

TABLE IV
 PROTON MAGNETIC RESONANCE DATA^a

Adduct	Chemical shifts, δ (ppm)			Rel intensities
	CH ₂ (CH ₂) ₅	Isolated -CH ₂ -	-CHX	
II	0.8-2.0 (m)	3.0 (m)	4.2 (5), $J_{HH} = 6$	13:2:1
III	0.8-2.0 (m)	2.7 (m)	4.1 (5), $J_{HH} = 6.5$ 6.0 (3), $J_{HH} = 6.5$	13:2:1:1
IV	0.8-2.0 (m)	2.8 (4), $J_{HH} = 6.0$, $J_{HH'} = 8.0$	4.2 (m) 6.0 (m)	13:2:1:1
V	0.8-2.0 (m)	4.0 (m)	5.9 (3), $J_{HH} = 6.5$	13:2:1
VI	0.7-2.1 (m)	3.2 (4), $J_{HH} = 5.5$, $J_{HH'} = 5.0$	4.2 (m)	13:2:1
VII	0.8-2.2 (m)	3.3 (3), $J_{HH} = 5.5$	4.4 (m)	13:2:1
VIII	0.8-2.2 (m)	2.7 (6), $J_{HH} = 6.5$, $J_{HF} = 18$	4.2 (5), $J_{HH} = 6.0$	13:2:1
IX	0.7-2.2 (m)	2.2-3.2 (m)	4.4 (m)	13:2:1
X	0.7-2.2 (m)	2.2-3.0 (m)	4.3 (m)	13:2:1
XI	0.7-2.7 (m)		4.0-4.8 (m)	15:1
XII	0.8-2.2 (m)	2.9 (m)	4.4 (m)	13:2:1
XIII	0.7-3.1 (m)		4.3 (m)	15:1
XIV	0.8-2.1 (m)	2.8 (4), $J_{HH} = 5.5$, $J_{HH'} = 5.0$	4.2 (5), $J_{HH} = 5.5$	13:2:1
XVII	0.7-2.1 (m)	2.5-3.3 (m)	4.4 (m)	13:2:1
XVIII	0.7-2.1 (m)	2.4-3.3 (m)	4.4 (5), $J_{HH} = 6.5$	13:2:1
XIX	0.7-2.1 (m)	2.6-3.2 (m)	4.4 (m)	13:2:1

^a In parentheses is given the multiplicity of the peak; the coupling constants are in cycles per second.

the usual manner and the organic layer distilled to give 2.4 g of product, bp 54-55° (0.8 mm), identified as CF₂=CFCH₂CHCl-(CH₂)₅CH₃. The pmr and ir spectra were consistent with the above structure.

Registry No.—II, 459-78-9; III, 23885-03-2; IV, 1071-51-8; V, 10575-86-7; VI, 1070-27-5; VII, 1070-26-4; VIII, 23885-08-7; IX, 461-01-8; X, 23885-10-1; XI, 23885-11-2; XII, 23885-12-3; XIII, 23885-13-4;

XIV, 23885-14-5; XVII, 23885-15-6; XVIII, 23885-16-7; XIX, 23885-17-8; CF₂BrCF₂CH=CH(CH₂)₅CH₃, 23885-18-9; CF₂BrCFCICH=CH(CH₂)₅CH₃, 310-63-4; CF₃CHBrC≡CCH₂(CH₂)₄CH₃, 23885-20-3; CF₃CBr=CHCHBr(CH₂)₅CH₃, 23885-21-4; CF₃CBBr₂CH=CH(CH₂)₅CH₃, 23885-22-5; CF₂=CFCH₂CHBr(CH₂)₅CH₃, 23942-63-4; CF₂=CFCH₂CHCl-(CH₂)₅CH₃, 23885-23-6; copper chloride, 7447-39-4; ethanolamine, 141-43-5.

Aluminum Chloride Catalyzed Diene Condensation. V.^{1,2} Selectivity-Reactivity Relationship of Dienophiles toward Butadiene, Isoprene, and 2-Trifluoromethylbutadiene

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The relative rates of reactions of isoprene and butadiene, k^i/k^b , with tetracyanoethylene, methyl acrylate-aluminum chloride complex, fumaryl chloride, vinylidene cyanide, maleic anhydride, dimethyl fumarate, dimethyl acetylenedicarboxylate, methyl acrylate, acrylonitrile, and dimethyl maleate were determined and plotted against the *reactivities* (the second-order rate constants with cyclopentadiene in dioxane at 20°) of the dienophiles. The k^i/k^b value increases with the increasing reactivity of the dienophile, in contrast to the accepted selectivity-reactivity relationship. Corresponding data for the 2-trifluoromethylbutadiene-butadiene pair of substrates are reported. The selectivity, based on the relative rate of the *s-cis* species, increases with the increasing reactivity of the dienophiles, here the selectivity being in favor of butadiene. The mechanistic implications of these results are discussed in connection with the selectivity-reactivity relationship and varying electrophilic character of the dienophiles. From the normal position taken by the methyl acrylate-aluminum chloride complex in the correlation line, the mechanism of the aluminum chloride catalyzed diene condensation is assumed to be one of the variety of the Diels-Alder reactions.

