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THE SOLUTION PHOTOCHEMISTRY OF SUBSTITUTED CYCLOHEPTATRIENES

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Abstract—The solution photochemistry of several ethoxycarbonyl- and ethoxycarbonyl-methoxy-substituted cycloheptatrienes has been investigated. The results have been used to analyse the directional specificity of ring-closure and 1,7-hydrogen migration reactions. This specificity is interpreted in terms of polarisation within the S_1 state which undergoes either (a) allowed photochemical reactions to give the observed products directly or (b) isomerisation to a *trans, cis, cis*-cyclohepatriene which then reacts via allowed ground-state processes. In at least two instances the directional specificity of the ring-closure reaction is wavelength dependent and this is attributed to the differing reactivities of the S_1 and S_2 states.

Cycloheptatrienes undergo three types of light-induced isomerisation, namely aromatisation to toluene derivatives, 1,7-hydrogen shifts and ring closure to bicyclo(3.2.0)hepta-2,6-dienes.[1] Only the latter two processes are important in solution and our attention was originally attracted to them due to (a) the apparent directional specificity of the ring closure reaction where two products were possible[2-8] and (b) the apparent lack of photoreactivity of the bicyclo(3.2.0)hepta-2,6-dienes produced. A consideration of the published work showed a marked absence of data on systems possessing electron-withdrawing substituents and we therefore turned our attention firstly to the ethoxycarbonylcycloheptatrienes. In the light of data published by Chapman *et al.*[2] on methoxycycloheptatrienes a subsequent logical extension of the work led to an examination of ethoxycarbonylmethoxycycloheptatrienes. Some results have been reported in preliminary form.[9-12]

RESULTS AND DISCUSSION

Photochemistry of ethoxycarbonylcycloheptatrienes in quartz

On irradiation of a nitrogen purged 0.05 M benzene solution of 7-ethoxycarbonylcycloheptatriene[13] (7E-CHT, 1*) in quartz with a medium pressure mercury arc, seven new peaks were observed by glc. These corresponded to eight isomeric photoproducts, the relative concentrations of which varied with time, although very little material was lost due to polymerisation. All products have been isolated by preparative glc of reaction mixtures irradiated for lengths of time most suitable for isolation of the individual component. The identified products consisted of (a) the three alternative ethoxycarbonylcycloheptatrienes (E-CHT's) (b) four ethoxycarbonylbicyclo(3.2.0)hepta-2,6-dienes (E-BCHD's) and (c) a tetracyclic isomer.

(a) *Ethoxycarbonylcycloheptatrienes.* 1E-CHT (2) rapidly built up to a maximum concentration of 7% after 0.2 hr, and had decayed totally after 11.0 hr. It was identified by glc comparison with an authentic sample prepared by thermolysis of 7E-CHT (1) (Experimental). 2E-CHT (3) *and* 3E-CHT (4) could not be separated by glc. Their combined concentrations reached a maximum value of 62% after 1 hr at which time the ratio 3:4 was 4:1 (NMR). At longer conversion times this ratio decreased, being 1:3 at a combined concentration of 17%. These products were no longer detectable after 31 hr. Their structures follow from NMR spectra (Table 1) and decoupling data of the two mixtures mentioned above.

Irradiation of a nitrogen purged 0.05 M benzene solution of 1E-CHT (2) in quartz resulted in rapid conversion to a mixture consisting of mainly 3 and 4 and virtually identical to that obtained from 7E-CHT (1) apart from the absence of a minor photoproduct which arises directly from 1 (*vide infra*). The high reactivity of 1E-CHT (2) does not prevent its build up to 7% on irradiation of 7E-CHT (1). This fact, coupled with the decrease in the 3:4 ratio with time, indicates the sequence $1 \rightarrow 2 \rightarrow 3 \rightarrow 4$ via a series of 1,7-hydrogen shifts. None of the cycloheptatrienes were detectable in the final photomixture.

(b) *Ethoxycarbonylbicyclo*(3.2.0)*hepta*-2,6-*dienes.* The structures of these compounds followed principally from their highly characteristic NMR spectra. Of particular diagnostic value is the fact that the cyclobutene olefinic protons do not couple with the ring junction protons.[14] The data for the parent system and the ethoxycarbonyl-derivatives are summarised in Table 2.

4E-BCHD (5) rapidly attained a maximum concentration of ~2% which thereafter remained unchanged. It was not formed on irradiation of 1E-CHT (2) and the inference that it is a primary photoproduct of 7E-CHT (1) was confirmed from its NMR spectrum (Table 2). The ethoxycarbonyl group probably occupies the *exo* position but this is not proven. The apparent photo-inertness of 5 parallels our observations with the parent diene.

3E-BCHD (6) reached a maximum concentration of 5.5% after 6 hr and thereafter slowly decayed. Its NMR spectrum (Table 2) showed clearly that the ester function was attached to the cyclopentene double bond of a bicyclo(3.2.0)hepta-2,6-diene. Kinetic evidence (*vide infra*) clearly indicated 6 as the correct structure. This has been confirmed by comparison with an authentic specimen synthesised from the known ketone 9[15] via the sequence outlined in Scheme 2.

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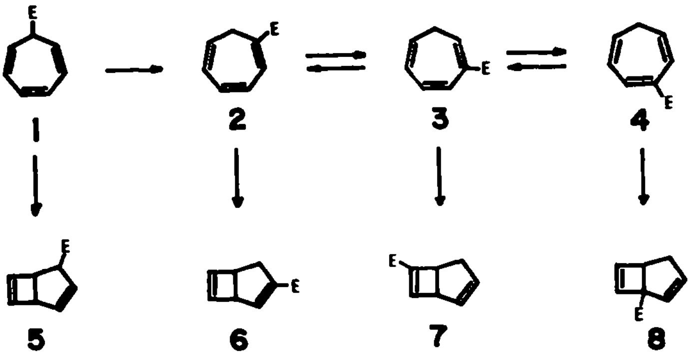
[*] In structures reproduced in this paper ethoxycarbonyl- and methoxy-substituents are represented by E and M respectively.

