Aluminum Chloride Catalyzed Diene Condensation. VI.[1,2] Partial Rate Factors of 2-Phenyl-, 2-Chloro-, 2-Trifluoromethyl-, and 2-Cyanobutadienes in Reactions with Methyl Acrylate. A Differential Hammett Correlation

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Received July 27, 1970

The para:meta ratios of the adducts and relative rates, 2-substituted butadiene as opposed to butadiene, of the aluminum chloride catalyzed and the uncatalyzed Diels–Alder reactions of 2-substituted butadienes (RC_4H_5, R = Ph, Cl, CF_3, and CN) with methyl acrylate at 20° were determined to obtain the partial rate factors, $prf^{(c)}$ and $prf^{(u)}$, for the formation of the respective adducts in both modes of the reactions. These two sets of prf's, including the prf's for 2-methyl-, 2,3-dimethyl-, and *trans*-1-methylbutadienes, were successfully correlated by a differential form of the Hammett equation, $\log prf^{(c)} - \log prf^{(u)} = \rho\sigma^+$. This correlation is regarded as a consequence of the electronic interaction between the diene substituent R and the dienophile substituent through a quasibenzene conjugation system that is conceived of in the four-center transition state.

In contrast to their recent importance in the theoretical studies of the multicenter reactions, the Diels–Alder reactions have not been sufficiently supplied with reliable exact experimental data on the substituent effects on their rates. Although the systematic study by Sauer, *et al.*,[3] among other less extensive studies, recently gave quantitative data supporting the well-known Alder rule on the rate,[4] the problem of orientation in the Diels–Alder reactions remains open yet. The preferential ortho/para orientation, irrespective of the electron-releasing or electron-withdrawing characteristics of the diene substituents, may be assumed to be a rule, but many of the reported isomer ratios are suspect or at best only semiquantitative.[5] Yet these orientation phenomena seem to have been regarded as indicating the failure of the polarity consideration of the electronic theory in understanding the characteristics of the Diels–Alder reactions.

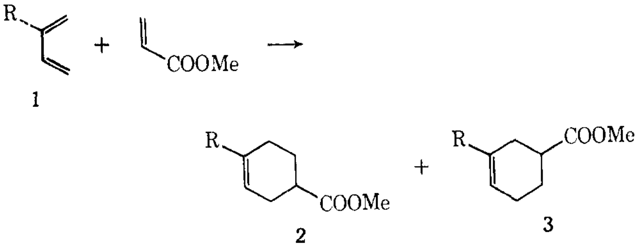
Therefore, it is of interest to obtain the kinetically controlled isomer ratios of high accuracy on which the theoretical arguments can be safely based. In this article the reactions of 2-phenyl-, 2-chloro, 2-trifluoromethyl-, and 2-cyanobutadienes with methyl acrylate, both uncatalyzed and aluminum chloride catalyzed, are studied with respect to the para:meta product ratios and the rates relative to unsubstituted butadiene, as the continuation of our previous studies on the isoprene[6] and *trans*-piperylene[7] cases.

Method and Results

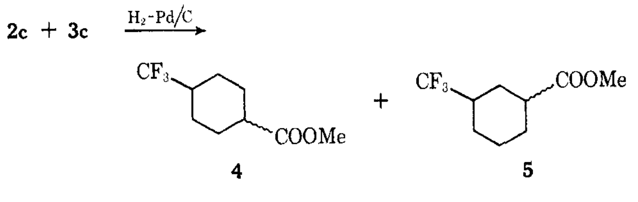
The reactions for the isomer ratio and relative rate determinations were carried out at 20°,[8] and the general pattern of the experimental design is analogous with that described in the previous papers.[6,7]

Para:Meta Ratio.—The products from reactions with 2-phenylbutadiene (**1a**) were hydrolyzed with alkali to obtain the mixture of **2a** (acid) and **3a** (acid) freed from some neutral by-products. After removing pure **2a** (acid) by recrystallization, the remainder was reconverted to the ester (**2a** + **3a**) and the isomeric composition was determined by the nmr spectroscopy.

