reference compound, mp 152–153 °C.

Anal. Calcd for $C_{11}H_{17}NO_3S$: C, 54.30; H, 7.04. Found: C, 54.28; H, 7.14.

Cyclohexanecarboxamide with 2. The yellow solution was kept overnight at room temperature, whereupon cyclohexylammonium tosylate separated: yield, 2.44 g (90%); mp 181–183 °C (lit.[21] mp 184 °C); reference compound, mp 183–184.5 °C.

Reaction of Malonamide with 2. A mixture of malonamide (1.02 g, 10.0 mmol), 2 (3.92 g, 10.0 mmol), and CH_3CN (40 mL) was heated for 1 h under reflux. The pale yellow mixture that resulted was filtered to give 0.19 g of a solid (mp 338–341 °C dec) presumed to be ammonium tosylate (lit.[19] mp 345–346 °C). The filtrate was concentrated on a rotary evaporator, and the residual material was triturated with Et_2O (50 mL) to give crude 2-(tosyloxy)malonamide as a yellow, crystalline solid: yield, 2.20 g (81%); mp 162–172 °C dec. Treatment of 0.5 g of the crude product with H_2O (20 mL) returned 0.33 g of product as a white powder; mp 183.5–185.5 °C; ^1H NMR (Me_2SO-d_6) δ 2.43 (s, 3 H), 5.07 (s, 1 H), 7.2–8.1 and 7.57 (overlapping AA′BB′ m and br s, 8 H), 2.06 and 3.37 (weak s, impurities).

Anal. Calcd for $C_{10}H_{12}N_2O_5S$: C, 44.11; H, 4.44. Found: C, 44.13; H, 4.29.

(The NMR spectrum and elemental composition were obtained for the product from another run).

Reaction of α-Phenylacetamide with 2 in Ethanol. A solution of α-phenylacetamide (1.35 g, 10.0 mmol) and 2 (3.92 g, 10.0 mmol) in ethanol (35 mL) was heated for 30 min under reflux. The resulting colorless solution was passed through anhydrous $MgSO_4$ and concentrated on a rotary evaporator to an oil mixed with some crystalline material. The mixture was then taken up in CH_2Cl_2 (30 mL), and the solution was washed with H_2O (2 × 30 mL), dried ($MgSO_4$), and concentrated to a yellow oil. The oil was kept open to the atmosphere for 14 h (to ensure the removal of PhI) and subsequently crystallized from ligroin to give 0.74 g of ethyl benzylcarbamate, mp 44–46.5 °C (lit.[22] mp 44 °C). The filtrate, upon cooling at ca. −20 °C, gave 0.15 g more of product, mp 45–47.5 °C; combined yield, 0.89 g (50%).

Registry No. H_3CCONH_2, 60-35-5; $H_3CCH_2CONH_2$, 79-05-0; $(CH_3)_2CHCONH_2$, 563-83-7; $(CH_3)_3CCONH_2$, 754-10-9; $CH_3(CH_2)_3CH_2CONH_2$, 628-02-4; $CH_3(CH_2)_5CH_2CONH_2$, 629-01-6; $CH_3(CH_2)_9CH_2CONH_2$, 1120-16-7; $CH_2{=}CHCH_2CONH_2$, 28446-58-4; $PhCH_2CONH_2$, 103-81-1; $H_3CNH_2\cdot HOTs$, 2840-20-2; $H_3CCH_2NH_2\cdot HOTs$, 102520-37-6; $(CH_3)_2CHNH_2\cdot HOTs$, 63458-89-9; $(CH_3)_3CNH_2\cdot HOTs$, 63458-91-3; $H_3C(CH_2)_3CH_2NH_2\cdot HOTs$, 102520-38-7; $H_3C(CH_2)_5CH_2NH_2\cdot HOTs$, 102520-39-8; $H_3C(CH_2e_6CH_2NH_2\cdot HOTs$, 102520-40-1; $CH_2{=}CHCH_2NH_2$-HOTs, 102520-41-2; $PhCH_2NH_2\cdot HOTs$, 14613-34-4; PhI(OTs)OH, 27126-76-7; $H_2NCOCH_2CONH_2$, 108-13-4; $H_2NCOCH(OTs)CONH_2$, 102520-43-4; $PhCH_2NHCO_2CH_2CH_3$, 2621-78-5; cyclobutanecarboxamide, 1503-98-6; cyclohexanecarboxamide, 1122-56-1; cyclobutylamine 4-methylbenzene sulfonate, 102520-42-3; cyclohexylamine 4-methylbenzene sulfonate, 53050-53-6.

