

Minimum electrophilicity principle in photocycloaddition formation of oxetanes

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ABSTRACT: The regio- and stereoselectivity of some Paternó–Büchi reactions are studied within a density functional framework with B3LYP exchange-correlation energy functional and 6-31G** basis set. It is shown that although in most cases the Minimum Polarizability and the Maximum Hardness Principles (MPP and MHP) successfully predict the major oxetane products of these reactions, but in all of the considered reactions, with no exception, the main products have the lesser electrophilicity values than the minor isomers, and therefore the Minimum Electrophilicity Principle (MEP) correctly predicts the most stable stereoisomer of the reaction. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: cycloaddition reaction; Paternó–Büchi reaction; oxetane; maximum hardness principle; minimum polarizability principle; minimum electrophilicity principle; density functional

INTRODUCTION

Although the Paternó–Büchi reaction,¹ that is the photocycloaddition of ketons and aldehydes to olefins (Scheme 1), discovered nearly one century ago, but it is also a topic of studies.^{2–12} As it is shown in Scheme 1, different regioisomers of oxetane can be formed depending on whether O atom in the excited carbonyl group makes a bond with the C₁ or C₂ atom of the ene molecule. Mechanistic studies^{13–16} have shown that there are two distinct mechanisms for this reaction, depending on the electron density at the ene molecule. For electron-rich olefins, addition generally proceeds through attack of the n-π* carbonyl compound (singlet or triplet) on ground state olefin. The triplet additions appear to involve a long-lived biradical with time for bond rotation before ring closure,¹⁷ but short-lived biradical which produce in singlet addition has no sufficient time for bond rotations.¹⁸ In the other hand, for electron-deficient olefins the addition involves attack of the singlet excited carbonyl on the ene, which can react stereospecifically to give oxetane. But the experimental results show that the product ratios are not always simply predicted from the stability of the intermediate radicals.

The elucidation of the rules which govern intermolecular energy transfer is one of the most pressing and fascinating problems in organic chemistry. During the

past few years many attempts have been made to introduce new concepts, which are related to stability or reactivity of molecules. Prominent among these are the electronic chemical potential,¹⁹ hardness²⁰ and polarizability, whose analytical and operational definitions are given as follows:

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{v(\vec{r})} \cong -\frac{IP + EA}{2} \quad (1)$$

$$\eta = \left(\frac{\partial^2 E}{\partial N^2} \right)_{v(\vec{r})} \cong \frac{IP - EA}{2} \quad (2)$$

$$\langle \alpha \rangle = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (3)$$

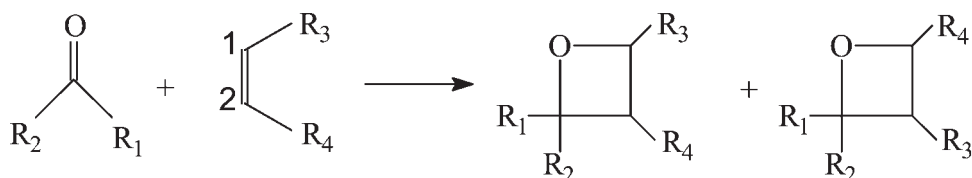
where IP and EA are the first vertical ionization energy and electron affinity, respectively, and α_{xx}, α_{yy}, and α_{zz} are the diagonal elements of polarizability tensor. Following Janak's theorem,²¹ these parameters can be approximated in terms of the energies of HOMO and LUMO molecular orbitals as:

$$\mu' \cong \frac{\varepsilon_L + \varepsilon_H}{2} \quad (4)$$

$$\eta' \cong \frac{\varepsilon_L - \varepsilon_H}{2} \quad (5)$$

Based on these concepts some principles are found in computational chemistry. Two commonly used of these principles are the Maximum Hardness Principle (MHP)^{22–26} and the Minimum Polarizability Principle (MPP).²⁷ According to these principles, hardness and

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Scheme 1. A general representation of the considered photocycloaddition reaction

polarizability are indices of stability or reactivity and the preferred direction of a chemical reaction is toward greater hardness and lesser polarizability. A formal proof of the MHP was given by Pearson and Chattaraj,²⁴ which relied on the constancy of both the external and chemical potentials. These conditions will put heavy constraints on the applicability of MHP. Although Sebastian²⁸ tried to show that the proof is in error, but 1 year later he reported some error in his used examples.²⁹ This principle was also proved by using variational principles.³⁰ A constructive discussion on MHP is collected by Geerlings *et al.*³¹ in a review article. Since these principles were proposed, numerous calculations^{32–37} have been carried out to verify these principles; but in some cases^{38–41} they were somewhat broken down.

Parr *et al.*⁴² have proposed electrophilicity index as a measure of energy lowering due to the maximal electron flow between donor and acceptor. They defined electrophilicity index as:

$$\omega = \frac{\mu^2}{2\eta} \cong \frac{(\text{IP} + \text{EA})^2}{4(\text{IP} - \text{EA})} \quad (6)$$

Using Janak's approximation,²¹ this relation has the following form:

$$\omega' \cong \frac{(\varepsilon_L + \varepsilon_H)^2}{4(\varepsilon_L - \varepsilon_H)} \quad (7)$$

The usefulness of this quantity as a stability descriptor has been demonstrated by many authors^{43–48} and its utility has been documented in a comprehensive review article.⁴⁹ Some authors considered the variation of electrophilicity along the reaction path.^{50,51} Recently Noorizadeh and Maihmi⁵² showed that the major product of a Diels–Alder reaction has always less electrophilicity than the minor product and therefore, they have claimed that the electrophilicity index can be used as an indicator for regioselectivity in this reaction. It is also shown that for those exothermic chemical reactions in which the number of moles decreases or at least remains constant, the most stable species (products) have the lowest sum of electrophilicities. Therefore it is concluded that *It seems that there is a tendency in atoms to arrange themselves so that the obtained molecule reaches the minimum electrophilicity.* This rule is called the Minimum Electrophilicity Principle (MEP).

