Theoretical Studies on E2 Elimination Reactions. Evidence That Syn Elimination Is Accompanied by Inversion of Configuration at the Carbanionic Center

Robert D. Bach,* Robert C. Badger, and Timothy J. Lang

Contribution from the Department of Chemistry, Wayne State University, Detroit, Michigan 48202.

Received September 27, 1978

Abstract: A theoretical treatment of the stereochemical course of alkene-forming elimination reactions is discussed. Based on frontier molecular orbital theory and ab initio molecular orbital calculations it is concluded that the feasibility of both syn and anti modes of elimination is enhanced by maximizing the overlap of the developing carbanionic orbital at C_β with the C_α-leaving group σ^* orbital. Furthermore, the less favored mode of syn elimination occurs by the concerted process of leaving-group expulsion at C_α and the concomitant inversion of configuration at C_β.

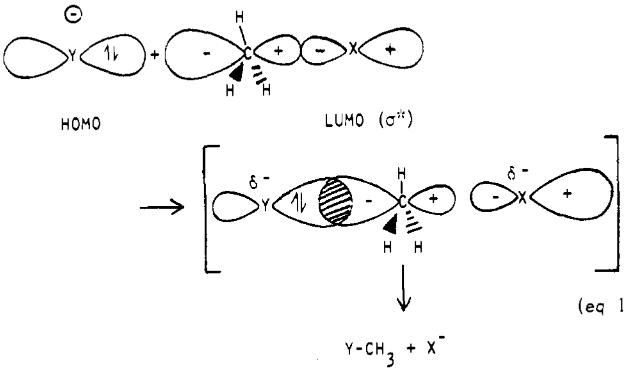
Introduction

The stereochemical course of 1,2 elimination reactions that form alkenes is defined to be syn or anti depending upon whether the two vicinal groups depart from the same or the opposite face of the developing carbon–carbon double bond. Both of these processes are now accepted as normal modes of bimolecular elimination. Mechanistic rationale for this important class of reactions developed simultaneously with stereochemical studies on S_N2 nucleophilic substitution. Hughes[1] first recognized that 1,2 elimination may be considered an internal nucleophilic substitution at the carbon bearing the leaving group by the developing electron pair at the β carbon. Ingold[2] suggested that the same kind of "quantal effects" that control Walden inversion may be responsible for influencing both anti- and syn-coplanar concerted eliminations. He also implied that syn elimination involving extensive proton transfer might involve inversion affording net syn-periplanar stereospecificity. Conceptually, the mechanism for anti elimination has become well accepted but controversy still surrounds the subtle features of syn elimination. There is, however, general agreement that syn-coplanar E2 elimination involves a transition state with considerable carbanion character.[3]

Theoretical studies on elimination reactions have been rather limited. Earlier efforts by Fukui were directed at an explanation of the origin of the reasons for the preferred anti elimination pathway.[4] Extended Hückel[5a] and ab initio[5b] calculations on ethyl chloride have suggested that its thermal decomposition involved elimination of HCl by a unimolecular concerted syn (i.e., suprafacial) pathway. On the basis of CNDO/2 calculations Lowe[6a] suggested that syn elimination proceeds through an E1cB-like transition state and Sedlacek[6b] has suggested that through-space or through-bond interactions dominate the preferred mode of elimination. We now report the results of a theoretical study on 1,2 elimination that provides convincing evidence that syn elimination is attended by concomitant inversion of configuration at the developing carbanion center.

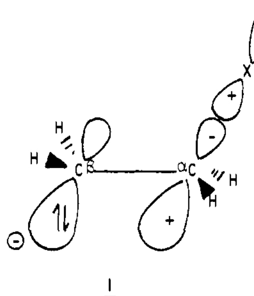
Results and Discussion

A comparison of S_N2 displacement reactions at carbon with both syn and anti elimination pathways motivated us to initiate an ab initio MO investigation of elimination reactions. The frontier molecular orbitals[6c] involved in a simple Walden inversion are typically the lone pair of an anion or the nonbonding electrons (HOMO) of the nucleophile and the vacant σ^* orbital (LUMO) of the σ bond involved in displacement (eq 1). Occupation of the antibonding σ^* C–X bond by electron density from the attacking nucleophile causes C–X bond rupture with ultimate displacement of the leaving group. This

