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ETHOXYACETYLENE AND ETHYL VINYL ETHER, DIPOLAROPHILES OF OPPOSITE REGIOCHEMISTRY IN DIAZOMETHANE CYCLOADDITIONS[1]

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Abstract: Diazomethane adds to ethoxyacetylene to give a 96 : 4 mixture in favor of 4-ethoxypyrazole (**3**) which had been identified as the only product in a previous study. This result contrasts the behavior of ethyl vinyl ether which gives 3-ethoxy-1-pyrazoline (**2**). Transition structures for the four possible regioisomers are determined by MNDO-PM3 calculations. The regioselectivity is explained on the basis of the PM3 calculations and their perturbational analysis using the program PERVAL. Distortions of the dipolarophiles in the transition structures due to closed-shell repulsions lead to FMO interactions which favor the experimental regiochemistry.

Cycloadditions of diazomethane are characterized by high reactivity of the 1,3-dipole towards electron deficient olefins.[2] However, also ethyl vinyl ether and ethoxyacetylene yield the correspoending adducts in slow reactions. The regiochemistry in the cycloadditions of ethoxyacetylene and ethyl vinyl ether is of interest because these dipolarophiles display opposite orientational behavior. Although it was postulated originally that ethyl vinyl ether gives **1** as the only product [3], it was later established that **2** represents the correct structure of the cycloadduct.[4] Ethoxyacetylene on the other hand seems to form **3** exclusively.[5] The change from a double to a triple bond, viz. from ethyl vinyl ether to ethoxyacetylene, inverts the regiochemistry.

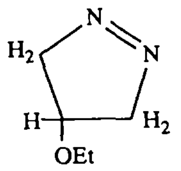
The regiochemistry of the cycloaddition of ethyl vinyl ether to diazomethane has been used as an argument in mechanistic discussions of 1,3-dipolar cycloadditions.[4,6] In particular, it was claimed that it supports the hypothesis of biradical intermediates. The revised structure **2** and the regiochemistry in cycloadditions of mono-substituted electron-deficient dipolarophiles would indeed be in agreement with the hypothesis. However, stereospecifically deuterated cis- and trans-2-D-ethyl vinyl ether retain the stereochemistry during the reaction, thus giving experimental evidence for the concerted nature of this cycloaddition.[7] FMO theory as an attempt to rationalize regiochemistry within the scope of a concerted, but not necessarily synchronous reaction, fails to explain the observed regiochemistry for ethyl vinyl ether, while ethoxyacetylene behaves as expected on this basis.[2]

Using a recently developed perturbational program [8] which includes polar interactions, covalent stabilizations and non-covalent repulsions we were able to show that closed-shell repulsions may have an important influence on the regiochemistry in 1,3-dipolar cycloadditions.[9-10] The regiospecificity in cycloadditions of diazomethane to mono-substituted olefins follows automatically from this approach.[9] Important conclusions from these studies seem to be that the discussion of reactivity and regioselectivity in terms of the FMO model may be successful in many cases due to the dominance of the frontier orbital interactions, and that false interpretations may be the consequence of the inherent approximations and not necessarily of a change in mechanism. FMO theory not only neglects other than the frontier orbital interactions in a reactive complex but also denies any influence of polar or closed-shell interactions. In the general case, however, these contributions also have to be accounted for, as is suggested by the Klopman-Salem approach$^{11-13}$ or by our perturbational treatment of chemical reactivity.^{14,15} Another deficiency may be that in FMO discussions the analysis is normally based on ground state structures and properties of the reactants.

So far we have treated only olefinic and no acetylenic dipolarophiles. Here we try to rationalize the regioselectivity for the two related dipolarophiles, ethyl vinyl ether and ethoxyacetylene. Neither the biradical approach nor FMO theory gives a consistent picture for both dipolarophiles. At the same time the cycloaddition of ethoxyacetylene to diazomethane is repeated because this reaction had been carried out at a time where NMR spectroscopy was not yet used routinely to check the crude reaction mixture for regiochemical isomers.

