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The Diels-Alder Reactions of Polychloro-2,4-cyclohexadienones

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2,3,4,5,6,6-Hexachloro-, 2,3,4,6,6-pentachloro-, and 2,4,6,6-tetrachloro-2,4-cyclohexadienones were found to undergo Diels-Alder reactions when the compounds were heated with such dienophiles as acrylic acid, methyl acrylate, methyl vinyl ketone, acrylonitrile, and ethyl vinyl ether. It was concluded, chiefly through analysis of these NMR spectra, that the reactions proceed stereospecifically to give a series of 7-substituted and polychlorinated bicyclo-[2.2.2]oct-5-en-2-ones, which is in agreement with the endo rule. The stereospecificity of these adducts does not, however, agree with the results of calculations by means of the perturbation method.

The Diels-Alder reaction is one of the most popular and useful reactions for organic chemists.[1] Accordingly, a number of theoretical studies have been made on the various problems concerning the reaction mechanism.[2] The arguments, however, have not been settled in many respects.[3] One of the most important questions is the nature of the factor that determines the final orientation between the diene and dienophile.[4,5] Most recently, Herndon and Hall have made a quantitative prediction, on the basis of the second-order perturbation calculations, on the relative reactivities and adduct structures in several competitive Diels-Alder reactions.[6] In that case, both the dienes and the dienophiles have been assumed to be axially symmetric and planar molecules. The predictions are in fairly good agreement with the experimental results. It may be worthwhile, then, to test the applicability of Herndon and Hall's method to the Diels-Alder reaction, where neither component is a symmetrical molecule. In the present experiment, unsymmetrical molecules were chosen both as the dienophiles and as the dienes. In relation to the choice of the compound, it should be mentioned here that the Diels-Alder reactions easily proceed, in spite of Woodward's prediction,[5] if a dienophile with an electron-donating substituent is added either to a polyhalogenated diene like haxachlorocyclopentadiene[7] or to an α,β-unsaturated, exocyclic carbon compound like dehydroindigo.[8] The diene components investigated here (Fig. 1) are polyhalogenated compounds, and all have an exocyclic carbonyl group in conjugation with the double bond. Thereupon, one would expect that the experimental results would not be in accordance with the theoretical predictions. Therefore, the structures of the adducts obtained were carefully investigated by means of their NMR spectra. Since the reactions were found to be stereospecific, the mechanisms were speculated about from various standpoints, such as the second-order perturbation energies and the steric hindrances in the course of the reactions.

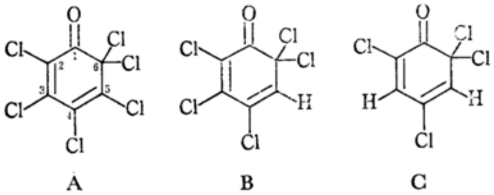

Fig. 1. Polychloro-2,4-cyclohexadienones.

Experimental

Materials. The synthesis of 2,3,4,5,6,6-hexachloro-2,4-cyclohexadienone (A) and its Diels-Alder reactions have been reported previously.[9] 2,3,4,6,6-Pentachloro-2,4-cyclohexadienone (B) was prepared by the follow-

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[1] K. Alder and G. Stein, *Angew. Chem.*, **50**, 510 (1937).

[2] a) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley, New York, N. Y. (1961), p. 432. b) M. Charton, *J. Org. Chem.*, **31**, 3745 (1966). c) M. Imoto, "Fuka-Hanno (Addition Reactions)," Tokyo Kagaku Dojin Co., Ltd., Tokyo (1967), p. 163.

[3] J. Sauer, *Angew. Chem. Intern. Ed. Engl.*, **6**, 16 (1967).

[4] K. Fukui, *J. Chem. Phys.*, **20**, 722 (1952).

[5] R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 4388 (1967).

[6] W. C. Herndon and L. H. Hall, *Theoret. Chim. Acta*, **7**, 4 (1967).

[7] K. L. Williamson, *J. Am. Chem. Soc.*, **85**, 516 (1963)

[8] R. Pummerer and H. Fiesselmann, *Ann. Chem.*, **544**, 206 (1940).