The **2b**:**3b** ratio was determined by glpc assuming an equal molar ion current intensity of the isomers. The **2c**:**3c** ratio was determined in a similar way, except that some additional experiments were required for assignment of the glpc peaks because the authentic specimen of neither isomer was accessible. Thus the mixture (**2c** + **3c**) was quantitatively converted to the saturated derivatives (**4** + **5**) whose glpc peaks were identified by comparison with those of **4** and **5** derived from authentic *p*- and *m*-trifluoromethylbenzoic acids, respectively.



a, R = Ph; **b**, R = Cl; **c**, R = CF_3; **d**, R = CN



Since the mixture, **2d** + **3d**, could not be separated under all the glpc conditions we tried, it was converted to **8** + **9** by the process shown in Scheme I and their glpc peaks were identified by comparison of the retention times with those of authentic specimens of **8** and **9** which were synthesized from *trans*-cyclohexane-1,4-dicarboxylic acid and isophthalic acid, respectively. Both the conversions, from **2d** + **3d** to **6** + **7** and from **6** + **7** to **8** + **9**, were satisfactorily quantitative. This allowed us to assign each of the peaks of the **6** + **7** mixture to one or the other of **6** and **7** unambiguously and to adopt their ratio as the desired ratio of **2d**:**3d**.

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(1) Paper V: T. Kojima and T. Inukai, *J. Org. Chem.*, **35**, 1342 (1970).

(2) Preliminary communication: T. Inukai and T. Kojima, *Chem. Commun.*, 1334 (1969).

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

(4) K. Alder, *Experientia, Suppl.*, **2**, 86 (1955).

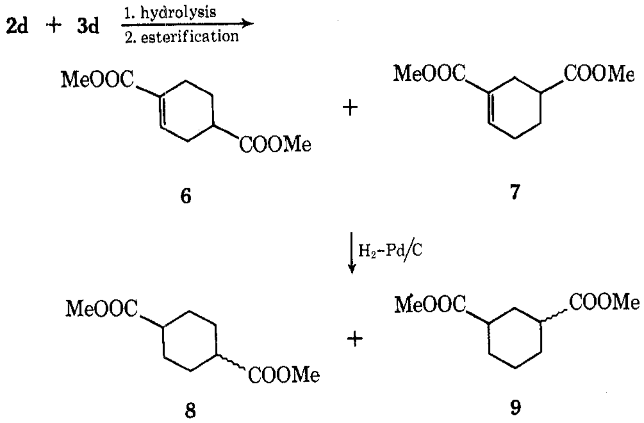
(5) See, for example, J. Sauer, *Angew. Chem.*, **79**, 76 (1967).

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

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

(8) Some of the uncatalyzed reactions were carried out in the dark in an air-conditioned room (about 20°), for they required a few months to afford a sufficient amount of the adduct for further study.

SCHEME I



The isomer ratios thus determined, together with some previous results, are summarized in Table I.

TABLE I

ISOMER RATIOS OF PRODUCTS FROM REACTIONS AT 20°

Substituent	Uncatalyzed, para:meta	Catalyzed,[a] para:meta
2-Ph	80:20[b,c]	97:3
2-Cl	87:13[b,d]	98:2
2-CF_3	55:45[b]	51:49
2-CN	84:16[a]	73:27
2-Me[e]	69.5:30.5[b]	95:5
	ortho:meta	ortho:meta
1-Me[f]	90:10[b]	98:2

[a] In benzene solution. [b] No solvent was used. [c] The ratio has been reported [I. N. Nazarov, Yu. A. Titov, and A. I. Kuznetsova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1270 (1959); *Chem. Abstr.*, **54**, 1410 (1960)] to be 4.5:1 (at 150°) and 7.3:1 (at room temperature). [d] The para isomer was reported as the main product.[30] [e] Reference 6. [f] Reference 7.

Relative Rates.—The competitive reaction techniques were employed for the determination of relative rates of 2-substituted butadiene as opposed to butadiene. In the case of 2-cyanobutadiene, however, they were calculated from the second-order rate constants of the respective Diels–Alder reactions, because the competitive reactions might be complicated by the probable concomitant condensation between 2-cyanobutadiene and butadiene.

The second-order rate constants, k^u, of the uncatalyzed reaction between 2-cyanobutadiene and methyl acrylate (MA) in benzene are shown in Table II. The Arrhenius parameters are calculated to be E_a = 15.0 kcal/mol, log A (l./mol sec) = 4.4.

TABLE II

SECOND-ORDER RATE CONSTANTS, k^u, OF UNCATALYZED REACTION BETWEEN **1d** AND MA IN BENZENE[a,b]

Temp, °C	k^u, l./(mol sec) × 10^7
20	1.38
36.4	7.78
45.3	15.0
60.5	31.5

[a] Initial concentration of **1d**, 1.30–2.57 mol/l.; that of MA, 3.62–5.06 mol/l. [b] Rate of formation of the product (**2d** + **3d**) was followed with glpc analysis with 1,2-diphenylbutane as the internal standard.

