

## MNDO INVESTIGATION OF THE 1,2-REARRANGEMENT OF SINGLET CARBENES AND NITRENES

GERNOT FRENKING\* and JOCHEN SCHMIDT

Institut für Organische Chemie der Technischen Universität Berlin, Strasse des 17 Juni 135,  
 D-1000 Berlin 12, West Germany

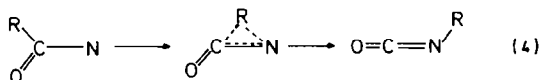
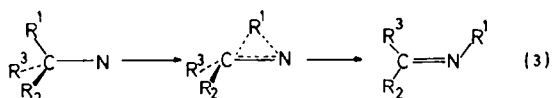
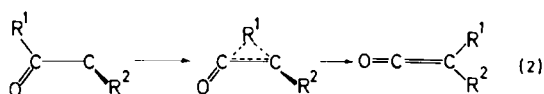
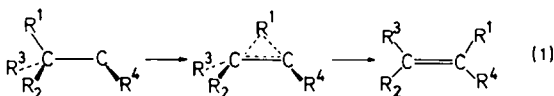
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**Abstract**—1,2-Rearrangement of substituted methylcarbenes, carbonylcarbenes, methylnitrenes and carbonylnitrenes have been calculated for singlet states by MNDO. The alteration in the electronic structure along the reaction course has been investigated by calculation and analysis of the transformation matrices between the MO's of the educts and the transition states. Migratory aptitudes are discussed as well as factors by which they may be determined. The effect of substituents at different positions has been investigated and conformational influences are discussed. As far as experimental results exist, the calculated data agree very well and offer a detailed understanding for the reaction mechanism and substituent effects.

1,2-Rearrangements of carbenes and nitrenes are not only a versatile route to various classes of compounds utilized in preparative organic chemistry; they also constitute an attractive problem being tackled from a theoretical point of view. Several reviews appeared in the last few years summarizing preparative and theoretical results being known so far as well as unsolved problems.<sup>1</sup> This paper is aimed to provide information and explanations from semiempirical SCF calculations and is focussed on the following four reaction types (chart 1).

All the rearrangements (1)–(4) have been calculated by MNDO<sup>2</sup> for the singlet states. Such an approach may be criticized. It is known that the ground states of carbenes and nitrenes are often triplets.<sup>3</sup> On the other hand most of the experimental results could best be understood when the reaction course proceeds via singlets.<sup>4</sup> A singlet course was also concluded from experiments.<sup>5</sup> Furthermore, calculated triplet transition states were found to be much higher in energy and therefore intersystem crossing may occur before reaching the top of the barrier.<sup>3a</sup>

Another critical point is that MNDO disfavors non-classical structures, thereby producing activation barriers of rearrangements being too high. Our calculations using  $R = H, F, Cl, CH_3, C_2F_5, OCH_3$  and  $SCH_3$  in reactions (1)–(4) yielded carbenes and nitrenes as minima on the energy hyperface with the exception of chlorine substituted carbonylcarbene and carbonylnitrene. However, nearly all evidence points to the occurrence of concerted reactions in migration from C=O to a nitrene center involved in the Lossen, Curtius and Hofman rearrangements.<sup>6</sup> Also the nitrene rearrangements are believed to proceed via a concerted mechanism.<sup>7</sup> In the case of the Wolff rearrangement, the occurrence of free carbonylcarbenes is dependent on the reaction procedure.<sup>8a</sup> The mechanism of the Wolff rearrangement has extensively been discussed by Strausz<sup>8b</sup> who showed that the oxirene structure explains the carbon scrambling found in photochemical decompositions.<sup>23</sup> He also calculated formylmethylene to be a minimum and more stable than oxirene.<sup>8b</sup> However, a more sophisticated approach shows that formylmethylene rearranges without any barrier to ketene.<sup>9a,b</sup> A recent *ab initio* calculation including CI shows that also methylcarbene is not a minimum on the energy hyperface but rearranges without barrier to ethylene.<sup>9c</sup> Under such circumstances it may be questioned if a model using free carbenes and nitrenes is adequate to investigate reactions (1)–(4). We do think that this is reasonable for the following reasons: (a) experimental results on migratory aptitudes are independent if the reaction is likely to proceed via free carbenes or if a concerted mechanism is involved;<sup>10</sup> (b) we are focussing mainly on relative energies of the transition states which are shown to be running parallel to the experimental migratory aptitudes as far as they are determined, independent if the reaction might be concerted or not; (c) a comparison of the calculated structures of methylcarbene and diazomethane showed the latter to be very much carbene-like. The electronic structure (HOMO mainly  $p_z$  of  $\alpha$ -carbon) and charge distribution (negative charge at  $\alpha$ -carbon) was very similar. The conclusion is that the results obtained from the calculations on free car-



benes mimic the relative activation barriers even in cases when a concerted mechanism is involved. Furthermore, MNDO calculations on carbene rearrangements previously published<sup>11</sup> gave reliable data on the stereochemistry similar to other methods.<sup>12</sup> "The fact that this approach appears to work does, in itself, provide justification for the strategy."<sup>13</sup>