It was shown in previous papers that the methyl acrylate-aluminum chloride complex (MA-AlCl₃)¹ is a more discriminating dienophile than uncomplexed methyl acrylate in reactions with isoprene-butadiene³

or *trans*-piperylene-butadiene⁴ pairs of diene substrates, whereas the former dienophile is more reactive than the latter.¹ The higher selectivity was also found in stereochemical (*endo-exo*)⁴⁻⁶ and orientational (*meta-para* or *ortho-meta*)^{3,4} phenomena. These ob-

(1) Part IV: T. Inukai and T. Kojima, *J. Org. Chem.*, **32**, 872 (1967).

(2) Presented in part: Abstracts, 18th Symposium on Organic Reaction Mechanism of the Chemical Society of Japan, Kyoto, Japan, Oct 1967, p 122; Abstracts, 22nd Annual Meeting of the Chemical Society of Japan, Tokyo, Japan, April 1969, p 1658.

(3) T. Inukai and T. Kojima, *J. Org. Chem.*, **31**, 1121 (1966).

(4) T. Inukai and T. Kojima, *ibid.*, **32**, 869 (1967).

(5) T. Inukai and T. Kojima, *ibid.*, **31**, 2032 (1966).

(6) J. Sauer and J. Kredel, *Tetrahedron Lett.*, 731 (1966).

servations apparently contradict the accepted selectivity-reativity relationship, according to which the more reactive reagents should be the less selective species and *vice versa*.⁷

This anomaly may be supposed to occur because the reaction of MA-AlCl₃ as a dienophile (the aluminum chloride catalyzed Diels-Alder reaction) proceeds by a mechanism different from that of methyl acrylate (uncatalyzed) reaction. If this is shown to be true we could draw a better inference on the mechanism of the Diels-Alder reactions by contrasting their characteristics to those of the catalyzed modification that is presumably more polar in nature. The anomalous selectivity-reativity relationship may, however, be a characteristic feature of the Diels-Alder reactions in general.

We therefore undertook to examine fully this relationship by using a series of common dienophiles covering a wide range of dienophilic reactivity and to investigate whether the MA-AlCl₃ complex is singular or not with respect to the selectivity-reativity relationship.

Results

The relative rates of isoprene *vs.* butadiene, k^i/k^b , and of 2-trifluoromethylbutadiene *vs.* butadiene, k^t/k^b , toward several dienophiles were determined mostly by the competitive reaction technique similar to that reported earlier.^{3,4} The reaction conditions and results for the isoprene-butadiene pair of dienes are summarized in Table I. The corresponding data for the 2-trifluoromethylbutadiene-butadiene pair are shown in Table II. The relative rates, k^t/k^b , for dimethyl maleate and maleic anhydride are those calculated from the second-order rate constants of respective reactions, which are presented in Table III. There is no reason for this inhomogeneity of the method adopted except that we could not afford to use 2-trifluoromethylbutadiene sufficiently to carry out the competitive experiments.

Since the adducts are thermally stable at the reaction temperature of 20°, it is unlikely that the observed relative rates are thermodynamically influenced. Indeed it was ascertained experimentally in some cases that the observed ratio is kinetically determined.

The *meta* to *para* ratios of the products from isoprene and unsymmetrical dienophiles are listed in Table IV.

Discussion

We wish to have an appropriate measure of reactivities of the dienophiles in order to test the selectivity-reativity relationship. Although obviously the reactivity of a reagent is an entity not expressible by a single number in a quantitative manner, it is useful to define a convenient scale, applicable to a particular type of reaction, on which various reagents will lie in an order almost invariable when the substrate varies. As the measure of the reactivities of the dienophiles, the second-order rate constants of the reactions with cyclopentadiene in dioxane at 20°⁸ will be employed, although it would be preferable to use the rate constants of the reactions of the dienophiles with butadiene,

(7) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1963, p 162.

(8) J. Sauer, H. Wiest, and A. Mielert, *Chem. Ber.*, **97**, 3183 (1964).

