

## Deazetation of a Bicyclic Azo Compound: Resolution of a Stereochemical Ambiguity and Conformational Analysis of a Biradical

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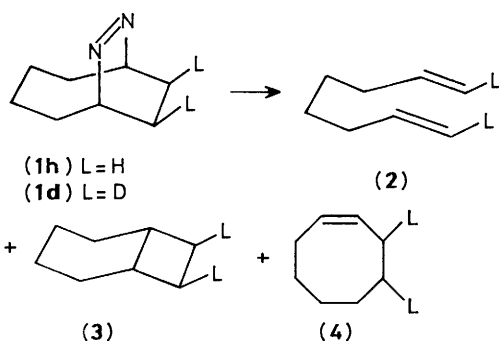
Development of a new approach has permitted a fuller analysis of the stereochemistry of deazetation of the stereospecifically deuterated azo compound (**1d**) than could be achieved previously, in that it has proved possible to analyse  $[1,8-^2\text{H}_2]$ octa-1,7-diene for *E,E*-, *E,Z*-, and *Z,Z*- content. This has given results for the thermal and photochemical reactions that can be rationalised in terms of partial conformational equilibration of the biradical.

Stereochemical studies have given considerable insight into the deazetation of cyclic and bicyclic azo compounds.<sup>1</sup> In particular, 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH)<sup>2-6</sup> and analogues are remarkable in that thermal and photochemical deazetations have been shown to proceed with predominant inversion of configuration, an observation for which several rationales have been proposed. More recently, we have reported that the next higher homologue, 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO), shows a similar inversion, but the choice of possible mechanisms is more restricted.<sup>7</sup>

Some years ago,<sup>8</sup> we reported the unusual stereochemistry of thermal deazetation of the deuterated 7,8-diazabicyclo[4.2.2]dec-7-ene (**1d**) and suggested that the results were due to incomplete equilibration of various conformations of the derived biradical. We report here full details of that study, a new approach to the analysis of the stereochemistry which has permitted the resolution of a residual stereochemical ambiguity in that work, and corresponding results for deazetation of (**1d**) on direct and sensitised photolysis.

### Results

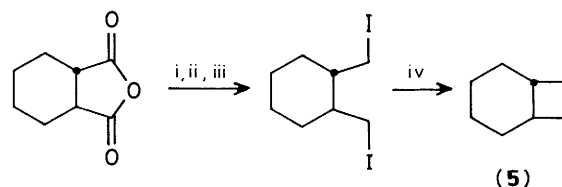
*Studies of the Unlabelled Compounds.*—Thermolysis, direct or sensitised photolysis of (**1**)<sup>9</sup> afforded three  $\text{C}_8\text{H}_{14}$  products (Scheme 1) which were isolated by preparative gas chrom-



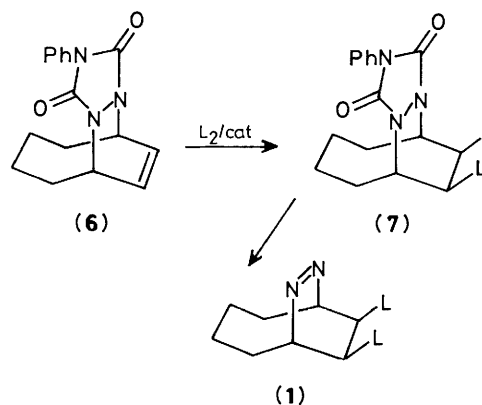
Scheme 1.

atography (g.c.) and were shown to be spectroscopically and chromatographically identical with authentic material. They were octa-1,7-diene (**2**), *cis*-bicyclo[4.2.0]octane<sup>10</sup> (**3**), and *cis*-cyclo-octene (**4**). All three were shown to be stable under the thermolysis conditions. No other products >1% were observed by g.c. In particular, vinylcyclohexane, a known product<sup>11</sup> from secondary pyrolysis of (**2**) and (**4**), was absent.

Another potential product, *trans*-bicyclo[4.2.0]octane (**5**), was synthesised by a route analogous to that used for the



Scheme 2. Reagents: i,  $\text{LiAlH}_4$ ,  $\text{Et}_2\text{O}$ ; ii,  $\text{TsCl}$ , pyridine; iii,  $\text{NaI}$ ,  $\text{Me}_2\text{CO}$ ; iv,  $\text{BuLi}$ ,  $\text{Et}_2\text{O}$



Scheme 3.

synthesis of *trans*-bicyclo[4.2.0]oct-3-ene<sup>12</sup> and outlined in Scheme 2. It was absent from reactions of (**1**) (<1% of the *cis*-isomer), and control experiments, in which (**5**) was co-pyrolysed or co-photolysed with (**1**) under the standard conditions, showed that, if it had been formed, it would have survived.

*Synthesis of Deuteriated Compounds and Stereochemical Assignments.*—Replacement of  $\text{H}_2$  by  $^2\text{H}_2$  in the synthesis of (**1**) (Scheme 3) led to (**7d**) and (**1d**). Even this constrained bicyclic olefin showed the presence of  $[^2\text{H}_3]$ -material in the product by mass spectrometry (m.s.) and bridgehead deuterium by  $^2\text{H}$  n.m.r., when palladium on carbon was used as the catalyst. However, Wilkinson's catalyst gave (**7d**) containing no  $[^2\text{H}_3]$ -material and no bridgehead deuterium.

