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Diels–Alder Reaction of *para*-Substituted Allyl and 2-Propynyl Benzoates with Hexabromo- and Tetrabromo-5,5-dimethoxy-1,3-cyclopentadienes

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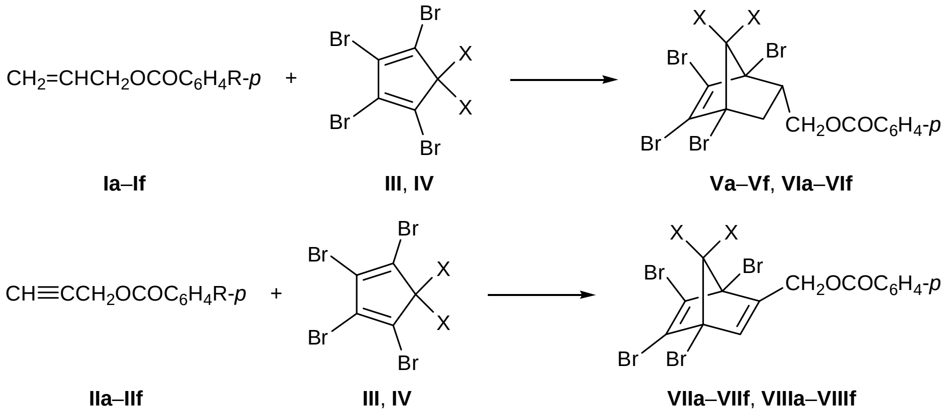
Abstract—*para*-Substituted 2-propynyl benzoates are more reactive than the corresponding allyl esters in the Diels–Alder reactions with hexabromo- and tetrabromo-5,5-dimethoxy-1,3-cyclopentadienes. The cycloaddition is favored by the presence of both electron-donor and electron-acceptor substituents in the aromatic ring, in keeping with the “neutral” reaction scheme. The reactivity of the addends is likely to be determined not only by their donor–acceptor properties but also by the localization energy.

The reactivity of addends in Diels–Alder reactions is commonly interpreted in terms of donor–acceptor interactions which are quantitatively estimated through the stabilization energy [1–5]; for this purpose, pair interactions between all occupied orbitals of one reagent and vacant orbitals of the other are considered. Three types of Diels–Alder reactions are distinguished [6]. Reactions in which diene acts as donor while dienophile acts as acceptor are governed by the interaction between the highest occupied molecular orbital (HOMO) of the diene and lowest unoccupied molecular orbital (LUMO) of the dienophile (the process is favored by the presence of donor substituents in the diene and acceptor substituents in the dienophile). In reactions where diene acts as acceptor, and dienophile as donor, the determining interaction is that between the LUMO of the diene and HOMO of the dienophile; here, the reactivity of the system increases when the dienophile contains donor substituents and the diene contains acceptor groups. Reactions following the “neutral” scheme involve both kinds of the HOMO–LUMO interactions between the addends; donor and acceptor substituents in the 4π and 2π components weaken one HOMO–LUMO interaction and enhance

Scheme 1.



I–**VIII**, R = OMe (**a**), Me (**b**), H (**c**), Cl (**d**), Br (**e**), NO_2 (**f**); **III**, **V**, **VII**, X = Br; **IV**, **VI**, **VIII**, **X =** OMe.

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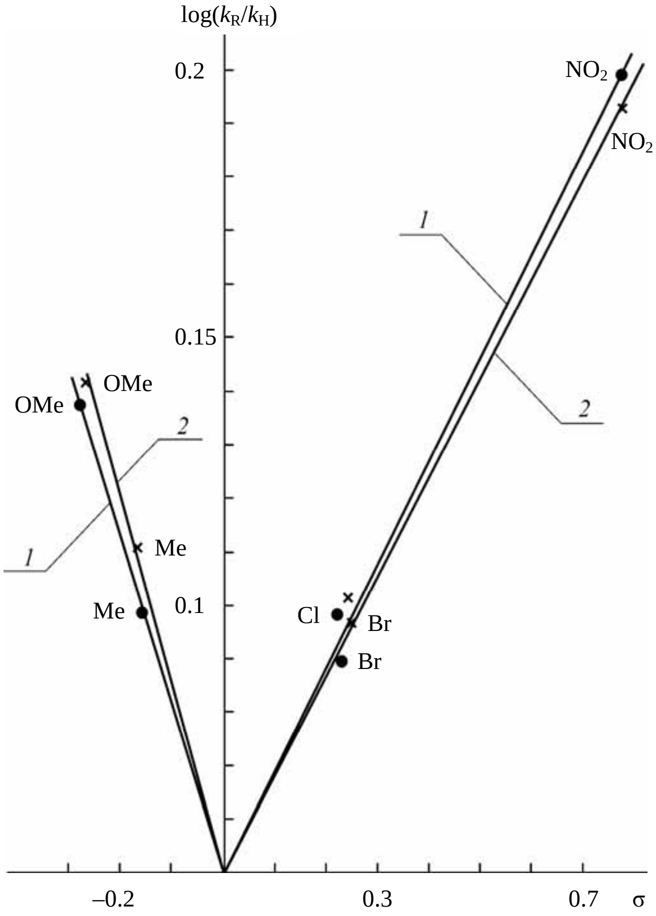

