Exclusive *syn*-Addition in Diels–Alder Additions to a 1-Hydroxycyclopenta-2,4-diene

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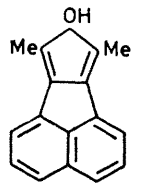
Summary In the Diels–Alder reactions of 7,9-dimethyl-8*H*-cyclopent[*a*]acenaphthylen-8-ol (**1**) with several dienophiles the observed adducts arise by addition to the face of the diene bearing the hydroxy-group.

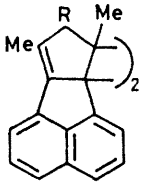
FUKUI and his coworkers have suggested[1] that the HOMO of a cyclopentadiene is biased towards the side of the molecule bearing a 1-heteroatom with a lone electron pair. Such a bias should result in a preferred addition of dienophiles *syn* to the heteroatom.† Relevant experimental observations of additions to 1-acetoxy-,[2] 1-halogeno-,[3] and pentachloro-[4] cyclopentadienes *do not* show a uniform preference for *syn*-addition. We describe the high *syn*-selectivity observed in the addition of several dienophiles to the novel hydroxycyclopentadiene (**1**).

Solutions of (**1**) were prepared by boiling the dimer (**2**; R = OH)[5] in benzene (30 min). Dissociation of the dimer in the presence of dimethyl fumarate gave a single adduct (73%), assigned the structure (**3**) since it was converted into the γ-lactone (**4**; R = CO_2Me) by hydrolysis to the diacid (KOH–EtOH–H_2O), lactonisation (MeC_6H_4-SO_3H-*p* in boiling toluene), and esterification (CH_2N_2). Treatment of the lactone (**4**; R = CO_2Me) with sodium methoxide in methanol gave (**3**) as the only product. The adducts formed from (**1**) and dimethyl maleate, maleic anhydride, and *N*-phenylmaleimide are all formed by *endo*-addition *syn* to the hydroxy-group. The dimethyl maleate and maleic anhydride adducts are cleanly converted into (**3**) (NaOMe–MeOH followed by CH_2N_2) and the *N*-phenylmaleimide adduct is formed from the maleic anhydride adduct and aniline in boiling xylene.

With methyl acrylate, (**1**) gave a *ca.* 1:1 mixture of *endo*- and *exo*-adducts; the *anti*-configuration† of the hydroxy-group in the *exo*-adduct was shown by conversion of the corresponding acid into the γ-lactone (**4**; R = H)‡ which gives the adduct (**5**) when treated with sodium methoxide in methanol. The *exo*-adduct is formed (in low yield) by sodium methoxide–methanol epimerisation of the *endo*-acrylate adduct. The diacetate (**2**; R = OAc)[5] dissociates in boiling benzene to give the acetate of (**1**) which, with methyl acrylate, gives only the *endo*-adduct (**6**). This suggests that *exo*-addition of acrylate to the alcohol (**1**) is favoured by hydrogen bonding and/or the small size of the hydroxy-group. A repulsive interaction of the larger acetoxy-group with an *exo*-substituent is revealed in the addition of the acetate of (**1**) with dimethyl fumarate which gives the acetate of (**3**) and its 7-epimer in a ratio of *ca.* 2:1.



(1)



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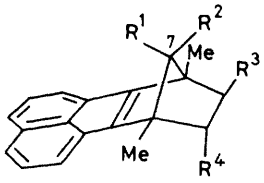

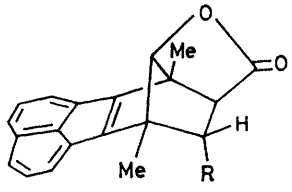

(4)

(3) R^1 = H, R^2 = OH, R^3 = R^4 = CO_2Me
(5) R^1 = R^4 = H, R^2 = OH, R^3 = CO_2Me
(6) R^1 = R^3 = H, R^2 = OAc, R^4 = CO_2Me
(7) R^1 = R^3 = H, R^2 = OH, R^4 = Ph

Since both (**1**) and its acetate give only the *endo-anti*-adducts with *N*-phenylmaleimide no evidence is available for hydrogen bonding effects favouring the formation of *endo-anti*-adducts. Moreover, addition of styrene to (**1**) gives the product (**7**) *via* *endo*-addition *syn* to the hydroxy-group; hydrogen bonding effects would be expected to be minimal in this case. For several of the adducts described the 7-epimers were prepared by reduction ($NaBH_4$) of the 7-ketones formed either by adduction to 7,9-dimethylcyclopent[*a*]acenaphthylen-8-one,[5] or by oxidation (CrO_3.2-pyridine–CH_2Cl_2) of the adducts themselves. The 7-epimers of the adducts were stable to the conditions employed for adduction showing that the adducts are the products of kinetic control. The ^1H n.m.r. spectra of the acetates epimeric at C-7 show, as expected,[6] that the acetyl methyl-group is more shielded ($\Delta\delta$ *ca.* 0·2 p.p.m.) and the C-7 proton less shielded ($\Delta\delta$ *ca.* 0·2 p.p.m.) in the *syn*-norbornenes.† The acetate of the adduct (**7**) displays an acetoxy methyl-group at δ 2·20 and the C-7 hydrogen resonance at δ 4·72; the C-7 epimer shows corresponding

† *syn*-Addition leads to an *anti*-norbornene derivative.

‡ The best method is with *p*-toluenesulphonic acid in boiling benzene; dicyclohexylcarbodi-imide is less effective, giving the acylurea as the major product.

signals at δ 2·0 and 5·10 respectively. The strongly preferred *syn*-additions to (**1**) support the suggestion of an orbital bias in the 1-heteroatom substituted cyclopentadienes[1] and indicate that steric effects are probably responsible for the several examples of preferred *anti*-addition previously reported.[3,4]

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