

Modification of Regioselectivity in Cycloadditions to C₇₀ under Microwave Irradiation

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The regioselectivity of the cycloaddition of *N*-methylazomethine ylide to C₇₀ can be modified by using microwave irradiation as the source of energy. Under microwave irradiation and by choosing the appropriate solvent and irradiation power, the 5–6 isomer is the major product, a situation that is in contrast to conventional heating where the 1–2 isomer predominates. Moreover, isomer 7–21, which represents 13% of monoadducts under classical heating, is not formed under microwave irradiation and with ODCB as solvent. Theoretical calculations predict an asynchronous mechanism and suggest that the modification of the regiochemical outcome is related to the relative energies and hardnesses of the transition structures involved.

Introduction

Microwave radiation is a nonconventional energy source whose popularity and synthetic utility in organic chemistry have increased considerably in recent years.¹ Microwave heating uses the ability of some materials (liquids and solids) to transform electromagnetic energy into heat. Characteristically, the use of microwaves can lead to significant decreases in reaction times, cleaner reactions that are easier to work up than those from conventional heating, and in many cases, higher yields. Despite the great practical advantages inherent in these properties, in the majority of studied reactions the chemical reactivity is unchanged (products obtained by microwave irradiation are identical to the obtained by classical heating), and no changes in isomeric distribution are observed. Under microwave irradiation, superheating to temperatures above the conventional boiling point can be produced² and decreases in reaction time are not surprising. Nevertheless, a milestone work by Stuerger³ showed that controlling the heating rate can modify isomeric distribution induced by the change in microwave power. The temperature profiles achieved by microwave heating are not accessible with a conventional heating bath and can allow kinetic control. A careful review of the literature shows that in other reactions the chemo-, regio-, and stereoselectivity can be modified or even inverted by the use of microwaves in comparison to

conventional heating.⁴ Consequently, interest in microwave irradiation as a technique in organic chemistry has increased considerably.

As part of our research into cycloaddition reactions under microwaves,⁵ we have successfully applied this methodology to cycloaddition reactions involving [60]-fullerene.⁶ In most cases, as expected, yields have been improved and reaction times were reduced.

Although cycloadditions to C₆₀ have been extensively studied in recent years,⁷ much less work has been performed in the chemistry of C₇₀ as a result of its low abundance and high cost. Moreover, the lower symmetry of C₇₀ gives rise to more isomers than C₆₀; whereas C₆₀ contains a single type of [6,6] bond, C₇₀ contains four different [6,6] bonds (Figure 1). In a similar way to C₆₀, cycloaddition reactions with C₇₀ take place exclusively on [6,6] bonds, and the 1–2 and 5–6 bonds⁸ are the most reactive ones, in this order.⁹

Within this context and in connection with our program on the application of microwaves to the chemistry of fullerenes,^{6,10–12} we decided to evaluate the potential of microwave irradiation to modify the regioselectivity in the formation of cycloadducts with [70]fullerene.

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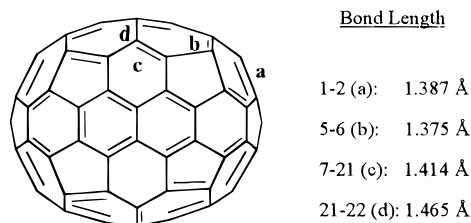
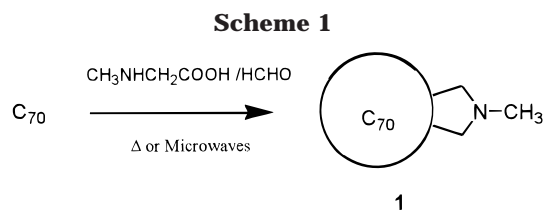


Figure 1. [6,6] Bond lengths of C_{70} .



Results and Discussion

Theoretical calculations for cycloadditions to [70]-fullerene are scarce.¹³ However, ab initio calculations for the Diels–Alder cycloaddition with butadiene¹⁴ have been performed recently. It was shown that attack at the 1–2 bond is preferred from a thermodynamic point of view and that 5–6 attack seems to be kinetically favored. Additions to other bonds are thermodynamically unfavored by at least 6 kcal/mol. With this result in mind and considering the heating rate and the decrease in reaction times achieved using microwaves, we believed that microwave radiation should favor the kinetic product (5–6 adduct) in cycloaddition reactions to C_{70} .

Cycloaddition of azomethine ylides to C_{60} is one of the most powerful methods for derivatizing fullerenes.¹⁵ *N*-Methylpyrrolidinofullerenes have been extensively prepared,¹⁶ and their properties have been studied.¹⁷ In addition, it has been reported¹⁸ that cycloaddition of azomethine ylides to [70]fullerene, under classical heating conditions (Scheme 1), affords the three monoadducts **1a–c** (Figure 2), namely, **1a** (isomer 1–2), **1b** (isomer 5–6), and **1c** (isomer 7–21) adducts in a 46:41:13 ratio. For this reason, we decided to use the cycloaddition of azomethine ylides to C_{70} as a model.

The low polarity of C_{70} (10^{-3} D) prevents the absorption of the radiation by this substrate. Microwave radiation must be absorbed by the solvent, and as a consequence, the nature of the solvent must have a significant influence on the course of the reaction.

To demonstrate the influence of microwave irradiation in relation to the solvent polarity, we chose toluene ($\mu =$

0.36 D), chlorobenzene ($\mu = 1.69$ D), and *o*-dichlorobenzene (ODCB) ($\mu = 2.50$ D)¹⁹ as solvents. The reactions carried out using conventional heating were performed in a round-bottomed flask immersed in a graphite bath preheated at the corresponding temperature. The reactions using microwave irradiation were performed in cylindrical flasks in a focused microwave reactor,²⁰ equipped with an infrared temperature detector, at refluxing temperature. Reaction times were chosen to prevent the formation of bisadducts, which could modify the ratio of monoadducts if they were to react at different rates. To check the reproducibility, entries 2 and 7 were duplicated, and the ratio of monoadducts differed in less than 1%. In all cases, after column chromatography, the isomer distributions in the crude mixtures were evaluated by integration of the methyl signals in the ¹H NMR spectra: $\delta = 2.52$ for **1c**, $\delta = 2.61$ for **1b**, and $\delta = 2.74$ for **1a**.