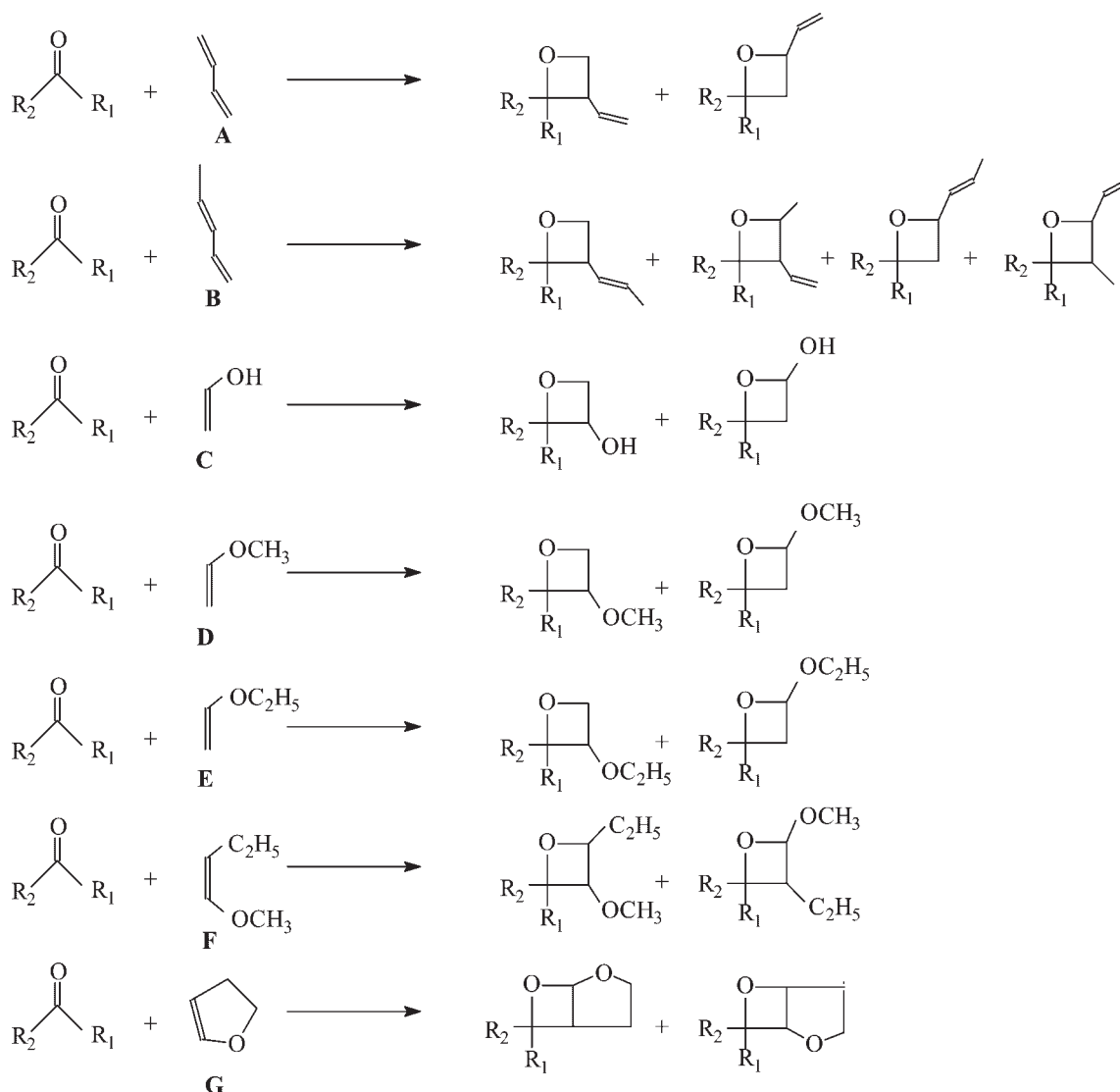
In the present study we apply the MHP, MPP, and MEP to interpret the regio- and stereoselectivity in some Paternó–Büchi reactions and compare the validity of the old principles (MHP and MPP) with the new one (MEP) in the considered reactions.

COMPUTATIONAL DETAILS

Equilibrium geometries for the products of different Paternó–Büchi reactions (79 stereoisomers) were obtained by full optimization within a density functional framework (B3LYP exchange–correlation energy functional^{53–56}) and using the most popular basis sets, 6-31G**. Vibrational frequencies were also calculated for optimized structures in order to check if there was a true minimum. For each structure zero-point energy (ZPE) correction had been taken into account in calculating the energies. Polarizabilities were evaluated using Eqn (3). The values of the electronic chemical potential and the chemical hardness were obtained by using Janak's approximation from the one-electron energies of the HOMO and LUMO frontier molecular orbitals (Eqns (4) and (5)). With these quantities at hand, the global electrophilicity was calculated for each molecule using Eqn (7). The electronic chemical potential, hardness and electrophilicity values were also calculated for each oxetane molecule using vertical ionization potential and electron affinity energies (Eqns (1), (2), and (6)). To compute these parameters we only need to do a geometry optimization on the neutral molecules (N -electron system), plus single point calculations on the cation ($N - 1$) and anion ($N + 1$) forms of the molecule at the neutral geometry. All the calculations were performed with the GAUSSIAN 98W program.⁵⁷

