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Theoretical study on the Diels–Alder reaction of bromo-substituted 2*H*-pyran-2-ones and some substituent vinyls

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Abstract: A DFT study of the reactivity, regio- and stereoselectivity of Diels–Alder reactions between 3-bromo, 5-bromo, and 3,5-dibromo-2*H*-pyran-2-ones and some weakly activated and unactivated alkenes was performed using the density functional theory (DFT). Four possible reaction channels, which are related to the formation of *meta*- and *para*- and *endo*- and *exo*-cycloadducts, were explored and characterized. The energy and natural bond orbital analysis showed that the *meta*-regioselectivity on the *exo* pathway was preferred and followed an asynchronous concerted mechanism with a polar nature in all Diels–Alder cycloadditions. Moreover, the activation free energies of the Diels–Alder cycloadditions of 3,5-dibromo-2*H*-pyran-2-one were lower than those for 3-bromo-2*H*-pyran-2-one and 5-bromo-2*H*-pyran-2-one, which is in line with experimental observations. DFT-based reactivity indices clearly predicted the regiochemistry of the isolated cycloadducts.

Keywords: bromo-2*H*-pyran-2-ones; DFT study; reaction mechanism; reactivity indices; regio- and stereoselectivity.

INTRODUCTION

During investigations on the role of substituents on the cycloaddition reaction of 2*H*-pyran-2-ones, it was found that 3-bromo and 5-bromo-2*H*-pyran-2-ones are the most interesting and unique, and have useful features.[1–5] These two 2*H*-pyran-2-ones are ambident dienes[3] and react with electron-rich, electron-poor and electron-neutral dienophiles with good regio- and stereoselectivity.[4,6,7] The cycloadditions of 2*H*-pyran-2-one itself are not selective.[5] Moreover, in contrast to the bromo-pyrones, 4-chloro-2*H*-pyran-2-one, in line with 2*H*-pyran-2-one itself, is neither ambident diene nor undergoes regioselective cycloadditions.[8] It undergoes cycloadditions only with electron-deficient dienophiles that were stereoselective, but not regioselective.[3a] During the course of a study of 2*H*-

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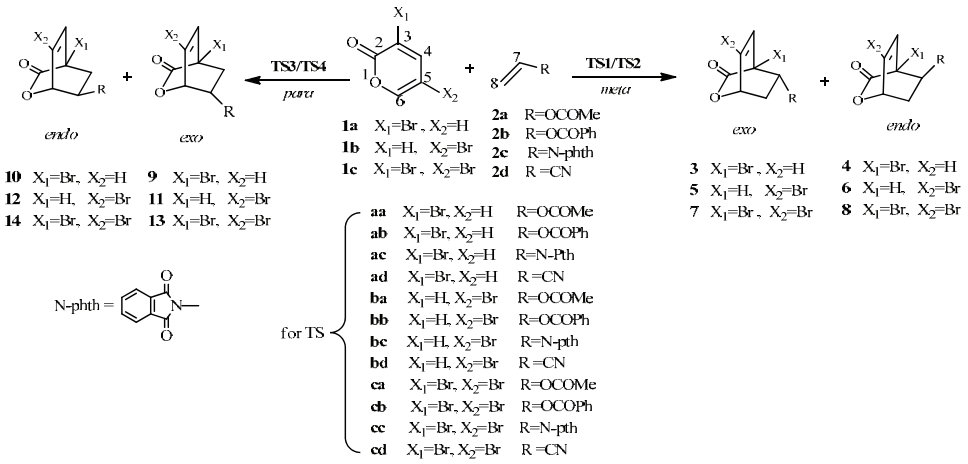
-pyran-2-ones, Cho and co-workers investigated 3,5-dibromo-2*H*-pyran-2-one in Diels–Alder (DA) reactions with a series of electronically and sterically distinct dienophiles.[3b] Their results showed that it is a highly potent ambident diene, being more reactive and stereoselective than monobromo-2*H*-pyran-2-ones, and thus capable of generating a variety of bicycloadducts in much higher chemical yields and *endo*/*exo* rations than monobromo-2*H*-pyran-2-ones.[3]

