Divergent Relative Migratory Aptitudes of Double and Triple Bonded Groups in Cyclopentadiene and Cycloheptatriene Systems

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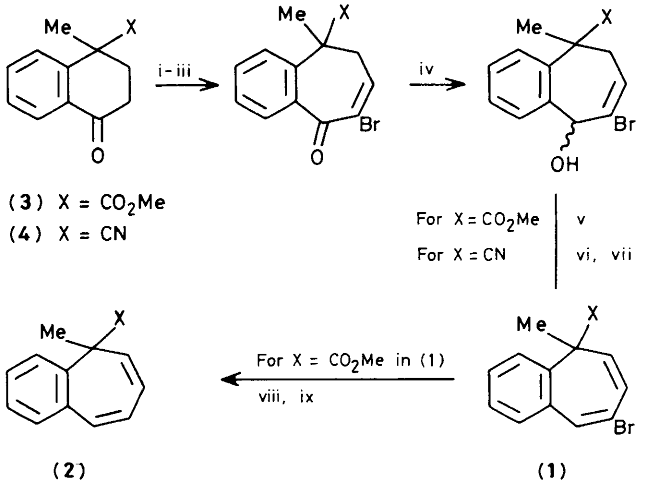
In cyclopentadiene systems 1,5-shift of triple bonded groups is much slower than that of double bonded groups whereas in the cycloheptatrienes (**1**) and (**2**), C≡N and CHO have very similar migratory aptitudes and (**2**; X = C≡CCOPh) rearranges at 60 °C whilst (**1**; X = *E*-CH=CHCOPh) is unchanged at this temperature; variations of strain in the bridged transition states [(**8**) compared to (**9**), and (**10**) compared to (**11**)] may explain these results.

For indenes, cyclopentadienes, heteracyclopentadienes, and cyclohexadienes the tendency of groups to undergo 1,5-sigmatropy follows the order: CHO > MeCO > H > CO_2Me > CN ~ C≡CH > alkyl.[1] This order can in large part be explained by postulating secondary MO interactions between the migration frame and the π^* orbital of the migrating unsaturated group.[1] However the very slow rearrangement of the nitrile group in 1,3-dimethylindenes[1] appears inconsistent with its good electron accepting ability, and the reported easy migration of CN in a cycloheptatriene and a benzocycloheptatriene.[2] We report 1,5-migratory aptitudes for double and triple bonded groups in the benzocycloheptatrienes (**1**) and (**2**). These establish that the migratory aptitudes of triple bonded groups depend strongly on the migratory framework.

The benzocycloheptatrienes (**1**) and (**2**) were prepared (Scheme 1) *via* ring-expansion of the tetralones (**3**) and (**4**).† The ester (**1**; X = CO_2Me) was converted into (**1**; X = CHO) *via* reduction ($Bu^i{}_2AlH$) and oxidation ($CrO_3 \cdot 2$pyridine,



Scheme 1. *Reagents:* i, Me_3SiCl, Et_3N, dimethylformamide; ii, $PhHgCBr_3$, $(CH_2OMe)_2$; iii, $AgBF_4$, MeOH, $(CH_2OMe)_2$; iv, $NaBH_4$, $CeCl_3$; v, MeOH, HCl; vi, CBr_4, Ph_3P, MeCN; vii, 1,8-diazabicyclo[5.4.0]undec-7-ene, C_6H_6; viii, $Bu^i{}_2AlH$, Et_2O; ix, Bu^nLi, Et_2O–H_2O.

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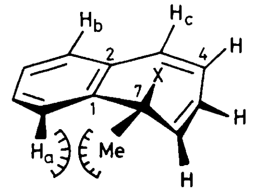
† The tetralone (**3**) was prepared by esterification of the known acid (ref. 3); tetralone (**4**) was obtained by Friedel–Crafts cyclisation of 4-cyano-4-phenylpentanoyl chloride obtained from the known methyl ester (ref. 3).

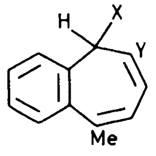
Table 1. Product and rate data for thermolyses

Compound	Product(s)	$10^4k/s^{-1}$ (t/°C) (Solvent)	$\Delta S^‡$/cal K^{-1} mol^{-1} [a]	$\Delta H^‡$/kcal mol^{-1} [a]
(**1**; X = CHO)	(**6**; X = CHO, Y = Br)	0.499 (114.4) (C_6D_6) 1.83 (127.1) „ 4.56 (138.7) „ 8.47 (147.1) „	−8.6 ± 2.7	27.16 ± 1.1
(**1**; X = CN)	(**6**; X = CN, Y = Br) and (**7**; X = CN, Y = Br)	0.473 (137.2) (C_6D_6) 1.20 (148.3) „ 2.64 (159.6) „ 5.97 (169.4) „ 3.31 (159.6) (CD_3CN) 5.84 (159.6) (CD_3OD)	−12.7 ± 1.8	27.2 ± 0.8
(**2**; X = CHO)	Mainly (**7**; X = CHO, Y = H)	2.25 (138.1) (C_6D_6) 3.42 (138.1) (CD_3CN)		
(**2**; X = CN)	Mainly (**7**; X = CN, Y = H)	0.392 (138.1) (C_6D_6)		
(**2**; X = C≡CCOPh)	(**6**; X = C≡CCOPh, Y = H) At 139 °C this gives (**7**; X = C≡CCOPh, Y = H)	0.358 (60.6) (C_6D_6) 0.937 (69.7) „ 2.55 (80.1) „ 8.35 (94.2) „ 3.70 (69.7) (CD_3OD)	−12.7 ± 1.1	22.1 ± 0.4

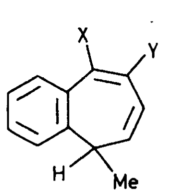
[a] 1 cal = 4.184 J.