All of the calculations have been performed with optimization of all geometrical parameters. Transition states have been determined rigorously as species having only one negative eigenvalue of the force-constant matrix.

### REACTION MECHANISM

The reaction mechanism of the 1,2 shift is characterized by movement of the C-R bonding (R being the migrating group) towards the empty p-orbital of the  $\alpha$ -carbon or nitrogen as shown in Fig. 1. This has been proven for methylcarbene by plotting the molecular orbital density maps of educt, transition state and ethylene.<sup>4b</sup> Following the shape of the MO's it revealed that the relevant C-H bonding MO, being the third highest in the carbene, becomes the second highest in the transition state and finally the C-C  $\pi$ -bonding HOMO in ethylene. Here, a different approach has been employed to yield information about the electronic alteration.

We calculated the transformation matrices between the MO's of the educt and the transition state, thereby expressing the MO's of the transition state  $C_{TS}$  in terms of the MO's of the educt  $C_E$ :

$$C_E = C_{TS}U$$

$$C_{TS}^{-1}C_E = U$$

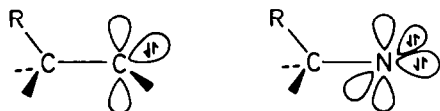


Fig. 1. Schematical orbital orientation for the 1,2R-shift of carbenes and nitrenes.

$C_{TS}^{-1}$  is easily constructed since the orthogonality of  $C_{TS}$  the transposed matrix is equal to the inverse. When other methods than MNDO are used it should be taken into account that the MO's have to be normalized.

Such a LCMO analysis has successfully been used for an analysis of orbital interaction of different reactions such as substitution and chelotropic addition along the reaction course,<sup>14a</sup> and for a comparative study of the electronic structure of neutral molecules and their radical cations.<sup>14b</sup> The transformation matrix for hydrogen migration in methylcarbene is shown in Table 1. The MO's of the educt are in columns, the MO's of the transition state are in rows; the eigenvalues of the occupied MO's are added to show the change in the energy values. Diagonal elements are underlined; they would equal 1 if no change had occurred.

The data in Table 1 correlate perfectly with the orbital density plot by Yates *et al.*<sup>4b</sup> obtained from *ab initio* calculations. The three lowest lying MO's remain nearly unchanged. The same holds true for the HOMO, whereas MO's 4 and 5 are mixing in such a way that they are practically exchanging their positions. The involvement of the empty p-AO of  $\alpha$ -carbon is demonstrated by the large coefficient of 0.30 which contributes the LUMO into the C-H bonding MO 5 of the transition state. The special merits of the transformation matrix are obvious. They show not only qualitatively the change in the sequence of the orbitals but provide quantitatively information about mixing of the orbitals. The transformation matrices for rearrangement of carbonylcarbene, methylnitrene and carbonylnitrene are omitted to limit the size of the paper. They show principally the same features as for methylnitrene but it should be remembered that these reactions are even more likely to involve a concerted mechanism.

### MIGRATORY APTITUDES

The following migratory aptitudes for 1,2-rearrangements of carbenes have been observed from experiments:<sup>1,15,16</sup>  $RS > H > CH_3 > OR$ ;  $C_2F_5 > F$ ;  $Cl > H > F$ . Fewer data are available for carbonylcarbenes, nitrenes and carbonylnitrenes, but

Table 1. Transformation matrix between the MO's of the educt (columns) and transition state (rows) for the 1,2H-shift of methylcarbene. MO eigenvalues  $\epsilon_i$  in eV