From the results presented in Table 1 it can be seen that there is a strong influence of the polarity of the solvent and of the heating technique used, and the following trends can be deduced:

Nonpolar Solvent. The use of toluene does not lead to any significant differences in the isomer distribution between conventional heating and microwave irradiation (entries 1 and 2), with **1a** being the predominant isomer. Toluene, as a nonpolar solvent, does not absorb microwaves efficiently, and the heating rate under microwave irradiation is similar to that produced under classical heating. Consequently, no differences in selectivity were found.

Polar Solvent. With a polar solvent such as ODCB, which absorbs microwaves efficiently, significant changes were observed and the product ratio depends on the heating technique used (see Table 1 and Figure 3). Under classical heating the ratio **1a:1b** changes to 1:1 (entry 5). This effect can be related to an increase in the reaction temperature, defined by the boiling point of the solvent, or to a change in the polarity of the solvent from toluene to ODCB.

Under microwave irradiation additional effects are observed; isomer **1c** was not observed in any case, regardless of the irradiation power, and the ratio **1a:1b** can be modified by changing the incident power, with **1b** being the predominant isomer at high power (entries 6–9).

This effect could be related to (i) the presence of “hot spots”; in this process the macroscopic temperature, under microwave irradiation, is not representative of the reaction temperature; (ii) the heating rate induced by microwaves, which cannot be achieved by conventional heating, on using high power and a polar solvent; or (iii) a selective interaction of the electromagnetic field with the transition state (**TS**) that gives rise to compounds **1a**, **1b**, and **1c** if they have differentiated polarities.

Intermediate Solvent. With a solvent of intermediate polarity, such as chlorobenzene, the influence of the solvent was confirmed and an intermediate situation between polar and nonpolar solvents was observed. Under classical heating the proportion of **1c** is reduced but the ratio **1a:1b** is maintained in relation to toluene (entries 1 and 3). Under microwave irradiation **1c** is still detected in a lower proportion (entry 4) while **1b** again becomes the major isomer, as is the case with ODCB.

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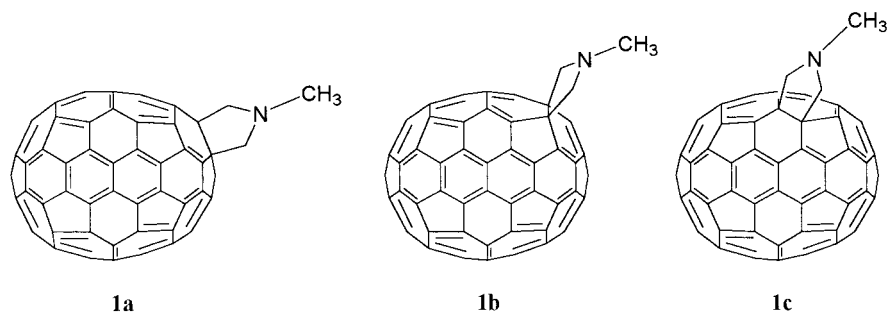


Figure 2. Cycloadducts 1a–c.

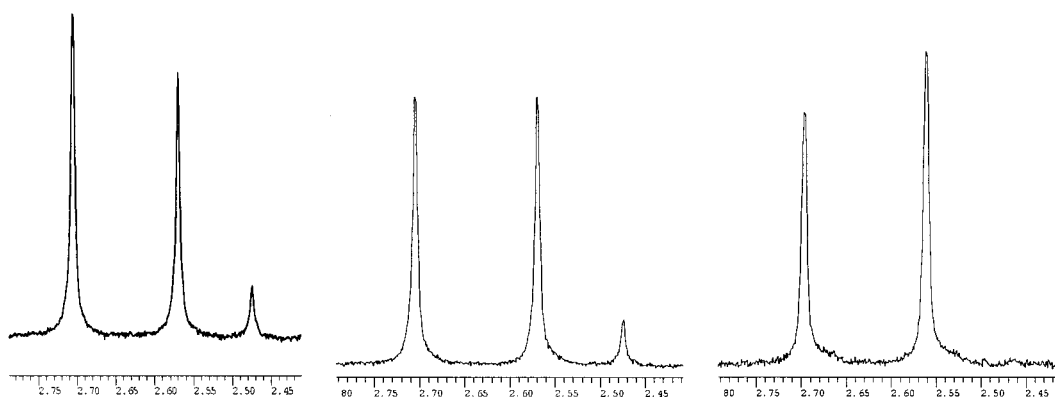


Figure 3. ¹H NMR region of the methyl group: (a) classical heating in toluene as solvent (entry 1, Table 1), (b) classical heating in ODCB as solvent (entry 5), and (c) microwave irradiation in ODCB at 180 W, 30 min (entry 8).

Table 1. Yield of Monoadducts and Isomer Distribution (1a:1b:1c) Using Classical Heating and Microwave Irradiation

entry	procedure	conditions	yield (%)	% 1a	% 1b	% 1c
1	classical heating ¹⁸	toluene, 120 min	45 ¹⁸	46	41	13
2	microwaves	toluene, 120 W, 30 min	32	48	44	8
3	classical heating	chlorobenzene, 120 min	35	50	43	7
4	microwaves	chlorobenzene, 120 W, 30 min	31	45	52	3
5	classical heating	ODCB, 120 min	32	46	46	8
6	microwaves	ODCB, 120 W, 30 min	39	50	50	0
7	microwaves	ODCB, 180 W, 10 min	21	43	57	0
8	microwaves	ODCB, 180 W, 30 min	37	45	55	0
9	microwaves	ODCB, 300 W, 15 min	37	47	53	0

To understand the origins of the observed regioselectivities, we performed a computational study on the modes of cycloaddition between *N*-methylazomethine ylide and C₇₀ to yield pyrrolidino[70]fullerenes 1a–c. Given the size of the system as a whole, we used the PM3 semiempirical²¹ Hamiltonian, because this method has proved useful in the study of other [3 + 2] cycloadditions.²² In addition, we checked the accuracy of PM3 by comparison with other 1,3-dipolar cycloadditions studied by our group using MP2 and B3LYP methodologies.^{23–25} In all of the cases studied, the HF/PM3 results were in good agreement with those obtained by SCF-MO and DFT.

