of f_1 in Table IV show clearly that in these sets we have a changeover from the predominance of one tautomer to that of the other. We conclude therefore that the method of Kabachnik cannot be universally applied.

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Application of the Hammett Equation to Nonaromatic Unsaturated Systems. VI. The Diels–Alder Reaction

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Rate constants taken from the literature for the reaction of sets of 1-substituted, 2-substituted, and 2,3-disubstituted 1,3-butadienes, and 9-substituted and 9,10-disubstituted anthracenes with various dienophiles and for the reaction of sets of *cis-* and *trans*-1,2-disubstituted and -1,1-disubstituted ethylenes with various dienes have been successfully correlated with the extended form of the Hammett equation $Q_X = \alpha\sigma_I + \beta\sigma_R + h$. Arguments are presented which show that for most of the reactions studied a concerted mechanism is involved. In some sets the available data did not permit any conclusions concerning the mechanism. The magnitude of the values of β obtained for several of the sets studied have been interpreted as evidence for a transition state which is closer to reactants than to adduct. Rates of per cent *endo*/per cent *exo* product formed in the reaction of 4-substituted cinnamoyl chlorides and cinnamic acids and of 4-nitrocinnamoyl and cinnamoyl derivatives with cyclopentadiene were also correlated with the extended Hammett equation; good results were obtained for the latter three sets. Rates of per cent 1,3/per cent 1,4 adduct formed in the reaction of substituted ethylenes with isoprene and of per cent *syn*/per cent *anti* adduct in the reaction of 2-substituted anthracenes with maleic anhydride have also been successfully correlated.

We have been engaged for some time in a study of the application of the Hammett equation[1] to nonaromatic unsaturated systems.[2] In this paper we extend our investigations to structural effects observed in the Diels–Alder and related reactions. In particular, we have studied the effect of substituents upon the reaction rates of dienes and dienophiles. Substituent effects upon the stereochemistry and the orientation in Diels–Alder reactions were also examined. Previous studies of structural effects upon the Diels–Alder reaction by means of the Hammett equation are extant.[3–8] In all of these studies, however, the substituents were bonded to a benzene ring attached to the diene or dienophile. No previous attempt to apply the Hammett equation or any other linear free-energy relationship to directly substituted dienes or dienophiles has been reported. We have therefore correlated by multiple linear regression analysis, sets of data taken from the literature with the extended Hammett equation

$$Q_X = \alpha\sigma_{I,X} + \beta\sigma_{R,X} + h \qquad (1)$$

For the correlation of disubstituted sets we have assumed that interaction terms[9] may be neglected and have used the equation

$$Q_X = \alpha\Sigma\sigma_{I,X} + \beta\Sigma\sigma_{R,X} + h \qquad (2)$$

The data used in the correlations are given in Table I. The σ_I constants were taken from our compilation.[10] The σ_R constants were obtained from the equation

$$\sigma_{R,X} = \sigma_{p,X} - \sigma_{I,X} \qquad (3)$$

The necessary σ_p constants were taken from the collection of Brown and McDaniel[11] when possible; otherwise they were obtained from previous papers in the series.[2]

For purposes of comparison, some of the substituted benzene sets previously correlated with the Hammett equation have been reexamined here by correlation with eq 1.

Results

Results of the correlations with eq 1 are set forth in Table II.

Substituent Effects on Diene Reaction Rates.—We have examined seven sets of substituted or disubstituted dienes (sets 1–7). Good-to-excellent results were obtained for sets 1–6. The elimination of the values for X = Et, *i*-Pr, and *t*-Bu from set 1 appears to give improved results (set 1A). This may be due to a steric effect of bulky groups in the 2 position of butadienes. Such groups may favor the formation of the s-*cis* conformation through which the Diels–Alder reaction proceeds. Because of these results, we included in set 2 only those singly substituted 1,3-butadienes which were members of set 1A. We have also considered that subset of set 2 which excludes all compounds in which one of the substituents is hydrogen (set 2A) to determine whether a second substituent introduces some change in α and β. The results show that no significant difference between values of α and β for sets 2 and 2A is observed. The results for set 6 seem to be improved by including in the set only those substituents which

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TABLE I
DATA USED IN CORRELATIONS

1. Rate constants of 2-substituted 1,3-butadienes with maleic anhydride in benzene at 25°[a]

X	Cl	H	Me	Et	*i*-Pr	*t*-Bu	OMe
k	0.019	0.19	0.57	1.15	2.2	5.6	1.9

2. Rate constants of 2,3-disubstituted 1,3-butadienes with maleic anhydride in benzene at 25°[a]

X^1, X^2	Cl, Cl	Cl, H	Cl, Me	H, H	H, Me	Me, Me
k	0.0009	0.019	0.12	0.19	0.57	2.0
	H, OMe					
	1.9					

3. Rate constants of 1-substituted 1,3-butadienes with maleic anhydride in dioxane at 30°[b]

X	OMe	Me	Ph	H
k_2	0.000841	0.000227	0.0000428	0.0000683

4. Rate constants of 2,3-disubstituted 1,3-butadienes with maleic anhydride in dioxane at 30°[b]

X^1, X^2	Me, Me	Me, H	H, H	Cl, H
k_2	0.000336	0.000154	0.0000683	0.00000690

5. Rate constants of 2,3-disubstituted 1,3-butadienes with tetracyanoethylene in tetrahydrofuran at room temperature[c]

X^1, X^2	Me, Me	Me, H	Me, Cl	H, Cl
k	240	15	1.5	0.002

6. Rate constants of 9-substituted anthracenes with maleic anhydride in dioxane at 130°[b]

X	Me	Et	OMe	H	Cl
k_2	0.112	0.0442	0.0163	0.00646	0.00192
	Br	CN	Ph	NO_2	
	0.00152	0.000042	0.00049	0.0000589	