$\epsilon_i$		-34.41	-22.32	-14.90	-14.51	-13.54	-8.72						
	i	1	2	3	4	5	6	7	8	9	10	11	12
-35.79	1	<u>0.99</u>	0.05	0.04	0.04	0.02	-0.01	-0.01	-0.01	-0.02	0.00	0.01	-0.01
-21.77	2	-0.06	<u>0.95</u>	0.05	0.23	-0.01	-0.01	0.05	-0.04	-0.16	0.06	0.00	-0.02
-15.85	3	0.05	0.14	<u>-0.93</u>	-0.26	-0.11	-0.00	0.03	0.02	0.13	-0.04	-0.02	0.08
-14.35	4	-0.02	-0.09	-0.24	<u>0.39</u>	0.88	0.02	-0.01	-0.03	-0.08	0.00	0.04	-0.10
-12.81	5	-0.01	-0.17	-0.22	0.79	<u>-0.42</u>	-0.12	-0.30	-0.00	0.03	0.09	0.04	-0.10
- 8.29	6	0.01	0.02	0.01	0.10	-0.06	<u>0.97</u>	-0.07	-0.07	0.17	-0.03	0.06	0.06
	7	-0.01	-0.02	-0.06	-0.25	0.01	0.09	<u>-0.66</u>	-0.17	-0.65	-0.01	0.09	-0.15
	8	0.01	-0.18	-0.13	0.11	-0.17	0.14	0.67	<u>-0.11</u>	-0.63	0.05	0.10	-0.13
	9	0.00	0.01	-0.01	0.01	0.00	0.08	-0.05	0.97	<u>-0.20</u>	0.04	0.10	0.09
	10	0.00	-0.01	0.02	0.14	-0.04	-0.00	-0.00	-0.03	-0.20	<u>-0.70</u>	-0.50	0.45
	11	-0.01	0.04	0.02	0.02	-0.02	-0.09	0.03	-0.05	0.09	-0.59	<u>0.79</u>	-0.02
	12	0.00	-0.03	0.01	0.02	-0.01	-0.05	-0.03	-0.13	-0.11	0.37	0.30	<u>0.85</u>

as far as they are determined they agree with the trend reported for carbenes.<sup>5,6,7b,8,17</sup> The calculated barriers for substituted methylcarbenes are listed in Table 2(a). Generally they are in agreement with the experimental trends listed above with two exceptions: The sequence of  $C_2F_5$  and F is reversed and  $OCH_3$  is calculated to have too low a barrier. However, there are two factors which have to be considered when relative migratory aptitudes are to be determined. Firstly, the calculated conformations are those ones with the migrating group gauche to the methine hydrogen and may not be the most stable one. In fact, in case of  $R=OCH_3$  this conformation was not even a minimum and had to be

fixed with a dihedral angle of  $90^\circ$ . The most stable conformation shows  $OCH_3$  syn to the methine proton (Table 4(a)) being  $4.5 \text{ kcal mol}^{-1}$  more stable; this increases the activation barrier to  $18.8 \text{ kcal mol}^{-1}$ .

The second factor concerns the influence of groups in syn or anti position upon the migratory aptitude, discussed in detail in the next section. Migration of hydrogen in methoxy-methylcarbene is different to that in methylcarbene. This can be seen in Table 4(a). The  $OCH_3$  group has a strong activating influence upon hydrogen migration, lowering the barrier to  $17.5 \text{ kcal mol}^{-1}$  which is now lower than  $18.8 \text{ kcal mol}^{-1}$  for  $OCH_3$ . The same effect reverses

Table 2. Calculated activation barriers for (a) methylcarbenes; (b) carbonylcarbenes; (c) methylnitrenes; (d) carbonylnitrenes. Heats of formation  $\Delta H_f$  in kcal/mol

(a)				(c)			
R	$\Delta H_f(E)$	$\Delta H_f(TS)$	$\Delta\Delta H_f$	R	$\Delta H_f(E)$	$\Delta H_f(TS)$	$\Delta\Delta H_f$
H	88.5	110.4	21.9	H	104.0	109.7	5.7
F	48.8	81.0	32.2	F	55.2	95.4	40.2
Cl	81.7	88.5	6.8	Cl	89.4	98.6	9.2
$C_2F_5$	-144.5	-106.9	37.6	$C_2F_5$	-135.9	-109.7	26.2
$CH_3$	82.9	110.1	27.2	$CH_3$	98.0	106.5	8.5
$SCH_3$	84.7	87.4	2.7	$SCH_3$	96.4	99.6	3.2
$OCH_3$	54.7*	69.0	14.3*	$OCH_3$	62.7	86.8	24.1

\*Dihedral angle  $RCCH$  fixed at  $90^\circ$ .