Afarinkia and co-workers studied the Diels–Alder reactions of 3- and 5-halo--substituted 2*H*-pyran-2-ones with poor electron-rich, electron-rich and deficient dienophiles.[7–9] Their experimental results showed that these cycloadditions proceed with excellent regioselectivity and very good stereoselectivity. In contrast, the 4-halo-substituted-2*H*-pyran-2-ones reactions proceed with only moderate regio- and stereoselectivity.[9] Furthermore, their results showed that the nature of halogen substituent had only a small, sometimes negligible, influence on the cycloaddition of 2*H*-pyran-2-ones, and also, in both the 3- and 5-substituted series, the distribution of the products did not appear to be significantly different.[8] Therefore, changing the halogen substituent did not significantly change the electronic demand of the 3- and 5-halo-substituted 2*H*-pyran-2-one, although it may influence their reactivity. Furthermore, they performed a range of calculations on substituted 2*H*-pyran-2-one cyclo-additions, at the B3LYP/6-31G level of theory, to demonstrate the advantage of 3- and 5-halo-substituted 2*H*-pyran-2--ones over 4-halo-substituted 2*H*-pyran-2-ones.[8,9]

Although there are many reports about the alternative synthetic routs,[3–9] there are no theoretical investigations about the detailed molecular mechanism and electronic parameters. As a part of a program directed toward the investigation of related DA cycloadditions, herein the results of a theoretical study on the mechanism of cycloaddition reactions between 3-bromo, 5-bromo and 3,5-dibromo-2*H*-pyran-2-ones **1a**–**c**, with a range of vinyl derivatives: vinyl acetate (**2a**), vinyl benzoate (**2b**), 2-ethenyl-1*H*-isoindole-1,3(2*H*)-dione (*N*-vinylphthalimide) (**2c**) and 2-propenenitrile (**2d**), to give the bridged bicyclic lactones **3**–**13** are presented (Scheme 1). The purpose of the present study was to provide a better understanding the mechanistic features of these processes, especially by localization and characterization of all stationary points involved in these formally [2+4]cycloadditions. A density functional theory (DFT) analysis was performed to explain both the *exo*/*endo* stereocontrol and regioselectivity of these processes in order to find a possible mechanism that may explain the different reactivity observed in each case.

Although DA cycloadditions of 5-bromo and 3,5-dibromo-2*H*-pyran-2-ones with poor electron-rich dienophiles **2a**–**c** were not prepared as part of experimental studies, the calculations based on them provided a better understanding of the trends, differences, and similarities between halogen substituted 2*H*-pyran--2-ones.



Scheme 1. The calculated possible reaction channels for the DA reaction of bromo-substituted 2*H*-pyran-2-ones **1a**–**c** with the vinyl derivatives **2a**–**d** at the B3LYP/cc-pVDZ level.

COMPUTATIONAL DETAILS

The density functional theory calculations were realized using the Gaussian 09 package.[10] The relative energies and free energies were computed at 298 K for the various stationary points at the B3LYP/cc-pVDZ level. The electronic structures of the stationary points were analyzed by the natural bond orbital (NBO) method.[11] The global reactivity indexes were estimated according to the equations recommended by Parr.[12] The global electrophilicity index, ω, is given by the following expression:[13]

$$\omega = \frac{\mu^2}{2\eta} \tag{1}$$

in terms of the electronic chemical potential, μ, and the chemical hardness, η. Both quantities may be approached in terms of the one-electron energies of the frontier molecular orbitals HOMO and LUMO, ε_H and ε_L,[14] as:

$$\mu = (\varepsilon_H + \varepsilon_L)/2 \tag{2}$$

$$\eta = \varepsilon_L - \varepsilon_H \tag{3}$$

Recently, Domingo introduced an empirical (relative) nucleophilicity index, N,[15] based on the HOMO energies obtained within the Kohn Sham scheme,[13] and defined as:

