

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

**Electronic Effects and Rates in the Diels-Alder Reaction<sup>1</sup>**ISAAC BENGHIAT<sup>2</sup> AND ERNEST I. BECKER<sup>3</sup>*Received January 2, 1958*

A kinetic study has been made of the reactivities of a series of methyl esters of substituted phenylpropionic acids with tetraphenylcyclopentadienone with the aim of defining the electronic effects of substituents on the rate of the Diels-Alder reaction. The reaction was followed by measuring the rate of evolution of carbon monoxide. The reactions were second order. The reaction products were isolated and characterized. The apparent ionization constants of the corresponding phenylpropionic acids in 50% aqueous ethanol were also determined. A plot of  $\log K/K_0$  of the ionization of the *m*- and *p*-substituted phenylpropionic acids against Hammett  $\sigma$ -constants gave a line whose slope was +0.69.

A plot of the logarithms of the rate constants against  $\log K/K_0$  gave a line whose slope was +1.10. Energies of activation for the reactions of the methyl esters of the *o*- and *p*-chlorophenylpropionic acids were 18.2 and 18.9 Kcal/mole.

The significance of the results obtained is discussed.

It is well known that the Diels-Alder reaction is accelerated by electron-withdrawing groups in the dienophile and by electron-releasing groups in the diene. Few quantitative studies have been made because of experimental difficulties due to side reactions or to dissociation of the product. Notable are those of Barnstorff and Meek<sup>4</sup> who investigated the effect of nuclear substituents on the dienophilic reactivity of *N*-phenylmaleimide and of DeWitt, Lester, and Ropp<sup>5</sup> who measured the rate of reaction between *p*-substituted 1-phenyl-1,3-butadienes and maleic anhydride. Bickford, Hoffman, Heinzelman, and Fore<sup>6</sup> have recently reported on some electronic and steric effects in maleic anhydride but the substituents, CH<sub>3</sub> and Cl, were on the double bond.

A previous paper from these laboratories<sup>7</sup> reported a preliminary investigation of the Diels-Alder reaction between tetracyclone (tetraphenylcyclopentadienone) and substituted acetylenes. It was found that the reaction is favored by electron-withdrawing substituents, that side-reactions such as polymerization or copolymerization do not occur, and that the reaction is irreversible because a benzene ring is formed by decarbonylation of the intermediate adduct. These properties of the reaction permit a precise study of the kinetics of the Diels-Alder reaction. Based on a convenient time for the reaction and on the ease of introducing various groups into the phenylacetylene, the methyl esters of substituted phenylpropionic acids were

selected for study. The present paper reports on a kinetic study of the reactivities of a series of such methyl esters with tetracyclone with the aim of more specifically defining the electronic effects of substituent groups on the rate of the Diels-Alder reaction.

## EXPERIMENTAL

*A. Synthetic.* Tetracyclone, m.p. 220–221° (rep. m.p. 219–220°), was prepared by the method of Johnson and Grummitt.<sup>8</sup>

The substituted phenylpropionic acids were prepared by dehydrobromination of the corresponding cinnamic acid or ester dibromides with alcoholic potassium hydroxide essentially according to literature procedures.

Several methods were used for the esterification of these acids. Sulfuric acid in methanol was used for the esterification of phenylpropionic acid. This method gave poor results with *p*-methoxyphenylpropionic acid. However, dimethyl sulfate<sup>9</sup> gave satisfactory yields. Finally esterification with *N* HCl in methanol<sup>10</sup> was adopted as the standard esterification technique. The results are summarized in Table I.

Phenylcyclohexane, purchased from Distillation Products Industries, was purified according to Corson and Ipatieff,<sup>11</sup> b.p. 138.0–138.5° (32 mm.),  $n_D^{25}$  1.5221 (rep.  $n_D^{25}$  1.5254,  $n_D^{25}$  1.5190<sup>13</sup>).

*B. Apparent ionization constants.* A solution of about 0.75 mmole of the substituted phenylpropionic acid, accurately weighed, in 50 ml. of 50 volume percent of aqueous ethanol was titrated potentiometrically under a nitrogen atmosphere with 0.1N NaOH. Ethanol was added during the titration to keep the composition of the solvent constant.

A Beckman Model G pH meter was used for the titration. The electrodes were Beckman #1190-42 and #1170.<sup>14</sup> The pH meter was standardized against aqueous buffer solution at pH of 5. Standardization was checked against aqueous buffer solution at pH of 2.

