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DETERMINATION OF REGIOSELECTIVITY OF CYCLOADDITION REACTIONS FROM ELECTRONEGATIVITY OF THE ACTIVE CENTRES

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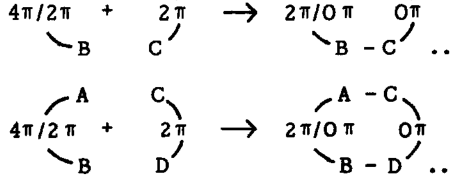
Abstract : An equation has been derived in terms of inherent electronegativity of the active centres, which can be utilised to determine the regioselectivity of the cycloaddition reactions.

Introduction : Regioselectivity of cycloaddition reactions[1] was determined previously by the methods[2] which were applicable to M.Os and inapplicable to GVB orbitals[3]. But pericyclic reactions can be explained both in terms of M.Os.[1] and GVB orbitals[4]. So, the purpose of this communication is to report a novel technique to determine the regioselectivity of the cycloaddition reactions, which is independent of the type of the orbitals used to explain the reactions.

Derivation of an Eqn. : The relationship between electronegativity and energy is well known[5]. Paar has shown the equivalence of Sanderson's electronegativity and chemical potential (dE/dN)[6]. Both Sanderson[7] and Parr[8] have drawn attention to the electronegativity equalisation as a possible guiding principle in chemical reactions. With these ideas in mind, an equation has been derived here in terms of electronegativity of the active centres in order to determine the regioselectivity of the nonpolar cycloaddition reactions. Let the active centres of the cycloaddition reactions shown in Fig.1 are all carbon atoms and χ_A, χ_B, χ_C and χ_D are the inherent electronegativities of the active centres A , B , C and D respectively. Since the active centres are all uncharged species, all the electrostatic energy terms may be neglected for simplicity and so covalent energy term has only been considered for the energy change associated with the covalent bond formation between the two active centres. Since covalent energy term is proportional inversely to the difference in size and in energy



....(i)

....(ii)

Fig. 1. Cycloaddition reactions

of the participating orbitals and since inherent electronegativity is such a parameter which is related to both the energy and size of the orbital, so it can be said that the covalent energy term is proportional inversely to the inherent electronegativity difference between the participating active centres. Now, since in a concerted cycloaddition reaction covalent bond formation occurs at both the ends of cycloaddition reactants simultaneously, so the energy change associated with the formation of bonds A − D and B − C in the cycloaddition reaction (i) in Fig. 1, $E_1 = K_1 / (\chi_A - \chi_D)(\chi_B - \chi_C)$, K_1 being the proportionality constant. Similarly, the energy change associated with the formation of bonds A − C and B − D in the cycloaddition reaction (ii) in Fig. 1, $E_2 = K_2 / (\chi_A - \chi_C)(\chi_B - \chi_D)$, K_2 being the proportionality constant. So,

$$\Delta E = E_1 - E_2 = K_1 / (\chi_A - \chi_D)(\chi_B - \chi_C) - K_2 / (\chi_A - \chi_C)(\chi_B - \chi_D) \ldots\ldots(i)$$

When the active centres are all carbon atoms with the same order of hybridisation, then $K_1 = K_2 = K$ (say) and then eqn. (i) becomes, $\Delta E = E_1 - E_2$

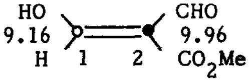
$$= K.(\chi_A - \chi_B)(\chi_C - \chi_D) / (\chi_A - \chi_D)(\chi_B - \chi_C)(\chi_A - \chi_C)(\chi_B - \chi_D) \quad \ldots\ldots\ldots(ii)$$

Section I :