Fig. 1. Correlation between the reactivity of esters **Ia**–**If** and Hammett substituent constants σ (chlorobenzene, 110°C): (*1*) reaction with diene **III**, (*2*) reaction with diene **IV**.

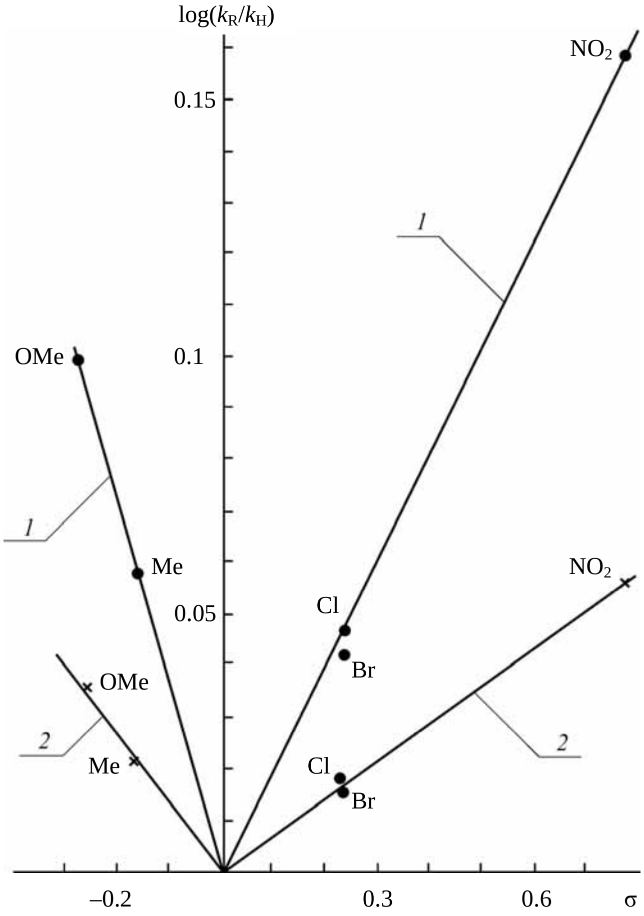

Fig. 2. Correlation between the reactivity of esters **IIa**–**IIf** and Hammett substituent constants σ (chlorobenzene, 110°C): (*1*) reaction with diene **III**, (*2*) reaction with diene **IV**.

the other, thus increasing the reactivity of the system. The neutral scheme of Diels–Alder reaction is characterized by *U*-shaped dependences between the reactivity and substituent constants σ.

Analysis of published data shows that, apart from donor–acceptor interactions between the addends, localization effects are also important in Diels–Alder reactions [7, 8]. Localization effects destabilize the transition state, and they depend on the ease of transformation of the initial π-systems of the diene and dienophile in the course of cycloaddition [7, 8].

In the present work we examined the kinetics of the Diels–Alder reactions of *para*-substituted allyl and 2-propynyl benzoates **Ia**–**If** and **IIa**–**IIb** with hexabromo-1,3-cyclopentadiene (**III**) and tetrabromo-5,5-dimethoxy-1,3-cyclopentadiene (**IV**) with the goal of elucidating factors determining the reactivity of the addends.

Donor–acceptor properties of dienophiles **Ia**–**If** and **IIa**–**IIf** were characterized by measuring their half-wave reduction potentials ($E_{1/2}$) relative to a saturated calomel electrode. Using the Briegleb equation [9], from the $E_{1/2}$ values we calculated the corresponding electron affinities E_A (Table 1). It is seen that the electron affinities of dienophiles **IIa**–**IIf** are lower than those of compounds **Ia**–**If**. The absolute values of E_A for compounds **Ia**–**If** and **IIa**–**IIf** are lower than that found for diene **III** but higher than the electron affinity of **IV**, i.e., diene **IV** is a stronger electron donor than dienophiles **Ia**–**If** and **IIa**–**IIf**. In keeping with the orbital donor–acceptor parameters of the ground state of esters **Ia**–**If** and **IIa**–**IIf**, compounds **Ia**–**If** should be more reactive than **IIa**–**IIf** toward dienes **III** and **IV**. In the Diels–Alder reactions of compounds **III** with dienophiles **Ia**–**If** and **IIa**–**IIf**, the reactivity of the system should be determined by the interaction between the HOMO of **Ia**–**If** and **IIa**–**IIf** and LUMO of **III**. In the reaction of **IV** with esters **Ia**–**If** and **IIa**–**IIf**, the interaction between the HOMO of **IV** and LUMO of **Ia**–**If** and **IIa**–**IIf** should be crucial.

