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ELECTRONIC EFFECTS AND RATES IN THE DIELS-ALDER REACTION

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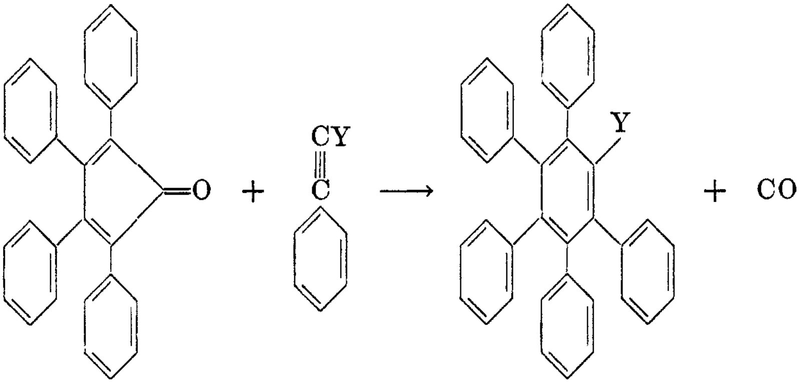
The kinetics of the Diels-Alder reaction has been the subject of an intensive investigation (1). Theories of electronic effects, however, have so far been employed only to interpret the structure of adducts between unsymmetrical dienes and dienophiles (2–6); they have not been applied to kinetic studies. It is the purpose of this paper to report the results of a preliminary investigation to apply a theory of electronic effects to the reaction rates of Diels-Alder reactions.

The reaction chosen for study is that between tetracyclone (tetraphenylcylopentadienone) and acetylenic dienophiles. These reactions proceed smoothly to give high-melting products in 80–90% yields (7–13). The progress of the reaction can be conveniently followed by determining the carbon monoxide which accompanies the reaction. In addition, Y may be changed so as to vary the polarity of the triple bond systematically.



Accordingly, phenylacetylenes in which Y = H, CH_3, CH_2OH, CHO, CO_2H, and CO_2CH_3, were each refluxed with tetracyclone in *p*-cymene or toluene until carbon monoxide was no longer evolved. The adducts were readily isolated by distilling the *p*-cymene or toluene with steam and crystallizing the crude products from a suitable solvent. In the case of the hitherto unreported pentaphenyltoluene and pentaphenylbenzyl alcohol the ultimate analyses were in accord with the expected ones. Pentaphenylbenzyl alcohol was also converted to its acetate and pentaphenylbenzaldehyde was derivatized as the 2,4-dinitrophenylhydrazone. During the reaction using phenylpropiolic acid carbon dioxide was evolved as well as carbon monoxide. Tetracyclone probably did not influence this reaction since carbon dioxide was detected when a sample of phenylpropiolic

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[1] Taken from a thesis submitted by J. J. D. to the Graduate Faculty in partial fulfillment of the requirements for the degree of Master of Science.

TABLE I

RELATIVE RATES OF REACTION BETWEEN $PhC{\equiv}CY$ AND TETRACYCLONE

Y	MOLES[a]	SOLVENT	TIME FOR DECOLORIZATION, HOURS	YIELD, %
H	.05	Cymene	2	68
	.03	Toluene	11	85.5
CO_2H	.03	Cymene	2.25	16.5[b] 35.6[c]
	.03	Toluene	12	20[b] 27.5[c]
CH_3	.03	Cymene	80	81.7
CH_2OH	.03	Cymene	39.5	80
CO_2CH_3	.03	Cymene	12	89
CHO	.03	Cymene	9	81.2

[a] An equal number of moles of tetracyclone was used. [b] This is yield of pentaphenylbenzoic acid. Carbon dioxide was evolved as well as carbon monoxide. [c] This is the yield of pentaphenylbenzene.