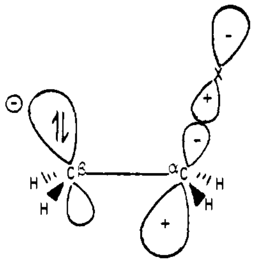


(eq 1)

picture also provides a simple rationale for why such displacements occur with inversion of configuration. Electron density in the occupied σ orbital (HOMO) of CH_3–X is maximized between the carbon and X atoms while the lobes of the antibonding σ^* orbitals, with the larger eigenvector coefficient on the carbon, are distorted toward the backside of the atoms to minimize antibonding interactions. In a similar fashion bonding electrons from the C_β–H occupy the back lobe of the developing carbanion in E_2- or E1cB-like transition states. Orbital mixing of these electrons with the empty σ^* orbital of the vicinal leaving group, which *initiates* C–X bond cleavage, is clearly favored in an anti-periplanar relationship as depicted in **1**. It is equally obvious that the syn-periplanar relationship in **2** represents a less favorable orbital arrangement for elimination that may be considered by analogy to S_N2 reactions to be tantamount to nucleophilic displacement by the C_β–H electron pair at C_α *with retention of configuration.* With this electronic configuration, carbon–carbon double bond formation can be facilitated by either extensive C–X bond breaking (i.e., an E1-like transition state) or by concomitant inversion of configuration at C_β. This simplified frontier MO approach has the advantage of providing a concept that is both easy to grasp and capable of theoretical tests through the use of ab initio molecular orbital calculations.



1



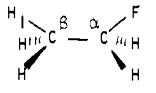
2

Table I. Optimized Geometries and Total Energies for Eclipsed (**3**) and Staggered (**4**) Ethyl Fluoride and for Syn (**7**) and Anti (**8**) Ethyl Fluoride Anion

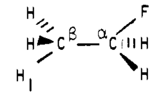
	STO-3G				4-31G				6-31G	
	3	**7**	**4**	**8**	**3**	**7**[a]	**4**	**8**[a]	**7**[b]	**8**[b]
					Bond Distances (Å)					
C_β-C_α	1.571	1.553	1.558	1.538	1.526	1.480	1.511	1.482	1.450	1.457
C_α-F	1.391	1.391	1.388	1.388	1.417	1.391	1.415	1.388	1.536	1.547
C_β-H_1	1.093		1.093		1.082		1.083			
C_β-H	1.093	1.103	1.093	1.106	1.082	1.103	1.082	1.106	1.103	1.106
C_α-H	1.104	1.110	1.106	1.108	1.077	1.110	1.078	1.108	1.110	1.108
					Bond Angles (deg)					
C_β-C_α-F	111.0	113.11	111.27	118.65	110.64	116.72	110.02	119.97	116.72	119.97
H_1-C_β-C_α	109.79		109.48		109.02		109.86			
H-C_β-C_α	110.15	104.33	110.06	103.79	111.65	113.35	110.84	110.57	113.35	110.57
C_β-C_α-H	109.82	114.50	109.09	110.92	111.98	113.54	111.62	110.82	113.54	110.82
θ[c]	−53.59	−66.66	53.81	67.57	−50.93	−44.58	52.61	52.56	−44.58	52.56
ϕ[d]	−55.07	−47.47	−56.32	−54.14	−49.66	−47.93	−50.25	−53.22	−47.93	−53.22
total energy, au	−175.749 28	−174.892 15	−175.753 24	−174.899 41	−177.839 76	−177.138 80	−177.844 96	−177.147 25	−177.328 72	−177.338 30

[a] All geometric parameters optimized except C_α–F, C_β–H, and C_α–H, which was maintained at their STO-3G values. [b] The only geometric parameters optimized were C_β–C_α and C_α–F; all other variables were maintained at their 4-31G values. [c] Inversion angle at the β carbon. [d] Angle comparable to θ but at the α carbon.