Experimental Results

Following the literature^{5}, ethoxyacetylene was reacted with excess diazomethane in etheral solution for two weeks at room temperature in the dark. After removal of all volatile material in vacuo, a 72% yield of colorless crystals was obtained which corresponded in melting point to the described 4-ethoxypyrazole. The ^{1}H-NMR spectrum confirms the structure. Besides the signals of the methyl and methylene protons of the ethoxy group only one additional singlet (2H) at 7.29 ppm is found. Tautomerization and rapid exchange of the NH-proton does not allow its identification and renders the pyrazole protons equivalent. This is in accordance with **3** and not with the regioisomeric product **4**. Expansion of the ^{1}H-NMR spectrum of the crude reaction mixture leads to additional signals of methylene and methyl protons. Recrystallization and analysis of the mother liquor allows the identification of the components. GC-MS reveals the presence of three compounds, displaying M^{+}-peaks m/z = 112, 112, and 126, respectively. One of the 112-peaks derives from 4-ethoxypyrazole, the other one corresponds to the regioisomer 3-ethoxypyrazole (**4**) as can be deduced from the ^{1}H NMR spectrum. In **4** the pyrazole protons are no longer equivalent, showing signals at 7.36 ppm and 5.65 ppm with a coupling constant of 2.3 Hz. The methylene and methyl protons appear at 4.21 ppm and 1.40 ppm. The third compound was assigned structure **5**, formed by reaction of **3** with excess diazomethane. Here the pyrazole protons appear at 7.15 ppm and 6.97 ppm, and the methyl protons of N-CH$_3$ at 3.74 ppm. Isolation of **4** and **5** was not attempted. The ratio of **3** : **4** was determined in an independent experiment by ^{1}H-NMR spectroscopy to 96 : 4. The reaction, although not completely regiospecific, confirms the original finding of the formation of 4-ethoxypyrazole as the dominant product. From the ratio of **3** : **4** a $\Delta\Delta G^{\ddagger}$ of 1.9 kcal/mol at 25°C can be calculated in favor of **3**.



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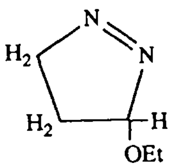

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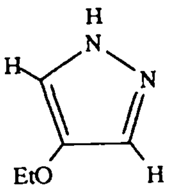

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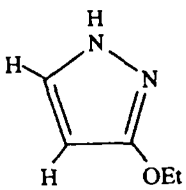

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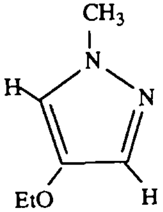

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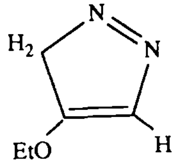

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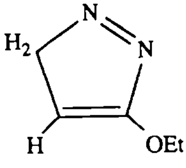

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Perturbational Analysis

The different orientation in the cycloadditions of ethoxyacetylene and ethyl vinyl ether presents a challange for a theoretical explanation. In earlier work we showed that a reasonable choice of transition structures for perturbational calculations can be made if they are modeled after ab-initio calculated transition structures. In almost all calculations of transition structures for (4+2) cycloadditions, regardless whether Diels-Alder reactions or 1,3-dipolar cycloadditions[16], it was found that the reacting centers are separated by about 2.1-2.3 Å in the transition state. In the case of unsymmetrical reactants it is obviously not expected that these separations are identical for the two new bonds.

In the present study we applied the following strategy: The transition structures for the regioisomeric cycloadducts of ethoxyacetylene and ethyl vinyl ether were determined by PM3, a reparametrized MNDO-AM1 method[17], using gradient methods. The complexes were separated into diazomethane and the dipolarophile, retaining their distorted structures. On the isolated molecules PM3 calculations were performed. These wavefunctions served as basis for the perturbation calculation.

$$\Delta E_{polar} = \sum_{k}\sum_{l} q_k q_l \gamma_{kl} \qquad \text{eq.1}$$

$$\Delta E_{polar} = 2 \sum_{l}^{L} \overset{occ}{\sum_{i}^{K}} \sum_{\mu}^{K} \sum_{\sigma}^{K} c_{i\mu} c_{i\sigma} V_{\mu\sigma,l} + 2 \sum_{k}^{K} \overset{occ}{\sum_{j}^{L}} \sum_{\nu}^{L} \sum_{\tau}^{L} c_{j\nu} c_{j\tau} V_{\nu\tau,k}$$
$$- 2 \sum_{ij} \sum_{\mu} \sum_{\sigma} \sum_{\nu} \sum_{\tau} c_{i\mu} c_{i\sigma} c_{j\nu} c_{j\tau} <\mu\sigma,\nu\tau> - \sum_{k}\sum_{l} C_k C_l \gamma_{kl} \qquad \text{eq.2}$$

