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The influence of protecting the hydroxyl group of β-oxy-α-diazo carbonyl compounds in the competition between Wolff rearrangement and [1,2]-hydrogen shift. Density functional theory study and topological analysis of the charge density

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Abstract. The influence of protecting the hydroxyl group of a β-oxy-α-diazo carbonyl compound on the competition between the Wolff rearrangement (WR) and the [1,2]-hydrogen shift (HS) was investigated theoretically. Stationary points on the potential-energy surface were located with the B3LYP density functional and the 6-31G** basis set. For the basic system geometry optimisations at B3LYP/6-311+G** were performed to validate the reliability of the B3LYP/6-31G** calculations. Single-point energy calculations were carried out at the B3LYP/6-311+G** level on the B3LYP/6-31G**-optimised geometries. Further insight into the processes was achieved with the aid of the theory of "atoms in molecules" of Bader. The calculated energy barriers qualitatively predicted the yields of HS and WR obtained experimentally. In order to rationalise the calculated energy barriers, it was necessary to take into account not only the electronegativity of the protective groups but also the alignment of the migrating groups with the depletion sites at the carbene centre. Further, when the hydroxyl group was not protected the existence of an intramolecular hydrogen bond played an important role in both HS and WR.

Key words: Wolff rearrangement – [1,2]-hydrogen shift – β-Oxy-α-diazo carbonyl compounds – Density functional theory calculation – Laplacian distribution of the charge density

1 Introduction

Rearrangement reactions of nitrogen, oxygen or carbon play an important role in chemistry. Among them the [1,2]-carbon and hydrogen shifts (HS) are of great importance and interest in organic synthesis and photochemistry [1–19]. Particularly, the isomerisation reactions of ketocarbenes are presently the subject of extensive studies [20–35]. López-Herrera and Sarabia [36, 37] departing from D-glyceraldehyde have recently designed a route aimed at synthesising 1-methyl-2-hydroxy synthons on asymmetric carbons, which constitute the skeleton of some antibiotic macrolides. The synthesis utilised the wolff rearrangement (WR) (Scheme 1) of α-ketodiazo compounds as its principal reaction step. The photolytical cleavage of the diazo compound presumably created a ketocarbene species, which rearranged (by migration of the methyl group at C_2 towards the carbene centre, C_4) to yield a ketene, which in turn reacted with methanol to give the ester. However, the product was not the ester but a β-diketone as a consequence of the shift of the hydrogen atom linked to C_5 (H_8). Moreover, the 100% yield indicated clearly its absolute predominance. Some strategies were addressed to avoid this competitive reaction. First, they thought that protection of the hydroxyl group in the β position, especially with electron-withdrawing substituents, could diminish the ability of hydrogen to undergo the transposition towards the carbene centre since it would be more strongly bonded to the adjacent carbon atom than before. In principle, the yields obtained supported that hypothesis (see Scheme 1 and Ref. [36]).

We have already studied these processes as well as some alternative reaction channels on the AM1 potential energy surface (PES) [38]. Subsequent ab initio and density functional theory (DFT) (B3LYP) studies carried out on a model system have shown that a hydrogen-bond interaction could condition the prevalence of the [1,2]-HS over the WR [39].

In this paper we report a theoretical study of the competing HS and WR reactions of hydroxymethyl-

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acetylmethylene (KC) as a model of the ketocarbene used experimentally, considering the influence of different protecting groups (R) (Scheme 1) on the yields. To that purpose several substituents are investigated: R = CH_3, $COCH_3$ being the methyl group representative of electron-releasing groups, and the acetyl of electron-withdrawing ones. It is well known that some carbenes (as in the present case) exhibit triplet ground states, with the first excited singlet state (the closed-shell singlet) lying very close to it in some cases [9, 11, 13]. In these situations intersystem crossings might take place and these would compete with the intramolecular rearrangements. In our case the singlet–triplet gap is predicted to be about 2 kcal/mol at UB3LYP/6-31G** level, and so both species can exist in rapid equilibrium [13]. Nevertheless, it has been reported that the shifts on the triplet ground-state PES have larger energy barriers than that on the first singlet-state PES [30, 32]. Therefore, in this paper we shall deal with the shifts on the first excited singlet-state PES, i.e. the one where the carbene has a σ^2 electronic configuration [6, 17]. Tunnelling effects were not considered in the present work on the basis of two assumptions [7, 8, 16]. First, the experiments were carried out at 274 K and second, the shifts (especially for the substituted system) involved movements of several heavy atoms (see later). The oxirene species [20, 30, 33, 35, 40] has not been taken into account since the product distribution does not show any hint of its role in the processes as probably has when the diazo and carbonyl groups are in inverted positions [37]. Nevertheless, theoretical studies are in progress to elucidate its participation.