RESULTS AND DISCUSSION

A number of Paternó–Büchi reactions between three simple carbonyl compounds (formaldehyde, acetaldehyde, and acetone) and seven olefins (A=1,3 butadiene; B=1,3 pentadiene; C=hydroxy ethylene; D=methoxy ethylene; E= ethoxy ethylene; F=1-methoxy 1-butene, and G=1,2 dihydro furane), which are shown in Scheme 2, are considered in this study. As it was mentioned, two different regioisomers are expected for



Scheme 2. The considered Paternó-Büchi reactions in this study

each reaction (B molecule, i.e. 1,3 pentadiene has possibilities of four different kinds of product formation), but the predominant oxetane product is that resulting from attack at the more highly substituted double bond.⁵⁸ Therefore, the first oxetane in each reaction is the experimentally major regioisomer^{4,58–62} in the presented scheme. These regioselectivities found agree well with the polarization of the carbonyl group in its $n-\pi^*$ excited state⁶³ and correspond to the general finding that electron-deficient alkenes react with triplet ketons to yield head-to-head adducts, while electron-rich alkenes lead to head-to-tail adducts.

To study the stereoselectivity of these reactions from theoretical point of view, the structures of different possible stereoisomers of the oxetane products (79 isomers) which are shown in Fig. 1 are considered here. According to the photochemistry rules and molecular orbital interactions,⁶⁴ it is expected that in the reactions of

acetaldehyde with olefins, the stereoisomers in which both of the substituents on the carbon of carbonyl and C2 atom of olefins are on the same side of ring (A6, B10, B16, B17, C6, D6, E6, F10, F11, and G3) are more favored than the *trans* isomers (A5, B9, B15, C5, D5, E5, F9, F12, and G5). All of the stable isomers in Fig. 1 are bolded. Structures of different stereoisomers were optimized and some parameters were calculated for each isomer. The obtained frontier molecular orbital energies (HOMO and LUMO) and polarizability values, with the calculated hardness and electrophilicity by using Janak's approximation (Eqns (5) and (7)) for these stereoisomers are gathered in Table 1. In this table, the lesser polarizability, greater hardness, and lesser electrophilicity values for each reaction are bolded to check the validity of the MPP, MHP, and MEP in prediction of the major product of a reaction. The failed principles are also given in the last column of the table. From the obtained results it