$$\varepsilon_{HOMO}(\text{Nu}) - \varepsilon_{HOMO}(\text{TCE}) \tag{4}$$

Nucleophilicity is referred to tetracyanoethylene (TCE), because it presents the lowest HOMO energy in a large series of molecules already investigated within the context of polar cycloadditions. This choice allows the convenient handling of a nucleophilicity scale of positive values. Recently, Domingo proposed two new electrophilic, P_k^+, and nucleophilic, P_k^-, Parr functions based on the atomic spin density distribution at the radical anion and cation of a neutral molecule.[16] The electrophilic, P_k^+, and nucleophilic, P_k^-, Parr functions, were obtained through the analysis of the Mulliken atomic spin density of the radical anion and cation by single-point energy calculations over the optimized neutral geometries using the

unrestricted UB3LYP formalism for radical species. The local electrophilicity indices, ω_k,[17] the local nucleophilicity indices, N_k,[198] were calculated using the following expressions:

$$\omega_k = \omega P_k^+ \quad (5)$$

$$N_k = N P_k^- \quad (6)$$

where P_k^+ and P_k^- are the electrophilic and nucleophilic Parr functions,[16] respectively.

RESULTS AND DISCUSSIONS

In the present study, the regio- and stereoselectivity of the cycloaddition reaction between bromo-substituted 2*H*-pyran-2-ones **1a**–**c** and vinyl substituents **2a**–**d** were studied, and then an analysis based on the reactivity indices of stationary points was performed.

*Study of the DA reactions of bromo-substituted 2*H*-pyran-2-ones **1a–c** with some vinyl derivatives (**2a–d**)*

Due to the asymmetry of bromo-substituted 2*H*-pyran-2-ones **1a**–**c**, four regio-isomeric channels are feasible for each of the DA reactions, *meta* and *para*, which are related to the *endo* and *exo* approach modes of the diene systems **1a**–**c** relative to the R group of the vinyl compounds **2a**–**d** (Scheme 1).

Analysis of the stationary points associated with these DA reactions indicated that they could occur *via* a one-step mechanism and consequently, four stereoisomeric TSs, named **TS1**, **TS2**, **TS3**, and **TS4**, and the corresponding products **3**–**13** were located and characterized. The activation and relative energies associated with these stationary points are given in Table I. Analysis of the geometries at the **TS** structures shows that the **TS**s of *meta* pathways correspond to asynchronous bond formation processes. The extent of bond formation along a reaction pathway is provided by the concept of bond order (BO).[19] These values are within the range of 0.180 to 0.636. These results show that for all DA reactions, **TS1** and **TS2** (*meta* pathways) are more asynchronous than **TS3** and **TS4** (*para* pathways), and that the **TSca**, **TScb** and **TScc** (for the *N*-phthalimide substituent) are the most asynchronous ones. The asynchronicity shown by the geometrical data is accounted for by the BO values.

Furthermore, the asynchronicity in bond formation at the **TS**s measured by $\Delta r = (r_2 – r_1)$ ranges from 0.72 to 1.10 at **TS1** and **TS2**, indicating that the **TS**s of *meta* process correspond to highly asynchronous bond-formation processes. Natural population analysis (NPA)[11] allowed the evaluation of the charge transfer (CT) along these DA reactions, at the TSs. Charge transfer (CT) plays a relevant role in most of organic reactions. In fact, in Diels–Alder reactions, the *CT* value is one of the most relevant characteristics of their transition states (**TS**s) and, in most cases, it is responsible of the height of their energy barrier. The calculated *CT* values for these DA reactions are given in Fig. 1. In general, the *CT* values in the **TS**s associated with the *para* pathways were lower than 0.090 e, in clear agree-

TABLE I. Activation energies, $\Delta E^{\#}$, activation free energies, $\Delta G^{\#}$, and reaction energies, ΔE_r, (all in kJ mol^{-1}), with the formation of DA cycloadducts between bromo-substituted 2*H*--pyran-2-ones **1a**–**c** and vinyl derivatives **2a**–**d** in the *meta* pathways