2 Theoretical methods

Quantum chemical calculations were carried out with the Gaussian94 program [40]. Geometry optimisations were performed via DFT [42–44] using the hybrid functional B3LYP [45, 46] and the 6-31G** basis set. Recent studies have reported DFT results on carbene rearrangements and they agree reasonably well with experimental results and with those employing more sophisticated *N*-electron treatments such us CCSD(T) or multiconfiguration self-consistent field techniques [9, 11–15, 33]. In order to further assess the reliability of the calculations reoptimisations at the B3LYP/6-311+G** level were performed for the basic system (without substituents) and minor modifications in the geometries and energies were detected. The nature of the stationary points was determined by analytically calculating the harmonic vibrational frequencies. In order to evaluate the basis truncation single-point calculations were also performed at the B3LYP/6-311+G** level on the B3LYP/6-31G** geometries. To obtain results more readily comparable with experiment $\Delta G^{\neq}$ values were also calculated within the ideal gas, rigid-rotor and harmonic oscillator approximations, as implemented in Gaussian packages. A temperature of 298.15 K and a pressure of 1 atm were assumed in the calculations.

To study the electronic effects induced by the protecting groups and their influence on the energy barriers the charge density computed at the B3LYP/6-311+G**//B3LYP/6-31G** level was analysed by means of the "atoms in molecules" theory of Bader [47]. In particular the topological properties of the bond critical point (BCP) linking that atom to the adjacent carbon atom (i.e. H_8—C_5, see Scheme 1), and the Laplacian distribution around the carbenic carbon (C_4) were analysed. The magnitude of the latter is especially interesting since it determines the position of the sites where the charge is locally accumulated or depleted [47–50]. Critical points of the negative Laplacian $-\nabla^2\rho(r)$ were computed with the BUBBLE program of the AIMPAC package [49]. We used the automated MORPHY program for localising critical points of $\rho(r)$, and for displaying contour maps of the Laplacian distribution [51].

3 Results and discussion

The optimised geometries of KC, of the transition state for HS (TS_{HS}) and of the transition state for WR (TS_{WR}) for R = H, CH_3 and $COCH_3$, respectively, are shown in Figs. 1–3. In Fig. 1 geometrical parameters at the B3LYP/6-311+G** level are included for comparison with the B3LYP/6-31G** results. Table 1 presents the B3LYP/6-31G** and B3LYP/6-311+G**//B3LYP/6-31G** energy barriers obtained in this work including the zero-point vibrational energy (ZPVE) correction for HS as well as $\rho(r)$ and $\nabla^2\rho(r)$ at the BCP of H_8—C_5, and the change in the dihedral angle between H_8 and a minima of $-\nabla^2\rho(r)$ [presumably in the valence shell of charge concentration (VSCC) of C_4, see later), located close to H_8 when going from KC to TS_{HS}. Table 2 gives the B3LYP/6-31G** and B3LYP/6-311+G**//B3LYP/6-31G** energy barriers including the ZPVE correction for WR as well as the change in the dihedral angle between C_1 and a minimum of $-\nabla^2\rho(r)$ around C_4 (presumably on the VSCC) (close to C_1) when going from KC to TS_{WR}. Energy barriers obtained at the B3LYP/6-311+G**//B3LYP/6-311+G** level for the system without substituents are also included in both tables for comparison. Figures 4 and 5 show the contour maps of the Laplacian, $\nabla^2\rho(r)$, in the migration planes in KC for R = H and CH_3, respectively.

Our B3LYP/6-311+G** calculations predict low energy barriers for both HS and WR reactions in agreement with the experimental activation energies reported for [1,2]-HS in some singlet carbenes [4, 5, 9, 13–15] and for WRs [33]. The B3LYP/6-31G** energy barriers are systematically higher by about 0.3–1.3 kcal/mol, with the largest difference taking place for WR when R = H (Tables 1, 2).