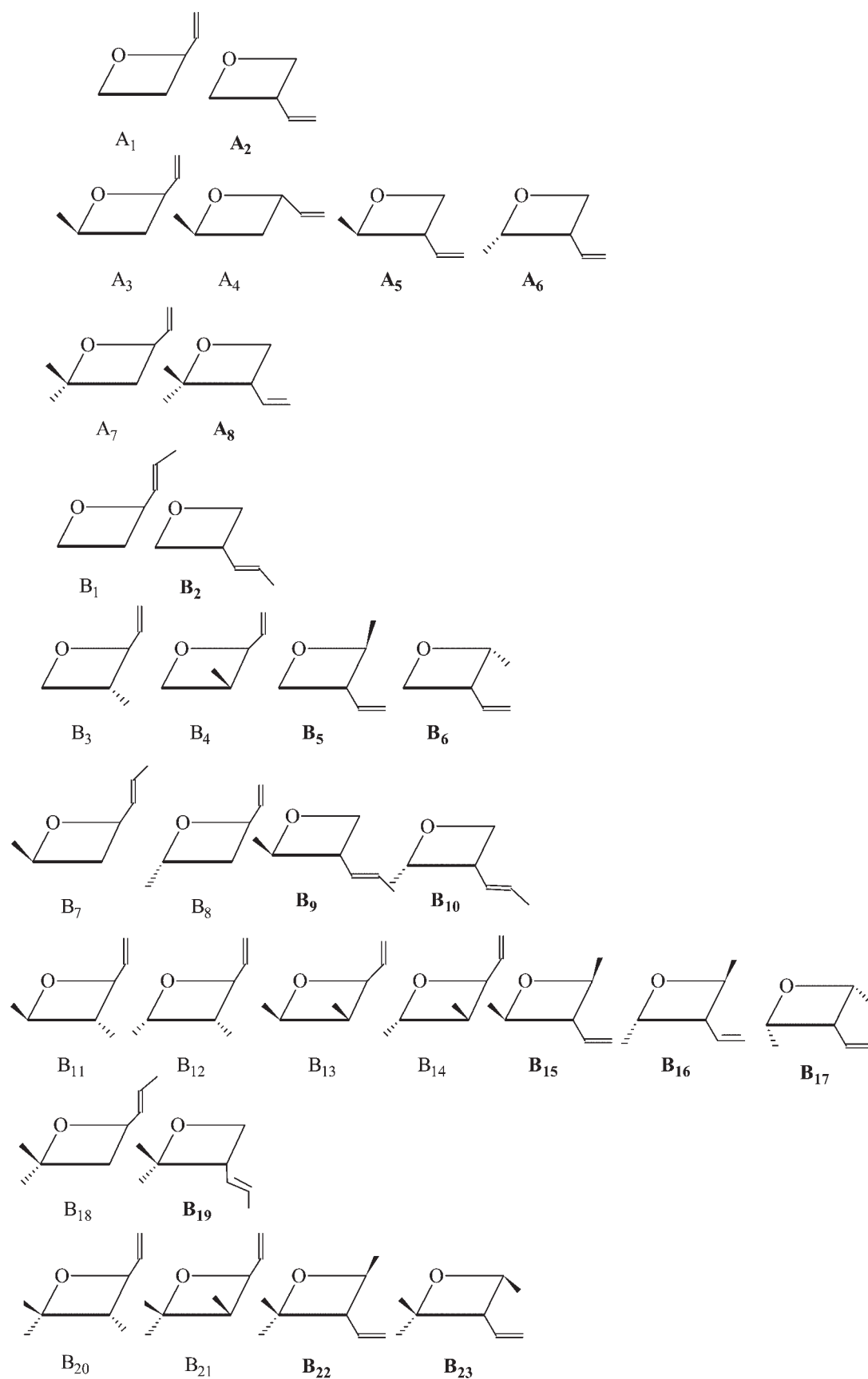


Figure 1. The considered stereoisomers in this study

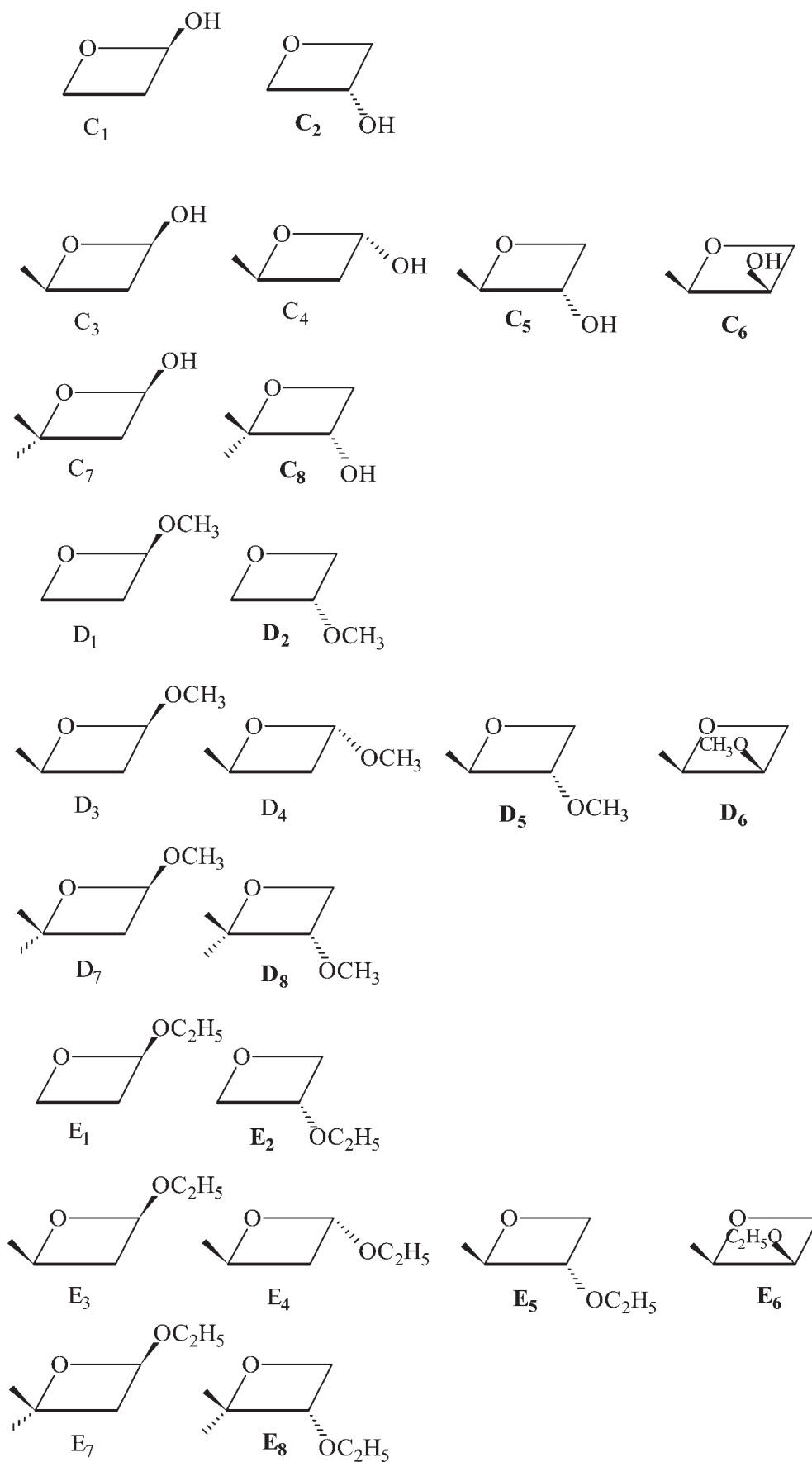


Figure 1. (Continued)

