

FULL PAPER

The [2+1] Cycloaddition of Singlet Oxycarbonylnitrenes to C₆₀

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Abstract Semiempirical and density functional calculations have been carried out to discuss the origin of the closed [5,6]-aza-bridged adduct obtained as a minor product in the reaction of singlet nitrenes with C₆₀. The results indicated that the most likely source is the direct addition of singlet nitrenes to a [5,6]-bond of C₆₀, in contradiction to the common belief that the [5,6]-bonds are not attacked in cycloaddition reactions to C₆₀.

Keywords Nitrene additions, Buckminsterfullerene, C₆₀, NCOOCH₃, AM1, B3LYP/6-31G**//AM1

Introduction

Heterofullerenes have recently attracted considerable attention in the field of fullerene chemistry as a result of their fascinating physical and chemical properties [1]. The current synthesis of nitrogen heterofullerenes in bulk quantities makes use of monoimino-[60]fullerenes as precursor species [1]. There are at least two synthetic routes to monoimino-[60]fullerenes. First, they can be obtained through a 1,3-dipolar cycloaddition (1,3-DC) of organic azides to C₆₀ followed by thermal N₂ extrusion [2]. Second, they can be synthesized by direct [2+1] cycloaddition to C₆₀ of oxycarbonylnitrenes generated *in situ* either by thermal elimination of N₂ from organic azides or by base-catalyzed α -elimination of O-4-nitrophenylsulfonylhydroxamic acid derivatives (see Scheme 1) [3]. Under thermolytic conditions, the former synthetic route yields the open [5,6]-aza-bridged as the main adduct observed, whereas the latter

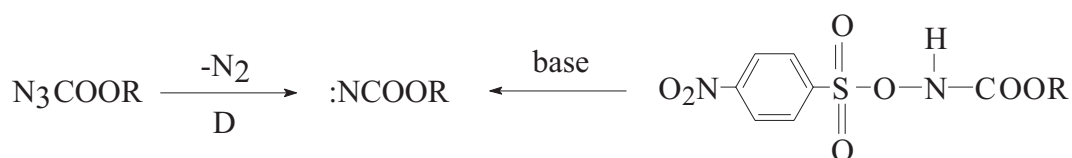
method affords closed [6,6]-aza-bridged product as the major regioisomer with certain amounts (*ca.* 10%) of open [5,6]-aza-bridged adduct [3]. Open [6,6] and closed [5,6]-aza-bridged isomers are not observed. This is not surprising at all considering that the regiochemistry of the addition reactions is governed by the drive to minimize the energetically unfavorable double bonds in pentagonal rings [4]. Hypothetical open [6,6] or closed [5,6]-structures require the introduction of three and two double bonds in five-membered rings, respectively [5].

Despite the great interest that the regiochemistry of cycloaddition reactions to fullerenes possesses [6], the reason for the different regiochemistry of the two aforementioned synthetic routes is not yet fully understood [3b]. Moreover, it is relevant to find new chemospecific cycloaddition routes to the synthesis of [5,6]-addition products. To our knowledge, only a direct addition reaction to a [5,6]-ring junction of C₆₀ has been reported to date [7]. Also, Meier and coworkers [8] found a direct Diels-Alder cycloaddition to the most reactive [5,6]-ring junction of C₇₀ [9].

As far as the 1,3-DC plus thermal N₂ elimination route is concerned, experimental [2c,h,j, 4a] and theoretical [10] results show that the initial attack to C₆₀ occurs at the shorter

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Dedicated to Professor Paul von Ragué Schleyer on the occasion of his 70th birthday