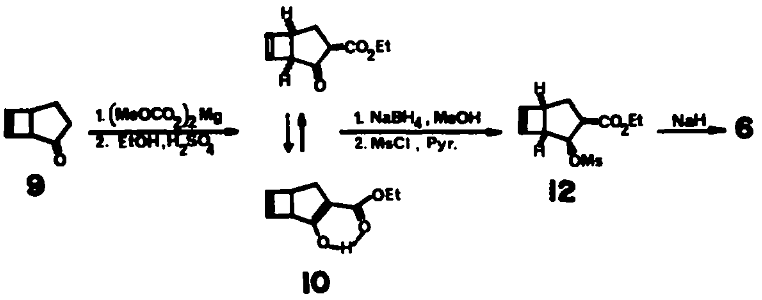
Table 1. Ring proton chemical shifts (τ), multiplicities and coupling constants (Hz) of cycloheptatrienes[a]

Compound	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)
7E-CHT (1)	4.60 dd;9,6	3.77 d(broad);9	3.38 t;3	3.38 t;3	3.77 d(broad);9	4.60 dd;9,6	7.49 t;6
1E-CHT (2)	-	2.78 d;9	3.30 M;2H		3.78 dd;9,5	4.46 dd;9,7	7.38 d;7;2H
2E-CHT (3)	3.55 t;7	-	2.90 d;10	3.35 dd;10,6	3.84 dd;8,6	4.70 dt;8,7	7.72 t;7;2H
3E-CHT (4)	4.59 dt;10,7	3.22 d;10	-	2.38 d;6	3.72 dd;10,6	4.39 dt;10,7	7.76 t;7;2H
4E,1M-CHT (46)	-	4.50 d;8	2.39 d;8	-	3.30 d;9	4.66 dd;9,7	7.47 d;7;2H
3E,1M-CHT (47)	-	4.10 s	-	2.63 d;6	3.74 dd;8,6	4.43 dd;9,6	7.48 d;6;2H
1E,3M-CHT (48)	-	2.97 d;2	-	4.04 dd;7,2	3.85 dd;9,7	4.68 dt;9,7	7.36 d;7;2H
1E,6M-CHT (49)	-	2.77 d;6	3.34 dd;10,6	3.76 dd;10,6	4.60 d;6	-	7.18 s;2H

[a] Single proton resonances unless otherwise stated. All spectra, measured in $CDCl_3$, exhibited normal ethoxycarbonyl signals; 46 to 49 showed an additional methoxy singlet.



Scheme 1.



Scheme 2.

Table 2. Ring proton chemical shifts (τ), multiplicities and coupling constants (Hz) of bicyclo(3.2.0)hepta-2,6-dienes[a]

Compound	H(1) and H(5)	H(4)	H(2) and H(3)	H(6) and H(7)
BCHD[14]	6.38;m 6.73;m	7.67;m	4.36;m;2H	3.67;d;3 3.92;d;3
1E-BCHD (8)	6.51;dd;10,4	7.40;ddt;17,10,3 7.80;dq;17,4	4.14;m 4.20;m	3.55;d;3 3.88;d;3
3E-BCHD (6)	6.22;m 6.61;m	7.46;m;2H	3.20;q;2	3.72;d;3 3.92;d;3
4E-BCHD (5)	6.22;m 6.65;m 6.38;m		3.98;m 4.34;m	3.63;d;3 3.87;d;3
6E-BCHD (7)	6.50;m;2H	7.58;m;2H	4.32;m;2H	2.97;s
7E, 5M-BCHD (50)	6.23;q;2.5	7.49;q;2;2H	4.15;dq;6,2 4.30;dt;6,2 *	3.14;s;2H
3E, 5M-BCHD (51)	6.34;q;2.5	7.30;t;2.5;2H	3.25;q;2	3.74;s;2H
1E, 3M-BCHD (55)[b]	c	c	5.37;t;2	3.66;d;3 3.86;d;3
5E, 3M-BCHD (56)[b]	6.35;m	7.15;dt;17,2 7.62;ddd;17,3,2	5.51;q;2	3.62;d;3 3.92;d;3
1E, 5M-BCHD (52)	-	7.44;m;2H	4.15;s;2H	3.51;d;3 3.60;d;3

[a] Single proton resonances unless otherwise stated. All spectra, measured in $CDCl_3$ unless otherwise stated, exhibited normal ethoxycarbonyl signals; 50 - 52, 55 and 56 showed an additional methoxy singlet.

[b] CCl_4

[c] This compound was only obtained as a mixture with 56 and these signals were not fully characterised.

6E-BCHD (7) reached a maximum concentration of 28% after 3.5 hr. Its NMR spectrum (Table 2) showed the ethoxycarbonyl function to be attached to the cyclobutene double bond and kinetic evidence (*vide infra*) showed 7 to represent the correct structure.

1E-BCHD (8) reached a maximum concentration of 22% after 8.5 hr. Its structure followed unambiguously from its NMR spectrum (Table 2), the key feature of which was the coupling of the single ring junction proton with the C(4)-methylene protons, J = 10 and 4 Hz. This shows that the substituent is at C(1).

(c) 2-*Ethoxycarbonylquadricyclene* (13). Of the four bicyclic products described 6, 7 and 8 decay on irradiation in quartz to give one major product (13, 70% after 43.0 hr). The mechanism of production of this compound will be the subject of a separate paper.[16]

Photochemistry of ethoxycarbonylcycloheptatrienes in pyrex

On irradiation in solution the ratio of any two primary products of one excited state must remain constant under conditions where neither is reactive. Since 6, 7 and 8 do not absorb above 290 nm and are stable on irradiation in pyrex the foregoing should hold for any pair of these which originate from ring-closure of the same cycloheptatriene. In Tables 3 and 4 are shown the results of irradiating 0.05 M benzene solutions of 1, 2 and various 3/4 mixtures through pyrex. These data establish 7 rather than the alternative 14 as the major bicyclic product and confirm other assignments. Table 3 clearly shows that 7 and 8 are derived from 3 and 4 respectively and that 7 therefore has the structure shown. In addition, on irradiation of 1E-CHT (2) (Table 4) the 7:6 ratio varied from 2:1 (0.25 hr) to 19:1 as the reaction proceeded. This confirmed that 6 arises from 2 and not 3. Finally the fact that 5 is only observed on irradiation of 7E-CHT (1) (Table 4) establishes its origin. We conclude that, as summarised in Scheme 1.