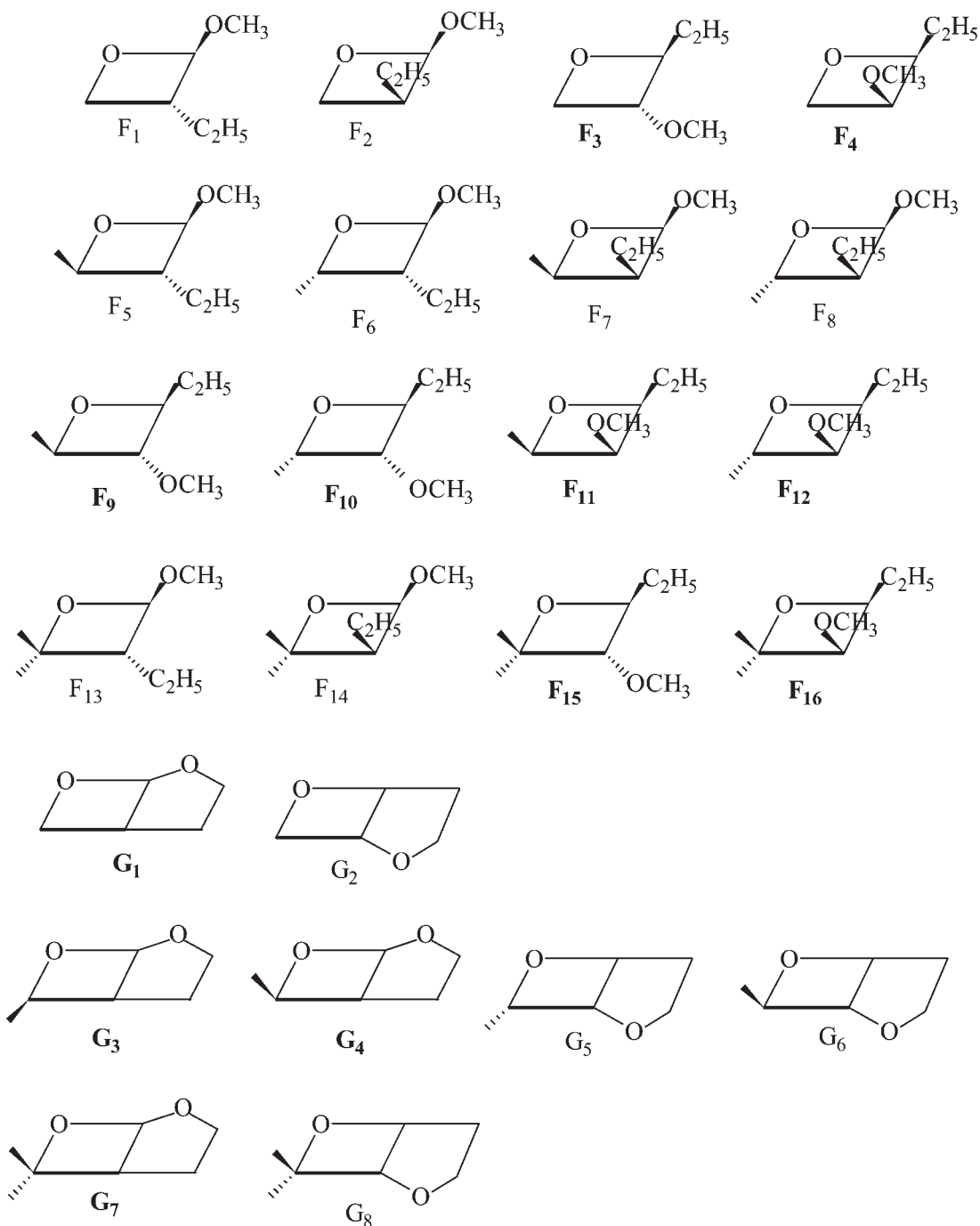


Figure 1. (Continued)

is found that nearly for most of the reactions (with six exceptions) the MPP is valid. Since the calculated polarizability is very sensitive to the quality of the basis set,³⁸ it seems that these exceptions may arise from the weakness of the used basis set (6-31G^{*}) and therefore the implementation of a larger basis set should minimize errors due to basis set incompleteness.

In contrast with the MPP, two other principles (MHP and MEP) are not so successful in predicting the major

products of the considered Paternó–Büchi reactions and nearly in all cases are failed. This difficulty may arise from the Janak's approximation, which seems to be inadequate in calculating the electrophilicity and hardness of these isomers. Therefore to remove this difficulty, the hardness and electrophilicity values for each oxetane were recalculated by using the ionization potential and electron affinity of the corresponding molecule (Eqns (2) and (6)), which are collected in Table 2. The results show

Table 1. Calculated frontier molecular orbital energies, polarizability, hardness, and electrophilicity values for different regioisomers of the considered reactions, using B3LYP/6-31G* method and the Janak's approximation