At the end of each titration, the electrodes were immersed in distilled water for one-half hour. The pH meter was

(1) Presented at the 132nd Meeting of the American Chemical Society, New York, N. Y., September 8 to 13, 1957, Abstracts, p. 32-P.

(2) Taken from the doctoral Dissertation of I. Benghiat presented to the Graduate Faculty of the Polytechnic Institute of Brooklyn, 1958.

(3) To whom inquiries should be directed.

(4) H. D. Barnstorff and J. S. Meek, 125th Meeting of the American Chemical Society, Kansas City, Mo., March 23 to April 1, 1954, Abstracts, p. 29-N.

(5) E. J. DeWitt, C. T. Lester, and G. A. Ropp, *J. Am. Chem. Soc.*, **78**, 2101 (1956).

(6) W. G. Bickford, J. S. Hoffmann, D. C. Heinzelman, and S. P. Fore, *J. Org. Chem.*, **22**, 1080 (1957).

(7) J. J. Dudkowski and E. I. Becker, *J. Org. Chem.*, **17**, 201 (1952).

(8) J. R. Johnson and O. Grummitt, *Org. Syntheses, Coll. Vol. III*, 806 (1953).

(9) K. Freudenberg and G. Wilke, *Ber.*, **85**, 78 (1952).

(10) P. Pfeiffer, *Ann.*, **411**, 148 (1916).

(11) B. B. Corson and V. N. Ipatieff, *Org. Syntheses, Coll. Vol. II*, 151 (1943).

(12) B. B. Corson and V. N. Ipatieff, *J. Am. Chem. Soc.*, **59**, 645 (1937).

(13) J. F. McKenna and F. J. Sowa, *J. Am. Chem. Soc.*, **59**, 471 (1937).

(14) Cf., H. K. Hall, Jr., *J. Phys. Chem.*, **60**, 63 (1956).

TABLE I  
 PHYSICAL CONSTANTS OF METHYL ESTERS OF SUBSTITUTED PHENYLPROPIOLIC ACIDS

Substituent	Method of Prepn. <sup>a</sup>	M.P., °C. or B.P., °C. (mm.)	Yield, %	Carbon		Analyses Hydrogen, %		Other Elements, %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
None <sup>b</sup>	1	128 (4 mm.)	74						
<i>m</i> -CH <sub>3</sub>	2	95 (0.6 mm.) <sup>c</sup>	69	75.84	75.92, 75.93	5.79	6.01, 6.23		
<i>p</i> -CH <sub>3</sub>	2	68-70	86	75.84	76.12	5.79	5.79		
<i>o</i> -Cl	2	39.5-40	74	61.71	61.62	3.63	3.62	18.22	18.52
<i>m</i> -Cl	1	28-30	50					18.22	17.77
<i>p</i> -Cl	1	92-94	94					18.22	17.86
<i>m</i> -NO <sub>2</sub>	2	51-52	18	58.54	58.51, 58.66	3.44	3.26, 3.42	6.83	6.54, 6.81
<i>p</i> -NO <sub>2</sub>	2	112-113	100	58.54	58.44	3.44	3.53	6.83	6.73
<i>m</i> -OCH <sub>3</sub>	2	124 (0.3 mm.) <sup>d</sup>	84	69.46	69.47, 69.35	5.30	5.65, 5.52		
<i>p</i> -OCH <sub>3</sub>	1	45-47	20	69.46	69.44	5.30	5.33		
<i>p</i> -OCH <sub>3</sub>	3	45	74						

<sup>a</sup> (1) Methanolic sulfuric acid; (2) methanolic hydrogen chloride<sup>10</sup>; (3) dimethyl sulfate.<sup>9</sup> <sup>b</sup>  $n_D^{22}$  1.5628 (C. Moureau, P. T. Muller, and J. Varin, *Ann. chim.*, [9] 2, 269 (1914), report  $n_D^{25}$  1.5618). <sup>c</sup>  $n_D^{24}$  1.5568. <sup>d</sup>  $n_D^{24.5}$  1.5663.