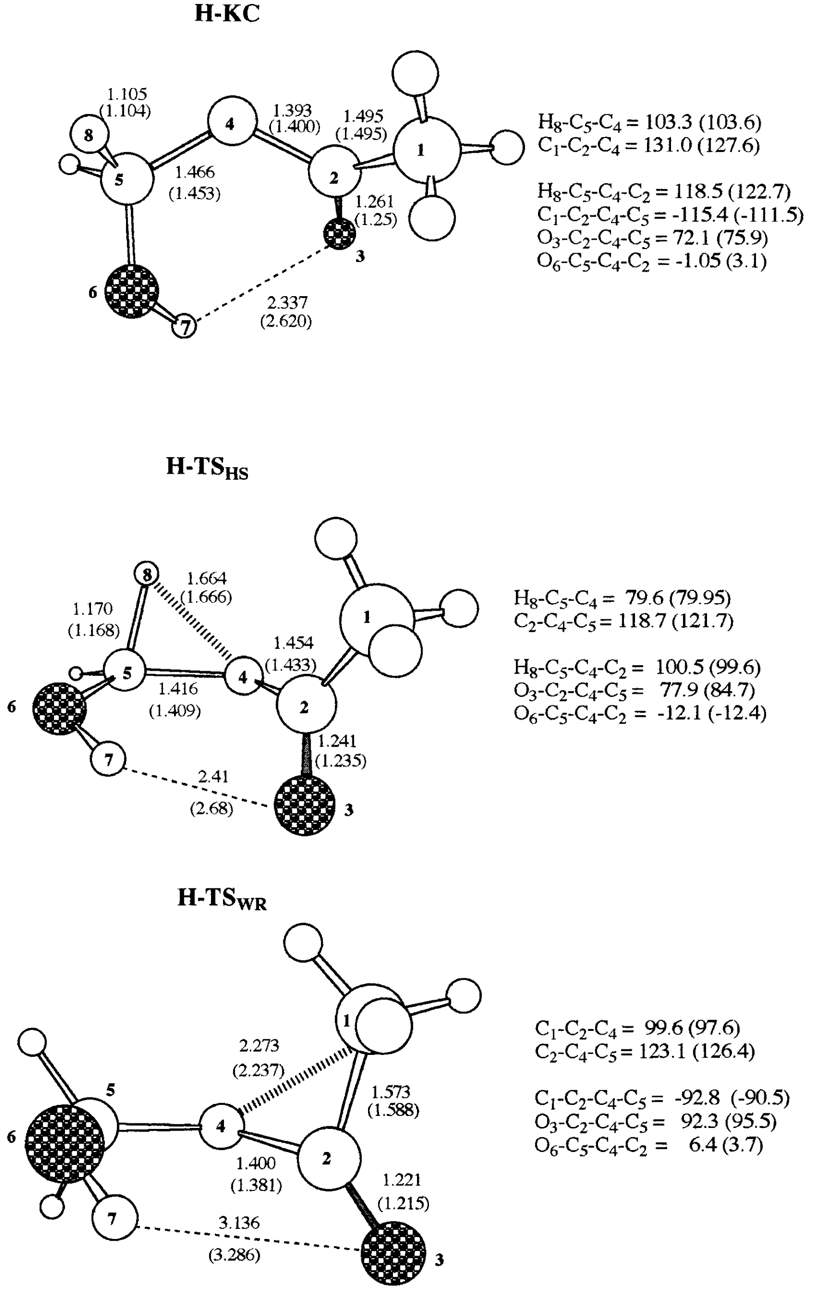
The B3LYP/6-311+G**//B3LYP/6-31G** free-enthalpy barriers predict the yields for HS and WR reactions in qualitative agreement with the experimental data (Scheme 1). In effect, by means of the relation

$$\%\mathrm{HS} = \frac{\exp\left[\frac{-\Delta G^{\neq}(\mathrm{HS})}{RT}\right]}{\exp\left[\frac{-\Delta G^{\neq}(\mathrm{HS})}{RT}\right] + \exp\left[\frac{-\Delta G^{\neq}(\mathrm{WR})}{RT}\right]} \times 100 \ ,$$

for R = H we obtain 85% of HS and 15% of WR, for R = CH_3 53% of HS and 47% of WR and for R = $COCH_3$ 10% of HS and 90% of WR. With the 6-31G** basis set the yields of HS obtained are higher especially in the case of R = CH_3. Thus our DFT calculations correctly predict the relative effect of both electron-withdrawing and electron-releasing substituents on HS and WR reactions of KC.

However, by considering only the electron-withdrawing or electron-releasing nature of the substituents the energy barriers obtained could not be satisfactorily explained. We evaluated the electronegativity of the different substituent groups using the expression pro-