In principle, two possible reaction paths are conceivable for 1,3-dipolar cycloadditions: the concerted and the stepwise mechanism.²⁶ The first pathway proceeds in a suprafacial manner for both reactants according to the

thermally allowed [$\pi 2_s + \pi 4_s$] mechanism (Scheme 2, path a).²⁷ The second pathway consists of a second-order nucleophilic addition of the 1,3-dipole over the dipolarophile to yield a zwitterionic intermediate, whose [5-*endo-trig*] ring closure leads to the corresponding five-membered cycloadduct (Scheme 2, path b).²² Previous studies^{25,28} on simple systems have shown that, in general, the concerted mechanism is preferred for non-metalled azomethine ylides. However, to assess the accuracy of PM3 for the system under study, we performed a prior computational study on the model reaction **2** + **3** → **4** (Figure 4) at both HF/PM3 and HF/6-31G* levels. In addition, the relative energies were calculated at the B3LYP/6-31+G*//HF/6-31G*+ $\Delta ZPVE$ level. The main geometrical data of the stationary points and the activation and reaction energies are reported in Figure 4 and in Table 2, respectively. From the results obtained we can conclude that PM3 is not biased against concerted

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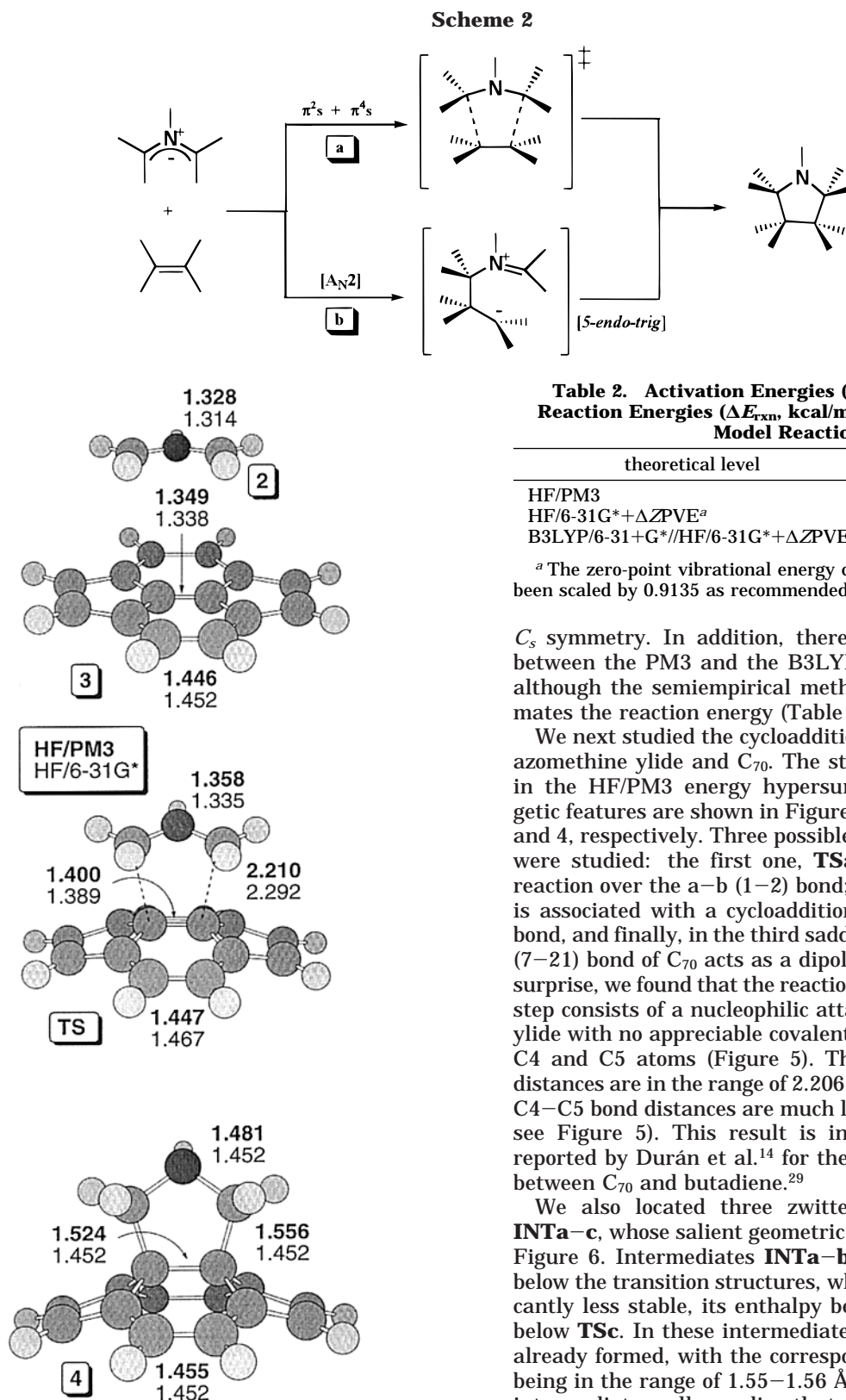


Figure 4. Ball and stick representations and chief geometric features of the fully optimized stationary points corresponding to the $2 + 3 \rightarrow 4$ model reaction. Distances are given in Å. In this and in other figures including ball-and-stick drawings, the different elements are represented by increasing order of shading as follows: H, C, N.

mechanisms for this processes, because it predicts a [$\pi 2_s + \pi 4_s$] concerted mechanism for the model reaction, with the corresponding transition structure (**TS**) possessing

(29) In the case of **TSb**, we located a concerted saddle point with similar C2–C3 and C4–C5 bond distances (2.556 and 2.592 Å, respectively). This structure was only 0.8 kcal/mol above **TSb** but had two imaginary frequencies (147.81 cm^{-1} and 74.11 cm^{-1}), the second one corresponding to the antisymmetric stretching of the C2–C3 and C3–C4 bonds being formed. Schleyer et al. found a similar result in their calculations on anionic [3 + 2] cycloadditions; see: Neumann, F.; Lambert, C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1998**, *120*, 3357.