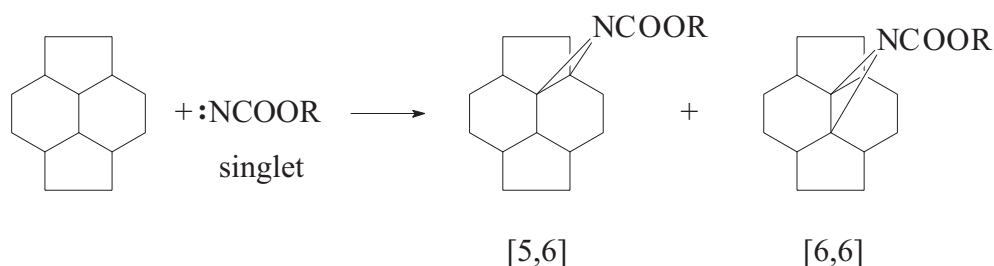
Scheme 1 Generation of oxycarbonylnitrenes by thermal elimination of N_2 from organic azides and by base-catalyzed *a*-elimination of *O*-4-nitrophenylsulfonylhydroxamic acid derivatives

and more reactive [6,6]-ring junctions yielding, first, a triazoline intermediate that, in a subsequent step, loses N_2 upon heating. Theoretical studies indicate that steric repulsions between the nitrene fragment and the leaving N_2 molecule during thermal triazoline decomposition protect the originally attacked [6,6]-bond and force the nitrene fragment to attack the adjacent [5,6]-ring junction [10]. The same conclusion most likely applies to the methanofullerenes generated from the reaction of diazo compounds with C_{60} [2b,4 a,11]. In this case, once the open [5,6]-methanofullerene is obtained, thermal equilibration between the open [5,6] and the closed [6,6]-regioisomers [2b,5,11 b,d-h] is reached upon further heating. The greater proportion of the latter indicates that the [6,6]-isomer is thermodynamically the most stable [11f,g]. This point was later confirmed through semiempirical and *ab initio* calculations at different levels of theory on the $\text{C}_{60}(\text{CH}_2)$ compound [5,12]. These calculations show that

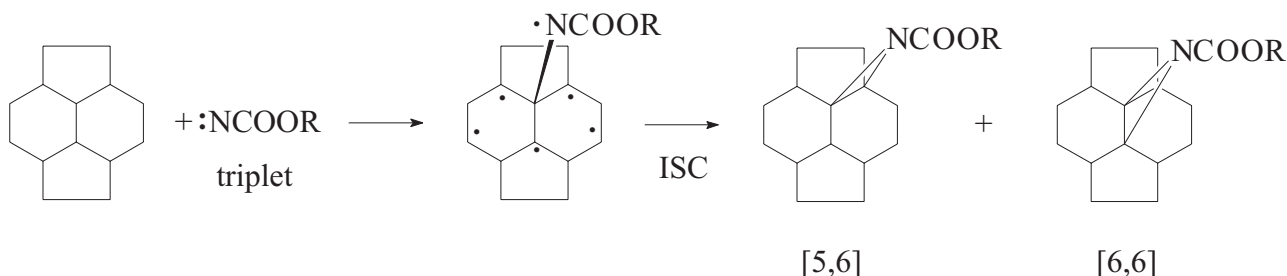
the closed [6,6]-adduct is about 5 kcal mol⁻¹ more stable than the open [5,6]-isomer [5,12]. AM1 calculations also show that closed [6,6]-isomers are more stable than [5,6]-adducts in fullerene silylene derivatives [13].

As regards the direct oxycarbonylnitrene addition, the fact that the major isomer is the [6,6]-adduct seems to indicate that the attack of nitrene to C_{60} takes place primarily to the [6,6]-ring junctions. This conclusion is supported by the experimental evidence showing that singlet carbenes and silylenes add exclusively to the [6,6]-ring junctions of C_{60} in one step [4a, 11f]. Less clear is the mechanistic origin of the *ca.* 10% of [5,6]-adduct obtained. At least two hypotheses can be formulated (see Scheme 2) [2, 3b]: first, the open [5,6]-product may be generated through the direct addition of singlet nitrenes to [5,6]-ring junctions; second, the addition of residual triplet nitrene to C_{60} may result in a mixture of [5,6] and [6,6]-regioisomers after intersystem crossover.