7. Rate constants of 9,10-disubstituted anthracenes with maleic anhydride in dioxane at 130°[b]

X^1, X^2	Me, Me	Et, Et	MeO, MeO	H, H	Cl, Cl
k_2	1.41	0.242	0.00191	0.00646	0.00028

8. Rate constants of cyclopentadiene with *trans*-1,2-disubstituted ethylenes at 40°[d]

X^1, X^2	$PhSO_2$, $PhSO_2$	Bz, $PhSO_2$	Bz, Bz	Ac, Ac
k_2	0.29	0.727	0.0384	0.009
	CN, CN	CO_2Me, CO_2Me		
	0.00328	0.00268		
X	CO_2Et, CO_2Et	CO_2H, CO_2H	CO_2Me, H	CN, H
k_2	0.0024	0.00222	0.0000622	0.0000475

9. Rate constants of cyclopentadiene with *cis*-1,2-disubstituted ethylenes in dioxane at 40°[d]

X^1, X^2	$PhSO_2$, $PhSO_2$	CN, CN	Bz, $PhSO_2$	Bz, Bz
k_2	0.00656	0.00318	0.000258	0.000257
	CO_2Me, CO_2Me	CO_2Me, H	CN, H	
	0.0000328	0.0000622	0.0000475	

10. Rate constants of cyclopentadiene with *trans*-1,2-disubstituted ethylenes in dioxane at 20°[e]

X^1, X^2	$PhSO_2$, $PhSO_2$	$PhSO_2$, Bz	Bz, Bz	CN, CN
k_2	0.115	0.0275	0.0136	0.000806
	CO_2Me, CO_2Me	CO_2Me, H	CN, H	
	0.000724	0.0000118	0.0000104	

11. Rate constants of cyclopentadiene with *cis*-1,2-disubstituted ethylenes in dioxane at 20°[e]

X^1, X^2	$PhSO_2$, $PhSO_2$	CN, CN	Bz, Bz
k_2	0.00194	0.00091	0.0000666
	CO_2Me, CO_2Me	CO_2Me, H	CN, H
	0.00000628	0.0000118	0.0000104

12. Rate constants of 9,10-dimethylanthracene with *trans*-1,2-disubstituted ethylenes in dioxane at 130°[e]

X^1, X^2	CN, CN	CN, CO_2Me	CO_2Me, CO_2Me
k_2	0.0453	0.0084	0.00215
	CO_2Et, CO_2Et	CN, H	CO_2Me, H
	0.00160	0.00145	0.000718
	Ph, H	Ph, CO_2Me	Me, CO_2Me
	0.00007	0.00002	0.000005
	Me, CN		
	0.000011		

13. Rate constants of 9,10-dimethylanthracene with *cis*-1,2-disubstituted ethylenes in dioxane at 130°[e]

X^1, X^2	CN, CN	CN, CO_2Me	CN, H	CO_2Me, CO_2Me
k_2	0.0435	0.0042	0.00145	0.0000205
	CO_2Me, H	Ph, H		
	0.000718	0.00007		

14. Rate constants of 9,10-dimethylanthracene with *trans*-3-substituted methacrylate in dioxane at 130°[e]

X	CN	CO_2Me	H	Ph	Me
k_2	0.0084	0.00215	0.000718	0.00002	0.000005

15. Rate constants of 9,10-dimethylanthracene with *trans*-3-substituted acrylonitriles in dioxane at 130°[e]

X	CN	CO_2Me	H	Me
k_2	0.0453	0.0084	0.00145	0.000011

16. Rate constants of 2,3-dimethylbutadiene with *trans*-1,2-disubstituted ethylenes in dioxane at 100°[f]

X^1, X^2	Bz, Bz	$PhSO_2$, $PhSO_2$	Bz, $PhSO_2$	CN, CN
k_2	0.0144	0.0106	0.00772	0.000224

17. Rate constants of 2,3-dimethylbutadiene with *cis*-1,2-disubstituted ethylenes in dioxane at 100°[f]

X^1, X^2	Bz, Bz	$PhSO_2$, $PhSO_2$	Bz, $PhSO_2$	CN, CN
k_2	1.94	12.8	4.13	19.4

18. Rate constants of 1,1-disubstituted ethylenes with 9,10-dimethylanthracene in dioxane at 130°[e]

X^1, X^2	Me, CO_2Me	Me, CN	CN, H	CO_2Me, H	Ph, H
k_2	0.000148	0.000205	0.00145	0.000718	0.00007

