Structure and Reactivity in Medium-ring Olefins

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IT is now well established that *trans* double bonds in medium-ring olefins are much more reactive than their acyclic counterparts,[1] and this has been ascribed to steric strain. For lack of accurate structural data, it has hitherto been difficult to define what types of strain occur and to estimate their relative importance. Recent *X*-ray studies have provided such data for the cycloundecatriene, humulene[2] (I), and the cyclodecatriene, germacratriene[3] (II), as their silver nitrate adducts. Before using these structures for arguments concerning reactivity it is necessary to consider two questions.

(1) Are the ring conformations found in the solid silver nitrate adducts similar to those adopted in solution before reaction?

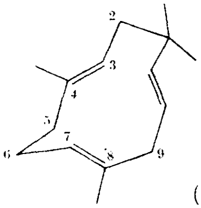
(2) Does the complexing of a double bond with a silver ion induce changes in hybridization with consequent changes of bond lengths and angles?

There is an obvious general similarity between the stereochemistries and conformations of the cyclisation products, (III) [4] and (IV) [5] (obtained by reaction with aqueous *N*-bromosuccinimide), and the conformations (I) and (II) of the olefin rings found in the silver nitrate adducts. As evidence for the second point we can cite two cases. *X*-Ray work has shown that *cis,cis,cis*-1,4,7-cyclononatriene has, within experimental error, the same structure both in the free state[6] and in its silver nitrate adduct.[7] The same is true of *trans,trans,trans*-1,5,9-cyclododecatriene[8] and its nickel complex. Though meagre we accept this evidence as indicating that the parameters found for the trienes (I) and (II) in their silver nitrate adducts faithfully reflect their structures before reaction in solution.

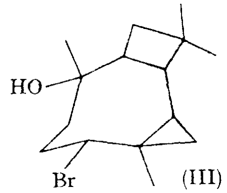
In an elegant analysis of the reaction of various olefins with di-imide, Garbisch *et al.*,[10] have had remarkable success in predicting their relative rates of reaction by resolving the steric strain about the reactive bond into (*inter alia*) bond-angle and torsional (sp^3–sp^2) contributions, and comparing these in the starting materials and products. Following this approach we have estimated the difference in strain energy between the 3,4 and 7,8 bonds of humulene (I) and between the 4,5 and 8,9 bonds of germacratriene (II) and have compared them with the corresponding observed reactivities. Germacratriene (II) is the simpler to compute as the sp^3–sp^2 torsional angles match so closely for each double bond, *viz*:

3,4	86°	5,6	64°
7,8	87°	9,10	61°

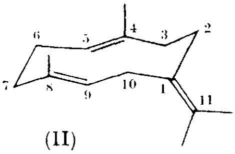
Other factors, such as non-bonded interactions between reagent and substrate, entropies of activation, bond-angle strain and nucleophilicities should also match closely for both double bonds. Another source of strain energy arises from a twisting about the axis of the double bond such that the planes of the pairs of substituents at each end are no longer parallel—a distortion only likely to be significant in endocyclic *trans* double bonds. This type of sp^2–sp^2 torsional strain was thought by Garbisch to make a negligible contribution in the cases he considered: an example is illustrated in the Newman projection (V) along the 4,5 bond of germacratriene. For this bond $\omega = 16°$ (whence $E_s = 2{\cdot}0$ kcal.†), whereas for the 8,9 bond $\omega = 20°$ ($E_s = 3{\cdot}2$ kcal.), a difference of *ca.* 1·2 kcal. and this seems to be the only substantial difference in strain energies between the two double bonds. Any reaction in which this particular strain can be relieved in the transition state would, therefore,



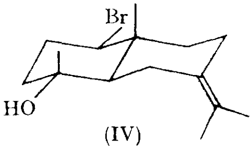
(I)



(III)



(II)



(IV)

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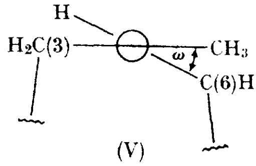
† sp^2–sp^2 torsional strain energy is estimated using the function $E_s = 8\omega^2$ cal./mole derived for ethylene (F. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules", D. Van Nostrand Co. Inc., New York, 1945, p. 183).

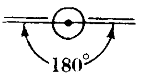
lead to a higher reaction rate for the 8,9 double bond.