The second-order rate constants, k^c, of the aluminum chloride catalyzed reaction of **1d** with MA (the MA–$AlCl_3$ complex as the dienophile[9]) were determined according to the method described previously.[9] The pseudo-first-order rate constants at several levels of aluminum chloride concentration were determined, and the second-order rate constants, k^c, were calculated (Table III). It should be noted that the contribution of the uncatalyzed reaction to the total rate is negligible and the rate of an individual kinetic run is first order to the concentration of **1d** alone, since the concentration of MA–$AlCl_3$ is determined by the analytical concentration of aluminum chloride and hence is essentially constant throughout a kinetic run.

TABLE III

DETERMINATION OF CATALYZED RATE CONSTANT, k^c, OF REACTION OF **1d** WITH MA–$AlCl_3$ IN BENZENE AT 40° [a]

$AlCl_3$,[b] mmol/l.	$AlCl_3$,[c] mmol/l.	MA, mmol/l.	$k_1 \times 10^6$ (sec^{-1})[d]	$k^c \times 10^4$ [e] (l./mol sec)
5.8	5.1	101	1.90	3.70
11.6	10.9	20.2	4.22	3.86
18.3	17.6	89.6	6.90	3.91
25.4	24.7	198.0	9.37	3.79

[a] Initial concentration of **1d**, 32.1 mmol/l. [b] Uncorrected. [c] Corrected for partial deterioration of $AlCl_3$ (0.7 mmol/l.), which was determined from the intercept of $[AlCl_3]$ on extrapolation to zero k_1. [d] $k_1 = t\ (sec)^{-1} \times 2.303 \log (a/a - x)$ where a is the initial concentration of **1d**. [e] $k^c = k_1$ divided by $[AlCl_3]_{cor}$.

The temperature dependence of k^c is shown in Table IV and the Arrhenius parameters are calculated to be E_a = 11.3 kcal/mol, log A (l./mol sec) = 4.4.

TABLE IV

SECOND-ORDER RATE CONSTANTS, k^c, OF CATALYZED REACTION BETWEEN **1d** AND MA–$AlCl_3$ IN BENZENE[a]

Temp, °C	k^c, l./(mol sec) × 10^5
10.0	5.79
20.0	11.6
30.0	18.9
40.0	38.1

[a] Initial concentration of **1d**, 32–62 mmol/l.; that of MA, 87–521 mmol/l.; $[AlCl_3]_{cor}$, 5.13–46.1 mmol/l.

The corresponding k^u and k^c of the reactions with butadiene as the diene component at 20° are 1.00 × 10^{-8} l./(mol sec) and 1.15 × 10^{-3} l./(mol sec), respectively,[9] and these values are used for calculation of the relative rates of **1d**. The relative rates of 2-substituted butadienes, as well as some other previous data for ready reference, are listed in Table V.

TABLE V

RELATIVE RATES AT 20°[a,b]

Substituent	Uncatalyzed reaction	Catalyzed reaction
2-Ph	23.1	94.5
2-Cl	1.29[c]	0.553
2-CF_3[d]	17.7[c]	0.320
2-CN	13.8	0.101
2-Me	1.89[e,f]	12.1[g]
2,3-Me_2	3.43[f]	36.2[g]
1-Me[h]	1.19[c]	6.47

[a] Reactivity of unsubstituted butadiene is taken as unity for each set of relative rate data; note that the rate constants for the catalyzed reactions are 10^5 times as large as those for the corresponding members of the uncatalyzed reactions.[9] [b] In benzene solution unless otherwise indicated. [c] In absence of solvent. [d] Reference 1. [e] 2.16 in absence of solvent, ref 6. [f] Present work. [g] Reference 6. [h] Reference 7.

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[9] T. Inukai and T. Kojima, *J. Org. Chem.*, **32**, 872 (1967).