Table 1. Half-wave reduction potentials $E_{1/2}$ and electron affinities E_A of dienophiles **Ia**–**If** and **IIa**–**IIf** and dienes **III** and **IV**

Comp. no.	$E_{1/2}$, eV	E_A, eV
Ia	–1.57	–0.24
Ib	–1.49	–0.16
Ic	–1.41	–0.07
Id	–1.29	0.05
Ie	–1.27	0.05
If	–0.93	0.42
IIa	–1.51	–0.18
IIb	–1.44	–0.11
IIc	–1.39	–0.05
IId	–1.37	0.03
IIe	–1.36	0.02
IIf	–0.97	0.38
III[a]	–	0.73
IV[a]	–	≤–0.303

[a] Data of [10].

The reactions kinetics were studied by polarography, following variation of the height of the reduction wave ($E_{1/2}$) of one of the addends with time (τ). Preliminarily, we examined polarographic behavior of dienophiles **Ia**–**If** and **IIa**–**IIf** and dienes **III** and **IV** at a dropping mercury electrode in dimethylformamide using tetraethylammonium iodide as supporting electrolyte. We found that the presence of dienophiles **Ia**–**If** or **IIa**–**IIf**, chlorobenzene, and cycloaddition products **V**–**VIII** in the reaction mixture does not interfere with polarographic determination of the current concentration of dienes **III** and **IV** (Table 2). The results of kinetic measurements showed that the reactions under study are characterized by low energies of activation (E_a) and large negative entropies of activation ($\Delta S^{\neq}$), indicating the concerted mechanism of cycloaddition (Table 2). The reactivity of dienophiles **Ia**–**If** and **IIa**–**IIf** toward dienes **III** and **IV** increases upon introduction of both electron-donor and electron-acceptor substituents into the aromatic ring (Figs. 1, 2). Obviously, the process can be regarded as a neutral version of the Diels–Alder reaction which involves symmetric arrangement of the HOMOs and LUMOs of dienes **III** and **IV** and dienophiles **Ia**–If and **IIa**–**IIf**.

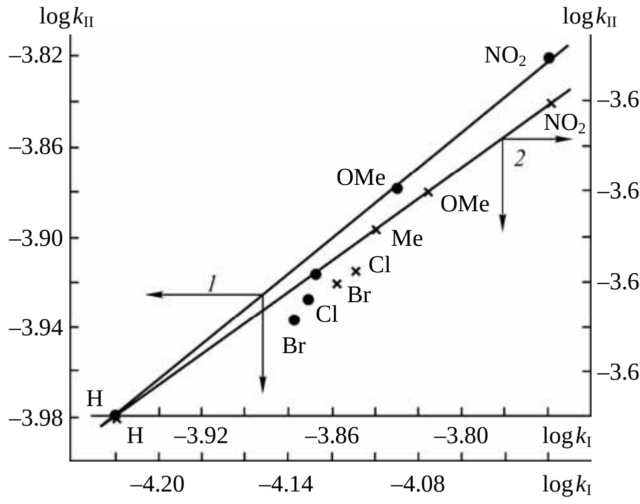

Fig. 3. Relative reactivities of esters **I** (logk_I) and **II** (logk_{II}) (chlorobenzene, 110°C): (*1*) reaction with diene **III**, (*2*) reaction with diene **IV**.

According to the data in Table 2, diene **III** is less reactive than **IV** in the examined reaction series. A probable reason is the presence of two geminal methoxy groups in molecule **IV** (instead of two bromine atoms in **III**). This leads to increase of the LUMO and HOMO energies of diene **IV**. As a result, the contribution of the interaction HOMO(diene)–LUMO(dienophile) to reduction of the activation barrier increases, and the reactivity of diene **IV** rises. Dienophiles **IIa**–**IIf** are considerably more reactive than **Ia**–**If**. Presumably, 2-propynyl esters **IIa**–**IIf** are characterized by lower localization energies and higher energies of the bonds being formed [11].