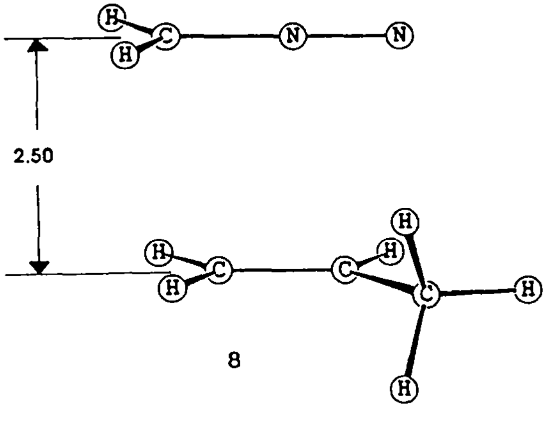
In this analysis we apply a modified version of our program PERVAL which is based on the MNDO approximation of Dewar[18] in the PM3 parametrization. This parametrization of the MNDO formalism tries to correct for the overestimation of the intermolecular repulsive interactions of the MINDO/3 or MNDO method. The extension of the theoretical approach from MINDO to MNDO increases the computation time of the perturbation calculation because the polar interactions are no longer calculated according to the simple equation 1 but according to eq. 2. In eq.1 $q_{k(l)}$ represents the charges of the atoms concerned and γ_{kl} stands for the repulsion of two electrons in spherical charge clouds (s-orbitals) at atoms k and l. In eq.2 it is necessary to take account explicitely of the core-electron attraction integrals $V_{\mu\sigma l}$ where $\mu\sigma$ stands for an electron in the overlap density of orbitals μ and σ at atom k of system K, and l is an atom of system L. Similarly, $V_{\nu\tau k}$ is the

Table 1:Comparison of perturbation calculations for complex **8** using different semiempirical schemes . Energies in kcal/mol.

semiempirical procedure	charge interaction	non-covalent repulsion	covalent stabilization	sum pertub. energies	ΔH_f CH_2N_2	ΔH_f propene	ΔH_f **8**	$\Delta\Delta H_f$ a)
MINDO/3	-0.03	41.3	-5.5	35.8	22.0	12.3	70.0	0.1
MNDO	-1.3	37.8	-3.1	33.3	69.1	8.0	110.1	0.3
AM1	-1.9	21.2	-4.2	15.1	63.9	9.4	88.6	0.2
MNDO-PM3	-1.7	26.0	-4.0	20.3	62.7	8.3	90.9	0.4

a)$\Delta H_f(\mathbf{8}) - \Delta H_f(CH_2N_2) - \Delta H_f(\text{Propene}) - \Sigma$perturbation energies

core-electron attraction integral of an electron in system L and the core of atom k in system K. The terms $<\mu\sigma,\nu\tau>$ are intermolecular electron repulsion integrals, C_k and C_l are the core charges of atoms k and l. γ_{kl} has the same meaning as in eq.1. The significance of the eigenvector coefficients c in eq.2 is self-explanatory. The interpretation of eq.2 remains the same as that of eq.1. It is the coulombic interaction of the two molecules due to their polarity. Because part of the nuclear repulsion is included in eq. 2 this has to be taken into consideration in the calculation of the non-covalent repulsion. Different types of two-center electron repulsion integrals have to be evaluated in the MNDO approximation for the calculation of the excitation energies in the perturbation treatment. Besides this the evaluation of the second-order or covalent stabilization remains the same as in the MINDO/3 approximation. The consequence of these changes, in particular the modification of the nuclear repulsion in PM3, is indeed a drastic decrease of the repulsive interaction of two molecules by a factor of about two. A similar reduction is obtained if the AM1 parametrization[19] is applied. This problem is demonstrated in comparative calculations in table 1 where results for a molecular complex of diazomethane and propene (**8**) are listed. The non-covalent repulsions between the two molecules are reduced by ca. a factor of two in changing from the MINDO/3 to the AM1 or PM3 parametrization. An analogous difference is found for MNDO and AM1. Whereas the covalent stabilizations remain very similar an increase in the polar interactions can be detected between MINDO/3 on one side and MNDO, AM1, or PM3 on the other. This seems to be due to the treatment of the two-center electron repulsions where in the latter treatments non-spherical charge distributions are considered.