Entry	Species	**TS**	$\Delta E^{\#}$	$\Delta G^{\#}$	ΔE_r
1	**1a+2a→3a**-*exo*	**TS1aa**	108.48	166.33	–48.53
2	**1a+2a→4a**-*endo*	**TS2aa**	112.94	169.31	–46.22
3	**1a+2b→3b**-*exo*	**TS1ab**	112.12	168.26	–49.94
4	**1a+2b→4b**-*endo*	**TS2ab**	116.66	170.56	–45.98
5	**1a+2c→3c**-*exo*	**TS1ac**	106.75	163.59	–28.80
6	**1a+2c→4c**-*endo*	**TS2ac**	112.64	168.23	–27.73
7	**1a+2d→3d**-*exo*	**TS1ad**	117.59	171.64	–29.45
8	**1a+2d→4d**-*endo*	**TS2ad**	107.65	161.71	–33.67
9	**1b+2a→5a**-*exo*	**TS1ba**	92.82	150.75	–69.94
10	**1b+2a→6a**-*endo*	**TS2ba**	102.04	157.18	–65.45
11	**1b+2b→5b**-*exo*	**TS1bb**	98.36	154.17	–68.60
12	**1b+2b→6b**-*endo*	**TS2bb**	100.47	155.97	–66.38
13	**1b+2c→5c**-*exo*	**TS1bc**	64.58	120.92	–75.89
14	**1b+2c→6c**-*endo*	**TS2bc**	76.74	131.41	–71.40
15	**1b+2d→5d**-*exo*	**TS1bd**	108.51	162.17	–51.16
16	**1b+2d→6d**-*endo*	**TS2bd**	100.17	153.82	–54.83
17	**1c+2a→7a**-*exo*	**TS1ca**	94.23	151.39	–62.01
18	**1c+2a→8a**-*endo*	**TS2ca**	100.63	156.30	–59.89
19	**1c+2b→7b**-*exo*	**TS1cb**	98.40	153.68	–63.50
20	**1c+2b→8b**-*endo*	**TS2cb**	100.22	155.34	–59.66
21	**1c+2c→7c**-*exo*	**TS1cc**	91.26	148.47	–43.06
22	**1c+2c→8c**-*endo*	**TS2cc**	101.83	157.25	–41.22
23	**1c+2d→7d**-*exo*	**TS1cd**	106.23	160.32	–41.75
24	**1c+2d→8d**-*endo*	**TS2cd**	98.22	152.36	–45.00

ment with the non-polar character of these pathways. On the other hand, the *CT* values at the **TS**s of the DA reactions of **1a**–**c** and **2a**–**c** in the most favorable regioisomeric pathways (*meta–exo*), were between 0.205 and 0.157 e, which indicate the polar nature of the *meta* channels in these DA reactions. Only the most unfavorable DA reactions of **1a**–**c** and **2d** presented low *CT* values (lower than 0.050 e). These results with the proposal that for the DA reactions of **1a**–**c** with **2a**–**d**, an increase in the polar character as the reaction proceeds is accompanied by an acceleration of the reaction.[7–9]

The energy barrier ($\Delta E^{\#}$) and activation Gibbs free energy values ($\Delta G^{\#}$), related to the occurrence of transition states for the DA reactions of **1a**–**c** with **2a**–**d** are lower for the *meta* approaches than those for the *para* ones (Table I). The measured stereoselectivity indicated that the *meta–exo* cyclization modes are more favorable than the *meta–endo* ones, leading to the formation of *meta–exo* adducts for the DA reactions of **1a**–**c** with **2a**–**c**, while the lowest barrier energies for the DA reactions of **1a**–**c** with **2d** occur on the *meta–endo* pathway, which yields the *meta–endo* cycloadducts **4d**, **6d** and **8d**. Therefore, the presence of a cyano group

