1,5-Shift of Unsaturated Groups; Migratory Aptitudes of Substituted Vinyl Groups and Evidence for *Exo*-Selectivity

By Douglas J. Field and David W. Jones*

(*Department of Organic Chemistry, The University, Leeds* LS2 9JT)

Summary For the 1,5-sigmatropic shift converting (**1**; X = *E*-substituent) into (**2**), migratory aptitude correlates with the resonance electron-accepting ability of the substituent X; *Z*-olefins migrate faster than their *E*-isomers, and (**6**) racemises faster than (**7**) in accord with migration *via* an *exo*-arrangement (**4**) rather than an *endo*-arrangement (**5**).

Marked differences in the migratory aptitude of unsaturated groups in 1,5-sigmatropic shift (HCO $\gg$ MeCO $\gg$ CH=CH$_2$ or CO$_2$Me)[1,2] can be explained in part by assuming transition state (TS) interaction between the π^*-orbital of the migrating group and the HOMO of the diene system. For the migrating groups studied so far resonance, inductive, steric, bond-strength, and secondary interaction effects[2] may differ. To investigate variations of migratory aptitude with the electron-accepting ability of the migrating group while keeping other effects fairly constant we have studied racemisation of the *E*-vinyl substituted indenes (**1**). These would be expected to racemise by 1,5-shift of the vinyl group to give the transient and symmetric isoindenes (**2**) which by 1,5-hydrogen shift would give the 2-vinylindenes (**3**). The required 1-vinylindenes were prepared from 1-formyl-1,3-dimethylindene[3] by Wittig or Wadsworth–Emmons reactions coupled when necessary with other standard procedures.† On thermolysis at temperatures within the range used for the kinetic measurements (Table) the indenes (**1**) generally underwent clean conversion into the 2-vinylindenes (**3**).‡ Racemisations of all the indenes followed good first-order kinetics. The activation parameters recorded (Table) agree with racemisation by concerted 1,5-vinyl shift to an isoindene (**2**) rather than dissociation to radicals or ions which recombine at C(1), C(2), and C(3) of the indene system. The observed conversion of *Z*-(**1**; X = Ph) into a mixture of *Z*- and *E*-(**3**; X = Ph) could be interpreted as due to the intervention of configurationally unstable vinyl radicals.[4] However, the independently measured rate of conversion of *Z*-(**3**; X =

---

† The *Z*- and *E*-olefins were separated by short-column chromatography on Kieselgel G (Merck) or Kieselgel G-silver nitrate (4:1).

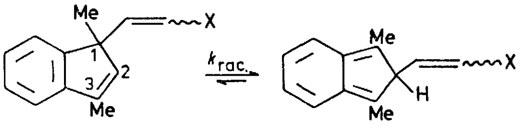
‡ The *E*-isomer (**1**; X = Me) gave a mixture of *E*- and *Z*- (**3**; X = Me), and (**1**; X = H) gave a complex product mixture.

TABLE. Rate data for racemisations in diphenyl ether.

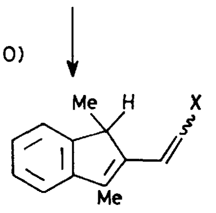
	Indene (**1**) X	Temperature range of measurements/°C	$10^5\,k_{rac}/s^{-1}$ at stated temperatures (°C)	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	$\Delta H^{\ddagger}$/k cal mol^{-1}
(i)	H	210—240	0·157 (180),[a] 7·89 (230), 14·29 (240)	−11·09±3·28	33·85±1·64
(ii)	*E*-Me	—	4·62 (230)	—	—
(iii)	*E*-Ph	200—230	44·03 (230), 12·06 (210), 1·28 (180)[a]	−12·90±1·02	31·15±0·49
(iv)	*E*-$C_6H_4NO_2$-*p*	—	40·78 (210)	—	—
(v)	*E*-CHO	160—190	20·73 (180)	−12·56±0·33	28·79±0·15
(vi)	*E*-CO_2Et	180—210	4·37 (180)	−10·75±0·38	31·02±0·18
(vii)	*Z*-Me	—	21·93 (230)	—	—
(viii)	*Z*-Ph	180—210	6·28 (180), 56·90 (210)	−10·26±0·75	30·91±0·35
(ix)	*Z*-$C_6H_4NO_2$-*p*	160—190	17·12 (180)	−13·22±0·53	28·69±0·24
(x)	MeC=CH_2	—	2·24 (240)	—	—

[a] Value extrapolated using the given activation parameters.

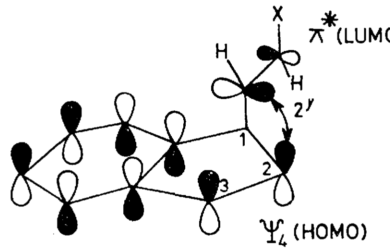
Ph) into the *E*-isomer (n.m.r.) *quantitatively* accounts for the *E*-(**3**; X = Ph) present at several points during the thermolysis of *Z*-(**1**; X = Ph). The conversion of *Z*-(**1**; X = Ph) into (**3**; X = Ph) is therefore highly stereoselective in accord with the occurrence of concerted 1,5-vinyl migration.



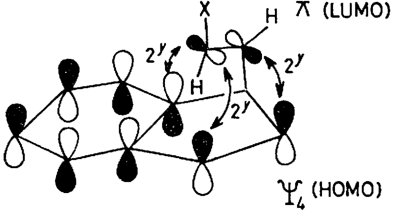
(1) (2)



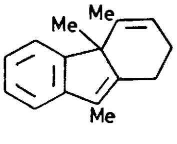
(3)



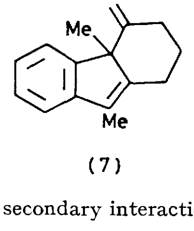
(4)



(5)



(6)



(7)

2^y = secondary interaction.