[9] a) S. Kumamoto, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan., Ind. Chem. Sect.)*, **64**, 188 (1961). b) K. Somekawa, H. Uemura and S. Kumamoto, *ibid.*, **72**, 2012 (1969).

ing method. 2,3,4,6-Tetrachlorophenol (16 g) was mixed with *t*-butyl hypochlorite[10] (11 g) at 0°C. The mixture was then kept at 40°C for 30 min, and the *t*-butanol thus produced, together with the excessive *t*-butyl hypochlorite, was removed under reduced pressure.[11] The remaining yellow liquid (18 g) was B (Found: C, 28.16; H, 0.60; Cl, 65.64%. Calcd for C_6HOCl_5: C, 27.56; H, 0.38; Cl, 66.02%. IR: $\nu_{C=O}=1718\ cm^{-1}$, NMR: $\delta_H=6.9$ ppm from TMS in the carbon tetrachloride solution). It is suspected, from the small NMR peak downfield from B, that B contains as impurities small amounts of 2,4,5,6,6-pentachloro-2,4-cyclohexadienone (B′) or 2,3,4,4,6-pentachloro-2,5-cyclohexadienone. Since, however, no Diels-Alder products of B′ were obtained, no further description of the properties will be made in this paper. 2,4,6,6-Tetrachloro-2,4-cyclohexadienone (C) was analogously prepared from 2,4,6-trichlorophenol (10 g) and *t*-butyl hypochlorite (10 g).[11] 11.5 g of the product were obtained; the properties were as follows:

Found: C, 31.70; H, 1.08; Cl, 60.43%. Calcd for $C_6H_2OCl_4$: C, 31.58; H, 0.88; Cl, 61.00%. $\nu_{C=O}=1715\ cm^{-1}$, $\delta_H=6.58$, 7.08 ppm, $J_{H-H}=2.0$ cps. The compounds used as the dienophiles were extra-pure-grade chemicals supplied by the Tokyo Kasei Ind. Co., Ltd., and were further purified before the experiments. The purities of the samples were proved by gas chromatography to be above 95%.

Procedure. In general, the reaction was carried out by refluxing a nearly equimolar mixture of a diene and a dienophile on a water bath. The precipitated product was separated from the remaining solution and was recrystallized from one of the following solvents: toluene, benzene, petroleum benzine, or petroleum ether. When the product was an oily substance, column-chromatography on activated alumina was used to purify the material. The reaction conditions, yields, mp, analytical data, and characteristic IR absorption bands of the pure products are summarized in Tables 1, 2, and 3. Chromatographic separations of the filtrates were also carried out on columns of alumina or on TLC of silica gel (Wakogel B-5) in order to detect possible isomeric by-products. No products other than those in Table 1 were, however, detected. Moreover, the products which were given by slow reactions at room temperature were identical with those in Table 1, indicating that no isomerizations had occurred under the present experimental conditions (Table 1).

Measurement and Analysis of NMR Spectra. The spectra were obtained by the use of a Varian A-60 analytical NMR spectrometer. The concentrations of the samples were kept at 0.5—5 mol %, and a small amount of TMS was dissolved in the solution as an internal reference. The obtained spectra were analyzed by the use of an electronic computer.*1 The computer programs for calculating the energies and the intensities for ABC[12] and ABCD[13] spin systems were made by the present authors.*2 The calculations were repeated until the calculated energy and intensity came within ±0.3 cps and ±10 % respectively of the observed values.

Results and Discussion

The results of elementary analyses for the reaction products are summarized in Table 2. The results are in good agreement with the values calculated for the rational formula which correspond to 1 : 1 adducts of the reactants. The characteristic IR absorption bands of the products are shown in

