All three α-azidovinyl ketones were identified by comparison with authentic samples prepared by the two other methods.[3]

Reaction of the α-Azidovinyl Ketones with Triphenylphosphine. —The azidovinyl ketone (0.01 mol) was allowed to react with 0.01 mol of triphenylphosphine in 50 ml of ether at room temperature. Nitrogen evolution was observed and the iminophosphorane precipitated partly from the mixture. After 1 day the solution was cooled, and the precipitate was filtered, washed with petroleum ether, and dried.

α-**(Triphenylphosphinimino)chalcone (16a)** was obtained as a yellow crystalline product in 87–93% yield and was recrystallized from carbon tetrachloride–petroleum ether: mp 163–163.5°; nmr ($CDCl_3$) τ 1.6–2.9 (three multiplets), 3.75 (d, 1 H, J = 7 Hz). *Anal.* Calcd for $C_{33}H_{26}NOP$ (483): C, 77.50; H, 5.09. Found: C, 77.65; H, 5.29.

α-**(Triphenylphosphinimino)benzylideneacetone (16b)** was obtained in 88% yield and recrystallized from carbon tetrachloride–petroleum ether: mp 166–166.5°; nmr ($CDCl_3$) τ 1.5–3.0 (three multiplets), 3.38 (d, 1 H, J = 8 Hz), 7.72 (s, 3 H). *Anal.* Calcd for $C_{28}H_{24}NOP$ (421): C, 79.81; H, 5.70. Found C, 80.08; H, 5.92.

α-**(Triphenylphosphinimino)ethylideneacetophenone (16c)** was obtained in 86% yield and recrystallized from carbon tetrachloride: mp 146–147°; nmr ($CDCl_3$) τ 1.9–2.9 (two multiplets), 4.2–4.7 (dq, 1 H), 7.92 (dd, 3 H, J = 7 and 1 Hz). *Anal.* Calcd for $C_{28}H_{24}NOP$ (421): C, 79.81; H, 5.70. Found: C, 79.76; H, 5.78.

The ir spectra (KBr) of the iminophosphoranes showed the expected C=O bands at 1630–1600 and C—P bands at 1410–1430, 1120, and 990–1000 cm^{-1}.

Registry No.—**3a,** 26309-08-0; **3b,** 26309-09-1; **3c,** 26309-10-4; **5b,** 26309-13-7; **9,** 26309-11-5; **10,** 26309-12-6; **16a,** 26309-14-8; **16b,** 26309-15-9; **16c,** 26309-16-0.

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The Nature of the Ortho Effect. VI. Polarographic Half-Wave Potentials

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Twenty-seven sets of polarographic half-wave potentials and related data for ortho-substituted benzene derivatives have been correlated with the equations $Q_X = \alpha\sigma_{I,X} + \beta\sigma_{R,X} + \psi r_V + h$ and $Q_X = \alpha\sigma_{I,X} + \beta\sigma_{R,X} + h$. Significant correlations were obtained with 18 of the sets correlated with the former, and 22 of the sets correlated with the latter equation. The results obtained for correlations with the former equation show that, in general, ψ is not significant. As successful correlations were obtained with the latter equation in most cases, there is no steric effect exerted by ortho substituents in the majority of the sets studied. Their effect is generally purely electrical in nature. The magnitude and composition of the electrical effect seems to be independent of the medium but strongly dependent on the group being reduced.

In continuation of our interest in the nature of the ortho effect, it seemed worthwhile to extend our investigations to polarographic half-wave potentials. The problem seems to have first been studied by Bennett and Elving,[1] who reported a correlation of $E_{0.5}$ values for 2-substituted nitrobenzenes with the Taft $\sigma_o{}^*$ constants by means of the simple Hammett equation

$$Q_X = \rho\sigma_X + h \quad (1)$$

Zuman[2] has studied the correlation of $E_{0.5}$ values for ortho-substituted benzene derivatives with the equation

$$\Delta E_{0.5,X} = \rho\sigma_{o,X}{}^* + \delta E^\circ{}_{S,X} \quad (2)$$

in an attempt to determine the presence or absence of steric effects. Hussey and Diefenderfer[3] have correlated $E_{0.5}$ values for 2-substituted phenyl bromides and iodides with the simple Hammett equation using σ_o constants defined by the expression

$$\sigma_o = 2.4\sigma_I + (1 - \text{S.F.})\sigma_R \quad (3)$$

where S.F. is a steric hindrance factor defined as the fraction of overlap between the reaction site radius and the substituent radius. The radii were obtained from data on the resolution of diphenyls. As we have recently shown[4] that the $E_S{}^\circ$ values proposed by Taft[5] as a measure of the steric effect of ortho substituents are in fact electrical effect parameters, it seemed useful to investigate the correlation of $E_{0.5}$ values with the aim of determining whether or not a steric effect is present.