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Toward a Transition-State Model in the Asymmetric Alkylation of Chiral Ketone Secondary Enamines by Electron-Deficient Alkenes. A Theoretical MO Study

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The processes involved in the asymmetric alkylation of chiral ketone secondary enamines, by electron-deficient alkenes, are theoretically simulated by ab initio SCF calculations, using ethyleneamine and propenal as prototype structures. It is shown that a compact activated complex might compensate to a large extent the steric hindrance by attractive MO interactions, arising from frontier orbitals. The corresponding structure of lowest energy, compatible with asymmetric induction, is the chair-like intermediate, with an s-cis conformation for the propenal moiety.

The alkylation of carbonyl compounds, through their tertiary enamine derivatives, by electron-deficient alkenes, is widely used in synthesis chemistry and constitutes the so-called Stork's first method.[3,4] In this field, the use of imines,[5] the reaction of which occurs via their tautomeric secondary enamines, provides an extension of the aforementioned method. It is worth noting that the imine method gives alkylations on the more substituted α carbon,[6] contrary to the case of tertiary enamines. This characteristic has recently been exploited for synthesizing compounds bearing a quaternary carbon center. A general method using imines arising from a chiral amine and yielding α,α-disubstituted chiral cyclanones has been proposed.[7] Both chemical and optical high yields are obtained, according to the sequence of reactions depicted in Scheme I. The high diastereofacial selectivity which is actually observed (~90%) remains to be rationalized on the grounds of simple molecular models.

A previous approach related to analogous situations has been made by Seebach et al.[8] in which a model of the

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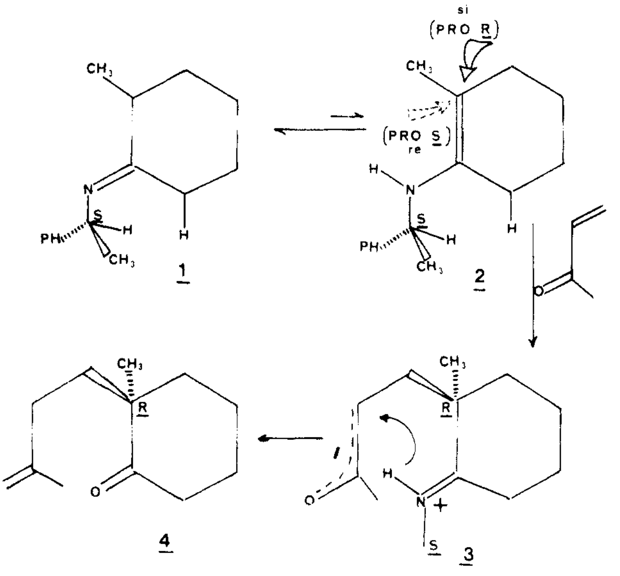
Scheme I. Reaction Sequence as Experimentally Described in Reference 7



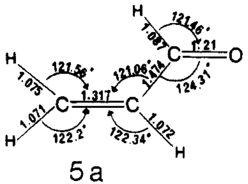
transition state is deduced from the analysis of the reaction products. We have adopted here a different strategy, based on a quantum mechanical study of the reactants approach, leading to the transition state. Our aim was to delineate the electronic and steric aspects encountered in various types of geometrical arrangements, on the one hand, and then to propose a simple workable model allowing for experimental testing, on the other hand.