| Molecule | ϵ_H | ϵ_L | α | η' | ω' | Failed principle |
|----------|--------------|--------------|----------------|----------------|----------------|------------------|
| A1 | -0.24516 | 0.01982 | 53.272 | 0.13249 | 0.04791 | MEP, MHP |
| A2 | -0.24448 | 0.01309 | 52.994 | 0.12879 | 0.05197 | |
| A3 | -0.24416 | 0.0208 | 64.131 | 0.13248 | 0.04707 | MEP, MHP |
| A4 | -0.24362 | 0.0218 | 64.348 | 0.13269 | 0.04637 | |
| A5 | -0.24253 | 0.0143 | 64.381 | 0.12843 | 0.05068 | |
| A6 | -0.24247 | 0.0131 | 63.635 | 0.12777 | 0.05148 | |
| A7 | -0.24256 | 0.02197 | 74.685 | 0.13227 | 0.04599 | MEP, MHP |
| A8 | -0.24042 | 0.01354 | 74.531 | 0.12698 | 0.05067 | |
| B1 | -0.23515 | 0.02752 | 66.016 | 0.13134 | 0.04103 | MEP |
| B2 | -0.24164 | 0.02169 | 65.575 | 0.13167 | 0.04593 | |
| B3 | -0.24326 | 0.01961 | 64.547 | 0.13144 | 0.04757 | MEP, MHP, MPP |
| B4 | -0.24374 | 0.01775 | 53.734 | 0.13075 | 0.04883 | |
| B5 | -0.24337 | 0.00928 | 65.303 | 0.12633 | 0.05422 | |
| B6 | -0.24296 | 0.00883 | 64.828 | 0.12590 | 0.05443 | |
| B7 | -0.23594 | 0.01385 | 79.184 | 0.12489 | 0.04937 | MEP, MHP |
| B8 | -0.23381 | 0.02980 | 77.144 | 0.13181 | 0.03947 | |
| B9 | -0.23927 | 0.02283 | 77.124 | 0.13105 | 0.04468 | |
| B10 | -0.23987 | 0.02156 | 76.235 | 0.13072 | 0.04558 | |
| B11 | -0.24236 | 0.02082 | 75.308 | 0.13159 | 0.04662 | MEP, MHP, MPP |
| B12 | -0.24105 | 0.02234 | 75.150 | 0.13170 | 0.04541 | |
| B13 | -0.24172 | 0.01863 | 74.326 | 0.13015 | 0.04780 | |
| B14 | -0.24201 | 0.01969 | 74.821 | 0.13085 | 0.04722 | |
| B15 | -0.24102 | 0.01533 | 75.214 | 0.12818 | 0.04967 | |
| B16 | -0.24070 | 0.01404 | 74.567 | 0.12737 | 0.05042 | |
| B17 | -0.24092 | 0.01021 | 75.844 | 0.12557 | 0.05299 | |
| B18 | -0.23312 | 0.03001 | 87.528 | 0.13157 | 0.03919 | MEP, MHP |
| B19 | -0.23786 | 0.01677 | 87.500 | 0.12732 | 0.04799 | |
| B20 | -0.23997 | 0.02233 | 85.553 | 0.13115 | 0.04515 | MEP, MHP, MPP |
| B21 | -0.24103 | 0.01999 | 84.830 | 0.13051 | 0.04680 | |
| B22 | -0.23906 | 0.01444 | 85.507 | 0.12675 | 0.04976 | |
| B23 | -0.23938 | 0.00991 | 86.384 | 0.12465 | 0.05281 | |
| C1 | -0.25684 | 0.07834 | 36.8103 | 0.16759 | 0.02377 | MEP, MHP, MPP |
| C2 | -0.24590 | 0.05858 | 37.0207 | 0.15224 | 0.02881 | |
| C3 | -0.25522 | 0.07743 | 47.7013 | 0.16633 | 0.02376 | MEP, MHP, MPP |
| C4 | -0.25488 | 0.08042 | 47.5303 | 0.16765 | 0.02270 | |
| C5 | -0.24366 | 0.06333 | 47.9237 | 0.15349 | 0.02648 | |
| C6 | -0.24455 | 0.05973 | 47.5703 | 0.15214 | 0.02807 | |
| C7 | -0.25321 | 0.07071 | 57.9742 | 0.16195 | 0.02571 | MEP, MHP, MPP |
| C8 | -0.24192 | 0.06119 | 57.9754 | 0.15155 | 0.02694 | |
| D1 | -0.25662 | 0.09166 | 48.129 | 0.17414 | 0.01953 | MEP, MHP |
| D2 | -0.24631 | 0.06966 | 48.051 | 0.15798 | 0.02469 | |
| D3 | -0.25513 | 0.09552 | 58.970 | 0.17532 | 0.01817 | MEP, MHP |
| D4 | -0.25585 | 0.09713 | 59.266 | 0.17646 | 0.01786 | |
| D5 | -0.24354 | 0.07813 | 58.836 | 0.16084 | 0.02126 | |
| D6 | -0.24399 | 0.07395 | 58.559 | 0.15897 | 0.02274 | |
| D7 | -0.25442 | 0.09141 | 69.614 | 0.17293 | 0.01921 | MEP, MHP |
| D8 | -0.24162 | 0.07415 | 68.949 | 0.15789 | 0.02221 | |
| E1 | -0.25521 | 0.09462 | 59.431 | 0.17492 | 0.01843 | MEP, MHP |
| E2 | -0.24532 | 0.07186 | 59.267 | 0.15859 | 0.02372 | |
| E3 | -0.25402 | 0.09704 | 70.233 | 0.17552 | 0.01755 | MEP, MHP |
| E4 | -0.25236 | 0.09711 | 70.336 | 0.17474 | 0.01724 | |
| E5 | -0.24181 | 0.07623 | 69.720 | 0.15912 | 0.02156 | |
| E6 | -0.24193 | 0.07297 | 69.315 | 0.15745 | 0.02266 | |
| E7 | -0.25306 | 0.09199 | 80.973 | 0.17253 | 0.01880 | MEP, MHP |
| E8 | -0.23972 | 0.07538 | 79.926 | 0.15755 | 0.02143 | |
| F1 | -0.25505 | 0.08501 | 69.310 | 0.17003 | 0.02126 | MEP, MHP |
| F2 | -0.25579 | 0.08463 | 69.153 | 0.17021 | 0.02151 | |
| F3 | -0.24399 | 0.07468 | 69.556 | 0.15934 | 0.02249 | |
| F4 | -0.24327 | 0.07156 | 69.057 | 0.15742 | 0.02341 | |
| F5 | -0.25383 | 0.08911 | 80.207 | 0.17147 | 0.01978 | MEP, MHP, MPP |
| F6 | -0.25211 | 0.08407 | 80.023 | 0.16809 | 0.02100 | |

(Continues)