TABLE 1. REACTIONS AND PRODUCTS

Reaction condition					Product		
Dienone	(g)	Dienophile* Z	(g)	Time (hr)	Yield (%)	Mp (°C)	Symbol
B	5.3	COOH	1.5	0.5	48	219—220.5	I
B	5.4	CO_2CH_3	1.8	13	57	96.5—98	II
B	5.3	C≡N	1.3	11	36	170—171	III
B	5.2	$COCH_3$	1.6	3	29	120—121	IV
B	10.2	OC_2H_5	3.2	15	60	oil	V
C	9.7	COOH	5.6	7	28	201—202	VI
C	5.1	CO_2CH_3	1.9	12	52	124—125	VII
C	5.1	C≡N	1.4	14.5	26	158—159.5	VIII
C	10.0	$COCH_3$	3.0	8	31	137—139	IX
C	21.5	OC_2H_5	8.9	10	55	oil	X

* CH_2=CH-Z

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10) H. M. Teeter, R. C. Bachmann, E. W. Bell and J. C. Cowan, *Ind. Eng. Chem.*, **41**, 849 (1949).

11) L. Denivelle and R. Fort, *Compt. rend.*, **235**, 1514 (1952); *Chem. Abstr.*, **48**, 553 (1954).

*1 A model OKITAC 5090 computer at the computer center of Kyushu University was used for this purpose.

12) C. A. Reilly and J. D. Swalen, *J. Chem. Phys.*, **32**, 1378 (1960).

13) a) C. A. Reilly and J. D. Swalen, *ibid.*, **34**, 980 (1961). b) J. W. Emsley, J. Feeney and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, Oxford (1965), p. 426.

*2 The matrix elements of the secular determinant for the ABCD system were examined all over again. The results are in agreement with those obtained by Reilly and Swallen[13a]; some errors were found, however, in the table given by Emsley *et al.*[13b]

Table 2. Analytical data of the products

Product	Formula	Found (%)				Calcd (%)			
		C	H	Cl	N	C	H	Cl	N
I	$C_9H_5Cl_6O_3$	31.94	1.38	52.34	—	31.94	1.49	52.38	—
II	$C_{10}H_7Cl_5O_3$	34.10	1.88	49.52	—	34.10	1.99	49.32	—
III	$C_9H_4Cl_5NO$	33.94	1.18	55.52	4.46	33.84	1.26	55.50	4.39
IV	$C_{10}H_7Cl_5O_2$	35.36	2.11	52.50	—	35.82	2.10	52.65	—
V	$C_{10}H_9Cl_5O_2$	34.62	2.22	52.09	—	35.50	2.68	52.41	—
VI	$C_9H_6Cl_4O_3$	35.49	1.92	46.06	—	35.56	1.99	46.65	—
VII	$C_8H_8Cl_4O_3$	37.77	2.60	44.57	—	37.77	2.53	44.59	—
VIII	$C_9H_5Cl_4NO$	37.82	1.67	49.48	4.90	37.93	1.77	49.70	4.92
IX	$C_{10}H_8Cl_4O_2$	40.44	2.71	46.88	—	39.81	2.67	46.99	—
X	$C_{10}H_{10}Cl_4O_2$	39.04	3.18	45.79	—	39.55	3.32	46.64	—

Table 3. Characteristic absorption bands of adducts (IR, cm^{-1})

Adduct	Absorption due to transformation of dienone		Absorption of substituent, Z,* due to transformation of dienophile		
	$\nu_{C=O}$	$\nu_{C=C}$	νZ (C=O,	C≡N,	C-O)
I	1765	1600	1712		1242
II	1765	1615	1736		1215
III	1770	1610		2260	
IV	1764	1610	1713		
V	1762	1611			1118
VI	1770	1618	1715		1242
VII	1771	1618	1735		1212
VIII	1770	1615		2260	
IX	1762	1622	1721		
X	1762	1620			1120

* CH_2=CH-Z

Table 3. The presence of a double bond is suggested (third column). However, there are no signs of the absorption bands due to the mono-substituted ethylenes. The sharacteristic absorption bands of the substituents (Z), on the other hand, are clearly observed, as are given in the table from the fourth column to sixth. As may be seen from the frequencies, the substituents are not likely to be conjugated with any unsaturated groups. The frequencies of the carbonyl absorption bands (1762—1771 cm^{-1}) in the second column are close to that of octachloro-3-cyclohexenone (1779 cm^{-1}).[14] Therefore, the presence of a polychloro-3-cyclohexenone ring is indicated.[*3] The above facts suggest strongly that the product is a 4+2 adduct which could be obtained by a Diels-Alder reaction between the polyhalogenated dienone and the monosubstituted ethylene.