Salient features of Eqn. (ii) : (a) Reaction (i) will be more favoured over reaction (ii) when $\Delta E = -$ ve. For opposite situation $\Delta E = +$ ve. (b) If $\chi_A = \chi_B$ or / and $\chi_C = \chi_D$, then $\Delta E = 0$ i.e. regioselectivity does not arise. Regioselectivity arises only when $\chi_A \neq \chi_B$ and $\chi_C \neq \chi_D$. (c) When $\chi_A \neq \chi_B \neq \chi_C \neq \chi_D$, then two cases may arise : (i) $\chi_A > \chi_B$ and $\chi_D > \chi_C$ or $\chi_A < \chi_B$ and $\chi_D < \chi_C$: Here, the numerator in eqn. (ii) is always − ve. So, high − high / low − low electronegative attachment of the active centres (which corresponds to E_1) will be more favoured over high − low electronegative attachment (which corresponds to E_2) provided the denominator is + ve. But in case the denominator is − ve then the reverse order of combination is more favoured. (ii) $\chi_A > \chi_B$ and $\chi_D < \chi_C$ or vice-versa : In this case, the numerator of eqn. (ii) is always + ve. So, here high − low electronegative attachment of the active centres (which now corresponds to E_1) will be more favoured over high − high / low − low electronegative attachment (which now corresponds to E_2) provided the denominator is − ve. But in case the denominator be + ve then the reverse order of combination will be more favoured. (d) If at least one factor of the denominator in eqn. (ii) be zero then the energy change (ΔE) will be maximum i.e. regioselectivity is expected to be maximum. Here, the favoured combination will be one in which active centres having identical inherent electronegativity are joined together — a process associated with maximum energy change. (e) Eqn. (ii) can explain why Lewis acid catalysed cycloaddition reaction is more regioselective than the uncatalysed reaction[9]. When a Lewis acid is used as a catalyst in a cycloaddition reaction, the electronegativity of the active centre directly joined to the substituent participating in the complex formation with the Lewis acid, will increase (say, χ_D increases). Then the value of the fraction $(\chi_C - \chi_D)/(\chi_A - \chi_D)(\chi_B - \chi_D)$ will increase[10] in eqn. (ii). Other fraction of the right hand side of eqn.(ii) will remain unchanged. Obviously, Δ E if negative for uncatalysed reaction will be more negative for the Lewis acid catalyed reaction i.e. regioselectivity of the reaction will increase.

Section II :

Application of Eqn. (ii) : The inherent electronegativity of an active centre in a cycloaddition reactant can be calculated by Huheey's method[11] from the a and b values of the substituents joined to the active centre viz. the inherent electronegativity of the C_1 - active centre in the compound 1 can be calculated from the a and b values of the substituents H (a = 7.17, b = 12.85) and OH (a = 10.80, b = 8.86) and is found to be 9.16 (Fig. 2). Similarly, the inherent electronegativity of the other active centre (C_2) can be calculated from the a and b values of CHO and CO_2Me. In case the substituent be a ring residue then for calculating the inherent electronegativity of the active centre, the a and b values of the ring residue directly joined to the active centre are considered, which in turn can be determined from the a and b values of its substituents. After determining, as stated above, the inherent electronegativities of the active centres in each reactant the regioselectivity of a cycloaddition reaction can be predicted by use of eqn. (ii) (see Section I). As for example, when the inherent electronegativities of the active centres of the cycloaddition reactants mentioned in Table 1 are inserted in eqn. (ii) then the sign of Δ E can be determined from which regioselectivity can be easily predicted. In this case, high - high/low - low mode of combination has been assumed to be associated with the energy change E_1 and high - low mode of combination has been assumed to be associated with the energy change E_2. So, here negative value of Δ E means high - high/low - low electronegative attachment of the active centres and positive value of Δ E means high-low electronegative attachment of the active centres. Although a few examples have only been furnished in Table 1 the prediction of regioselectivity by use of eqn. (ii) has been found to be in agreement with the experimental observation for many other thermal and photochemical cycloaddition reactions[18].

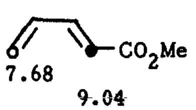
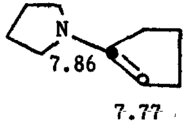
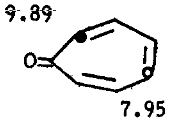
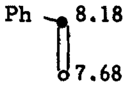
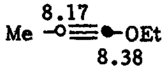
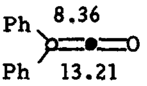
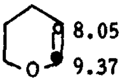
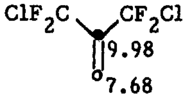
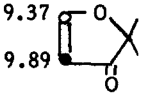
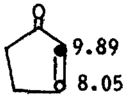
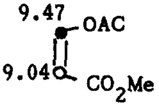
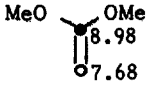
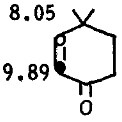