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Results and Discussion

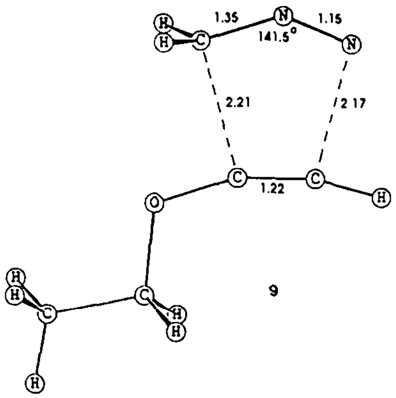
The structure and the heats of formation of the reactants and the products were determined by PM3 calculations with complete geometry optimization. The pertinent results are collected in table 2. From the heat of formation the reaction enthalpies are calculated to -42.2, -42.5, -60.8 and -59.8 kcal/mol for **1**, **2**, **6**, and **7**, respectively. The high negative reaction enthalpy can be taken as an indication for an early transition state which should allow the application of FMO theory.

Table 2: Heat of formation of reactants, products and transition structures according to PM3 calculations on optimized geometries (kcal/mol).

compound or complex	ΔH_f	ΔH_f(individual constituents) CH_2N_2	dipolarophile	Σ
CH_2N_2	61.0			
$HC{\equiv}C\text{-}OC_2H_5$	15.1			
$H_2C{=}CH\text{-}OC_2H_5$	-30.0			
1	-11.2			
2	-11.5			
6	15.3			
7	16.3			
9	107.7	76.5	24.2	100.7
10	108.3	78.4	24.0	102.4
11	64.7	77.1	-20.3	56.8
12	62.3	80.6	-23.9	56.7

The transition structures for the formation of the regioisomeric adducts **1**,**2**,**6** and **7** were calculated using gradient minimization techniques as incorporated in the AMPAC program package of Dewar.[19] In all four cases it was possible to locate transition structures which had only one negative eigenvalue in the Hessian matrix, proving that these are saddle points in the potential energy hypersurface. Their structures are displayed in formulas **9** - **12**. Before discussing details of the complexes it is noteworthy to mention that the transition structures, which lead to the experimentally observed cycloadducts, have in both cases lower heats of formation than those of the isomeric products. It is rewarding to see that PM3 seems to be adequate to describe the experimental findings in our cases.

There are some common features in all four transition structures. The distance of the reacting centers is about 2.2 Å ± 0.1 Å, except for the CN-bond distance in **12**, which is calculated to 2.36 Å. The bond distance at the side where the substituent is located is always slightly greater than that of the two other reacting atoms. Diazomethane assumes a bent structure with an average NNC-angle of 140°, slightly smaller than in the transition structure for the reaction of diazomethane and ethylene.[20] The CN-bond length in diazomethane has a value of 1.36 ± 0.1 Å, the length of the NN-bond is 1.15 Å. The structure of diazomethane is only marginally different in the four transition structures. The characteristic distortion of the dipolarophiles is the bending of the hydrogen atoms and the substituent out of the plane of the π-system and away from diazomethane. This can be interpreted as the gradual movement of these groups into the position which they assume in the final products. The origin of this movement should be partially closed-shell repulsion between the molecules and partially



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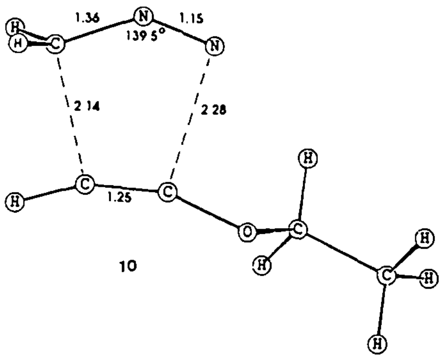