Fig. 1. Optimised structures of hydroxymethylacetylmethylene (*KC*), the transition state for the hydrogen shift (TS_{HS}), and the transition state for the Wolff rearrangement (TS_{WR}) at the B3LYP/6-31G** level and the B3LYP/6-311+G** levels (*in parentheses*), together with relevant geometrical parameters for the system without substituents (R = H). Bond lengths are in angstrom and angles in degree



posed by Boyd and Boyd [52]. [1]The values obtained for R = CH_3, H and $COCH_3$ are 2.549, 2.556 and 2.572, respectively, correlate well with the value of $\rho(r)$ and the Laplacian $\nabla^2\rho(r)$ calculated at the H_8—C_5 BCP (Table 1). We see from Table 1 that the magnitude of $\rho(r)$ grows slightly with the electronegative character of R. Moreover, the behaviour of $\nabla^2\rho(r)$ indicates that the more electronegative R the greater the accumulation of charge at the BCP of H_8—C_5, and, consequently, the stronger the H_8—C_5 bond. However, while for R = $COCH_3$ the energy barrier for HS is about 3.0 kcal/mol greater than that for R = H in agreement with the greater electron-withdrawing ability of —$OCOCH_3$ compared with that of —OH, the energy barrier for HS for R = CH_3 is 0.3 kcal/mol greater than that for R = H in spite of the fact that CH_3 is an electron-releasing group. Therefore, some other factor not yet considered by us must be playing an important role in this process.

In this respect, the degree of distortion necessary for the reaction to occur has been reported to be important in the determination of the energetic cost of certain HS. Evanseck and Houk [4] studied [1,2]-HS in some

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[1] First they define an electronegativity factor as, $F_A = r_H/N_A[\rho(r_c)]r_{AH}$, where r_H is the distance from the BCP of the hydrogen nucleus, N_A is the number of valence electrons of atom A, $\rho(r_c)$ is the electron density at the BCP r_c, and r_{AH} is the internuclear distance. The electronegativity of a group is then defined as a potential function of that factor by adjusting the two parameters to give the values of 1.00 and 4.00 for Li and F, respectively according to the Pauling values: $\chi_A = 1.938\ (F_A)^{-0.2502}$

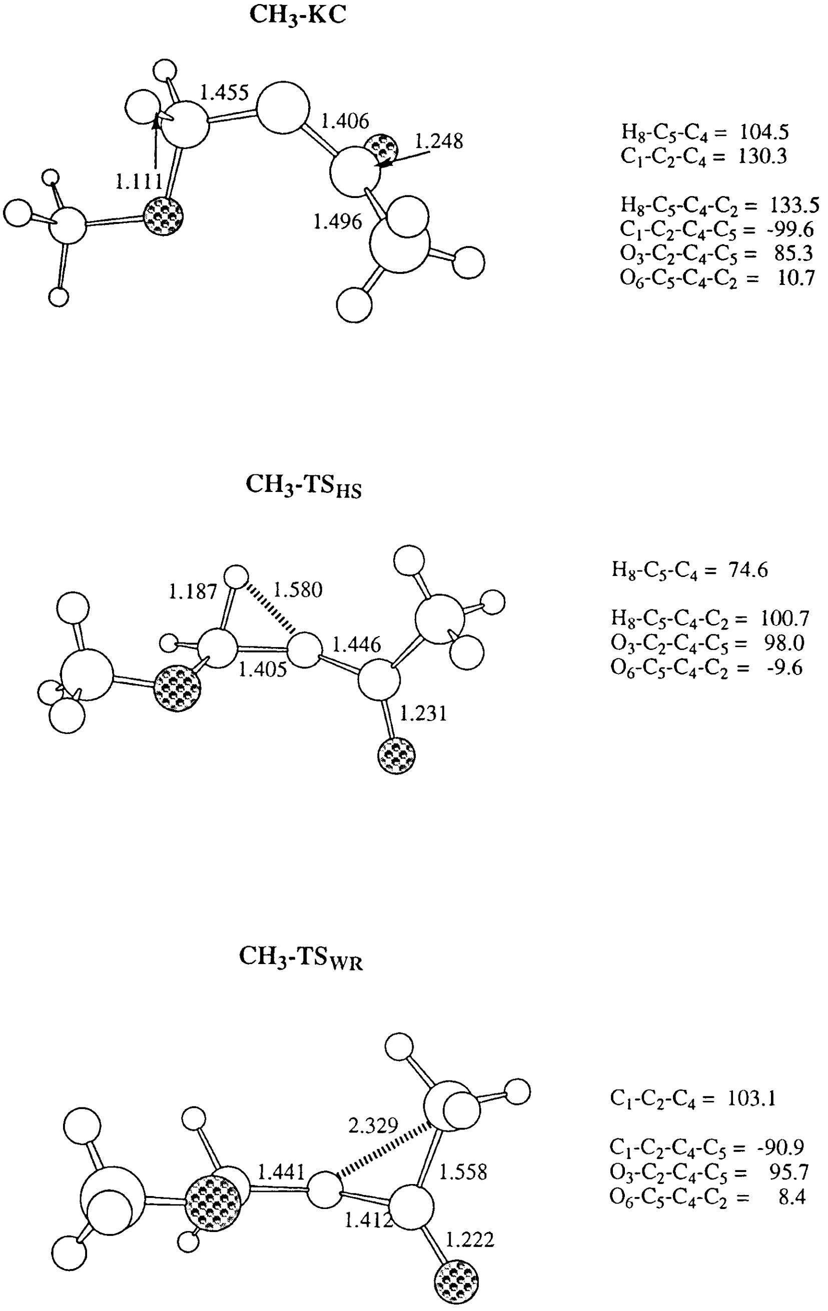

Fig. 2. Optimised structures of *KC*, TS_{HS} and TS_{WR} at the B3LYP/6-31G** level, together with relevant geometrical parameters for the system substituted with R = CH_3. Bond lengths are in angstrom and angles in degree