19. Rate constants of cinnamaldehyde with substituted ethylenes at 170°[g]

X	OBu	O-*i*-Bu	Ph	CO_2R	4-MeC_6H_4
k_2	0.00604	0.00598	0.002	0.0005	0.0026

20. Relative rates of 1-(4′-substituted phenyl)-1,3-butadiene with maleic anhydride in dioxane at 25°[h]

X	H	MeO	Me	NO_2	Cl
k_X/k_H	1	2.65	1.11	2.75	0.586

21. Relative rates of 1-(4′-substituted phenyl)-1,3-butadiene with maleic anhydride in dioxane at 35°[h]

X	H	MeO	Me	NO_2	Cl
k_X/k_H	1	2.33	1.29	0.300	0.632

22. Relative rates of 1-(4′-substituted phenyl)-1,3-butadiene with maleic anhydride in dioxane at 45°[h]

X	H	MeO	Me	NO_2	Cl
k_X/k_H	1	2.40	1.37	0.280	0.636

23. Log 10^3k_r of 3-substituted methylphenylpropiolates with tetracyclone in phenylcyclohexane at 175.6°[i]

X	MeO	Me	H	Cl	NO_2
Log 10^3k_r	0.238	0.207	0.170	0.458	0.758

24. Log 10^3k_r of 4-substituted methylphenylpropiolates with tetracyclone in phenylcyclohexane at 175.6°[i]

X	MeO	Me	H	Cl	NO_2
Log 10^3k_r	0.076	0.100	0.170	0.352	0.889

25. Equilibrium constants of 6,6-di(4′-substituted phenyl)-fulvene tetracyanoethylene in $CHCl_3$ at 20°[j]

X	MeO	H	Br	Cl
k	325000	11000	3300	2600

26. *endo/exo* ratio in adduct of 4-substituted cinnamoyl chlorides with cyclopentadiene in acetone or toluene at 55°[k]

X	NO_2	Cl	H	MeO
r	1.78	2.03	2.03	1.94

27. *endo/exo* ratio in adduct of 4-substituted cinnamic acids with cyclopentadiene in acetone or toluene at 55°[k]

X	NO_2	Cl	H	MeO
r	0.429	0.667	0.754	0.887

28. *endo/exo* ratio in adduct of 4-nitrocinnamoyl derivatives with cyclopentadiene in acetone or toluene at 55°[k]

X	Cl	OH	OMe	NH_2
r	1.78	0.429	0.389	0.333

29. *endo/exo* ratio in adduct of cinnamoyl derivatives with cyclopentadiene in acetone or toluene at 55°[k]

X	Cl	OH	OMe	NH_2
r	2.03	0.754	0.786	0.515

TABLE I (*Continued*)

30. *para/meta* ratio in adduct of substituted ethylenes with isoprene[l]

X	Ph	CHO	CO_2Me	CO_2Et	CN	Ac	NO_2
r	3.5	1.8	2.0	1.9	2.2	2.3	3.7

31. *syn/anti* ratio in adduct of maleic anhydride with 2-substituted anthracenes[m]