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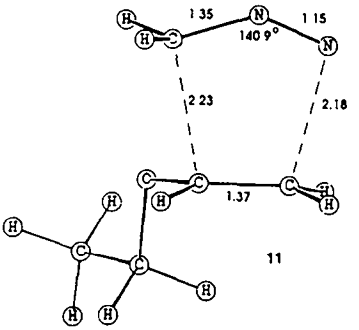

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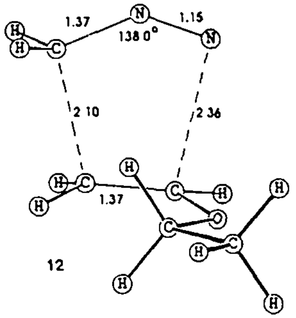

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rehybridization of the carbon atoms at the multiple bonds in order to achieve a better overlap with the relevant orbitals of diazomethane.

Another remarkable feature concerns the position of the ethyl groups of the ethoxy substituent in the two regioisomeric transition structures, **9** and **11**, as compared with **10** and **12**. The alkyl group in **9** and **11** is in a position relative to diazomethane which leads to the smallest closed-shell repulsion. The distance between the atoms of the CH_2-group of diazomethane and those of the CH_2-group of the substituent is the greatest possible. In **9** all heavy atoms lie in one plane. In **10** and **12**, however, the ethyl groups are perpendicular to the plane of the ring. The closed-shell repulsion in the orientation, where the substituent is at the nitrogen side of diazomethane, does not lead to the same kind of distortion as in **9** and **11**. The reason for the different behavior can be found in the type of repulsive potential which results from the CH_2-group of diazomethane.In **10** and **12** it originates from a single nitrogen atom whereas in **9** and **11** it stems from the CH_2-group. The hydrogen atoms seem to force the ethyl group into a symmetrical position with respect to their location in the latter case, or, in other words, if the ethyl group in **9** and **11** would move similarly as in **10** and **12** it would feel more repulsive interactions from one hydrogen atom than from the other. In order to avoid this the alkyl substituent rests in a symmetrical position with respect to the CH_2-group. Whereas this argument holds exactly for ethoxyacetylene it is only qualitatively correct for ethyl vinyl ether. As we will see this distortion has consequences for the character of the molecular orbitals of the dipolarophile, which interact as HOMOs and LUMOs with the relevant

Table 3: Perturbation calculations for complexes **9** - **12** (kcal/mol).

complex	charge interaction	non-covalent repulsion	covalent stabilization	Σ	HO_{CH2N2} $LU_{dipolarophile}$	$HO_{dipolarophile}$ LU_{CH2N2}
9	-2.9	44.9	-27.5	14.4	-13.7	-5.3
10	-2.1	42.9	-26.4	14.4	-11.5	-5.3
11	-2.8	44.9	-27.0	15.1	-13.1	-6.0
12	-1.0	43.6	-28.0	14.7	-11.7	-8.7

orbitals of diazomethane.

The result of the perturbational analysis of the transition structures is collected in Table 3. The interaction due to the polar character of the molecules ranges from -1.0 to -2.9 kcal/mol, the non-covalent repulsion is almost twice as high as the covalent stabilization. The total perturbation energies are of the order of +14 to +15 kcal/mol, showing not much differentiation between the regioisomeric products. While the identical value of +14.4 kcal/mol for the sum of the perturbation energies for **9** and **10** does not reflect the experimental preference for one isomer, the different values for **11** and **12**, however, do reproduce the experimental result qualitatively. It has to be recollected that the starting point of the perturbational calculations is not identical for **9** and **10**, and **11** and **12**, respectively. In our earlier treatment of diazomethane cycloadditions we based the analysis of all cycloadditions on the structure of diazomethane as found for the transition structure of the reaction with ethylene, and on ground state structures of the dipolarophiles. Thus, we were able to compare directly the results of the perturbation caculations. Here, however, we have slightly different structures of diazomethane and more distinct differences for the dipolarophiles. Therefore, we must take into account the distortion energies of the reaction partners. We find that the sum of the heats of formation of the reacting molecules in the transition structures **9** and **10** are 100.7 kcal/mol and 102.4 kcal/mol, respectively. This means that it is energetically 1.7 kcal/mol more expensive to distort the molecules for the transition structure **10** than for **9**. If we take this into consideration in the evaluation of the perturbation calculations, the formation of **9** is favored, in agreement with the experiment. In the case of **11** and **12** the sum of the heats of formation of the isolated molecules in their distorted structures is identical. Therefore, the perturbation calculations can be compared directly. As was pointed out above these values do indeed favor slightly the experimentally observed regioisomer.