carbenes and tried to rationalise the yields in terms of the dihedral angle of the position of the migrating hydrogen atom relative to an a priori vacant *p* orbital at the carbene centre. More recently, Reed and Modarelli [12] have indicated that the yields of [1,2]-HS in some diazo compounds correlate well not only with the strength of the C—H bond (H being the migrating atom), but also with the position of that atom relative to the empty *p* orbital at the carbene centre. In addition, Shustov et al. [14] have remarked on the stabilising effect of the interaction between the occupied σ orbital of a C—H bond with the vacant *p* orbital at the carbene centre (σ_{CH}-p) and the interaction between the nonbonding carbene sp^2 with the antibonding σ* orbital of the vicinal C—Cl bond (n-σ_{CCl}*) in the equilibrium between the cis/trans conformers of ethylchlorocarbene and chloromethylchlorocarbene controlling the product distribution. This kind of through-space interaction ("hyperconjugation") was also utilised by Sulzbach et al. [15] in their study of HS and carbon shifts in some carbenes to explain the stabilisation of both the carbenic precursors and the transition structures that lead to the preferred products.

In the theory of "atoms in molecules" the Laplacian distribution determines the sites of local charge accumulation [$\nabla^2\rho(r) < 0$], "lumps", and of charge depletion [$\nabla^2\rho(r) > 0$], "holes". The alternate maxima and minima in this distribution that appear for atoms account for the shell structure of an atom. The more external surface of charge accumulation is the VSCC, which is spherical for an isolated atom. When this atom combines with others this surface is no longer homoge-

Fig. 3. Optimised structures of *KC*, TS_{HS} and TS_{WR} at the B3LYP/6-31G** level, together with relevant geometrical parameters for the system substituted with R = $COCH_3$. Bond lengths are in angstrom and angles in degree