1

Fig. 2

Polar Effect : If at least one of the active centres in each cycloaddition reactant is similarly substituted then the inherent electronegativity of such similarly substituted active centres will be indentical ; then according to Section I (d) above, the preferred mode of combination will be one that involve joining of the active centres having identical inherent electronegativity. In such cases, mere determination of the relative order of electronegativity of the active centres in each cycloaddition reactant is

Table - 1

Cycloaddition reaction type	Reactants with inherent electronegativities of their active centres		Sign of ΔE	Predicted regio-selectivity	Observed regio-selectivity	Ref.
	A	B				
(4 + 2) Thermal			- ve	h-h/1-1 (high-high/ low-low)	h-h/1-1	12
			+ ve	h-1 (high-low)	h-1	13
(2 + 2) Thermal			+ ve	h-1	h-1	14
			+ ve	h-1	h-1	
(2 + 2) Photo			- ve	h - h/1 -1	h-h/1-1	15
			- ve	h - h/1-1	h-h/1-1	16
			+ ve	h-1	h-1	17

sufficient to determine the mode of combination (i.e. high - high/low - low or high - low mode of attachment) of the active centres. And the relative order of electronegativity of the active centres in each cycloaddition reactant can then be determined qualitatively from the polar effect of the substituents present with the active centres and for this purpose we need not require to calculate the inherent electronegativity of the active centres by Huheey's method. Now, the substituents (other than hydrogen) commonly in use in organic chemistry can be categorised into four types (I-IV) on the basis of the nature of polar effect exerted by them (see below). For all these

W=CO_2Me, COMe, CHO, etc.

D=OMe, Cl, Br, etc.

J=Ph, CH=CH_2, etc.

M=CH_3, CH_2

(a) (b) (c) (d)

Fig. 3

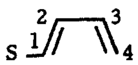
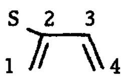
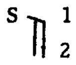
four types of substituents, the relative order of electronegativity of the active centres in a cycloaddition reactant such as 1 - substituted ethylene can be determined from the polar effect of the substituents as follows :

(i) For type I substituent(W): -I and - R effects are present: In this case electronegativity of both the ethylenic carbon active centres will increase but the increase will be much higher at the carbon directly joined to the substituent than the remote carbon as -I effect of the substituent decreases with the increase of the distance (Fig. 3a).

(ii) For type II substituent (D) : - I and + R effects are present :
Here, the electronegativity of the ethylenic carbon directly joined to the substituent will increase but that of the remote carbon will decrease. This is obvious because - I effect is much stronger than + R effect and decreases with the increase of the distance (Fig. 3b).

(iii) For type III substituent (J) : Conjugative effect is present :
In this case, the conjugative effect of the substituent will try to decrease the

Table - 2

Compound*	Type of substituent	Relative order of electronegativity of the active centres
	I - IV	$X_1 > X_4$
	I	$X_1 > X_4$
	II - IV	$X_1 < X_4$
	I - IV	$X_1 > X_2$

* S = Substituent

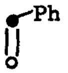
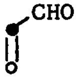
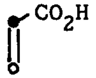
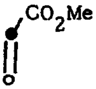
electronegativity of both the ethylenic carbons whereas − I effect of the Sp^2 carbon of the substituent will try to increase the electronegativity of both the ethylenic carbons and the latter effect will be appreciable at the carbon directly joined to the substituent and negligible at the romote carbon. Hence, the electronegativity of the ethylenic carbon directly joined to the substituent will be more than that of the remote carbon (Fig. 3c).

(iv) For type IV substituent (M) : Hyperconjugative effect is present :

If the substituent be CH_3 or CH_2 group, then the situation becomes unique. Although the inherent electronegativity of CH_3 / CH_2 group is slightly greater than that of hydrogen, the former has a higher electron donating power than the latter because of its greater charge capacity[11b]. Such a substituent (CH_3 or CH_2) when attached to ethylenic carbon will exert hyperconjugative effect. The result is that the electronegativity of both the adjacent and remote carbon will decrease but the decrease will be less on the adjacent carbon and more on the remote carbon because the adjacent carbon will experience an additional electron pull (by induction) toward the Sp^3 hybridised carbon of methyl or methylene group. So the electronegativity of the ethylenic carbon bearing the CH_3/CH_2 group will be higher than that of the unsubstituted ethylenic carbon (Fig. 3d).