It is convenient at this point to review our method for ascertaining the presence or absence of steric effects. There are several possible cases to consider,[6] of which four are of major interest to us. They are (1) the steric effect obeys a linear free-energy relationship.[5] Then, if a suitable steric effect parameter is available, we may write a linear free-energy relationship including electrical and steric terms. For a steric effect parameter we have chosen the van der Waals radius of that atom or group of atoms of the substituent which is bonded to the benzene ring. Then, in this case, we write the linear free-energy relationship[4,7,8]

$$Q_X = \alpha\sigma_{I,X} + \beta\sigma_{R,X} + \psi r_{V,X} + h \quad (4)$$

(2) The steric effect does not obey a linear free-energy relationship. In this case, we may write for any particular datum in the set

$$Q_X = \alpha\sigma_{I,X} + \beta\sigma_{R,X} + S_X + h \quad (5)$$

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(1) C. E. Bennett and P. J. Elving, *Collect. Czech. Chem. Commun.*, **25**, 3213 (1960).
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TABLE I

1. $E_{0.5}$ 2-XC_6H_4I, 66% EtOH–H_2O, 0.01 *M* Et_4NBr, 25°[a]

I	OH	Br	NH_2	Cl	Me	Ph	H
1.235	1.49	1.30	1.56	1.34	1.683	1.48	1.65

2. $E_{0.5}$ 2-XC_6H_4I, 90% EtOH–H_2O, 0.06 *M* LiCl, 0.2 *M* KOAc, 0.013 *M* AcOH, 25°[b]

H	Cl	Br	Me	MeO	EtO	OH[c]	CO_2H	Ph
1.68	1.56	1.50	1.70	1.60	1.64	1.55	1.47	1.61

3. $E_{0.5}$ 2-XC_6H_4I, H_2O, 1.0 *M* $LiClO_4$[d]

H	Me	Et	Ph	NH_2	OH	OMe	OEt
1.655	1.688	1.685	1.570	1.565	1.535	1.567	1.587

F	Cl	Br	CF_3
1.374	1.375	1.322	1.343

4. $E_{0.5}$ 2-XC_6H_4I, H_2O, 0.1 *M* Me_4NCl[d]

H	Me	Et	Ph	NH_2	OH	OMe	OEt
1.467	1.495	1.478	1.327	1.416	1.391	1.393	1.405

F	Cl	Br	CF_3
1.205	1.203	1.153	1.190

5. $E_{0.5}$ 2-XC_6H_4Br, H_2O, 0.1 *M* Me_4NCl[d]

H	Me	NH_2	OH	OMe	OEt	CF_3	F	Cl
2.07	2.12	2.01	1.97	1.93	1.99	1.67	1.69	1.69

6. $E_{0.5}$ 2-XC_6H_4OTs, Me_2NCHO, 0.05 *M* Et_4NI, 25°[e]

F	Cl	NH_2	OMe	Me	NMe_2	NO_2[b]
1.332	1.337	1.422	1.431	1.420	1.740	1.118, 1.330

H
1.429

7. $E_{0.5}$ 2-XC_6H_4OTs, Me_2SO, 0.05 *M* Et_4NI, 25°[e]

F	Cl	NH_2	OMe	Me	NMe_2	NO_2[b]	H
1.452	1.436	1.501	1.527	1.497	1.608	1.484	1.491

8. $E_{0.5}$ 2-XC_6H_4OTs, MeCN, 0.05 *M* Et_4NI, 25°[e]

F	Cl	NH_2	OMe	Me	NMe_2	NO_2[c]	H
1.409	1.407	1.441	1.508	1.510	1.455	1.378	1.463

9. $E_{0.5}$ 2-XC_6H_4OTs, C_5H_5N, Et_4NI, 25°[f]

Cl	F	NH_2	NMe_2	OMe	Me	H
1.313	1.328	1.398	1.388	1.427	1.400	1.415

10. $E_{0.5}$ 2-XC_6H_4OTs, PhCN, Et_4NI, 25°[g]

Cl	F	NH_2	NMe_2	Me	OMe	H
1.414	1.427	1.450	1.440	1.475	1.468	1.452

11. $E_{0.5}$ 2-XC_6H_4OTs, equimolar C_5H_5N–Me_2NCHO, Et_4NI, 25°[g]

Cl	F	NH_2	NMe_2	Me	OMe	H
1.297	1.313	1.392	1.379	1.387	1.409	1.381

12. $E_{0.5}$ 2-XC_6H_4CHO, 66% EtOH–H_2O, 0.01 *M* Et_4NBr, 25°[a]

H	I	Cl	MeO	OH	Me
1.506	1.248	1.331	1.494	1.504	1.493

13. $E_{0.5}$ 2-XC_6H_4CHO, 60% EtOH–H_2O, pH 1.73, 25°[a]

H	I	Cl	MeO	OH	Me
1.000	0.827	0.868	0.960	1.050	0.962

14. $E_{0.5}$ 2-XC_6H_4CHO, 60% EtOH–H_2O, pH 2.25, 25°[a]

H	I	Cl	MeO	OH	NH_2[c]	Me
1.022	0.850	0.895	0.994	1.070	1.030	0.990

15. $E_{0.5}$ 2-XC_6H_4CHO, 60% EtOH–H_2O, pH 2.59, 25°[a]

H	I	Cl	MeO	OH	Me
1.051	0.876	0.918	1.020	1.098	1.018

16. $E_{0.5}$ 2-XC_6H_4CHO, 60% EtOH–H_2O, pH 3.16, 25°[a]

H	I	Cl	OH	NH_2[c]	Me
1.088	0.914	0.970	1.134	1.090	1.062

17. $E_{0.5}$ 2-XC_6H_4CHO, H_2O, pH 0, 20°[h]

H	OH	OMe	Me	Cl	Br	I	NHAc
0.780	0.850	0.775	0.720	0.693	0.698	0.707	0.765

CHO	CO_2H	NH_2[c]	CO_2Me
0.465,[i] 0.776	0.684	0.843	0.722

18. $E_{0.5}$ 2-XC_6H_4CHO, H_2O, pH 13, 20°[h]