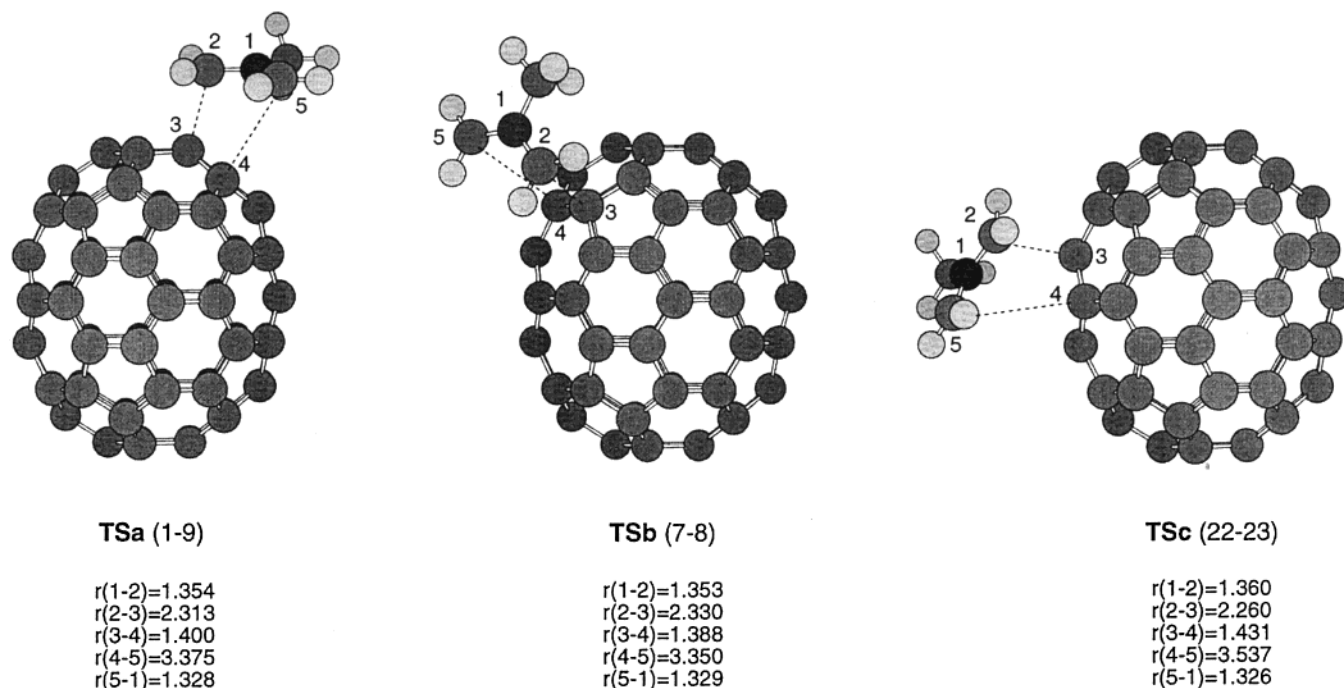


Figure 5. Ball and stick representations and chief geometric features of the RHF/PM3 fully optimized saddle points **TSa–c**. See Figure 4 caption for additional details.

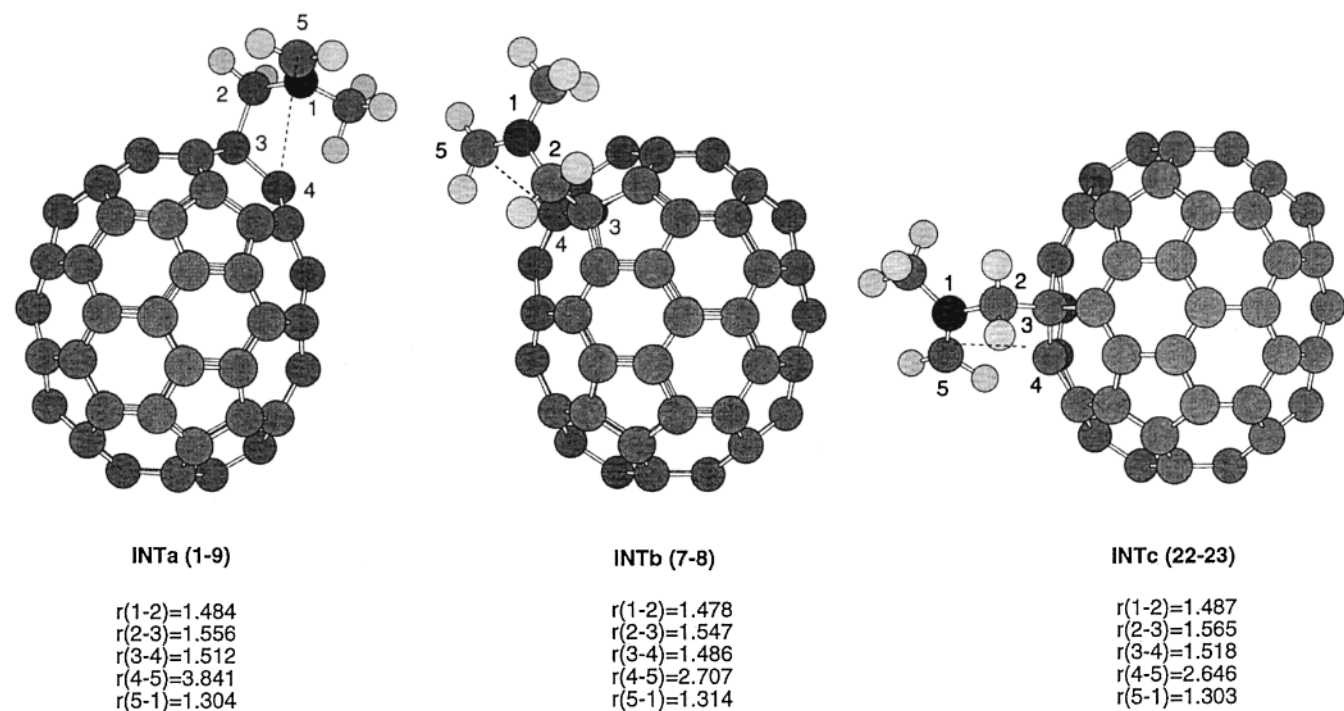


Figure 6. Ball and stick representations and chief geometric features of the RHF/PM3 fully optimized stationary points **INTa–c**. See Figure 4 captions for additional details.

kcal/Å (deg) were unsuccessful. Similarly, the computed reaction coordinates showed no barrier on passing from the intermediates to the products. The energies of these cycloadducts and their main geometric features are given in Table 3 and Figure 7, respectively. According to our previous results on the model reaction, it seems very likely that the enthalpies of reaction are overestimated at the RHF/PM3 level.