Elaboration of a Model on the Grounds of Experiment

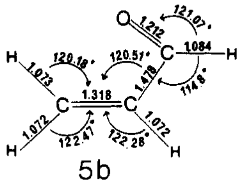
Let us first describe the typical reaction sequence displayed in Scheme I, in order to point out the salient facts that take place along the whole process. This procedure will allow us to elaborate a simplified reaction model, apt to be numerically tested by quantum calculations. The imine **1** is prepared from racemic 2-methylcyclohexanone and (*S*)-(−)-1-phenylethylamine. It is reversibly transformed into its tautomeric enamine **2**. The latter reacts with methyl vinyl ketone to give zwitterion **3**, which undergoes proton transfer, and finally, after hydrolysis, yields the (*R*)-(+)-diketone **4** with an enantiomeric excess of 91%. The alkylation essentially takes place on the pro-R face of **2**, in a quasi-axial fashion which corresponds to the least motion path. The proton transfer in the intermediate **3** is assumed to be fast, provided that the zwitterion *has a favorable geometry.*

All these considerations are supported by the fact that Michael additions to cyclohexenones, usually predominantly occur through axial attack,[9] as, for example, in Corey's cyclopropanation of cyclohexenones.[10] Another series of qualitative arguments can be derived from the electronic nature of the reactants. The π system of the enamine **2**, having two couples of paired electrons located on three centers, is isoelectronic with an allylic anion having two electrons in a MO of high energy. This moiety can thus be regarded as a "soft" nucleophile in terms of the HSAB theory.[11] Its interaction with the "soft" acid center of the conjugated ketone is therefore very likely to be dominated by frontier orbital interactions.[12] Obviously, all these points have to be tested in a theoretical approach; they are just recalled here for locating the problem in a familiar chemical way of looking at stereoselectivity. Collecting the preceding arguments, we can use a reasonable guideline for building up a computable model. It consists in considering that the transition state will preserve to a large extent the geometry of the optimal approach of the reactants, the latter being in turn ruled by a balance between MO interactions and steric (nonbonded) effects.

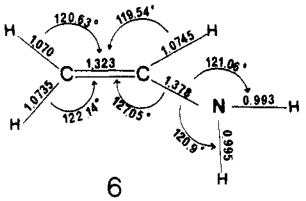
The very large size of the molecules depicted in Scheme I prevents them from being used in a quantum mechanical calculation at ab initio grade, and much simpler prototypes are requested. Structures **5a**, **5b**, and **6** have been selected for an exploratory scanning of the various reaction possibilities. Let us now consider the formation of a bond between the terminal carbons of **5** and **6**. The stable molecular geometry of both reactants is nearly planar, so that the most favorable overlap is obtained when the reacting molecules are located in parallel planes, as shown in Figure 1. Two limiting structures can be formed, according to **7** and **8**. Both have the same terminal <C|C> overlap, but, taking the enamine as fixed, they differ in the relative position of the carbonyl compound. In **7**, the reaction partners minimize all kinds of steric interactions, but it is clear that the chiral center α to the nitrogen atom lies far away from the rest of the system, in such a way that small or no asymmetric induction is expected. In the compact structure **8**, the chiral center lies much closer to the rest of the system and thus is likely to induce chiral interactions. But, at first glance, this type of structure suffers from steric congestion: it will be disfavored, unless attractive interactions may result from MO factors. Five types of structures have been studied, in order to examine various hypotheses: the already mentioned *all-trans* loose geometry of **7** and four compacts geometries **9** to **12** displayed in Figure 2. They can be classified into two sets. The three atoms of **6** and the three carbons of **5** can be arranged so as to form a pseudo-six-membered ring. The latter is boat-shaped in **9** and **10**, the only difference of which comes from the relative position of the carbonyl with respect to the cycle concavity. The chair forms **11** and **12**



5a



5b



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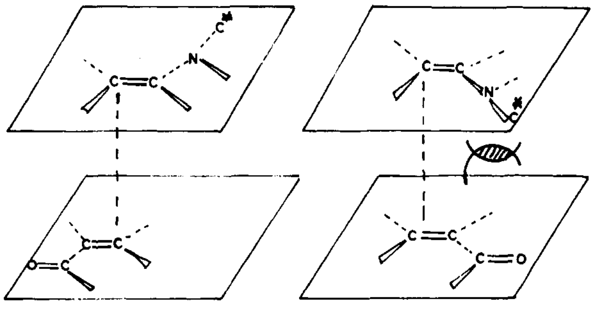

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Figure 1. Loose and compact approaches of the reactants.

