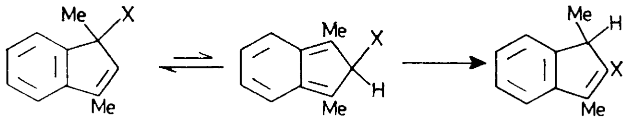
1,5-Shift of Unsaturated Groups

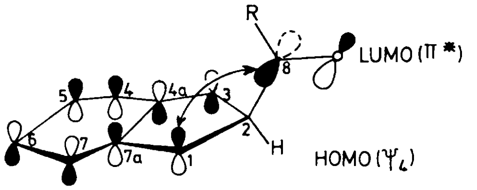
By Douglas J. Field, David W. Jones,* and Geoffrey Kneen
(*Department of Organic Chemistry, The University, Leeds* LS2 9JT)

Summary Racemisation rates for the indenes (**1**) provide migratory aptitudes for acyl, vinyl, ethynyl, nitrile, and alkyl groups, as well as hydrogen; it is proposed that the fast migration of formyl, acetyl, and benzoyl groups is, at least in part, due to a secondary interaction involving the carbonyl π^* orbital.

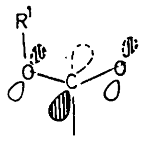
Although considerable progress has been made in understanding substituent effects in cycloaddition reactions,[1] large substituent effects in electrocyclic and sigmatropic processes are less well understood.[2] For the 1,5-sigmatropic shift no adequate explanation has been offered for the greater migratory aptitudes of unsaturated groups (acyl,[3a] aryl,[3b] butadienyl[3c] and vinyl[3d]) compared to alkyl groups. Racemisation of the aldehyde (**1**; X = CHO) has been shown[3a] to involve *only* a concerted 1,5-formyl migration to the transient isoindene (**2**; X = CHO). We have studied the racemisation of a range of indenes (**1**) to determine the migratory aptitudes for a variety of groups (X). We observe a wide variation of migratory aptitude for which a tentative explanation is advanced.



(1) (2) (3)



(4)



(5)

The optically active indenes were prepared from the acid (**1**; X = CO_2H)[3a] or the aldehyde (**1**; X = CHO)[3a] by standard procedures. Our results for different migrating acyl groups (Table) reveal a wide spread of migratory aptitudes; the formyl group migrates *ca.* 10^3 times more rapidly than acetyl, which migrates *ca.* 10^4 times more rapidly than the methoxycarbonyl group. The formyl, acetyl, and benzoyl groups migrate more readily than hydrogen [entry (vii)

Table], but the methoxycarbonyl group migrates *ca.* 10^2 times more slowly than hydrogen. The slow migration of the ethynyl and nitrile groups [entries (viii) and (ix)] suggests that increased *s*-character in the migrating bond is not *the* dominant factor determining the more ready migration of acyl than alkyl groups. Neither are inductive effects dominant, as the indenes [(**1**); X = CH_2OAc, CH_2CHO, and dioxolan-2-yl] fail to racemise at temperatures up to 240 °C. Considerably more rapid rearrangement of the formyl than the vinyl group [entry (xiii)] supports an important transition state (TS) interaction between the highest occupied indene orbital and the π^* orbital of the migrating group. When steric and other effects are very similar, migratory aptitude parallels the increased electron accepting ability in the migrating group (lower π^* energy). This is observed for the benzoyl-indenes [entries (x)—(xii)] and the phenyl and *p*-nitrophenyl esters [entries (iv) and (v)]. The substituent effects are small, however, and indicate little polarity change in going from the ground state to the rearrangement TS. This is supported by the small solvent effect observed for the racemisation of (**1**; X = CHO), which is only 1·3 times more rapid in dimethylformamide than in decalin. In these respects the 1,5-acyl shift resembles the Diels–Alder reaction in which interaction of one pair of frontier molecular orbitals is assumed to be dominant[1] yet little polarity can be detected by solvent or substituent effects.[4] Like the Diels–Alder reaction the 1,5-acyl shift is subject to catalysis by Lewis acids; racemisation of (**1**; X = COMe) is 70 times faster in the presence of BF_3.