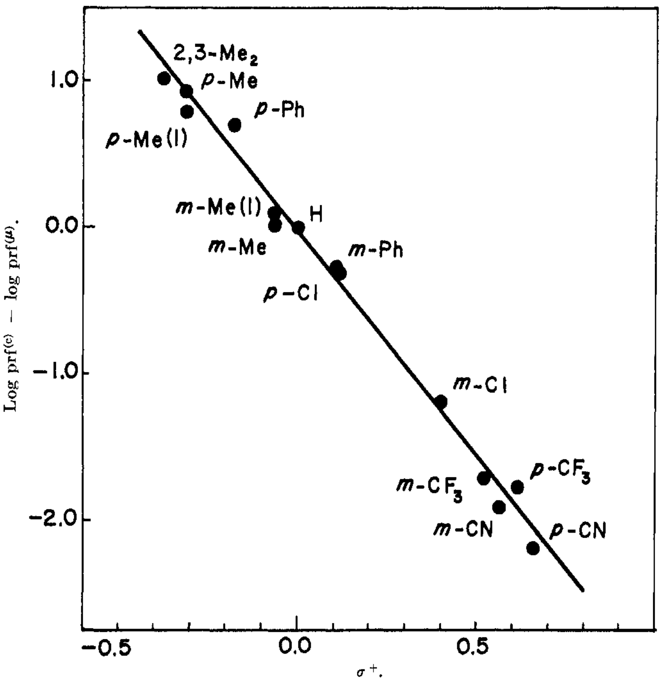

Figure 1.—Plot of log prf$^{(c)}$ − log prf$^{(u)}$ *vs.* σ^+. The points for 1-methylbutadiene have the mark (l) attached.

Discussion

Since the isomer ratios and relative rates were obtained from reactions at 20° at which temperature the products are thermally stable, it can be safely assumed that these results are kinetically controlled.

As to the isomer ratios the following rules are observed. (1) With the substituents capable of electron release by the inductive or mesomeric mechanism (Me, Ph, and Cl), the degree of para (or ortho) orientation is enhanced by the change of the dienophile from MA to MA–AlCl$_3$. (2) The percentage of meta for the dienes with the electron-withdrawing substituents increases, but to a relatively lesser degree, by the same change of the dienophile. (3) In no case does the meta exceed the para however.

Rules 1 and 2 are apparently in harmony with the expectation from the electronic theory, since MA–AlCl$_3$ is more electrophilic than MA.[1] However, the fact that the meta per cent of 2-Ph or 2-Me is greater than that of 2-CN in the uncatalyzed reactions is peculiar. The rule 3 agrees with, and reconfirms, the accepted general ortho or para orientation in the Diels–Alder reactions[5] and obviously contradicts the prediction from the polarity consideration.[10] It may be argued that the steric hindrance in the transition state prevents the predominance of the meta product,[11] the orientation that would otherwise be the case. This view cannot be born out, however, since the less bulky CN group gives less meta per cent than the CF$_3$ group; note that the difference of the substituent constants $\sigma_p^+ - \sigma_m^+$, of CN group (0.097) is about the same as that of the CF$_3$ group (0.092),[12] suggesting a similar isomer ratio for both groups on the electronic basis. Consequently, this peculiar orientation is deemed to be a genuine property of the Diels–Alder reactions.

The relative rate is related to the reactivities of the s-cis subspecies of the diene, $\bar{k}_{\text{cis}}$, and the cisoid–transoid equilibrium constant, K = [s-cis]/[s-trans], by eq 1.[1]

$$\text{relative rate} = [\bar{k}_{\text{cis}}{}^{\text{R}}/\bar{k}_{\text{cis}}{}^{\text{H}}][K^{\text{R}}/(1 + K^{\text{R}})]/[(1 + K^{\text{H}})/K^{\text{H}}] \quad (1)$$

Alder's generalization that electron-releasing diene substituents facilitate the reaction[4] should apply to $\bar{k}_{\text{cis}}$. However, since the effect of R on the K value will be manifold in origin, the observed relative rates may not follow a simple trend as will be seen by inspection of Table V. Unfortunately, the ratio of $\bar{k}_{\text{cis}}{}^{\text{R}}/\bar{k}_{\text{cis}}{}^{\text{H}}$ cannot be evaluated because the K values are not known to a required accuracy.

It is possible to qualitatively rationalize the results if we assume that K's for 2-Ph-, 2-Cl-, 2-CN-, and 2-CF$_3$-butadienes are greater than K^{H}.[13] Thus the conformational factor is dominant in determining the relative rates of the uncatalyzed reactions, whereas in the catalyzed reactions this factor is heavily overshadowed by the other factor, $\bar{k}_{\text{cis}}{}^{\text{R}}/\bar{k}_{\text{cis}}{}^{\text{H}}$, since MA–AlCl$_3$ is more sensitive to the substituent effect than free MA.[1]

For the convenience of the quantitative analysis of the reactivities that follows, the partial rate factors, prf$^{(u)}$ and prf$^{(c)}$, for the uncatalyzed and catalyzed reactions, respectively, were calculated from the isomer ratio and relative rate data. The results are shown in Table VI.