The deuteriated position and its geminal partner were readily discerned in the 220 MHz  $^1\text{H}$  n.m.r. spectra of both (**1d**) and (**7d**), so their relative stereochemistry could be assigned by lanthanide induced shift studies which were carried out for both (**1h**) and (**1d**) and (**7h**) and (**7d**). It was clear that addition of deuterium to (**6**) had taken place from the face of the double bond *syn* to the heteroatoms. This is consistent with the results of Dyllick-Brenzinger<sup>13</sup> on the conformational analysis of

**Table 1.** Isotopic distribution in products from deazetation of (**1d**) determined by  $^2\text{H}$  n.m.r.

Product	$\delta$ (assignment)	Mode of deazetation		
		Heat (170 °C)	$h\nu$ (direct)	$h\nu$ (sensitised)
Octadiene ( <b>2</b> )	5.07 ( <i>E</i> )	88	81	67
	5.13 ( <i>Z</i> )	12	19	13
Bicyclo-octane ( <b>3</b> )	1.84 ( <i>exo</i> )	99	90	73
	1.68 ( <i>endo</i> )	<1	10	27

bicyclo[4.2.2]decenes, which implied a conformer in which one of the methylenes of the four carbon bridge would prevent access to the *anti*-face of the double bond.

Samples of (**7d**) from deuterogenation sometimes contained a few percent of the unsaturated precursor (**6**) which could not be separated by crystallisation or chromatography. For synthesis, such samples were carried through to the azo compound directly, but for analysis, they were purified by treatment with hydrogen peroxide in formic acid, which converted the precursor (**6**) into its epoxide, preparative thin layer chromatography, and repeated recrystallisation. Quantitative analysis was then by m.s., which showed for a typical sample 94.2%  $^2\text{H}_2$ , 5.2%  $^2\text{H}_1$ , 0.6%  $^2\text{H}_0$ , and by  $^2\text{H}$  n.m.r., which showed only one signal for any sample of (**1d**) or (**7d**). Upper limits on the magnitude of the *anti*-deuterium signal, by comparison with the  $^{13}\text{C}$  satellites were <2% for (**1d**) and <1% for (**7d**).

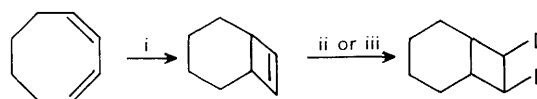
Catalytic hydrogenation of bicyclo[4.2.0]oct-7-ene<sup>14</sup> afforded the bicyclo-octane required for comparison above (Scheme 4). Reduction, instead, with deuteriodi-imide gave deuteriated bicyclo-octane<sup>15</sup> in which the deuteriated position and its geminal partner were readily discerned in the  $^1\text{H}$  n.m.r. spectrum. The  $^2\text{H}$  n.m.r. spectrum showed two signals at  $\delta$  1.84 and 1.67, in the ratio of 82:18. Assuming preferential reaction on the convex side of the molecule, *i.e.* the *exo*-face of the double bond, the signal at 1.84 is due to the *exo*-7,8-positions.

Hydroboration<sup>16</sup> of octa-1,7-diyne using bis(1,2-dimethylpropyl)borane followed by deuteronolysis with [ $O$ - $^2\text{H}_1$ ]acetic acid gave [ $1,8$ - $^2\text{H}_2$ ]octa-1,7-diene in which one of the doublets near  $\delta$  5.0 was almost absent and in which the remaining doublet showed a coupling constant of 17 Hz, showing it to be due to the terminal *cis*-protons. Quantitative analysis was by  $^2\text{H}$  n.m.r. which showed only one signal and none, above the level of the  $^{13}\text{C}$  satellites, at the shift expected for a *cis*-deuterium (<1%).

$^2\text{H}$  N.m.r. Analysis of the Hydrocarbon Products from (**1d**) and Control Experiments.—Deazetation of (**1d**) led to the same three products as for (**1h**). Separation by preparative g.c. and analysis by  $^2\text{H}$  n.m.r. gave the results for (**2**) and (**3**) shown in Table 1. In every case, (**4**) showed the deuterium equally distributed between the allylic and saturated positions, with none at the vinyl position.

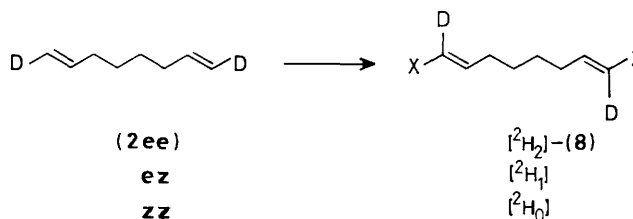
In each case, (**2**) was formed with less retention of configuration than (**3**), which gave cause for concern that the diene was undergoing secondary *cis-trans* isomerisation in the reaction. Subjection of (**1h**) plus (**2ee**) (*ca.* 10 mol%) to all three modes of reaction, followed by  $^2\text{H}$  n.m.r. analysis of the hydrocarbons, showed no deuterium in the *Z*-position or elsewhere, ruling out *cis-trans* isomerisation and also 2 + 2 cycloaddition to form (**3**) or any other secondary reaction of the diene.

Complete Analysis of the Stereochemistry of the Diene.—The  $^2\text{H}$  n.m.r. analysis could only give the ratio of total *E*- to total *Z*-deuterium in the diene, but the proportions of the *E,E*-, *E,Z*-, and *Z,Z*-isotopomers were not accessible by direct spectroscopic

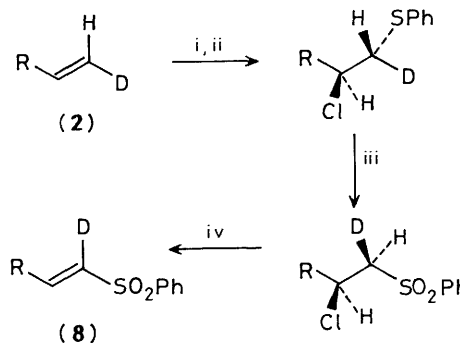


**Scheme 4.** Reagents: *i*,  $h\nu$ ; *ii*,  $\text{H}_2$ , Pd/C, L = H; *iii*,  $\text{N}_2\text{D}_2$ , L = D

methods such as n.m.r. ( $^1\text{H}$  or  $^2\text{H}$ ) or m.s. However, they could be determined by an indirect chemical method combined with m.s., since a stereospecific substitution reaction in which *E*-deuterium is retained and *Z*-deuterium is lost would translate stereochemical information into deuterium content (Scheme 5).