The computed activation barriers for the reaction between *N*-methylazomethine ylide and C₇₀ are signifi-

cantly smaller than that calculated for the model reaction and those reported by Durán et al.¹⁴ for the isoelectronic thermal cycloaddition between butadiene and C₇₀ (see Table 3). Given the loss of polarity on passing from the reactants to the products, it is expected that these values would be larger in solution, according to the experimental³⁰ and computational²⁵ results reported by Huisgen and by our group, respectively, for 1,3-dipolar cycloadditions. An analysis of the distortion enthalpies for **TSa–c** (Table 4) reveals that the ΔH_{dis} values are similar

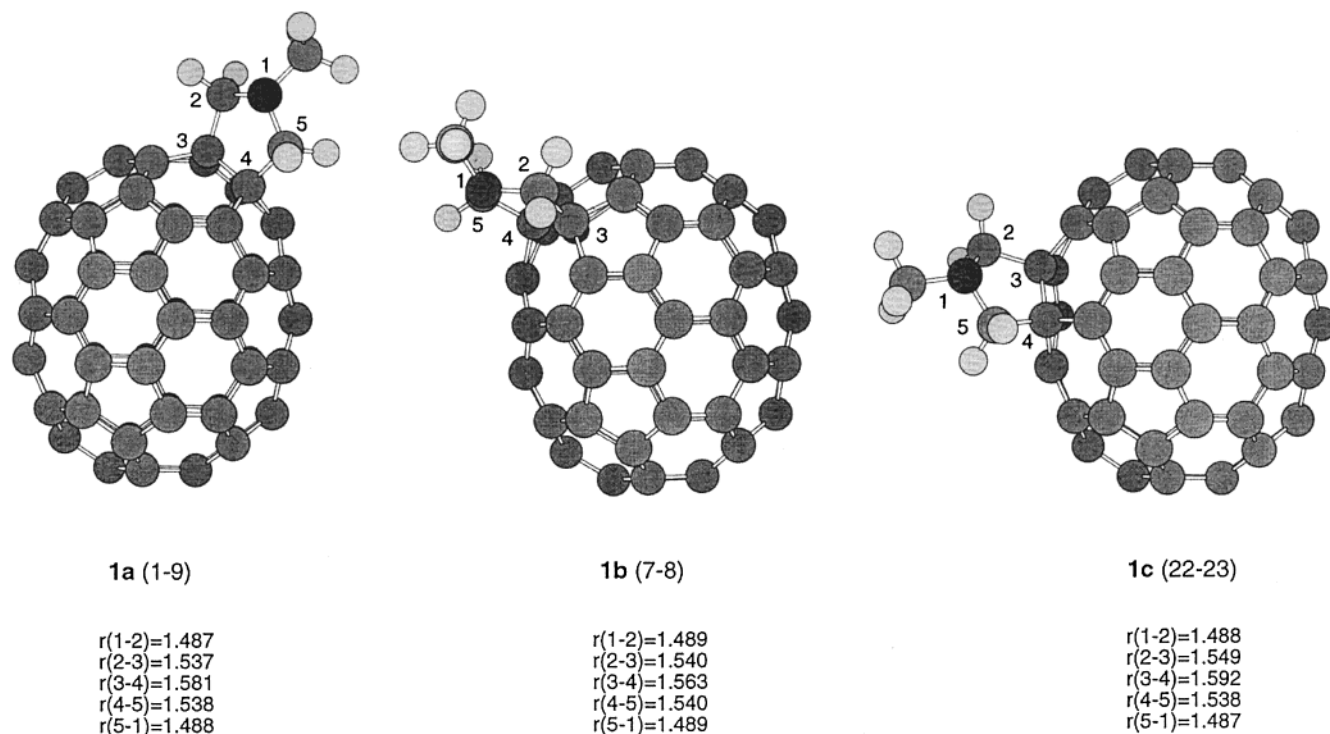


Figure 7. Ball and stick representations and chief geometric features of the RHF/PM3 fully optimized cycloadducts **1a–c**. See Figure 4 caption for additional details.