 TABLE II  
 PHYSICAL CONSTANTS, APPARENT IONIZATION CONSTANTS (24°), AND SIGMA CONSTANTS OF SUBSTITUTED PHENYLPROPIOLIC ACIDS IN 50% ETHANOL (VOL.) AT 24°C. AND SPECIFIC RATE CONSTANTS OF THE ESTERS

Substituent	Found	Lit., M.P., °C.	Apparent $pK_a$	$pH$ at Mid-Point <sup>a</sup>	$K \times 10^4$	Sigma <sup>b</sup>	Specific Rate Constants of the Esters
							$\times 1000$ (molal <sup>-1</sup> sec. <sup>-1</sup> )
None	136-137	135-136 <sup>c</sup>	3.40	3.45	3.98	0.00	1.48
<i>m</i> -CH <sub>3</sub>	135-136 <sup>d</sup>	109.5 <sup>e</sup>	3.44	3.48	3.63	-0.04	1.61
<i>p</i> -CH <sub>3</sub>	148-149 dec.	150 <sup>f</sup>	3.53	3.57	2.95	-0.13	1.25
<i>o</i> -Cl	134-135	132-133 dec. <sup>f</sup>	3.26	3.32	5.50	0.14	2.97
<i>m</i> -Cl	140-143	140-141 <sup>g</sup>	3.15	3.23	7.08	0.25	2.87
<i>p</i> -Cl	192-194	192-193 dec. <sup>h</sup>	3.20	3.27	6.31	0.20	2.25
<i>m</i> -NO <sub>2</sub>	143	143.7-144.4 <sup>h</sup>	2.96	3.08	11.0	0.44	5.73
<i>p</i> -NO <sub>2</sub>	202 dec.	201-202 <sup>i</sup>	2.87	3.02	13.5	0.53	7.75
<i>m</i> -OCH <sub>3</sub>	107-108	109 <sup>j</sup>	3.36	3.41	4.37	0.04	1.73
<i>p</i> -OCH <sub>3</sub>	139 dec.	141-143 dec. <sup>k</sup>	3.63	3.66	2.34	-0.23	1.19

<sup>a</sup> The  $pH$  at the half-neutralization point is recorded for comparison with the apparent  $pK_a$  values obtained using equation 1. <sup>b</sup>  $\log K_{ion}$  (substituted phenylpropionic acid)  $-\log K_{ion}$  (phenylpropionic acid). <sup>c</sup> T. W. Abbott, *Org. Syntheses*, Coll. Vol. II, 515 (1943). <sup>d</sup> From CS<sub>2</sub>. *Anal.* Calcd. for C<sub>10</sub>H<sub>8</sub>O<sub>2</sub>: C, 74.99; H, 5.03; Neut. equiv., 160.2. Found: C, 75.03, 75.10, H, 4.85, 4.89; Neut. equiv., 162.6. <sup>e</sup> W. Müller, *Ber.*, 20, 1212 (1887). <sup>f</sup> F. G. Baddar, L. S. Assal, and N. A. Doss, *J. Chem. Soc.*, 461 (1955). <sup>g</sup> M. M. Otto, *J. Am. Chem. Soc.*, 56, 1393 (1934). <sup>h</sup> M. S. Newman and S. H. Merrill, *J. Am. Chem. Soc.*, 77, 5549 (1955). <sup>i</sup> F. G. Baddar and L. S. Assal, *J. Chem. Soc.*, 1267 (1948). <sup>j</sup> J. I. Jones and T. C. James, *J. Chem. Soc.*, 1600 (1935). <sup>k</sup> E. Bergmann and A. Bondi, *Ber.*, 66, 278 (1933).

recalibrated against aqueous buffer before each titration.

Apparent ionization constants were calculated using the equation<sup>15</sup>:

$$pK_a = pH - \log \frac{[\text{salt}] + [H^+]}{[\text{acid}] - [H^+]} \quad (1)$$

In these calculations, corrections for liquid junction potentials were neglected; unit activities were assumed and  $pH$  readings were assumed to be equal to the logarithms of the reciprocals of the hydrogen-ion concentrations.

Two titrations were made on each acid at 24°. There was no change in  $pK_a$  values calculated at 30%, 50% and 70% neutralization. Maximum deviation of  $pK_a$  values between pairs of determinations was  $\pm 0.015$  units. The results are listed in Table II. A plot of  $\log K/K_0$  of the ionization of the *m*- and *p*-substituted phenylpropionic acids in 50% aqueous ethanol against Hammett sigma values showed the expected linearity. The slope of the line calculated by the method of least squares is  $+0.69$  (see Fig. 1).