TABLE VI

PARTIAL RATE FACTORS AT 20°[a]

	Uncatalyzed		Catalyzed	
R	prf$_{\text{para}}^{(u)}$	prf$_{\text{meta}}^{(u)}$	prf$_{\text{para}}^{(c)}$	prf$_{\text{meta}}^{(c)}$
2-Ph	37	9.2	183	5.7
2-Cl	2.2	0.34	1.1	0.022
2-CF$_3$	19.5	16	0.33	0.31
2-CN	23	4.4	0.15	0.055
2-Me	2.7	1.15	23	1.2
2,3-Me$_2$	3.4	3.4	36	36
	prf$_{\text{ortho}}^{(u)}$	prf$_{\text{meta}}^{(u)}$	prf$_{\text{ortho}}^{(c)}$	prf$_{\text{meta}}^{(c)}$
1-Me	2.1	0.24	13	0.30

[a] prf$_{\text{para}}^{(u)}$, for example, means the relative rate of formation of the para isomer, in units of the uncatalyzed reactivity of unsubstituted butadiene in one of the two degenerate orientations. The partial rate factors for the catalyzed reactions are in units of the catalyzed reactivity of butadiene. *Cf.* footnote *a* to Table V.

Differential Hammett Correlation.—It is easy to eliminate the unknown conformational factors appearing in eq 1 and to derive eq 2, in which $k_{\text{cis}}{}^{\text{R}}$'s are the rates

$$\text{prf}^{(c)}/\text{prf}^{(u)} = [k_{\text{cis}}{}^{\text{R(c)}}/k_{\text{cis}}{}^{\text{H(c)}}]/[k_{\text{cis}}{}^{\text{R(u)}}/k_{\text{cis}}{}^{\text{H(u)}}] \quad (2)$$

of formation of isomeric products based on the normalized concentration of the s-cis subspecies of the

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[10] Some articles of interest in this connection are J. Kazan and F. D. Greene, *J. Org. Chem.*, **28**, 2965 (1963); D. L. Fields, T. H. Regan, and J. C. Dignan, *ibid.*, **33**, 390 (1968); C. K. Bradsher and J. A. Stone, *ibid.*, **33**, 519 (1968); and T. L. Kwa, O. Korver, J. W. Hartgering, and C. Boelhouwer, *Tetrahedron*, **24**, 5711 (1968).

[11] The steric strain between the carboxylate and R group will be greater, if it is of any significance, in the transition state toward the meta isomer than the para when the diene and dienophile approach to each other in parallel planes in the endo fashion.

[12] The same can be shown in terms of Hammett σ constants.

[13] Steric repulsion in the s-trans conformation is generally assumed when R is bulky. 2-Cyanobutadiene in hexane shows uv absorption of $\epsilon_{\max}$ 11,500 ($\lambda_{\max}$ 217 mμ), which extinction coefficient is more compatible with the s-cis rather than the s-trans conformation. The electronic effect of the cyano group on $\epsilon_{\max}$ will not be great since 1-cyanobutadienes show normal extinction coefficients for transoid 1,3-dienes: *trans*-1-cyanobutadiene, $\epsilon_{\max}$ 25,500 ($\lambda_{\max}$ 240 mμ); *cis*-1-cyanobutadiene, $\epsilon_{\max}$ 25,400 ($\lambda_{\max}$ 240 mμ), both in hexane solution.

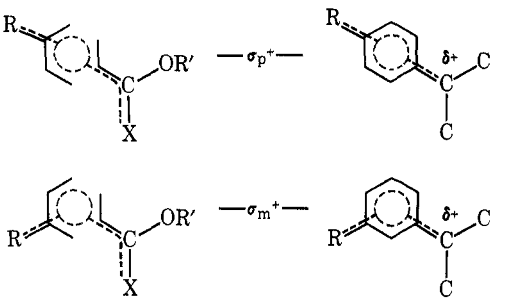
dienes. It is of interest to examine the interrelation of the two sets of prf's by means of eq 3, so to say a

$$\log \mathrm{prf}^{(c)} - \log \mathrm{prf}^{(u)} = \rho\sigma^{+} \tag{3}$$

differential Hammett correlation. Figure 1 shows the plot ($\rho = -3.07$, $r = 0.994$, $s^2 = 0.015$). In this correlation σ_p^+ and σ_m^+ are used for $\mathrm{prf}_{\mathrm{para}}$ and $\mathrm{prf}_{\mathrm{meta}}$, respectively, of 2-substituted butadienes, and $\sigma_{p\text{-Me}}^+$ (as a substitute for $\sigma_{o\text{-Me}}^+$)[14] and $\sigma_{m\text{-Me}}^+$ for $\mathrm{prf}_{\mathrm{ortho}}$ and $\mathrm{prf}_{\mathrm{meta}}$, respectively, of 1-methylbutadiene.[16]

Such a way of application of σ_p^+ and σ_m^+ will be rationalized by contrasting the four-center transition states of the Diels–Alder reactions with the transition states of SN1 solvolysis of the aryldimethylcarbinyl chlorides on whose rates σ^+ were defined (Scheme II).