(b)				(d)			
R	$\Delta H_f(E)$	$\Delta H_f(TS)$	$\Delta\Delta H_f$	R	$\Delta H_f(E)$	$\Delta H_f(TS)$	$\Delta\Delta H_f$
H	63.6	74.2	10.6	H	74.0	74.9	0.9
F	14.1	42.3	28.2	F	29.1	60.4	31.3
Cl	—*	—*	—*	Cl	—*	—*	—*
$C_2F_5$	-170.9	-152.7	18.2	$C_2F_5$	-158.4	-152.7	5.7
$CH_3$	56.0	71.0	15.0	$CH_3$	65.4	68.1	2.7
$SCH_3$	53.9	54.2	0.3	$SCH_3$	66.0**	66.0**	<0.1**
$OCH_3$	14.6	30.7	16.1	$OCH_3$	29.0	47.2	18.2

\*No minimum was found for the carbene.

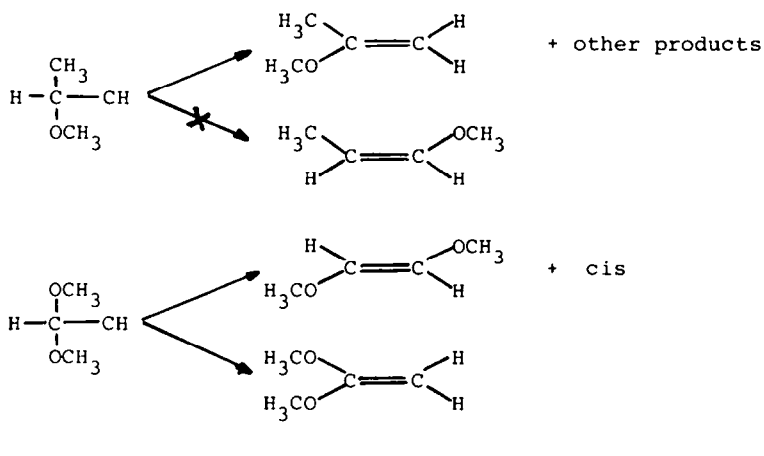
\*No minimum was found for the nitrene structure.

\*\*Nitrene structure and transition state have been found but differed by  $<0.1 \text{ kcal/mol}$ .

the sequence of F and  $C_2F_5$  when both groups are in competition. The activation height for migration of  $C_2F_5$  in  $C_3F_7-CH$  was calculated to be  $4.5 \text{ kcal mol}^{-1}$  lower than F. As it will be shown later, fluorine has the strongest promoting influence upon migratory aptitudes besides  $OCH_3$ . The calculated data in Table 2(a) are therefore in full agreement with experimental trends. However, they show that in determining relative migratory aptitudes, the activating influences of the competing groups are very important. The  $OCH_3$  group is intrinsically a comparatively fast migrating substituent, which is often over-compensated by its ability to lower the activation barriers of other groups. This is demonstrated by the experimental results of Kirmse and Buschoff.<sup>18</sup>

charge was found.<sup>19</sup> Here again, the charge distribution could not be correlated to the calculated energy values. The same holds true for the eigenvalues of a particular MO. This is not surprising in the light of the foregoing discussion. Especially in the carbonyl compounds, the transition states show nearly a unity transformation matrix and it is very arbitrary to single out a special orbital to be dominant.

But it is possible to shed some light on the problem from a different point of view. As the groups are rearranging as anions rather than cations, the whole reaction may be seen as nucleophilic attack towards the carbene or nitrene  $\alpha$ -position. Then, the reaction would be more  $S_N2$  or  $S_N1$  type as it is more or less



With only one alkoxy group, the activating influence favors migration of hydrogen and alkyl. When  $OCH_3$  and H both are promoted by another alkoxy group, they both rearrange smoothly with predominant  $OCH_3$  migration, dependent on the reaction conditions.

The activation barriers for the carbonylcarbenes Table 2(b) are lower than for methylcarbenes, but show the same trend. They agree with experiments as far as reported.

The data for nitrenes in Table 2(c) show a difference. While for some of the substituents (F, Cl,  $OCH_3$ ,  $SCH_3$ ) the barrier becomes larger, for others it is smaller. In some cases, this reverses the sequence compared to the carbenes, e.g. hydrogen should now migrate faster than chlorine. This is experimentally not yet proven. It is noticeable that only groups bonded by atoms having lone-pair orbitals show an increased barrier. This may be caused by the larger lone-pair repulsion resulting from two nitrogen lone-pairs. In going from the nitrenes to the carbonylnitrenes (Table 2(d)), similar alterations are found as for the carbenes. All barriers are lowered, and no minimum for chlorine could be found. From all the candidates in Table 2(d) only fluorocarbonylnitrene might possibly exist as free nitrene.