H	OH[c]	OMe	Me	Cl	Br	I	NHAc
1.40	1.62	1.62	1.38	1.39	1.264	1.197	1.247

CO_2H[c]	NH_2	CHO
1.34	1.555	1.317,[i] 1.462

19. $E_{0.5}$ 2-XC_6H_4CHO, H_2O, pH 13, 20°, second wave[h]

H	OH[c]	OMe	Me	Cl	Br	I	NHAc
1.23	1.22	1.245	1.16	1.043	1.066	1.117	1.05

CO_2Me
1.097

20. $E_{0.5}$ 2-$XC_6H_4NO_2$, 66% EtOH–H_2O, 0.01 *M* Et_4NBr, 25°[a]

H	I	Br	Cl	OH	NH_2	Ph	Me
0.935	0.816	0.860	0.866	0.990	1.030	0.928	1.005

CO_2H	CO_2Et	CHO	NO_2
0.526, 0.968	0.826	0.640	0.570

21. $E_{0.5}$ 2-$XC_6H_4NO_2$, 60% EtOH–H_2O, pH 1.73, 25°[a]

H	I	Br	Cl	OH	NH_2	Ph	Me
0.326	0.204	0.263	0.256	0.246	0.372	0.290	0.358

CO_2H	CHO	CO_2Et	NO_2
0.304	0.228	0.282	0.134

22. $E_{0.5}$ 2-$XC_6H_4NO_2$, 60% EtOH–H_2O, pH 2.25, 25°[a]

H	I	Br	Cl	OH	NH_2	Ph	Me
0.366	0.232	0.294	0.306	0.284	0.422	0.341	0.390

CO_2H	CHO	CO_2Et	NO_2
0.340	0.286	0.313	0.168

23. $E_{0.5}$ 2-$XC_6H_4NO_2$, 60% EtOH–H_2O, pH 3.16, 25°[a]

H	I	Br	Cl	OH	NH_2	Ph	Me
0.430	0.306	0.396	0.410	0.362	0.488	0.412	0.525

CO_2H	CHO	CO_2Et	NO_2
0.420	0.346	0.400	0.230

24. E_S 2-$XC_6H_4NO_2$, 50% MeOH–H_2O, pH 12.5, 26°[j]

Cl	OMe	NH_2	OH[c]	Me	H
−0.81	−0.90	−0.95	−0.88	−0.93	−0.83

25. $E_{0.5}$ 2-$XC_6H_4NO_2$, 50% MeOH–H_2O, pH 12.5, 46°[j]

Cl	OMe	NH_2	OH[c]	Me	H
−0.91	−0.97	−1.08	−1.09	−1.07	−1.06

26. E_S 2-$XC_6H_4NO_2$, 50% MeOH–H_2O, pH 12.5, 46°[j]

Cl	OMe	NH_2	OH[c]	Me	H
−0.81	−0.89	−0.96	−0.91	−0.91	−0.84

27. $E_{0.5}$ 2-$XC_6H_4C_{10}H_{11}Fe$, MeCN, 0.2 *M* $LiClO_4$, 25°[k]

MeO	EtO	Me	F	Cl	Br	I	NO_2
0.292	0.295	0.340	0.359	0.386	0.388	0.389	0.444

CO_2Me	CH_2OH	Ph	H	CO_2H
0.380	0.352	0.340	0.343	0.373

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where S_X is the steric effect of the substituent and does not obey a linear free-energy relationship.

(3) The steric effect is constant. Then

$$Q_X = \alpha\sigma_{I,X} + \beta\sigma_{R,X} + h' \quad (6)$$

where

$$h' = h + S_X \quad (7)$$

(4) The steric effect is nonexistent. Then

$$Q_X = \alpha\sigma_{I,X} + \beta\sigma_{R,X} + h \quad (8)$$

Obviously eq 7 and 8 are equivalent. To determine the presence or absence of a steric effect, the data are correlated with eq 4 and 8.

The data used are set forth in Table I. The presence of a significant steric effect will not be indicated by a successful correlation with eq 4. Although this is a necessary condition for the existence of a steric effect, in case 1 it is not sufficient. The conclusive evidence for the existence of such a steric effect is provided by the confidence level of ψ, the coefficient of the Van der