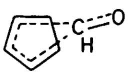
(**5**)



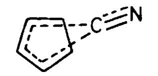
(**6**)



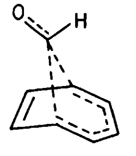
(**7**)



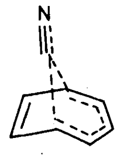
(**8**)



(**9**)



(**10**)



(**11**)

CH_2Cl_2). Treatment of the intermediate alcohol (**1**; X = CH_2OH) with Bu^nLi and aqueous work-up gave (**2**; X = CH_2OH) which on Swern oxidation gave (**2**; X = CHO). The latter was converted into (**2**; X = CN) *via* its oxime. The aldehyde (**1**; X = CHO) gave the olefin (**1**; X = CH=CBr_2) (Ph_3P, CBr_4) which with Bu^nLi afforded (**2**; X = C≡CH). The latter gave (**2**; X = C≡CCOPh) upon reaction with PhCOCl, Et_3N, $PdCl_2{\cdot}2Ph_3P$ (cat.), and CuI (cat.).

As shown in structure (**5**) a 7,7-disubstituted benzocycloheptatriene is destabilised by peri-like interaction of a C-7 substituent with an *ortho*-proton (H_a) of the benzo-group. 1,5-Shift of X in (**5**) relieves this interaction (the C-Me bond in the product forms an angle of *ca.* 45° with the C–H_a bond) replacing it by peri-like interaction of H_b and H_c. Accordingly any equilibrium between (**5**) and its 1,5-shift product should favour the latter and so enable ready observation of the 1,5-shift. As shown by the thermolysis results (Table 1) this proved to be the case. Thermolyses of the compounds (**1**) and (**2**) were conducted in degassed solvents and followed by 90 MHz ^1H n.m.r. measurements. For the compounds in Table 1 rearrangement proceeded cleanly to give the products (**6**) of simple 1,5-shift of X and/or the products (**7**) derived from them by 1,5-hydrogen shift. The activation parameters and solvent rate effects (Table 1) support the occurrence of concerted 1,5-shifts, as does our failure to observe cross-over products when (**1**; X = CN) and (**2**; X = CHO) rearrange together.

Acetylene and nitrile migration occur readily in the cycloheptatriene system; the acetylene (**2**; X = C≡CCOPh) rearranges at 60 °C and the simple acetylene (**2**; X = C≡CH) rearranges at 145 °C (210 min) to give mainly (**7**; X = C≡CH, Y = H). Moreover it is clear that in the cycloheptatriene system triple bonded groups compete favourably with the best migrators about the cyclopentadiene system.[1,4] Thus rearrangement of the nitrile (**1**; X = CN) is only slightly slower than rearrangement of the aldehyde (**1**; X = CHO) (Table 1), and the olefin (**1**; X = *E*-CH=CHCOPh) is unchanged at 80 °C (30 min)‡ indicating slower rearrangement than observed for (**2**; X = C≡CCOPh). The order of migratory aptitude CHO > COMe > CO_2Me observed in indenes[1] is maintained in the cycloheptatrienes (**1**); (**1**; X = CHO) rearranges at 114 °C whereas (**1**; X = COMe) requires heating at 175 °C (110 min) for complete conversion into a mixture of (**6**; X = COMe, Y = Br) and two unidentified naphthalenes. Rearrangement of (**1**; X = CO_2Me) requires heating at 205 °C (2 h) and gives 5-bromo-7-methoxycarbonyl-7-methyl-2,3-benzonorcaradiene rather than a product of 1,5-CO_2Me shift. For the cycloheptatriene system the order of migratory aptitude:

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‡ At 100 °C (45 min) the olefin undergoes an entirely different reaction which is currently under study.

CHO > CN, C≡CH > COMe > CO_2Me > alkyl prevails. The improved position of the triple bonded groups in this order is attributable to reduced strain in bridged rearrangement transition states (T.S.). Thus for rearrangement of formyl in a cyclopentadiene the bridged T.S. (**8**) resembles a cyclopropane whereas the T.S. (**9**) for CN migration resembles a methylenecyclopropane. Accordingly the T.S.s (**8**) and (**9**) should reflect the much greater stability of cyclopropane than methylenecyclopropane (13.6 kcal mol^{-1}).[5] For formyl and nitrile migration about cycloheptatriene the bridged T.S.s (**10**) and (**11**) incorporate units resembling cyclopentane and methylenecyclopentane which have very similar energies.[5] Migration of triple bonded groups should therefore be more favourable in 7- than 5-ring dienes. The bridged T.S.s depicted in (**8**)—(**11**) derive from important secondary interaction involving the π^* orbital of the migrating group.[1] This probably occurs at an early stage in the separation of the originally bonded centres.[6]

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References

1 D. J. Field, D. W. Jones, and G. Kneen, *J. Chem. Soc., Perkin Trans. 1*, 1978, 1050, and cited references; R. J. Bushby and D. W. Jones, *J. Chem. Soc., Chem. Commun.*, 1979, 688.

2 E. Ciganek, *J. Am. Chem. Soc.*, 1967, **89**, 1458.

3 G. N. Walker and D. Alkalay, *J. Org. Chem.*, 1971, **36**, 491.

4 D. J. Field and D. W. Jones, *J. Chem. Soc., Perkin Trans. 1*, 1980, 714.

5 P. v. R. Schleyer, J. E. Williams, and K. R. Blanchard, *J. Am. Chem. Soc.*, 1970, **92**, 2377.

6 R. W. Alder and W. Grimme, *Tetrahedron*, 1981, **37**, 1809.

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