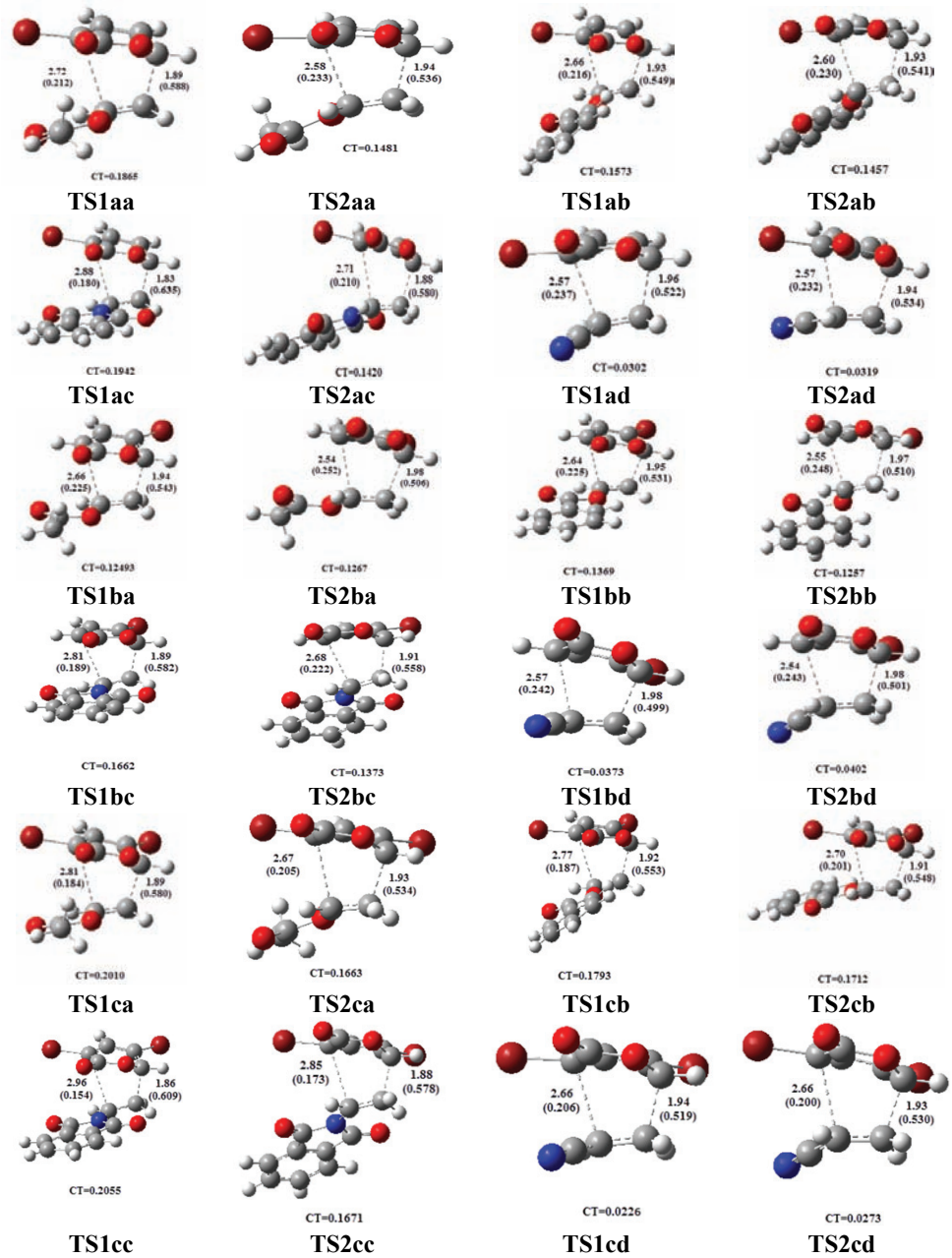


Fig. 1. Optimized geometries (B3LYP/cc-pVDZ) of the transition structures involved in the *meta* pathways of the DA reactions between the bromo-substituted 2*H*-pyran-2-ones **1a**–**c** and the vinyl derivatives **2a**–**d**. The bond distances are given in Å, the Wiberg bond indices are given in parenthesis and the natural charges (*CT*) of the **TS**s are also given.

on the dienophile, neither changes the stereoselectivity (*exo* to *endo*), nor increase the energy barriers relative to the other dienophiles.

On the other hand, the results of energy values in Table I showed that the DA reactions of **1a**–**c** with **2a** and **2b** are less stereoselective than the cycloadditions to dienophiles **2c** and **2d**. These differences in stereoselectivity could be explained as follows.

