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APPLICATION OF FORCE FIELD CALCULATIONS TO ORGANIC CHEMISTRY—V[1]

STERIC INTERPRETATION OF ELECTROPHILIC TRANSANNULAR ADDITION TO JUXTAPOSED DOUBLE BONDS

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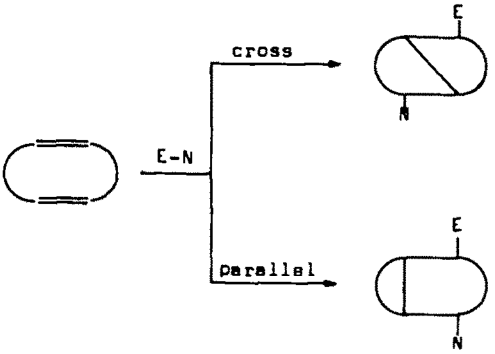
Abstract—The course of electrophilic addition to a molecule having two isolated double bonds in close proximity to give a transannular cross or parallel bridged product, depends on the thermodynamic stability of the products. If the difference in calculated steric energies between neutral hydrocarbon skeletons of the cross and parallel adducts exceeds 10 kcal/mol then the more stable product is formed exclusively, whereas if the energy difference is less than 10 kcal/mol both types of transannular products can be formed. Several examples apparently not conforming to this empirical rule are discussed.

Over the two decades since its inception by Westheimer in 1956,[2] the empirical force field (molecular mechanics) method has been developed to a stage where now not only static and dynamic conformational problems but also steric aspects of organic reactions are being handled with success, usually with an accuracy comparable to or higher than that of the best semi- and non-empirical quantum chemical calculations.[3]

For those reactions where the highest energy intermediates are defined with some confidence, such as acid-catalyzed ester hydrolysis[4] and esterifications,[5] nucleophilic addition to ketones,[6] chromic acid oxidation of alcohols,[7] and carbonium ion reactions,[8] the energy of the transition state can be readily estimated by molecular mechanics on the basis of the presumed structure.[3] However, this approach is not directly applicable to the majority of other reactions, where we have little knowledge of reaction intermediates. Nevertheless, if the highest barrier along the reaction coordinate is close enough to either the initial or final state, molecular mechanics can be advantageously used to estimate the steric contribution to activation energy. Thus, on the assumption of a product-like transition state, selective C–C bond cleavage in the catalytic hydrogenation of strained cage hydrocarbons,[9,10] and selective formation of two adamantene dimers[11] have been successfully interpreted by steric energy calculations. This paper describes further application of this latter approach to the interpretation of an intramolecular ring closure reaction.

Attack of an electrophile to a molecule having two isolated double bonds in spatial proximity usually leads to transannular bridge formation, for which two formal possibilities, cross and parallel, exist (eqn 1).



(1)

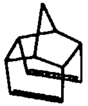
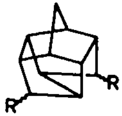
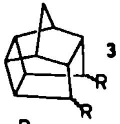
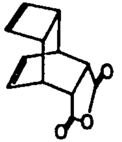
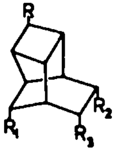
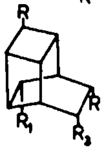
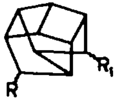
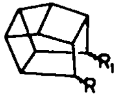
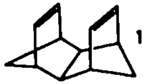
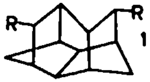
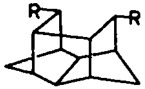
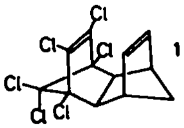
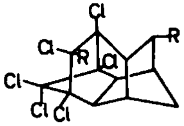
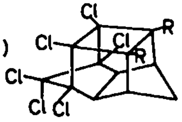
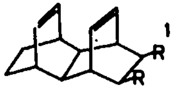
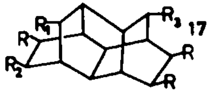
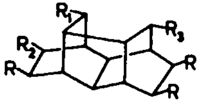
(E: electrophile, N: counter ion)

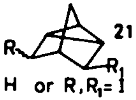
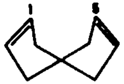
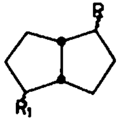
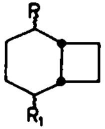
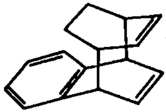
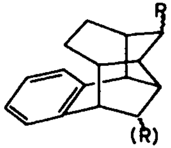
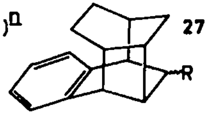
Experimental results on this type of reaction have been confusing. In some cases only the cross or the parallel bridged product is isolated, while in other cases both products are formed simultaneously (Table 1). Recently, Inagaki *et al.*[12] advanced a perturbation theory to interpret those cases where preferential cross bridging takes place. While the orbital mixing effect must certainly be working when cross bridging occurs, a general theory must explain why and to what extent parallel addition takes place in other systems. Shortcomings arising from a general ignorance of steric effects in previous molecular orbital treatments have recently been brought to attention.[13] We propose here that this reaction is likely to be under product development control and that accordingly comparison of steric energies among possible products should provide a uniformly reasonable interpretation.