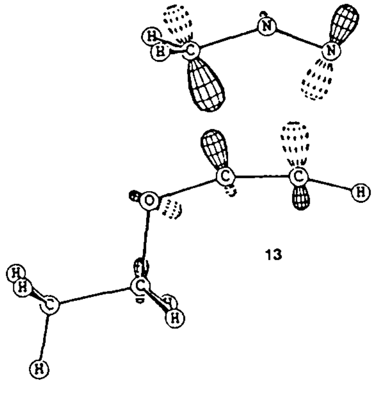
FMO theory in its qualitative form has been used to rationalize reactivity and regioselectivity in (4+2) cycloadditions. It is claimed that the magnitude of the frontier molecular orbital interactions determines reactivity and regioselectivity. This theory provides a very successful basis for the interpretation of many experimental observations. Applied to our problem of regiochemistry in diazomethane cycloadditions of ethoxyacetylene and ethyl vinyl ether it would require that the FMO interactions favor the experimental regiochemistry. Table 3 gives relevant information.The regioisomeric transition structures of the cycloaddition of ethoxyacetylene and diazomethane (**9** and **10**) display unequal FMO interactions. The HOMO(diazomethane) - LUMO(ethoxyacetylene) stabilization is greater by ca. a factor of two. This fits the general expectation for diazomethane cycloadditions.[9] As table 4 shows this result does not follow immediately from the FMO separations. The differences in stabilization should be smaller on this basis. However, an inspection of formulas

15 and **16**, respectively **17** and **18**, shows that the orientation of the orbitals in **16** and **18** is less favorable for a stabilization of the transition structure than in **15** and **17**. The simple reactivity model which incorporates both changes in orbital energies and in eigenvector coefficients in one picture, viz. the FMO separations, is reflected properly by the calculated stabilization.

Table 4: HOMO - LUMO energies (eV) for reactants in ground state and in transition structures.

compound	ground state		in **9**		in **10**		in **11**		in **12**	
	HO	LU	HO	LU	HO	LU	HO	LU	HO	LU
$HC\equiv C\text{-}OC_2H_5$	-10.15	2.14	-10.85	0.50	-9.97	0.89				
$H_2C{=}CH\text{-}OC_2H_5$	-9.57	1.27					-10.10	0.57	-9.36	0.93
H_2CN_2	-9.22	0.88	-9.01	-0.69	-9.01	-0.78	-9.02	-0.71	-9.01	-0.88

There is no distinction of the transition structures **9** and **10** on the basis of the weaker interaction, the stronger one, however, favors the experimental regiochemistry. **13** and **14** reproduce the structures of the FMOs of the 1,3-dipole (HOMO) and the dipolarophile (LUMO) for the regioisomers. An interpretation of regiochemistry in terms of the magnitude of eigenvector coefficients in this dominating interaction as judged by the size of the orbital lobes is not possible, the sizes of the orbitals being too similar to allow a discrimination. The different way of distortion of the dipolarophile in the transition states, however, provides an interpretation of the preference for **6**. LUMO(ethoxyacetylene) in **9** has less enolether character than in **10**. Due to the position of the ethyl group the antibonding enolether orbital in **9** is perpendicular to the plane of the ring, but not so in **10**. As a consequence, the ethoxyacetylene LUMO has a lower energy in **9** than in **10**, leading to a smaller FMO gap and a higher stabilization energy. In conclusion, it can be stated that the preference for **9** is the consequence of a better HOMO(diazomethane) - LUMO(ethoxyacetylene) interaction due to distortions of the dipolarophile resulting from closed shell repulsions.