Path A



Path B



Scheme 2 The two mechanisms proposed to explain the formation of [5,6] and [6,6]-aza-bridged adducts

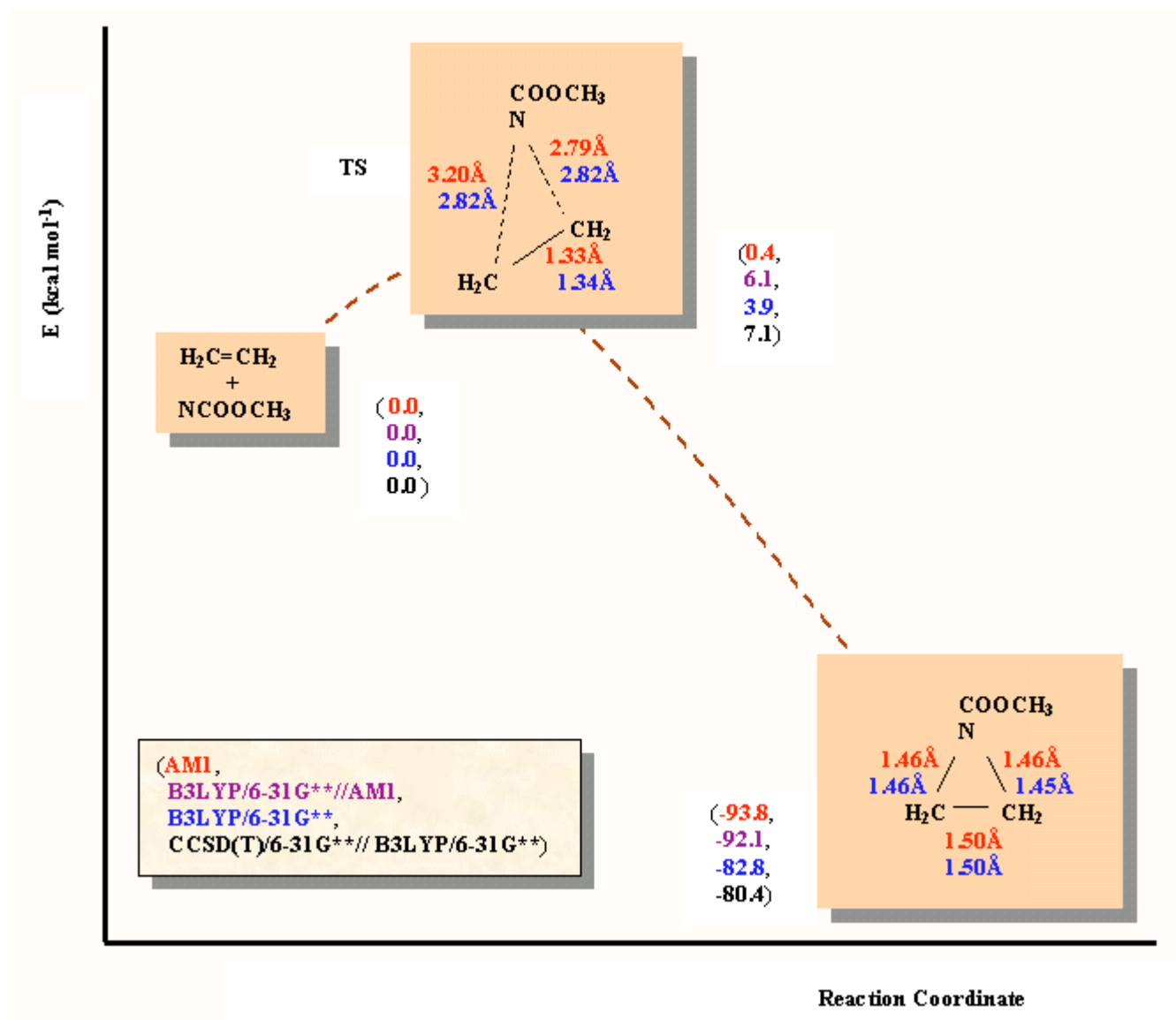


Figure 1 Reaction energies and energy barriers (in kcal mol^{-1}), and the most relevant geometrical parameters (Å) for the TS and the product of the cycloaddition of singlet NCOOCH_3 to ethylene obtained at different levels of theory

In this work we have carried out an analysis of the direct cycloaddition of singlet methoxycarbonylnitrene to the [6,6] and [5,6]-bonds of C_{60} through semiempirical and density functional calculations. The results point out the direct addition of singlet nitrenes to the [5,6]-ring junctions as the most probable source of the open [5,6]-aza-regioisomer obtained.