TABLE II

Set	α	β	ψ	h	R[a]	F[b]	r_{12}[c]	r_{13}[c]	r_{23}[c]
1A	−0.631	−0.0432	−0.174	1.88	0.966	18.34[i]	0.068	0.584	0.145
1B	−0.753	−0.0719		1.61	0.944	20.52[h]	0.068		
2A	−0.355	−0.0722	−0.0293	1.70	0.855	4.537[m]	0.235	0.453	0.140
2B	−0.371	−0.0783		1.66	0.853	8.00[k]	0.235		
3A	−0.584	−0.0454	−0.0996	1.81	0.965	36.34[g]	0.151	0.295	0.439
3B	−0.625	−0.0870		1.64	0.955	46.65[g]	0.151		
4A	−0.529	−0.0872	−0.0951	1.59	0.959	30.71[g]	0.151	0.295	0.439
4B	−0.568	−0.127		1.44	0.948	40.14[g]	0.151		
5A	−0.789	−0.118	−0.0706	2.17	0.974	31.32[h]	0.049	0.384	0.381
5B	−0.825	−0.141		2.06	0.971	49.14[g]	0.049		
6A$_1$	−0.310	−0.272	−0.0454	1.46	0.803	1.810[n]	0.096	0.223	0.149
6A$_2$	−0.230	−0.120	−0.0369	1.47	0.960	3.943[n]	0.681	0.249	0.205
6B$_1$	−0.318	−0.269		1.39	0.801	3.568[n]	0.096		
6B$_2$	−0.236	−0.118		1.41	0.947	8.765[n]	0.681		
7A$_1$	−0.144	−0.117	−0.0283	1.52	0.872	3.163[n]	0.096	0.223	0.149
7A$_2$	−0.179	−0.161	−0.0253	1.52	0.974	6.275[n]	0.681	0.249	0.205
7B$_1$	−0.149	−0.115		1.48	0.867	6.063[m]	0.096		
7B$_2$	−0.183	−0.159		1.48	0.963	12.78[m]	0.681		
8A$_1$	−0.134	0.0128	0.0362	1.43	0.715	1.046[n]	0.096	0.223	0.149
8A$_2$	−0.264	−0.182	0.0374	1.42	0.991	18.41[n]	0.681	0.249	0.205
8B$_1$	−0.128	0.0103		1.49	0.699	1.908[n]	0.096		
8B$_2$	−0.257	−0.185		1.47	0.978	22.24[l]	0.681		
9A$_1$	−0.148	−0.0204	−0.0631	1.50	0.851	2.622[n]	0.096	0.223	0.149
9A$_2$	−0.240	−0.163	−0.0631	1.49	0.972	5.660[m]	0.681	0.249	0.205

Set	s_{est}[d]	s_α[d]	s_β[d]	s_ψ[d]	s_h[d]	t_α[e]	t_β[e]	t_ψ[e]	t_h[e]	n[f]
1A	0.0563	0.130	0.0813	0.112	0.179	4.853[i]	0.531[q]	1.552[o]	10.52[g]	8
1B	0.0638	0.118	0.0896		0.0407	6.396[i]	0.803[p]		39.39[g]	8
2A	0.0509	0.117	0.0767	0.106	0.166	3.032[l]	0.942[p]	0.276[q]	10.24[g]	9
2B	0.0468	0.0929	0.0676		0.0286	3.994[i]	1.157[p]		57.98[g]	9
3A	0.0411	0.0663	0.0536	0.0658	0.112	8.817[g]	0.848[p]	1.515[o]	16.12	12
3B	0.0440	0.0648	0.0492		0.0229	9.654[g]	1.767[o]		71.55[g]	12
4A	0.0411	0.0662	0.0536	0.0657	0.112	7.991[g]	1.629[o]	1.446[o]	14.25[g]	12
4B	0.0435	0.0641	0.0487		0.0227	8.868[g]	2.605[l]		63.35[g]	12
5A	0.0497	0.0969	0.0652	0.0848	0.139	8.147[g]	1.807[o]	0.833[p]	15.66[g]	9
5B	0.0484	0.0849	0.0573		0.0325	9.711[g]	2.469[l]		63.46[g]	9
6A$_1$	0.116	0.217	0.142	0.270	0.406	1.427[p]	1.919[o]	0.168[r]	3.593[l]	7
6A$_2$	0.0283	0.0748	0.0876	0.0659	0.0994	3.073[p]	1.370[p]	0.560[q]	14.78[l]	5
6B$_1$	0.101	0.185	0.122		0.0723	1.720[o]	2.199[m]		19.24[g]	7
6B$_2$	0.0229	0.0599	0.0709		0.0173	3.945[m]	1.658[p]		81.55[g]	5
7A$_1$	0.0389	0.0729	0.0476	0.0904	0.136	0.1971[o]	2.455[m]	0.313[q]	11.19[i]	7
7A$_2$	0.0164	0.0434	0.0508	0.0382	0.0576	4.125[o]	3.167[o]	0.662[q]	26.35[l]	5
7B$_1$	0.0342	0.0627	0.0415		0.0245	2.369[m]	2.767[m]		60.37[g]	6
7B$_2$	0.0139	0.0364	0.0430		0.0105	5.043[l]	3.701[m]		140.8[g]	5
8A$_1$	0.0414	0.0776	0.0507	0.0963	0.145	1.732[o]	0.253[r]	0.375[q]	9.882[i]	7
8A$_2$	0.0135	0.0357	0.0418	0.0314	0.0474	7.394[m]	4.361[o]	1.191[p]	29.90[l]	5
8B$_1$	0.0367	0.0672	0.0445		0.0263	1.909[o]	0.232[r]		56.49[g]	7
8B$_2$	0.0148	0.0387	0.0459		0.0112	6.636[l]	4.024[m]		131.2[g]	5
9A$_1$	0.0324	0.0608	0.0397	0.0754	0.114	2.434[m]	0.0513[q]	0.0837[p]	13.20[g]	7
9A$_2$	0.0247	0.0653	0.0764	0.0575	0.0868	3.679[o]	2.124[p]	1.097[p]	17.14[l]	5