TABLE II

PHYSICAL CONSTANTS OF SUBSTITUTED PENTAPHENYLBENZENES

Y	M.P., °C.	SOLVENT	ANALYSES					
			C		H		N	
			Calc'd	Found	Calc'd	Found	Calc'd	Found
H	251[a]	Acetic acid						
CO_2H	357.5–358.5[b]	Acetic acid						
CH_3	284	Acetic acid	94.05	93.91	5.95	5.95		
CH_2OH	296	*n*-Butanol	90.95	90.82	5.78	5.63		
CH_2OCOCH_3	311	Xylene	88.27	87.75	5.70	5.50		
CHO	265[c]	Acetic acid						
$CH{=}NNHC_6H_3(NO_2)_2$ =*2,4*	294		77.44	77.53	4.53	4.54	8.40	8.61
$COOCH_3$	342[d]	*p*-Cymene						

[a] Reference (14) reports m.p. 251°. [b] Reference (7) reports m.p. 345°. [c] Reference (8) reports m.p. 263–265°. [d] Reference (9) reports m.p. 342°.

TABLE III

DIPOLE MOMENTS OF C_6H_5Y

Y	$\mu \times 10^{18}$	REFERENCE
CH_3	0.4	16
CH_2OH	1.72[a]	17
CO_2H	1.78	18
CO_2CH_3	2.06	16
CHO	2.75	16

[a] An average value.

acid was refluxed alone in *p*-cymene or in toluene. This side reaction may account for the low yields obtained. Dilthey (7, 9) has not reported this partial decarboxylation. The results of the experiments are summarized in Tables I and II.

TABLE IV

ABSORPTION MAXIMA OF C_6H_5Y AND $C_6H_5C{\equiv}CY$

Y	DOUB AND VANDENBELT (19) C_6H_5Y		CAMPBELL, *et al.*, (20)	THIS WORK $C_6H_5C{\equiv}CY$
	λ_1, mμ	λ_2, mμ	mμ	mμ
H	203.5	254		234
CH_3	206.5	261	262	237
CH_2OH			258.5	238.5
CO_2H	230	273		247
CO_2CH_3				255
CHO	249.5	—		263.5

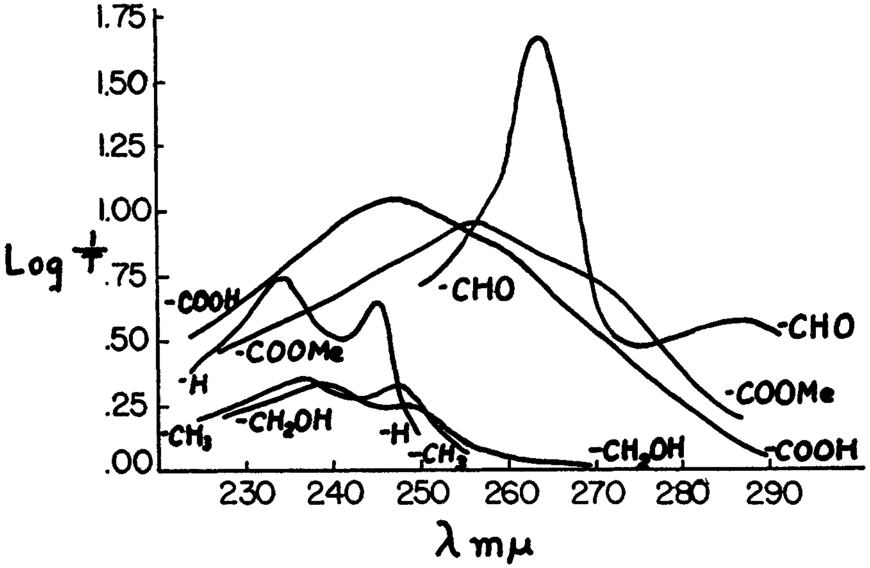


FIG. 1. ULTRAVIOLET ABSORPTION SPECTRA OF $PhC{\equiv}CY$ where Y = H, CH_3, CH_2OH CHO, CO_2H, and CO_2CH_3.

The data of Table I lead to the conclusion that the relative rates of reaction are governed by the electronegativities of the groups Y: the greater the electron-withdrawing character of Y, the faster is the rate. The dipole moments of the groups Y when attached to a benzene ring are listed in Table III for comparison with the rates in Table I.