SCHEME II



Diels–Alder reaction
(X = O or O:AlCl$_3$)

solvolysis

The success of the correlation in a differential form, eq 3, means that the *change* of the substituent effects on the free energy of activation due to the change of the electronic characteristics of the dienophile substituent, from COOMe to COOMe-AlCl$_3$, is linearly correlated with σ_R^+. This will be regarded as resulting from the transmission of the substituent effects in both series of the reactions through a benzene-like conjugation system, though it may not be planar, that is conceived of in the four-center or multicenter transition state.[17a]

It should be noted that neither eq 4 nor 5 hold, as will be evident from the fact that the isomer ratios in both the reaction series do not follow the correlation

$$\log k_{\mathrm{cis}}^{\mathrm{R(c)}}/k_{\mathrm{cis}}^{\mathrm{H(c)}} = \rho^{(c)}\sigma^{+} \tag{4}$$

$$\log k_{\mathrm{cis}}^{\mathrm{R(u)}}k_{\mathrm{cis}}^{\mathrm{H(u)}} = \rho^{(u)}\sigma^{+} \tag{5}$$

$\log \mathrm{prf}_{\mathrm{para}} - \log \mathrm{prf}_{\mathrm{meta}} = \rho(\sigma_p^+ - \sigma_m^+)$. It is concluded, therefore, that, although the *interrelation* between the two sets of the reactivity data for the catalyzed and uncatalyzed Diels–Alder reactions is electronically intelligible in terms of eq 3, the orientation phenomena in none of these reactions are explicable by the conventional electronic considerations.[17b] A perturbational molecular orbital treatment for the orientation has been reported to give good predictions for methyl- and phenylbutadienes,[18] but the exactly same calculation on 2-cyanobutadiene that presents a more diagnostic case turned out to give meta orientation in disagreement with the experimental results.[19] Therefore, more elaborate MO calculations are required in order to obtain a satisfactory solution of the problem using one-step transition models.

Experimental Section

Melting points are uncorrected. Identification of the products, either pure specimens or uncontaminated binary mixtures of isomers, were made by their satisfactory nmr spectra (a Varian A-60A spectrometer) and elemental analyses.

Substituted 1,3-Butadienes.—**1a** was prepared by the published procedure,[20] bp 64–66° (15 mm) [lit.[21] bp 60° (15 mm)]. **1b** was prepared according to the known method,[22] bp 58° (lit.[22] bp 59.4°). **1c** is the same as that described previously.[1] 3-Hydroxy-3-cyano-1-butene was prepared in 70% yield by addition of hydrogen cyanide to methyl vinyl ketone in methanol below −5°,[23,24] and its acetate[27] was pyrolyzed[27] to obtain **1d**, bp 34–36° (40 mm) [lit.[27] bp 34–36° (33 mm)]. **1-Cyanobutadiene** was synthesized from crotonaldehyde by the method of Gudgeon, *et al.*,[28] bp 47–56° (31.5 mm) [lit.[28] bp 48–58° (24 mm)]. Cis (pure) and trans (containing about 4% cis) isomers separated by preparative glpc (polyethylene glycol column)[29] were used for uv measurements.

Authentic Diels–Alder Adducts.—A. **2a** (acid) and **3a** (acid) were prepared from **1a** and acrylic acid by the known method:[20] **2a** (acid), mp 157–159.7° (lit.[20] mp 157–158°); **3a** (acid), mp 96.5–97.5° (lit.[20] mp 87–88°). These were converted to the methyl esters with diazomethane: **2a**, mp 58.7–59.7° (lit.[20] mp 57–58°); **3a**, bp 154–155° (6 mm). B. **2b** (acid) was obtained by alkaline hydrolysis[30] of the adduct of **1b** and methyl acrylate by the method of Meek and Trapp,[30] mp 109.5–110.5° (lit.[30] mp 113–114°). Its methyl ester, **2b**, showed bp 98–101.5° (10 mm). The oily by-product, **2b** (acid) plus **3a** (acid),[30] of the alkaline hydrolysis of the above adduct was passed through a silica gel column and was converted to the methyl ester, bp 94–95.6° (8 mm), which was found to consist 60% of **2b** and 40% **3b** by glpc. C. See ref 1 for **2c** and **3c**. D. The mixture of **2d** plus **3d** was obtained from reaction of **1d** with methyl acrylate in benzene at 20°, 2 months, bp 150°–151.5° (15 mm).