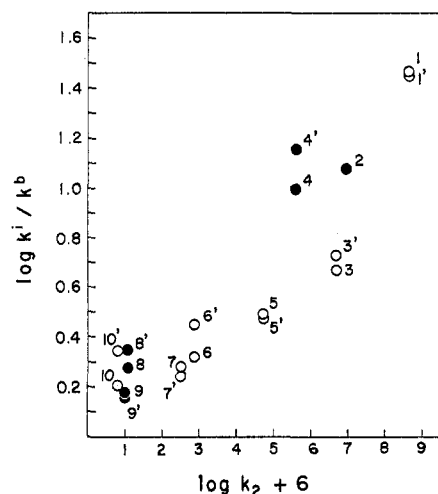


Figure 1.—The relation between relative rates of isoprene *vs.* butadiene, k^i/k^b , at 20° and reactivities of dienophiles: k_2 (ref 8) in unit of l./mol sec. The numerals attached to the points correspond to the set numbers of Table I: O, symmetrical dienophile; ●, unsymmetrical dienophile.

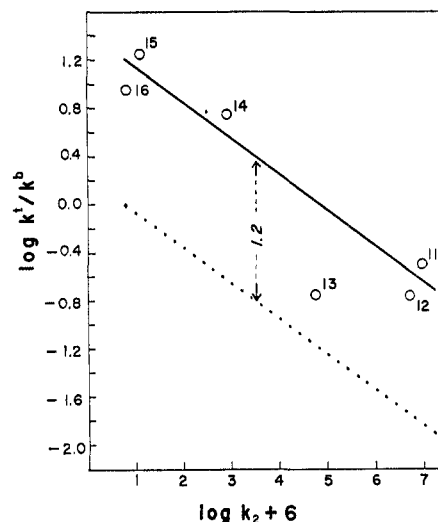


Figure 2.—The relative rates of 2-trifluoromethylbutadiene *vs.* butadiene, k^t/k^b , at 20° and reactivities of dienophiles: k_2 (ref 8) in unit of l./mol sec. Maleic anhydride, 13; dimethyl maleate, 16; others correspond to the set numbers of Table II.

the standard substrate, if they were available. Since the reactivity of MA-AlCl₃ cannot be obtained in this standard system, the rate constant in benzene solution at 20° determined in a somewhat indirect way (see Experimental Section) was used as a substitute.⁹

The correlation between the observed relative rate and reactivity is plotted in log-log scale in Figures 1 and 2. It appears from Figure 1 that the dienophiles of symmetrically substituted ethylene structure define a rising curve, although the scatter is considerable. The upward deviation of the unsymmetrical dienophiles is reasonable because their transition complexes would be more polarized than those from the symmetrical dienophiles, so as to receive more the stabilizing effect of the methyl substituent. It should be noted that, although

(9) (a) This can be justified because the rate of Diels-Alder reactions is comparatively solvent (and even phase) insensitive.^{9a,10} (b) A. Wassermann, "Diels-Alder Reactions," Elsevier Publishing Co., Amsterdam, 1965, pp 50-52.

(10) See, e.g., J. Sauer, *Angew. Chem.*, **79**, 76 (1967).

TABLE I
(Continued)

Dienophile, mmol	Isoprene mmol	Butadiene, mmol	Solvent, g	Reaction period, days	Product ratio ^b	k^i/k^b	
						Obsd	Avg
Set 9. Acrylonitrile, Benzene							
19.6	437.5	722.0	397	240	1.02	1.68	1.52
20.6	510.6	770.4	339	240	0.903	1.36	
Set 9'. Acrylonitrile, None							
18.9	290.1	521.2	None	62	0.845	1.51	1.51
9.43	318.1	625.0	None	62	0.769	1.51	
Set 10. Dimethyl Maleate, Benzene							
7.35	297.7	545.4	413	240	0.854	1.57	1.61
7.70	301.3	998.6	352	240	0.496	1.64	
Set 10'. Dimethyl Maleate, None							
7.29	295.8	448.1	None	144	1.185	2.26	2.22
3.47	280.9	484.4	None	142	1.23	2.18	

^a Dienophile and solvent are given for each set. ^b Mole ratio of isoprene adduct to butadiene adduct. ^c Previous work; see ref 3.

TABLE II
RELATIVE RATES, 2-TRIFLUOROMETHYLBUTADIENE *vs.* BUTADIENE,
 k^t/k^b , AT *ca.* 20°^a

Dienophile, mmol	2-CF ₃ -butadiene, mmol	Butadiene, mmol	Solvent, g ^b	Reaction period, days	Product ratio ^c	k^t/k^b	
						Obsd	Avg
Set 11. Ma-AlCl ₃							
10.0 ^d	99.97	85.12	23.1	1/6	0.381	0.315	0.320
10.0 ^d	99.97	125.1	20.5	1/6	0.271	0.330	
Set 12. Fumaryl Chloride							
1.96	102.6	167.9	117.0	2	0.106	0.175	0.173
1.96	102.2	44.37	122.0	14	0.398	0.171	
Set 14. Dimethyl Fumarate							
19.1	28.67	582.7	315.0	39	0.269	5.80	5.65
4.72	26.21	697.3	322.0	38	0.206	5.51	
Set 15. Dimethyl Fumarate							
5.00	49.16	50.88	None	69	15.37	17.0	17.7
5.23	49.14	66.56	None	69	12.96	18.4	

^a Dienophile is given for each set. ^b Benzene solvent. ^c Mole ratio of the 2-CF₃-butadiene adduct to butadiene adduct. ^d Methyl acrylate (10.0 mmol) and aluminum chloride (4.0 mmol); see ref 1 for the basis of this expression.