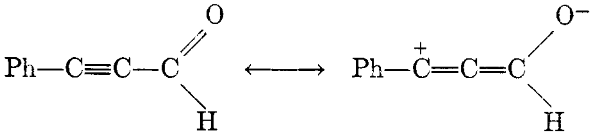
The rapid reaction with phenylacetylene may be due partially to its smaller size and partially due to acid catalysis (15). With phenylpropiolic acid the rapid rate may be due to acid catalysis because an examination of Fisher-Hershfelder models shows no large differences in size of the groups Y except when Y = H.

It was of interest to see whether the results of this investigation could be correlated with the work of Doub and Vandenbelt (19) wherein values were obtained for the displacing effect associated with directional displacement of electrons to or from the benzene ring depending on the character of the groups. These values were expressed in terms of the shift of the ultraviolet absorption maxima. This same type of shift in the absorption maximum was observed with the acetylenic dienophiles studied here. Their absorption spectra were determined in methanol solution, employing a Carey Recording Spectrophotometer, over the range 205–295 mμ. The intensity of the shift was found to be as follows for the pertinent compounds (table IV and Figure 1):

$$CHO > CO_2CH_3 > CO_2H > CH_2OH > CH_3.$$

The fact that 1-phenyl-1-propyne and 3-phenyl-2-propyn-1-ol exhibit two absorption maxima does not detract from the main argument since the absorption maxima of the latter are shifted bathochromically with respect to those of the former.

The above data are consistent with either the cationoid-anionoid (6, 21–23) or the ion-molecule pair (24) mechanisms for the Diels-Alder reaction. Thus, a transitory electronic structure for the acetylenic dienophile may be presumed which reacts with the tetracyclone.



EXPERIMENTAL[2]

All temperatures are corrected.

Starting materials. These were prepared according to established procedures save for 3-phenyl-2-propyn-1-ol, so that only physical constants are given herein. Tetracyclone (25) melted at 219–220°. Dibenzyl ketone boiled at 166–167° (10 mm.), m.p. 34.5–35.0°. Phenylacetylene (b.p. 142–144°), phenylpropiolaldehyde [b.p. 86–87° (5 mm.); n_D^{20} 1.6025], and phenylpropiolic acid, m.p. 135.5–136.5°, were prepared according to references 26, 27, and 28, respectively. Methyl phenylpropiolate was prepared by treating phenylpropiolic acid with diazomethane, b.p. 139–141° (25 mm.), n_D^{30} 1.557 [reported (29), b.p. 132–133° (16 mm.), n_D^{25} 1.5618]. 1-Phenyl-1-propyne (b.p. 70–71° (12 mm.), n_D^{20} 1.560) was prepared according to Bogert and Davidson (30). The reported constants are b.p. 71–74° (15 mm.) (31), and n_D^{20} 1.5600 (32).

3-Phenyl-2-propyn-1-ol. Into a 300 ml., round-bottom flask fitted with a Hahn condenser were placed 11 g. (0.085 mole) of phenylpropiolaldehyde, 14 ml. (0.014 mole) of a molar solution of freshly distilled aluminum isopropoxide in 2-propanol, and 225 ml. of dry 2-propanol. The flask was heated on steam-bath and the contents refluxed until acetone could no longer be detected in the distillate, about four hours. The Hahn condenser was replaced with a condenser set for downward distillation and the 2-propanol was distilled at atmospheric pressure. After cooling to room temperature, the reaction mixture was hydrolyzed with

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[2] Analyses were carried out by Drs. Weiler and Strauss, 164, Banbury Road, Oxford, England.

cold, dilute hydrochloric acid (10 ml. of concentrated acid in 75 ml. of water), and then extracted with three 25-ml. portions of benzene. The combined benzene extracts were washed with 25 ml. of water, dried over sodium sulfate, and distilled, discarding the benzene and a small forerun, to give 7.3 g. (0.055 mole, 65%) of colorless 3-phenyl-2-propyn-1-ol, b.p. 129–130° (10 mm.), n_D^{25} 1.5873 [reported (33) b.p. 107° (2 mm.), n_D^{25} 1.5835].