Table 1. (Continued)

| Molecule | ϵ_H | ϵ_L | α | η' | ω' | Failed principle |
|------------|--------------|--------------|----------------|----------------|----------------|------------------|
| F7 | -0.25628 | 0.08056 | 79.877 | 0.16842 | 0.02292 | |
| F8 | -0.25429 | 0.08808 | 80.277 | 0.17119 | 0.02017 | |
| F9 | -0.24161 | 0.08145 | 80.313 | 0.16153 | 0.01985 | |
| F10 | -0.24163 | 0.07593 | 80.137 | 0.15878 | 0.02162 | |
| F11 | -0.24237 | 0.07233 | 79.902 | 0.15735 | 0.02297 | |
| F12 | -0.24074 | 0.07797 | 80.001 | 0.15936 | 0.02078 | |
| F13 | -0.25115 | 0.08291 | 90.534 | 0.16703 | 0.02119 | MEP, MHP |
| F14 | -0.25476 | 0.07901 | 90.657 | 0.16689 | 0.02314 | |
| F15 | -0.23970 | 0.07419 | 90.545 | 0.15695 | 0.02182 | |
| F16 | -0.24019 | 0.07176 | 90.382 | 0.15598 | 0.02274 | |
| G1 | -0.25801 | 0.08185 | 53.6543 | 0.16993 | 0.02283 | MEP |
| G2 | -0.24943 | 0.08243 | 54.0777 | 0.16593 | 0.02101 | |
| G3 | -0.25568 | 0.07971 | 64.3313 | 0.16770 | 0.02308 | MEP |
| G4 | -0.25611 | 0.08694 | 64.6881 | 0.17153 | 0.02086 | |
| G5 | -0.24442 | 0.08867 | 65.0183 | 0.16655 | 0.01821 | |
| G6 | -0.24795 | 0.08670 | 65.1323 | 0.16733 | 0.01942 | |
| G7 | -0.25392 | 0.07809 | 74.9083 | 0.16601 | 0.02328 | MEP |
| G8 | -0.24341 | 0.08413 | 75.5807 | 0.16377 | 0.01936 | |

The major isomers are bolded. All values are in a.u.

that by using these more accurate relations, only in four cases the MHP is broken down (C and E molecules with acetone, F molecule with all of the carbonyl compounds); whereas surprisingly in all reactions, with no exception, the MEP is valid and this principle correctly predicts the main product of each reaction. In fact in all reactions, the experimentally observed predominant products are consistently associated with lower values of electrophilicity and it seems that the MEP is the most successful principle in the study of a Paternó-Büchi reaction. Again the failure of MHP in some cases may arise from the

weakness of the used basis set and the difference between the chemical potentials of the compared molecules; because as it is mentioned in the introduction section, the constancy of chemical potential is one of the conditions of MHP. But these difficulties are not seen in electrophilicity because as it was shown in our previous paper,⁵² this index is not so dependent to the selected basis set and the obtained trend for the electrophilicities of a given series of molecules does not vary with the change in the used basis set. In the other hand, the results show that the *cis* stereoisomer of each oxetane has lesser electrophilicity

Table 2. Calculated vertical ionization energy, electron affinity, hardness and electrophilicity values for different regioisomer of the considered reactions, using B3LYP/6-31G* method

| Molecule | IE | EA | η | ω | Failed principle |
|------------|---------|---------|----------------|----------------|------------------|
| A1 | 0.32939 | 0.10597 | 0.11171 | 0.21210 | |
| A2 | 0.33282 | 0.10085 | 0.11598 | 0.20269 | |
| A3 | 0.32522 | 0.10613 | 0.10954 | 0.21232 | |
| A4 | 0.32477 | 0.10650 | 0.10913 | 0.21304 | |
| A5 | 0.32656 | 0.10053 | 0.11301 | 0.20175 | |
| A6 | 0.32741 | 0.09808 | 0.11467 | 0.19735 | |
| A7 | 0.32101 | 0.10489 | 0.10805 | 0.20984 | |
| A8 | 0.32221 | 0.09661 | 0.11280 | 0.19439 | |
| B1 | 0.31475 | 0.10753 | 0.10361 | 0.21514 | |
| B2 | 0.32008 | 0.10315 | 0.10846 | 0.20644 | |
| B3 | 0.32463 | 0.10261 | 0.11101 | 0.20554 | |
| B4 | 0.32572 | 0.10044 | 0.11264 | 0.20154 | |
| B5 | 0.32811 | 0.09498 | 0.11657 | 0.19195 | |
| B6 | 0.33641 | 0.09335 | 0.12153 | 0.18996 | |
| B7 | 0.31482 | 0.10286 | 0.10598 | 0.20576 | |
| B8 | 0.31132 | 0.10839 | 0.10146 | 0.21702 | |
| B9 | 0.31249 | 0.09170 | 0.11039 | 0.18499 | |
| B10 | 0.31602 | 0.10066 | 0.10768 | 0.20154 | |

(Continues)

Table 2. (Continued)