(a) The photo-interconversion of the cycloheptatrienes 1–4 would lead to the establishment of a photostationary state containing essentially only 3 and 4 in a ratio strongly favouring 4. The production of 6 on irradiation of 3/4 mixtures and the high yield of 7 on irradiation of such mixtures rich in 4 demonstrate the reversibility of steps 2→3 and 3→4. There is no experimental evidence for the reversibility of step 1→2.

(b) Each cycloheptatriene ring closes to a single bicyclo(3.2.0)hepta-2,6-diene, i.e. closure of 2, 3 and 4 is directionally specific. We have synthesised the alternative products of ring closure of 2 and 3, i.e. 15 and 16

Table 3. Dependence of initial relative rates of formation of 7 and 8 on initial proportions of 3 and 4[a]

Starting ratio [2E-CHT (3)] : [3E-CHT (4)]	Formation rate ratio [6E-BCHD (7)] : [1E-BCHD (8)]
3.0	2.9
1.0	1.0
0.25	0.32

[a] Irradiation of 0.05 M benzene solutions in pyrex

respectively, via routes to be published.[16] Neither was detectable by glc in our photomixtures. We have so far failed to achieve a synthesis of the bicyclic diene 14, the alternative ring closure product of 4.

Since our preliminary communication Linstrumelle[17] has published results very similar to those described so far although the bicyclic dienes 5 and 6 were not isolated.

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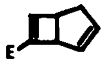

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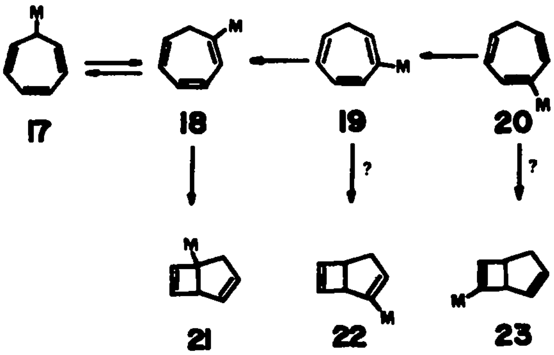
Photochemistry of methoxycycloheptatrienes

These systems have been most thoroughly investigated by Chapman *et al.*[2] and Scheme 3 gives the essential details of their results. Irradiation of the 7- or 1-isomers (17 or 18) led to the establishment of a photostationary state between these two. This was bled to a single bicyclic diene, 21. No 2 or 3-substituted cycloheptatrienes or their photoproducts were produced. On irradiation of the 3-methoxy compound (20) the major bicyclic product was 21 indicating that 1,7-hydrogen shifts lead in the opposite direction to that observed for the ethoxycarbonyl systems. In addition the formation of a cyclobutanone and a cyclopentanone on acid hydrolysis of a photomixture from 20 is in agreement with, but by no means proof of, ring closure of 19 and 20 to 22 and 23 respectively. The dienes 21, 22 and 23 correspond to cycloheptatriene ring closures which are directionally the opposite of those observed by us for the corresponding ethoxycarbonyl systems.

Our experiments with the latter systems are the first in which a complete monosubstituted series of cycloheptatrienes have been ring closed photochemically. These data together with the admittedly less complete details concerning the methoxycycloheptatrienes clearly indicate that mesomerically electron donating and withdrawing groups have specific and opposite effects on the direction of light-induced ring closure. In addition the 1,7-hydrogen shift sequences appear to proceed in opposite senses.



Scheme 3.

Polarisation of the excited state

In all cases so far investigated both the ring-closure and hydrogen shift reactions proceed via the singlet excited state as evidenced by the absence of quenching by oxygen and the failure of attempts to sensitize such reactions. The contrast between the results for methoxy- and ethoxycarbonyl-cycloheptatrienes is a clear indication that electronic as opposed to steric factors are responsible for the directional specificity of the processes under consideration. We have attempted to rational-

Table 4. Products of 100 hr irradiation of 0.05 M de-oxygenated benzene solutions in pyrex

	Products/%				
Starting material	3/4	5	6	7	8
7E-CHT (1)	10	1	2	71	14
1E-CHT (2)	1	0	4	76	19
2E-CHT (3) 3E-CHT (4) } 1:1	0	0	2	70	26

ise the data in terms of the effect of substituents on the direction of polarisation of the excited state. Although our treatment is at best an over-simplification of the situation, the correlation with experiment and hence the predictive value are excellent. The following summarises our approach.

Ring closure reactions. In the S_1 state of cycloheptatriene itself the polarisation will be in one of the directions shown in 24 and 25, and this will change on introduction of a substituent onto a double bond. For the ring-closure reaction polarisation in a 1,4- and 3,6-sense will be important. In order to decide in which of these directions polarisation will be greater we have considered the effect of substituents on the relative stabilities of the extreme cases 26 and 27 in which complete charge separation has occurred in a 1,4-sense in 26, a 3,6-sense in 27. Important and equal contributions of these canonical forms in the case of cycloheptatriene itself would correspond to 24. The importance of forms of this type is in agreement with molecular orbital results which show the strengthening of the C(2)–C(3) and C(4)–C(5) bonds coupled with weakening of the C(1)–C(2), C(3)–C(4) and C(5)–C(6) bonds in the first excited state of a hexatriene.[18] These bonding characteristics together with the fact that, in terms of homoconjugation, the S_1 state of cycloheptatriene should prefer 1,6-antarafacial interaction (a Möbius array[19]) rather than the suprafacial interaction of the ground state,[20] indicate that the spectroscopic S_1 state of this molecule may relax to a conformation of C_2 symmetry (28). In contrast to the boat-like ground state[21] this possesses an ideal geometry for 1,4- or 3,6-ring closure as indicated. The canonical forms 26 and 27 are, in a bonding sense, intermediate between the cycloheptatriene and the bicyclo(3.2.0)hepta-2,6-dienes formed in a 1,4-sense and a 3,6-sense respectively. It is therefore reasonable to assume that if 26 makes a larger contribution than 27 to the overall structure of the S_1 state ring closure will take place in a 1,4-sense. Apart from the bonding favouring ring-closure in this sense the greater charge difference between the 1 and 4 as opposed to the 3 and 6 positions could well result in distortion of 28 along the reaction path required for 1,4-ring closure. In 26 the arrows show the required nature, electron donating or withdrawing, of a substituent at each olefinic carbon if it is to stabilize 26 with respect to 27. Based on these arguments, and assuming polarisation in the sense of 26 and 27 rather than with the charges reversed, we conclude that:

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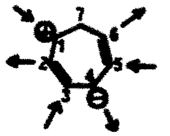

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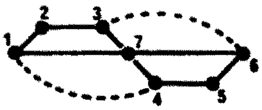

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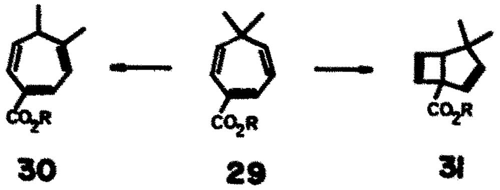
(1) An electron donating substituent at positions 1, 3 or 5 or an electron accepting substituent at positions 2, 4 or 6 should result in a 1,4-ring closure.