This is the first time that the Meerwein-Ponndorf-Verley reduction has been applied to an acetylenic aldehyde. The relative ease of obtaining pure solvents, simple apparatus, and facile isolation of the product gives this procedure preference over other methods which have been reported for this compound: $PhC{\equiv}CMgBr + (CH_2O)_3$ (34), $PhC{\equiv}CMgBr + CH_2O$ (35), and that of Bert (36)—a five-step synthesis.

Reactions with tetracyclone. These reactions were performed in a similar manner; the reaction forming pentaphenylbenzene is described as being typical and the reaction forming pentaphenylbenzoic acid is described because of the two products obtained.

Pentaphenylbenzene. A mixture of 5.10 (0.050 mole) of phenylacetylene and 19.22 g. (0.050 mole) of tetracyclone in 130 ml. of *p*-cymene (washed with sulfuric acid to remove unsaturation) was refluxed in a flask fitted with a nitrogen inlet tube and a reflux condenser. Nitrogen was passed through the flask throughout the reflux. Zero time was taken as the first drop of reflux. The same flask, heating mantle and condenser were used throughout. Deliberate testing showed that the interval for heating to zero time was reproducible within 5 minutes. A strip of filter paper moistened with a 1% solution of palladium^{II} chloride was suspended in the effluent gas stream and immediately turned black. The strip was changed until, after 15 minutes' exposure, it was not darkened. At this time the solution was practically decolorized. Upon cooling to room temperature, crystals deposited and were filtered to give 12.3 g., m.p. 249–250°, after drying at 50°. The filtrate was distilled with steam, and the residue filtered, dried, washed with *n*-hexane, (m.p. 249–250°), combined with the previous crop and recrystallized from acetic acid to give 15.1 g. (0.033 mole, 66%) of pentaphenylbenzene, m.p. 251°.

Pentaphenylbenzoic acid. A solution of 11.53 g. (0.030 mole) of tetracyclone and 4.38 g. (0.030 mole) of phenylpropiolic acid was refluxed in 130 ml. of *p*-cymene. The effluent gases were bubbled through a solution of barium hydroxide and the gases emerging at that point were tested for carbon monoxide. A white, crystalline precipitate formed rapidly in the barium hydroxide solution.

The *p*-cymene solution was concentrated and allowed to cool giving a colorless precipitate which weighed 2.48 g. (4.94 mmole, 16.5%) after recrystallization from *p*-cymene, and melted at 357.5–358.5°. The mother liquors were combined and concentrated giving two crops of colorless crystals which after recrystallization weighed 4.90 g. (10.7 mmole, 35.6%) of pentaphenylbenzene, m.p. 251°. Steam-distillation of the filtrate afforded 7.52 g. of a light brown material which softened at 80° and melted widely. This was not examined further.

When a solution of phenylpropiolic acid was either heated above its melting point or refluxed in *p*-cymene, carbon dioxide was evolved as shown by a positive test with barium hydroxide solution.

Pentaphenylbenzyl acetate. Pentaphenylbenzyl alcohol was dissolved in an excess of acetic anhydride at 60°. Cooling gave colorless crystals which after recrystallization from xylene, melted at 311°.

Pentaphenylbenzaldehyde 2,4-dinitrophenylhydrazone was prepared from equivalent quantities of pentaphenylbenzaldehyde and 2,4-dinitrophenylhydrazine according to Shriner and Fuson (37); m.p. 294°.

SUMMARY

The Diels-Alder reaction between tetracyclone and phenylpropargylic derivatives has been investigated. It was found that the rates increased in the order named as CH_3, CH_2OH, CO_2CH_3, and CHO were substituted for Y in $PhC{\equiv}CY$.

These results are in accord with the usual mechanisms for the Diels-Alder reaction and also with the measured dipole moments and absorption spectra.

During the course of the research several new compounds were synthesized: pentaphenyltoluene, pentaphenylbenzyl alcohol and its acetate, and the 2,4-dinitrophenylhydrazone of pentaphenylbenzaldehyde. The Meerwein-Ponndorf-Verley reaction has been successfully applied in the reduction of phenylpropiolaldehyde to 3-phenyl-2-propyn-1-ol.

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