Other Authentic Samples. Methyl 4-Trifluoromethylcyclohexane-1-carboxylate (*cis*-**4** and *trans*-**4**).—α,α,α-Trifluoro-*p*-toluic acid (Aldrich Co.) was hydrogenated in acetic acid with platinum oxide catalyst at 80° under hydrogen pressure of 40 atm, and the product was converted (MeOH and H$_2$SO$_4$) to the methyl ester, bp 90–90.5° (20 mm), whose isomeric composition was 77:23, presumably rich in the cis isomer.

Methyl 3-trifluoromethylcyclohexane-1-carboxylate (*cis*-**5** and *trans*-**5**) was prepared from α,α,α-trifluoro-*m*-toluic acid (Aldrich Co.) in the same way as above, bp 90–91° (20 mm), and had an isomeric composition of 88:12, presumably rich in the cis isomer.

Dimethyl *trans*-1,4-cyclohexanedicarboxylate (*trans*-**8**) was prepared by esterification (MeOH and H$_2$SO$_4$) of *trans*-1,4-cyclo-

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(14) Evidently $\sigma^+_{o\text{-Me}}$, free from proximity effects, is ideal if it were available. Recently a $\sigma^+_{o\text{-Me}}$ value (−0.233) was claimed[15] from the rate study of the pyrolytic elimination reactions of esters on the assumption that the proximity effects are negligible. This value also fits nicely in the correlation line.

(15) G. G. Smith, K. K. Lum, J. A. Kirby, and J. Posposil, *J. Org. Chem.*, **34**, 2090 (1969).

(16) Brown and Okamoto's σ^+ [H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958)] was used.

(17) (a) See ref 1 for the evidence and discussions against the cationic two-step mechanism for the aluminum chloride catalyzed reactions. (b) For some previous works on structural effects of the Diels–Alder reactions in terms of the Hammett-type equations, see M. Charton, *J. Org. Chem.*, **31**, 3745 (1966), and references therein.

(18) J. Feuer, W. C. Herndon, and L. H. Hall, *Tetrahedron*, **24**, 2575 (1968).

(19) Unpublished work with H. Sato.

(20) J. S. Meek, R. T. Merrow, D. E. Ramey, and S. J. Cristol, *J. Amer. Chem. Soc.*, **73**, 5563 (1951).

(21) C. C. Price, F. L. Benton, and C. J. Schmidle, *ibid.*, **71**, 2860 (1949).

(22) W. H. Carothers, I. Williams, A. M. Collins, and J. E. Kirby, *ibid.*, **53**, 4203 (1931).

(23) M. Tanaka and J. Murata, *Kogyo Kagaku Zasshi*, **60**, 433 (1957).

(24) Levulinonitrile was the main product when the addition of hydrogen cyanide was carried out by the descriptions of ref 25 and 26.

(25) E. O. Leopold and H. Vollmann, U. S. Patent 2,166,600 (July 18, 1939).

(26) C. S. Marvel and N. O. Brace, *J. Amer. Chem. Soc.*, **70**, 1775 (1948).

(27) M. Tanaka, T. Nishimura, and J. Murata, *Kogyo Kagaku Zasshi*, **60**, 435 (1957).

(28) H. Gudgeon, R. Hill, and E. Isaac, *J. Chem. Soc.*, 1926 (1951).

(29) J. G. Grasselli, B. L. Ross, H. F. Huber, and J. M. Augl, *Chem. Ind. (London)*, 162 (1963).

(30) J. S. Meek and W. B. Trapp, *J. Amer. Chem. Soc.*, **74**, 2686 (1952).

hexanedicarboxylic acid (Aldrich Co.) and showed mp 66–66.3° (lit.[31] mp 69°). The ester was epimerized (MeONa in absolute MeOH) to a mixture *trans*-**8** (75%) and *cis*-**8** (25%).

Dimethyl 1,3-cyclohexanedicarboxylate (**9**) was obtained from isophthalic acid by hydrogenation with platinum oxide catalyst at 60°, 40 atm, in acetic acid, followed by esterification, bp 129.5–130.5° (10 mm) [lit.[31] *cis*-**9**, bp 130.6° (10 mm); *trans*-**9**, bp 140° (20 mm)]. The product consisted of 84% of *cis*-**9** and 16% of *trans*-**9**.

Determination of Isomer Ratios.—The Diels-Alder reactions were carried out at 20° starting from approximately equimolecular amounts of the dienes and dienophiles in a similar way as in the previous work.[6,7] The assumption was made that the isomer ratios were equal to the glpc peak area ratios (FID by a Hitachi K 53 instrument equipped with a suitable Golay column).