Method of calculation

The size of the systems studied prevents the use of *ab initio* molecular quantum mechanical methods to perform geometry optimizations. Therefore, full geometry optimizations without symmetry constraints have been carried out with the

AM1 semiempirical method [14] as implemented in the AMPAC 6.0 [15], a quantum chemistry program from Semichem, Inc. All zero-gradient structures have been characterized by a vibrational analysis. For all stationary points, single-point B3LYP [16] energy calculations have been performed at the AM1-optimized geometries employing the 6-31G** basis set [17] (B3LYP/6-31G**//AM1) and with the help of the Gaussian-98 program [18]. Recent studies on the dimerization of carbenes [19] and addition of carbenes to alkenes [20] prove the validity of the B3LYP combined with the 6-31G* basis set approach to treat reactions in which singlet carbenes intervene. We have further tested the validity of the B3LYP/6-31G**//AM1 approach employed in this work by calculating the [2+1] cycloaddition of singlet NCOOCH_3 to ethylene using different methodologies. The reaction en-

Table 1 AM1 C-C bond distance (\AA) between the two attacked carbon atoms of C_{60} , together with AM1 standard enthalpy of formation (ΔH_f^0), reaction enthalpy (ΔH_r), and enthalpy barriers (ΔH^\ddagger) for the [2+1] cycloaddition of singlet $NCOOCH_3$ to C_{60} . [a]

Species	Label	R(C-C) [b]	ΔH_f^0	ΔH_r	ΔH^\ddagger
<i>Reactants</i>					
	C_{60}		973.3		
	$NCOOCH_3$		36.7		
<i>TS</i>					
	[6,6]	1.385	1010.4		0.4 (3.6)
	[5,6]/5	1.464	1010.4		0.4 (3.2)
	[5,6]/6	1.464	1010.4		0.4 (3.7)
<i>Adducts</i>					
	Closed [6,6]	1.563	920.5	-89.5 (-78.7)	
	Open [6,6]	2.200	929.5	-80.5 (-76.0)	
	Open [5,6]/5	2.201	915.7	-94.5 (-81.9)	
	Open [5,6]/6	2.200	916.2	-93.8 (-81.7)	
	Closed [5,6]/5	1.620	941.5	-68.5 (-61.9)	
	Closed [5,6]/6	1.620	942.7	-67.3 (-61.8)	

[a] All energy values are given in kcal mol^{-1} . Values in parentheses are reaction energies and energy barriers calculated at the ab initio B3LYP/6-31G**//AM1 level

[b] The experimental [6,6] and the [5,6]-bond lengths in C_{60} are 1.401 and 1.458 \AA [27], while the AM1-optimized bond lengths are 1.385 and 1.464 \AA , respectively