(2) For 3,6-ring closure the opposite should apply.

(3) If the influence of a 1, 3, 4 or 6 substituent is opposed by that of a 2 or 5 substituent the former would be expected to direct ring closure, assuming comparable electronic properties.

To our knowledge all known examples of the light-induced ring closure of cycloheptatrienes are in accord with these conclusions. In addition to the compounds in Schemes 1 and 3, methyl thujate (29) gives 31[6] (Scheme 4) and the methylated cycloheptatrienes 32 and 36 (Scheme 5) and 38 and 40 (Scheme 6) all give ring closure to a single bicyclic diene[1,3-5] in accord with electron donation from a methyl group. In the case of 38 the effect of the C(3)–Me group should direct ring closure; in the case of 40 the effects of the C(1)- and C(6)-groups will counteract each other leaving the directional effect of the C(2)–Me.



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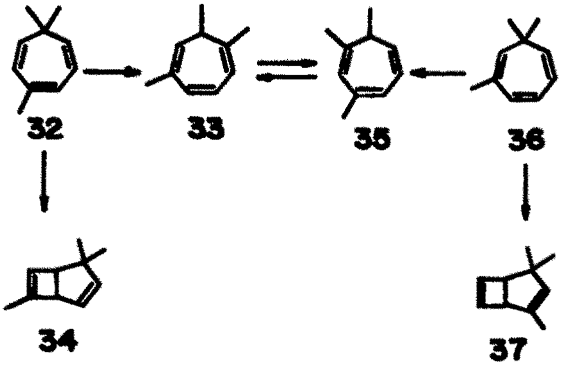
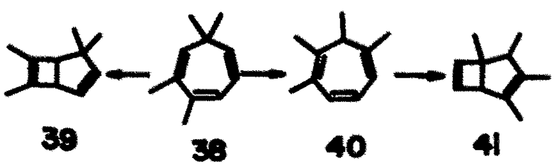


Scheme 5.



Scheme 6.

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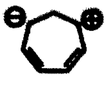

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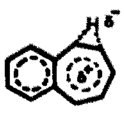

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All of the above results indicate (a) that the directional specificity of the photochemical ring closure of cycloheptatrienes is a result of excited state polarisation and (b) that the excited state involved is polarized in the sense indicated by 26 and 27 (and 24) rather than with the charges reversed. It is gratifying that since our preliminary communications,[9,10] Libit[22] and Tezuka and Kikuchi[23] have published theoretical treatments which support our conclusions that the S_1 state of cycloheptatriene is polarized as depicted in 24. However, Hückel calculations[22] did not allow prediction of ring closure directions for monosubstituted cycloheptatrienes, although it was claimed that this was possible for 1,7-hydrogen shifts assuming that hydrogen migrated as a positively charged species to the more negative adjacent carbon. Our analysis in terms of the relative importance of 26 and 27 gives entirely the opposite result in that hydrogen migrates as a hydride-like species to the more positive adjacent carbon. As shown in the following section the agreement with experiment is excellent.

1,7-Hydrogen and 1,7-methyl-shifts. Experimental determination of the relative efficiencies of individual 1,7-shifts is particularly difficult since the product may itself be photoreactive with respect to further hydrogen shifts and/or ring closure. The net result of such a complex photochemical process involving light absorption by a number of intermediate species depends on other things, relative extinction co-efficients, lamp characteristics, etc. besides the intrinsic chemical reactivities of individual excited states. However, in the first instance, we shall neglect such factors and concentrate on the expected effect of a substituent on the tendency for $H^{\ominus}$ (or $CH_3^{\ominus}$) to undergo 1,7-migration within a particular excited state. Based on the effect of a substituent on the relative stabilities of 26 and 27, the estimated relative efficiencies of 1,7-hydrogen migration for both an electron acceptor (A) and an electron donor (D) in a monosubstituted series of cycloheptatrienes are shown in Scheme 7, assuming that migration of $H^{\ominus}$ (or $CH_3^{\ominus}$) to the more positive centre takes place and recognising that the effect of a 1, 3, 4 or 6 substituent should be greater than that of a 2 or 5 substituent. For the sake of completeness one should also consider the relative importance of 42 and 43, completely polarized in a 1,6-sense. This, of course, gives exactly the same prediction. Although it is not always clear from the published data to what extent a reaction sequence has been allowed to go to completion, these data and our own, as indicated below, are clearly in excellent agreement with Scheme 7.

(1) *Electron accepting substituents* (*A*)

(a) 1-Cyano-[8] and 1-benzoyl-cycloheptatriene[24] both yield the corresponding 2-substituted derivative.

(b) Our work has shown: (i) That 7E-CHT (1) undergoes rapid conversion to the 2-isomer (3), only small amounts of the 1-isomer (2, 7%) building up. The 2-isomer is slowly converted to the 3-isomer (4) which finally becomes the major monocyclic isomer present. (ii) Irradiation of the 1-isomer (2) rapidly gives the 2-isomer (3) but no 7-isomer (1) is produced as evidenced by the lack of production of its bicyclic photoproduct (5). (iii) Irradiation of a mixture of 2- and 3-isomers (3 and 4) gives about 5% of 1-isomer (2). This is to be expected since the interconversion of 2 and 3 should be faster than that of 3 and 4.

(2) *Electron donating substituents* (*D*)

(a) 1-Methoxy- and 1-thiomethyl-cycloheptatrienes[2,8] give the predicted 7-substituted derivatives as the sole hydrogen shift products.