Similarly, the relative order of electronegativity of the active centres in 1 - substituted and 2-substituted dienes can be determined from the polar effect of the substituent. All these have been summarised in Table 2. Following the Table 2, the relative order of electronegativity of the active centres in the cycloaddition reactants A & B (Table 3) and in the compounds 2 - 5 (Fig.4) have been determined as depicted in the diagrams[23]. Since according to Section I (d) above,

Table - 3

Sl. no.	Reactant A (4π)	Reactant B (2π)	Ref.
1	 S=Ph,CO_2H,Me		19
2	 S = Ph, OMe		20
3	 S = CO_2H, Me		21
4		 S=CH=CH_2, CO_2Me	22, 19b
5			20b

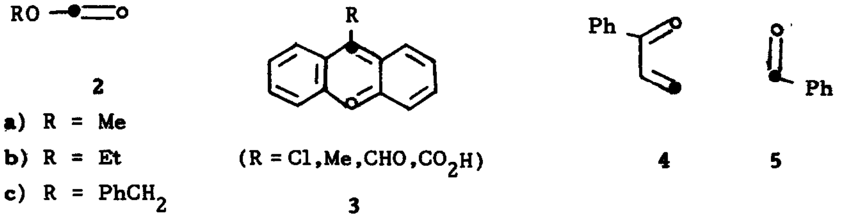
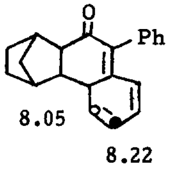
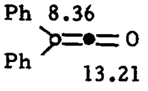
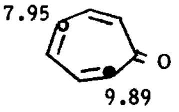
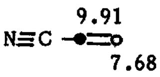


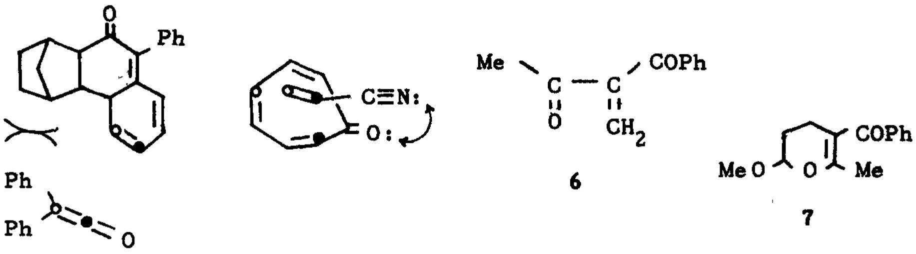
Fig.4

the favoured combination will involve attachment of the active centres having identical electronegativity, so dimerization^{24} of the compounds 2 and 3 and cycloaddition reaction^{25} involving 4 and 5 will go through high-high/low-low electronegative attachment of the active centres. Similarly, the cycloaddition reactions involving the substrates A and B of Table 3 can be predicted to occur by high-high/low-low electronegative attachment of the active centres because the inherent electronegativity of the methylene carbon active centre in each substrate (A or B) can be expected to be identical. All these predictions are in accord with the experimental observations.

Disagreement : The disagreement between the predicted regioselectivity and observed regioselectivity may arise mainly due to (i) steric interaction and (ii) lonepair-lonepair or dipole-dipole interaction^{26}. As for example, the thermal (2+2) cycloaddition reac-

Table - 4

Cycloaddition reaction type	Reactants with inherent electronegativities of their active centres		Sign of ΔE	Predicted regioselectivity	Observed regioselectivity	Ref.
	A	B				
(2 + 2) Thermal			-ve	h-h/l-l	h-l	27
(4 + 2) Thermal			-ve	h-h/l-l	h-l	13



(a) (b) (c) (d)