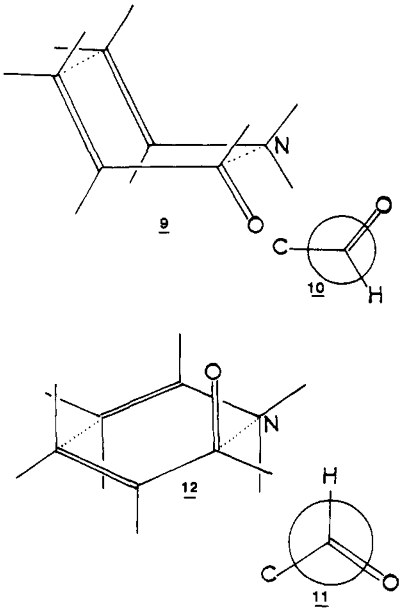


Figure 2. Boat- and chair-like structures of the compact approach. In 10 and 11 only the carbonyl group conformation is drawn; the rest of the system is identical with 9 and 12, respectively.

also differ by the carbonyl position, which is pseudoaxial in 12 and pseudoequatorial in 11. It is worth noting that 9 and 11, on the one hand, and 10 and 12, on the other hand, are respectively s-trans and s-cis, if one refers to the ketone component. It must be clear that the preceding labeling is only of practical use but does not really correspond to geometrical properties of the usual six-membered ring compounds.

Method of Calculation

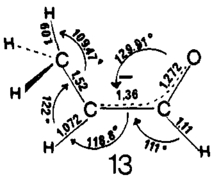
Ab initio calculations were carried out by using the Gaussian series of programs,[13] with the 3-21G basis set.[14] All geometries were optimized by using a gradient algorithm.[15] Two levels of optimization were used. In a first step, all geometrical parameters of **5a**, **5b**, and **6** were optimized. The next step of the calculation was achieved by keeping the reactants in parallel planes and freezing the CH and NH bond lengths, with all other parameters being optimized, for structures **9** to **12**. A preliminary scan of the reactants approach was done, in order to set the interplane distance at a significant value. We have selected the distance of 2.75 Å, which corresponds to a region where the overlap between the π systems becomes noticeable and where further approach fastly becomes endothermic. The related $\langle C_2|C_3\rangle$ π overlap displayed in Figure 4 is ~0.1 and the overall repulsion energy is >10 kcal·mol^{-1} with respect to infinite separation. These numbers are suitable for use in the forthcoming perturbation theory analysis.

Table I

compd	energy (au)	rel energy (kcal mol^{-1})
6	-132.326444	
5a	-189.689880	
5b	-189.689884	
5 + **6** (infinite d)	-322.016324	0.00
9	-321.995306	13.19
10	-321.996254	12.59
11	-322.000934	9.65
12	-322.002313	8.79
7	-322.003870	7.81
15	-321.873685[a]	89.50
13	-190.242640	
14	-132.704364	

[a] The isodesmic reaction **13** + **14** → **15** + H_2, where the energy of H_2, calculated with the same basis set is -1.1229500 (au), is exothermic (ΔE = -31.15 kcal mol^{-1}). If one compares the experimental C-C bond energy (84.0 kcal mol^{-1}) vs. the H_2 bond energy, we have a -19.5 kcal mol^{-1} balance, in the same direction. Our thermodynamic balance, just taking into account the electronic energy, therefore is in reasonable agreement with these data. The split-valence basis used in these calculations is adequate for delocalized ionic species, without using polarization functions, as it would be necessary dealing with more compact species.