(15) S. Glasstone, *Textbook of Physical Chemistry*, Second Edition, D. Van Nostrand Co., Inc., New York, N. Y., 1946, p. 1003.

*C. Kinetic measurements.* The reaction was followed by measuring the rate of evolution of carbon monoxide.

1. *Apparatus.* The reaction flask was a 35-ml. or 50-ml. round bottom flask with a wide neck (20 mm. OD) which was 180 mm. long. The flask was fitted with a 19/38 tapered joint and a side arm of 1 mm. bore capillary tubing. A 13 mm. tube closed at the lower end and with a 19/38 tapered joint in the center extended to the bulb of the flask. A tungsten hook was sealed into the lower end of the tube. A sample cup (13 mm. OD  $\times$  19 mm. long) was fitted with a platinum loop so that it could be suspended from the tungsten hook.

The flask was supported in the constant temperature bath by means of a clamp which was attached to a shaking device. The sample cup dropped from the hook into the flask when operation of the shaker was started.

The capillary side arm of the reaction flask was connected to a cooling coil which in turn was connected (using capillary tubing) by way of a three-way stopcock to a Fisher Precision Hempel Gas Burette. One of the side arms of the three-way stopcock served as a vent to the atmosphere.

2. *Kinetic experiments.* A typical run was carried out as follows. Two millimoles of tetracyclone and 10 ml. of phenylcyclohexane were placed in the reaction flask. Three car-

borundum boiling chips were added. The flask was flushed with nitrogen. It was then stoppered with a 19/38 tapered cap and placed in the constant temperature bath. The side-arm of the flask was connected to the cooling coil. Twenty min. were allowed for the flask to reach the temperature of the bath (separate experiments had shown that 13 min. were adequate) with the flask vented to the atmosphere by way of the three-way stopcock. At the end of this time, the three-way stopcock was adjusted so that the flask was connected to the gas burette. Mercury was the confining liquid in the gas burette.

When the volume in the gas burette had remained constant for 0.5 hr., the cap on the reaction flask was replaced by the jointed tube and the pendant sample cup which contained 2 mmoles of the substituted methyl phenylpropiolate. After an additional 15 min., the initial volume was recorded and the timer and the shaker were started simultaneously. The sample cup dropped into the reaction flask when the shaker was started. Volume readings were taken at one-minute intervals initially, but at longer intervals at the reaction proceeded. Errors in volume readings were minimized by a preliminary equalization of the pressures of the system and the compensating tube just before the final reading was to be taken. Then the stopcock was closed again, the pressures were equalized exactly and the volume recorded. The reaction was followed to 80–94% completion. About 80 readings were taken during each run and used in the calculation of the specific rate constant. A portion of these readings for the reaction between tetracyclone (2 mmole) and methyl phenylpropiolate (2 mmole) in phenylcyclohexane (10 ml.) at 175.6° are shown for a typical run:

$t$ , min.	Vol. CO, ml.	$t$ , min.	Vol. CO, ml.
0.00	4.50	140.00	40.00
20.00	18.05	160.00	41.32
40.00	25.65	180.00	42.20
59.00	30.31	200.00	42.95
80.00	33.90	220.00	43.72
100.00	36.50	240.00	44.50
120.00	38.50	Infinity	53.50 (calcd.)

The rate constants for the Diels-Alder reaction of the esters are listed in Table II. Each rate constant is the average of two or more runs.

Rate constants are expressed in terms of molalities rather than molarities because of the uncertainty of the volume of the solution at 175.6°. Assuming that the density of the solution at 175.6° is the same as that of the phenylcyclohexane at 175.6° (0.82 g./ml.), the specific rate constants in units of sec.<sup>-1</sup> molar<sup>-1</sup> are 10% greater than the specific rate constants (sec.<sup>-1</sup> molal<sup>-1</sup>) reported in this study. This difference does not affect the relative values of the rate constants. The same values are found for the Hammett rho constant and for the energies of activation regardless of the concentration units used for the specific rate constants. An error in the energy of activation could result because the change of about 2% in the molar concentration due to the 30° change in temperature produces a corresponding error in the specific rate constant. The error in log  $k$  (from which energy of activation is derived) is less than the error in  $k$ .