TABLE III
RELATIVE RATE, k^t/k^b ,
FROM KINETIC MEASUREMENTS AT 20°

Dienophile, mmol/l. ^a	R	2 R-butadiene, mmol/l. ^a	Solvent	k_2 , l./mol sec	k^t/k^b
A. Dimethyl Maleate					
6894	CF ₃	1079	None ^b	2.27×10^{-8}	9.00
7717	H	324.7	None ^b	2.52×10^{-9}	
B. Maleic Anhydride					
493.6	CF ₃	150.4	Benzene	5.08×10^{-6}	0.19
157.1	H	244.7	Benzene	2.71×10^{-5}	

^a Initial concentration ^b In excess of dimethyl maleate.

TABLE IV
 ISOMER DISTRIBUTION OF ISOPRENE ADDUCTS^a

Dienophile	<i>meta</i> , %	<i>para</i> , %
MA-AlCl ₃ ^b	5.0	95.0
Vinylidene cyanide ^c	8.7	91.3
Methyl acrylate ^b	30.5	69.5
Acrylonitrile ^{c,d}	25.5	74.5

^a From reaction at *ca.* 20°. ^b Previous work; see ref 3. ^c A Hitachi K53 gas chromatograph with a Golay column HB 2000-90 (polypropylene glycol, 90 m) was used; peak area ratio was assumed to be equal to the isomer ratio. ^d The literature reports *meta* 21.8%, *para* 78.2%: J.-C. Soula, D. Lumbroso, M. Hellin, and F. Coussemant, *Bull. Soc. Chim. Fr.*, 2059 (1966).

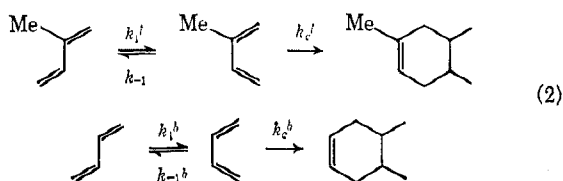
the reactivity scale is numerically presented, it is not more than semiquantitative in principle;¹¹ hence a quantitative significance cannot be attached to the shape (*i.e.*, straight, concave, or convex) of the correlation line. The trend is, however, definitely that the more reactive dienophiles are generally more selective, which is opposite to the normal selectivity-reativity relationship. To the level of accuracy of this correlation and argument the MA-AlCl₃ should not be regarded as a singular dienophile.

The selectivity to be compared with the reactivity, in theoretical considerations, must properly be in terms of the ratio of rates of reactions of *s-cis* subspecies of isoprene and butadiene, k_c^i/k_c^b , rather than the observed relative rate, k^i/k^b . The relation between these two ratios is expressed by eq 1, where k values are

$$k^i/k^b = [k_c^i/k_c^b][k_1^i/(k_{-1} + k_1^i)][(k_{-1}^b + k_1^b)/k_1^b] \\ = [k_c^i/k_c^b][K^i/(1 + K^i)][(1 + K^b)/K^b] \quad (1)$$

$$\cong [k_c^i/k_c^b][K^i/K^b] \quad (1')$$

related to eq 2 on the assumption that the cisoid-transoid interconversion is much faster than the diene



condensation. Since K^i/K^b is a constant under the uniform experimental conditions, the relationship between selectivity and reactivity holds irrespective of the true value of K^i/K^b .¹²

The reaction series of 2-trifluoromethylbutadiene *vs.* butadiene (Figure 2) includes both cases, $k^t > k^b$ and $k^t < k^b$, making the selectivity-reativity correlation appear complicated at first sight. In the similar way as above the observed ratio, k^t/k^b , is expressed by eq 3,

$$k^t/k^b = [k_c^t/k_c^b][K^t/(1 + K^t)][(1 + K^b)/K^b] \\ \cong [k_c^t/k_c^b][K^t/(1 + K^t)/K^b] \quad (3)$$

where the meaning of the symbols is self-evident. The dienophiles may be expected to react with the *s-cis* subspecies of 2-trifluoromethylbutadiene slower than

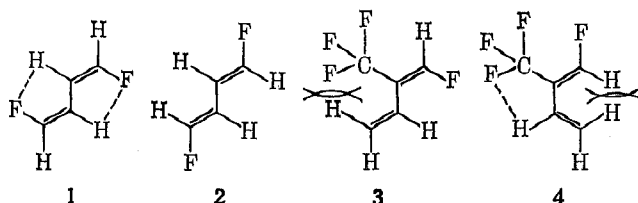
(11) The order of reactivity of dienophiles will be inverted only in exceptional cases of reactions with very electrophilic dienes like hexachlorocyclopentadiene (Diels-Alder reactions with inverse electron demand¹⁰).