Table 1 summarizes reported experimental results along with differences in calculated steric energies (SE) between the cross and parallel products. For technical reasons, calculations were performed on the hydrocarbon skeletons, using Engler (E)[14] and 1971 Allinger (A)[15] force field models. With both force fields, energy minimization was achieved by the pattern search method.[14] Computational results are tabulated in Table 2.

The first two examples (1, 4) in Table 1 represent cases where *only* cross bridged product (2, 5) is obtained and

Table 1. Electrophilic addition to molecules having juxtaposed double bonds. Calculated strain energy (SE) difference between cross and parallel adducts (kcal/mol)

Diene		Electrophile	Adduct (% yield)		Ref	SE(cross)-SE(parallel)[a]
			Cross-type	Parallel-type		
	1	Br_2	 2(100) R = Br	 3(0)	16	-10.24(E)[b,d] -10.61(A)[c,d]
	4	Br_2	 5(100) R = Br, R_1,R_2 = -O-CO-, R_3 = CO_2H	 6(0)	17	-12.68(E) -9.23(A)
	7	Br_2	 8(-)[e] R = Br, R_1 = +	 9(-)[e]	19	-12.02(E)[f] -12.78(A)[f]
	10	I_2	 11(42)[g] R = I	 12(10-20)[g]	20	-4.82(E) -3.89(A)
	13	Br_2	 14(21) R = Br	 15(22)	21	h
	16	Br_2	 17[i] R = CO_2CH_3, R_1,R_2 = -O-CO-, R_3 = Br	 18[i]	22	-1.43(E) -7.67(A)

 19	$Hg(OAc)_2$ I_2	 20(0)	 21(96) R=OH, R_1=H or R,R_1=I	23 24	27.1(Exp/E)[j] 31.1(Exp/E)[k]
 22	CH_3OCH_2OAc	 23(66)	 24(0) R=CH_2OCH_3, R_1=OAc	26	-15.3(Exp)[l] -18.22(E)[m] -17.21(A)[m]
 25	$Hg(OAc)_2$	 26(36)[n] R = OH	 27(12)[n]	38	-15.40(A)

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[a] Energy difference corresponding to that between hydrocarbon skeletons. See Table II for calculated enthalpies and strain energies of these skeletons. [b] Based on Engler force field, ref. 14. [c] Based on 1971 Allinger force field, ref. 15. [d] Taken from ref. 18. [e] 8 is an imaginary intermediate. See text. [f] Steric energy of 8 (1,3-bishomocubane) taken from ref. 25. [g] Crystalline 12 was isolated only in a 0.008 molar scale run while in a 0.13 molar scale run liquid product was isolated in about 60 % crude yield, from which, after deiodination,pure 11 (R=H) was isolated in 42 % yield. See ref. 21. [h] Same as above. See text. [i] The structure of product dibromide (yield not reported) has not been fully characterized. Ref. 22. [j] Based on revised strain energy of nortricyclane (42.8 kcal/mol) derived from revised enthalpy (19.8 kcal/mol; H. K. Hall, Jr., C. D. Smith and J. H. Baldt, J. Am. Chem. Soc., 95, 3197 (1973)) and Schleyer's increment scheme (P. v. R. Schleyer, J. E. Williams and K. R. Blanchard, J. Am. Chem. Soc., 92, 2377 (1970)). Strain energy of cross product (20) is based on Engler force field calculations, ref. 14. [k] Based on strain energy of nortricyclane (38.8 kcal/mol) by combustion analysis (H. K. Hall, Jr. et al., loc. cit.). [l] R. H. Boyd, S. N. Sanwal, S. Shary-Tehrany and D. McNally, J. Phys. Chem., 75, 1264 (1971). [m] Taken from ref. 14. [n] Yield based on isolated alcohol after treatment with $NaBH_4$.