The second order rate constants were obtained graphically from a plot of  $1/V_{\infty} - V_t$  vs.  $t$ , where  $V_{\infty}$  is the final volume of carbon monoxide and  $V_t$  is the volume at time,  $t$ . Straight line relations were observed in all instances.  $V_{\infty}$  could not be determined conveniently experimentally because it increased slowly for several days. Accordingly, it was calculated from successive fractional lives by the following method.

3. *Calculation of the final reading.* In the second order reaction in which the reactants are present in equivalent amounts,

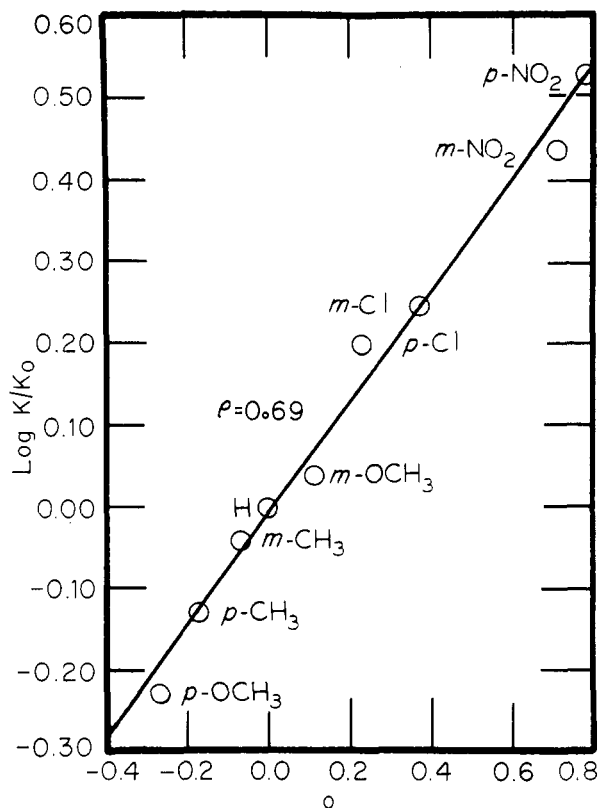


Fig. 1. Relationship between log  $K/K_0$  for substituted phenylpropionic acids and Hammett's  $\sigma$ -constants

$$kt = \frac{1}{c} - \frac{1}{c_0} = \frac{1}{x_{\infty} - x} - \frac{1}{x_{\infty}} \quad (2)$$

where  $x$  is the amount by which the concentration of a product has increased since  $t = 0$ , and  $x = 0$  at  $t = 0$ . Suppose  $x$  is experimentally known as a function of  $t$  over some limited time interval. Equation (2) will apply if the  $x$ ,  $t$  axes are translated so that the experimental curve begins at the origin. Suppose that in the time interval  $(0, t_1)$  the reaction concentration falls to the fraction  $\alpha$  of its initial value, and in the interval  $(t_1, t_2)$  again falls to the same fractional amount so that  $c_1 = \alpha c_0$ ,  $c_2 = \alpha^2 c_0$ ,  $x_1 = c_0(1 - \alpha)$ , and  $x_2 = c_0(1 - \alpha^2)$ . Then  $x_2/x_1 = 1 + \alpha$ ; and, from (2),  $t_2/t_1 = 1 + 1/\alpha$ . These relations may be used to evaluate  $x_{\infty}$  and hence  $k$ , as follows. For an arbitrarily chosen  $\alpha$ , a value of  $t_1$  is estimated from the graph. Then  $t_2$  is calculated from the last equation. The corresponding value of  $x$  is read from the graph and is compared with  $x_2 = x_1(1 + \alpha)$ . Successive approximations of  $t_1$  are made until consistent values are obtained. Now  $x_{\infty}$  is given by  $x_1/(1 - \alpha)$  and values of  $k$  may be calculated from Equation 2.

In the present work  $x_{\infty}$  was calculated for  $\alpha = 0.5$  and checked for values of  $\alpha$  equal to 0.6 and 0.7. The agreement was excellent.

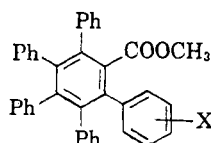
4. *Isolation of products.* Methyl pentaphenylbenzoate was filtered from the reaction mixtures from several runs. The yield of ester, m.p. 341–342° (rep. m.p. 342°<sup>27</sup>) was 80.3%. An additional 18% of ester was obtained by concentration of the filtrates.

