Pericyclic Reactions.[1] The Synthesis and Reactions of Deuterium Labelled Cyclohexa-1,4-diene and Cyclohexa-1,3-diene

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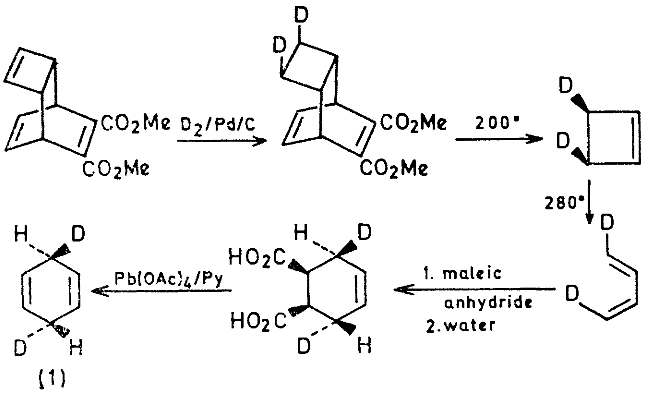
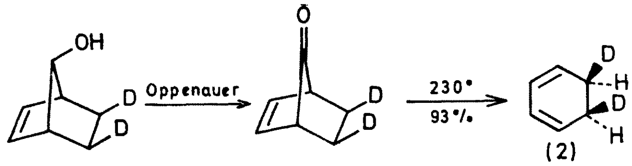
Summary The stereospecific syntheses of *trans*-3,6-dideuteriocyclohexa-1,4-diene (1) and *cis*-5,6-dideuteriocyclohexa-1,3-diene (2) are outlined; decomposition of these compounds to benzene and hydrogen shows that only cyclohexa-1,4-diene loses hydrogen stereospecifically; dehydrogenation of (1) and (2) by a variety of reagents is non-stereospecific.

WE report here the synthesis of the stereospecifically labelled cyclohexadienes (1) and (2) by the routes illustrated in Scheme 1† and Scheme 2.‡ We have used these compounds to examine two groups of potentially pericyclic reactions.



SCHEME 1

One of these groups of reactions is the fragmentation to give benzene and hydrogen. There is a growing body of evidence[8] that cyclohexa-1,4-diene fragments thermally by a concerted process; one of the necessary pieces of evidence, the loss of *cis* hydrogens, has been obtained[9] using *cis*-3,6-dimethylcyclohexa-1,4-diene, which loses hydrogen much more readily than the *trans*-isomer. Our compound (1) provides direct evidence that the parent compound also loses hydrogen stereospecifically *cis*, since pyrolysis of (1) gives monodeuteriobenzene with very little benzene or dideuteriobenzene (Table 1). In the case of cyclohexa-1,3-diene no concerted processes have been claimed in either thermal decomposition (where *trans* loss of HD would be allowed) or photochemical decomposition (where *cis* loss of H_2 or D_2 would be allowed). For the thermal reaction, a radical chain process has been suggested.[10] For the photochemical reaction, it has been suggested[11] that the photochemically excited molecules decay to their thermally excited ground states before decomposition.



SCHEME 2

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† Except for the selective hydrogenation, none of the reactions[2] used in Scheme 1 is new; however the presence of the isotope is new. The pyrolysis results prove that both the synthetic sequence and the pyrolysis are stereospecific. It is true that we have not, strictly, shown that the cyclohexadiene is not the *cis*-isomer losing HD in a *trans*-manner; this is obviously rather unlikely. The stereochemistry shown in Scheme 1 is inferred from the Woodward–Hoffmann rules[3] and from many precedents; its consistency, involving, as it does, at least six pericyclic reactions starting from COT, is compelling. We might note in particular that the opening of cyclobutene and the Diels–Alder reaction of butadiene are also shown by this sequence to be stereospecific.