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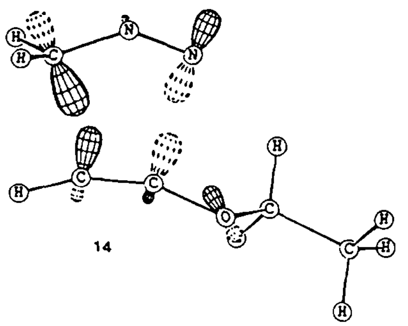

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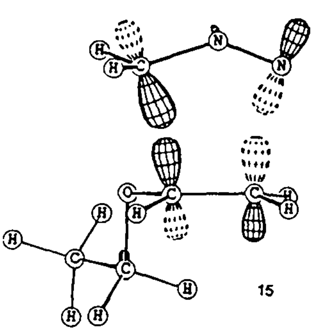

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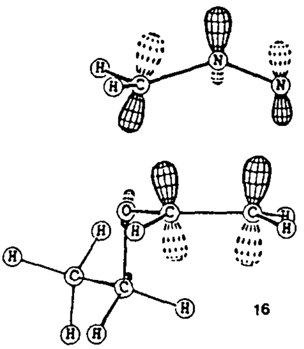

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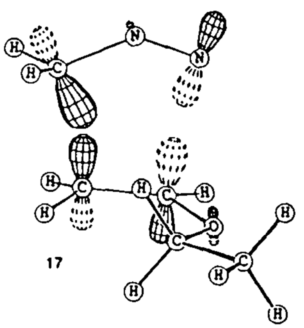
The situation is slightly different for the transition structures **11** and **12**. **11** has a higher HOMO(diazomethane) - LUMO(ethyl vinyl ether)- but a lower HOMO(ethyl vinyl ether) - LUMO(diazomethane) interaction than **12**. The sum of both stabilizations favors **12**. This is the result of a remarkable increase of the HOMO(ethyl vinyl ether) - LUMO(diazomethane) interaction by 2.7 kcal/mol which overrides the loss in the other FMO interaction. A simple explanation results again from the difference in the structure of ethyl vinyl ether in **11** and **12**. The representation of the FMOs in **15** - **18** for both regioisomers provides the explanation. In **18** the HOMO of the dipolarophile has enolether character whereas in **16** it has negligible contributions from oxygen. Therefore, their energies are different (see Table 4), giving a higher lying HOMO in **18** than in **16**. The reduced FMO gap in **18** leads to the increase in stabilization and rationalizes the experimental result. It can be stated again that the distortions of the dipolarophile due to closed shell repulsions are important for the regiochemistry.



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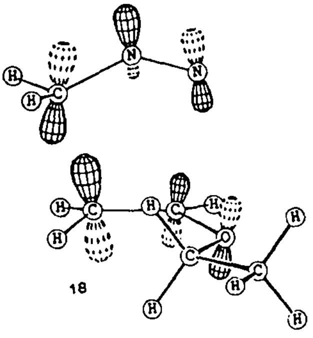

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Conclusion

The regiochemistry of the cycloadditions of diazomethane to ethoxyacetylene and ethyl vinyl ether is reproduced by PM3 calculations of the transition structures. The different distortions of the alkyl groups in the ene- or yne-ether in **9** and **11**, and in **10** and **12** respectively, which are the consequences of different closed shell repulsions between the CH_2-group of diazomethane and the substituent, and the N-terminus of diazomethane with the same substituent, can be made responsible for the regiochemistry. FMO interactions which result from these distortions in the transition structures favor the experimental regiochemistry. Thus, FMO theory which takes proper account of molecular distortions in transition structures seems to provide a consistent and elegant interpreatation of regiochemistry. The explanation of the orientational behaviour of the two dipolarophiles does not require the assumption of a change in the concerted nature of these cycloadditions.

Experimental

Reaction of ethoxyacetylene with diazomethane: 2.33 g (33 mmol) ethoxyacetylene in 3 ml hexane [21] were reacted with 2.10 g (50 mmol) diazomethane [22] in 140 ml diethylether at room temperature for 14 days in the dark. All volatile material was then removed under vacuum. 2.70 g (72% relative to ethoxyacetylene) of a colorless crystalline material with m.p. 67°C (Lit.[5] 67-68°C) were isolated. ^1H NMR($CDCl_3$):δ= 1.37[t,J=7.0 Hz,3H,-CH_2CH_3], 3.94[q,J=7.0 Hz,2H, -CH_2CH_3], 7.29[s,2H].- MS(70 eV):*m/z*(%) = 112(36,M^+) ,84(100, M-C_2H_4).