We chose ethyl fluoride as our theoretical model substrate employing hydride ion as the base. Ethyl fluoride, in both eclipsed (**3**) and staggered (**4**) conformations, was exhaustively



3



4

minimized[7] using a 4-31G basis set (Table I). The eclipsed conformer, **3**, was calculated to be 3.26 kcal/mol higher in energy than **4**. The hydride ion induced syn and anti elimination of HF from **3** and **4** was an exothermic process with a calculated ΔH of −21.71 and −18.45 kcal/mol,[9] respectively:

$$CH_3CH_2F + H^- \rightarrow H_2 + CH_2{=}CH_2 + F^- \quad (2)$$

A preliminary scan of the STO-3G potential energy surface for syn elimination was performed by maintaining a symmetry plane containing H_1-C_β-C_α-F in **5**. The hydride ion preferred an approach along the C_β-H_1 axis. With the H_1-H_2 internuclear distance as the independent variable, an energy minimum was realized with an H_1-H_2 bond distance of 0.74 Å, which is a fully bonded hydrogen molecule. The C_β-H_1 distance had been increased by 71% while the C_α-F distance remained essentially unchanged (<1% stretch). In a similar fashion, elongating the C_β-H_1 bond by 80% resulted in a charge of −0.38 on C_β and a reduction in C_β-H_1 Mulliken overlap population from 0.383 (in **4**) to 0.043. These data strongly suggest that the C_β-H_1 bond ruptures well in advance of the departure of fluoride ion.

These conclusions were further verified when an extended (4-31G) basis set was utilized for examination of the minimum-energy pathway for both syn and anti elimination. Stretching the C_β-H_1 bond distance in both **5** and **6** at 10% intervals and minimizing the remaining variables[7] demonstrated that in both model eliminations the reaction exhibited concerted E2 character but that proton abstraction by H^- was well advanced relative to departure of F^-. For example, at 0, 40, 60, and 100%, C_β-H_1 bond elongation in syn elimination, **5**, the H_1H_2 bond distances were 1.59, 0.94, 0.85, and 0.79 Å, respectively. The comparable C_α-F bond distances were 1.46, 1.55, 1.58, and 1.82 Å, respectively. The same trend was noted for anti elimination, **6**, where the hydrogen molecule (H_1-H_2 = 0.84 Å) was formed rapidly while the C_α-F bond was stretched only ~10% at 80% C_β-H_1 bond elongation. Calculated activation energies (relative to products) of 21.6 and 11.6 kcal/mol were estimated for the syn- (**5**) and anti- (**6**) elimination with both maxima at ≃30% C_β-H_1 bond stretch.

Our principal objective in this study was to ascertain the stereochemical fate of the inversion angle, θ, at C_β as the elimination progressed. Employing a 4-31G basis set, we approached the problem first by elongating the C-F bond at 10% intervals and examining only the hybridization, or inversion angle, at the developing carbanion in both **5** and **6**. As seen in Figure 1, a relatively smooth change in hybridization from sp^3 to sp^2 ($\theta = 0°$) is apparent as anticipated for anti elimination. In contrast, syn elimination is attended by a more rapid change in θ, reaches planarity at C_β at 38% C-F elongation, and *attains a positive value of θ* at about 50% cleavage of F^-. Secondly, we examined the dependence of θ on C_β-H_1 bond elongation but with the additional refinement of minimizing all pertinent variables.[7] These results are also presented in Figure 1 and a facile inversion at C_β occurs after ≃60% proton removal. At this point ($\theta = -52°$) displacement of F^- commences and when θ is +7° (100% C_β-H stretch) the C-F bond has been elongated by 28%.

These data provide gratifying support for the qualitative frontier MO picture given above. Very little C-F bond rupture was evident in **5** until the inversion process was in motion to effectively initiate π-bond formation. Elimination of ethyl fluoride is in excellent agreement with what one would anticipate for a relatively poor leaving group with a very strong base.[10] The calculated reactant-like position of the transition state along the reaction coordinate is in good accord with what one would expect for a highly exothermic reaction.