(12) Approximate eq 1' holds in this case, since K^i and K^b are much smaller than 1 (see later discussions).

with that of butadiene because the trifluoromethyl group is electron withdrawing.¹³ It then should be the term $K^t/(1 + K^t)/K^b$ that makes k^t larger than k^b in reactions with less selective dienophiles; to paraphrase, 2-trifluoromethylbutadiene has a higher population of *s-cis* conformer than butadiene such that the observed rate, k^t , may happen to be larger than k^b when k_c^b is not sufficiently greater than k_c^t .¹⁴ This view sets the lower limit of $\log K^t/[(1 + K^t)/K^b]$ at *ca.* 1.2 from the correlation of Figure 2.

Although direct physical studies on the conformation of 2-trifluoromethylbutadiene have not been reported, the notion of larger K^t than K^b values can be supported on the following bases. (A) The stabilizing interaction between hydrogen and halogen atoms at the 1,3-position is well known.¹⁵ In particular the higher thermodynamic stability of *cis,cis*-1,4-difluorobutadiene (1) over *trans,trans*-1,4-difluorobutadiene (2), which is otherwise supposed to be more stable, was ascribed to this sort of interaction (Chart I).¹⁷ Irrespective of

CHART I



the true reason why this stability order prevails in these cases, we may infer that 2-trifluoromethylbutadiene would have similar stabilization by taking an *s-cis* form (3), whereas the *s-trans* form (4) is sterically strained (Chart I). (B) Uv absorption of 2-trifluoromethylbutadiene in hexane was found at λ_{\max} 215 μ (ϵ_{\max} 11,000 \pm 1000). This extinction coefficient falls in the general range of ϵ_{\max} values for the *cis* 1,3-dienes and seems to be too small for the *trans* dienes.

These reasons are not enough alone to conclude that the compound predominantly takes the *s-cis* form, but support the conclusion that K^t is larger than K^b . Incidentally, K^b is generally believed to be *ca.* 0.03 at room temperature,¹⁸ and may be even smaller according to more precise, microwave studies which failed to detect the *cis* form.¹⁹

The selectivity-reativity correlation line in terms of the relative rates of *s-cis* subspecies, k_c^t/k_c^b , will be located somewhere below, and shifted parallel to, the dotted line drawn in Figure 2. The more reactive dienophiles are more selective, the selectivity here being in favor of unsubstituted butadiene over 2-tri-

(13) J. Sauer, D. Lang, and A. Mielert, *Angew. Chem.*, **74**, 352 (1962).

(14) The increasing order of the reaction rate, 2-methyl- < 2-ethyl- < 2-isopropyl- < 2-*t*-butylbutadiene, for the Diels-Alder reactions with maleic anhydride, was explained with the increasing steric hindrance in the transoid conformation.¹⁶

(15) D. Craig, J. J. Shipman, and R. B. Fowler, *J. Amer. Chem. Soc.*, **83**, 2885 (1961).

(16) See ref 17 and the literature cited therein.

(17) H.-G. Viehe, *Angew. Chem.*, **75**, 783 (1963); H.-G. Viehe and E. Franchimont, *Chem. Ber.*, **97**, 602 (1964).

(18) (a) J. G. Aston, G. Szasz, H. W. Woolley, and F. G. Brickedde, *J. Chem. Phys.*, **14**, 67 (1946); (b) W. B. Smith and J. L. Massingill, *J. Amer. Chem. Soc.*, **83**, 4301 (1961).

(19) D. R. Lide, Jr., *J. Chem. Phys.*, **37**, 2074 (1962). For isoprene see D. R. Lide, Jr., and M. Jen, *ibid.*, **40**, 252 (1964).

fluoromethylbutadiene, and again the MA-AlCl₃ is not singular.

Consequently, the relation between selectivity and reactivity in the Diels-Alder reactions is opposite to the selectivity rule, which is expressed in an explicit form by eq 4.^{6,20} The prerequisite for this equation is

$$\frac{\text{selectivity of hot reagent}}{\text{selectivity of cold reagent}} = \frac{\delta_R \Delta F^{\ddagger}_H}{\delta_R \Delta F^{\ddagger}_C} = \frac{\alpha_H \delta_R \Delta \bar{F}^{\circ}_H}{\alpha_C \delta_R \Delta \bar{F}^{\circ}_C} \quad (4)$$

($\alpha_H < \alpha_C$)

that the reactions to be compared are *similar* in nature or belong to the same series. The limiting cases of application of eq 4, *i.e.*, very high and very low reactivity, quite appeal to the intuition, but in the moderate range of reactivity no convincing justification has been demonstrated.²¹ Although the electrophilic aromatic substitutions, for example, are thought of as similar in some respect, there is no experimental evidence for this selectivity rule as far as the authors are aware. It is indeed difficult to examine the relationship in such cases, because those complications such as the prior equilibrium generating the true reagent (*e.g.*, nitronium ion) or the solvation of the species involved make the concentration of the true reagent, hence the rate constant of the elementary step, unknown.²² The Diels-Alder reactions are comparatively free from these complications²³ and there was expected a fair opportunity of examining the relationship.