In order to decide on the most probable structures for the adducts, the NMR spectra were carefully examined. Examples of the analyzed spectra are shown in Figs. 2—4. The chemical shifts (δ) and the coupling constants (J) thus obtained are summarized in Tables 4 and 5. As a consequence, the

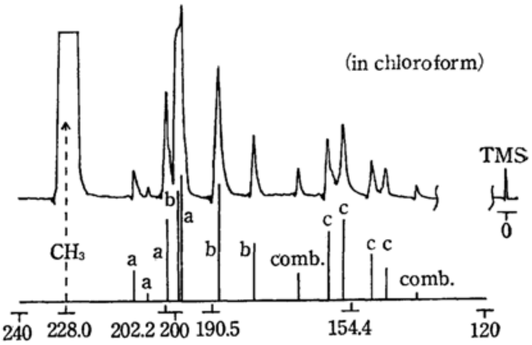

Fig. 2. Adduct of A with methyl acrylate (NMR, cps).

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[14] S. Kumamoto, Thesis, Kyushu University (1962).

[*3] Carbonyl absorption bands are known to shift to frequencies higher by 10—25 cm^{-1} if a chlorine atom is attached to the carbon atom alpha to the carbonyl group.[15] Hence, the difference between the carbonyl absorptions of octachloro-3-cyclohexenone and those of the adducts in Table 3 may be reasonably explained as due to the difference in the number of alpha chlorine atoms.

[15] K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, and Nankodo Co., Ltd., Tokyo (1962), p. 42.

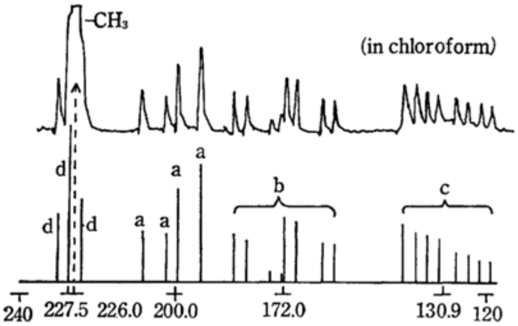


Fig. 3. Adduct of B with methyl acrylate (NMR, cps).

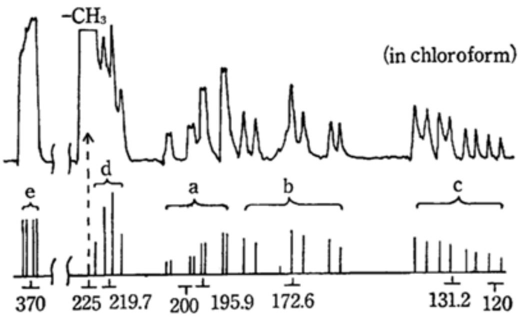


Fig. 4. Adduct of C with methyl acrylate (NMR, cps).

TABLE 4. CHEMICAL SHIFTS OF ADDUCTS (NMR, cps)

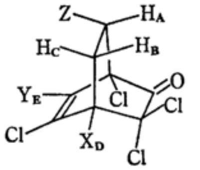
Run	Adduct ((Dienone)+(Z)[a])	Solvent	Chemical shift (δ)[d]					
			H_A	H_B	H_C	H_D	H_E	H_Z
1	((A)+(COOH))[b]	S1	233.6	204.1	178.1	—	—	938
2	I	S1	227.3	180.3	148.9	247.5	—	731
3	VI	S1	216.0	178.2	145.4	232.3	390.0	563
4	((A)+(CO_2CH_3))	S1	233.6	195.2	167.8	—	—	219.6
5	((A)+(CO_2CH_3))	S2	202.2	190.5	154.4	—	—	228.0
6	II	S1	227.0	173.8	139.3	248.5	—	220.2
7	II	S2	200.0	172.0	130.9	227.5	—	226.8
8	VII	S1	210.5	169.5	133.7	229.7	380.0	222.0
9	VII	S2	195.9	172.6	131.2	219.7	370.0	225.0
10	((A)+(C≡N))	S2	213.6	200.1	163.8	—	—	—
11	III	S2	213.4	183.5	145.6	231.0	—	—
12	VIII	S2	207.2	182.8	141.4	221.5	377.5	—
13	((A)+($COCH_3$))	S2	212.2	185.7	151.5	—	—	262.0
14	IV	S2	210.5	167.3	116.5	228.7	—	136.5
15	IX	S2	206.0	168.2	116.8	220.7	266.5	136.0
16	((A)+(OC_2H_5))	S2	236.2	198.1	145.5	—	—	216,72
17	V	S2	233.2	174.7	119.1	212.2	—	216,72