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)	$\Delta S^‡$/cal K^{-1} mol^{-1}	$\Delta H^‡$/kcal mol^{-1}
(i)	CHO	50—80	5480 (140)[a]	−11·41 ± 2·21	22·08 ± 0·75
(ii)	COMe	140—165	5·11 (140)	−10·23 ± 1·16	28·31 ± 0·5
(iii)	CO_2Me	—	5·34 (255)	—	—
(iv)	CO_2Ph	225—255	14·46 (255), 0·00065 (140)[a]	−7·51 ± 0·49	36·77 ± 0·25
(v)	$CO_2C_6H_4NO_2$-*p*	—	23·3 (255)[b]	—	—
(vi)	CONHMe	—	4·30 (245)	—	—
(vii)	H	—	*ca.* 0·05 (140)[c]	—	—
(viii)	C≡CH	—	*ca.* 0·22 (245)	—	—
(ix)	C≡N	—	*ca.* 0·19 (245)	—	—
(x)	$COC_6H_4SO_2Me$-*p*	130—160	10·23 (140)	−7·20 ± 0·45	28·98 ± 0·19
(xi)	COPh	140—180	4·97 (140), 146 (180)	−8·76 ± 0·88	28·91 ± 0·37
(xii)	COC_6H_4OMe-*p*	—	75·5 (180)	—	—
(xiii)	$CH=CH_2$	210—240	0·00375 (140)[a]	−11·09 ± 3·28	33·85 ± 1·64

[a] Value extrapolated using the given activation parameters. [b] Rate of formation of the 2-isomer (**3**) (measured by n.m.r.). [c] Estimated rate prior to onset of catalysis; racemisation of 1-methyl-3-t-butylindene proceeds at a similar rate (J. Almy and D. J. Cram, *J. Amer. Chem. Soc.*, 1970, **92**, 4316).

In view of the small substituent effects observed when steric factors are similar, the rapid decrease in migratory aptitude in the series CHO ≫ COMe ≫ CO_2Me, although in accord with increasing energy of the carbonyl π^* orbital,[5] is probably accentuated by other factors. If the rearrangement TS resembles the high energy isoindenes (**2**) it can be envisaged as being derived from (**4**) by tilting the carbonyl group to secure a good overlap of carbonyl (π^*) and indene (ψ_4) orbitals. Migration with the acyl oxygen remote from the indene ring as in (**4**) (*exo*-TS) allows a bonding secondary interaction between the MO's [see (**4**)]. Migration with the acyl oxygen over the indene ring (*endo*-TS) introduces anti-bonding between the π^* coefficient at O and C(7a). Accordingly an *exo*-TS may be favoured for formyl and acetyl migration, although for the latter electronic destabilisation must be balanced against the steric disadvantage of migration with the methyl group over the indene ring. For methoxycarbonyl and related groups the π^* orbital has the form shown in (**5**). Thus anti-bonding between C(7a) and a π^* coefficient at O is unavoidable. This explanation also applies if the rearrangement TS is early; repulsive interaction then involves C(3) of the indene system.† Similar migratory aptitude differences in cyclohexadienes[6] can also be explained in this way.

(*Received*, 13*th August* 1976; *Com.* 939.)

---

† If as it migrates along the line of the C(1)—C(2) bond the acyl group occupies a plane at *ca.* 90° to that bond, antibonding interaction will be present between the *endo*-oxygen and both C(3) and C(7a).

[1] K. N. Houk, *Accounts Chem. Res.*, 1975, **8**, 361; K.-L. Mok and M. J. Nye, *J.C.S. Perkin I*, 1975, 1810.

[2] *E.g.*, B. J. Arnold, P. G. Sammes, and T. W. Wallace, *J.C.S. Perkin I*, 1974, 409, 415; C. W. Jefford, A. F. Boschung, and C. G. Rimbault, *Tetrehedron Letters*, 1974, 3387; R. Huisgen and H. Mayr, *J.C.S. Chem. Comm.*, 1976, 55, 57; M. J. S. Dewar and L. E. Wade, *J. Amer. Chem. Soc.*, 1973, **95**, 290; G. R. Krow and J. Reilly, *ibid.*, 1975, **97**, 3837; D. A. Evans and A. M. Golob, *ibid.*, p. 4765.

[3] (a) D. J. Field, D. W. Jones, and G. Kneen, *J.C.S. Chem. Comm.*, 1975, 754, and cited references; (b) L. L. Miller and R. F. Boyer, *J. Amer. Chem. Soc.*, 1971, **93**, 650; (c) L. A. Paquette and M. J. Carmody, *ibid.*, 1975, **97**, 5841; T. L. Gilchrist, C. J. Moody, and C. W. Rees, *J.C.S. Chem. Comm.*, 1976, 414; (d) C. D. Anderson, J. T. Sharp, E. Stefaniuk, and R. S. Strathdee, *Tetrahedron Letters*, 1976, 305.

[4] J. Sauer, *Angew. Chem. Internat. Edn.*, 1967, **6**, 16.

[5] O. Eisenstein, J. M. Lefour, and C. Minot, *Tetrahedron Letters*, 1976, 1681.

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