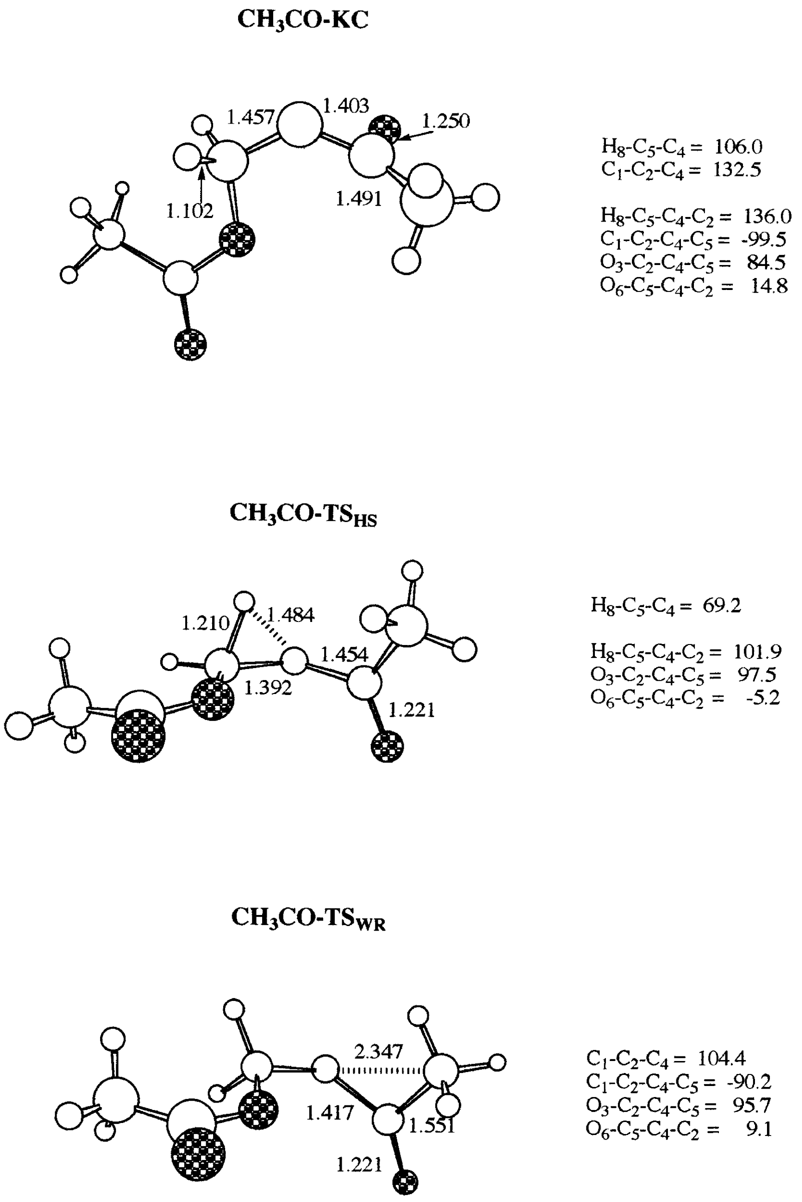

Table 1. Energy barriers and free enthalpies for the transition state for the hydrogen shift for the different substituents studied at B3LYP/6-311+G** and B3LYP/6-31G** (*in parentheses*) levels, with zero-point vibration energy (*ZPVE*) included (from unscaled B3LYP/6-31G** harmonic frequencies). For R = H the energy barrier at the B3LYP/6-311+G**//B3LYP/6-311+G** level is included for comparison (*in brackets*). Values of the charge density, $\rho(r)$, and of the Laplacian, $\nabla^2\rho(r)$, at the H_8—C_5 bond critical point. Dihedral angle of H_8 with respect to a local minimum, localised close to it, of the Laplacian distribution around C_4

	—CH_3	—H	—$COCH_3$
$\Delta E^{\neq}$ (kcal/mol)	0.90(1.41)	0.64(0.84)[0.81]	3.61(4.13)
$\Delta G^{\neq}$ (kcal/mol)	1.96(1.81)	1.21(1.75)	4.01(5.03)
ρ (r(H_8—C_5)) (a.u.)	0.2654	0.2679	0.2728
$\nabla^2\rho$ (r(H_8—C_5)) (a.u.)	−0.8627	−0.8900	−0.9123
Δ(H_8—C_5—C_4—cp_1) (degree)	−20.9	−12.8	−31.7

Table 2. Energy barriers and free enthalpies for the transition state for the Wolff rearrangement for the different substituents studied at B3LYP/6-311+G** and B3LYP/6-31G** (*in parentheses*) levels, with ZPVE included (from unscaled B3LYP/6-31G** harmonic frequencies). For R = H the energy barrier at the B3LYP/6-311+G**//B3LYP/6-311+G** level is included for comparison (*in brackets*). Dihedral angle of C_1 with respect to a local minimum, localised close to it, of the Laplacian distribution around C_4

	—CH_3	—H	—$COCH_3$
$\Delta E^{\neq}$ (kcal/mol)	1.06(1.53)	1.26(2.45)[1.64]	1.80(2.72)
$\Delta G^{\neq}$ (kcal/mol)	2.03(2.49)	2.24(3.53)	2.72(3.64)
Δ(C_1—C_2—C_4—cp_2) (degree)	−7.4	−5.3	−8.5

neous but maxima, minima and saddle points of $-\nabla^2\rho(r)$ appear on it. Interestingly, the maxima can be bonded or nonbonded. The first are related to the bonds formed and the latter to lone-electron pairs. On the other hand, the minima on the VSCC are sites susceptible to attack by nucleophiles [45, 48, 50]. The singlet carbene has a zone of charge accumulation (given by a

