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DIELS-ALDER ADDUCTS OF 1,1-DISUBSTITUTED OLEFINS

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In the Diels-Alder addition of trans 1,2-disubstituted or 1,1-disubstituted olefins to cyclohexadiene or cyclopentadiene there is a competition between two groups for the endo position. In this preliminary study we examine the structure of adducts obtained with a series of 2-substituted acrylonitriles and 2-substituted methyl acrylates to account for the factors determining the ratio of adducts with 1,1-disubstituted olefins.

The dienophiles 2-chloroacrylonitrile (1a), 2-bromoacrylonitrile (1b), methyl 2-chloroacrylate (1c), methyl 2-bromoacrylate (1d) and ethyl 2-acetoxyacrylate (1e) were allowed to react in benzene with cyclopentadiene and cyclohexadiene. The structures of the adducts follow from a consideration of the ratio of products (see table 1) and the NMR spectra of the adducts. The shielding effect of the double bond in substituted norbornenes leads to a shift of 4-6 c.p.s. of the methyl signal of the endo adduct of methyl acrylates to high field with respect to the methyl signal of the exo adduct. In 2-methylnorborn-5-enes the endo methyl is shifted to high field by 11-20 c.p.s. with respect to the signal of the corresponding exo methyl; these shifts are independent of other substituents at the 2 position and will be helpful in the determination of structure of other Diels-Alder adducts.

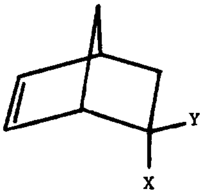
Observation of this shift permitted assignment of structure to the adducts of the unsaturated esters - the endo-exo ratios were very similar to those obtained with the corresponding acids[1]. Conflicting[2,3,4] structures have been assigned to the adducts of cyclopentadiene with 2-chloroacrylonitrile. Although the substituents do not permit a structural assignment based upon the observed shielding effect we are able to deduce the structures by consideration of the ratio of adducts. Reaction of methyl 2-chloroacrylate with cyclopentadiene shows that chlorine preferentially adopts the endo position. Comparison of the ratio of adducts with methyl acrylate (76:24)[5] and acrylonitrile (60:40)[6] suggests that adduct (2a) would be the expected product with 2-chloroacrylonitrile and the ratio of major adduct to minor adduct should be enhanced by comparison with methyl 2-chloroacrylate; this is the case. The similar adduct ratios obtained with both cyclohexadiene and cyclopentadiene and the two halonitriles are taken to indicate that in each case in the major isomer the halogen adopts the endo position. Hydrolysis of the adducts confirms these structural assignments. Thus adduct (5a) in aqueous potassium hydroxide at 100° gives largely a mixture of the epimeric acids (6)[7] but adduct (4a) gives mainly bicyclic acids (7) and (8). The stereochemistry of the leaving group determines the nature of the product in a manner similar to the S_N1 acetolysis of the tosylates of endo-bicyclo (2,2,2) oct-5-en-2-ol[8] and exo-bicyclo (2,2,2) oct-5-en-2-ol[9], but we believe the lack of reactivity of the adducts to aqueous silver nitrate solution[3] shows that our hydrolysis has S_N2 character.

Earlier results[1,10] have shown that alkyl or halo groups adopt the endo position in preference to the carboxyl group. From our results it is clear that halo groups but not the acetoxyl group adopt the endo position in preference to the carbomethoxy or cyano group. Although it may be argued that the important factor controlling the stereochemistry of addition of 2-alkylacrylic acids to dienes[10] is steric in origin we believe that with halogen substituted olefins the stereochemical control is largely electronic. In just the same way that multiple bonds stabilise the endo transition state relative to the exo by secondary orbital interaction[11] halogen atoms may stabilise the endo route by mixing of the non-bonded electrons.

TABLE 1

Yields of Adducts of 1,1-disubstituted Olefins with Cyclopentadiene and Cyclohexadiene

Diene	Dienophile	Temperature°	% Yield	
			Adduct 2 or 4	Adduct 3 or 5
Cyclopentadiene	1a	75	80.5	19.5
	1b	75	75	25
	1c	75	64	36
	1d	75	65	35
Cyclohexadiene	1a	75	82	18
	1c	120	75	25
	1d	120	77	23
	1e	120	32	68
	1a	142	80	20



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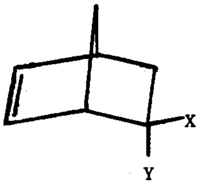

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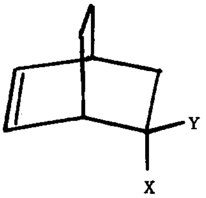

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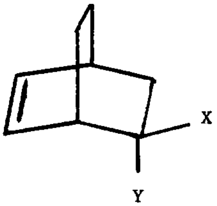

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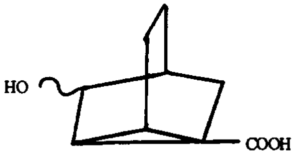

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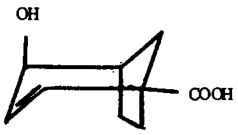

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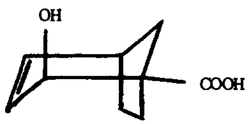
a: X = Cl Y = CN

b: X = Br Y = CN

c: X = Cl Y = COOMe

d: X = Br Y = COOMe

e: X = OAc Y = COOEt



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