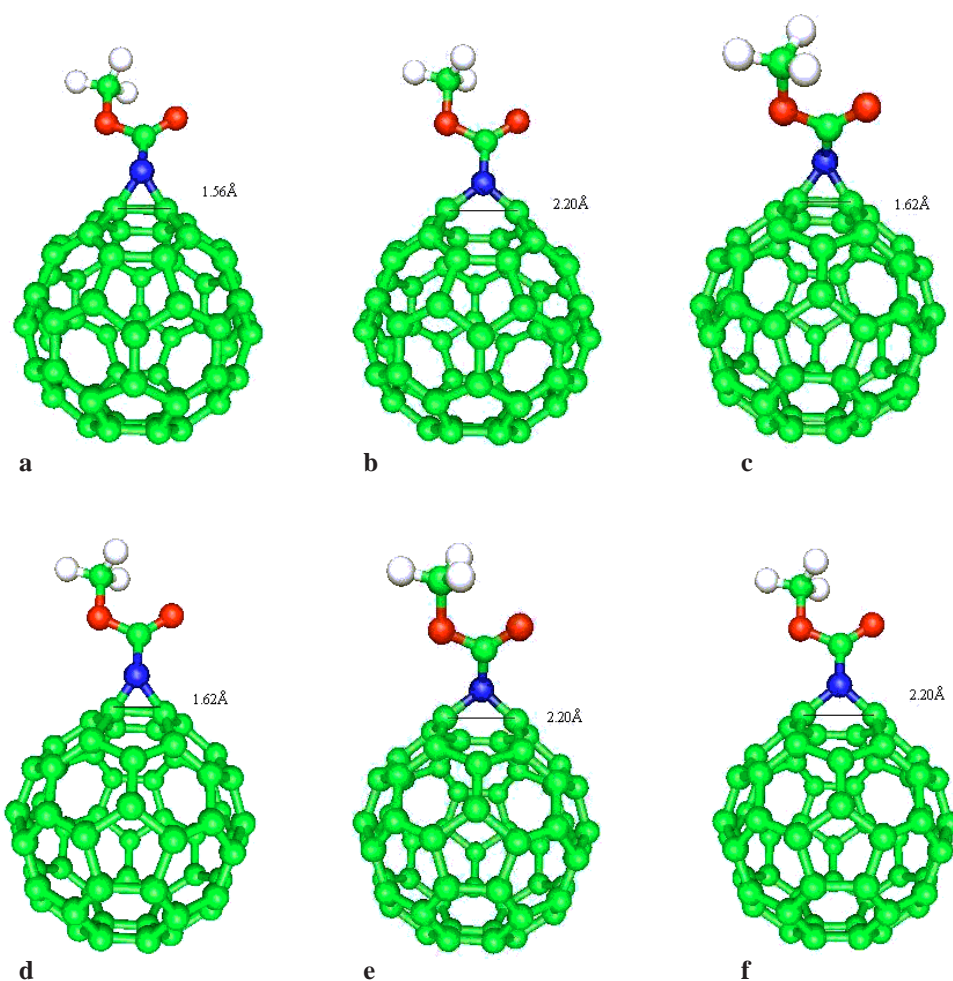
ergies, energy barriers, and the transition state (TS) geometries obtained with the different methods are shown in Figure 1. For the AM1 TS, we have checked by following the intrinsic reaction path [21] that the TS connects reactants and products. This TS has reactant-like character as expected from the small barrier and high exothermicity of the reaction, its geometry being similar to that found for the addition of carbenes to alkenes [20,22]. As one can see, AM1 predicts a concerted and asynchronous attack for this [2+1] cycloaddition, while the B3LYP/6-31G** method yields a concerted and synchronous attack. The asynchronous character of the AM1 TS is likely the result of the interaction between the oxygen atom of the carbonyl group and a hydrogen atom of ethylene. This interaction is probably overestimated at the AM1 level. Remarkably, the B3LYP/6-31G** geometry of the product is practically coincident to that optimized at the AM1 level. As compared to the CCSD(T)/6-31G**//B3LYP/6-31G**, the B3LYP/6-31G**//AM1 reaction energy is too exothermic and the energy barrier is slightly too small. However, from a qualitative point of view, the B3LYP/6-31G**//AM1 result does not differ significantly from more sophisticated B3LYP/6-31G** and CCSD(T)/6-31G**//B3LYP/6-

31G** calculations and therefore the B3LYP/6-31G**//AM1 approach seems to be a reliable method in order to draw qualitative conclusions. Finally, it is worth mentioning that we have made use of the AM1 main geometrical parameters of the TS in Figure 1 as the starting point in the search for the TS structures corresponding to the different nitrene attacks to C_{60} .