Set	α	β	ψ	h	R	F	r_{12}	r_{13}	r_{23}
9B$_1$	−0.159	−0.0160		1.41	0.812	3.872[n]	0.096		
9B$_2$	−0.251	−0.158		1.39	0.937	7.162[n]	0.681		
10A$_1$	−0.0736	0.00441	0.00799	1.45	0.760	1.366[n]	0.096	0.223	0.149
10A$_2$	−0.137	−0.0924	0.00803	1.44	0.9995	345.1[l]	0.681	0.249	0.205
10B$_1$	−0.0723	0.00386		1.46	0.757	2.684[n]	0.096		
10B$_2$	−0.135	−0.0930		1.45	0.997	187.3[i]	0.681		
11A$_1$	−0.151	−0.0378	−0.0326	1.43	0.854	2.701[n]	0.096	0.223	0.149
11A$_2$	−0.243	−0.179	−0.0327	1.42	0.981	8.516[n]	0.681	0.249	0.205
11B$_1$	−0.157	−0.0355		1.38	0.844	4.941[m]	0.096		
11B$_2$	−0.249	−0.177		1.37	0.971	16.24[m]	0.681		
12A	−0.379	−0.235	−0.157	1.70	0.987	25.77[l]	0.333	0.556	0.060
12B	−0.509	−0.281		1.46	0.942	11.89[l]	0.333		
13A	−0.226	−0.196	−0.135	1.16	0.962	8.370[n]	0.333	0.556	0.060
13B	−0.338	−0.236		0.954	0.900	6.416[m]	0.333		
14A	−0.230	−0.202	−0.130	1.18	0.975	13.00[m]	0.333	0.556	0.060
14B	−0.339	−0.240		0.979	0.917	7.900[m]	0.333		
15A	−0.239	−0.203	−0.131	1.21	0.975	12.84[m]	0.333	0.556	0.060
15B	−0.348	−0.242		1.01	0.918	8.032[m]	0.333		

TABLE II (*Continued*)

Set	α	β	ψ	h	R	F	r_{12}	r_{13}	r_{23}
16A	−0.230	−0.239	−0.139	1.26	0.998	88.88[m]	0.341	0.580	0.032
16B	−0.344	−0.271		1.05	0.931	6.522[n]	0.341		
17A	−0.141	−0.230	−0.0789	0.846	0.708	2.339[n]	0.010	0.614[m]	0.163
17B	−0.201	−0.241		0.730	0.696	3.753[m]	0.010		
18A	−0.436	−0.336	−0.0405	1.41	0.952	16.08[i]	0.090	0.627	0.111
18B	−0.466	−0.338		1.35	0.951	28.07[g]	0.090		

Set	s_{est}	s_α	s	s_ψ	s_h	t_α	t_β	t_ψ	t_h	n
9B$_1$	0.0312	0.0571	0.0378		0.0224	2.778[m]	0.422[q]		62.87[g]	5
9B$_2$	0.0259	0.0677	0.0802		0.0196	3.709[m]	1.975[o]		71.11[g]	5
10A$_1$	0.0198	0.0372	0.0243	0.0462	0.0696	1.977[o]	0.181[r]	0.173[r]	20.86[g]	7
10A$_2$	0.00163	0.00430	0.00503	0.00379	0.00571	31.76[l]	18.36[l]	2.122[p]	252.6[i]	5
10B$_1$	0.0173	0.0317	0.0210		0.0124	2.282[m]	0.184[r]		118.0[g]	7
10B$_2$	0.00270	0.00705	0.00834		0.00204	19.18[i]	11.15[i]		713.2[g]	5
11A$_1$	0.0314	0.0588	0.0384	0.0730	0.110	2.573[m]	0.983[p]	0.446[q]	13.00[g]	7
11A$_2$	0.0191	0.0506	0.0592	0.0446	0.0672	4.800[o]	3.025[p]	0.0735[q]	21.09[l]	5
11B$_1$	0.0281	0.0514	0.0341		0.0201	3.052[l]	1.043[p]		68.61[g]	7
11B$_2$	0.0168	0.0439	0.0519		0.0127	5.666[l]	3.409[m]		107.8[g]	5
12A	0.0280	0.0811	0.0567	0.0598	0.0927	4.668[l]	4.136[m]	2.623[o]	18.37[i]	6
12B	0.0482	0.110	0.0927		0.0345	4.611[i]	3.031[m]		42.39[g]	6
13A	0.0356	0.103	0.0722	0.0760	0.118	2.191[o]	2.722[o]	1.771[p]	9.829[i]	6
13B	0.0466	0.107	0.0897		0.0334	3.165[m]	2.635[m]		28.56[g]	6
14A	0.0287	0.0830	0.0581	0.0611	0.0948	2.776[o]	3.472[m]	2.132[o]	12.41[i]	6
14B	0.0423	0.0969	0.0815		0.0303	3.494[l]	2.949[m]		32.27[g]	6
15A	0.0294	0.0851	0.0595	0.0627	0.0972	2.813[o]	3.411[m]	2.092[o]	12.41[i]	6
15B	0.0428	0.0981	0.0824		0.0307	3.551[l]	2.934[m]		32.82[g]	6
16A	0.0110	0.0318	0.0250	0.0236	0.0365	7.255[m]	9.561[m]	5.881[o]	34.41[i]	5
16B	0.0463	0.107	0.103		0.0332	3.223[m]	2.631[o]		31.54[i]	5
17A	0.0814	0.197	0.109	1.64	0.246	0.716[p]	2.112[m]	0.483[q]	3.445[i]	11
17B	0.0774	0.146	0.101		0.0500	1.370[p]	2.386[l]		14.62[g]	11
18A	0.0533	0.126	0.0734	0.108	0.163	3.470[i]	4.583[i]	0.376[q]	8.642[g]	9
18B	0.0493	0.0910	0.0678		0.0336	5.117[i]	4.992[i]		40.17[g]	9