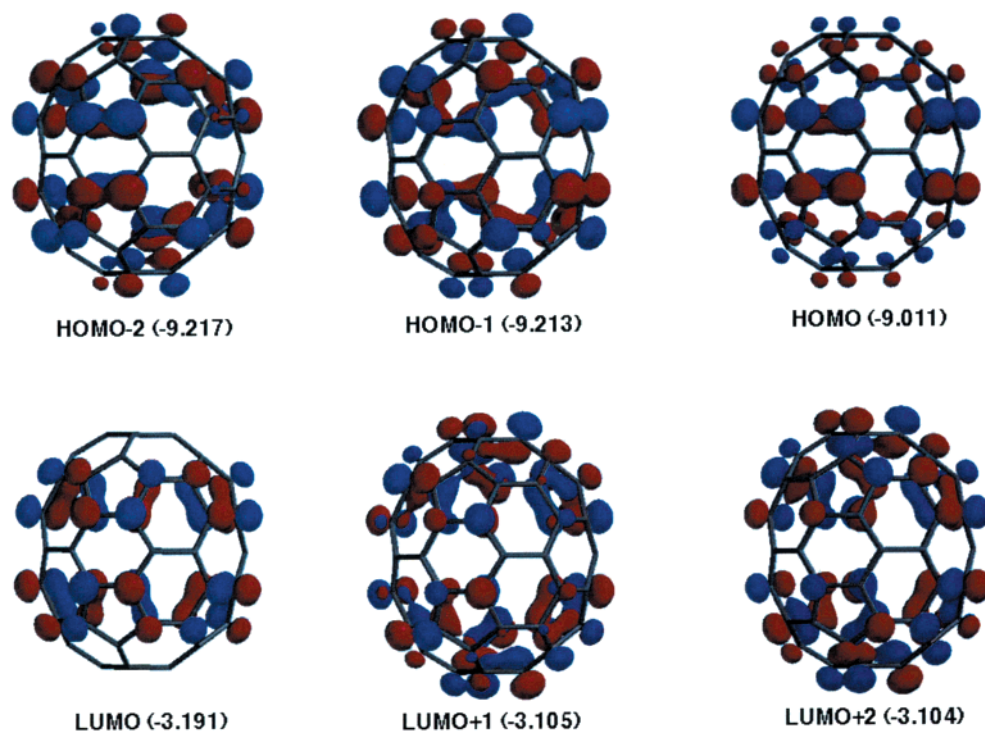


Figure 8. Plot of selected molecular orbitals of C_{70} , computed at the RHF/PM3 level. Number in parentheses are the orbital energies and are given in eV.

for both the C_{70} and the azomethine moieties. Therefore, most of the small activation barrier in this reaction stems from the distortion of the reactants in the corresponding transition structure. However, the total ΔH_{dis} value for

TS_c is ca. 2.6 kcal/mol larger than those found for **TS_a–b**, thus suggesting that the regiocontrol of the reaction is related to the larger distortion of the equatorial positions on passing from C_{70} to **TS_c**, as well as from the electronic distortion of the azomethine moiety. Thus, whereas the heats of formation of **TS_a** and **TS_b** are very similar (Table 3), that of **TS_c** is 1.19 kcal/mol larger. If the corresponding free energies are calculated at the

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Table 3. HF/PM3 Heats of Formation (ΔH_f , kcal/mol) and Relative Enthalpies (ΔH^\ddagger ,^a ΔH_{int} ,^b ΔH_{rxn} ,^c kcal/mol) for the Stationary Points Found in the Reaction between *N*-Methylazomethine Ylide and C₇₀ to Yield Regioisomers **1a–c**

regioisomer	TSa–c		INTa–c		1a–c	
	ΔH_f	ΔH^\ddagger	ΔH_f	ΔH_{int}	ΔH_f	ΔH_{rxn}
a (1–2)	925.74	3.44	904.34	–17.96	851.19	–71.13
b (5–6)	925.72	3.42	904.24	–18.06	849.01	–73.31
c (7–21)	926.91	4.61	919.53	–2.77	867.76	–60.56

^a Computed as $\Delta H^\ddagger = \Delta H_f(\text{TS}) - [\Delta H_f(\text{C}_{70}) + \Delta H_f(\text{CH}_2\text{N}(\text{CH}_3)\text{CH}_2)]$. ^b Computed as $\Delta H_{\text{int}} = \Delta H_f(\text{INT}) - [\Delta H_f(\text{C}_{70}) + \Delta H_f(\text{CH}_2\text{N}(\text{CH}_3)\text{CH}_2)]$. ^c Computed as $\Delta H_{\text{rxn}} = \Delta H_f(\mathbf{1}) - [\Delta H_f(\text{C}_{70}) + \Delta H_f(\text{CH}_2\text{N}(\text{CH}_3)\text{CH}_2)]$.

boiling temperatures of toluene, chlorobenzene, and ODCB (384, 405, and 454 K, respectively) it is found that **TSa** is 2.7–3.0 kcal/mol above **TSa** and **TSb** (see Table 4). At 384 K this energy difference corresponds to a **1a**:**1b**:**1c** ratio of 48.96:49.69:1.35 under kinetic control. This regiomer distribution is in fair agreement with that found experimentally (vide supra). If we consider that the computed dipole moment of **TSa** is ca. 0.5 D larger than those of **TSa** and **TSb**, it is expected that the relative proportion of **TSa** in toluene solution would be larger than that computed in the gas phase.

Why are **TSa–b** so asynchronous? From the FMO standpoint, the shape of the molecular orbitals of C₇₀ shows an unfavorable topology for a [$\pi 2_s + \pi 4_s$] mechanism, with the exception of **TSb**. For instance, in the HOMO of C₇₀ the a–b subunit has a phase dislocation that makes the interaction with the LUMO of *N*-methylazomethine ylide difficult. In addition, there are no LUMO coefficients for the a–b subunit in C₇₀. Therefore, the HOMO of *N*-methylazomethine ylide must interact with the LUMO + 1 and LUMO + 2 of C₇₀. In the case of **TSb**, the local symmetry of the b atoms of C₇₀ is adequate both at the HOMO and at the LUMO, although the atoms involved do not have the largest coefficients. Finally, in all of the MOs reported in Figure 8 there is a nodal plane that contains the “equatorial” e-atoms. As a consequence, no covalent interaction of these atoms with the carbon atoms of the 1,3-dipole can be expected. Therefore, **TSa** must be the transition structure of highest energy, as well as the most asynchronous one.

The next question to be addressed is why **TSa** is more disfavored under microwave irradiation. To answer this question, the polarity and the polarizability of the transition structures involved must be taken into account. The plots of the electrostatic potential of **TSa–b** on the electron density surface are shown in Figure 9. From these data it is clear that most of the negative charge of the fullerene moiety in **TSa** and **TSb** (ca. 0.14 e, see Table 4) is located at the carbon adjacent to the carbon–carbon bond being formed. In **TSa**, however, the negative charge (0.18 e, Table 4) is delocalized all around the C₇₀ subunit. Therefore, this latter saddle point exhibits a more homogeneous charge distribution for the bulky fullerene moiety than **TSa** or **TSb**. On the other hand, the absolute hardnesses (η) of these stationary points computed according to the following eq 1³¹ show that **TSa**

$$\eta = \frac{\epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}}{2} \quad (1)$$

is the softest saddle point (Table 4). In addition, the isotropic polarizability volumes, α'_{av} , computed according

to eq 2 where α_{av} is the average polarizability (eq 3) show

$$\alpha'_{\text{av}} = \frac{\alpha_{\text{av}}}{4\pi\epsilon_0} \quad (2)$$

$$\alpha_{\text{av}} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (3)$$

that **TSa** is the most polarizable transition structure (Table 4). In summary, this latter transition structure should interact less efficiently with the oscillating electric field of the microwaves,^{32a} thus favoring the formation of the remaining cycloadducts under kinetic control. Similarly, since **TSb** has the highest hardness and the lowest polarizability, its formation should be favored under microwave irradiation, thus explaining the change in regioselectivity with respect to classical heating.