We next chose to examine an extreme E1cB elimination that utilized syn (**7**) and anti (**8**) ethyl fluoride anions:

$$^-CH_2CH_2F \rightarrow CH_2{=}CH_2 + F^- \quad (3)$$

Our initial efforts in the study of the elimination of F^- from the β carbanions **7** and **8** employed the STO-3G basis set. We found that both **7** and **8** were thermodynamically stable, gas-phase species and that **8** was more stable than **7** by 4.56 kcal/mol. Maintaining the symmetry plane passing through C_β, C_α, and F, we developed a minimum-energy pathway for F^- elimination from **7** and from **8** with C_α-F bond elongation as the assumed reaction coordinate. Three basic features of this elimination pathway are worthy of note. First, a plot of C_β inversion vs. C_α-F bond stretch is particularly revealing

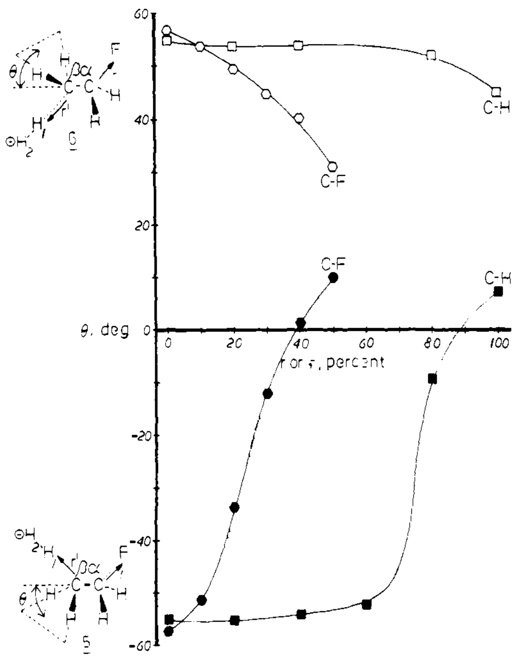


Figure 1. Plot of the angle of inversion, θ, vs. the percentage of C-F (hexagons) and C-H (squares) bond elongation, relative to their calculated bond lengths (4-31G basis set) in the ground state during syn (**5**) and anti (**6**) elimination.

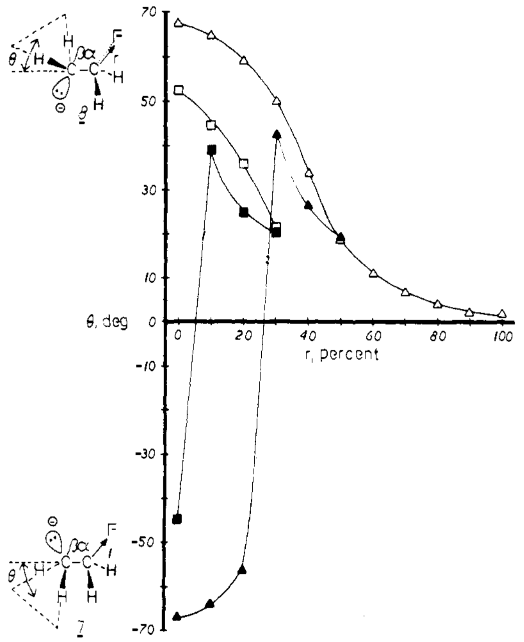
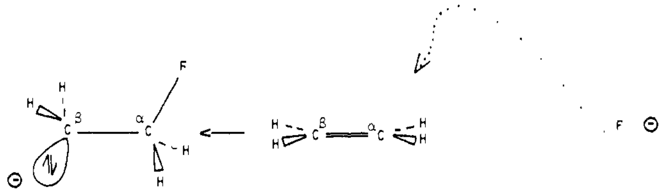


Figure 2. Plot of the angle of inversion, θ, vs. the percentage of C-F bond elongation relative to the calculated C-F bond distances in ethyl fluoride in **3** and **4** during syn (**7**) and anti (**8**) expulsion of F$^-$. Both STO-3G (triangles) and 4-31G (squares) basis sets were used.