Set	α	β	ψ	h	R	F	r_{12}	r_{13}	r_{23}
19A	−0.236	−0.106	−0.0762	1.30	0.751	1.725[n]	0.210	0.616	0.010
19B	−0.296	−0.118		1.18	0.729	2.841[n]	0.210		
20A$_1$	−0.446	−0.326	0.0787	0.780	0.865	7.943[i]	0.283	0.350	0.099
20A$_2$	−0.402	−0.760	−0.0866	1.04	0.893	7.856[k]	0.121	0.307	0.423
20B$_1$	−0.421	−0.326		0.904	0.861	12.90[h]	0.283		
20B$_2$	−0.431	−0.699		0.901	0.888	13.08[h]	0.121		
21A$_1$	−0.259	−0.0263	0.0203	0.308	0.856	7.305[k]	0.283	0.350	0.099
21A$_2$	−0.245	−0.0265	0.00943	0.323	0.865	5.917[l]	0.121	0.307	0.423
21B$_1$	−0.253	−0.0263		0.340	0.854	12.13[h]	0.283		
21B$_2$	−0.242	−0.0331		0.338	0.864	10.32[i]	0.121		
22A$_1$	−0.262	−0.326	0.0131	0.360	0.854	7.160[k]	0.283	0.350	0.099
22A$_2$	−0.245	−0.0345	0.000108	0.378	0.867	6.047[l]	0.121	0.307	0.423
22B$_1$	−0.258	−0.0326		0.381	0.853	12.01[h]	0.283		
12B$_2$	−0.245	−0.0346		0.378	0.867	10.58[i]	0.121		
23A$_1$	−0.301	−0.0311	0.0686	0.361	0.823	5.589[k]	0.283	0.350	0.099
23A$_2$	−0.278	−0.107	0.0284	0.421	0.828	4.367[m]	0.121	0.307	0.423
23B$_1$	−0.279	−0.0311		0.469	0.807	8.386[i]	0.283		
23B$_2$	−0.269	−0.127		0.465	0.826	7.510[k]	0.121		
24A	0.253	0.143	−0.122	−0.687	0.986	11.73[n]	0.231	0.431	0.207
24B	0.201	0.153		−0.865	0.905	4.542[n]	0.231		
25A	0.351	0.0631	0.00841	−1.06	0.975	6.288[n]	0.231	0.431	0.207
25B	0.355	0.0624		−1.05	0.974	18.67[m]	0.231		
26A	0.230	0.155	−0.0749	−0.751	0.9997	498.6[l]	0.231	0.431	0.207
26B	0.198	0.161		−0.860	0.968	14.86[m]	0.231		
27A	0.121	0.120	0.0251	0.302	0.935	20.94[g]	0.057	0.159	0.158
27B	0.125	0.124		0.343	0.928	30.90[g]	0.057		

Set	s_{est}	s_α	s_β	s_ψ	s_h	t_α	t_β	t_ψ	t_h	n
19A	0.0687	0.175	0.143	0.140	0.213	1.352[p]	0.745[p]	0.543[q]	6.097[i]	8
19B	0.0637	0.126	0.131		0.0428	2.346[m]	0.906[p]		27.66[g]	8
20A$_1$	0.0995	0.155	0.111	0.164	0.264	2.872[l]	2.940[i]	0.481[q]	2.959[i]	12
20A$_2$	0.0899	0.145	0.253	0.175	0.279	2.771[l]	3.008[l]	0.494[q]	3.718[i]	10
20B$_1$	0.0951	0.140	0.106		0.0545	3.010[i]	3.074[i]		16.61[g]	12
20B$_2$	0.0849	0.126	0.208		0.0488	3.425[i]	3.355[i]		18.46[g]	10
21A$_1$	0.0402	0.0628	0.0447	0.0661	0.107	4.132[i]	0.588[q]	0.308[q]	2.893[l]	12
21A$_2$	0.0395	0.0639	0.111	0.0771	0.123	3.833[i]	0.238[r]	0.122[r]	2.635[l]	10

TABLE II (*Continued*)

Set	s_{est}	s_α	s_β	s_ψ	s_h	t_α	t_β	t_ψ	t_h	n
$21B_1$	0.0381	0.0560	0.0424		0.0218	4.512^i	0.620^q		15.60^g	12
$21B_2$	0.0367	0.0543	0.0900		0.0211	4.451^i	0.368^q		16.03^g	10
$22A_1$	0.0419	0.0654	0.0466	0.0688	0.111	4.011^i	0.700^q	0.191^r	3.245^j	12
$22A_2$	0.0397	0.0641	0.112	0.0775	0.123	3.826^i	0.309^q	0.139^r	3.068^l	10
$22B_1$	0.0396	0.0581	0.0440		0.0226	4.437^i	0.741^p		16.82^g	12
$22B_2$	0.0368	0.0545	0.0903		0.0211	4.504^i	0.383^q		17.87^g	10
$23A_1$	0.0518	0.0809	0.0577	0.0852	0.137	3.721^i	0.539^q	0.806^p	2.627^l	12
$23A_2$	0.0543	0.0876	0.153	0.106	0.168	3.172^j	0.699^q	0.269^q	2.501^l	10
$23B_1$	0.0508	0.0747	0.0565		0.02913	3.738^i	0.549^q		16.13^g	12
$23B_2$	0.0506	0.0749	0.124		0.0290	3.588^i	1.020^p		16.01	10
24A	0.0204	0.0545	0.0343	0.0520	0.0773	4.638^o	4.172^o	2.351^p	8.881^m	5
24B	0.0369	0.0902	0.0614		0.0272	2.232^o	2.487^o		31.75^g	5
25A	0.0335	0.0893	0.0561	0.0853	0.127	3.934^o	1.125^p	0.099^r	8.405^m	5
25B	0.0238	0.0581	0.0396		0.0175	6.109^l	1.578^p		59.95^g	5
26A	0.00305	0.00812	0.00510	0.00775	0.0115	28.29^l	30.34^l	9.663^m	65.18^j	5
26B	0.0209	0.0511	0.0348		0.0154	3.880^m	4.624^l		55.73^g	5
27A	0.0167	0.0224	0.0218	0.0251	0.0417	5.430^g	5.491^g	1.001^p	7.243^g	13
27B	0.0167	0.0220	0.0215		0.00849	5.684^g	5.743^g		40.37^g	13