(b) 3-Methoxycycloheptatriene gives a complex mixture but principal products are the 7- and 1-methoxycycloheptatrienes and the ring closure product of the latter.[2]

(c) 1-Methylcycloheptatriene gives 98% of the predicted 7-isomer and 2% of the 2-isomer.[8]

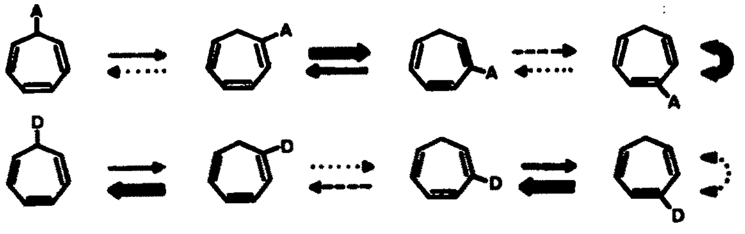
(d) Irradiation of the 2,7,7- and 3,7,7-trimethylcycloheptatrienes 32 and 36 (Scheme 5)[1,3,4] results in a specific methyl shift in the direction predicted for $CH_3^{\ominus}$-like migration. The products 33 and 35 undergo light-induced interconversion via 1,7-hydrogen shifts exactly as would be predicted. In the case of 35 both the 1- and 3-methyl groups direct hydrogen migration to give 33. In the case of 33 the directive effect of the 1-methyl will outweigh that of the 5-methyl resulting in formation of 35.

(e) The tetramethyl derivative 38 (Scheme 6)[1,5] also possesses Me groups whose directive effects should oppose each other. As predicted the 3-substituent dominates and 1,7-Me migration to give 40 takes place.

(3) *Combined electron accepting and electron donating substituents*

Apart from our own work (*vide infra*) only one cycloheptatriene comes into this category. Irradiation of methyl thujate (29, Scheme 4)[6] results in predicted Me migration to give 30, and predicted ring closure to give 31. In 30 both the 1-methyl and 3-methoxycarbonyl groups would direct 1,7-hydrogen migration to give back 30 itself. No other cycloheptatrienes are observed. Of interest is the fact that 30, in contrast to 29, does not undergo ring closure. We attribute this to steric factors (*vide infra*).

Recently Swenton *et al.*[25] have investigated the effect of substituents on the balance between light-induced ring closure and 1,7-hydrogen shifts in 1,2-benzotropilidines. Their results were best accommodated in terms of a transition state of type 44 for the 1,7-hydrogen shift. This



Scheme 7. Relative 1,7-hydrogen shift efficiencies (A = electron acceptor, D = electron donor): → enhanced by 1, 3, 4 or 6 substituent; ➡ enhanced by 2 or 5 substituent; → no substituent effect; - - -→ retarded by 2 or 5 substituent; ······→ retarded by 1, 3, 4 or 6 substituent.

is clearly in good agreement with our analysis of such shifts within cycloheptatrienes.

Preparation of ethoxycarbonylmethoxycycloheptatrienes

A logical extension of Chapman's and our own work was the investigation of systems containing both a methoxy- and an ethoxycarbonyl-grouping. We hoped to prepare compounds in which the substituent effects (a) reinforced each other (b) opposed each other.

Alkaline hydrolysis of the product of thermal decomposition of ethyldiazo-acetate in anisole has been reported to give phenylacetic acid and a methoxycycloheptatriene carboxylic acid.[26] The latter has subsequently been shown to be the 1,4-disubstituted compound **45**.[27]

From this reaction we have been able to isolate cycloheptatrienes of four disubstituted types. From the distilled thermal decomposition mixture the 1,4-derivative **46** (preparative glc) and the two 1,3-disubstituted derivatives **47** and **48** (preparative tlc) were isolated. The 1,6-disubstituted isomer **49** was prepared by benzene sensitized irradiation of **47** using a low pressure mercury lamp. The yield after dry column chromatography on silica gel was ~50%. The structures of **46**–**49** followed unambiguously from their NMR spectra which are summarised in Table 1.

Photochemistry of ethoxycarbonylmethoxycycloheptatrienes

The substituents in **47**–**49** are all in a 1,3-relationship. They will therefore be discussed together since 1,7-hydrogen shift sequences represent potential pathways for their interconversion. Initially nitrogen purged 0.005 M benzene solutions were irradiated in pyrex. In each case rapid production ethoxycarbonylmethoxybicyclo(3.2.0)hepta - 2,6 - dienes (E-M-BCHD's) took place. The products produced on consumption of starting material and their yields are given in Table 5. The bicyclic products were isolated by preparative tlc and identified from their NMR spectra (Table 2) and their thermal opening in degassed benzene to the corresponding cycloheptatrienes (Experimental).

These results indicate that of **47**, **48** and **49** only **47** and **49** ring close and in each case closure is again directionally specific. In the case of **47**, in which the substituent effects should oppose each other, the directive effect of the OMe function is dominant, and closure to 7E-5M-BCHD (**50**) occurs. Both substituents have the same directive influence in **49** and the predicted product is that obtained, 3E-5M-BCHD (**51**). The production of **50** and **51** on irradiation of **47** and **48** indicates that hydrogen shifts may compete effectively with ring closure and in Scheme 8 are shown the seven cycloheptatrienes which may be involved in this system, as a result of sequential 1,7-hydrogen migrations. Clearly the approach employed in Scheme 7 could become complex for two substituents but may be simplified for 1,3-related substituents with respect to the estimated relative efficiencies of individual 1,7-hydrogen shifts as shown in Scheme 8. It is immediately apparent from this Scheme that such hydrogen shifts should take place in an overall anti-clockwise direction to give products. Thus **48** should be converted to **49** via **47** which is exactly what the product distributions in Table 5 demonstrate.

The photochemistry of 4-ethoxycarbonyl-1-methoxycycloheptatriene (**46**)

On irradiation of a nitrogen purged 0.005 M benzene solution of 4E-1M-CHT (**46**) through pyrex a very slow reaction took place to give a single product, conversion being complete after 400 hr (compare Table 5). On irradiation through quartz with the same lamp the time required was 16 hr. The product was identified as 1E-5M-BCHD (**52**) on the basis of its NMR spectrum (Table 2) and its essentially quantitative conversion back to **46** on attempted tlc or glc analysis.

