

INTERRELATION OF ADDITION REACTIONS  
OF HEXACHLOROCYCLOPENTADIENE AND BROMINE  
TO N-ARYLIMIDES OF ENDO- AND  
EXO-BICYCLO[2,2,1]HEPT-5-ENE-2,3-DICARBOXYLIC ACIDS

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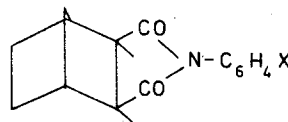
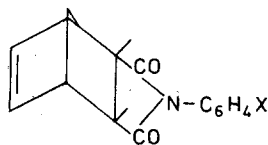
Received July 5, 1982

Accepted November 17, 1982

A comparative analysis of the relative reactivities of N-arylimides of endo- and exo-bicyclo[2,2,1]hept-5-ene-2,3-dicarboxylic acids for the addition reactions of hexachlorocyclopentadiene and bromine has been carried out. According to different correlations the transition states of these two processes are shown to be similar.

Проведён сопоставительный анализ относительных реакционных способностей N-арлимидов эндо- и экзо-бицикло [2,2,1] гепт-5-ен-2,3-дикарбоновых кислот в реакциях присоединения гексахлорциклопентадиена и брома. На основании различных корреляционных соотношений показана близость переходных состояний этих двух процессов.

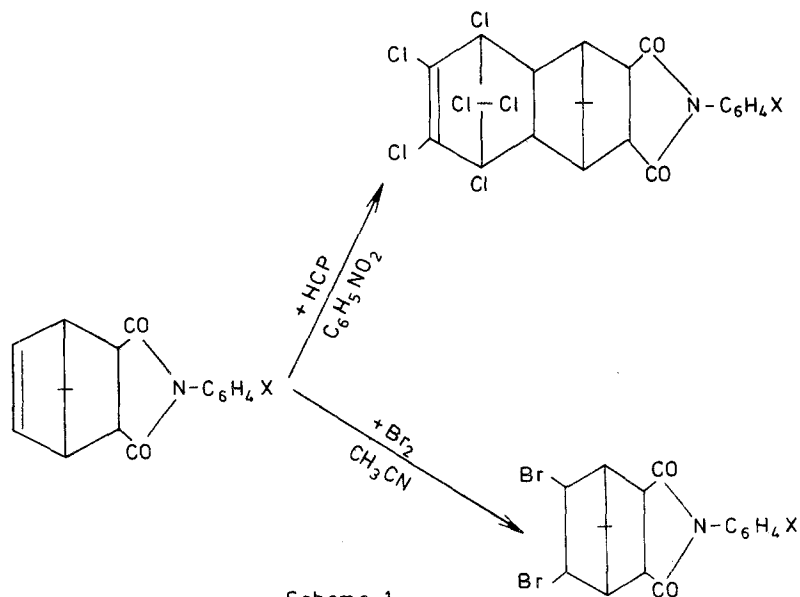
For the first time we have made an attempt to elucidate the general and distinctive properties of the addition of hexachlorocyclopentadiene (HCP) and bromine to N-arylimides of endo- (Run I) and exo- (Run II)-bicyclo[2,2,1]hept-5-ene-2,3-dicarboxylic acids having the structures:



where

X = p-OH (I), p-CH<sub>3</sub>O (II), p-CH<sub>3</sub> (III), H (IV), m-CH<sub>3</sub>O (V), p-Cl (VI), p-Br (VII), m-COOH (VIII), m-Cl (IX), p-NO<sub>2</sub> (X).

Results of kinetic investigations for these two reactions (Scheme 1) have been reported previously /1-6/.



The kinetics of addition reactions of HCP and bromine was studied in nitrobenzene at 393–423 K and acetonitrile at 233 to 283 K, respectively.

By the extrapolation of experimental data /2, 3/, the logarithms of rate constants for the addition reactions of HCP ( $\lg k_{\text{HCP}}$ ) and bromine ( $\lg k_{\text{Br}_2}$ ) at 298 K were obtained.

Data of Table 1 indicate a parallelism in the rates of these reactions, apparently due to the resemblance of electron demands in both cases: electron-donating substituents in aromatic nuclei of imides (I–IV) increase the rate of both reactions, whereas electron-accepting ones (VI–X) decrease it.

Presumably, the greater reactivity of bromine (by a factor of  $10^9$ ) compared with HCP in the experimental runs (Table 1) can be attributed to the greater electron affinity of molecular bromine ( $E_A = 1.48$  eV /5/ compared to HCP  $E_A = 0.62$  eV /6/) and to the lower molecular volume of the former, which facilitates its approach to the reaction center in the formation of a non-classical bromonium complex.