The data (Table) show that electron-withdrawing groups increase the rate of vinyl migration; thus *E*-(**1**; X = CHO) racemises 132 times more rapidly than (**1**; X = H) at 180 °C, and a *p*-nitro group accelerates *E*-β-styryl migration by *ca.* 3·4 [Table entries (iii) and (iv)]. On the other hand electron-supplying groups slow down migration. An *E*-methyl group [entry (ii)] slows vinyl shift by a factor of 0·58, and although accurate rate data were not obtainable we have observed that an *E*-methoxy- and an *E*-chloro-substituent both retard vinyl migration. As expected in the light of these latter observations there was no correlation between the migratory aptitude of the *E*-(CH=CHX) group and the σ_I value of the group X. However migratory aptitude correlated well with the σ_R^- value of X (correlation coefficient, r = 0·966), and even better with the rates of addition of morpholine to the olefins CH_2=CHX[5] (r = 0·976) (Figure). Correlation of migratory aptitude with the resonance electron-accepting ability of the group X supports the view[2,6] that more rapid rearrangement of unsaturated than saturated groups is, at least in part, associated with secondary interaction involving the π-system of the migrating group [see (**4**)]. However, this interaction does not appear to be associated with appreciable separation of charge; *E*-(**1**; X = CHO) racemises only 2·38 times faster in dimethyl sulphoxide than in diphenyl ether, and whilst morpholine addition to CH_2=CHX is accelerated by *ca.* 10^4 in going from X = CONHMe to X = COPh, the same substituent change produces an increase of only $10^{1\cdot25}$ in the racemisation rate of *E*-(**1**) (Figure).

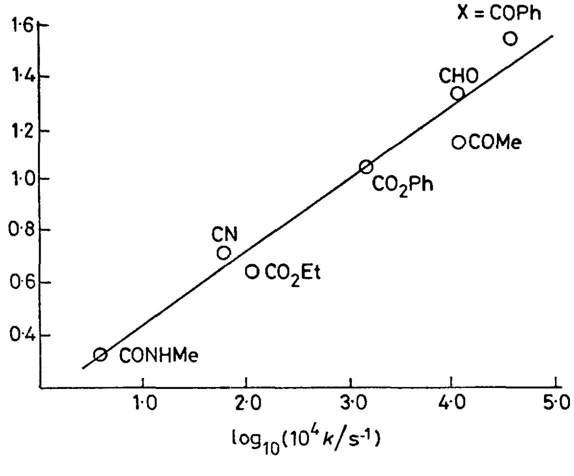


FIGURE. Plot of $\log_{10}10^5\,k$ for racemisation of the indenes (**1**) at 180 °C (ordinate) against $\log_{10}10^4\,k$ for addition of morpholine to the olefins CH_2=CHX (ref. 5) (abscissa).

Comparison of racemisation rates for corresponding *E* and *Z* olefins favours the suggestion that rearrangement preferentially involves an *exo*-arrangement of migrating

π-system and the indene fragment (**4**) rather than an *endo*-arrangement (**5**) which would be destabilised by repulsive secondary HOMO–LUMO interactions. The Table, entries (ii) and (vii), (iii) and (viii), and (iv) and (ix) show that *Z*-olefins racemise 4·2—4·9 times faster than their *E*-counterparts. Steric destabilisation of the *endo*-TS would be expected to be greater for the *Z* than the *E*-olefins and lead to more rapid rearrangement of the latter. On the other hand in going to an *exo*-TS a *Z*-olefin would be expected to experience the greater decrease in steric interaction and so rearrange more rapidly than its *E*-isomer as observed. Comparison of entries (iii) and (iv) and (viii) and (ix) shows that a *p*-nitro group is only slightly less effective at promoting migration of the *Z*-styryl group (rate increase 2·7) than the *E*-styryl group (rate increase 3·4). This suggests comparable conjugation of the nitro and aryl groups and the double bond at the TS's for migration of *Z*- and *E*-styryl groups. Whilst this is possible for an *exo*-TS, steric factors would be expected severely to curtail such conjugation in the *endo*-TS of *Z*-styryl migration. Further evidence on this point was obtained by synthesis of the olefins (**6**) and (**7**) in optically active form; at 250 °C (**6**) constrained to migrate *via* an *exo*-TS racemised 49·4 times faster than (**7**) which must rearrange *via* an *endo*-TS.

(*Received*, 30*th June* 1977; *Com.* 658.)

---

[1] P. Schiess and P. Funfschilling, *Tetrahedron Letters*, 1972, 5195.

[2] D. J. Field, D. W. Jones, and G. Kneen, *J.C.S. Chem. Comm.*, 1976, 873.

[3] D. J. Field, D. W. Jones, and G. Kneen, *J.C.S. Chem. Comm.*, 1975, 754.

[4] *Cf.* V. Rautenstrauch, G. Buchi, and H. Wüest, *J. Amer. Chem. Soc.*, 1974, **96**, 2576.

[5] H. Shenev, Z. Rappoport, and S. Patai, *J. Chem. Soc.* (*B*), 1970, 469.

[6] H. F. Semmelhack, H. N. Weller, and J. S. Foas, *J. Amer. Chem. Soc.*, 1977, **99**, 293.