[a] Multiple correlation coefficient. [b] F test for significance of regression. [c] Partial correlation coefficients of σ_I on σ_R, σ_I on r_V, and σ_R on r_V, respectively. [d] Standard errors of the estimate, α, β, ψ, and h. [e] "Student's t tests" for significance of α, β, ψ, and h. [f] Number of points in set. [g] 99.9% confidence level (cl). [h] 99.5% cl. [i] 99.0% cl. [j] 98.0% cl. [k] 97.5% cl. [l] 95.0% cl. [m] 90.0% cl. [n] <90.0% cl. [o] 80.0% cl. [p] 50% cl. [q] 20% cl. [r] <20% cl.

Waals radius term in eq 4. This confidence level is obtained by means of a "Student's t test" of ψ.

If ψ is not significant, this implies either (a) the existence of cases 2, 3, or 4, or (b) the choice of a steric parameter was incorrect. The data are now correlated with eq 8. If the correlations with eq 4 and 8 are both unsuccessful, this implies either case 1 and an incorrect steric parameter or case 2. It is not possible to distinguish between these situations at the present time. If the data are well correlated by eq 8, cases 1 and 2 may be ruled out, as the data in these cases must include a variable steric term which is not accounted for by eq 8. Thus lack of significance of ψ in correlations with eq 4 coupled with successful correlation with eq 8 indicates the existence of case 3 or case 4. These cases may be distinguished by comparing the experimentally observed value of h (that data point for which X = H), with the calculated value obtained from the correlation. In case 3, $h_{obsd} \neq h_{calcd}$, whereas in case 4 $h_{obsd} = h_{calcd}$.

The σ_I constants used in these correlations are from our compilation;[9] the σ_R constants were obtained from the equation

$$\sigma_R = \sigma_p - \sigma_I \qquad (9)$$

using the σ_p values of McDaniel and Brown.[10] Values of r_V were taken from the collection of Bondi[11] or were group values calculated by us.[4] The correlations were carried out by multiple linear regression analysis.[12]

In several of the sets studied, ionizable substituents were excluded[13] because at the pH of the medium in which the $E_{0.5}$ values were determined, these groups are ionized to some extent. Results for sets 6–11 are considerably improved by exclusion of the values for the amino and dimethylamino groups. These groups seemed to deviate considerably in correlations of the $E_{0.5}$ values for the corresponding meta- and para-substituted phenyl tosylates in some of the sets. The nitro group was excluded from sets 6–8 as it is reportedly reduced by a mechanism differing from that common to the other groups in the set.[14] Sets 20–23 were correlated both including and excluding the values for the hydroxy and amino groups as it has been suggested that they are reduced by a mechanism differing from that which is observed for the other substituents.[15]

Results

Results of the correlations are presented in Table II. Sets labeled A were correlated with eq 4; sets labeled B were correlated with eq 8.

The confidence levels of r_{12}, r_{13}, and r_{23} are all <90.0% unless otherwise noted.

Halobenzenes.—Of the four sets of iodobenzenes (sets 1–4), two gave excellent, one gave good, and one gave poor results for correlations eq 4. With eq 8, one set gave good and three sets gave excellent correlations. The bromobenzenes (set 5) gave an excellent correlation with both eq 4 and 8.

Phenyl Tosylates.—Best results were obtained for correlations excluding the amino and dimethylamino groups (sets 6–$11A_2$ and 6–$11B_2$). Four sets did not give significant correlations with eq 4, one set gave poor results, and one set gave fair results. With eq 8, one set gave very good, one fair, and two produced poor results; two sets did not give significant correlations.

Benzaldehydes.—Of the eight sets of benzaldehydes (sets 12–19), one gave very good, one fair, and three gave poor results. Three sets did not give significant correlations with eq 4. Correlation with eq 8 gave poor results for four sets, excellent for one set, fair for one set. Two sets did not give significant results.

Nitrobenzenes.—The four sets of nitrobenzenes in neutral or acid media (sets 20–23) were correlated both with (A_1 and B_1 sets) and without (A_2 and B_2 sets) the values for the amino and hydroxy groups. The results are not greatly affected by the exclusion of these values.