The raw material was recrystallized from n-pentane. The mother liquor was concentrated until a yellow oily product remained. This product was analyzed by ^1H NMR (Fig. 1) and GC/MS. 3-Ethoxypyrazole: ^1H NMR($CDCl_3$): δ= 1.40[t,J=7.0 Hz,3H,-CH_2CH_3], 4.21[q,J=7.0 Hz,2H,-CH_2CH_3], 5.65[d,J=2.3 Hz,1H], 7.36[d,J=2.3 Hz,1H].- MS(70 eV):*m/z*(%) = 112(68,M^+),84(100,M^+-C_2H_4). N-Methyl-4-ethoxypyrazole: ^1H NMR($CDCl_3$): δ = 1.27[t,J=7.0 Hz,3H, -CH_2CH_3], 3.86[q,J=7.0 Hz,2H,-CH_2CH_3], 3.74[s,3H,N-CH_3], 6.97[s,1H], 7.15[s,1H].- MS(70 eV):*m/z*(%) = 126(100,M^+),98(100,M-C_2H_4).

In order to establish the ratio of **3** : **4** an independent experiment was carried out under identical conditions. The raw product of this reaction was analyzed by ^1H NMR and gave a ratio of **3** : **4** of 96 : 4.

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References

1. PMO Analysis of Cycloadditions, part 6. For part 5 see: R. Sustmann, P.Daute, R. Sauer and W. Sicking, *Tetrahedron Lett.* **1988**, *29*, 4699.
2. R. Huisgen, in "*1,3-Dipolar Cycloaddition Chemistry*" A. Padwa, Ed., John Wiley & Sons, New York 1984, Vol.1, p.1.
3. A. D. Yakonov, *J. Gen. Chem. USSR* **1947**, *17*, 67; *C.A.* **1948**, *42*, 902h.
4. R. A. Firestone, *J. Org. Chem.* **1976**, *41*, 2212.
5. S. H. Groen and J. F. Arens, *Rec. Trav. Chim. Pays-Bas* **1961**, *80*, 879.
6. R. A. Firestone, *J. Org. Chem.***1968**, *33*, 2285; *ibid.* **1972**, *37*, 2181.
7. K. N. Houk, to be published.
8. R. Sustmann and W. Sicking, *Chem. Ber.* **1987**, *120*, 1323.
9. R. Sustmann and W. Sicking, *Chem. Ber.* **1987**, *120*, 1653.
10. R. Sustmann and W. Sicking, *Chem. Ber.* **1987**, *120*, 1471.
11. G. Klopman, *J. Am. Chem. Soc.* **1968**, *90*, 223.
12. L. Salem, *J. Am. Chem. Soc.* **1968**, *90*, 543.
13. A. Devaquet and L. Salem, *J. Am. Chem. Soc.***1969**, *91*, 3793.
14. R. Sustmann, A. Ansmann and F. Vahrenholt, *J. Am. Chem. Soc.* **1972**, *94*, 8099.
15. R. Sustmann and F. Vahrenholt, *Theor. Chim. Acta* **1973**, *29*, 305.
16. K. N. Houk, *Pure & Appl. Chem.* **1989**, *61*, 643.
17. J. J. P. Stewart, *J. Comput. Chem.* **1989**, *10*, 109, 221.
18. M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.* **1977**, *99*, 4899.
19. M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.* **1985**, *107*, 3902.
20. G. Leroy and M. Sana, *Tetrahedron* **1975**, *31*, 2091.
21. A hexane solution was purchased from Aldrich and purified by distillation. The concentration of ethoxyacetylene in this solution was determined by GLC.
22. Diazomethane was prepared from Diazald (Aldrich); see: Fieser & Fieser, "Reagents for Organic Chemistry", John Wiley & Sons, 1967, Vol 1, p.191.