‡ The dideuterioalcohol in Scheme 2, a known compound of known stereochemistry,[4] was oxidised by a reaction[5] known in the undeuteriated series. The thermal loss of carbon monoxide is of a known kind,[6] but has not been used or observed before in this simple case.[7]

Our results conform with these suggestions: we find that pyrolysis, flash photolysis or continuous irradiation of (2) give benzene with non-stereospecific loss of H_2, HD, and D_2 (Table 1). A lower isotope effect, which indicates a high effective "temperature," is noticeable in the photolysis experiments.

TABLE 1

Deuterium content of the benzene product by decomposition of (1) *and* (2)

Compound	Conditions	%d_0[a]	%d_1[a]	%d_2[a]	%d_3[a]
(1)[b]	340°/1 hr.	2·5	94	3·5	0
(2)[c]	400°/1 hr.	6	29	63	2
(2)[c]	continuous irradiation	14	37	47	2
(2)[c]	flash photolysis	12	37	47	4
(2)[c]	flash photolysis with added excess of CH_4	12	39	42	7

[a] Measured by low-voltage mass spectrometry on benzene separated from the reaction mixture by gas chromatography.
[b] Estimated by low-voltage mass spectrometry to be $>96\%$ d_2.
[c] Estimated by low-voltage mass spectrometry to be $>94\%$ d_2.

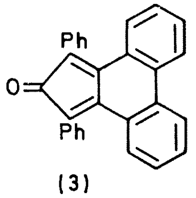
The other group of reactions which we have studied is that involving the transfer of hydrogen to other molecules. We find that cyclohexa-1,4-diene is smoothly dehydrogenated both by anthracene and by phencyclone (3), to give 9,10-dihydroanthracene and dihydrophencyclone (4)§ respectively. These reactions could, in principle, take a symmetry-allowed course which would be stereospecific. The observed reactions are, however, non-stereospecific (Table 2). The cyclohexa-1,3-diene (2) is converted into benzene by DDQ, chloranil, and other reagents, in each case, with no marked stereospecificity (Table 2).

TABLE 2

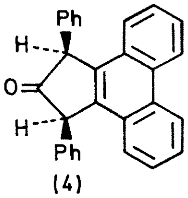
Deuterium content of the reaction products produced by decomposition of (1) *and* (2) *in the presence of hydrogen acceptors*

Reactions	Benzene produced %d_0	%d_1	%d_2	Reduced product %d_0	%d_1	%d_2
(1) + anthracene 235°/5 days	4	51[a]	45	52[b]	43[b]	5[b]
(1) + phencyclone 120°/4 hr.	5	35	60	56[c]	41[c]	3[c]
(2) + DDQ 100°/16 hr.	7·5	27·5	65			
(2) + chloranil 100°/16 hr.	10	29	61			
(2) + diethyl azodicarboxylate 20°/2 hr.	9	35	56			
(2) + benzenediazonium-2-carboxylate 60°/12 hr.	19[d]	33[d]	48[d]			

[a] The high d_1 value is due to concurrent unimolecular decomposition of (1), see above. [b] The product is 9,10-dihydroanthracene in 100% yield. [c] The product is (4), in 70% yield. [d] Since the d_0 value is not equal to the d_2 value, the benzene is not coming equally from benzyne and (2); benzene is a very minor product.



(3)



(4)

The results with (2) are similar to those of Trost,[13] who studied the dehydrogenation of *cis*-1,2-dideuterio-1,2-dihydroacenaphthene. Like his, our results give evidence for a slight preference for *cis*-abstraction, which may be due to an ion-pair effect. With our compounds the allowed, concerted reactions of (1) and (2) with these reagents would lead directly to an aromatic product. Evidently this favourable feature is still not enough to make the reaction follow, to any great extent, the concerted pathway.

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§ The stereochemistry of dihydrophencyclone was established as *cis*: lithium aluminium hydride reduction of (4) gave an alcohol whose trichloroacetyl isocyanate[12] derivative showed protons in the n.m.r. spectrum, in addition to those on aromatic rings as a two-proton doublet (τ 4·95) and a one-proton triplet (τ 3·73). *trans*-Dihydrophencyclone, to give this result, would have to give rise to two coincidences, one of chemical shift and one of coupling constants.

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