a) CH=CH-Z. b) An adduct of A and acrylic acid. c) S1=Pyridine, S2=chloroform.
d) Expressed in cycles per second downfield from tetramethylsilane resonance.

TABLE 5. COUPLING CONSTANTS OF ADDUCTS (cps)

Run*	J_{AB}	J_{AC}	J_{BC}	J_{BD}	J_{CD}	J_{DE}	J_{EA}
1	9.8	5.8	−13.2				
2	9.6	6.5	−13.7	3.0	3.0		
3	9.6	6.7	−13.7	3.0	3.0	2.5	1.0
5	9.1	5.6	−13.1				
7	9.5	6.4	−13.5	3.1	3.1		
9	9.5	6.4	−13.5	3.0	3.0	2.5	1.0
10	9.4	5.4	−13.5				
11	9.7	5.8	−13.8	3.0	3.0		
12	9.8	5.6	−14.2	3.0	3.0	2.5	1.0
13	9.2	6.0	−12.9				
14	9.6	6.6	−13.7	3.0	3.0		
15	9.6	6.6	−13.5	3.0	3.0	2.5	0.7
16	8.0	3.0	−13.8				
17	8.0	3.2	−14.2	3.0	3.0		

* Equal to run numbers of Table 4.



X=Y=Cl; from A
X=H, Y=Cl; from B
X=Y=H; from C
$Z=CO_2H$, CO_2CH_3,
C≡N, $COCH_3$ or OC_2H_5

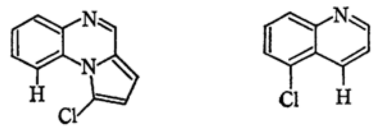
Fig. 5. The steric structures of adducts.

mutual orientation between the diene and the dienophile components in the adduct molecules were deduced to be as are shown in Fig. 5. The reasons will be described in detail below.

In the case of methyl acrylate adducts, one can clearly notice that the signals b and c of the adducts become increasingly complex upon the variation of the diene component from A to B (Figs. 2 and 3). The analysis shows that the proton H_D is almost equally coupled to H_B and H_C, but not to H_A (Table 5). The newly-appearing signals, d, in Fig. 3 should correspond to the proton at the 5-position of B, which should be found at the bridge head in the adduct molecule. Therefore, it may be suggested that the α-methine and β-methylene groups of the dienophile component are bonded to the 2- and 5-positions respectively of the diene component, B.

Similar arguments with the adduct obtained from C and methyl acrylate also indicate that the mutual orientation of the two components is the same as that in the case of B and methyl acrylate. In the case of the adduct obtained from A, one should notice at first that the coupling constants among the protons H_A, H_B, and H_C are almost the same as those in the adducts from B or C (Table 5). Therefore, the steric arrangements of these three protons may be expected to be the same among the three adducts. In addition, the replacement of the bridge head proton, H_D, with a chlorine atom, *i.e.*, the variation of the diene from B to A, is seen to have much greater effects on the chemical shifts of the protons H_B (+18.5 cps) and H_C (+23.5 cps) than on H_A (+2.2 cps), as is shown in Run 4 and Run 6 of Table 4. One may think, then, that the methylene group of the dienophile component is bonded to the 5-position of A. In other words, the orientation of the diene with respect to the dienophile component is the same between the adducts obtained from A, B, and C.