X	NO_2	H	NHAc	NMe_2
r	0.64	1	1.08	1.22

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TABLE II

RESULTS OF CORRELATIONS

Set	α	β	h	R[a]	F[b]	r[c]	s_{est}[d]	s_α[d]	s_β[d]	s_h[d]	n[e]	cl[f]
1	−4.75	−4.02	−0.534	0.939	14.90	0.617	0.347	0.873	1.08	0.205	7	97.5
1A	−3.86	−3.88	−0.809	0.996	57.93	0.556	0.136	0.394	0.425	0.104	4	90.0
2	−4.12	−3.85	−0.811	0.989	87.31	0.659	0.219	0.321	0.633	0.160	7	99.9
2A	−3.96	−3.23	−0.721	0.988	21.29	0.818	0.369	0.781	1.81	0.369	4	90.0
3	−4.08	−4.25	−4.30	0.980	12.41	0.869	0.197	1.74	1.01	0.140	4	90.0
4	−2.96	−1.65	−4.16	0.99999	20408.	0.384	0.00625	0.0148	0.0340	0.00520	4	99.5
5	−8.91	−13.3	−1.28	0.975	9.598	0.636	0.835	2.07	6.38	1.39	4	90.0
6	−3.15	−2.41	−2.09	0.897	12.42	0.181	0.610	0.773	1.16	0.342	9	99.0
6A	−3.84	−4.23	−1.92	0.986	35.45	0.0889	0.289	0.497	1.05	0.214	5	95.0
7	−3.07	−0.366	−1.17	0.874	3.237	0.599	1.05	1.42	1.63	0.694	5	90.0
7A	−4.93	−6.91	−2.23	0.993	33.09	0.793	0.349	0.655	1.68	0.345	4	90.0
8	2.58	8.07	−6.13	0.925	20.77	0.0903	0.523	0.679	1.66	0.620	10	99.0
8A	2.61	7.69	−6.04	0.787	4.078	0.497	0.589	1.09	3.03	1.46	8	90.0
9	2.46	0.905	−5.62	0.871	6.270	0.303	0.543	0.760	2.35	0.665	7	90.0
9A	3.84	5.32	−8.00	0.934	6.784	0.530	0.471	1.06	3.81	1.67	5	90.0
9B	2.33	0.944	−5.40	0.924	8.797	0.301	0.433	0.611	1.87	0.543	6	90.0
9C	2.70	1.35	−5.85	0.892	1.950	0.854	0.573	2.30	8.15	4.16	4	90.0
10	2.08	12.6	−7.11	0.981	52.31	0.303	0.375	0.524	1.62	0.459	7	99.5
10A	2.68	14.5	−8.15	0.942	7.894	0.530	0.458	1.03	3.71	1.62	5	90.0
11	2.66	1.98	−6.54	0.894	5.991	0.271	0.617	0.863	2.91	0.769	6	90.0
11A	4.40	8.25	−9.67	0.983	14.15	0.550	0.363	0.829	3.21	1.34	4	90.0
11B	2.50	2.35	−6.31	0.975	19.43	0.278	0.329	0.464	1.56	0.418	5	90.0
12	1.70	5.90	−4.82	0.859	9.824	0.747	0.764	1.24	3.33	0.596	10	99.0
12A	3.31	6.14	−6.23	0.996	236.9	0.695	0.175	0.337	0.857	0.190	7	99.9
13	3.73	−6.56	−4.78	0.793	2.548	0.791	0.946	1.81	6.10	0.844	6	90.0
13A	2.03	1.32	−4.14	0.976	20.22	0.846	0.315	0.689	2.56	0.308	5	95.0
14	0.643	11.5	−3.59	0.963	12.77	0.786	0.522	1.61	4.10	0.416	5	90.0
14A	3.12	6.22	−4.36	0.9998	1160.0	0.889	0.0559	0.255	0.594	0.0740	4	99.0
15	1.21	12.0	−3.25	0.968	7.385	0.824	0.681	2.33	6.94	0.545	4	90.0
16	2.12	16.5	−8.75	0.993	37.94	0.851	0.167	0.670	2.37	1.21	4	90.0
17	1.20	−1.84	−0.189	0.996	70.09	0.851	0.0666	0.267	0.945	0.483	4	90.0
18	1.46	5.89	−4.19	0.998	290.5	0.573	0.0593	0.187	0.414	0.0732	5	99.5
19	−1.32	−1.43	−2.70	0.9988	427.2	0.290	0.0303	0.129	0.0490	0.0315	5	99.5
20	−0.662	−1.08	−0.0542	0.969	15.47	0.140	0.127	0.206	0.266	0.0932	5	90.0
21	−0.670	−0.948	−0.0158	0.983	28.64	0.140	0.0948	0.142	0.183	0.0640	5	95.0
22	−0.719	−0.990	−0.00683	0.987	38.36	0.140	0.0794	0.129	0.167	0.0585	5	95.0
23	0.709	0.318	0.224	0.985	33.34	0.140	0.0594	0.0968	0.124	0.0437	5	95.0
24	0.848	0.715	0.200	0.989	43.34	0.140	0.0716	0.117	0.151	0.0527	5	97.5
25	−3.51	−4.51	4.04	0.9986	182.9	0.394	0.0874	0.251	0.258	0.0873	4	90.0
26	−0.0614	−0.0204	0.306	0.744	0.620	0.232	3.11	0.0633	0.0669	0.0311	4	90.0
27	−0.302	−0.301	−0.123	0.996	58.26	0.232	0.0216	0.0439	0.0464	0.0216	4	90.0
28	1.52	0.386	−0.453	0.937	3.573	0.981	0.205	4.01	2.78	2.55	4	90.0
29	1.05	0.418	−0.109	0.991	26.20	0.981	0.0601	1.18	0.816	0.748	4	90.0
30	0.226	−0.768	0.352	0.537	0.812	0.417	0.131	0.307	0.613	0.118	7	90.0
30A	0.708	1.19	−0.0854	0.919	6.181	0.402	0.0576	0.177	0.539	0.117	6	90.0
31	−0.262	−0.123	0.0166	0.953	4.932	0.457	0.0642	0.139	0.0898	0.0620	4	90.0

[a] Multiple correlation coefficient. [b] *F* test for significance of regression. [c] Partial correlation coefficient of σ_I on σ_R. [d] Standard errors of estimate, α, β, h. [e] Number of points in set. [f] Confidence level.

are spherically symmetric and for which, therefore, steric inhibition of resonance cannot occur (set 6A). We shall consider the question of steric inhibition of resonance in more detail below. The results for set 7 are poor. We again consider this to be due to steric inhibition of resonance, and perhaps to other steric factors as well. Exclusion of the dimethoxy compound from the set results in a much improved correlation (set 7A). Models show that the methoxy groups should be rotated out of the plane of the rings by a significant amount.

Substituent Effects on Dienophile Reaction Rates.—We find it convenient to consider three classes of dienophiles: (1) *trans*-1,2-disubstituted (sets 8, 10, 12, 14–16), (2) *cis*-1,2-disubstituted (sets 9, 11, 13, 17), and (3) 1,1-disubstituted dienophiles (set 18). Our results for the *trans*-1,2-disubstituted dienophiles are from good to excellent. Elimination of those compounds in set 8 in which one of the substituents is hydrogen resulted in a very poor correlation (set 8A) which it is interesting to note has values of α and β which are not significantly different from those obtained for set 8. We believe the poor correlation obtained for set 8A is due to the comparatively narrow range of substituent type of which the set is composed. The same results obtain set 10A when monosubstituted dienophiles are omitted from set 10. If we exclude monosubstituted ethylenes from set 12, however, a very great improvement in correlation results (set 12A). Furthermore, the values of α obtained for these two sets are significantly different, although the values of β are not. We believe that this may be due to difference in steric effects between mono- and disubstituted dienes reacting with the 9,10-dimethylanthracene, and that these steric effects are not present when the diene reactant is cyclopentadiene. To account for our results we propose the presence of essentially constant steric effects of one magnitude for monosubstituted ethylenes and of another magnitude for disubstituted ethylenes reacting with 9,10-dimethylanthracene. In sets 14 and 15 one of the two substituents is held constant. Exclusion of the monosubstituted compound from set 14 gives improve results (set 14A) as is expected in view of the fact that sets 14 and 15 are subsets of set 12.