**Scheme 5.**



**Scheme 6.** Reagents: *i*, PhSCl,  $\text{CH}_2\text{Cl}_2$ ; *ii*, Heat, DMSO; *iii*, mCPBA,  $\text{CH}_2\text{Cl}_2$ ; *iv*, NaOAc, DMSO

This was achieved for X =  $\text{SO}_2\text{Ph}$  by the sequence shown in Scheme 6:<sup>17</sup> *i*, anti-Markovnikov addition,<sup>18</sup> *ii*, isomerisation to the bis-Markovnikov adduct,<sup>18</sup> *iii*, oxidation to the sulphone, and *iv*, elimination of HCl. This was followed by multiple recrystallisations, first to constant melting point, then to constant integration of the 220 MHz n.m.r., and finally to constant m.s., with three concordant runs on different days. This was to remove any *cis*-vinyl sulphone or 2-sulphonyloctadiene from the anti-Markovnikov adduct, either of which would throw out the analysis. Whether or not episulphonium ions are intermediates in the first two steps is debatable,<sup>19</sup> but overall *trans*-addition would certainly be expected. For the elimination step, the combination of weak base and dipolar aprotic solvent was chosen because it had been shown in other cases<sup>20</sup> to favour *trans* rather than *gauche* elimination. These expectations were confirmed experimentally by subjecting (**2ee**) (>99% *E* by  $^2\text{H}$  n.m.r.) to this procedure. It afforded (**8d<sub>2</sub>**) without loss of deuterium.

In practice, crude mixtures of  $\text{C}_8\text{H}_{14}$  products were used to avoid any possibility of isotopic fractionation on preparative g.c. Also, since octadiene gave *M* - 1 and *M* - 2 fragments on electron impact (e.i.) and both *M* + 1 and *M* - 1 using methane chemical ionisation (c.i.), the deuterium analysis of the diene was carried out on the crude bis(chloro sulphide) from step (*i*) using e.i.m.s. This seemed satisfactory, since the addition was quantitative, so there was no opportunity for fractionation

**Table 2.** Products and stereochemistry from deazetation of (1)

Mode of deazetation	Heat (170 °C)	<i>hν</i> (direct)	<i>hν</i> (sensitised)
Product percentages:			
Octadiene	47	78	74
Bicyclo-octane	35	17	20
Cyclo-octene	18	5	6
Mass spectrometric results:			
% (2ee)	79	64	43
(2ez)	20	33	53
(2zz)	1	3	4
net % <i>E</i> -d	89	81	69
<sup>2</sup> H N.m.r. results:			
<i>E</i> : <i>Z</i> - <sup>2</sup> H in (2)	88:12	81:19	67:13
<i>exo</i> : <i>endo</i> - <sup>2</sup> H in (3)	>99: 1	90:10	73:27

of isotopes, and octadiene was the only product which could react with the sulphenyl chloride to give a bis-adduct showing peaks in the relevant region of the m.s. Deuterium analysis of the disulphone (8) was by ammonia c.i.m.s. For both, clean molecular ion regions were obtained in high intensity, and the peak ratios for unlabelled material were in good agreement with those calculated from standard values of natural abundances. For labelled material, correction for natural abundance of heavy isotopes was by a least squares fitting of the <sup>2</sup>H<sub>0</sub>:<sup>2</sup>H<sub>1</sub>:<sup>2</sup>H<sub>2</sub> ratios to as many peaks as possible in the molecular ion group.

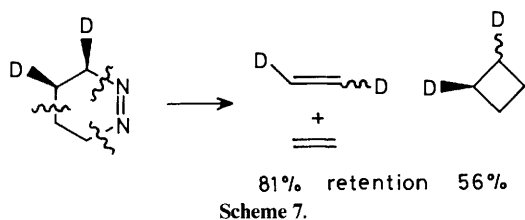
Subjection of samples of (2) from deazetation of (1) to this procedure led to the disulphone (8) for which the deuterium content was determined by m.s. as above. Correction for small amounts of <sup>2</sup>H<sub>0</sub> and <sup>2</sup>H<sub>1</sub> material in the diene gave the stereochemical results indicated in Table 2. It is worth noting that the good agreement between the values for the %*E*-deuterium in (2) determined directly by <sup>2</sup>H n.m.r. and indirectly by chemistry plus m.s. further supports the validity of the analysis.

## Discussion

*Validity of the Biradical Mechanism.*—The results from deazetation of azo compounds have generally been discussed in terms of biradical intermediates, unless the stereochemistry, or some other unusual feature, requires a more complex explanation,<sup>21</sup> with singlet-triplet differences being attributed to a spin correlation effect<sup>22</sup> (s.c.e.) on the lifetime of the biradical.

For example, in a parallel study of DBO,<sup>7</sup> the unexpected stereochemistry led us to postulate one bond cleavage followed by conformational changes in the diazenyl biradical, but this is not needed to explain the results presented here.

Again, in their studies of the thermolysis of monocyclic six-membered ring azo compounds, Dervan<sup>23</sup> found that the cleavage to two olefins was more stereospecific than the coupling to form cyclobutanes (Scheme 7). They explained this in terms of a competition between a concerted three bond cleavage leading to olefins stereospecifically, and a biradical



process leading to both cleavage and coupling with the same, lower, stereospecificity, *via* a partially stereorandomised biradical. This is actually the reverse of the results presented here, in which the coupling is more stereospecific. While there may be such a concerted component in our thermal reaction, it cannot account for the observed difference between the cleavage and coupling.