The remaining esters were prepared by heating one equivalent of tetracyclone with 1.1 equivalents of substituted phenylpropionic ester at 175° overnight. The properties are recorded in Table III.

## RESULTS

A plot of log  $K/K_0$  of the ionization of the  $m$ - and

TABLE III  
PHYSICAL PROPERTIES OF METHYL 2-ARYL-3,4,5,6-TETRAPHENYLBENZOATES



X	M.P., °C.	Carbon, %		Hydrogen, %		Other Element, %	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
<i>m</i> -CH <sub>3</sub>	306-307	88.00	87.95	5.83	6.09		
<i>p</i> -CH <sub>3</sub>	297-298	88.00	87.88	5.83	5.91		
<i>o</i> -Cl	331-332	82.44	82.46	5.05	5.03	6.58	6.25
<i>m</i> -Cl	309-310	82.44	83.05	5.05	5.05	6.58	6.43
<i>p</i> -Cl	284-285	82.44	82.51	5.05	5.08	6.58	6.72
<i>m</i> -NO <sub>2</sub>	260-261	80.86	81.21	4.95	5.04	2.49	2.40
<i>p</i> -NO <sub>2</sub>	272-274	80.86	81.15	4.95	5.13	2.49	2.55
<i>m</i> -OCH <sub>3</sub>	255-256	85.37	85.54	5.66	5.36		
<i>p</i> -OCH <sub>3</sub>	256-257	85.37	85.70	5.66	5.62		

*p*-substituted phenylpropionic acids in 50% aqueous ethanol against Hammett  $\sigma$  constants showed the expected linearity. The value of the constant obtained from the slope by the method of least squares was +0.69. The correlation coefficient,<sup>16</sup>  $r$ , was 0.99, the standard deviation,<sup>16</sup>  $s$ , was 0.03, and  $n$  was 9. Newman and Merrill<sup>17</sup> obtained a  $\rho$  constant of +0.81 from their measurements in 35% dioxane.

Our relative acid strengths, expressed as  $\log K/K_0$ , correspond closely to those reported by Newman and Merrill<sup>17</sup> for these same acids in 35% aqueous dioxane.

The logarithms of the rate constants have been plotted against  $\log K/K_0$ . The slope of the line calculated by the method of least squares is +1.10, with  $r = 0.97$ ,  $s = 0.07$ , and  $n = 9$  (see Fig. 2). Rates for the *o*-chloro ester were omitted in the calculation of the rho value.

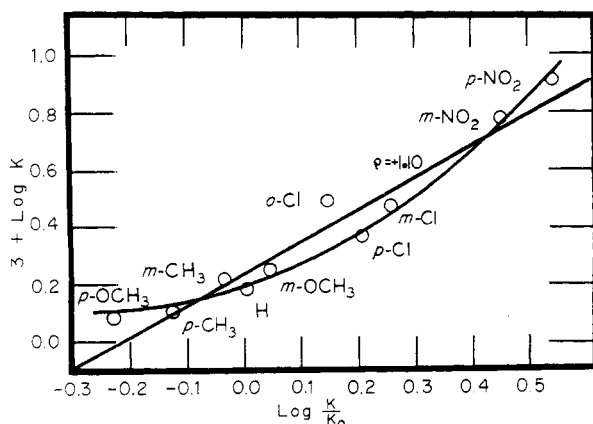


Fig. 2. Relationship between  $\log k$  and  $\log K/K_0$  for substituted phenylpropionic acids

Specific rate constants of the methyl esters of the *o*- and *p*-chlorophenylpropionic acids were deter-

(16) H. H. Jaffe, *Chem. Revs.*, **53**, 191 (1953).

(17) M. S. Newman and S. H. Merrill, *J. Am. Chem. Soc.*, **77**, 5552 (1955).

mined at three temperatures in order to permit calculation of the energies and entropies of activation. Results are shown in Table IV.