A comparative analysis of the absolute values of reaction constants ( $\rho$ ) for N-arylimides (I–X) provides evidence in favor of the proximity of the transition states of both cycloaddition reactions.

Table 1  
 Logarithms of rate constants for cycloaddition reactions of HCP\* and bromine\*\* to H-arylimides  
 of endo- and exo-bicyclo[2,2,1]hept-5-ene-2,3-dicarboxylic acids at 298 K

Nos	Substituent X	Run I			Run II		
		lg (k <sub>x</sub> )HCP	lg (k <sub>x</sub> )Br <sub>2</sub>	lg (k <sub>x</sub> )Br <sub>2</sub> / (k <sub>x</sub> )HCP	lg (k <sub>x</sub> )HCP	lg (k <sub>x</sub> )Br <sub>2</sub>	lg (k <sub>x</sub> )Br <sub>2</sub> / (k <sub>x</sub> )HCP
I	p-OH	-7.84	0.83	8.77	-7.46	1.12	8.58
II	p-CH <sub>3</sub> O	-7.93	0.70	8.63	-7.61	0.96	8.57
III	p-CH <sub>3</sub>	-8.07	0.60	8.67	-7.69	0.87	8.56
IV	H	-8.18	0.48	8.66	-7.82	0.78	8.60
V	m-CH <sub>3</sub> O	-8.21	0.46	8.55	-7.88	0.68	8.49
VI	p-Cl	-8.34	0.31	8.65	-7.98	0.56	8.54
VII	p-Br	-8.40	0.29	8.69	-8.01	0.55	8.56
VIII	m-COOH	-8.45	0.19	8.64	-8.13	0.46	8.64
IX	m-Cl	-8.54	0.13	8.67	-8.14	0.45	8.60
X	p-NO <sub>2</sub>	-8.85	-0.24	8.61	-8.53	0.05	8.58

\*In nitrobenzene

\*\*In acetonitrile

Table 2

Parameters of the Hammett and correlation equations  $y = ax + b$  describing the interrelation of the rate constants for the addition reactions of HCP and bromine to N-arylimides of endo- and exo-bicyclo[2,2,1]hept-5-ene-2,3-dicarboxylic acids at 298 K

Runs	x	y	a( $\rho$ )	b(lg $k_0$ )	r <sup>a</sup>	S <sup>b</sup>	n <sup>c</sup>
I	$\delta$	lg ( $k_x$ ) <sub>HCP</sub>	(-0.869±0.035)	(-8.170±0.004)	0.993	0.036	10
	$\delta$	lg ( $k_x$ ) <sub>Br<sub>2</sub></sub>	(-0.897±0.036)	( 0.489±0.004)	0.994	0.037	10
	lg ( $k_x$ ) <sub>Br</sub>	lg ( $k_x$ ) <sub>HCP</sub>	0.968±0.018	-8.644±0.007	0.999	0.017	10
II	$\delta$	lg ( $k_x$ ) <sub>HCP</sub>	(-0.889±0.026)	(-7.812±0.003)	0.996	0.027	10
	$\delta$	lg ( $k_x$ ) <sub>Br<sub>2</sub></sub>	(-0.879±0.041)	( 1.085±0.005)	0.992	0.042	10
	lg ( $k_x$ ) <sub>Br<sub>2</sub></sub>	lg ( $k_x$ ) <sub>HCP</sub>	1.005±0.021	-8.576±0.014	0.998	0.019	10

<sup>a</sup>Correlation coefficient; <sup>b</sup>Standard deviation; <sup>c</sup>Number of measurements

As is seen from Table 2,  $\rho$  changes only slightly upon going from the reactions of cycloadditions with HCP to those of bromination. This fact is in agreement with the conclusion resulting from the interpretation of  $\rho$  as a characteristic of the transition state, implying that under identical conditions the reactions proceeding through similar transition states, should have similar values of  $\rho$  /7/.

Quantitative studies of these two cycloaddition reactions permit to derive an equation of their interrelation. This equation was found from the kinetic data of Table 1 by the least-squares method. The parameters of this relationship are given in Table 2. Excellent correlation coefficients of the dependences  $\lg(k_x)_{Br_2} - \lg(k_x)_{HCP}$  for both experimental runs indicate the validity of the interrelation for these two cycloaddition reactions.

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