R = Phenyl.—The adduct, 11.0 g, from the aluminum chloride catalyzed reaction was heated in aqueous methanolic sodium hydroxide (NaOH 4 g, MeOH 15 ml, H_2O 25 ml) for 16 hr. After dilution with water the mixture was washed with ether, and the aqueous layer acidified with dilute hydrochloric acid to precipitate the acids. The precipitates were recrystallized from benzene to obtain 6.1 g of pure **2a** (acid). The benzene mother liquor on vacuum evaporation to dryness left 3.5 g of crystals, which was treated with diazomethane in ether to recover the mixture of **2a** plus **3a**, 3.1 g, by vacuum distillation. The **2a**:**3a** ratio of this mixture was found to be 92:8 by the relative nmr peak heights at τ 7.60 and 7.37 (characteristic of **2a** and **3a**, respectively, in 10 wt % benzene solution with tetramethylsilane as internal standard), by referring to the calibration curve prepared by use of known artificial mixtures of **2a** and **3a**. The product from the uncatalyzed reaction was treated similarly but no attempt was made to set aside pure **2a** (acid) before nmr analysis. The limit of experimental uncertainty is estimated at ±1% absolute.

R = Cl.—An R-45 Golay column (45 meter polypropylene glycol 550, Hitachi) was used for the glpc analysis of **2b**:**3b** ratio; **3b** eluted faster than **2b**.

R = CF_3.—The glpc analysis of the adduct from the uncatalyzed reaction by means of a PEG 4000-45 Golay column (45-m polyethylene glycol 4000, Hitachi) gave two peaks, peak A (faster elute, 55%) and peak B (45%). The adduct was hydrogenated at NTP with Pd on carbon to obtain the **4** plus **5** mixture in over 96% yield. It exhibited four glpc peaks, in order of elution, of trans-**5** (4.6%), *cis*-**4** (38.1%), *trans*-**4** (15.5%), and *cis*-**5** (41.8%), all being identified by coincidence of retention times with those of the authentic samples. Therefore the ratio of **2c**:**3c** in the original adduct is reckoned to be 53.6:46.4 in good agreement with that directly found by peak A and peak B above, which are now ascribed to **2c** and **3c**, respectively.

R = CN.—The adduct, 2.00 g, was heated with aqueous sodium hydroxide (7.4 g of NaOH in 35 ml of H_2O) under reflux for 45 hr, and the resulting solution was acidified with hydrochloric acid to precipitate almost all of the dicarboxylic acids. The precipitates were collected by filtration and washed with a small volume of water, and the combined aqueous solution was treated in order to recover further crops of the hydrolysis product, which were proved to be minute. The combined product weighed 2.57 g; so it must contain some sodium chloride. It was converted to **6** + **7** by treatment with diazomethane in methanol, bp 95–101° (2 mm); overall yield from **2d** + **3d** was 92%. This mixture gave on glpc with a Golay column HB 2000-45 (polypropylene glycol, Hitachi) two peaks, peak A (faster elute, 73%) and peak B (27%), which were identified with **6** and **7**, respectively, in the following way. The mixture, **6** plus **7**, was hydrogenated at NTP with Pd on carbon to afford **8** plus **9** in 95% yield. The saturated product gave, on glpc analysis with the same column, four peaks, *trans*-**9** (9.1%), *cis*-**8** (57.9%), *trans*-**8** (17.9%), and *cis*-**9** (15.1%). The predominant isomer of the Diels-Alder reaction therefore belongs to the para series.

Competitive Reactions.—The reaction conditions used were quite similar to those described in the previous papers.[1,6,7] For the cases of **1a** and 2,3-dimethylbutadiene was used isoprene as the competitor in place of the standard substrate butadiene. The ratios of the products from two dienes were determined by quantitative glpc using appropriate calibration curves for peak area ratio *vs.* molar ratio.

Kinetic experiments were carried out in a similar manner to the previous work,[1,9] and some of experimental details are summarized in Tables II, III, and IV.

Registry No.—**2b**, 27705-05-1; **2d**, 20594-59-6; **3a**, 27705-07-3; **3b**, 27705-08-4; **3d**, 27705-09-5; *cis*-**4**, 27705-10-8; *trans*-**4**, 27705-11-9; *cis*-**5**, 27705-12-0; *trans*-**5**, 27705-13-1; aluminum chloride, 7446-70-0; 2-phenylbutadiene, 2288-18-8; 2-chlorobutadiene, 126-99-8; 2-trifluoromethylbutadiene, 381-81-7; 2-cyanobutadiene, 5167-62-4; methyl acrylate, 96-33-3.

Acknowledgment.—The authors express their sincere thanks to Professor O. Simamura of Tokyo University for his kind interest and encouragement throughout this series of study. They also thank Mr. T. Nakamura for his valuable technical assistance.

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