TABLE IV  
SPECIFIC RATE CONSTANTS (MOLAL<sup>-1</sup> SEC.<sup>-1</sup>) AT VARIOUS TEMPERATURES FOR THE REACTION BETWEEN METHYL CHLOROPHENYLPROPIOLATES AND TETRACYCLONE

Subst.	$t$ , °C.	1000 k
<i>o</i> -Cl	166.5	1.93
	175.6	2.97
	196.0	7.17
<i>p</i> -Cl	166.2	1.49
	175.6	2.25
	195.2	5.65

Energies and entropies of activation calculated from the data in Table IV are recorded in Table V. The entropy of activation was calculated in accordance with the usual equations<sup>18</sup>

$$k = Ae^{-E_a/RT} \quad \text{and} \quad A = e^{\frac{kT}{h}} e^{\Delta S^\ddagger/R}$$

TABLE V  
ENERGIES AND ENTROPIES OF ACTIVATION TETRACYCLONE WITH METHYL ESTERS OF *o*- AND *p*-CHLOROPHENYLPROPIOLIC ACID

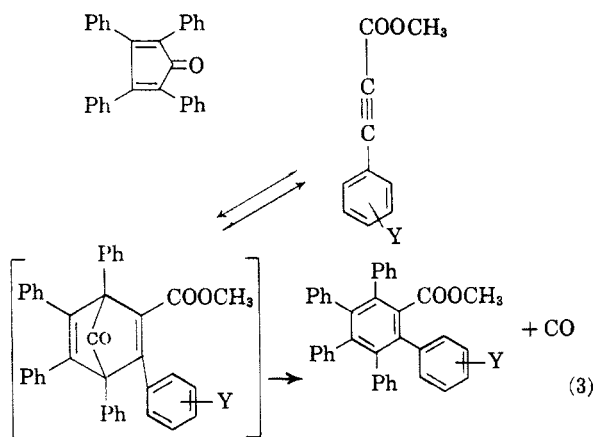
	<i>o</i> -Cl	<i>p</i> -Cl
$E_a$ , Kcal. mole <sup>-1</sup>	18.2 <sup>a</sup>	18.9 <sup>a</sup>
$\log_{10} A$ , sec. <sup>-1</sup> , molal <sup>-1</sup>	6.3	6.6
$\Delta S^\ddagger$ at 175.6°C., e.u. <sup>b</sup>	-32.3	-31.3
$\Delta S^\ddagger$ at 175.6°C., e.u. <sup>c</sup>	-18.6	-17.6

<sup>a</sup> Correlation coefficients,<sup>16</sup>  $r$ , and standard deviations,<sup>16</sup>  $s$ ; *o*-Cl,  $r = 1.000$ ,  $s = 0.00$ ,  $n = 3$ ; *p*-Cl,  $r = 0.996$ ,  $s = 0.035$ ,  $n = 3$ . <sup>b</sup> Standard state of 1 molal solution. <sup>c</sup> Standard state of 1 mole per gram of solvent.

(18) S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes*, McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 199, 417.

## DISCUSSION

There is no drift in second-order rate constants in reactions followed up to 94% completion. This result is consistent with either the formation of the adduct in the rate-determining step, followed by rapid elimination of carbon monoxide, or the formation of the adduct by a rapid equilibrium followed by the elimination of carbon monoxide in the rate-determining step (Equation 3). These



two alternatives are kinetically indistinguishable by merely measuring the rate of evolution of carbon monoxide.<sup>19</sup> However, the first alternative is favored because the energies and entropies of activation of the reaction are comparable to those found in typical Diels-Alder reactions.<sup>20</sup> In the study of a Diels-Alder reaction in which hydrogen was eliminated from the adduct, Jarvie and Janz<sup>21</sup> also found that the kinetic parameters fell within the range for typical Diels-Alder association reactions. The absence of a marked difference in the entropies of activation found in this study from those of Diels-Alder reactions between simpler adducts is surprising in view of the presence of the phenyl groups in tetracyclone. This result, however, is in accordance with Wassermann's conclusion<sup>22-24</sup> that the transition state is non-planar.

The reactivities of the esters of the meta- and para-substituted phenylpropionic acids are in the order expected from the values of the sigma constants of the corresponding acids. The positive sign means simply that the reaction is accelerated by electron-withdrawing substituents. The rates are in the same sequence as the corresponding sigma values except for *m*-CH<sub>3</sub> and *o*-Cl. With *m*-methyl the substituted ester is more reactive than

the unsubstituted one. Jaffe<sup>16</sup> has noted that substituent constants may vary due to polarizability effects, and that occasionally, *m*-methyl substituents appear to be electron-attracting. In a study of the chlorination of *p*-(substituted benzyloxy)benzoic acids, Jones<sup>25</sup> found that the *m*-methyl group produced a greater acceleration of the reaction than the *p*-methyl group did.