Similarly, the double inversion, which is characteristic of azo compounds containing the DBH unit,<sup>2-6</sup> is not observed, so none of the special mechanisms postulated to account for this need apply in the present case. Thus, neither the recoil mechanism,<sup>4</sup> nor the concerted loss of nitrogen and C-C bond formation by a  $\sigma_2 + \sigma_2$  process (9),<sup>2</sup> nor backside attack (S<sub>H</sub>i) in a diazenyl biradical (10)<sup>3</sup> need be involved.



(9)

(10)

The results presented in Table 2 are, in fact, typical of what is observed in deazetation of azo compounds through biradical intermediates, with a small loss of stereochemistry in the thermal reaction and a much greater loss of stereochemistry in the triplet sensitised process.<sup>22</sup> Thus, while we have not ruled out alternatives, a 1,4-biradical is the most economical explanation for our results, and is assumed in the discussion below.

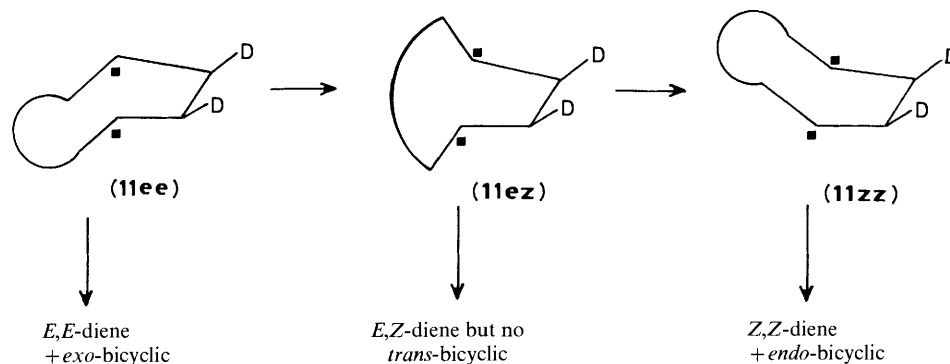
*Stereochemistry.*—In our preliminary communication,<sup>8</sup> which concerned the thermal reaction, we postulated a Scheme which showed partially equilibrating conformations of cyclo-octane-1,4-diyl (11), but in which we deliberately avoided drawing the conformation of the four carbon chain (see below). We showed (11) being generated in a conformation (11ee) which can lead to products with complete retention of configuration or relax to conformation (11ez). Cleavage of this leads to (2ez), but coupling could only lead to the *trans*-bicyclo-octane, which is not observed. Since *endo*-(3d) is also not observed, it would seem that (11zz) is not populated, leading to the prediction that (2zz) should not be observed either.

While it was not possible to test this prediction using <sup>2</sup>H n.m.r. alone, the combination of chemistry and m.s. described above made possible the necessary discrimination, showing that all the *Z*-deuterium was in (2ez) and that (2zz) was absent, fully confirming the prediction.

The experimental results in Table 2 were dissected into the percentages of cleavage and coupling coming from each conformation of the biradical, which are shown in Table 3.

Firstly, for the thermolysis, the proportion of (2zz) is low, as implied by Scheme 8. Thus, for the thermally generated biradical, conformation (11zz) is, indeed, not populated to any significant extent, or, more strictly, no products are formed from it.

Secondly, the stereospecificity of the sensitised photolysis is lower than that of the thermolysis. Thus the singlet biradical from thermolysis forms 88% of its products from the conformation in which it is born (11ee) and <1% from (11zz), whereas for the triplet biradical, the initial conformation gives only 50% of the products, and 9% are formed from (11zz). This is most simply explained by a normal spin correlation effect which extends the lifetime, and permits greater exploration of conformation space. While some recent reports<sup>24</sup> suggest that triplet biradicals react preferentially through regions of high inter-system crossing efficiency, this is not obviously so, in this case.



Scheme 8.

Table 3. Percentage of (2) + (3) from conformations of (11)

Mode of deazetation	Heat (170 °C)	<i>hν</i> (direct)	<i>hν</i> (sensitised)
From (11ee)	88	69	50
(11ez)	12	27	41
(11zz)	0	4	9

Thirdly, the direct photolysis lies in between the thermolysis and direct photolysis in its degree of stereospecificity. This has been a common observation since the classic study of Bartlett and Porter.<sup>22</sup> It may be due to a number of factors, unrelated to the intrinsic behaviour of the biradical, such as the difference in temperature at which the thermal and photochemical reactions are carried out, or to a certain amount of intersystem crossing in the azo compound leading to a triplet biradical and thus products with lower stereospecificity.

**Conformational Analysis of the Biradical.**—We have used Molecular Mechanics<sup>25</sup> to study the conformations of cyclo-octanediyI (11). Our model is very simple, using the parameters proposed by Allinger<sup>26</sup> for carbon centred radicals and considering the two radical centres as independent, thus neglecting, among other factors, multiplicity.

We found several minima within 10 kJ mol<sup>-1</sup> of the global minimum, and classified them according to whether *cis*-deuteriation would give rise to (2ez) (*EZ* type) or to (2ee) or (2zz) (*EE/ZZ* type). The global minimum was of the *EZ* type but there was an *EE/ZZ* type only 5.5 kJ mol<sup>-1</sup> higher in energy. It may be significant that even for the triplet biradical, which clearly has more time to relax, only 9% of the products are formed from (11zz) which is predicted to be uphill from (11ez). While there is likely to be little quantitative significance in the calculation, it supports our analysis in terms of this type of conformational equilibration.

The finding of several low energy minima, of each type, differing mainly in the torsional angles about the four carbon chain confirms the wisdom of not specifying the conformation of this part of the molecule in detail in Scheme 8.