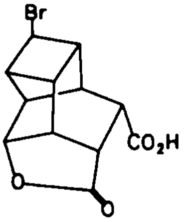
Table 2. Calculated enthalpies and strain energies for polycyclic molecules (kcal/mol)

Compound	ΔH_f^o E[a]	ΔH_f^o A[b]	Strain energy E[a]	Strain energy A[b]
Tetracyclo[4.2.2.$0^{2,5}$.$0^{3,7}$]decane (5, R,R_1,R_2,R_3=H)	20.87	23.74	54.35	57.43
Pentacyclo[5.4.1.$0^{2,9}$.$0^{3,6}$.$0^{4,8}$]dodecane (5a')	25.04	30.54	62.84	68.53
Pentacyclo[6.4.0.$0^{2,5}$.$0^{3,7}$.$0^{6,11}$]dodecane (5b')	21.75	23.21	59.55	61.21
Tetracyclo[4.4.0.$0^{2,5}$.$0^{3,8}$]decane (6, R,R_1,R_2,R_3=H, Dihydrobasketane)[c]	33.55	32.97	67.03	66.66
Pentacyclo[4.3.1.$0^{2,5}$.$0^{3,9}$.$0^{4,7}$]decane (9, R,R_1=H, Dihydropentaprismane)	60.35	65.02	87.89	92.64
Pentacyclo[7.3.0.$0^{2,6}$.$0^{3,11}$.$0^{4,8}$]dodecane (11, R=H)	8.72	11.50	46.72	49.30
Pentacyclo[7.2.1.$0^{2,6}$.$0^{3,10}$.$0^{4,8}$]dodecane (12, R=H)	13.54	15.39	51.34	53.39
Pentacyclo[9.4.0.$0^{2,7}$.$0^{3,12}$.$0^{4,9}$]tetradecane (17, R,R_1,R_2,R_3=H)	-8.94	-21.27	39.12	27.11
Pentacyclo[8.3.1.$0^{2,7}$.$0^{3,11}$.$0^{4,9}$]tetradecane (18, R,R_1,R_2,R_3=H)	-7.51	-13.60	40.55	34.78
Tricyclo[3.2.0.$0^{3,6}$]heptane (20, R=H)	45.92	54.13	69.95	78.32
cis,cis-1,5-Cyclooctadiene (22, twist boat)		24.82		11.68
5,6-Benzotetracyclo[6.3.1.$0^{2,7}$.$0^{4,11}$]dodecane (26, R=H)		26.36[d]		
5,6-Benzotetracyclo[6.4.0.$0^{2,7}$.$0^{4,11}$]dodecane (27, R=H)		41.76[d,e]		
Tetracyclo[6.3.1.$0^{2,7}$.$0^{4,11}$]dodecane (26a)	-10.80	-11.71	32.94	32.36
Tetracyclo[6.4.0.$0^{2,7}$.$0^{4,11}$]dodecane (28a)	5.75[e]	7.57[e]	49.49[e]	51.64[e]

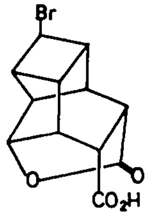
[a] Based on Engler force field, ref. 14. [b] Based on 1971-1972 Allinger force field, ref. 15. [c] N. A. Sasaki, R. Zunker and H. Musso, Chem. Ber., 106, 2996 (1973). [d] Steric energy in gas phase at 25°. For definition, see ref. 15a. [e] Eclipsed conformation. Twist form is so unstable that it is transformed into eclipse form in the course of energy minimization.

no parallel adduct observed.[17,18] In both examples, the hydrocarbon skeleton of the cross product (2, 5) is about 10 kcal/mol more stable than that of parallel product (3, 6).[18a] If this energy difference reflects that between the transition states leading to the two types of products, the exclusive formation of cross product can be readily rationalized. The cross bridge product 5 was first assigned a 5-membered lactone structure 5a based on IR C=O absorption at 1770 cm^{-1}.[17] However, the skeletal twist in 5 imposed by the cross transannular bridging would seem to render the 6-membered lactone 5b more easily formed and more stable than 5a. Calculations on hydrocarbon models revealed that 5b' is considerably more stable than 5a' (Table 2), and recent X-ray analysis of lactone 5 has actually confirmed the 6-membered lactone structure 5b.[19]

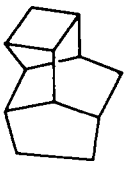
It was proposed that the cross bridged intermediate 8 intervenes in the bromination of hypostrophene (7).[20] The assumption of 8 rather than 9 seems quite reasonable seeing that the calculated energy difference between them is as large as those in the two examples mentioned above. Thus, up to this point the results of our analysis agree well with the orbital mixing theory.