We attempted to find factors which may determine the size of the activation barrier. In previous papers on 1,2-rearrangement in carbenium ions a correlation could be established between the eigenvalue and degree of localization of the LUMO and the calculated barrier, whereas no influence of the positive

concerted. The sequence in migratory aptitudes  $SCH_3 > Cl > OCH_3 > F$  follows the same pattern found in nucleophilic reactions.<sup>20</sup> But then, H and CH<sub>3</sub> should migrate much faster because  $H^-$  and  $CH_3^-$  are very strong nucleophiles. However, in the rearrangements (1)–(4) the migrating groups have not only to be good nucleophiles but also good leaving groups.  $H^-$  and  $CH_3^-$  are extremely poor leaving groups and hence do not rearrange that easily. From this point of view it may be said that the migratory aptitude of a group in carbene and nitrene rearrangement is largely determined by its ability to act as nucleophile and leaving group. Iodine should be one of the best migrating groups.

What makes the difference in migratory aptitudes when going from the carbenes to the carbonylcarbenes, nitrenes and carbonylnitrenes? To a first approximation, the situation of the migrating group may be taken as the same in all four reactions. In this case, the center of nucleophilic attack should determine the reaction rate which should be mainly influenced by the eigenvalue of the LUMO which is always localized at the p-orbital of the carbene or nitrene  $\alpha$ -atom. In fact, the LUMO's of the carbonylnitrenes are by far the lowest, being typically 2.5 eV lower than carbenes, respectively. The LUMO's of the nitrenes and carbonylcarbenes are on an average 1.0–1.2 eV lower than the respective carbenes and this may explain the lower energy values. For substituents with lone-pair orbitals, the barriers increase for the nitrenes compared to the carbenes because of additional electronic repulsion.

## SUBSTITUENT INFLUENCES

The ability of  $\beta$ -alkoxy groups to enhance substantially the migration of other groups has already been noted and is experimentally proven.<sup>18</sup> Table 3(a) shows the activating barriers for H-migration of  $\beta$ -substituted methylcarbene with substituents at  $\beta$ -C syn to the methylhydrogen.

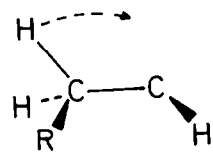
All the calculated groups promote H-migration relative to hydrogen. The data indicate also that the order of stabilization follows the order of  $\pi$ -donation ability which is reasonable since in the beginning of the reaction positive charge is developed at the  $\beta$ -C atom. Even  $C_2F_5$  is a better donor than hydrogen because p-orbitals are available. The correlation between donor ability and activation barrier is clearly demonstrated in Fig. 2(a) where the differences in the APS<sup>22</sup> bond-order of the  $C_\beta$ -R bond between the carbene and the transition state are plotted against the energy values.

All groups show a smaller decrease or even an increase for the bond order  $C_\beta$ -R in the transition state than hydrogen.  $\pi$ -Donor stabilization should be independent if the substituent at  $\beta$ -C is syn or anti to the methin proton. However, Table 3(b) shows that the barriers are now nearly unaffected by F, Cl and  $C_2F_5$  relative to H. As the data for the APS bond-order are practically the same in syn or anti position, donor stabilization cannot be responsible for this difference. The reason may rather be the smaller CC-lone pair angle in the transition state, which causes a stronger electronic repulsion with F, Cl and  $C_2F_5$ , compensating the donor stabilization effect. The conformations of  $SCH_3$  and  $OCH_3$  in the transition state avoid strong lone pair repulsion as it will later be shown in detail.

The same  $\pi$ -conjugative stabilization applies also when the substituents are in  $\alpha$ -position, but now the effect upon the barrier is opposite and much stronger since a truly empty p-orbital is stabilized in the carbene. Largest activation barriers are now found for

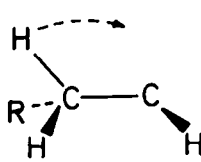
Table 3. Calculated activation barriers (kcal/mol) for hydrogen migration in substituted methylcarbenes. (a)  $\beta$ -syn substitution; (b)  $\beta$ -anti substitution; (c)  $\alpha$ -substitution

(a)



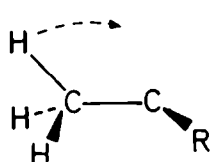
R	$\Delta H_r(E)$	$\Delta H_r(TS)$	$\Delta\Delta H_r$
H	88.5	110.4	21.9
F	43.7	62.4	18.7
Cl	75.8	96.2	20.4
$C_2F_5$	-149.1	-128.4	20.7
$CH_3$	83.1	102.2	19.1
$SCH_3$	82.3	101.9	19.6
$OCH_3$	50.2	67.7	17.5

(b)