Results and discussion

The standard enthalpies of formation of reactants, TSs, and adducts, together with reaction enthalpies and enthalpy barriers for the different [2+1] cycloadditions of singlet $NCOOCH_3$ to C_{60} are collected in Table 1. The geometries of the different regioisomers and TSs are depicted in Figures 2 and 3, respectively. There are two possible adducts and TSs corresponding to the [5,6]-attack, the so-called [5,6]/5 and [5,6]/6. In the former, the methoxycarbonyl substituent of the nitrene faces the pentagonal ring, while in the latter this substituent faces the hexagonal ring (see Figures 2 and 3).

Figure 2 The six possible AM1 regioisomers that can be obtained in the singlet NCOOCH_3 addition to C_{60} : (a) the closed [6,6], (b) the open [6,6], (c) the closed [5,6]/5, (d) the closed [5,6]/6, (e) the open [5,6]/5, and (f) the open [5,6]/6



Further, as commented in the Introduction, the [5,6] and [6,6]-adducts can be either open or closed, thus giving six possible regioisomers for $\text{C}_{60}(\text{NCOOCH}_3)$. All open structures have C-C bond lengths between the two attacked carbon atoms of 2.20 Å, while this C-C bond distance for closed structures differs for the [5,6] and [6,6]-bonds, being 1.62 and 1.56 Å for the former and the latter, respectively (see Table 1). These values are close to those found for C_{60}O and $\text{C}_{60}(\text{CH}_2)$ at the HF/3-21G level of theory [12]. For instance, this C-C bond length is 2.20 and 1.59 Å in the open [5,6] and closed [6,6]-adducts of $\text{C}_{60}(\text{CH}_2)$, respectively [12].

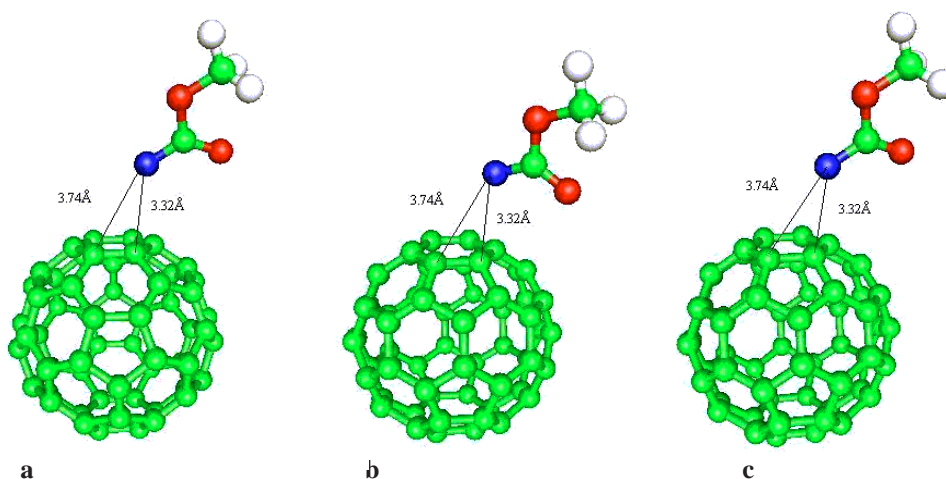
From the AM1 enthalpies of formation of the different adducts one can see that the open [5,6]-aza-bridged adducts are the most stable regioisomers. In particular, the open [5,6]-isomers are 4-5 kcal mol⁻¹ more stable than the closed [6,6] both at the AM1 and B3LYP/6-31G**//AM1 levels. Similar results have been reported for C_{60}O [13] at the HF/6-31G**//HF/3-21G level of theory. On the contrary, for a series of methanofullerenes, the MNDO [2b] and PM3 methods [5] and the HF and local and nonlocal DFT approaches using double zeta plus polarization basis sets [12], yield the closed [6,6] as the most stable regioisomer in agreement with experimental results [11f,g]. Remarkably, for the same series

of methanofullerenes AM1 incorrectly predicts the open [5,6]-isomer to be more stable than the closed [6,6] [5]. For this reason it was concluded [5] that the AM1 method overestimates the stability of the [5,6] as compared to the [6,6]-regioisomers. In contrast to this result and comparing the AM1 and B3LYP/6-31G**//AM1 relative stabilities of the different regioisomers in Table 1, we have found that the AM1 method affords a good estimate of the relative stabilities of the regioisomers of monoimino-[60]fullerenes.