**Conclusion.**—We have developed and verified an experimental protocol which can be applied to as little as 10 mg of substrate, and which will extend the usefulness of deuterium as a stereochemical label. In general, methyl has a significant steric bulk, and also an electronic effect, so, while methyl labels sometimes make analysis easier, deuterium is to be preferred in principle since it represents the smallest possible perturbation. The particular problem addressed here has been noted by others.<sup>27</sup>

We have applied the method to a system which appears to be straightforward and uncontroversial, where a model involving a biradical intermediate and a spin correlation effect can account for all the data. We have pushed this simple model a little further by applying Molecular Mechanics to the biradical to give results which fit well with the experimental data. It seems appropriate to use such a model when it fits and only look for alternatives when it fails, as we had to do in the case of our parallel study of DBO.

### Experimental

<sup>1</sup>H N.m.r. spectra were recorded on a Perkin-Elmer R34 at 220 MHz. Chemical shifts are reported in p.p.m. downfield from internal tetramethylsilane. <sup>2</sup>H N.m.r. spectra were recorded on a Bruker WH400 machine at 61.4 MHz. Chemical shifts are reported relative to internal CDCl<sub>3</sub> = 7.24 p.p.m. I.r. spectra were recorded on a Perkin-Elmer 680B machine and u.v. spectra were recorded on a Perkin-Elmer 552. Mass spectra (m.s.) were recorded on a Kratos MS80 instrument. Analytical gas chromatography (g.c.) was performed using packed columns and nitrogen as carrier on a Pye Unicam 204, or using capillary columns and helium as carrier on a Carlo Erba 2450TP, fitted with a Grob type split/splitless injector. Preparative g.c. was performed using the latter instrument fitted with 4 or 10 mm diameter columns. M.p.s were uncorrected. Elemental analyses were carried out by Butterworth Laboratories, Teddington, Middlesex. Light petroleum refers to the fraction b.p. 30–40 °C purified by extraction with concentrated sulphuric acid, washing with water, passage through a column of alumina, and distillation through a 500 × 30 mm Vigreux column. Alumina refers to alumina activity I for chromatography.

**4-Phenyl-2,4,6-triazatricyclo[5.4.2.0<sup>2,6</sup>]tridec-12-ene-3,5-dione.**—4-Phenyl-1,2,4-triazolidine-3,5-dione (4.40 g, 25 mmol) in ethyl acetate (25 cm<sup>3</sup>) was stirred in an ice-bath during the dropwise addition (30 min) of *t*-butyl hypochlorite (5.0 cm<sup>3</sup>, 43 mmol). Stirring was continued 1 h at room temperature, when the red solution was concentrated under reduced pressure and redissolved in ethyl acetate (25 cm<sup>3</sup>). Cyclo-octa-1,3-diene was added dropwise until the red colour was discharged, when a precipitate formed. This was filtered off to give 4-phenyl-2,4,6-triazatricyclo[5.4.2.0<sup>2,6</sup>]tridec-12-ene-3,5-dione (5.40 g, 76%), m.p. 202–203 °C (lit.,<sup>28</sup> 203–204 °C).

**4-Phenyl-2,4,6-triazatricyclo[5.4.2.0<sup>2,6</sup>]tridecane-3,5-dione.**—4-Phenyl-2,4,6-triazatricyclo[5.4.2.0<sup>2,6</sup>]tridec-12-ene-3,5-dione (17.10 g, 60 mmol), 10% palladium on carbon (0.54 g), and ethyl acetate (300 cm<sup>3</sup>) were stirred under an atmosphere of hydrogen in a conventional hydrogenator, until uptake of hydrogen ceased. The mixture was filtered through Celite and concentrated under

reduced pressure to give 4-phenyl-2,4,6-triazatricyclo[5.4.2.0<sup>2,6</sup>]tridecane-3,5-dione (16.70 g, 97%), m.p. 174–176 °C (lit.,<sup>28</sup> 178–180 °C).

7,8-Diazabicyclo[4.2.2]dec-7-ene.—Using the general procedure of Adam,<sup>29</sup> 4-phenyl-2,4,6-triazatricyclo[5.4.2.0<sup>2,6</sup>]tridecane-3,5-dione (1.71 g, 6 mmol) gave, after sublimation (100 °C, 20 mmHg), 7,8-diazabicyclo[4.2.2]dec-7-ene (0.41 g, 50%), m.p. 94–95 °C (lit.,<sup>30</sup> 93–95 °C).

[12,13-<sup>2</sup>H<sub>2</sub>]-4-Phenyl-2,4,6-triazatricyclo[5.4.2.0<sup>2,6</sup>]tridecane-3,5-dione.—4-Phenyl-2,4,6-triazatricyclo[5.4.2.0<sup>2,6</sup>]tridec-12-ene-3,5-dione (5.08 g, 18.0 mmol), Wilkisons catalyst (0.25 g), toluene (50 cm<sup>3</sup>), and ethyl acetate (50 cm<sup>3</sup>) were stirred 18 h under an atmosphere of deuterium. The mixture was filtered and concentrated under reduced pressure and the residue recrystallised from methanol to give [12,13-<sup>2</sup>H<sub>2</sub>]-4-phenyl-2,4,6-triazatricyclo[5.4.2.0<sup>2,6</sup>]tridecane-3,5-dione (3.93 g, 76%). The product showed the appropriate differences in its <sup>1</sup>H n.m.r. spectrum, but also the presence of a trace of the unsaturated precursor which could not be removed by recrystallisation or chromatography. The sample was pure enough for synthesis of the azo compound, but not for deuterium analysis.