The signals for H_B invariably appear in a field lower by 34.2—55.6 cps than those for H_C in chloroform (Table 4). There may be two explanations for this nonequivalence of the geminal protons. Granting the configuration in Fig. 5 to be correct, one would expect that H_B would be considerably deshielded because it is very close (*ca.* 2.5 Å) to the chlorine atom alpha to the carbonyl group of the polychloro-3-cyclohexenone ring. There are a number of examples of such van der Waals shifts (Fig. 6). The H_C proton, on the other hand, is shielded because of the anisotropy of the carbon-carbon double bond. The joint effect of these two factors seems to give a reasonable explanation of the observed difference between H_B and H_C.



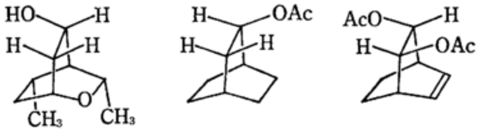
−60 cps[a)] −29 cps[b)]

Fig. 6. Van der Waals shifts induced by chlorines.

a) C. F. Raymond *et al.*, *J. Org. Chem.*, **29**, 2440 (1964).
b) F. A. L. Anet, *J. Chem. Phys.*, **32**, 1274 (1960).

The vicinal coupling constants for bicyclic systems similar to the compounds under investigation have been studied by several investigators. Some relevant examples are shown in Fig. 7. It is generally found in these examples that J_{cis} is larger than J_{trans}. Both of these coupling constants decrease with the electron-withdrawing property of the substituent (Z) attached to the ethylene group. The same could be said of the cases of bicyclo-[2.2.1]-heptane derivatives.[16)] It is reasonable to expect that the vicinal coupling constants of the adducts under investigation will follow the same trend as those described above.

On this basis, it may be suggested that H_B and H_C are, respectively, at the *cis*- and *trans*-positions



$J_{trans}=3.6$[a)] $J_{trans}=2.6$[b)] $J_{trans}=6.0$[b)]
$J_{cis}=9.8$ $J_{cis}=8.2$

Fig. 7. Vicinal coupling constants in bicyclo-[2.2.2]ring system.

a) J. S. Webb *et al.*, *J. Am. Chem. Soc.*, **84**, 3183 (1962).
b) K. Tori *et al.*, *Chem. Ber.*, **97**, 2798 (1964).

$$\left.\begin{array}{l} J_{AB}=9.1\text{—}9.8, \\ \quad 8 \text{ (when } Z=OC_2H_5) \\ J_{AC}=5.4\text{—}6.7, \\ \quad 3 \text{ (when } Z=OC_2H_5) \end{array}\right\}$$

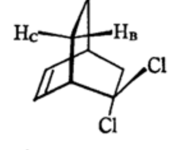


Fig. 8. Configuration.

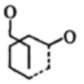
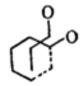
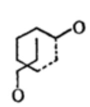
[16)] K. L. Williamson, *J. Am. Chem. Soc.*, **85**, 516 (1963).

with respect to H_A (Fig. 8). This suggestion is further confirmed by observing the large vicinal coupling constant (9.1 cps) of the maleic anhydride adduct,[9a] where only *cis*-coupling might be expected to be present. The values for the geminal coupling constant (J_{BC}) and the long-range coupling constant (J_{AE}) are also resonable for this type of bicyclic compound.[17–19] The configuration which is in best agreement with the above discussion is thus concluded to be the one shown in Fig. 5.

Since the reaction products were found to be stereospecific, as has been described above, an attempt has been made to elucidate the reaction mechanism by the use of a simple molecular orbital method.*4 The charge densities in the electron systems of a diene, A, and a dienophile, methyl vinyl ketone (F), are shown in Fig. 9. On the basis of the charge densities of the two components (Fig. 9), the β carbon of the dienophile may be expected to be attracted to the cardon atom at the 2-position of the cyclohexadienone system. Since the experimental result is just the opposite of this prediction, however, the electrostatic attraction in the ground state is not considered to play an important role in the reaction mechanism. If the reaction proceeds *via* a one-step, cyclic, concerted mechanism,[6] the relative preferences among several different geometries in the activated states may be compared by evaluating the stabilization energy for the interacting electron systems in each case. The stabilization energies were estimated by the second-order perturbation method for the three orientations shown in Table 6. The molecular planes of the diene and dienophile (below) were assumed to be parallel to each other.

