ISIR, Osaka Univ.*, **23**, 71 (1966).

9) P. R. Wells and W. Adcock, *Aust. J. Chem.*, **18**, 1365 (1965).

10) A. Fischer, J. D. Murdoch, J. Packer, R. D. Topsom, and J. Vaughan, *J. Chem. Soc.*, **1957**, 4358; A. Fischer, H. H. Fountain, and J. Vaughan, *ibid.*, **1959**, 1310; see also Ref. 21.

11) P. R. Wells and W. Adcock, *Aust. J. Chem.*, **19**, 221 (1966).

12) C. Eaborn, P. Golborn, R. E. Spillett, and R. Taylor, *J. Chem. Soc.*, **1968**, 1112; R. W. Bott, R. E. Spillett, and C. Eaborn, *Chem. Commun.*, **1965**, 147.

13) C. Eaborn and A. Fischer, *J. Chem. Soc., B*, **1969**, 152.

14) C. W. Hurd, *J. Amer. Chem. Soc.*, **47**, 2777 (1925); *J. Org. Chem.*, **13**, 164 (1948).

15) J. Sauer, R. Huisgen, and A. Hauser, *Chem. Ber.*, **91**, 1461 (1958).

16) T. Jacobs, S. Winstein, J. W. Ralls, and J. Robson, *J. Org. Chem.*, **11**, 27 (1946).

17) W. Schneider and F. Kunau, *Ber.*, **54**, 2304 (1921); S. Ruhemann and S. Levy, *ibid.*, **53**, 270 (1920).

18) L. Friedmann and H. Shechter, *J. Org. Chem.*, **26**, 2522 (1961).
19) Huang-Minlon, *J. Amer. Chem. Soc.*, **68**, 2487 (1946); D. Todd, "Organic Reactions," Vol. 4, Chap. 8, John Wiley and Sons (1949).
20) G. Lock, *Monatsh.*, **83**, 865 (1952).
21) A. Fischer, W. J. Mitchell, G. S. Ogilvie, J. Packer, J. E. Packer, and J. Vaughan, *J. Chem. Soc.*, **1958**, 1462.
22) H. H. Hodgson and S. Birtwell, *ibid.*, **1943**, 321.
23) H. H. Hodgson and D. E. Hathway, *ibid.*, **1944**, 538.
24) R. E. Bowman, *ibid.*, **1950**, 322.
25) M. J. S. Dewar and P. J. Grisdale, *J. Amer. Chem. Soc.*, **84**, 3541 (1962).
26) F. C. Whitmore and A. L. Fox, *ibid.*, **51**, 3363 (1923).
27) G. J. Leuck and R. P. Perkins, *ibid.*, **51**, 1831 (1929).
28) H. G. Rule and S. B. Thompson, *J. Chem. Soc.*, **1937**, 1764.
29) E. D. Bergmann and J. Blum, *J. Org. Chem.*, **26**, 3214 (1961).
30) A. Bryson, *J. Amer. Chem. Soc.*, **82**, 4862 (1960).
31) H. H. Hodgson and S. Birtwell, *J. Chem. Soc.*, **1943**, 468; *ibid.*, **1944**, 539; A. Bryson and R. W. Mattews, *Aust. J. Chem.*, **16**, 401 (1963).
32) W. G. Brown, "Organic Reactions," Vol. 6, John Wiley and Sons (1942), Chap. 10.
33) S. W. Chaikin and W. G. Brown, *J. Amer. Chem. Soc.*, **71**, 122 (1949); D. S. Noyce and G. V. Kaiser, *J. Org. Chem.*, **34**, 1008 (1969).
34) E. Berliner and N. Shieh, *J. Amer. Chem. Soc.*, **79**, 3849 (1957).
35) n=15; *p*-MeS, *p*-Ph, 2-Naph, *p*-Me, *p*-Et, *p*-*i*-Pr, *p*-*t*-Bu, *p*-F, *p*-Cl, *p*-Br, *m*-Me, *m*-F, *m*-Cl, *m*-Br, and H derivatives were employed for the calculation.
36) a) Data taken from J. D. Roberts and J. A. Yancey, *J. Amer. Chem. Soc.*, **73**, 1011 (1951); b) Data taken from D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).
37) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons (1964).
38) Y. Yukawa, Y. Tsuno, and M. Sawada, unpublished.
39) n=19; *p*-Me, *m*-Me, *p*-Et, *p*-F, *m*-F, *p*-Cl, *m*-Cl, *p*-Br, *m*-Br, *p*-MeO, *p*-MeS, *p*-NH_2, *p*-NO_2, *m*-NO_2, *m*-I, H, *m*,*m*-Me_2, 2-Naph, and *p*-Ph.
40) In the case of the detritiation for 3α and 4α series,[12,13] ρ is calculated to be −6.43 and *r*, 1.13 (R=0.997, s=±0.14, n=7; 3-Me-α, 3-Cl-α, H-α, 4-Me-α, 4-F-α, 4-Cl-α, and 4-Br-α). The precise *r* value in the corresponding benzene system can not be determined because of insufficient data.
41) L. K. Creamer, A. Fischer, B. R. Mann, J. Packer, R. B. Richards, and J. Vaughan, *J. Org. Chem.*, **26**, 3148 (1961); A. Bryson and R. W. Matthews, *Aust. J. Chem.*, **16**, 401 (1963).
42) K. C. C. Bancroft and G. R. Howe, *Tetrahedron Lett.*, **1967**, 4207.
43) W. Adcock and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **89**, 379 (1967).
44) M. J. S. Dewar, R. Golden, and J. M. Harris, *ibid.*, **93**, 4187 (1971).
45) D. S. Noyce and R. W. Nichols, *Tetrahedron Lett.*, **1972**, 3889.
46) D. A. Forsyth, *J. Amer. Chem. Soc.*, **95**, 3594 (1973).
47) P. R. Wells, S. Ehrenson, and R. W. Taft, "Progress in Physical Organic Chemistry," Vol. 6, Interscience (1968), p. 147.
48) $\rho_{t,3\alpha}=1.90$ was employed (see Table 6).