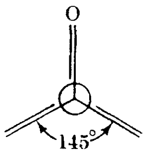
(V)

Epoxidation should be a suitable reaction for detecting such a difference since π–π transannular interactions between the double bonds would be expected to be unimportant in the transition state, and it involves a minimal geometric change, *cf.*, diagrams (VI) and (VII) (projections along the C–C bond before and after epoxidation) in which the projected angles contract from 180° to 145°. In the event reaction of (II) with buffered peracetic acid (1 mole) gave the 8,9- and 4,5-monoxides in a ratio of 65 : 35, implying (see Garbisch, eq. 1) a difference of *ca.* 0·4 kcal. between the respective activation energies, *i.e.*, 1/3 of the sp^2–sp^2 torsional strain difference is relieved in reaching the transition state. The high reactivity of the strained trisubstituted double bonds is clear from the isolation of only a trace of the tetrasubstituted 1,11-oxide, (ω = 1° in the silver nitrate adduct).

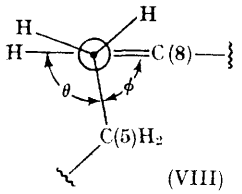
Reaction of humulene with peracid (1 mole) gave > 95% of the 7,8-monoxide,[11] corresponding to $\Delta\Delta F^* > 1\cdot7$ kcal. The sp^2–sp^2 torsional strains are $\omega_{3,4} = 8°$, $E_s = 0\cdot5$ kcal., and $\omega_{7,8} = 18°$, $E_s = 2\cdot6$ kcal., giving a difference $\Delta E = 2\cdot1$ kcal., which, if 1/3 is again relieved in the transition state, is too small to account for the difference in reactivity. In this ring, however, the sp^3–sp^2 torsion angles for the two bonds differ considerably, and taking our previous model for epoxidation it can be seen from the Newman projections along the 6,7-bond [(VIII) and (IX)] that the torsion angle (θ) is effectively reduced by *ca.* 35°.‡ Reference to the figures in the Table shows that in this case epoxidation *decreases* this type of strain by ~1·1 kcal. for bond 7,8, but *increases* it by ~1·8 kcal. for bond 4,5.



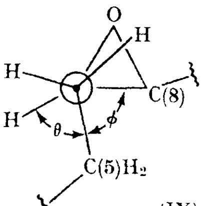
(VI)



(VII)



(VIII)



(IX)

TABLE

sp^3–sp^2 Torsional strain energies in humulene and its monoxides§

	Humulene		Monoxides	
Bond	$\theta°$	E_s (kcal./mole)	$\theta°$	E_s (kcal./mole)
2,3	54	0·02	19	1·10
4,5	71	0·16	36	0·90
6,7	103	0·65	68	0·10
8,9	85	0·74	50	0·20

(θ is defined in projections (VIII) and (IX): values for humulene are calculated from *X*-ray results,[2] and for the monoxides are estimated from models).

§ sp^3–sp^2 torsional potential functions have the general form, $E_s = K\ (1 + \cos 3\theta)$ if the three substituents on the sp^3 atom are identical. Though this is not true for the cases considered here, the function probably yields reasonable estimates in view of the limited ranges of θ achievable. K is the half height of the potential barrier. Values of $2K$ (kcal./mole) for relevant compounds are: propene[12] (2·0), isobutene[13] (2·2), *cis*-butene[14] (0·8), propene oxide[15] (2·6),2,3-*cis*-butylene oxide[16] (1·6). As it is well established that the rotational barrier is considerably lower for *cis*-1,2-disubstituted olefins than for the corresponding *trans*-compounds,[14] extrapolation to trisubstituted olefins would suggest the use of two different values of K, *viz*, 1·0 when the alkyl group is *cis* to H and 0·4 when *cis* to another alkyl group; the appropriate values for epoxides would be 1·3 and 0·8 respectively.

The combination of sp^3–sp^2 and sp^2–sp^2 torsional strains gives a difference of ~5·0 kcal., which, if 1/3 is relieved in the transition state, would account for the observed disparity of rates.

We regard these estimates of energy differences as, at best, semi-quantitative, but believe that they

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‡ This picture of epoxidation involving only a twisting about the double bond with little change in remainder of the molecule is reasonable, at least in the early stages of reaction, since C–C–C bond angles are similar in olefins and epoxides and there are only slight changes in C–C bond lengths. The twisting already present in the double bonds in the cases above make this simple picture even more probable. This description implies that ϕ is the same in (VIII) and (IX); however, this does not mean that ϕ is the angle to be used for the estimation of torsional strain in (IX) as it would describe the dihedral angle only if the C–C bond of the oxide were a straight line between the two carbon atoms rather than the 'bent bond' generally accepted for three-membered ring compounds. Thus θ, the only angle to change, is a better estimate for the torsion angles.

illustrate the importance of the contribution made by sp^2–sp^2 torsional strain to the high reactivity of medium-ring *trans*-olefins and that in certain circumstances, *e.g.*, germacratriene, this may be much larger than the familiar sp^3–sp^2 torsional strains.

(*Received, September 8th,* 1967; *Com.* 962.)

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