However, the results of the present study indicate that the electrophilicity of the dienophiles is the determining factor. The influence of the diene substituents on rate of reaction may be greater the more electrophilic the dienophile is;²⁴ since there is a general parallelism between the reactivity of the dienophiles and their presumable electrophilicity, k_c^i/k_c^b and k_c^b/k_c^t will increase with the increasing reactivity. The intramolecular selectivity (Table IV) can be similarly explained. This explanation may not be unconditionally accepted, however, because the actual weight of this factor cannot be estimated. The reason for emphasizing this reservation in this particular case is that the present knowledge of principal factors determining the substituent effect in the Diels-Alder reactions is only rudimentary and the conventional argument based on the electrophilicity of the reagents is not well grounded.²⁵ The electrophilicity factor,

(20) Here δ_R is an operator that gives the substituent (R) effect on the operand and α is a parameter measuring the approximate fractional displacement of the transition state along the reaction coordinate from reagents to products.⁶

(21) In hydrogen abstraction by free radicals the selectivity rule seems to apply, but the electronegativity of radicals must also be taken into account: W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, pp 154, 170.

(22) L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 35 (1963).

(23) That the diene and dienophile themselves are the *true* reagents is vindicated by the practical absence of effects of medium and additives on rates and the generally clean second-order rate law of the reactions.

(24) (a) This idea will require a theoretical proof. Empirical support may be rendered by the following data concerning hydrogen abstractions from nuclear-substituted toluenes by the free radicals (R \cdot) of similar R-H dissociation energy (103-104 kcal/mol) (Hammett ρ vs. σ^+): 0 (ref 24b), -0.3 (ref 24c), -0.35 (ref 24d), and -0.66 (ref 24e) for Me \cdot , Ph \cdot , *t*-BuO \cdot , and Cl \cdot , respectively, in the order of increasing electron affinity of the radicals. (b) R. E. Pearson and J. C. Martin, *J. Amer. Chem. Soc.*, **85**, 354 (1963). (c) W. A. Pryor, J. T. Echolo, Jr., and K. Smith, *ibid.*, **88**, 1189 (1966). (d) H. Sakurai and A. Hosomi, *ibid.*, **89**, 458 (1967). (e) G. A. Russell and R. C. Williamson, Jr., *ibid.*, **86**, 2357 (1964).

(25) The fact that *ortho* (>*meta*) or *para* (>*meta*) orientation of Diels-

in cooperation with the high polarizability of the 1,3-diene electron system, will make the precise topography of the energy surface of the transition state sensitive to the variation of the reagents. In such a case the α value (eq 4) might increase as the electron affinity of the dienophile substituent increases, because it must lose the conjugative share of the α,β double bond electrons as the reorganization of electrons proceeds to complete the two new σ bonds.²⁶

In conclusion, the aluminum chloride catalyzed diene condensation is thought to be one of the variety of normal Diels-Alder reactions because its position in the reactivity-selectivity correlation is not singular.²⁷

Experimental Section

All melting points are uncorrected. Nmr spectra were taken using a Varian A-60A spectrometer on 10 wt % carbon tetrachloride solutions containing tetramethylsilane as internal standard. The glpc analyses were carried out with an Ohkura Model 1200 and a Hitachi K23 instrument using appropriate calibration curves for peak area ratio *vs.* molar ratio, unless otherwise indicated.

Reagents.—Butadiene used is as described in the previous paper.²⁸ Commercial isoprene was distilled and was gas chromatographically homogeneous. 2-Trifluoromethylbutadiene was prepared from 1,1,1-trifluoroacetone (Aldrich) by the known method,²⁹ bp 35-36° (lit. bp 41-42°, 29 35.0-35.5°³⁰). Dimethyl maleate, acrylonitrile, methyl acrylate, and MA-AlCl₃ complex are the same as described previously.^{5,28} Vinylidene cyanide, bp 52.5-53° (12 mm) [lit.³¹ bp 50.5° (10 mm)], was prepared by the method of Adris, *et al.*³¹ Tetracyanoethylene (Aldrich) was used directly as obtained. Other dienophiles were prepared by the known methods and had correct boiling or melting points: dimethyl acetylenedicarboxylate, bp 74.5-76.5° (7 mm); dimethyl fumarate, mp 101°; fumaryl chloride, bp 52-52.5° (12 mm); maleic anhydride, mp 53°. Solvents were purified in the usual way and were anhydrous.