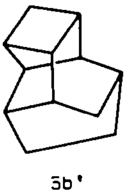
5a



5b

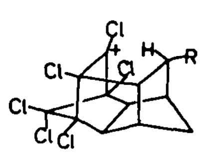


5a'



5b'

In contrast to the cleanly selective bridging in 1 and 4, tetracyclododecadiene 10 gives the parallel as well as the cross bridged product in apparent violation of the orbital mixing rule. In terms of the strain energy difference, however, this result is hardly surprising. The calculated steric energy difference between **11** and **12** is considerably smaller than those in the previous examples. If we assume here that these values are proportional to but overestimate the actual enthalpy difference between the product development states for cross and parallel transannular bond formation, we can still rationalize the concomitant formation of the parallel addition product **11** on steric grounds alone. The highly strained birdcage hydrocarbon derivative **15** must have been formed through **15a**, with which the strain energy of **14** should be compared. Thus, similar product distribution for the reactions from **10** and **13** is understandable.



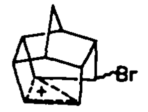
15a

The bromination product from **16** has not been thoroughly studied.[22] Prediction of the product structure, either **17** or **18** or both, is difficult due to large discrepancy in the SE(cross)–SE(parallel) values from the two force fields employed, but one would expect a mixture of **17** and **18** with the former probably predominating.

Norbornadiene (**19**) provides a case of dramatic dominance of steric energy; no cross bridged product (**20**) has ever been detected, the parallel bridged product with the nortricyclane skeleton (**21**) being formed exclusively.[23,24] This apparently abnormal behavior is compatible with the extemely high strain calculated for the cross product (**20**) compared to **21**. The significantly smaller distance (*ca.* 2.4 Å) between the two juxtaposed double bonds of norbornadiene compared with those (*ca.* 3 Å) in the other diolefins[25] cited in Table 1, and the consequent interaction between them even in the ground state, are expected to diminish the energy barrier leading to the parallel product **21**.

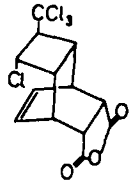
The overwhelming stability of the bicyclo[3.3.0]octane system relative to the bicyclo[4.2.0]octane system is well-known.[14a] The central point of the electrophilic addition to cyclooctadiene (**22**) is, therefore, not the exclusive formation of **23** over **24**,[26] but rather the reason why transannular cyclization occurrs on a flexible monocyclic substrate like **22**. It is only recently that the prevailing conformation of this diene in solution has been confirmed to be the twist-boat form (**22**, C_2 point group).[27–29] In this conformation, C1 and C5 are closer than in other potential conformers such as boat and chair.[28] According to X-ray analysis of *syn*-3,7-dibromo-**22**, the C1–C5 distance is 3.45 ± 0.03 Å.[30] The corresponding distance in **22** relaxed in the Allinger force field[15b] is 3.272 Å. Transannular cross bridging in **22** from this conformation appears to fit the least motion principle.[31]

We also checked the possibility of twisting conformations in the ground state of the other dienes discussed in Table 1. Twisting of **1**, for example, around the axis passing through the two norbornane-bridgehead C atoms would relieve the repulsion within the eclipsed ethano bridge and promote cross bridge formation.† However, according to molecular mechanics calculations by Allinger force field,[15] all the substrate dienes discussed above have, except for **22**, "eclipsed" double bond arrangement at their global energy minima.[25]‡ Thus, in the product development stage of the electrophilic addition reactions, which we consider here as the rate-determining stage, carbon nuclei must move from the initial "eclipsed" configuration to that close to the product, either cross or parallel. It is attractive to assume a long-lived "π complex" intermediate like **1a**, incorporating an aromatic 2π-electron system, in order to allow nuclear movements to occur, though it should be noted that in the perturbational treatment based on the orbital mixing rule[12] it is not necessary to take the movements of nuclei into account. However, the concomitant formation of parallel addition product can be best explained by the long-lived intermediate whose fate is determined by steric energy change accompanying the nuclear movements.



1a

The steric interpretation of the transannular bridging mode presented above should not in principle be limited to electrophilic additions but should be extendable to other reactions under product development control. We note here, however, three cases which show the danger there can be in overestimating steric effects.