Fig.5

tion between the substrates A and B (Table 4) favours high - low electronegative attachment of the active centres[27] rather than high-high/low-low electronegative attachment although eqn.(ii) predicts the latter. The steric interaction in the high-high/low-low approach is probably responsible for the disagreement (Fig.5a). Another case of disagreement was observed in the thermal (4+2) cycloaddition reaction[13] between 1 - cyanoethylene and cycloheptenone (Table 4). Although eqn.(ii) predicts high-high/low-low electronegative attachment of the active centres, yet the reaction goes through high-low electronegative joining of the active centres because in the former approach serious lone pair - lone pair interaction[28a] is present (shown by double headed arrow in Fig.5b). In the case of intramolecular cycloaddition reaction ring strain[28b,c] or transannular interaction[29] may be present which may sometimes become too important to jeopardise the prediction by eqn.(ii).

Discussion : Although cycloaddition reactions with heterodienes and heterodienophiles have not been considered here yet there is no reason why eqn.(ii) will not be applicable for such thermal reactions if electrostatic energy term does not play any important role. As a typical example of such thermal reactions, the compound **2a** is found to react[30] with compound **6** in benzene at r.t. to produce compound **7** (96%) (Fig.5) by high-high/low--low electronegative attachment of the active centres which is in accord with the prediction by Section I(d). But photocycloaddition reactions involving heterodienes and heterodienophiles are complicated because of the possibility of excitation by nonbonding electrons.

In our electronegativity method, the inherent electronegativities of the active centres in the excited state of a molecule have been assumed to be identical with those in the ground state and regioselectivity has been determined accordingly. Although this is merely an approximation and may not necessarily hold good for all photoexcited molecules yet our method has been found to be suitable in predicting the regioselectivity of many photocycloaddition reactions on the basis of this approximation. The most advantage of the electronegativity method is its wider applicability because the method is independent of the type of the orbitals used to explain the cycloaddition reactions. So a practical organic chemist will find this method very useful as it does not involve advanced chemical calculation. Of course, sometimes solvent effect[31] or homoconjugation[32] plays an important role on the regioselectivity of the cycloaddition reaction for which due consideration should then be made.

References and notes :

1 (a). Hoffmann, R.; Woodward, R.B. *The Conservation of Orbital Symmetry,* Verlag-Chemie. Academic Press. **1970.**

(b). Gleiter, R.G.; Bohm. M.C. *Pure & Appl. Chem.* **1983,** 55,237.

2 (a). Houk. K.N. *J.Am. Chem. Soc.* **1973,** 95, 4092.

(b). Epiotis. N.D. *J.Am. Chem. Soc.* **1973,** 95, 5624.

3. Goddard. W.A.; Ladner. R.C. *J.Chem. Phys.* **1969,** 51, 1073.

4. Goddard. W.A. *J.Am. Chem. Soc.* **1972,** 94, 793; Pal. S.K. *Ind. J.Chem.* **1987,**26B(4) 312-317.

5. Klopman, G. *Chemical Reactivity and Reaction Paths* Klopman. G. Ed. Wiley New York. **1974,** 66.

6. Thomson. C.(Sr.Reporter). *Theoretical Chemistry* The Royal Society of Chemistry. London. **1981,** Vol 4.

7. Sanderson. R.T. *Chemical Bonds and Bond Energy* 2nd Edn. Academic Press. New York. **1976.**

8. Paar. R.G.; Donnelly. R.A.; Levy. M.; Palke. W.E. *J.Chem. Phys.* **1972,** 68, 3801.

9. Fleming. I. *Frontier Orbitals and Organic Reactions* John Wiley & Sons. **1976;** Bridges. A.J.; Fisher. J.W. *Tetrahedron Letters* **1983,** 24(5), 447-450.

10. Let χ_{D*} represents the inherent electronegativity of the active centre D in the catalysed reaction, so the said fraction will then be converted into

$(\chi_C - \chi_{D*}) / (\chi_A - \chi_{D*})\ (\chi_B - \chi_{D*})$

In the uncatalysed reaction, let ΔE is - ve and $\chi_A > \chi_B$ & $\chi_D > \chi_C$.