(9) M. Charton, *J. Org. Chem.*, **29**, 1222 (1964).
(10) D. H. McDaniel and H. C. Brown, *ibid.*, **23**, 420 (1958).
(11) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).
(12) K. A. Brownlee, "Statistical Theory and Methodology in Science and Engineering," 2nd ed, Wiley, New York, N. Y., 1965; E. L. Crow, F. A. Davis, and M. W. Maxfield," "Statistics Manual," Dover Publications, New York, N. Y., 1960.
(13) Reference 2, p 49.
(14) Footnote *e*, Table I.
(15) Reference 2, p 78.

With eq 4, three sets gave good and one set gave very good results. With eq 8, three sets gave excellent and one set gave very good results. Of the three sets of nitrobenzenes in alkaline media, one gave fair correlation with eq 4, whereas two did not give significant correlations. With eq 8, two sets gave poor results and one set did not give significant correlation.

Phenylferrocenes.—The phenylferrocenes (set 27) gave excellent correlations with both eq 4 and eq 8.

Overall, significant correlations with eq 4 were obtained for 18 of the 27 sets studied, whereas, for correlation with eq 8, 22 sets gave significant results.

Discussion

Steric Effect.—We may now consider the question of the presence of steric effects in terms of our previous discussion. Only one of the 27 sets correlated with eq 4 gave a significant value of ψ, and even in this case ψ was barely significant. We conclude that we may reject the existence of a steric effect related to the van der Waals radii of the group. As successful correlations were obtained with eq 8 in 22 of the 27 sets studied, we may exclude the existence of a steric effect represented by some other parameters other than the van der Waals radius in most if not all cases. We may also exclude the existence of a steric effect which does not obey a linear free-energy relationship (case 2) at least in those sets which are correlated by eq 8. As for those five sets which are not correlated by eq 8, no conclusions can be reached as the lack of correlation may be due to causes other than the presence of a steric effect. Since in those sets which are correlated by eq 8, the value for X = H lies on the correlation line, $h_{obsd} = h_{calcd}$ and we may reject the possibility of the existence of a constant steric effect (case 3). We are forced to the conclusion that, in general, the polarographic data studied in this work exemplify the absence of any steric effect (case 4). This result is in agreement with our findings for other ortho substituted benzene data.[4,6-8,16] It again *refutes* the often quoted concept that the so-called proximity effect of ortho substituents is largely steric in nature.

Magnitude of the Electrical Effect.—The magnitude of the electrical effect is measured by the value of α. The bromobenzenes give the largest value of α. Somewhat smaller values are found for the iodobenzenes. The benzaldehydes and nitrobenzenes give about the same average value of α of 0.3. Thus, for bromobenzenes α is about 2.7 times the value of α observed for benzaldehydes and nitrobenzenes. The tosylates gave an average value of α of 0.2.

Composition of the Ortho Electrical Effect.—We may conveniently describe the composition of the electrical effect of a substituent in terms of ϵ where[17]

$$\epsilon = \beta/\alpha \tag{10}$$

(16) M. Charton and B. I. Charton, *J. Org. Chem.*, **33**, 3872 (1968).

For the purpose of calculating values of ϵ, α, and β, values taken from the correlations with eq 8 were used as, in general, best results were obtained for correlation with eq 8. Values of ϵ are in Table III. The values

TABLE III

VALUES OF ϵ

Set	ϵ	Set	ϵ	Set	ϵ
1	0[a]	11	0.71	20	0.77
2	0[a]	12	0.55	21	0[a]
3	0[a]	13	0.70	22	0[a]
4	0.22	14	0.71	23	0[a]
5	0.17	15	0.70	25	0[a]
7	0.87	17	...[b]	26	0.81
8	0.72	18	0.73	27	0.99
10	0.69				

[a] β was not significant. [b] α was not significant.

of ϵ obtained for the iodobenzenes lie in the range 0–0.2. The value for the bromobenzenes lies in the same range. There does not seem to be any effect of solvent on ϵ values, although the data are too scanty to make this conclusion certain. An average value of ϵ of 0.7 is obtained for the benzaldehyde (excluding set 17). There seems to be no dependence of ϵ on pH or on medium. With the exception of sets 20 and 26 for which ϵ equals 0.8, the nitrobenzenes generally have low values of ϵ. Again, there seems to be no dependence on pH. It is interesting that, although the magnitude of the electrical effect is about the same for benzaldehydes as for nitrobenzenes, the composition of the electrical effect is very different. We are unable at the present time to explain this observation.

The phenylferrocenes give a value of ϵ of 0.99. It is difficult to compare this result with the other values obtained, however, as this represents the results of the correlation of chronopotentiometric quarter-wave potentials, whereas the other ϵ values have generally been obtained for polarographic half-wave potentials.

The results obtained show clearly the impossibility of defining a single generally useful set of ortho-substituent constants to be used for all ortho-substituted sets.[18] The values of ϵ obtained range from 0 to 0.99.

The Inclusion of the Unsubstituted Member of the Set.—It has been noted that the value of hydrogen (the unsubstituted compound) frequently does not lie on the correlation line for ortho-substituted compounds. This does not seem to be the case for polarographic half-wave potentials. Inclusion of the value for hydrogen in all sets seems, if anything, to have improved the correlations. We conclude that in the case of polarographic data, the value for the unsubstituted compound does in fact lie on the correlation line.

(17) M. Charton, *J. Amer. Chem. Soc.*, **86**, 2033 (1964).

(18) M. Charton, *ibid.*, **91**, 6649 (1969).