Purification and Analysis of [12,13-<sup>2</sup>H<sub>2</sub>]-4-Phenyl-2,4,6-triazatricyclo[5.4.2.0<sup>2,6</sup>]tridecane-3,5-dione.—[12,13-<sup>2</sup>H<sub>2</sub>]-4-Phenyl-2,4,6-triazatricyclo[5.4.2.0<sup>2,6</sup>]tridecane-3,5-dione (0.10 g, 0.35 mmol) in formic acid (0.5 cm<sup>3</sup>) in an n.m.r. tube was treated with hydrogen peroxide (30%; 0.2 cm<sup>3</sup>) and heated at 60 °C until n.m.r. analysis showed disappearance of the traces of vinyl protons. The mixture was poured into water and extracted with dichloromethane, and the extract was dried and concentrated under reduced pressure to give crude product. This was subjected to preparative t.l.c. on silica gel, eluting with 20% acetone in light petroleum. The faster running band was recrystallised from methanol–chloroform; δ<sub>D</sub>(CHCl<sub>3</sub>) 2.18 only (>99%); m.s., after correction for natural abundance of heavy isotopes, showed <sup>2</sup>H<sub>0</sub> (0.6%), <sup>2</sup>H<sub>1</sub> (5.2), <sup>2</sup>H<sub>2</sub> (94.2).

[9,10-<sup>2</sup>H<sub>2</sub>]-7,8-Diazabicyclo[4.2.2]dec-7-ene.—[12,13-<sup>2</sup>H<sub>2</sub>]-4-Phenyl-2,4,6-triazatricyclo[5.4.2.0<sup>2,6</sup>]tridecane-3,5-dione was converted as above into the labelled azo compound, which showed the appropriate differences in the <sup>1</sup>H n.m.r.; δ<sub>D</sub>(CHCl<sub>3</sub>) 1.70 only (>98%).

Normal Work-up Procedure for C<sub>8</sub> Hydrocarbons.—The light petroleum solution from synthetic or exploratory reactions was passed down a column of alumina (200 × 10 mm), which was flushed with more light petroleum. This removed water, by-products, sensitiser, residual azo compound, any oxidation products, and essentially everything except C<sub>8</sub> hydrocarbons. The eluant was concentrated through a 500 × 30 mm Vigreux column or a 200 × 10 mm column packed with glass helices, depending on the volume. The residue was analysed by g.c., <sup>1</sup>H or <sup>2</sup>H n.m.r., or separated by preparative g.c. for further analysis as appropriate.

cis-Bicyclo[4.2.0]octane.—Cyclo-octa-1,3-diene (7.00 g) in light petroleum (700 cm<sup>3</sup>) was irradiated under nitrogen, in a quartz immersion well apparatus, using a 500 W medium-pressure mercury lamp for 15 days after which time g.c. analysis showed almost complete conversion into a single product. The solution was filtered through a short column of silica gel to remove polymer and oxidation products. Palladium on carbon (5%; 0.1 g) was added, and the solution was stirred for 18 h under an atmosphere of hydrogen. The mixture was filtered through Celite and concentrated first through a 500 × 30 mm

Vigreux column, and then through a 200 × 10 mm helix packed column to give a residue which was flash distilled (b.p. <160 °C). Preparative g.c. (30% SE30) gave bicyclo-octane (1.12 g, 16%; >99% pure by g.c.); δ<sub>H</sub>(CDCl<sub>3</sub>) 1.15–1.75 (10 H, m), 1.83 (2 H, m), and 2.28 (2 H, br s); δ<sub>C</sub>(CDCl<sub>3</sub>) 23.0, 24.7, 28.2, and 33.3.

[7,8-<sup>2</sup>H<sub>2</sub>]-cis-Bicyclo[4.2.0]octane.—The above experiment was repeated, omitting the hydrogenation step, to afford bicyclo[4.2.0]oct-7-ene (2.63 g, 38%), after preparative g.c., which was stored over calcium chloride for the next step; δ<sub>H</sub>(CCl<sub>4</sub>) 1.30–1.75 (8 H, m), 2.84 (2 H, br t), and 6.07 (2 H, br s).

Bicyclo[4.2.0]oct-7-ene (1.08 g, 10 mmol), ethan[<sup>2</sup>H<sub>1</sub>]ol (10 cm<sup>3</sup>) and potassium azodicarboxylate (3.88 g, 20 mmol) were stirred under nitrogen during the slow addition of [<sup>O-2</sup>H<sub>1</sub>]-acetic acid (2.5 cm<sup>3</sup>). The mixture was poured into aqueous sodium hydrogen carbonate and extracted with light petroleum. The extract was washed with water and after work-up and preparative g.c. gave [7,8-<sup>2</sup>H<sub>2</sub>]-cis-bicyclo[4.2.0]octane (0.80 g, 73%); δ<sub>D</sub>(CHCl<sub>3</sub>) 1.84 (82%) and 1.68 (18%).

trans-Bicyclo[4.2.0]octane.—trans-Cyclohexane-1,2-dicarboxylic anhydride (3.08 g, 20 mmol) in THF (30 cm<sup>3</sup>) was added dropwise to a suspension of lithium aluminium hydride (1.60 g, 42 mmol) in THF (20 cm<sup>3</sup>) stirred under nitrogen. Stirring was continued 0.5 h at room temperature and 2 h at reflux. The mixture was cooled in an ice-bath and a ground mixture of sodium sulphate decahydrate and Celite was added to it; the mixture was then filtered and the residue washed with ether. The combined filtrate and washings were concentrated under reduced pressure to yield crude trans-cyclohexane-1,2-diyl-dimethanol (2.62 g, 91%), pure by n.m.r.

The diol (2.62 g, 18 mmol) in anhydrous pyridine (10 cm<sup>3</sup>) was stirred and cooled in ice during the slow addition of toluene-*p*-sulphonyl chloride (7.63 g, 40 mmol) in pyridine (15 cm<sup>3</sup>). Stirring was continued at room temperature 1 h after which the mixture was poured onto crushed ice to afford a solid which was filtered off and recrystallised from MeOH (4.76 g, 58%), m.p. 106–108 °C.