As χ_D increases to χ_{D*}, then $\chi_C - \chi_{D*} > \chi_C - \chi_D$ i.e. the numerator of the said fraction will increase. Now let us consider two cases :

(i) when $\chi_A > \chi_D$ and $\chi_B > \chi_D$ in the uncatalysed reaction :

Here, as χ_D increases to χ_{D*} then $\chi_A - \chi_{D*} < \chi_A - \chi_D$ and $\chi_B - \chi_{D*} < \chi_B - \chi_D$

So, $(\chi_A - \chi_{D*})(\chi_B - \chi_{D*}) < (\chi_A - \chi_D)(\chi_B - \chi_D)$.

Since the numerator increases but denominator decreases, so the value of the said fraction will increase.

(ii) when $\chi_A > \chi_D$ and $\chi_B < \chi_D$ in the uncatalysed reaction :

Suppose, $\chi_A - \chi_D = |a|$ and $\chi_B - \chi_D = |b|$

Here, as χ_D increases to χ_{D*} in the catalysed reaction, then

$\chi_A - \chi_{D*} < \chi_A - \chi_D$ and $\chi_B - \chi_{D*} > \chi_B - \chi_D$

Now, suppose, $\chi_{D*} = \chi_D + x$ where x is a + ve quantity.

So, $\chi_A - \chi_{D*} = |a| - x$ and $\chi_B - \chi_{D*} = |b| + x$

then, $(\chi_A - \chi_{D*})(\chi_B - \chi_{D*}) = (|a| - x)(|b| + x)$

$$= |a|\,|b| - x\,(|b| - |a|) - x^2$$

Now, when $|b| - |a|$ is equal to zero or greater than zero then in both the cases right hand side is less than $|a|\,|b|$ i.e.

$(\chi_A - \chi_{D*})(\chi_B - \chi_{D*}) < |a|\,|b| < (\chi_A - \chi_D)(\chi_B - \chi_D)$

Here also, the numerator increases but denominator decreases, so the value of the said fraction will increase.

11 (a). Huheey. J.E. *J. Phys. Chem.* **1965**, 69, 3284; *ibid.* **1966**, 70,2086; Huheey. J.E. *J. Org. Chem.* **1966**, 31, 2365.

(b). Huheey. J.E. *Inorganic Chemistry - principles of structure and reactivity* 3rd Edn. Harper International. **1983**.

(c). 100% equalisation of electronegativity was considered in calculating the electronegativity of unknown substituent/active centre by Huheey's method.

12. Cunnigham. R.: Damishefsky. W. *J. Org. Chem.* **1965**, 30, 3676; Barchtold. C.A.; Ciabattoni. J.; Tunick. A.A. *ibid*, 3679.

13. Kitahara. Y.; Uyehara. T. *Chem and Ind.* **1971**, 354; Shoji. Y.; Takeshita. H.; Ito.S. *Tetrahedron Letters* **1969**, 1815.

14. Kimbrough. R.D.; Hurd. C.D. *J.Am. Chem. Soc.* **1960**, 82, 1373; Arens. J.F.*Angew. Chem.* **1958**, 70 631.

15. Margaretha. P. *Helv. Chem. Acta.* **1974**, 57, 1866.

16. Ogino. T.; Kubota. T.; Manaka. K. *Chem. Letters* **1976**, 323; Ogino. T.; Yamada. K.; Isogai. K. *Tetrahedron Letters* **1977**, 2445.

17. Mitra. R.B.; Le Mahen. R.; Bass. T.D.; Corey. E.J. *J.Am. Chem. Soc.* **1964**, 86, 5570; Brown. E.L.; Nelson. P.J.; Kelin K.; Koch. T.H.; Chapman. O.L. *J. Am. Chem. Soc.* **1968**, 90, 1657.

18. Sano. T.; Toda. J.; Tsuika. Y. *Chem. Pharm. Bull.* **1983**, 31(1), 356-9.; Partridge. J.J.; Chadha. N.K.; Uskokovic. M.R. *J. Am. Chem. Soc.* **1973**, 95, 532.; Baghi. J.F.; Bogri. T. *Tetrahedron Letters* **1969**, 1639.; Kelly. R.B.; Zameckik.