An attempt was also made to partially optimize the zwitterionic structure **15**.[16] As an end result, no clear-cut



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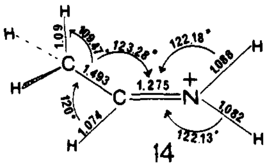

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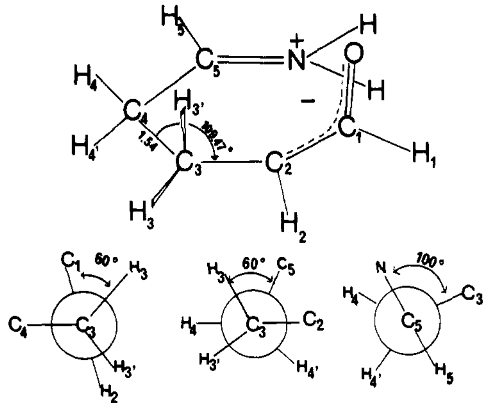

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energy minimum emerged, but the important point to note is that, in the vicinity of the geometry described in **15**, the potential energy varies rather smoothly, so that no im-

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[15] The analytical method of W. C. Davidson and L. Nazareth, further developed by M. Peterson and K. Peterson, is found as a routine link in the aforementioned series of programs.

[16] Many technical difficulties were encountered. SCF convergence was very difficult to obtain. The calculation was carried out as follows: we first optimized the ionic structures **13** and **14** separately. Then the resulting density matrices were used as an initial guess for **15**. The following strategy was adopted: (i) optimization of the C_3C_4 bond length; then the following degrees of freedom were optimized; (ii) rotation of the NH_2=CH plane around C_5C_4; (iii) rotation of the CHO–CH plane around C_2C_3; (iv) rotation in block of the optimally adapted NH_2=CH–CH_2 and CHO–CH–CH_2 units around C_3C_4.

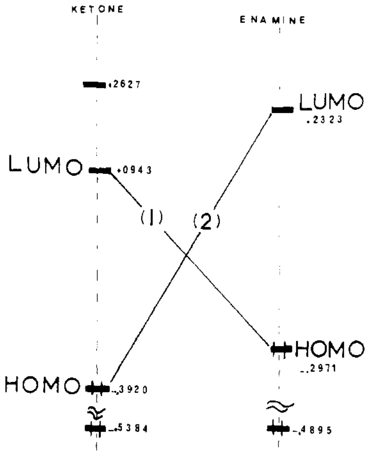


Figure 3. Calculated energies, in au, of the frontier orbitals of **5** and **6**.

portant driving force exists which would force the system to drastically change its conformation. The latter point bears important qualitative meaning. It shows that although **15** might be regarded as a local energy minimum, this moiety is not likely to be formed due to its high energy. A facile proton transfer from NH_2 to C_2 occurring more or less concomitantly with the C–C bond formation would indeed prevent the system from passing through a high energy zwitterionic transient species (vide infra the discussion). The calculated data are displayed in Table I.

Discussion about the Calculated Results

First of all, the data of Table I reveal that, as expected, the trans–trans structure **7** has the lowest energy. But, at quite the same energy, we also find compact chair structures **11** and **12**. The boat structures **9** and **10** are less stable, but lie not too far in energy from the most stable one. A first trend emerges from this comparison: *the compact structures are not appreciably disfavored with respect to the approach which minimizes all steric factors (7)*. Looking at structure **9**, we see that the maximum number of bonds are eclipsed, so that the maximum of repulsive nonbonded interactions is likely to take place. It is therefore clear that some extra stabilization comes from MO interactions, and we will examine this point in detail. We will first focus our attention on the boat structures, in order to point out the main MO features which compensate the nonbonded interactions, and then, in a second step, we will compare the boat and chair structures.