The ditosylate (4.76 g, 10.5 mmol), sodium iodide (3.45 g, 23 mmol), and acetone (25 cm<sup>3</sup>) were stirred 60 h at room temperature. The mixture was filtered, concentrated under reduced pressure, and the residue taken up in light petroleum; the solution was then refiltered and reconcentrated under reduced pressure to afford a product which showed a trace of residual tosylate from its <sup>1</sup>H n.m.r. spectrum. Filtration chromatography over silica gel (80 × 20 mm), eluting with light petroleum gave the di-iodide (3.10 g, 81%), pure by n.m.r.

The di-iodide (3.10 g, 8.5 mmol) in anhydrous ether (10 cm<sup>3</sup>) was stirred under nitrogen during the addition of butyl-lithium [*ca.* 1 mol dm<sup>-3</sup>, in light petroleum (10 cm<sup>3</sup>)]. After 10 min, t.l.c. analysis showed the absence of di-iodide. The mixture was heated for 1 h under reflux, cooled, quenched with water (0.5 cm<sup>3</sup>), passed through an alumina column, concentrated through a helix-packed column, and short path distilled (b.p. <160 °C). Preparative g.c. gave trans-bicyclo[4.2.0]octane<sup>31</sup> (0.43 g, 46%; >99% by g.c.); δ<sub>H</sub>(CCl<sub>4</sub>) 1.25 (4 H, m), 1.45 (2 H, m), 1.56 (2 H, m), 1.70 (4 H, m), and 1.90 (2 H, br s); *m/z* 110 (*M*<sup>+</sup>, 6%), 95 (9), 82 (46), 81 (45), 69 (37), 68 (48), and 67 (100).

[1,8-<sup>2</sup>H<sub>2</sub>]Octa-1,7-diene.—A solution of borane–dimethyl sulphide complex (4.0 cm<sup>3</sup>, 40 mmol) in anhydrous diglyme (17.6 cm<sup>3</sup>) was stirred under nitrogen at 0–5 °C (ice-bath) during the dropwise addition of 2-methylbut-2-ene (8.5 cm<sup>3</sup>, 80 mmol). Stirring was continued at room temperature for 2 h after which the mixture was recooled to 0–5 °C and octa-1,7-diene (1.60 cm<sup>3</sup>, 12.5 mmol) was added. Stirring was continued at

room temperature 2 h after which the mixture was recooled to 0–5 °C and deuterium oxide (0.5 cm<sup>3</sup>) and [*O*-<sup>2</sup>H<sub>1</sub>]acetic acid (15 cm<sup>3</sup>) were added. The mixture was heated under reflux for 2 h and then poured into water and extracted with light petroleum. The extract was washed with water, filtered through alumina, concentrated through a helix-packed column, and short path distilled (b.p. < 160 °C). Preparative g.c. gave [1,8-<sup>2</sup>H<sub>2</sub>]octa-1,7-diene (0.19 g, 14%) and integration of the vinyl regions in its <sup>1</sup>H n.m.r. showed 86.4% incorporation of deuterium; δ<sub>D</sub>(CCl<sub>4</sub>) 5.07 (>99%).

*General Procedure for Photochemical and Thermal Reactions.*—The labelled or unlabelled azo compound in light petroleum was irradiated with a 500 W medium-pressure mercury lamp for the direct photolysis, the reaction being monitored by u.v. spectroscopy by the disappearance of the azo ππ\* band at 386 nm. For sensitised photolysis, 3-methoxyacetophenone was added as sensitiser, and irradiation was in a Rayonet apparatus fitted with '300 nm' lamps. Careful consideration of the u.v. spectra and lamp output showed that essentially all the light was absorbed by the sensitiser, and none by the azo compound. Thermal reactions were carried out in Carius tubes sealed under nitrogen and containing 4-t-butylpyrocatechol (10–20 mg) as a radical inhibitor.

*Preparative Pyrolysis of 7,8-Diazabicyclo[4.2.2]dec-7-ene.*—7,8-Diazabicyclo[4.2.2]dec-7-ene (0.25 g) and 4-t-butylpyrocatechol (10 mg) in light petroleum (25 cm<sup>3</sup>) in a Carius tube were heated for 69 h at 160–70 °C. Work-up, as above, and preparative g.c. gave three fractions: octa-1,7-diene (60 mg, 30%), *cis*-bicyclo-octane (46 mg, 23%), and cyclo-octene (28 mg, 14%). Each was spectroscopically and chromatographically identical with authentic material.

*Preparative Pyrolysis of [9,10-<sup>2</sup>H<sub>2</sub>]-7,8-Diazabicyclo[4.2.2]dec-7-ene.*—The experiment described above for the unlabelled compound was repeated, using the labelled compound (0.25 g), to afford the same three fractions, 64, 48, and 26 mg respectively, which were characterised by g.c. and <sup>1</sup>H n.m.r. and analysed by <sup>2</sup>H n.m.r.

*Preparative Direct Photolysis of [9,10-<sup>2</sup>H<sub>2</sub>]-7,8-Diazabicyclo[4.2.2]dec-7-ene.*—[9,10-<sup>2</sup>H<sub>2</sub>]-7,8-Diazabicyclo[4.2.2]dec-7-ene (150 mg) in light petroleum (25 cm<sup>3</sup>) was irradiated for 51 h under nitrogen. Work-up, addition of unlabelled bicyclo-octane and cyclo-octene as carriers, and preparative g.c. gave three fractions which were analysed by <sup>2</sup>H n.m.r.

*Preparative Sensitised Photolysis of [9,10-<sup>2</sup>H<sub>2</sub>]-7,8-Diazabicyclo[4.2.2]dec-7-ene.*—[9,10-<sup>2</sup>H<sub>2</sub>]-7,8-Diazabicyclo[4.2.2]dec-7-ene (100 mg), 3-methoxyacetophenone (80 mg), and light petroleum (20 cm<sup>3</sup>) were irradiated for 16 days under nitrogen. Work-up, addition of unlabelled carriers, and preparative g.c. gave three fractions which were analysed by <sup>2</sup>H n.m.r.