Modification of selectivities and accelerations of rates in microwave-induced reactions have been related to the presence of “hot spots” and superheating of solvents. In this context, Mingos described that polar solvents can be heated to 18–26 K above the boiling point.^{2a} Similarly, hot spots have been detected, especially in heterogeneous reactions. In these hot spots temperatures up to 100–200 K above the bulk temperature have been measured. In this way the bulk temperature is not representative of the reaction temperature.^{2b}

It is worth noting that purely thermal arguments predict a larger production of **1a** under microwave irradiation, which is the opposite to the result found experimentally (see Tables 1 and 4). Therefore, we propose that if the hardness parameters of the corresponding transition structures are sufficiently different, formation of the product connected with the hardest transition structure is preferred under microwave irradiation.

To obtain some information on the properties and stability of cycloadducts **1a–c**, full geometry optimizations were carried out. Some relevant parameters of cycloadducts are gathered in Table 5.

Theoretical data predict that **1b** is the lowest energy isomer, being more stable than **1a** and **1c** by 2.18 and 18.75 kcal, respectively (Figure 7, Table 5). These results are in line with those found for other C₇₀ adducts.¹⁴ Accordingly, the bond distance between both sp³ carbon atoms in the C₇₀ framework is shorter in **1b** (1.563 Å) than that in **1a** (1.581 Å) and **1c** (1.592 Å). It is known that an increase in the bond distance between the two sp³ atoms results in destabilization,^{33a} and these results are in agreement with those determined experimentally by X-ray crystallography (1.584 Å for the adduct with the 5–6 bond and 1.603 Å for the adduct with the 1–2 bond) for Diels–Alder adducts of *o*-quinodimethane to C₇₀.^{33b} In a similar way to C₆₀ derivatives, cycloadducts **1a–c** show a higher HOMO and LUMO than the pristine C₇₀ (–3.19 and –9.01 eV) as a consequence of the saturation of one double bond. It should be remarked that the LUMO levels in *N*-methylpyrrolidino[70]fullerenes **1a–c**

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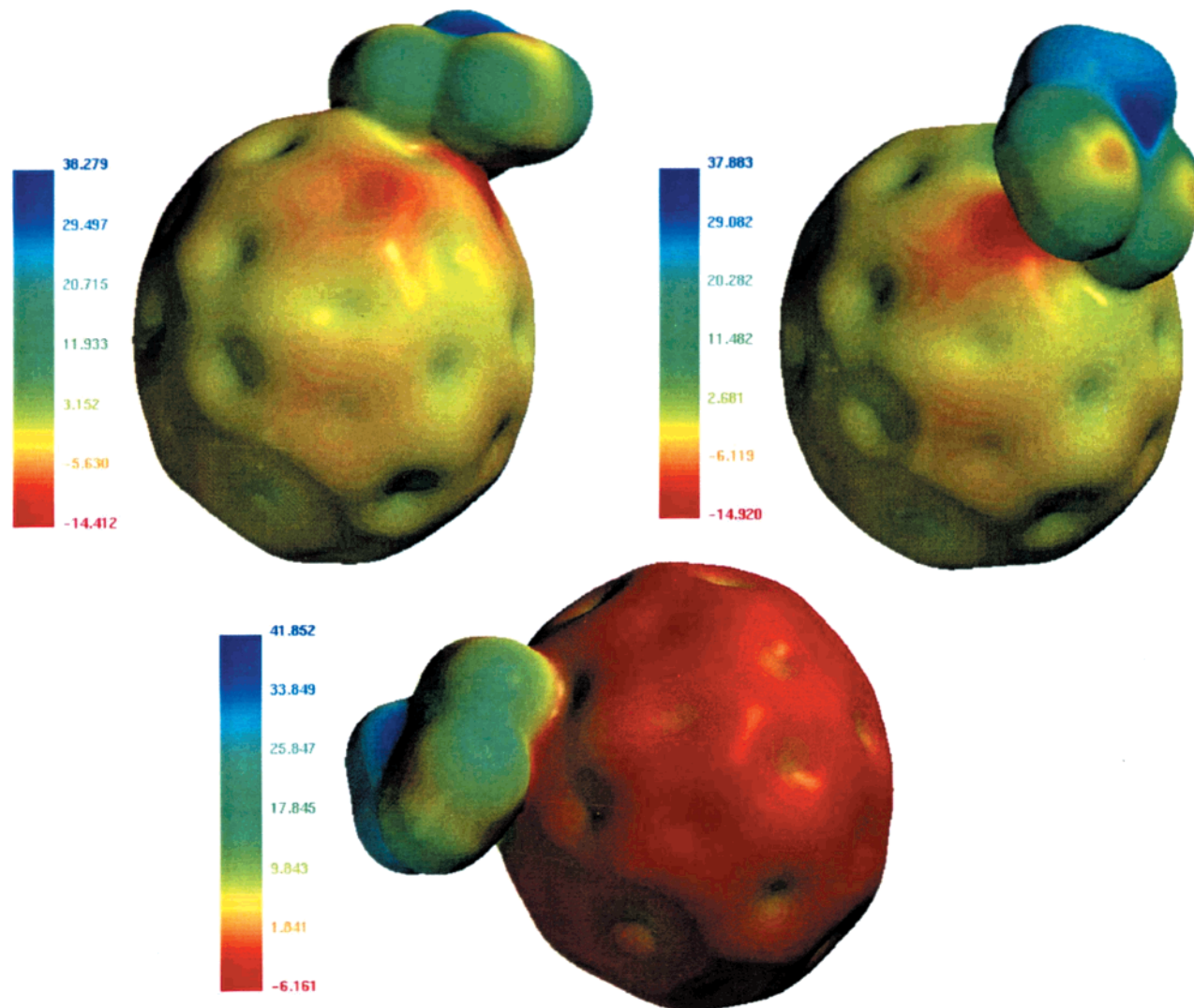
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Table 4. Fullerene Moiety Charges (Σq , e), Dipole Moments (μ , D), Hardnesses^b (η , eV), Average Polarizability Volumes^c (α'_{av} , Å³), Free Energies (ΔG° , kcal/mol), and Distortion Enthalpies (ΔH_{dis} , kcal/mol) of Transition Structures TSa–c