The lack of stereoselectivity in the cycloadditions of vinyl acetate **2a** presumably arises from a lack of strong secondary orbital interactions, suggesting that the cycloaddition to the weakly activated dienophile may be much more susceptible to steric interaction.[7] This was confirmed from the results of the cycloadditions of 2-ethenyl-1*H*-isoindole-1,3(2*H*)-dione (**2c**), where the reactions are highly *exo* selective. Here, the steric congestion arises directly from an unfavorable steric interaction between the second nitrogen substituent and the bromine atom in the **TS**, leading to the *endo* cycloadduct. Therefore, **TS1ac**, **TS1bc** and **TS1cc** leading to the *exo* cycloadduct are favored. This does not arise in the **TS** of *endo* cycloadduct of vinyl benzoate **2b** since the benzoate group can swing away from the bromine in the transition state. Moreover, the *endo* predomination in the cycloaddition of 2-propenenitrile (**2d**) is attributed to secondary orbital interactions and therefore it was not expected that cycloaddition to the bromo-2*H*-pyran-2-ones **1a**–**c** would give an *endo* to *exo* ratio of nearly one.

As can be seen in Table I and Scheme 1, it is possible to correlate the calculated energy of the transition state to the final yield of the cycloadducts **3**–**13**. The calculated values of all transition states confirmed that the ones likely to be the most abundant are the **3**, **5** and **7** isomers in all cases, which occurred in the DA reactions of **1a**–**c** with **2c**. The cycloadditions of **1a**–**c** with **2d** in all of reactions had the highest relative energy and it was expected to be the most disfavored cycloadduct.

The results of calculated free activation energies ($\Delta G^{\#}$) for DA reactions of 3,5-dibromo-2*H*-pyran-2-one (**1c**) with **2a**, **2b** and **2d** demonstrate the lowest activation free energy, while an increasing barrier energy has been seen for **1c** and **2c**.With considering FMO approach (Table II), broadly speaking, 3-bromo, 5-bromo and 3,5-dibromo-2*H*-pyran-2-one should undergo normal and inverse electron demand cycloadditions with dienophiles bearing weakly electron-donating (**1a**–**c**) and electron-withdrawing (**2d**) substituents, respectively.

DFT-based reactivity indices

The molecular DFT-based parameters, electronic chemical potential (μ), chemical hardness (η), global electrophilicity (ω) and global nucleophilicity (N) of the reactants **2a–d** and **1a–c** are displayed in Table II.

As can be seen in Table II, the bromo-2*H*-pyran-2-one derivatives **1a**–**c** are more electrophilic than the dienophiles **2a**–**d** and 3,5-dibromo-2*H*-pyran-2-one

(**1c**) with the highest electrophilicity (ω = 2.43 eV) being classified as a strong electrophile on the electrophilicity scale.[20] On the other hand, **1a** has a high nucleophilicity index, N = 2.52 eV, and thus is classified as a strong nucleophile on the nucleophilicity scale.[21] This ambiphilic behavior is the consequence of the presence of the enone and oxygen atom inside **1a**–**c**. The electronic chemical potential (μ) of the bromo-2*H*-pyran-2-one derivatives **1a**–**c** are lower than those of the dienophiles, **2a** (–0.134), **2b** (–0.156) and **2c** (–0.130), indicating that charge transfer along the corresponding reactions will occur from the dienophiles **2a**–**c** to the electron deficient dienes **1a**–**c**. While as expected, a CN group (**2d**) decreases the chemical potential and increases the electrophilicity toward the dienophiles **2a**–**d**, and hence, these results are in agreement with the increase in the activation energy.

TABLE II. HOMO and LUMO energies, electronic chemical potential, μ, chemical hardness, η, (all in a.u.), global electrophilicity, ω, and nucleophilicity, N (both in eV), for the reactants obtained at the B3LYP/cc-pVDZ level of theory

Species	E_{HOMO}	E_{LUMO}	μ	η	ω	N
1a	–0.24366	–0.07747	–0.160	0.166	2.09	2.52
1b	–0.24586	–0.07990	–0.162	0.166	2.15	2.40
1c	–0.24777	–0.08881	–0.168	0.158	2.43	2.41
2a	–0.25309	–0.01470	–0.134	0.238	1.02	2.27
2b	–0.25205	–0.06044	–0.156	0.192	1.71	2.29
2c	–0.24195	–0.01862	–0.130	0.223	1.03	2.57
2d	–0.26633	–0.08384	–0.178	0.182	2.28	1.90