Authentic samples of Diels-Alder adducts required for the quantitative glpc analyses of the products were prepared by reactions at *ca.* 20° for varying periods according to the rate of the reaction of each pair of the diene and dienophile. Their physical constants are listed in Table V. Proofs of structures of the four new compounds are as follows.

The isoprene-vinylidene cyanide adduct gave the following nmr data: τ 4.61 (m, 1 H), 7.30 (m, 2 H), 7.72 (br s, 4 H), and 8.21 (d, $J = 2$ cps, 3 H).

Anal. Calcd for C₉H₁₀N₂: C, 73.9; H, 6.9; N, 19.1. Found: C, 73.7; H, 7.1; N, 18.8.

The 2-trifluoromethylbutadiene-dimethyl fumarate adduct gave the following nmr data: τ 3.66 (m, 1 H), 6.31 (s, 6 H), 6.94-7.33 (m, 2 H), and 7.33-7.83 (m, 4 H).

Anal. Calcd for C₁₁H₁₃F₃O₄: C, 49.6; H, 4.9. Found: C, 49.5; H, 5.1.

The 2-trifluoromethylbutadiene-methyl acrylate adduct gave the following nmr data: τ 3.65 (m, 1 H), 6.30 (s, 3 H), and 7.1-8.5 (m, 7 H).

Anal. Calcd for C₉H₁₁F₃O₂: C, 51.9; H, 5.3. Found: C, 52.0; H, 5.2.

Alder reactions is observed irrespective of the electronic characteristics of the substituent R in 1-R- or 2-R-butadienes cannot be explained on the basis of the electronic theory.

(26) (a) It can be misleading in general to assume a higher reactivity to a reagent simply because of its lower selectivity, as has been sometimes done, even in comparison of a series of reactions of presumed similarity. (b) It was recently reported that the Hammett ρ value for E2 reaction of *para*-substituted phenyl β -chloroethyl sulfones is larger with a stronger amine (faster reaction) under uniform reaction conditions: Y. Yano and S. Oae, Abstract, 22nd Annual Meeting of the Chemical Society of Japan, Tokyo, April 1969, p 1648.

(27) In paper I of this series was proposed a different view which is not retainable now.

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TABLE V
 PHYSICAL CONSTANTS OF DIELS-ALDER ADDUCTS

Diene- ophile ^a	Mp or bp of butadiene adduct, °C (mm)	Mp or bp of isoprene adduct, °C (mm)	Mp or bp of 2-CF ₃ -butadiene adduct, °C (mm)
1	201.5-202 ^b	115-116 ^c	
4	100-105 (9) ^d	114 (10) ^e	
5	99 ^f	63.5-64 ^g	106 ^h
	116.5-118 (5)	125-127.5 (5)	
6	94.5 (3) ⁱ	127-129.5 (6) ^j	114.5 (5) ^e
7	100.5-102 (2.5) ^k	132-134 (5) ^l	
8	73-73.5 (20) ^m	90-93 (20) ⁿ	112 (30) ^e
9	76 (19) ^o	93 (20) ^p	
10	110.5 (5) ^q	121.5-121.7 (6) ^r	119-120 (5) ^e

^a Dienophile number corresponds to the set number of Table I.
^b Literature mp 201-202°: W. J. Middleton, R. E. Heckert, E. L. Little, and C. G. Krespan, *J. Amer. Chem. Soc.*, **80**, 2783 (1958). ^c Literature mp 114-116°: C. A. Stewert, Jr., *J. Org. Chem.*, **28**, 3320 (1963). ^d Literature bp 114° (10 mm): ref 31. ^e New compound; see text for identification. ^f Literature mp 101-102°: L. F. Fieser and R. C. Novello, *J. Amer. Chem. Soc.*, **64**, 802 (1942); ^g Literature mp 63-64°: O. Diels and K. Alder, *Justus Liebigs Ann. Chem.*, **470**, 101 (1929). ^h Literature mp 107-107.5°: A. L. Henne and P. E. Hinkamp, *J. Amer. Chem. Soc.*, **76**, 5147 (1954). ⁱ Literature bp 137° (20 mm): I. N. Nazarov and V. F. Kucherov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 329 (1954); *Chem. Abstr.*, **49**, 5329 (1955). ^j Literature bp 149-149.5° (20 mm): A. A. Petrov and N. P. Sopov, *Sb. Statei Obshch. Khim.*, **2**, 853 (1953); *Chem. Abstr.*, **49**, 5329 (1955). ^k Literature bp 138.5-139.5° (10 mm): N. P. Sopov and V. S. Milkashevskaya, *Zh. Obshch. Khim.*, **26**, 1914 (1956); *Chem. Abstr.*, **51**, 4968 (1957); ^l Literature bp 151.5-152.5° (10 mm): footnote k. ^m Literature bp 80-82° (23 mm): E. D. Bergmann and D. F. Hermann, *J. Appl. Chem.* (London), **3**, 42 (1953). ⁿ Literature bp 85-86° (15 mm): H. E. Hennis, *J. Org. Chem.*, **28**, 2570 (1963). ^o Literature bp 83° (20 mm): A. A. Petrov and N. P. Sopov, *J. Gen. Chem. USSR*, **17**, 2228 (1947); *Chem. Abstr.*, **42**, 4957 (1948). ^p Literature bp 102-104° (25 mm): I. N. Nazarov, Yu. A. Titov, and A. I. Kuznetsova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1412 (1959); *Chem. Abstr.*, **54**, 1409 (1960). ^q Literature bp 114-115° (5 mm): footnote i. ^r Literature bp 149.5-150° (20 mm): footnote j.