Let us look at the energy diagram of Figure 3, where the dominant MO interactions are outlined. During the approach of the terminal carbon atoms, in order to form a bond, two stabilizing two-electron interactions must be taken into account, between the HOMO and the LUMO of each system, respectively. This interaction is depicted according to (1) and (2). The perturbation interaction arising from two nondegenerate levels is $\sim S^2/\Delta E$, where S is the overlap and ΔE the energy gap separating the levels. On considering, to a first approximation, that the overlap S is roughly the same in both cases for the terminal carbon atoms, we see that the interaction (1) is more important than its counterpart (2) because ΔE is smaller in the latter case. The overall overlap, i.e., taking into account all the interacting centers, even increases this dichotomy (vide infra). This couple of interactions is detailed in Figure 4. In the drawing, the size of the π lobes is approximately proportional to the calculated coefficients, and, since we are looking at the formation of a C–C bond, the overlap has been taken as positive between these centers, thus fixing the relative signs of the other contributions.

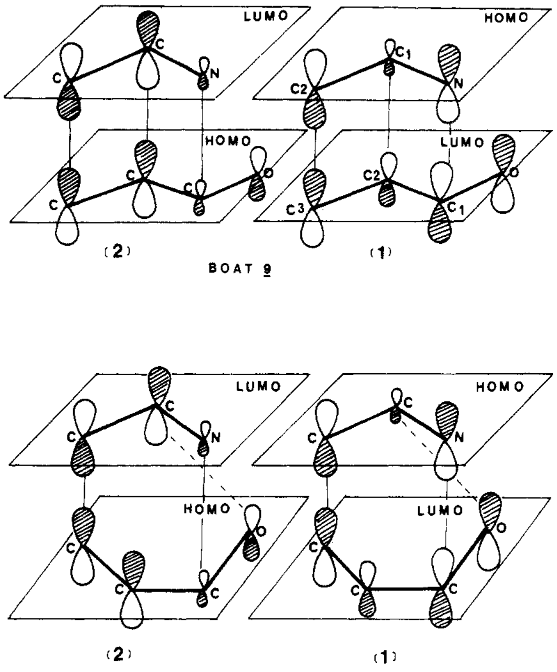


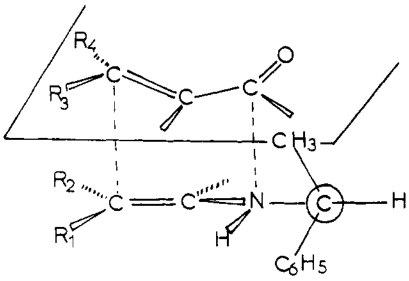
Figure 4. MO pattern for the interactions described in Figure 3 according to (1) and (2). The size of the lobes is roughly proportional to the calculated coefficients.

The most important interaction, (1) of Figure 3, arising between the HOMO of the donor (enamine) and the LUMO of the acceptor (propenal) is displayed in the right part of Figure 4. We see that once the terminal lobes are arranged in a bonding fashion, an attractive interaction also takes place between the N center and the carbon of the carbonyl group. A secondary repulsive interaction is found between carbon 2 of the ketone and carbon 1 of the enamine, but the corresponding coefficients are small compared to those which interact in a bonding fashion. In the upper left part is shown the second (weaker) interaction, (2), between the HOMO of the propenal moiety and the LUMO of the enamine. We see that two repulsive interactions arise, an important one between C_2 of the ketone and C_1 of the enamine, both having large coefficients, and a weaker one between C_1 of the ketone and N (small coefficients). We can summarize these qualitative arguments as follows: the dominant interaction (1) is largely attractive. In the second interaction (2), the bonding effects are compensated by antibonding contributions of the rest of the system. It is therefore clear that if we have the possibility of maintaining the bonding effects and of minimizing the antibonding ones, we will have an even better stabilizing balance. These requirements are fulfilled in the chair structures displayed in the bottom of Figure 4. In the leading interaction (bottom right), we see that C_2 of the ketone and C_1 of the enamine are no longer in coincidence, so that only the stabilizing interactions remain. In the interaction (2) (bottom left), the attraction now dominates over repulsion since the important antibonding contribution, not being in coincidence, is minimized, the remaining one still involving small coefficients. A secondary effect also results from the position of the oxygen atom, in the s-cis conformation, as shown in broken lines in the bottom of Figure 4. This attraction arises in both (1) and (2), between the oxygen and C_1 of the enamine. This extra stabilization is not present in the s-trans conformation of propenal, **11**, but is operative in structure **12**.