(Figure 2). After 25% C_α-F bond elongation the syn anion has undergone almost total inversion of configuration and the *syn elimination pathway merges with and becomes indistinguishable from the anti mode of F$^-$ elimination from **8**.* Secondly, we observed that the pathway for loss of F$^-$ was reminiscent of the observation of Lehn[12] on the approach of H$^-$ to formaldehyde in this model study of nucleophilic addition to sp^2-hybridized carbon. The reverse of F$^-$ elimination from **8** would be that of nucleophilic addition of F$^-$ to ethylene. On the basis of microscopic reversibility we predict that at C_α-F distances larger than $\simeq$4 Å at the fluoride ion approaches the HC_αH bisector in the nodal plane of the π bond and the C_β-C_α-F angle is 180°. For C_α-F distances between 4 and 2.5 Å the C_β-C_α-F angle smoothly decreases from 180 to 115.5°. Finally, for C_α-F distances between 2.5 and 1.4 Å the C_β-C_α-F angle slowly increases to 118.7° affording the energetically favored anti anion **8** where the developing carbanion at C_β can be stabilized by mixing with the σ* C-F orbital at C_α. The third feature of the STO-3G pathway is that the plot of total energy vs. C_α-F bond elongation smoothly increases in energy from reactants to products with no apparent intervening transition state, the reaction enthalpies[9] being +128.58 and +133.14 kcal/mol for elimination from **7** and **8**, respectively (eq 3). Because of the problems typically associated with theoretical treatments of carbanions, we have also employed the extended 4-31G and 6-31G basis sets to examine the overall energetics of F$^-$ elimination from the β carbanions **7** and **8**.



Examining the elimination of F$^-$ from both **7** and **8** with the 4-31G basis set, we found the reactions (eq 3) to be exothermic with enthalpies[9] of −19.57 and −14.26 kcal/mol, respectively. The enthalpy difference reflects the higher (5.30 kcal/mol) ground-state energy of the syn carbanion. The energies of both carbanions were necessarily optimized (Table I) by holding the C-F bond distance fixed since exhaustive minimization led directly to elimination products (eq 3). Consistent with this observation, we found that the syn carbanion undergoes inversion at C_β to form the anti anion *without energy of activation.* This may be a reflection of the exothermicity of the loss of F$^-$ from these anions in their syn- and anti-periplanar conformations. It should be noted that the 90° conformer (C_β-C_α bond rotation), where the C-F bond and the filled lobe at C_β are orthogonal and a minimum rate of elimination is predicted,[14] is thermodynamically stable and the inversion barrier of that conformer is 7.0 kcal/mol.[13] A plot of C_β inversion vs. C-F bond stretch in both **7** and **8** employing the 4-31G basis set is given in Figure 2. Immediate exothermic inversion is noted and anti elimination ensues. The exothermicity of F$^-$ elimination is a consequence of the high electron affinity of the leaving group and both **7** and **8** are thermodynamically unstable if a reasonable pathway for elimination is available. These observations prompted us to briefly examine the effect of dihedral angle (H_1-C_β-C_α-F) on elimination reactions. The well-known "DePuy postulate"[14] states in effect that the rates of elimination will be maximized in either a syn (0°) or anti (180°) conformation with the latter being preferred (all other things being equal). We have examined the effect of dihedral angle on elimination of F$^-$ from carbanions **7** and **8** and find that the isoergic point ($\Delta E = 0$) for F$^-$ expulsion is attained at dihedral angles of ~20 and 144°, respectively. Thus, anti E1cB elimination from ethyl fluoride anion is predicted to be endothermic unless the deviation from anti periplanarity is less than 36°. The more restrictive requirements on the dihedral angle (<20°) for syn elimination are consistent with the principles of orbital overlap outlined above.

Using the 6-31G basis set, we obtained results which were essentially identical with those achieved with the 4-31G basis set. Employing the 6-31G basis set on the 4-31G-determined optimal geometries, we found that the elimination of F$^-$ from **7** and **8** was also exothermic with calculated enthalpies[9] of −21.16 and −16.03 kcal/mol, respectively. As noted above with the 4-31G basis set, full optimization (6-31G) of **7** and **8** resulted in the elimination products. Therefore, the results obtained from the 4-31G and the 6-31G basis sets lead to the same conclusion—both **7** and **8** are unstable, gas-phase carbanions. However, when the inversion angles, θ, at C_β in **7** and **8** were maintained at their approximately tetrahedral 4-31G values, the C_β–C_α and the C_α–F bond distances could be optimized (Table I). A rigid C_β inversion barrier of 7.60 kcal/mol (relative to **8**) was calculated when all other geometric parameters were maintained constant (4-31G).