| Molecule | IE | EA | η | ω | Failed principle |
|------------|---------|---------|----------------|----------------|------------------|
| B11 | 0.32089 | 0.10329 | 0.10880 | 0.20671 | |
| B12 | 0.31951 | 0.10401 | 0.10775 | 0.20809 | |
| B13 | 0.32066 | 0.10069 | 0.10998 | 0.20178 | |
| B14 | 0.32094 | 0.10123 | 0.10986 | 0.20280 | |
| B15 | 0.32252 | 0.09998 | 0.11127 | 0.20052 | |
| B16 | 0.32264 | 0.09775 | 0.11245 | 0.19645 | |
| B17 | 0.33283 | 0.09273 | 0.12005 | 0.18857 | |
| B18 | 0.30849 | 0.10707 | 0.10071 | 0.21433 | |
| B19 | 0.31099 | 0.09400 | 0.10850 | 0.18896 | |
| B20 | 0.31612 | 0.10255 | 0.10679 | 0.20518 | |
| B21 | 0.31761 | 0.10005 | 0.10878 | 0.20044 | |
| B22 | 0.31749 | 0.09609 | 0.11070 | 0.19315 | |
| B23 | 0.31911 | 0.09166 | 0.11373 | 0.18546 | |
| C1 | 0.35718 | 0.15393 | 0.10163 | 0.32131 | |
| C2 | 0.34484 | 0.13691 | 0.10397 | 0.27904 | |
| C3 | 0.34706 | 0.14800 | 0.09953 | 0.30781 | |
| C4 | 0.34649 | 0.15049 | 0.09799 | 0.31504 | |
| C5 | 0.33645 | 0.14008 | 0.09818 | 0.28911 | |
| C6 | 0.33960 | 0.13366 | 0.10297 | 0.27189 | |
| C7 | 0.34086 | 0.13642 | 0.10222 | 0.27857 | MHP |
| C8 | 0.33119 | 0.13193 | 0.09963 | 0.26910 | |
| D1 | 0.34888 | 0.16178 | 0.09355 | 0.34843 | |
| D2 | 0.33635 | 0.14281 | 0.09677 | 0.29656 | |
| D3 | 0.34273 | 0.16008 | 0.09132 | 0.34605 | |
| D4 | 0.34372 | 0.16161 | 0.09106 | 0.35054 | |
| D5 | 0.32872 | 0.14664 | 0.09104 | 0.31026 | |
| D6 | 0.33449 | 0.14112 | 0.09668 | 0.29246 | |
| D7 | 0.33839 | 0.15273 | 0.09283 | 0.32479 | |
| D8 | 0.32446 | 0.13746 | 0.09350 | 0.28525 | |
| E1 | 0.34385 | 0.16002 | 0.09192 | 0.34526 | |
| E2 | 0.33265 | 0.14171 | 0.09547 | 0.29462 | |
| E3 | 0.33838 | 0.15720 | 0.09059 | 0.33888 | |
| E4 | 0.33543 | 0.15941 | 0.08801 | 0.34779 | |
| E5 | 0.32383 | 0.14020 | 0.09182 | 0.29316 | |
| E6 | 0.32752 | 0.13758 | 0.09497 | 0.28472 | |
| E7 | 0.33437 | 0.15032 | 0.09202 | 0.31911 | MHP |
| E8 | 0.31999 | 0.13651 | 0.09174 | 0.28393 | |
| F1 | 0.34310 | 0.14850 | 0.09730 | 0.31048 | MHP |
| F2 | 0.34281 | 0.14675 | 0.09803 | 0.30561 | |
| F3 | 0.32847 | 0.14300 | 0.09274 | 0.29962 | |
| F4 | 0.32670 | 0.13906 | 0.09382 | 0.28904 | |
| F5 | 0.33758 | 0.15048 | 0.09355 | 0.31828 | MHP |
| F6 | 0.33507 | 0.14586 | 0.09461 | 0.30561 | |
| F7 | 0.34144 | 0.14072 | 0.10036 | 0.28957 | |
| F8 | 0.33656 | 0.14708 | 0.09474 | 0.30861 | |
| F9 | 0.32180 | 0.14352 | 0.08914 | 0.30363 | |
| F10 | 0.32384 | 0.13841 | 0.09272 | 0.28809 | |
| F11 | 0.32857 | 0.13476 | 0.09691 | 0.27690 | |
| F12 | 0.32008 | 0.14099 | 0.08954 | 0.29677 | |
| F13 | 0.33192 | 0.14245 | 0.09474 | 0.29692 | MHP |
| F14 | 0.33578 | 0.13683 | 0.09948 | 0.28067 | |
| F15 | 0.31782 | 0.13296 | 0.09243 | 0.27480 | |
| F16 | 0.31873 | 0.13118 | 0.09378 | 0.26983 | |
| G1 | 0.34803 | 0.14865 | 0.09969 | 0.30933 | |
| G2 | 0.33563 | 0.15473 | 0.09045 | 0.33229 | |
| G3 | 0.34239 | 0.14314 | 0.09964 | 0.29578 | |
| G4 | 0.34151 | 0.15038 | 0.09557 | 0.31649 | |
| G5 | 0.32682 | 0.15173 | 0.08755 | 0.32698 | |
| G6 | 0.33010 | 0.15292 | 0.08859 | 0.32919 | |
| G7 | 0.33681 | 0.13836 | 0.09923 | 0.28444 | |
| G8 | 0.32220 | 0.14421 | 0.08899 | 0.30555 | |

The major isomers are bolded. All values are in a.u.

than the *trans* form of the molecule and therefore are the major stereoisomers for the considered reaction; which is in accordance with the photochemistry rules. It is also mentioned that for those cases in which all of the considered principles are valid, the same stereoisomers are introduced as the stable and major products of that reaction. For example, in the reaction of 1,3 butadiene (A molecule) with acetaldehyde all principles predict the A6 as the major isomer of the reaction.

Therefore we have claimed that *at equilibrium, a system attempts to arrange its electronic structure to generate species with the lesser electrophilicity so that more stable isomers correspond to lesser electrophilicity values.* To generalize this principle, its validity is checking in some other organic reactions in our research group.

CONCLUSION

Although the MPP and MHP are not always successful in predicting the major product of a photocycloaddition reaction of a carbonyl group with an olefine (Paternó–Büchi reaction), but the results suggest that not only the MEP is able to predict correctly the regioselectivity during a photocycloaddition reaction, but also successfully predicts the major stereoisomer of such reaction. Therefore we have claimed that *at equilibrium, a system attempts to arrange its electronic structure to generate species with the lesser electrophilicity so that more stable isomers correspond to lesser electrophilicity values.*

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