As said before, there are two possible open [5,6]-adducts, the so-called open [5,6]/5 and open [5,6]/6 (see Figure 2). The open [5,6]/5 is about 0.5 kcal mol⁻¹ more stable than the open [5,6]/6, both at the AM1 and B3LYP/6-31G**//AM1 levels. We have not located the TS for the pyramidal inversion that connects the open [5,6]/6 and the open [5,6]/5 systems, although experimental NMR studies suggest that this process is almost barrierless [2a]. The same pyramidal inversion exists for the rest of the regioisomers.

The open [6,6] and the closed [5,6]-regioisomers are also minima in the potential energy surface of $\text{C}_{60}(\text{NCOOCH}_3)$. As compared to the closed [6,6] and the open [5,6]-adducts, the open [6,6] and the closed [5,6]-regioisomers are 9 and 35 kcal mol⁻¹ higher in energy, respectively. As commented be-

Figure 3 AM1 transition states corresponding to the three studied attacks in the singlet NCOOCH_3 addition to C_{60} : (a) the [6,6]-attack, (b) the [5,6]/5-attack, and (c) the [5,6]/6-attack



fore, the open [6,6] and the closed [5,6]-regioisomers are forced to locate three and two double bonds within five-membered rings of the fullerene, thus disrupting the preferred [5]radialene type bonding present in C_{60} [4,11 f]. No open [6,6] and closed [5,6]-regioisomers were found for the C_{60}O [12] and $\text{C}_{60}(\text{CH}_2)$ compounds [5, 12]. However, closed [5,6]-regioisomers were located with the PM3 method for $\text{C}_{60}(\text{CR}_2)$ with R being OMe, COOEt, COO^tBu, or Ph [5]. The authors found that these closed [5,6]-adducts were *ca.* 15 kcal mol⁻¹ higher in energy than the corresponding open [5,6]-isomers. In view of that, the stability of the closed [5,6]-regioisomer of $\text{C}_{60}(\text{NCOOCH}_3)$ could already be anticipated while that of the open [6,6]- $\text{C}_{60}(\text{NCOOCH}_3)$ is more unexpected, although it can not be attributed to a possible failure of the AM1 method, since the open [6,6]-adduct is even more stable as compared to the closed [6,6]-product at the B3LYP/6-31G**//AM1 level of theory.

At the AM1 level, the enthalpy barriers for the attack of singlet NCOOCH_3 to ethylene (Figure 1) and C_{60} (Table 1) are exactly the same, 0.4 kcal mol⁻¹. However, using the B3LYP/6-31G**//AM1 approach it is found that the attacks of singlet nitrene to C_{60} have slightly smaller energy barriers than the attack to ethylene. At the B3LYP/6-31G**//AM1 level of theory, the [6,6], [5,6]/5, and [5,6]/6 attacks have similar energy barriers, the [5,6]/5 attack being somewhat favored. For all these three TSs, the bond lengths of the two N-C forming bonds are rather large (3.32 and 3.74 Å) and the deformation enthalpies [a] of C_{60} and NCOOCH_3 are close to zero. Thus their geometry corresponds clearly to TSs with reactant-like character and concerted and asynchronous nature. However, as found for ethylene, the use of higher levels of calculation may give synchronous TSs.