The substituents in **46** are both expected to direct ring closure in a 1,4-sense to give the observed product. The very slow reaction must reflect steric hindrance to ring closure. This is presumably the reason why ring closure of **29** but not of **30** (Scheme 4) was observed by Chapman and Smith[6] on irradiation of methyl thujate (**29**). No other cycloheptatrienes or photoproducts derived from them were observed on irradiation of **46**. The predicted

Table 5. Products of irradiation of ethoxycarbonylmethoxycycloheptatrienes[a]

Starting material	Reaction time/hours	Products
3E, 1M-CHT (47)	1.0	7E, 5M-BCHD (50) 65% 3E, 5M-BCHD (51) 35%
1E, 3M-CHT (48)	1.0	7E, 5M-BCHD (50) 65% 3E, 5M-BCHD (51) 35%
1E, 6M-CHT (49)	2.0	3E, 5M-BCHD (51) 100%

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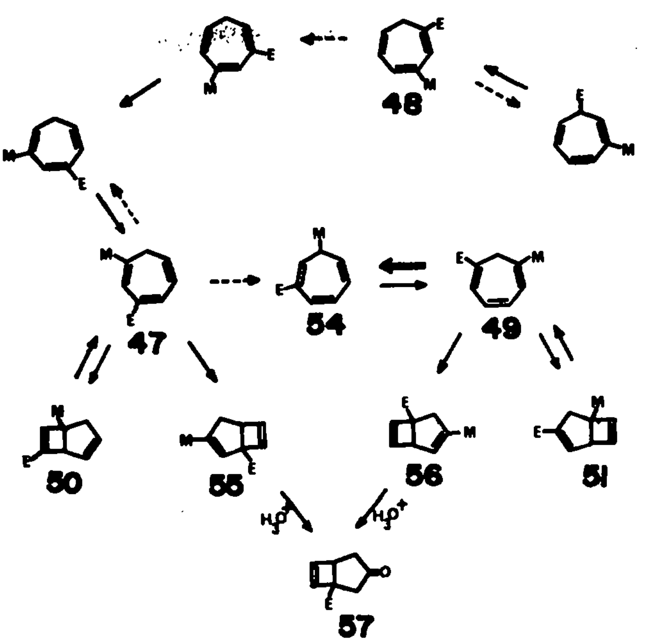
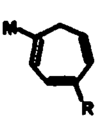
[a] Irradiation in pyrex of nitrogen purged benzene solution, 100W medium pressure. No loss of material due to polymerisation.

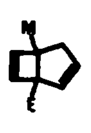


Scheme 8. Photochemistry of 47, 48 and 49. Relative 1,7-hydrogen shift efficiencies:→enhanced by two 1,3,4 or 6 substituents;→enhanced by a 2 or 5 sibstitutnt;——→ substituents oppose each other; retarded processes omitted.



45 R=COOH

46 R=E



52

53

1,7-hydrogen migration would give 53, which in turn would be predicted to undergo similar migration back to 46. The latter reaction is presumably fast relative to other processes. This appears to be a feature of 7-OMe-substituted cycloheptatrienes as witnessed by the lack of formation of ring closure products from 17, 53 and 54.

"*Abnormal*" *ring closure-reaction via an upper excited state*

Until our finding that the bicyclic dienes 6, 7 and 8 undergo photochemical conversion to the quadricyclene 13 such systems had appeared to be photochemically inert.[1-8,14] We have investigated the possibility that the bicyclic dienes 50 and 51 may also be photoreactive. The rather unexpected results are described below.

On irradiation of degassed 0.005 M benzene solutions of 50, 51 or a mixture of the two in pyrex, slow but complete conversion to two new products took place in ~75 hr. No material was lost to polymerisation. The products, formed in approximately 1:1 ratio were identified as 1E-M-BCHD (55) and 5E-3M-BCHD (56) (Scheme 8), the *alternative* ring closure products of 47 and 49 respectively! These enol ethers could not be separated due to their identical glc characteristics and their instability with respect to hydrolysis. Their structures follow from the NMR spectrum of the mixture (see Table 2) and the quantitative hydrolysis of this mixture to a single product, the ketone 57. The structure of the latter followed from spectral data, ν_{max}(CHCl$_3$): 1749, 1723 cm^{-1}; τ(CDCl$_3$): 3.77 (d; 3 Hz) and 3.83 (d; 3 Hz), C(6) and (C(7) AB; 6.44 (d; 9 Hz), 7.45 (dd; 17, 9 Hz) and 7.78 (d; 17 Hz), C(4) and C(5) ABX; 7.08 (d; 18 Hz) and 7.59 (d; 18 Hz), C(2) AB; 5.82 (q; 7 Hz) and 8.72 (t; 7 Hz), CO$_2$Et. When irradiation was commenced with pure 47, 49 was also produced in the initial stages. These results show that the bicyclic dienes 50 and 51 are able to open photochemically to the corresponding cycloheptatrienes which may then interconvert via 1,7-hydrogen shifts. This reversibility of ring closure provides an explanation for the apparent general lack of photoreactivity of bicyclo(3.2.0)hepta - 2,6 - dienes: ring opening will in many cases be a "hidden" process due to the photostationary state lying heavily on the ring-closed side as a result of the more favourable light absorbing characteristics of the cycloheptatrienes. In the present case the enol ethers 55 and 56 slowly accumulate due to their inability to compete with the α,β-unsaturated esters 50 and 51, and of course 47 and 49, for the light transmitted by pyrex.[b]

Inhibition of formation of the "abnormal" ring closure products 1E-3M-BCHD (55) *and* 5E-3M-BCHD (56) *by oxygen.* In a number of experiments carried out to produce 55 and 56 the ratio of these products showed differences which led us to consider deoxygenation variations as a possible cause. With this in mind sealed pyrex ampoules containing degassed and non-degassed 0.007 M solutions of 3E-1M-CHT (47) and 1E-6M-CHT (49) were irradiated on a conventional "merry-go-round" apparatus and the reactions monitored by NMR and glc. A typical set of product compositions is shown in Table 6. Whereas the relative rates of production of the "normal" products, 50 and 51, showed some differences, the striking finding was that the "abnormal" products, 55 and 56, were not produced at all in the presence of oxygen. Control experiments showed that these enol ethers are destroyed on irradiation under the non-degassed con-

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[b] On irradiation in quartz 55 and 56 rapidly polymerise.