The polar character of a cycloaddition process can be predicted using the electrophilicity difference of the reaction pair, $\Delta\omega$.[22] In this sense, the electrophilicity differences between the diene **1c** and the dienophiles **2a** and **2c** are about 1.40, indicating a large polar character for these cycloadditions, while the small $\Delta\omega$ between **1a** and **2b** (0.38 eV) and between **1b** and **2d** (0.21 eV) show a low polar character for these cycloaddition reactions. The Parr indices, local electrophilicity indices and local nucleophilicity indices for the atoms C6 and C3 of the pyrones **1a**–**c**, and C7 and C8 of the dienophiles **2a**–**d** are given in Table III (see Scheme 1 for atom numbering). The Parr functions (the electrophilic, P_k^+, and nucleophilic, P_k^-) were computed based on Mulliken atomic spin density analysis.

According the Domingo model,[15,17] along a polar cycloaddition involving asymmetric reagents, the most favorable reactive channel is that involving the initial two-center interaction between the most electrophilic center (ω_k) at the electrophile and the most nucleophilic center (N_k) at the nucleophile. According to this model, in the cycloaddition reactions of **1a–c** with dienophiles **2a–d**, the most favorable two-center interaction occurs between C6 of the dienes and C8 of

dienophiles **2a–d**, leading to the formation of the **3**–**13** regioisomers, which is in agreement with the experimental results.[7–9]

TABLE III. The Parr functions (P_k^-, P_k^+ / au), local electrophilicity indices (ω_k / eV) and local nucleophilicity (N_k / eV) indices for the C6 and C3 atoms of the pyrones **1a**–**c** and for atoms C7 and C8 of the dienophiles at the reactive sites for the reactants obtained at the B3LYP/cc-pVDZ level of theory

Species	k	P_k^-	P_k^+	N_k	ω_k
1a	C6	0.188	0.381	0.474	0.795
	C3	0.253	0.204	0.639	0.426
1b	C6	0.394	0.205	0.945	0.492
	C3	0.232	0.264	0.558	0.634
1c	C6	0.240	0.384	0.580	0.932
	C3	0.188	0.222	0.453	0.540
2a	C7	0.181	0.171	0.410	0.174
	C8	0.291	0.548	0.660	0.559
2b	C7	0.018	0.074	0.040	0.127
	C8	0.092	0.357	0.212	0.610
2c	C7	0.009	0.037	0.024	0.038
	C8	0.019	0.476	0.050	0.490
2d	C7	0.219	0.260	0.146	0.594
	C8	0.606	0.426	1.152	0.972

CONCLUSIONS

DFT computations using the B3LYP functional in conjunction with the cc-pVDZ basis set were used to analyze the outcome of the DA reactions of the bromo-2*H*-pyran-2-ones **1a**–**c** with some weakly activated and unactivated vinyls. The following conclusions could be inferred from the results of the energies:

I. The activation energies associated with the DA reaction of cyclic dienes **1a**–**c** with dienophile **2c** is more favorable than those for the reactions with **2a**, **b** and **2d**. The low reactivities of the dienophiles in these DA reactions correspond with their nucleophilic character.

II. While the DA reactions with **2a**–**c** are *exo* selective, the reaction with **2d** is *endo* selective.

III. 3,5-Dibromo-2*H*-pyran-2-one is more active than 3- and 5-bromo-2*H*--pyran-2-ones, having a lower energy barrier.

IV. These DA reactions proceed *via* a polar, regioselective and highly asynchronous process.

ИЗВОД

ТЕОРИЈСКА СТУДИЈА ДИЛС–АЛДЕРОВЕ РЕАКЦИЈЕ БРОМО-СУПСТИТУИСАНИХ 2*H*-ПИРАН-2-ОНА И НЕКИХ СУПСТИТУИСАНИХ ВИНИЛА

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Извршено је DFT испитивање реактивности, регио- и стереоселективности Дилс–Алдерове реакције између 3-бромо, 5-бромо и 3,5-дибромо-2*H*-пиран-2-она и неких слабо активираних и неактивираних алкена. Истражена су четири могућа реакциона пута, који обухватају формирање *мета*-, *пара*-, *ендо*- и *егзо*-циклоадукта. Анализа заснована на енергији и природним орбиталама показује да је преферирана *мета*-региоселективност и *егзо*-реакциони механизам.

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