R	$\Delta H_r(E)$	$\Delta H_r(TS)$	$\Delta\Delta H_r$
H	88.5	110.4	21.9
F	45.9	67.3	21.4
Cl	80.8	101.9	21.1
$C_2F_5$	-145.8	-123.9	21.9
$CH_3$	83.6	103.1	19.5
$SCH_3$	84.2	104.1	19.8
$OCH_3$	52.4	69.7	17.3

(c)



R	$\Delta H_r(E)$	$\Delta H_r(TS)$	$\Delta\Delta H_r$
H	88.5	110.4	21.9
F	8.4	47.8	39.4
Cl	65.1	95.3	30.2
$C_2F_5$	-156.5	-139.2	17.3
$CH_3$	70.8	93.7	22.9
$SCH_3$	60.7	90.9	30.2
$OCH_3$	5.8	49.3	43.5

R =  $OCH_3$  and F. Fig. 2(b) shows nearly a linear relationship between the difference in the APS bond order values  $C_\alpha$ -R and the calculated energies as listed in Table 3(c). Here, the strong  $\sigma$ -withdrawing of  $C_2F_5$  is effective in the transition state and lowers the barrier relative to hydrogen. The deviation for R =  $SCH_3$  may be explained by an artifact of the MNDO method which produces a linear carbene structure and, thereby, a too high APS value. It has already been noted that a 1,2-H-shift in methylchlorocarbene is drastically reduced relative to methylcarbene.<sup>1b</sup>

The substituent influence for the carbonylcarbenes at  $\alpha$ -position is completely analogous to the saturated carbenes as shown in Table 4.

Substituent influences at methylnitrene are shown in Table 5 and should be compared to the values for methylcarbene at anti position in Table 3(b). Due to the larger lone-pair repulsion (C-N bond shorter than C-C in carbenes) groups like Cl and  $C_2F_5$  now even increase the barriers, while the promoting effect of F is greatly reduced.

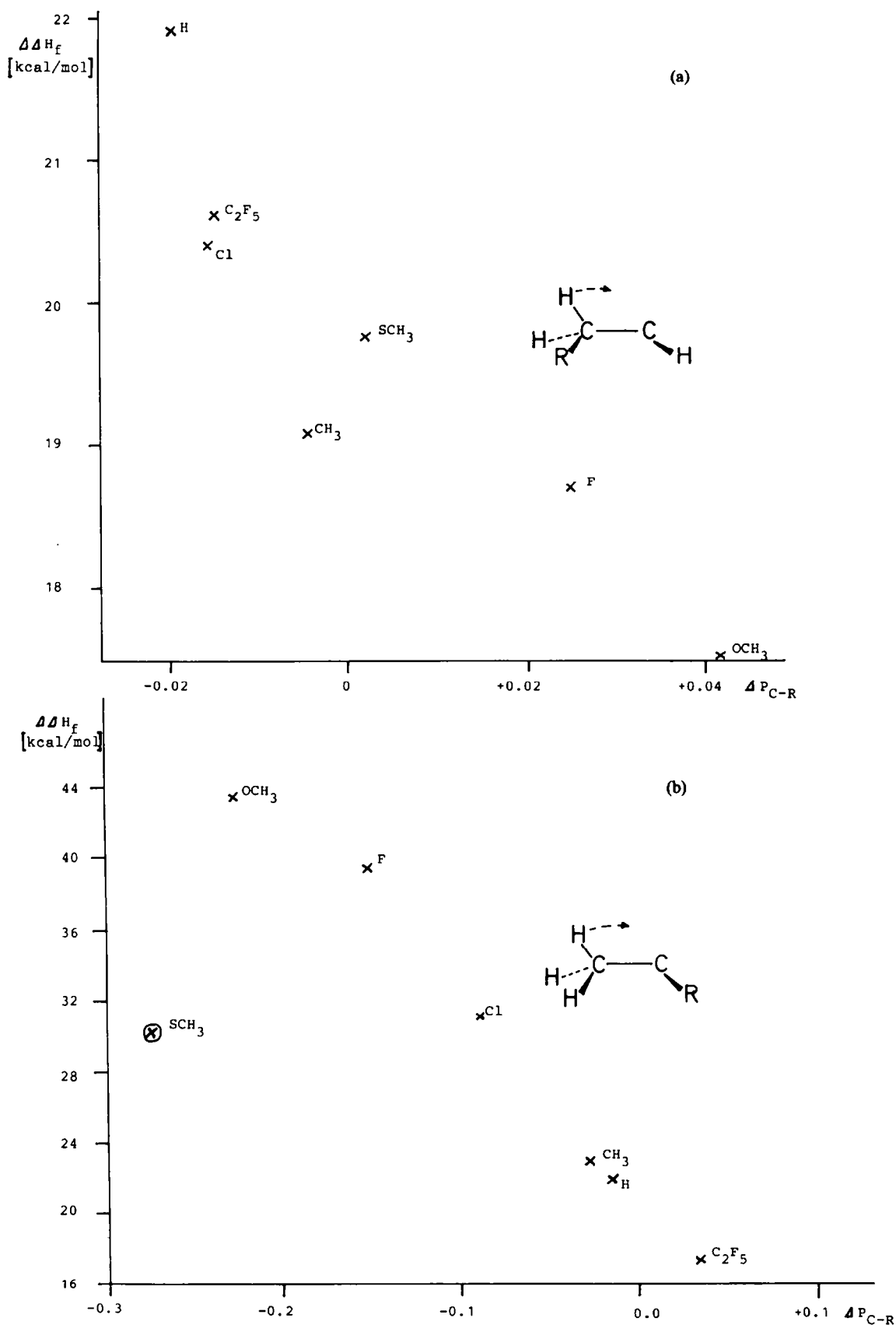
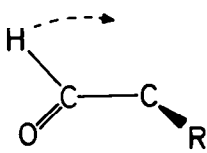