J; Beckett. B.A. *Can. J. Chem.* **1972**, 50, 3455.; Wiesher. K.; Poon.L.; Jirkovsky T.; Fishman. M. *Can. J. Chem.* **1969**, 47, 433.; Rosenberg. H.M.; Serve. P. *Can. J. Chem.* **1969**, 47. 4295.

19 (a). Titov. Y.A.; Kuznetsova. A.I. *Doklady. Akad. Nauk. SSSR.* **1959**, 126,586.; Kharasch. M.S.; Sternfeld. E. *J.Am. Chem Soc.* **1939**, 61, 2318.

(b). Titov. Y.A.; Kuznetsova. A.I. *Doklady. Akad. Nauk. SSSR.*Otdel.Khim. Nauk. **1960**, 1810, 1815.; Snyder. H.R.; Poos. G.I. *J.Am.Chem. Soc.***1949**, 71, 1057.

(c). Kuznetsova. N.V.; Kuznetsova. A.I.; Nazarov. I.N. *Zhur. Obschei. Khim.* **1955**, 25, 88.

20 (a). Pasche. W.; Lehmann. E. *Ber.* **1935**, 68, 1146.; Bluemenfeld. G. *ibid.* **1941**, 74, 524.; Alder. K.; Vagt. H.; Vogt. W. *Annalen.* **1949**, 165,135.: Ropp. G.A.; Coyner. E.C. *J.Am. Chem. Soc.* **1949**, 71, 1832.; Meck. J.S.; Lorenzi F.J.; Cristo. S.J. *ibid.* 1830.

(b). Wichterle. O. *Colln. Czech. Chem. Commun.*Eng.Edn.**1938**,10,497.; Gilchrist. T.L.; Storr. R.G. *Organic Reactions and Orbital Symmetry* 2nd Edn. Cambridge University Press. **1979**.

21. Alder. K.; Schumacher. M.; Wolff. D. *Annalen* **1949**, 79, 564.; Vogt. W.; Alder. K. *Annalen* **1949**, 120, 564.

22. Snyder. H.R.; Poos. G.I. *J.Am. Chem. Soc.* **1950**, 72, 4104.

23. Higher and lower electronegative active centres have been depicted by a black solid circle and a vacant circle respectively in all the diagrams of this paper.

24 (a). Mizuno. K.; Hashizume. T.; Otsuji. Y. *J. Chem. Soc. Chem. Commun.* **1983**, 14, 772-3.

(b). Greene. F.D.; Misrock. S.L.; Wolfe. J.R. *J.Am. Chem. Soc.* **1955**, 77, 3852.; Applequist. D.E.; Little. R.L.; Friedrich. E.C.; Wall. R.E. *ibid.* **1959**, 81, 452.

25. Alder K.; Haydn. J. *Annalen* **1950**, 201, 570.; Merrow. R.T.; Meek. J.S.;Ramney. D.E.; Cristol. S.J. *J.Am. Chem. Soc.* **1951**, 73, 5563.

26. Similar observation was noted in ref. 9.

27. Fish R.H. *J. Org. Chem.* **1969**, 34, 1127,; Koppitz. P.; Huisgen. R.; Feiler.L.A. *J.Am. Chem. Soc.* **1974**, 96, 2270.

28 (a). Another possibility is the presence of dipole-dipole interaction.

(b). Seto. H.; Tsunoda. S.; Ikeda. H.; Fujimoto. Y.; Tatsuno. T.; Toshioka. H.*Chem. Pharm. Bull* . **1985**, 33, 2594.

(c). Crimmins. M.T. *Chem. Rev.* **1988**, 88, 1453-1473.

29. Winkler. J.D.; Henegar. K.E. *J.Am. Chem. Soc.* **1987**, 109, 2850. See also ref. 28 (c).

30. Yamanchi. M.; Katayama. S.; Baba. O.; Watanaba. T.J. *Chem. Soc. Chem. Commun.* **1983**, 6, 281-2.

31. Pardo. L.; Branchadell. V.; Oliva. A.; Bertran. J. *Theo. Chem.* **1983**, 10, 255-60.

32. Mahain. C.; Schwager. L.; Carrupt. P.A.; Vogel. P. *Tetrahedron Letters* **1983**, 24(34), 3603-6.