4a

One is the addition of trichloromethyl radical to **4**, which gives only the adduct on the cyclobutene double bond (**4a**),[33] in accordance with the suggested necessity of a long-lived intermediate to effect bridge formation.[34]§

The second example of the limitation of our approach is the observation that the oxirane ring cannot induce cross bridge formation, but always gives parallel bridging. Two examples are reported (eqns 2 and 3). These reactions lead to thermally *less* stable parallel-bridged products. We suggest here a protonated oxirane intermediate like **13b**, in

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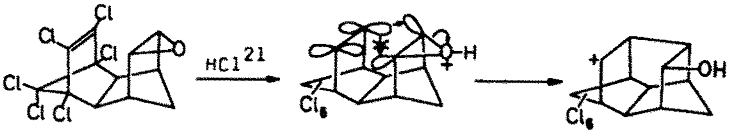
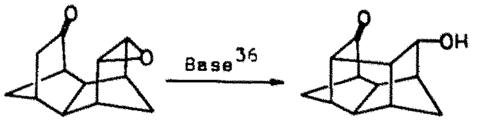
†Many substituted norbornanes do indeed have twisted structure, Ref. 32.

‡25 is missing in Ref. 25, which should have the lowest energy at the eclipsed conformation since there is as much as 20 kcal/mol calculated strain energy difference between the eclipsed and twisted forms of the non-benzo derivative (tricyclo[4.2.2.2^{2,5}]dodeca-3,7-diene) in favor of the former (unpublished results).

§Replacement of the acid anhydride group of 4 with more strongly electron withdrawing groups also suppresses the transannular reaction. Namely, the products of bromine addition are then exclusively *cis*-dibromides on the cyclobutane ring (Ref. 35). *These results* are clearly due to inductive effect and are not in conflict with the present interpretation.

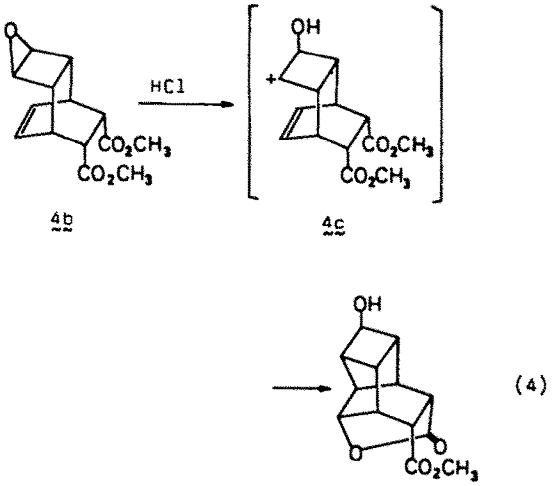


13a 13b (2)



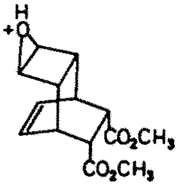
(3)

which the distance from the back lobe of the bent σ bond of the orixane ring to the diagonally juxtaposed p_z orbital of the double bond must be simply too large to allow formation of a cross bridge, unless such formation involved an extremely twisted intermediate. In contrast, however, HCl treatment of epoxy-4 (**4b**) gives only the cross-bridged product **4e** in quantitative yield (eqn 4),[37] which may appear to be in contradiction to the explanation given for eqns (2) and (3). As indicated by Sasaki,[37] it is reasonable to assume the ring-opened intermediate **4c**



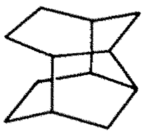
4b 4c (4)

rather than the protonated oxirane **4d** in view of the enormous strain expected in the protonated 5-oxabicyclo[2.1.0]pentane partial structure in the latter.

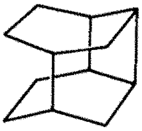


4d

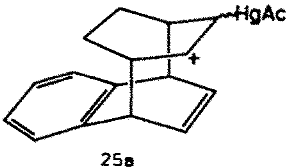
Finally, oxymercuration of 3,4 - benzotricyclo[4.2.2.$2^{2,5}$]dodeca - 3,7,9 - triene (**25**, Table 1)[38] presents the most serious obstacle against our steric analysis. Force field calculations on hydrocarbon skeletons indicate that the cross-bridged product (**26**, R=H) is 15 kcal/mol more stable than the parallel bridged product (**27**, R=H). This energy difference arises from the saturated portions of these molecules, as seen in the



26a



27a



25a

comparison between parent systems **26a** and **27a** (Table 2). Thus, one would have expected exclusive formation of **26**. However, one fourth of the product mixture was parallel-bridged **27** (R=HgX) while three fourths were cross-bridged **26** (R=HgX). The reason for the formation of **27** must be sought not in steric but in electronic effects, possibly including homoconjugation of the C=C bond of the likely intermediate **25a** with the aromatic ring.

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