In order to elucidate factors determining the reactivity of addends in the above Diels–Alder reactions, we examined the relation between their reactivity and selectivity. It is known [8, 12] that the reactivity–selectivity ratio may be sensitive to one or another factor affecting the reactivity; this relation was studied in detail in [12], and it was shown that more reactive reagent is characterized by greater (anomalous) selectivity when the relative reactivity is controlled by the energy of donor–acceptor interaction. When the reactivity is controlled by the localization energy, more reactive reagent is characterized by lower (normal) selectivity. Comparison of the reactivity of dienophiles **Ia**–**If** and **IIa**–**IIf** toward dienes **III** and **IV** (Fig. 3) revealed normal reactivity–selectivity ratio. Esters **IIa**–**IIf**, which are more reactive than **Ia**–**If**, exhibit lower selectivity: the slopes of the correlation straight lines in Fig. 3 are 0.78 and 0.35, respectively. This means that the reactivity of dienophiles **IIa**–**IIf** in the Diels–Alder reactions with compounds **III** and **IV** is controlled by the localization energy while the contribution of donor–acceptor interaction is much smaller.

Table 2. Kinetic parameters of the Diels–Alder reactions of esters **Ia**–**If** and **IIa**–**IIf** with dienes **III** and **IV** in chlorobenzene

Reactants	$k \times 10^6$, l mol^{-1} s^{-1}			E_a, kJ/mol	log*A*	$\Delta H^{\neq}$, kJ/mol	$-\Delta S^{\neq}$, J mol^{-1} K^{-1}
	100°C	110°C	120°C				
Ia, **III**	46.4	81.7	138.0	69.0	5.3	65.8	194.5
Ib, **III**	42.8	74.6	126.6	70.8	5.5	67.4	192.8
Ic, **III**	37.4	59.4	97.8	74.5	5.9	1.3	189.0
Id, **III**	42.0	73.7	122.0	70.8	5.5	67.4	192.8
Ie, **III**	41.7	72.9	118.5	74.5	6.0	71.3	189.0
If, **III**	57.7	93.5	163.5	63.2	4.6	60.0	200.4
Ia, **IV**	106.1	152.5	237.9	57.3	4.0	54.1	206.2
Ib, **IV**	89.7	143.1	215.9	59.4	4.2	56.2	204.2
Ic, **IV**	67.5	110.0	172.7	67.0	5.2	63.8	196.6
Id, **IV**	92.4	140.5	226.2	63.2	4.8	60.0	200.4
Ie, **IV**	91.0	138.8	218.1	60.2	4.4	57.1	203.3
If, **IV**	111.3	171.7	270.5	53.6	3.5	50.4	209.9
IIa, **III**	72.7	130.9	221.1	59.4	4.2	56	204.3
IIb, **III**	68.4	119.0	202.0	61.1	4.4	57.9	202.7
IIc, **III**	63.3	104.2	171.6	64.4	4.8	61.1	199.1
IId, **III**	66.2	115.9	191.8	61.5	4.5	58.3	201.9
IIe, **III**	65.6	114.7	200.6	62.2	4.5	59.2	201.4
IIf, **III**	92.9	150.5	263.1	58.4	4.1	55.2	205.2
IIa, **IV**	165.9	237.6	346.7	48.5	3.0	45.2	215.2
IIb, **IV**	149.9	230.1	229.5	51.9	3.4	48.5	211.7
IIc, **IV**	133.1	219.1	325.5	57.4	4.2	54.1	206.2
IId, **IV**	157.5	228.2	346.5	50.9	3.3	47.9	212.7
IIe, **IV**	150.8	227.4	339.1	51.5	3.4	48.3	212.3
IIf, **IV**	161.4	249.5	354.5	47.8	2.9	44.5	215.9

EXPERIMENTAL

Kinetic experiments were carried out with freshly prepared samples of dienophiles **Ia**–**If** and **IIa**–**IIf** and dienes **III** and **IV**; their purity was checked by TLC on KSK silica gel (100–150 mesh; unfixed layer) using benzene–1,2-dichloroethane–acetic acid (3 : 1 : 0.5) as eluent; development with iodine vapor.

Polarographic reduction of the addends was performed in a three-electrode cell at a dropping mercury electrode in DMF at 20°C using tetraethylammonium iodide as supporting electrolyte; the half-wave reduction potentials were measured relative to a saturated calomel electrode using a GWP-673 polarograph.

Diels–Alder reactions were carried out in ampules using equimolar amounts of the addends in chlorobenzene at 100, 110, and 120°C. The temperature was maintained with an accuracy of ±0.05°C using a U-10 temperature-controlling unit. The second-order rate constants were determined with an accuracy of ±5% by polarography (ON-101 instrument), following variation of the concentration of dienes **III** and **IV** [13]; the calculations were performed according to the following formula [14]:

$$k = 1/\tau[1/(c_0 - c_\tau) - 1/c_0],$$

where τ is the time, c_0 is the initial addend concentration, and c_τ is the current addend concentration.

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