The results obtained for the *cis*-disubstituted dienophile sets are not very good in most cases. Elimination of the monosubstituted ethylenes from set 9 did not significantly improve the results (set 9A). Inspection of models led us to conclude that in dimethyl maleate the carbomethoxy groups cannot be coplanar with the ring. This compound was therefore excluded from set 9 giving a significant, although small, improvement in the results (set 9B). Exclusion of the values for monosubstituted ethylenes and that for dimethyl maleate resulted in a poor correlation. Exclusion of the monosubstituted ethylenes from set 11 gives somewhat improved results (set 11A). Exclusion of the value for dimethyl maleate from set 11 also gave some improvement (set 11B). This set probably best represents the behavior of these compounds. Correlation in set 13 is improved by the omission of the value for dimethyl maleate (set 13A) in accord with the results obtained for sets 9 and 11.

In view of the fact that the values of α and β obtained for set 17 are different in sign results for this set are probably not significant. The results obtained for the 1,1-disubstituted ethylenes are excellent.

Substituent Effects on the Enone-Substituted Ethylene Cyclization.—The correlation obtained for the only set of this type studied is excellent.

Substituent Effects on Adduct Stereochemistry.—No correlation is observed for set 26. Fair to good results were obtained with sets 27–29. The lack of correlation in set 26 is perhaps indicative of the high reactivity of the dienophile resulting in a lack of discrimination in the stereochemistry.

Substituent Effects on Adduct Orientation.—The results obtained for set 30 are not significant. Elimination of the value for styrene (set 30A) resulted in a significant correlation. The results obtained for set 31 are fair.

Discussion

The Mechanism of the Diels–Alder Reaction.—The mechanism of the Diels–Alder reaction has recently been reviewed.[12] We do not intend to describe the mechanism in detail here, but rather to attempt to draw certain mechanistic conclusions from the correlations with eq 1. Let us consider the question of a concerted *vs.* a two-step mechanism. In order to clearly define what we mean by these terms, we consider any mechanism for which the reaction coordinate proceeds from reactants through a single transition state to products as concerted, and any mechanism for which the reaction coordinate proceeds from reactants through a transition state followed by an intermediate and then a second transition state to product as a two-step mechanism. Let us now consider what the effect of substituents on the diene must be in the case of the concerted mechanism. For the 2-substituted 1,3-butadienes

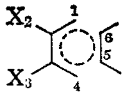
$$\log k_{\mathrm{X}_2} = \alpha_{12}\sigma_{\mathrm{IX}} + \alpha_{42}\sigma_{\mathrm{IX}_2} + \beta_{12}\sigma_{\mathrm{RX}_2} + \beta_{42}\sigma_{\mathrm{RX}_2} + h \quad (4)$$

where α_{12} represents the magnitude of the localized (inductive and/or field) effect at C_1 in the transition state, I, the other coefficients have analogous meanings. Then

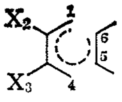
$$\log k_{\mathrm{X}_2} = \alpha\sigma_{\mathrm{IX}_2} + \beta\sigma_{\mathrm{RX}_2} + h \quad (5)$$

equivalent to eq 1 where

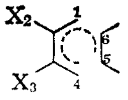
$$\alpha = \alpha_{12} + \alpha_{42} \qquad \beta = \beta_{12} + \beta_{42} \quad (6)$$



I



II



III

Now for the 2,3-disubstituted butadienes we may write

$$\log k\mathrm{X}_2\mathrm{X}_3 = \alpha_{12}\sigma_{\mathrm{IX}_2} + \alpha_{42}\sigma_{\mathrm{IX}_2} + \alpha_{13}\sigma_{\mathrm{IX}_3} + \alpha_{43}\sigma_{\mathrm{IX}_3} + \beta_{12}\sigma_{\mathrm{IX}_2} + \beta_{42}\sigma_{\mathrm{RX}_2} + \beta_{13}\sigma_{\mathrm{RX}_3} + \beta_{43}\sigma_{\mathrm{RX}_3} + h \quad (7)$$

If the reaction of the 2,3-disubstituted 1,3-butadienes is with a symmetric dienophile, such as maleic anhydride, we see then that the 2 and 3 positions are equivalent and therefore

$$\alpha_{12} = \alpha_{43},\ \alpha_{13} = \alpha_{42},\ \beta_{12} = \beta_{43},\ \beta_{14} = \beta_{42} \quad (8)$$

which leads to the equation

$$\log k_{\mathrm{X}} = \alpha(\sigma_{\mathrm{IX}_1} + \sigma_{\mathrm{IX}_2}) + \beta(\sigma_{\mathrm{RX}_1} + \sigma_{\mathrm{RX}_2}) + h \quad (9)$$

equivalent to eq 2.

We may proceed to a consideration of the effect of substituents on the diene in the case of the effect of substituents on the diene in the case of the twotesp mechanism. There are three possible cases with which we must concern ourselves: the first step

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[12] A. Wassermann, "Diels–Alder Reactions," Elsevier Publishing Co., Amsterdam, 1965.

is rate determining, the second step is rate determining, and both steps are comparable in rate. We shall consider the case in which the first step is rate determining. For 2-substituted 1,3-butadienes reacting with a symmetric dienophile we may have either or both of the transition states II or III. Considering transition state II, we write

$$\log k_{X_2} = \alpha_{42}\sigma_{IX_2} + \beta_{42}\sigma_{RX_2} + h \qquad (10)$$

equivalent to eq 1. For the 2,3-disubstituted 1,3-butadienes we write

$$\log k_{X_2X_3} = \alpha_{42}\sigma_{IX_2} + \alpha_{43}\sigma_{IX_3} + \beta_{42}\sigma_{RX_2} + \beta_{43}\sigma_{RX_3} + h \quad (11)$$