Conclusion

Our theoretical considerations prompt us to generalize that *the rate of both syn and anti elimination will be increased by maximizing overlap of the developing carbanion at C_β with the backside of the C_α leaving group.* Thus, the mechanism for syn elimination is in effect an E1cB process where expulsion of the leaving group occurs concomitantly with inversion at C_β. In a syn E2 (or E1cB) elimination, rehybridization at C_β will occur until the best balance between orbital overlap at C_α and loss of counterion bonding between the developing carbanion and the departing hydrogen-base pair is attained. This suggestion is consistent with existing experimental data,[3] where E1cB-like transition states have been invoked for syn elimination, and provides a rational explanation for the failure to observe hydrogen-deuterium exchange in E1cB reactions. We also extend these concepts to include pyrolytic syn elimination (Cope) and α',β (ylide) elimination where intramolecular syn 1,2 elimination should also be enhanced by inversion of configuration at the carbanionic carbon.

Acknowledgment. Support of this work by the National Science Foundation (CHE 76 21992) is gratefully acknowledged. We also wish to thank Professor N. A. LeBel for helpful discussions on the interpretation of these results. R.D.B. would like to thank Professor Roald Hoffmann for his generous hospitality during his sabbatical leave at Cornell, where the manuscript was written.

References and Notes

(1) E. D. Hughes, *J. Am. Chem. Soc.*, **57**, 708 (1935).
(2) C. K. Ingold, *Proc. Chem. Soc., London*, 265 (1962).
(3) (a) W. H. Saunders, Jr., and A. F. Cockerill, "Mechanisms of Elimination Reactions", Wiley-Interscience, New York, 1973; (b) J. Sicher, *Angew. Chem., Int. Ed. Engl.*, **11**, 200 (1972); (c) N. A. LeBel, *Adv. Alicyclic Chem.*, **3**, 195 (1971); (d) J. F. Burnett, *Surv. Prog. Chem.*, **5**, 53 (1969).
(4) K. Fukui, *Tetrahedron Lett.*, 2427 (1965); K. Fukui and H. Fujimoto, *ibid.*, 4303 (1965); *Bull. Chem. Soc. Jpn.*, **40**, 2018 (1967); K. Fukui, H. Hao, and H. Fujimoto, *ibid.*, **42**, 348 (1969); H. Fujimoto, S. Yamabe, and K. Fujiu, *ibid.*, **44**, 971 (1971).
(5) (a) I. Tvaroska, V. Klimo, and L. Valko, *Tetrahedron* **30**, 3275 (1974); (b) P. C. Hiberty, *J. Am. Chem. Soc.*, **97**, 6975 (1975).
(6) (a) J. P. Lowe, *J. Am. Chem. Soc.*, **94**, 3718 (1972); (b) J. Sedlacek, *Collect. Czech. Chem. Commun.*, **42**, 2027 (1977); (c) K. Fukui and H. Fujimoto, "Mechanisms of Molecular Migrations", Vol. 2, B. S. Thyagarjan, Ed., Interscience, New York, 1969, p 117; R. G. Pearson, *Acc. Chem. Res.*, **4**, 152 (1971).
(7) Calculations employed the GAUSSIAN 70 series of programs[8] with standard STO-3G and 4-31G basis sets. The geometry of both conformers of ethyl fluoride was first optimized with an STO-3G basis set and then exhaustively minimized with a 4-31G basis set using 0.02 Å and 2° increments. The geometries of the ethyl fluoride carbanions were similarly optimized by STO-3G (0.01 Å and 1° increments) and then with a 4-31G basis set but excluding C–H bond distances. A similar procedure was used with the geometries of the hydride-induced elimination except that 0.1 Å and 5° increments were used.
(8) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969); J. W. Hehre, R. Ditchfield, and J. A. Pople, *ibid.*, **54**, 724 (1971).
(9) The 4-31G total energies of H^- and H_2 are −0.422 44 and −1.126 82 au, respectively. The STO-3G, 4-31G, and 6-31G total energies of F^- are −97.613 32, −99.247 83, and −99.350 18 au, respectively. The fully optimized STO-3G and 4-31G total energies of ethylene are −77.073 92 and −77.922 15 au, respectively, while the 6-31G energy of the 4-31G optimized ethylene molecule is −78.004 42 au. The 6-31G total energies of the 4-31G optimized syn (**7**) and anti (**8**) ethyl fluoride anions are −177.320 88 and −177.329 06 au, respectively.
(10) The hydride ion is a relatively strong base. Its proton affinity in the gas phase exceeds the affinity of F^- by more than 50 kcal/mol.[11]
(11) A. Dedieu and A. Veillard, *J. Am. Chem. Soc.*, **94**, 6730 (1972).
(12) H. B. Bürgi, J. M. Lehn, and G. Wipff, *J. Am. Chem. Soc.*, **96**, 1956 (1974).
(13) The 90° conformer has a minimum energy when the inversion angle θ was 62° (total energy −177.129 40 au). The planar carbanion (C_β) had a total energy of −177.118 32 au with all variables optimized including the C–F bond distance. The geometries used to calculate the rotational barrier were optimized in a similar fashion with the exception of the syn ($\theta = 0°$) and anti ($\theta = 180°$) conformers.
(14) C. H. DePuy, R. D. Thurn, and G. F. Morris, *J. Am. Chem. Soc.*, **84**, 1314 (1962).