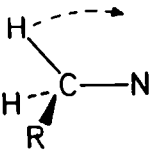
Fig. 2. Calculated activation barriers  $\Delta\Delta H_f$  (kcal/mol) versus differences in APS bond-order values  $\Delta P_{C-R}$  between educts and transition states for the 1,2H-shift in methylcarbenes (a)  $\beta$ -syn substituted; (b)  $\alpha$ -substituted.

Table 4. Calculated activation barriers (kcal/mol) for hydrogen migration in substituted carbonylcarbenes.



R	$\Delta H_f(E)$	$\Delta H_f(TS)$	$\Delta\Delta H_f$
H	63.6	74.2	10.6
F	-12.2	19.5	31.6
Cl	45.5	68.4	22.9
C <sub>2</sub> F <sub>5</sub>	-176.2	-166.7	9.4
CH <sub>3</sub>	42.2	55.8	13.6
SCH <sub>3</sub>	29.1	54.4	25.3
OCH <sub>3</sub>	-18.1	19.3	37.4

Table 5. Calculated activation barriers (kcal/mol) for hydrogen migration in substituted methylnitrenes.



R	$\Delta H_f(E)$	$\Delta H_f(TS)$	$\Delta\Delta H_f$
H	104.0	109.7	5.7
F	55.2	60.5	5.3
Cl	89.4	95.4	6.0
C <sub>2</sub> F <sub>5</sub>	-135.9	-127.9	8.1
CH <sub>3</sub>	98.0	101.3	3.3
SCH <sub>3</sub>	96.4	100.1	3.7
OCH <sub>3</sub>	62.7	65.8	3.1

Generally, substituent effect upon the migration barriers are mainly operative by their  $\pi$ -conjugative ability which decreases the energy sizes in case of  $\beta$ -substitution. This may further be influenced by lone-pair repulsion.  $\alpha$ -Substitution has a much greater influence than  $\beta$ -substitution.

#### CONFORMATIONAL INFLUENCES

In a recent paper, Nickon and Bronfenbrenner<sup>21</sup> (NB) proved experimentally that the conformation orientation of groups lacking axial symmetry in carbene rearrangement may even be more important than the eclipsed alignment of the C-R bond with the carbene lone-pair. As such influences have neither experimentally nor theoretically been investigated before, we

decided to include this problem in our work. We are following the notation suggested by NB using OCH<sub>3</sub> as an example. Orientation in migrating group is called M-orientation, in the thermal  $\alpha$ -C or N substituted group it is labeled T-orientation, while the syn and anti position at the methyl group being the migration origin are termed O-syn and O-anti orientation. By reference to an imaginary plane perpendicular to the C <sub>$\alpha$</sub> -C <sub>$\beta$</sub>  bond, two extreme positions may be labeled as face and edge. This is illustrated for the transition states of reactions (1)-(4) in Tables 6(a)-(d).

$\theta$  refers to the dihedral angle H<sub>3</sub>C-O-C-C <sub>$\beta$</sub>  for the carbenes and H<sub>3</sub>C-O-C-N for the nitrenes.