Equations equivalent to 10 and 11 can be obtained from a consideration of transition state III. Analysis of the case in which the second step is rate determining will give equation equivalent to 10 and 11. For the third case equations analogous to 4 and 7 are obtained. Comparing the concerted and two-step mechanisms we may draw the following conclusions. The rate constants for the reaction of the 2,3-disubstituted 1,3-butadienes with symmetric dienophiles should be successfully correlated by eq 2 giving values of α and β equal to those obtained by the correlation of the rate constants of 2-substituted 1,3-butadienes with eq 1, *if the mechanism is concerted.* The rate constants for the reaction of the 2,3-disubstituted 1,3-butadienes with symmetric dienophiles *should not be correlated by eq 2 unless X_2 and X_3 are identical,* and, in any event, values of α and β obtained from correlation of the rate constants of the 2,3-disubstituted 1,3-butadienes with eq 2 *should not* be equal to the values of α and β obtained for the correlation of the rate constants for the reaction of 2-substituted butadienes with eq 1.

In all of the above discussion, it is assumed that both mono- and disubstituted dienes are reacting with the same dienophiles under the same reaction conditions.

Our results for sets 1 and 2 show clearly that, on the basis of the above analysis, the 2- and 2,3-substituted 1,3-butadienes are reacting by the concerted mechanism, as successful correlation of the rate constants for the disubstituted compounds with eq 2 was obtained, and the values of α and β obtained therefrom are statistically in agreement with those obtained for the correlation of the rate constants of the monosubstituted dienes with eq 1. Successful correlation of the rate constants for the 2,3-disubstituted 1,3-butadienes with eq 2 in set 4 and to a lesser extent set 5 suggest that these compounds also react by the concerted mechanism.

The arguments we have presented above may also be applied to the reaction of 9-substituted and 9,10-disubstituted anthracenes with maleic anhydride. While the results obtained for set 7A are not good enough to be conclusive, they suggest that these compounds also react *via* the concerted mechanism.

The above analysis may also be applied to 1-substituted and both *cis*- and *trans*-1,2-disubstituted ethylenes reacting as dienophiles with symmetric dienes. Again we predict that the disubstituted compounds should be correlated by eq 2 in the case of the concerted mechanism, with α and β values equal to those obtained by correlating the monosubstituted compounds with eq 1. In the case of the two-step mechanism, correlation of disubstituted compounds with eq 2 will fail unless X_1 and X_2 are identical. Even then the values of α and β obtained should differ from those obtained for the monosubstituted ethylenes with eq 1. Let us first consider the *trans* compounds. While the data were not sufficient to permit comparison of separate sets of 1-substituted and *trans*-1,2-disubstituted ethylenes, we have several sets in which the entire set includes both monosubstituted and disubstituted compounds. A comparison of the values of α and β obtained including and then excluding the monosubstituted compounds will show that they have the same values of α and β as the disubstituted compounds. The results obtained for substituted ethylenes reacting with cyclopentadiene at 20° (sets 10 and 10A) and 40° (sets 8 and 8A) show clearly that α and β are unaffected by the exclusion of the monosubstituted compounds from the set. We conclude that this reaction proceeds through a concerted mechanism. In the case of the substituted ethylenes reacting with 9,10-dimethylanthracene (sets 12 and 12A) the value of β is unchanged on exclusion of the monosubstituted compounds from the set; the change in the value of α is within the standard deviation obtained for α_1 and the correlation with eq 2 is successful even though X_1 is not identical with X_2 for seven of the ten members of the set. We believe that this reaction also probably proceeds through a concerted mechanism. The reasonably good correlation with eq 2 obtained for set 16 which includes a compound for which X_1 and X_2 are not identical, suggest that these compounds may also react by the concerted mechanism.

With regard to the *cis*-1,2-disubstituted ethylenes, the successful correlation obtained of sets 9 and 11 and the good agreement between α and β values of sets 9B and C seem to indicate a concerted mechanism for the reaction of *cis*-1,2-disubstituted ethylenes with cyclopentadiene. The successful correlation obtained for set 13A suggests that the reaction of *cis*-1,2-disubstituted ethylenes with 9,10-dimethylanthracene also goes through a concerted mechanism.

In general, it would seem that the reactions studied have all shown a concerted mechanism. On the basis of this conclusion, we may now proceed to draw further inferences from the magnitude of the β values obtained for the substituted diene sets. If the transition state for the reaction were to be close to the product, the value of β should be small for the 1-substituted dienes and the 9-substituted anthracenes, as in the product the substituent is bonded to an sp^3 carbon atom and therefore the substituent cannot interact with a π-electron system. The observed values of β are fairly large; we therefore conclude that the transition state is closer to reactants than to product. This same argument may be applied to the β values observed for the *trans*-1,2-disubstituted ethylenes. The very much smaller values of β obtained for the *cis*-1,2-disubstituted ethylenes suggest that perhaps for these compounds the transition state is closer to product than it is for the corresponding *trans* compounds. It is interesting in this regard to note that the values of β obtained for the reaction of the *trans*-1,2-disubstituted ethylenes and the 1,1-disubstituted ethylenes with 9,10-dimethylanthracene while large are much less than the values obtained for the reaction of the *trans*-1,2-disubstituted ethylenes with cyclopentadiene or with 2,3-dimethyl-1,3-butadiene. This again may possibly be due to the location of the transition state on the reaction coordinate.