Table 6. Products of irradiation of cycloheptatrienes in degassed and non-degassed benzene[a]

Cycloheptatriene	Products (%)			
	50	51	55	56
47 degassed	14	18	18	50
47 non-degassed	35	65	0	0
49 degassed	14	22	6	58
49 non-degassed	23	77	0	0

[a] 0.007 M solutions; 95 hours' irradiation

ditions of Table 6. However, in the non-degassed experiments described in this Table very little material was lost and no glc or NMR signals corresponding to enol ether oxidation products were observable. We therefore conclude that oxygen prevents the formation of the "abnormal" products 55 and 56 as distinct from reacting with them subsequent to their formation.

A simple explanation of these results would be that the "normal" products 50 and 51 arise via the S_1 state, the "abnormal" products 55 and 56 via the T_1 state. The triplet reaction, resulting from a very inefficient intersystem crossing process could manifest itself over a long period due to the clean and *reversible* nature of the singlet process and the inability of the triplet products to compete for the available light. This was our initial interpretation of these results.[11]

An alternative explanation of the oxygen quenching phenomenon has been considered. Both the cycloheptatrienes 47 and 49 show two UV absorption bands as shown in Fig. 1 and it appeared possible that the "abnormal" ring closure products were the result of excitation into the higher energy band. This process would clearly be extremely slow in pyrex in agreement with observation. Air saturated benzene absorbs at longer wavelength than when deoxygenated[c] and this could prevent the required shorter wavelength excitation over the experimental time scale. That this explanation is correct was shown by irradiations in cyclohexane at 254 and 313 nm.

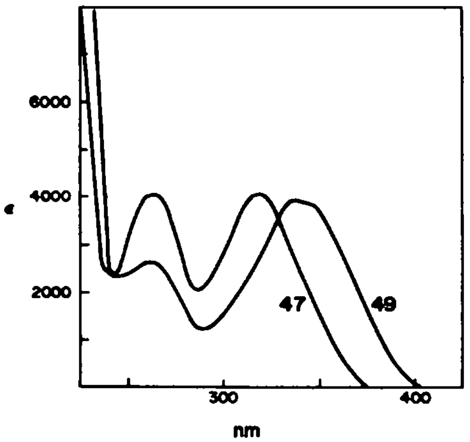

Fig. 1. UV spectra of 47 and 49 in ethanol.

Wavelength dependent photochemistry of 3E-1M-CHT (47) *and* 1E-6M-CHT (49) *in cyclohexane*

On 313 nm irradiation[d] of 0.005 M solutions of 47 and 49 in cyclohexane only the "normal" bicyclic dienes 50 and 51 were formed. Clearly in these experiments excitation took place within the long wavelength band of the starting materials (see Fig. 1).

Similar irradiations carried out at 254 nm,[e] i.e. involving excitation into the short wavelength bands of 47 and 49 (see Fig. 1), led in both cases to immediate production of both "normal" and "abnormal" dienes in approximately equal amounts. The reactions were insensitive to oxygen! In Fig. 2 is shown the initial formation of 51 and 56 from 49. Clearly the "abnormal" ring closure product 56 is a major primary product of excitation at 254 nm. The above results clearly provide convincing evidence that the oxygen quenching effect described in the previous section is due to the prevention of excitation into the shorter wavelength bands of 47 and 49 due to absorption caused by benzene–oxygen interaction.

Wavelength dependent photochemistry of E- and Z-hexa-1,3,5-trienes has been described.[30] In these cases ground state conformational factors coupled with extinction coefficient variations amongst the different conformers were put forward to explain the wavelength dependence of product distribution. Such factors would appear to be of no consequence in the cases of the cycloheptatrienes 47 and 49. The most straightforward explanation of the results is that subsequent to 254 nm excitation both 47 and 49 undergo chemical reaction via, at least in part, their relaxed S_2 states. Since, on irradiation of 49, 51 and 56 are initially produced in equal amounts (Fig. 2) the maximum amount of reaction via S_1 would be $\sim 50\%$ and ring closure from S_2 would be directionally specific and opposite to that of S_1. This is not unreasonable since the two states are bound to have different electron distributions. If, as seems highly unlikely, all product observed on 254 nm irradiation resulted from S_2 ring closure this reaction would be directionally non-specific.

trans,cis,cis-*Cycloheptatrienes as possible reaction intermediates*

We have described how the directional specificity of

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[c] This is thought to be the result of contact charge-transfer from benzene to oxygen.[28]

[d] Medium pressure mercury arc with a filter solution of 0.02 M potassium chromate in 1% aqueous potassium carbonate.[29]

[e] Low pressure mercury arc; no transmission below 200 nm.

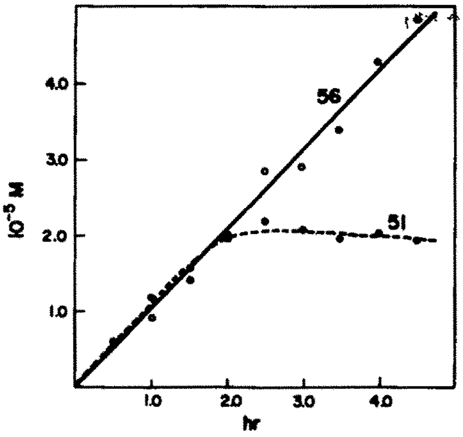

Fig. 2. Formation of 51 and 56 on irradiation at 254 nm of 49 (5×10^{-3} mol l^{-1}) in cyclohexane.

the light-induced ring closure and 1,7-hydrogen shift reactions are in agreement with reaction from an S_1 state whose electron distribution determines the direction in which the reaction will take place. However, in our opinion no evidence has been presented, here or elsewhere, which rules out the possibility of reaction via an intermediate ground-state *trans,cis,cis*-cycloheptatriene. Such a species could ring-close via the allowed conrotatory mode or undergo an allowed antarafacial 1,7-hydrogen shift. Clearly these reactions would necessitate the participation of the *trans* double bond. Thus, the directional specificity observed could reflect the specificity of the *cis-trans* isomerisation process. It turns out that such considerations lead to the same predictions in terms of directional specificity as one obtains for direct reaction from S_1. We have argued that if a substituent stabilises 26 with respect to 27 it will contribute more to the structure of the excited state and the ring closure and 1,7-hydrogen shift processes will take place in a 1,4- and a 1,7-sense respectively. The greater contribution of 26 should also favour relaxation of S_1 to a geometry suitable for cross-over to a ground state cycloheptatriene with a *trans*-1,2 as opposed to a *trans*-5,6 double bond. Ring closure and hydrogen shift reactions would then automatically involve C(1) and not C(6).