TS	Σq	μ	η	α'_{av}	ΔG°			ΔH_{dis}	
					384 K	405 K	454 K	C ₇₀	CH ₂ N(CH ₃)CH ₂
TSa (1–2)	–0.14	4.880	2.492	91.51	855.70	850.95	838.00	0.95	1.47
TSb (5–6)	–0.14	4.812	2.505	91.21	855.69	850.94	839.00	0.94	1.03
TSc (7–21)	–0.18	5.298	2.488	92.76	858.41	853.75	842.00	1.61	2.29

^a Total Mulliken charge of the C₇₀ fragment. ^b Computed according to eq 1. ^c Computed according to eq 2.

**Figure 9.** Electrostatic potentials mapped onto electron densities for transition structures TSa–c. Red and blue colors denote negative and positive charges, respectively. All values have been computed at the RHF/PM3 level and are given in kcal/mol.**Table 5.** Heats of Formation (kcal/mol) and Main Parameters of Pyrrolidino[70]fullerenes 1a–c Calculated at the PM3 Level

compound	attack	E (kcal/mol)	r (Å) ^a	HOMO (eV)	LUMO (eV)
1a	1–2	851.19	1.581	–8.74	–3.09
1b	5–6	849.01	1.563	–8.92	–3.03
1c	7–21	867.76	1.592	–8.87	–3.07
C ₇₀				–9.01	–3.19
1d			1.582	–9.14	–2.79
C ₆₀				–9.48	–9.14

^a r = bond length of sp³ atoms in C₇₀ framework.

are lower by 0.2–0.3 eV than those in *N*-methylpyrrolidino[60]fullerene **1d** (see Table 5). This fact suggests that pyrrolidino[70]fullerenes should be better acceptor systems than pyrrolidino[60]fullerenes.

Finally, the design of C₆₀-based covalently linked donor–acceptor systems that can simulate photosynthetic systems is an area of increasing interest.³⁴ With this purpose in mind, several molecules containing a pyrrolidino[60]fullerene moiety covalently linked to a donor fragment have recently been prepared,³⁵ and some of these systems have shown intramolecular photoinduced charge-transfer processes.³⁶ Considering the lower HOMO–LUMO gap in **1a–c** (5.65–5.89 eV, see Table

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5) compared to that in *N*-methylpyrrolidino[60]fullerene **1d** (6.35 eV), it would be interesting to prepare pyrrolidino[70]fullerene derivatives containing a donor fragment to study their excited-state interactions.

Conclusions

In conclusion, we have shown that the regioselectivity of the cycloaddition of azomethine ylides to C₇₀ can be modified by using microwave irradiation as the source of energy and by choosing the appropriate solvent and irradiation power. To the best of our knowledge, this result represents the first example where the 5–6 isomer is the major product in C₇₀ chemistry. Moreover, this is the first example of inversion of the regioselectivity in cycloadditions as a consequence of using microwave irradiation as opposed to classical heating, and it shows that microwave irradiation can be used efficiently to modify the reactivity and the selectivity of a given reaction. Our computational results suggest that this phenomenon can be explained by considering that, under kinetic control, microwave irradiation favors the formation of the product corresponding to the hardest and least polarizable transition structure. We believe that the model reported here can be extended to other competitive reactions involving polar transition states that possess different polarizabilities.

Experimental Section

Reagents used were commercially available and reagent grade. C₇₀ was purchased from Merck. ¹H NMR spectra were recorded at 200 MHz with a Varian Mercury 200 spectrometer. Chemical shifts are quoted on the δ scale (internal standard, TMS). Microwave irradiations were performed in a Maxidigest MX 350 (Prolabo) microwave reactor equipped with an IR temperature detector.

General Procedure. A mixture of C₇₀ (50 mg, 0.06 mmol), *N*-methylglycine (11 mg, 0.12 mmol), and paraformaldehyde (9 mg, 0.30 mmol) in 65 mL of solvent was irradiated in the microwave reactor under Ar, for the time and with the power indicated in each case. After cooling, the resulting brown solution was washed with water (2 × 50 mL), dried with Na₂SO₄, and concentrated in vacuo. The crude material was purified by column chromatography on silica gel using toluene/triethylamine (100:1) as the eluent to separate unreacted fullerene and possible higher adducts.

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Computational Methods. All semiempirical calculations were performed by means of the PM3 Hamiltonian.²¹ Transition structures were located using the eigenvector following algorithm³⁷ as implemented in MOPAC.³⁸ All stationary points were characterized by harmonic analysis.³⁹ The transition structures showed only one imaginary frequency in their diagonalized Hessian matrices and this was associated with nuclear motion along the reaction coordinate under study. Reaction intermediates, reactants, and products had positive defined Hessian matrices. Thermodynamic quantities were computed using the standard rigid rotor approximation.⁴⁰ The reported stationary points were refined until their gradient norm was below 0.20 kcal/mol·Å. In addition, the SCF convergence criteria were incremented 100 times, as suggested by Boyd et al.⁴¹ Electrostatic potentials were computed using the SPARTAN package.⁴²

The results for the model reaction were obtained using the GAUSSIAN 94⁴³ series of programs, with the standard 6-31G* and 6-31+G* basis sets.⁴⁴ Electron correlation was partially taken into account by means of the B3LYP functional.⁴⁵ Zero-point vibrational energies (ZPVEs) were scaled⁴⁶ by 0.9135.

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