The 2-trifluoromethylbutadiene-dimethyl maleate adduct gave the following nmr data: τ 3.62 (m, 1 H), 6.27 (s, 6 H), 6.72-7.18 (m, 2 H), and 7.18-7.61 (m, 4 H).

Anal. Calcd for C₁₁H₁₃F₃O₄: C, 49.6; H, 4.9. Found: C, 49.5; H, 5.0.

Competitive Experiments.—The reaction conditions are shown in Tables I and II. With no solvent runs the reactions were carried out in thick-wall, sealed tubes. The method of analysis of the relative rate is similar to that reported previously,³ except that in runs with fumaryl chloride the product was converted into the dimethyl ester by treatment with absolute methanol before glpc analysis. Carbowax 6000 (10 wt %) on Diasolid M (Nihon Chromato Industries Co., Ltd.) was used for analyses in sets 1, 1', 3, 3', and 6-15 (Tables I and II). For sets 4, 4', 5, and 5', Silicon DC 550 on Diasolid M (the same supplier) was employed.

Kinetic experiments were carried out in a conventional way in a thermostat, with a known amount of dimethyl *trans*-4-cyclohexene-1,2-dicarboxylate added as the internal standard for glpc analysis (silicon DC 550 column) of the product formed by appropriate intervals of reaction period.

Rate Constant of MA-AlCl₃-Cyclopentadiene Reaction in Benzene.—This reaction is too fast to measure directly in the usual way. The relative rate, cyclopentadiene *vs.* isoprene, in benzene at 20° toward MA-AlCl₃ was determined to be 646:1 by the competitive experiments similar to those described above (silicon DC 550 column). Since k^i/k^b is 12.1 (Table I) and $k^b = 1.15 \times 10^{-8}$ l/mol sec,¹ the desired rate constant is calculated to be 8.99 l/mol sec.

Proof of Kinetic Control of the Product Ratio.—The Diels-Alder adduct from butadiene (or isoprene) was treated with a large excess of isoprene (or butadiene) at room temperature for a period longer than that of the corresponding competitive experiment. It was ascertained by glpc that no cross-adduct was formed under the experimental conditions.

Registry No.—Butadiene, 106-99-0; isoprene, 78-79-5; 2-(trifluoromethyl)butadiene, 381-81-7; isoprene-vinylidene cyanide adduct, 23884-89-1; 2-(trifluoromethyl)-butadiene-dimethyl fumarate adduct, 23884-90-4; 2-(trifluoromethyl)butadiene-methyl acrylate adduct, 23884-91-5; 2-(trifluoromethyl)butadiene-dimethyl maleate adduct, 23884-92-6.

Preparation of Di- and Triaroylamides by Means of *n*-Butyllithium and Aroyl Halides. Influence of Lewis Bases¹

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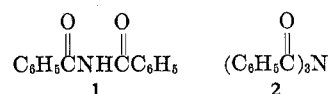
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Aroylations of the N-lithio salts of various amides, amines, and phthalimide have been accomplished by aroyl halides in the presence of Lewis bases such as 1,4-diazabicyclo[2.2.2]octane (dabco) to afford conveniently di- and triaroylamides in good to excellent yield. Presumably, the Lewis bases coordinate with the lithium cations and perhaps with the acid halides, resulting in enhanced reactivities of the nitrogen anions toward electrophiles, and of the carbonyl group of the acid chlorides toward nucleophiles.

Aroylation of amides and related organic nitrogen compounds to afford di- and triaroylamides such as 1 and 2, respectively, has been accomplished under a variety of conditions, but there does not appear to be a general method for synthesizing such compounds. For example, benzamide has been benzoylated by benzoyl chloride to afford dibenzamide (1) in some cases,² and tribenzamide (2) in others.³ An especially

interesting method of preparing amide 2 involves tribenzoylation of lithium nitride.⁴ Although good yields of di- and triaroylamides have often been reported,²⁻⁴ reaction times and conditions have usually been inconvenient. In addition, certain aroylations of amides have been limited to primary ones.³



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