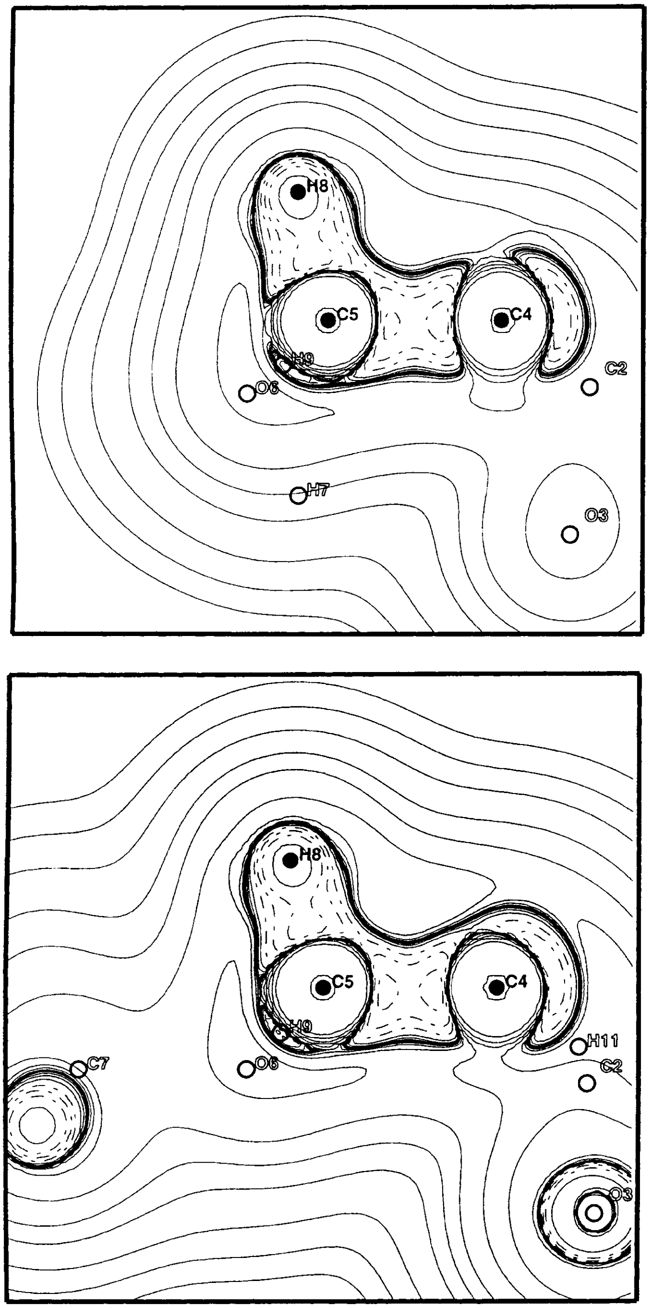

Fig. 4. Contour maps of the Laplacian distribution of the charge density, $\nabla^2\rho(r)$, in the H_8—C_5—C_4 plane of KC for the system without substituents (*above*) and for R = CH_3 (*below*). *Dashed lines* are negative zones (charge accumulation) and *solid lines* are positive zones (charge depletion)

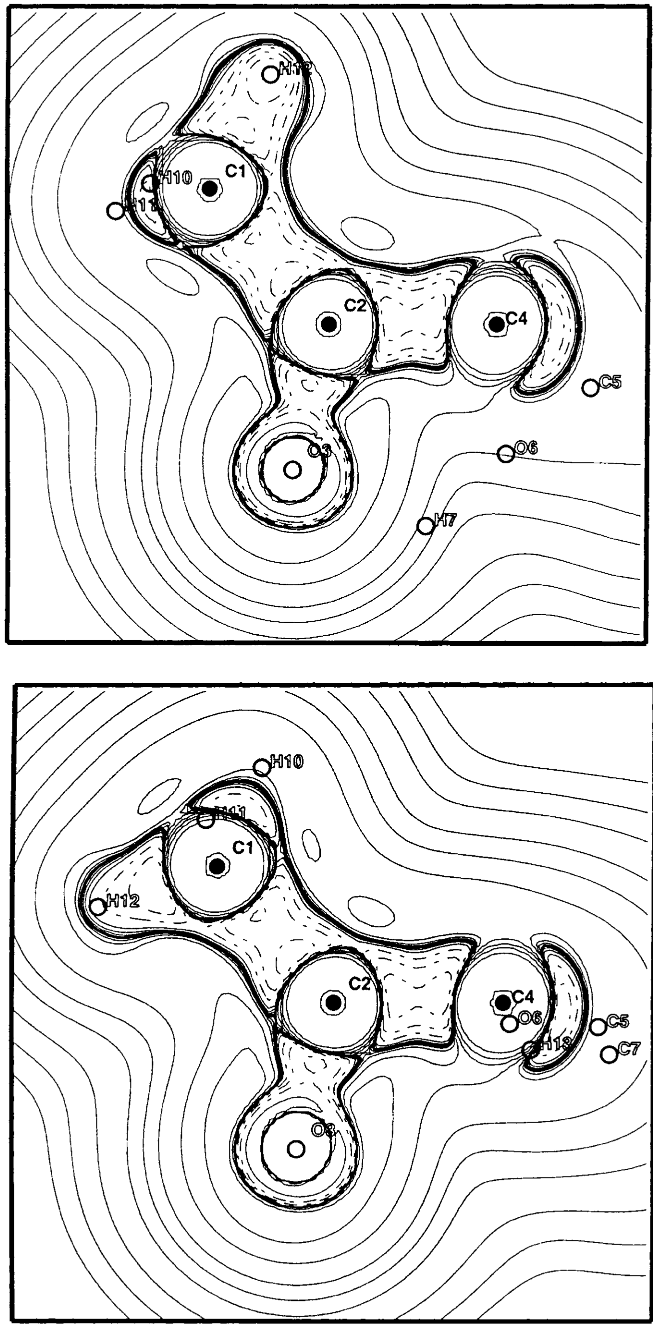

Fig. 5. Contour maps of the Laplacian distribution of the charge density, $\nabla^2\rho(r)$ in the C_1—C_2—C_4 plane of KC for the system without substituents (*above*) and for R = CH_3 (*below*). *Dashed lines* are negative zones (charge accumulation) and *solid lines* are positive zones (charge depletion)