Fig. 9. The charge density of 2,3,4,5,6,6-hexachloro-2,4-cyclohexadienone (A) and methyl vinyl ketone (F).

TABLE 6. STABILIZATION ENERGIES CALCULATED BY SECOND ORDER PERTURBATION METHOD (in β unit)

Inter-planar distance (Å)	Mutual orientations		
	 (*ortho-endo*)	 (*ortho-exo*)	 (*meta-endo*)
2.5	0.429	0.514	0.492
3.4	0.013	0.017	0.016

Geometries of A and F used for calculation.

A: $O–C_1$, 1.24Å; $C_1–C_2$, 1.43Å; $C_2–C_3$, 1.37Å; $C_3–C_4$, 1.45Å; $C_4–C_5$, 1.34Å; C–Cl, 1.76Å; $\angle OC_1C_2$, $\angle C_1C_2C_3$, $\angle C_2C_3C_4$, $\angle C_3C_4C_5$, 121°; $\angle$CCCl, 119.5°.

F: $O–C_1$, 1.24Å; $C_1–C_\alpha$, 1.45Å; $C_\alpha–C_\beta$, 1.34Å; $\angle OC_1C_\alpha$, $\angle C_1C_\alpha C_\beta$, 121°.

The calculations were made for the cases of two different interplanar distances, 3.4 and 2.5Å, and all π orbitals of the two components were taken into consideration.*5 The results are summarized in Table 6. The stabilization energies indicate that an *ortho-exo* addition is most favored. In actuality, however, *ortho-endo* adducts are produced exclusively. Thus, it is clear that Herndon and Hall's method is not powerful enough to cover all of the Diels-Alder reactions. For that matter, Woodward and Katz's simple method[20] can not be expected to give the answer, either.*6 The true cause of the formation of stereospecific products may be found either in steric factors or in electronic factors which can not be taken into consideration by simple molecular orbital calculation. Further investigation is being undertaken to solve this complex problem the results will be reported in later paper.

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17) R. C. Cookson, T. A. Crabb, J. J. Frankel and J. Hudec, *Tetrahedron*, *Suppl.*, **7**, 355 (1967).

18) P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1171 (1964).

19) K. Tori, Y. Takano and K. Kitahonoki, *Chem. Ber.*, **97**, 2798 (1964).

*4 The following parameters were used in the calculation.[2a)]
A: $h_{\ddot{O}}=2.0$, $h_{C_1}=0.3$, $h_{C_6}=0.1$, $h_{C_1}=2.0$, $K_{C=O}=1.4$, $K_{C_2-C_3,\,C_4-C_5}=1.1$, $K_{C-Cl}=0.4$. F: $h_{\ddot{O}}=2.0$, $h_{C_1}=0.3$, $K_{C=O}=1.4$, $K_{C_\alpha-C_\beta}=1.1$.

*5 The following formula was used for calculating the second-order perturbation energies.[6)]

$$\Delta E = 2\Big[\sum_{m}^{\text{occ.}}\sum_{n}^{\text{vac.}} - \sum_{m}^{\text{vac.}}\sum_{n}^{\text{occ.}}\Big]\frac{[\sum_{i,j} a_{m,i}b_{n,j}P_{mi,nj}]^2}{E_m - E_n}$$

The resonance integrals, $P_{mi,nj}$, were then calculated from the overlap integrals[21)] by the use of Mulliken's equation.[22)]

20) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

21) N. Tyutyulkov and P. Markov, *Montsh. Chem.*, **96**, 2030 (1965).

22) R. S. Mulliken, *J. Phys. Chem.*, **56**, 295 (1952).

*6 Polychloro-2, 4-cyclohexadienones (A, B, and C) are characterized by their high electron affinities and ionization potentials. Therefore, the situation is just the opposite of the case which Woodward and Katz have presumed in their discussion. It may be worth mentioning, in this connection, that the diene reacts with cyclopentadiene, but not with maleic anhydride.