Let us turn now to discuss the feasibility of the nitrene triplet addition pathway as possible route for the generation of the open [5,6]-aza-regioisomer. The methoxycarbonyl substituent in NCOOCH_3 lifts the degeneracy of the two 2p

degenerate orbitals of the parent nitrene NH [23]. The stabilization of one of the 2p orbitals due to the presence of this substituent is insufficient, however, to yield a singlet closed-shell ground state for NCOOCH_3 . The NCOOCH_3 species has a triplet ground state that is 13.1 kcal mol⁻¹ more stable than the lowest-lying singlet state at the B3LYP/6-31G** level [b]. Nonetheless, triplet NCOOCH_3 species generated under thermal conditions from N_3COOCH_3 are probably inaccessible, since one can expect that the crossover from the singlet to the triplet surface through spin-orbit coupling must be difficult for systems of such small size [24]. This, together with the low barrier for the direct attack of singlet NCOOCH_3 to the [5,6]-bond of C_{60} , prompt us to conclude that the direct singlet nitrene addition to a [5,6]-bond is most likely responsible for the obtention of the *ca.* 10% of closed [5,6]-aza-bridged regioisomer obtained in the cycloaddition of oxycarbonylnitrenes to C_{60} .

The present results show that the reactivity of [5,6] and [6,6]-ring junctions of C_{60} are similar, at least as far as the nitrene addition is concerned. In fact, our results slightly favor the [5,6]-attack both kinetically and thermodynamically. This attack is further favored if one takes into account that C_{60} contains 60 [5,6]-bonds and 30 [6,6]-ring junctions. Our result differs from experimental findings showing that the [6,6]-adduct is the major product obtained in the nitrene addition to C_{60} [3]. Since the energy differences between the [5,6] and [6,6]-attacks are small, one can expect that higher levels of calculation including the effect of the solvent will reproduce the experimental result. This notwithstanding, we believe that the qualitative conclusion reached by this work indicating that the [5,6] and [6,6]-bonds of C_{60} have similar reactivities in front of singlet nitrenes will not be altered in a significant way by the use of higher-level theoretical methods. This conclusion is surprising since it is commonly said that the [6,6]-bonds in fullerenes are more reactive than the [5,6]-ring junc-

[a] The deformation enthalpy is the enthalpy needed to modify the geometry of the reactants to that they have in the TS

[b] The triplet NCOOCH_3 has been optimized within the unrestricted formalism. The S^2 value for this system is 2.013 at the B3LYP/6-31G** level

tions [4,25]. This has been verified in a number of 1,3-DC and Diels-Alder (DA) cycloadditions, both experimentally [4,25] and theoretically [10,26]. However, there is a difference between the adducts obtained after [2+1] and 1,3-DC or DA cycloadditions that may explain the enhanced reactivity of the [5,6]-bonds in [2+1] cycloadditions. In DA and 1,3-DC the closed [5,6]-adducts are more stable than the open [5,6]-adducts, because in the open [5,6]-adducts the new formed six-membered and five-membered rings obtained after DA and 1,3-DC, respectively, are strained since they have to accommodate a large C-C bond length (about 2.20 Å). Moreover, closed [5,6]-adducts are energetically unfavorable as compared to the closed [6,6]-adducts given that they require the introduction of two double bonds in two five-membered rings of C₆₀. Therefore, the closed [6,6]-adducts become clearly the most stable regioisomer in DA and 1,3-DC. Not surprisingly, they are also the kinetically most favorable products, since as a common rule the most stable adduct has also the lowest TS. On the contrary, [2+1] cycloadditions yield three-membered rings that are not specially strained in the open [5,6]-configuration. As a result, open [5,6]-adducts are more stable than closed [5,6]-adducts and have almost the same energy as the [6,6]-adducts. This is the case not only for C₆₀(NCOOCH₃) but also for C₆₀O and C₆₀(CH₂) [12]. Accordingly, in the addition of singlet NCOOCH₃ to C₆₀, the [5,6] and [6,6]-attacks have similar barriers and exothermicities. More research is under way in our laboratory as to further elucidate this hypothesis.

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Supplementary material available Table listing the 3D coordinates of all calculated structures (reactants, TSs and adducts) in XYZ-format.

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