To resume the preceding analysis, we see that in the chair structures important attractive interactions are found, which are likely to compensate to a large extent the nonbonded repulsion resulting from a compact approach of the reactants. These MO effects are not too surprising. For example, they bear some analogy with the well-established endo rule of Diels–Alder reactions, which has been rationalized on similar grounds.[17,18]

A Compact Model for Asymmetric Induction

Structure **16** displays a compact model where the geometrical constraints are emphasized. Prior to an examination of asymmetric induction, let us go back to the geometry of the enamine **2** (Scheme I). Two series of problems arise regarding the N-substituents. First of all, assuming that the *N*-ethylene unit is planar, or nearly so, the most stable geometry corresponds to the smallest steric interaction between the ethylenic methyl and the smallest substituent on N, i.e., H in our case. This result is quite obvious upon the examination of molecular models and is commonly observed in alkenes. The problem of the conformation around N and the asymmetric carbon is more complex. Considering the fact that this carbon is linked to the conjugated N–C–C chain, we can infere that the conformation where CH lies in the nodal plane of the unsaturated system is preferred. This type of conformation is usually observed in α-substituted ketones or alkenes.[19] Moreover, in the actual molecule **2**, it corresponds to the least steric congestion when one takes into account the pseudoequatorial hydrogen beared by the closest saturated carbon of the cycle. The corresponding conformation is shown in **16**. Indeed, the flexibility of this structure remains important in the free molecule but might be substantially frozen in a compact activated complex. This optimal conformation creates two diastereotopic faces, one having a methyl group pointing in the superior half-space and the second having a phenyl group pointing in the inferior half-space (*in the case of an S carbon*). When both the methyl and the phenyl groups are allowed to rotate, they occupy volumes of very different sizes, and it is evident that the less hindered face is the one that contains the methyl substituent. In a compact approach, the ethylenic ketone will therefore preferentially come close to the enamine in the latter half-space. We now have to distinguish two cases: (i) If the R_3 and R_4 ketone substituents depicted in **16** are identical, as it is the case in methyl vinyl ketone, we observe the formation of *one* new asymmetric center, i.e., the ethylenic carbon of the former enamine, as experimentally established. (ii) If $R_3 \neq R_4$, the concomitant formation of a *second* asymmetric center might be predicted, provided that the same structure of the reaction transition state prevails.



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Another argument in favor of a compact activated complex is found in examining the evolution of the zwitterion which results from the initial C–C bond formation. In a compact geometry such as that in **15**, which is obtained through the least motion path starting from the chair geometry **12**, the hydrogen transfer from NH_2 to C_2 is easy since these centers are close to each other.[20] The energetic balance of **15** with respect to **5** + **6** (Table I) cannot be accurately compared to the actual reaction conditions where solvation is likely to play an important role in stabilizing the charged species. Nevertheless, the high calculated endothermicity induces one to think that the proton transfer might be more or less concerted with the addition step, in order to avoid, as much as possible, the creation of two opposite charges. This should not at all be the case in a zwitterion resulting from a loose approach, like 7, where many other reaction possibilities exist, among which is the reversible destruction of the intermediate restoring the uncharged reactants.

Conclusion

Two series of concluding remarks emerge from the above study. The first one is that the calculation shows that Michael-type additions might proceed through a compact activated complex. Moreover, this proposal is comforted by the actually observed asymmetric induction which could not be efficient in a "tail-to-tail" loose approach of the reactants. The second one is that our proposal allows for prediction of the synchronous formation of two asymmetric centers upon the use of an enamine like **2** and a β-substituted enone. The latter possibility remains to be experimentally tested.

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Registry No. Ethyleneamine, 593-67-9; propenal, 107-02-8.

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(20) A reaction similar to the ene synthesis was earlier proposed by one of us for a related situation, see ref 5b.