With *o*-Cl the  $\sigma$  value is in line when compared with the unsubstituted ester. However, when compared with the *m*- and *p*-Cl compounds, it is out of line, being too rapid. Increases in the rate of acid hydrolysis<sup>17</sup> and in the rate of basic hydrolysis<sup>26</sup> of substituted phenylpropionic esters have also been observed previously.

The points on the Hammett plot appear to exhibit a systematic curvature. Swain and Langsdorf<sup>27</sup> noted this curvature in polar reactions and attributed it to differences in the effectiveness of resonance interactions between the substituents and reacting center in the transition states. In the present study, the rate of reaction is greater than the expected value for both the *p*-nitro- and the *p*-methoxy-substituted esters. The effect observed here may be due to a solvent effect or to polarizability of the triple bond by strongly electron-attracting or electron-withdrawing groups. The curvature of the plot may be due to the electro-negativity of the triple bond<sup>28,29</sup> resulting in unequal interactions with positive and negative substituents. This can be determined from a pending study of substituted cinnamic esters with tetracyclone. (Wolinski<sup>30</sup> reports that pentaphenylbenzoic acid is formed, presumably with the loss of both carbon monoxide and hydrogen, from the reaction between tetracyclone and cinnamic acid.)

DeWitt, *et al.*,<sup>5</sup> noted a curvature in a Hammett plot for the reaction between substituted 1-phenylbutadienes with maleic anhydride in dioxane. They attributed this curvature to the polarizability of the *p*-methoxy group. The Hammett rho value of the reaction at 25° was -0.685. Okamoto and Brown<sup>31</sup> showed that DeWitt's data fitted a plot of  $\log k$  vs.  $\sigma^+$  much better than a plot of  $\log k$  vs.  $\sigma$ . ( $\sigma^+$  is the substituent constant applicable to electrophilic reactions.) On the basis of this result, Okamoto and Brown concluded that the Diels-Alder reaction proceeds by the radical-ion-pair mechanism which was postulated by Woodward.<sup>32</sup>

(19) A. A. Frost and R. G. Pearson, *Kinetics and Mechanism*, John Wiley & Sons, Inc., New York, N. Y., 1953, pp. 179-182.

(20) Footnote 19, p. 101.

(21) J. M. S. Jarvie and G. J. Janz, *J. Phys. Chem.*, **60**, 1430 (1956).

(22) A. Wassermann, *J. Chem. Soc.*, 828 (1935).

(23) A. Wassermann, *J. Chem. Soc.*, 612 (1942).

(24) W. Rubin and A. Wassermann, *J. Chem. Soc.*, 2205 (1950).

(25) B. Jones, *J. Chem. Soc.*, 1835 (1935).

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One would expect a correlation of the reactivity of the dienophile with Hammett (nucleophilic)  $\sigma$  values to go hand in hand with correlation of the reactivity of the diene with electrophilic  $\sigma^+$  values. Moreover, reactions which are known to proceed by a free-radical mechanism have been correlated with the Hammett equation.<sup>33</sup> In some cases the substituent effects are quite large. The difference between a primary radical mechanism with secondary electronic effects on one hand and a radical-ion mechanism on the other is a matter of degree rather than of kind. Therefore, a clear-cut decision between them is not possible. This result is consistent with current interpretations of the electronic processes involved in a reaction proceeding through a cyclic transition state.

The reactivity of the *o*-chloro ester is greater than would be expected from the value of the sigma constant of the corresponding acid. The energies

and entropies of activation for the *o*- and *p*-chloro esters are very similar and do not shed any light on the cause of this effect. Enhanced reactivities of the ortho derivatives were also noted by Newman and Merrill<sup>17</sup> for the esterification of substituted phenylpropionic acids. Roberts and Carboni<sup>26</sup> found that the saponification rates of the *o*-esters are rather faster than would be expected from the rates and ionization constants of the *m*- and *p*-substituted acids although the rates of reaction of the *o*-acids with diphenyldiazomethane in ethanol and in dioxane fit the Hammett plot very well. The reason for the enhanced activities of the *o*-esters on the Diels-Alder reaction and in esterification and hydrolysis reactions is not known.

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BROOKLYN 1, N. Y.

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(33) J. E. Leffler, *The Reactive Intermediates of Organic Chemistry*, Interscience Publishers, Inc., New York, N. Y., 1956, pp. 238-241.