The Magnitude and Composition of the Electrical Effect.—As a measure of the magnitude of the electrical effect we may take the α values. As the ratio ϵ is generally constant for a given system, where

$$\epsilon = \frac{\beta}{\alpha} \tag{12}$$

specifying α is sufficient to determine the magnitude of electrical effects. The composition may be conveniently described in terms of ϵ. Values of ϵ for the sets studied are reported in Table III.

TABLE III

VALUES OF ϵ

Set	ϵ	Set	ϵ	Set	ϵ	Set	ϵ
1A	1.01	8	3.13	16	7.78	23	0.449
2A	0.816	9B	0.405			24	0.843
3	1.04	10	6.06	18	4.03		
4	0.557	11B	0.940	19	1.08	27	0.998
5	1.49	12A	1.85	20	1.63	28	0.153
6A	1.10	13A	0.651	21	1.41	29	0.398
7A	1.40	14A	1.99	22	1.38		
		15	9.92				

The magnitude of the electrical effect of substituents on dienes seems to be dependent on the solvent and the dienephile, as is shown by a comparison of sets 1, 4, and 5. Comparison of values for sets 4 and 5 suggests that the composition of the electrical effect may also be solvent dependent although the data are insufficient to warrant a conclusion. The results for the 1-(4′-substituted phenyl)-1,3-butadienes show that the temperature dependence of α and β is small. Comparison of sets 3 and 4 seems to show that a 1-substituent exerts a greater effect on reaction rate than does a 2-substituent by a factor of 1.4. The magnitude and composition of the electrical effect in the 9-substituted and 9,10-disubstituted anthracenes (sets 6A and 7A) is about the same as that observed for the 1-substituted 1,3-butadienes (set 3). Although the 2-substituted and 2,3-disubstituted 1,3-butadienes show a range of ϵ values from 0.557 to 1.49, the uncertainties in α and β are so large that at the present the average value of about 1 adequately represents the composition of the electrical effect in these compounds.

trans-1,2-Disubstituted ethylenes (sets 8, 10, 12A, and 16) show comparatively small values of α when contrasted with the values observed for substituted olefins. The values of α obtained for the *cis*-1,2-disubstituted ethylenes are about the same as those obtained for the *trans*-1,2-disubstituted ethylenes; the value of α obtained for the 1 set of 1,1-disubstituted ethylenes is somewhat smaller but of the same order of magnitude. This result is not unexpected. In a comparison of reactants undergoing some given reaction under the same reaction conditions α is a function only of molecular geometry.[13] For the *cis*- and *trans*-1,2- and 1,1-disubstituted ethylenes, the distance and angle variables of which α is a function are of course approximately equal.

The comparison of the values of α obtained for the 3- and 4-substituted methyl phenylpropiolates (sets 23 and 24) with the values obtained for the disubstituted ethylenes suggests that acetylenic dienophiles are decidedly more susceptible to substituent effect. With respect to the composition of the electrical effect the value of ϵ obtained for set 24 is comparable to these observed for *cis*-1,2-disubstituted ethylenes and very much less than those values observed for the *trans* compounds.

In order to discuss the magnitude and composition of the electrical effect for the one set (set 25) of equilibrium constants available, we must consider this equilibrium in terms of the rates of the forward and reverse reactions. Writing

$$v_f = k_f C_{\text{diene}} \cdot C_{\text{dienophile}} \tag{13}$$

$$v_r = k_r C_{\text{adduct}} \tag{14}$$

and at equilibrium

$$v_r = v_f \tag{15}$$

we obtain

$$\frac{k_f}{k_r} = \frac{C_{\text{adduct}}}{C_{\text{diene}}\, C_{\text{dienophile}}} \tag{16}$$

For this reaction however,

$$K_e = \frac{C_{\text{adduct}}}{C_{\text{diene}}\, C_{\text{dienophile}}} \tag{17}$$

Then

$$\log K_{eX} = \log k_{fX} - \log k_{rX} \tag{18}$$

$$\log K_{eX} = \alpha_f \sigma_{IX} + \beta_f \sigma_{RX} + h_f - \alpha_r \sigma_{IX} - \beta_r \sigma_{RX} - h_r \tag{19}$$

$$\log K_{eX} = \alpha \sigma_{IX} + \beta \sigma_{RX} + h \tag{20}$$

where

$$\alpha = \alpha_f - \alpha_r,\ \beta = \beta_f - \beta_r,\ h = h_f - h_r \tag{21}$$

As α_f and α_r and β_f and β_r must be opposite in sign, we can now account in part for the large magnitude of α and β obtained for set 25.

To interpret our results for the effect of substituents on adduct stereochemistry, we must consider the type of data correlated. The over-all rate constant for the formation of adduct may be written in terms of the *endo* and *exo* rate constants as

$$k_t = k_{endo} + k_{exo} \tag{22}$$

Now let us write[14]

$$k_{exo} = p_{exo} k_t,\ k_{endo} = p_{endo} k_t \tag{23}$$

where p_{endo} and p_{exo} are the per cents of each stereoisomer obtained. Then

$$\frac{p_{endo} k_t}{p_{exo} k_t} = r = \frac{k_{endo}}{k_{exo}} \tag{24}$$

and

$$\log r = \log \frac{k_{endo}}{k_{exo}} = \alpha_n \sigma_{IX} + \beta_n \sigma_{RX} + h_n - \alpha_0 \sigma_{IX} - \beta_0 \sigma_{RX} - h_0 \tag{25}$$

$$\log r = \log \frac{k^{endo}}{k^{exo}} = \alpha \sigma_{IX} + \beta \sigma_{RX} + h \tag{26}$$

where

$$\alpha = \alpha_n - \alpha_0,\ \beta = \beta_n - \beta_0 \text{ and } h = h_n - h_0 \tag{27}$$

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[13] M. Charton, Abstracts, 137th National Meeting of the American Chemical Society, Cleveland, Ohio, April 1960, p 92-O; 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1961, p 57-T.