*Control Experiments using trans-Bicyclo[4.2.0]octane.*—A stock solution was made, containing *trans*-bicyclo-octane (10 mm<sup>3</sup>) and cyclo-octane (10 mm<sup>3</sup>) as internal standard in cyclohexane (10 cm<sup>3</sup>). 7,8-Diazabicyclo[4.2.2]dec-7-ene (10 mg) was dissolved in part of this (1 cm<sup>3</sup>), and portions (0.1 cm<sup>3</sup>) were sealed under nitrogen in four Pyrex tubes. Two were heated 52 h at 165 °C and two were used as controls. G.c. analysis showed the same ratio of *trans*-bicyclo-octane to cyclo-octane in all four tubes. Similar experiments were performed for direct and sensitised photolysis.

*Control Experiments using (E,E)-[1,8-<sup>2</sup>H<sub>2</sub>]Octa-1,7-diene.*—Light petroleum (20 cm<sup>3</sup>) containing (E,E)-[1,8-<sup>2</sup>H<sub>2</sub>]octa-1,7-

diene (25 mm<sup>3</sup>), 7,8-diazabicyclo[4.2.2]dec-7-ene (250 mg), and 4-t-butylpyrocatechol (10 mg) was sealed in a Carius tube which was then heated 72 h at 170 °C. Work-up and <sup>2</sup>H n.m.r. analysis showed only one signal, at δ 5.07. Similar experiments were performed for direct and sensitised photolysis.

(E,E)-1,8-Bisphenylsulphonylocta-1,7-diene.—Benzene-sulphenyl chloride was made from *N*-chlorosuccinimide (1.34 g, 10 mmol), thiophenol (1.10 g, 10 mmol), and dichloromethane (10 cm<sup>3</sup>) by the procedure of Fuchs.<sup>17</sup> Octa-1,7-diene was added dropwise until the orange colour was discharged. The mixture was then concentrated under reduced pressure, stirred with carbon tetrachloride (20 cm<sup>3</sup>), filtered, and reconcentrated to give a pale yellow oil. At this stage, n.m.r. analysis suggested a mixture of anti-Markovnikov and Markovnikov adducts.

The crude sample from above was dissolved in dry dimethyl sulphoxide (9 cm<sup>3</sup>) and heated at 100 °C for 1.5 h when n.m.r. analysis suggested the reaction was complete. The mixture was poured into iced water (10 cm<sup>3</sup>) which was then extracted with dichloromethane. The organic phase was washed with water, dried (MgSO<sub>4</sub>), and concentrated under reduced pressure to afford a yellow oil (2.22 g). This was dissolved in dichloromethane (20 cm<sup>3</sup>), stirred in an ice-bath, treated with 3-chloroperoxybenzoic acid (85%; 4.50 g) over 0.5 h, stirred 1 h at room temperature, and treated with saturated aqueous sodium metabisulphite (10 cm<sup>3</sup>) and sodium hydrogen carbonate (10 cm<sup>3</sup>). The aqueous phase was separated and extracted with dichloromethane and the combined organic phases were dried (MgSO<sub>4</sub>) and concentrated under reduced pressure to afford a pale yellow oil (2.44 g). This was dissolved in dimethyl sulphoxide (10 cm<sup>3</sup>) and anhydrous sodium acetate (1.64 g) was added; the mixture was then stirred at room temperature for 2 h after which it was poured into iced water (20 cm<sup>3</sup>). The mixture was extracted with dichloromethane, and the combined organic phases were dried (MgSO<sub>4</sub>) and concentrated under reduced pressure to afford (E,E)-1,8-bisphenylsulphonylocta-1,7-diene as a pale yellow oil, which crystallised with time (2.82 g, 72%, based on thiophenol), m.p. 147–148 °C (from methanol–chloroform) (Found: C, 61.75; H, 5.75; S, 16.3. C<sub>20</sub>H<sub>22</sub>O<sub>4</sub>S<sub>2</sub> requires C, 61.49; H, 5.75; S, 16.43%; ν<sub>max</sub>(CHCl<sub>3</sub>) 1 625 (m, C=C) and 1 317 and 1 143 (s, SO<sub>2</sub>); δ<sub>H</sub>(CDCl<sub>3</sub>) 1.49 (4 H, br t, *J* 6 Hz), 2.25 (4 H, br q, *J* 6 Hz), 6.33 (2 H, dt, *J* 15, 1.5 Hz), 6.95 (2 H, dt, *J* 15, 7 Hz), 7.58 (6 H, m), 7.88 (4 H, d, *J* 8 Hz); *m/z* (e.i.) 390 (*M*<sup>+</sup>, 1%), 249 (21), 195 (19), 143 (18), 125 (78), 107 (100), 77 (64); *m/z* (c.i., CH<sub>4</sub>) 394 (1%), 393 (4), 392 (9), 391 (39), and 390 (0).

*Analysis of [1,8-<sup>2</sup>H<sub>2</sub>]Octa-1,7-diene from Deazetation.*—In some cases, the diene was isolated by preparative g.c. and subjected to the above procedure, but generally, the concentrated solution of hydrocarbon products, obtained as in the 'general procedure' above was titrated with a slight excess of benzenesulphenyl chloride until the yellow colour persisted. The adduct was converted into the bis-sulphone (8) by the above procedure with avoidance of any crystallisations which might fractionate regioisomers or diastereoisomers and thus fractionate deuterium. The final product was recrystallised from methanol–chloroform to constant m.p., then to constant integration of the <sup>1</sup>H n.m.r., and then analysed by m.s. Recrystallisation and m.s. analysis were repeated until consistent data were obtained. There was no difference between runs which used isolated diene and crude hydrocarbons.

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