The Unusual Structures, Energies, and Bonding of Lithium-Substituted Allenes, Propynes, and Cyclopropenes

Eluvathingal D. Jemmis,[1] Jayaraman Chandrasekhar, and Paul von Ragué Schleyer*

Contribution from the Institut für Organische Chemie der Universität Erlangen-Nürnberg, 8520 Erlangen, West Germany. *Received August 13, 1978*

Abstract: Propyne and allene undergo sequential hydrogen-lithium exchange experimentally to give C_3H_3Li (two isomers), $C_3H_2Li_2$, C_3HLi_3, and C_3Li_4. Mono- and dilithiated cyclopropenes are also known. The structures and bonding of hypothetical isolated monomers with these compositions, investigated by ab initio molecular orbital methods, reveal remarkable features. While acetylide bonding, e.g., in propynyllithium (**1**), is the most favorable energetically, bridging lithiums are preferred over conventional placements. Allenyllithium (**11**), the simplest bridged molecule of this type, has a bent carbon skeleton ($\angle$CCC = 157.6°, STO-3G optimization) which better accommodates simultaneous Li bonding to C-1 and C-3. Even though Li is closest to C-2, bonding to that atom is indicated by the overlap populations to be negligible. The vinyl hydrogen of cyclopropene, with its enhanced acidity, exhibits a larger energy of replacement than that of ethylene. The methylene hydrogen behaves in the opposite way owing to the antiaromatic character of 3-cyclopropenyllithium (**5**). Examination of a number of structural possibilities indicated the most favorable forms, e.g., **17** for $C_3H_2Li_2$, with an acetylide and a bridging lithium. Two bridging lithiums in CLiC planes roughly at right angles are found in the lowest energy structures of C_3HLi_3 (**23**) and of C_3Li_4 (**36**), which in addition have one and two acetylide-type C–Li bonds, respectively. The orthogonal π systems, each involved in bonding a bridging lithium, are responsible for this arrangement. Numerous other forms of these isomers were considered. With few exceptions, classical structures based on the corresponding hydrocarbons were much less stable than alternative arrangements in which the multicenter bonding capabilities of lithium could be better utilized. Another example is 1,2-dilithiocyclopropene, which prefers the doubly bridged (**4a**) over the classical (**4**) structure.

New theories of bonding evolve from a knowledge of structural characteristics of sets of related molecules. The development of the bonding principles governing boranes, by Lipscomb and others, has brought order to a field where every

0002-7863/79/1501-2848$01.00/0