[14] O. Exner, *Collection Czech. Chem. Commun.*, **26**, 1 (1961).

As might be expected, the effect of a substituent attached to the carbonyl group (sets 28 and 29) is much greater than that of a substituent attached to the benzene ring. It would appear from our results that the stereochemistry of the Diels–Alder adduct is a function of substituent effects.

The data correlated in our study of orientation in Diels–Alder adducts are of the same type as that examined above in the question of the stereochemistry of the adduct. Equations analogous to 22–27 may be written. Our results show that substituent effects in the substituted ethylenes (set 30A) are important in determining the orientation in Diels–Alder adducts. The effect of a substituent in the 2-substituted anthracenes (set 31) on orientation is much smaller than is the effect in the substituted ethylenes, as might be expected from a comparison of the geometries.

Our results for the enone–ethylene cyclization (set 19) show that substituent effects are somewhat smaller here than those observed for the other reactions studied. Substituent effects seem to be comparable to those observed for *cis*-1,2-disubstituted ethylenes acting as dienophiles.

Steric Effects.—We have noted that large differences in the value of β are observed when we compare the reactions of *trans*-1,2-disubstituted ethylenes with cyclopentadiene (or with 2,3-dimethyl-1,3-butadiene), *trans*-1,2-disubstituted ethylenes with 9,10-dimethylanthracene, 1,1-disubstituted ethylenes with 9,10-dimethylanthracene, and *cis*-1,2-disubstituted ethylenes with cyclopentadiene, 2,3-dimethyl-1,3-butadiene, or 9,10-dimethylanthracene. It would seem that these differences in β are due to steric repulsions in the transition state in all of the reactions of the *cis* compounds, and to some extent in the reactions between the *trans*-12- and the 1,1-disubstituted ethylenes and 9,10-dimethylanthracenes.

In certain of the 9-substituted and 9,10-disubstituted anthracenes steric inhibition of resonance seems likely. It is of interest to calculate the interplanar angle θ made by the plane of the substituent with the plane of the anthracene ring system. The variation of σ_R with θ is given by

$$\sigma_{R},\ \theta_{X} = \sigma_{RX} \cos^2 \theta \qquad (28)$$

The observed rate constant may be expressed as

$$\log k_{X(obsd)} = \alpha\sigma_{IX} + \beta\sigma_{R,\theta X} + h \qquad (29)$$

Solving eq 29 for $\sigma_{R\theta}$; eq 28 for $\cos^2 \theta$, and combining, we obtain the relationship

$$\frac{\log k_{X(obsd)} - \alpha\sigma_{IX} - h}{\beta\sigma_{RX}} = \cos^2 \theta \qquad (30)$$

Values of θ calculated for the MeO, Ph, and NO_2 groups are 45, 90, and 90°, respectively. In the case of the latter two values, eq 30 gave negative values of $\cos^2 \theta$, and we have therefore considered θ to be 90°. For 9,10-dimethoxyanthracene, we obtain an average value of 58° for θ for the methoxy groups. The difference between this average value of θ and the value calculated for 9-methoxyanthracene is probably not significant.

We have attempted to calculate an average value of θ for the carbomethoxy groups in dimethyl maleate. No results could be obtained for sets 9B and 13A. Steric inhibition of resonance may be one of the factors involved in the surprisingly low reactivity of dimethyl maleate but in these sets some other factor must also be involved. For set 11B we may calculate an average value of θ of 41°. In this connection it should be noted that *cis*-dibenzoylethylene in sets 9 and 11 appears to be free of steric effects. Examination of models suggests that *cis*-dibenzoylethylene may not be distorted to the same extent as dimethyl maleate, and in fact the former may be essentially free of steric inhibition of resonance.

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Imino Lactones. III. The Cyclization of 4-Bromobutyranilide in Aqueous Solution[1a,b]

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The cyclization of 4-bromobutyranilide in aqueous solution has been investigated at 30° in the range of pH 2–14. The rate of cyclization is independent of pH in the range of pH 2–10 and is directly proportional to hydroxide ion activity at higher pH. Below pH 10, the sole reaction product is the imino lactone II, resulting from nucleophilic displacement by the neutral amide function. Cyclization of the amide anion at pH >10 yields both the imino lactone II and the pyrrolidone III in a ratio 1:9. The latter finding appears to constitute the first example of O^--5 ring closure with 4-substituted butyramides.

Recurrent interest in the nucleophilic properties of the amide function has led to several studies of the cyclization of 4-halo-N-substituted butyramides.[2–4] Fusion with solid potassium hydroxide or cyclization in organic solvents containing alkali bases gave 2-pyrrolidones; fusion in the absence of base or reaction in neutral or weakly basic organic media yielded derivatives of 2-iminotetrahydrofuran. In extension of our studies[5] on the chemistry of the imino lactone II in

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[1] (a) This work is taken from a dissertation presented by B. A. C. in partial fulfillment of the requirements for the Ph.D. degree, Yale University, 1966. (b) Financial support by the National Institutes of Health (Grant No. AM-04288) is gratefully acknowledged. (c) Predoctoral fellow of the National Institutes of Health, 1965–1966.

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