nonbonded maximum) and zones of charge depletion (Figs. 4, 5); therefore, the carbene species can be both nucleophiles (reacting with electrophiles through the "lump") or electrophiles (reacting with nucleophiles through the "holes"). In our case the processes take place between an electrophile (the H or the CH_3) and a nucleophile (the "holes" in the carbene). The ease of migration is measured by the difference in the dihedral angle of the migrating groups and the minima of the Laplacian distribution. In principle, there should be only two minima of $-\nabla^2\rho(r)$ in the VSCC above and below the molecular plane [47, 48, 50] located at about 0.7 Å; however, we found about four minima around C_4 in the range 0.6–0.9 Å. Interestingly, two of these points were located close to H_8 and C_1, indicating that the reactions are expected to be very fast, since the migrating groups would find a channel of charge depletion to attain the carbene centre. Moreover, this closeness of the migrating groups to the local charge depletions is related to the through-space hyperconjugation described previously.

In the present work we consider the difference in the dihedral angle between the migrating group and its associated minimum critical points —cp1 or cp2— (the closest to the group) of $-\nabla^2\rho(r)$ around C_4 between the reactant and the corresponding TS as a measure of the ease of the migration.

We see from Tables 1 and 2 that this geometrical factor [see $\Delta(H_8—C_5—C_4—cp_1)$ and $\Delta(C_1—C_2—C_4—cp_2)$, the differences in the dihedral angles] is more pronounced for the HS than for the WR, being for HS in agreement with the order of the barriers.

The relative geometrical ease of the HS for R = H compared with the cases R = CH_3, and $COCH_3$ comes from the existence of a hydrogen bond interaction in KC (Fig. 1) as already reported [39]. This hydrogen-bond interaction was confirmed in the present work by the location of a BCP between the H_7 and O_6 atoms [$\rho(r) = 0.0127$ a.u. and $\nabla^2\rho(r) = 0.0581$ a.u.]. The appearance of a ring critical point in $\rho(r)$ mirrors the closeness of the geometry. This interaction favours geometrically the migration of the hydrogen atom from C_5 to C_4 since it keeps part of the molecular skeleton in a quasiplanar arrangement (see the $O_6—C_5—C_4—C_2$ dihedral angle in Fig. 1) without contributing to the energy barrier since it remains practically unaltered at TS_{HS}. In Fig. 4 we present the contour maps of the Laplacian of charge density in the $H_8—C_5—C_4$ plane of KC for R = H and CH_3. Moreover from Fig. 4 it is apparent that when R = H the HS is much more favourable owing to the "hole" in the Laplacian distribution presented by C_4 for the hydrogen to move into. In contrast when R = CH_3 the "hole" does not appear in that plane.

Concerning the WR the energy barriers correlate with the calculated electronegativity of the three R substituents, the geometrical factor being much less important than for the HS and far less discriminating (Table 2). It is interesting to note that the WR for R = H is clearly handicapped with respect to the other two substituents because of the breaking of the $O_6H_7{\cdots}O_3$ hydrogen bond at TS_{WR} (Fig. 1). This energetic cost can also explain the larger theoretical barrier found for the WR than for the HS when R = H. In Fig. 5 we display the contour maps of the Laplacian distribution of the charge density in the $C_1—C_2—C_4$ plane of KC for R = H and CH_3. We see that when R = CH_3 C_4 has a wider "hole" to be occupied by C_1 in the WR.

4 Summary

The effect of protecting the hydroxyl group of KC (derived from the corresponding β-oxy-α-diazo carbonyl compound by photolysis) with R = CH_3 and $COCH_3$ at the B3LYP/6-311+G**//B3LYP/6-31G** level has been investigated. The predicted yields are in agreement with the experimental data, which render the [1,2]-HS to be preferred over the WR when the system is not protected. To correctly explain the order of the energy barriers besides the electronegativity of the protecting groups one must also consider the alignment of the migrating groups with the "hole" (given in the context of the theory of "atoms in molecules") in the carbene centre and in the present case the existence of an intramolecular $C—O{\cdots}H—O$ hydrogen-bond interaction.

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