M-face orientation is clearly favoured for methoxymethylcarbene because of oxygen p-lone-pair orientation towards the empty p orbital of  $\alpha$ -C, and avoided unfavourable sp<sub>2</sub> lone-pair repulsion as in M-face' orientation (Table 6(a)). The data provide useful information about the different strength of interaction: The less favourable sp<sub>2</sub> lone-pair orientation towards the empty  $\alpha$ -C orbital in M-edge'' nearly compensates the lone-pair repulsion in the M-face' orientation. M-edge' orientation is much higher in energy and confirms the result and interpretation of NB that an edge conformation for a migrating phenyl group is energetically very demanding. Because of better  $\pi$ -conjugative ability, edge conformations are favoured for O-syn and O-anti positions. O-anti-edge'' conformation avoids lone-pair repulsion and is energetically the lowest among the O-anti positions, while O-syn-edge' is a little lower than O-syn-edge''. O-syn orientation has very little influence upon the barriers whereas O-anti orientation is more important.

Large energy differences are also found for T-orientation which is reasonable when the conjugative influence discussed in the previous section is remembered. This accounts for the strong preference of the edge-orientation. T-edge'' conformation avoids O-C lone-pair repulsion and is clearly lower in energy than T-edge'.

Tables 6(b)-(d) show that the same trends are found for carbonylcarbenes, nitrenes and carbonylnitrenes. It becomes evident that for all four reactions conformational constraints in sterically hindered systems may be large and influence the reaction course as it has experimentally been shown by NB.

#### CONCLUSION

1,2-Rearrangements of saturated carbenes, carbonylcarbenes, saturated nitrenes and carbonylnitrenes prefer a transition state in which the C-R bond of the migrating group R is eclipsed to the empty p-orbital of the carbene or nitrene. This is in detail demonstrated by the transformation matrix between the MO's of the educt and the transition state. Migratory aptitudes can be understood in terms of nucleophilicity and leaving group character of the rearranging group. The reactions may be considered as intramolecular substitutions, being more S<sub>N</sub>2 or S<sub>N</sub>1 type as they are more or less concerted. The mutual influence of competing groups at  $\beta$  position is essential for discussing their rearrangement abilities. Activation barriers and reaction course may further be strongly influenced by conformational constraints especially for groups owning lone-pair orbitals.

Table 6. Different orientations of the methoxigroup in M, O-syn, O-anti and T-positions of the transition states for H-migration in (a) methoximethylcarbene; (b) methoxycarbonylcarbene; (c) methoximethylnitrene; (d) methoxycarbonylnitrene. Heat of formation  $\Delta H_f$  in kcal/mol.  $\theta$  refers to the  $H_3C-O-C-C$  dihedral angle of the carbenes and  $H_3C-O-C-N$  dihedral angle of the nitrenes, respectively

					opt.
$\theta$	$0^\circ$	$180^\circ$	$270^\circ$	$90^\circ$	$108.3^\circ$
$\Delta H_f$	96.5	78.7	77.4	70.8	69.0
					opt.
$\theta$	$90^\circ$	$270^\circ$	$180^\circ$	$0^\circ$	$0.7^\circ$
$\Delta H_f$	76.4	75.1	74.7	69.7	69.7
					opt.
$\theta$	$90^\circ$	$270^\circ$	$180^\circ$	$0^\circ$	$178.6^\circ$
$\Delta H_f$	71.8	70.2	68.4	69.9	67.7
					opt.
$\theta$	$270^\circ$	$90^\circ$	$0^\circ$	$180^\circ$	$181.5^\circ$
$\Delta H_f$	62.2	60.7	53.5	49.3	49.3
					opt.
$\theta$	$0^\circ$	$180^\circ$	$270^\circ$	$90^\circ$	$114.0^\circ$
$\Delta H_f$	51.3	39.1	35.2	33.0	30.7

(a)

(b)



Table 6 (Contd)

					opt.
	T-face'	T-face''	T-edge'	T-edge''	
$\theta$	$270^\circ$	$90^\circ$	$0^\circ$	$180^\circ$	$188.9^\circ$
$\Delta H_f$	28.5	28.2	22.7	19.5	19.3
<hr/>					
					opt.
	M-edge'	M-edge''	M-face		
$\theta$	$0^\circ$	$180^\circ$	$90^\circ$		$103.1^\circ$
$\Delta H_f$	107.8	100.0	87.7		86.8
<hr/>					
					opt.
	O-face'	O-face''	O-edge'	O-edge''	
$\theta$	$90^\circ$	$270^\circ$	$180^\circ$	$0^\circ$	$15.2^\circ$
$\Delta H_f$	68.9	67.6	67.4	65.9	65.8
<hr/>					
					opt.
	M-edge'	M-edge''	M-face		
$\theta$	$0^\circ$	$180^\circ$	$90^\circ$		$106.1^\circ$
$\Delta H_f$	62.3	59.3	48.3		47.2

(c)

(d)

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