It is not immediately obvious why geometrical isomerisation of the 3,4-double bond should be less important than 1,2 (or 5,6) isomerisation via the S_1 state of a cycloheptatriene and with this in mind we have performed MINDO/3 calculations on the S_1 state of cycloheptatriene itself.[31] Two energy minima were found with by far the more stable structure having a geometry of essentially C_2 symmetry as depicted in 28. In this structure the "angles of twist" about the C(1)–C(2) and C(3)–C(4) bonds relative to the planar arrangement of a normal double bond are 57.9 and 38.5° respectively. Thus, it seems likely that cross-over from S_1 to a ground-state *trans,cis,cis*-cycloheptatriene would be the more favoured geometrical isomerisation process. The production of the alternative ring closure products on excitation of 47 and 49 into their shorter wavelength bands would then reflect cross-over of the relaxed S_2 state to the alternative *trans, cis, cis*-ground-state.[f]

Further work on these systems is in progress.

EXPERIMENTAL

Benzene and cyclohexane were subjected to sulphuric acid, water, bicarbonate, water treatment and distilled from P_2O_5. Unless otherwise stated irradiations were carried out with a Hanovia 100W medium pressure mercury lamp. Thin layer chromatography was performed on Merck pre-coated silica gel F_{254} plates. Analytical glc was performed on a Perkin–Elmer F11 instrument using a polyethylene glycol adipate column, solid support either Chromosorb G or siliconised Embacel. Mixture compositions were estimated by the cutting out and weighing of individual peaks from photocopies of the glc traces. Preparative glc was performed on a Perkin–Elmer F21 instrument using a polyethylene glycol adipate column, solid support 60–80 mesh Chromosorb A. To prevent polymersion of the separated components benzene was placed in the traps before attachment to the instrument. UV spectra were recorded on a Unicam SP800 spectrometer using 95% ethanol as solvent, values given in nm (ϵ). IR spectra (liquid films) were recorded on a Perkin–Elmer 257 spectrometer, values in cm^{-1}. NMR spectra were recorded on a Varian Associates HA100 100 MHz spectrometer with TMS as an internal standard, chemical shifts in ppm. Hexamethyl benzene was used as a standard in estimating amounts of material lost due to polymerisation, etc. Mass spectra were recorded on an A.E.I. MS12 spectrometer at 70 eV, values in *m/e* (%).

1. 7E-CHT (1).[13] A soln of ethyl diazoacetate (25 ml) in benzene (400 ml) was irradiated in pyrex for 67 hr. The solvent and unreacted diazo compound were removed under water pump vacuum and the residue distilled through a Vigreux column to give a red–gold oil, 40–47°, 0.2 Torr (~ 7 g), shown to be ~ 90% homogenous by glc. Preparative glc gave 1, λ_{max} 256 (2320). ν_{max} 1740, 1608. NMR data Table 1. *m/e* 164 (M^+, 2.4), 91 (100), 65 (45), 63 (25).

2. 1E-CHT (2). A soln of 1 (995 mg) in benzene (16 ml) was heated in an evacuated sealed tube at 200–210° for 3 hr. After solvent removal the residue was distilled (0.1 Torr, 75°, air bath) and the resulting oil (982 mg) subjected to preparative glc (9 ft column, 160°). This gave (a) 2 (203 mg), λ_{max} 275 (3980), λ_{inf} 300 (3640). ν_{max} 1709, 1615. NMR data Table 1. *m/e* 164 (M^+, 12), 135 (42), 91 (100). (b) a 1:1 mixture (132 mg) of 3 and 4 *cf.* experiment 3.

3. 2E-CHT (3) *and* 3E-CHT(4). A N_2 purged soln of 1 (810 mg) in benzene (30 ml) was irradiated through quartz for 110 min. The solvent was removed under water pump vacuum and the residue distilled (0.5 Torr, 70°, air bath). Preparative glc of the distillate (9 ft column, 150°) gave a 4:1 mixture of 2 and 3. The NMR spectrum of the mixture unambiguously identified the major component as 3 (Table 1). Preparative glc of a distillate obtained after 43 hr irradiation of a similar soln gave a 1:3 mixture of 3 and 4. The NMR spectrum of this mixture unambiguously identified the major component as 4 (Table 1).

4. 4E-BCHD (5). Preparative glc of the distillate obtained in experiment 3 gave a minor component (6 mg) having a shorter retention time than the 3/4 mixture. It was identified as 5 solely on the basis of its NMR spectrum (Table 2).

5. 6E-BCHD (7) *and* 1E-BCHD (8). A N_2 purged soln of 1 (850 mg) in benzene (25 ml) was irradiated through quartz for 43 hr. After solvent removal and distillation (0.1 Torr, 70°, air bath) the resulting oil (777 mg) was subjected to preparative glc (3 ft column, 80°) to give (a) 8 (48 mg). End absorption, $\epsilon_{250} = 289$. ν_{max} 1725. NMR data Table 2. *m/e* 164 (M^+, 81), 135 (27), 91 (100), 43 (32). (b) 7 (146 mg) λ_{max} 225 (7650). ν_{max} 1719, 1600. NMR data Table 2. *m/e* 164 (M^+, 6), 135 (32), 91 (100), 43 (40).

6. 3E-BCHD (6). A 4:1 mixture (800 mg) of 2E-CHT (3) and 3E-CHT (4) from experiment 3 was irradiated in N_2 purged benzene (40 ml) through pyrex for 183 hr. The experiment was repeated 3 times and after removal of solvent the total material was subjected to distillation (0.3 Torr, 85°, air bath). Analytical

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[f] Based on simple MO-theory, excitation to S_2 would involve promotion of an electron from an orbital which is bonding between C(1)–C(2) and C(5)–C(6) to one which is antibonding.[18] No such change of the C(3)–C(4) interaction takes place and thus cross-over from S_2 to a *trans,cis,cis*-ground-state seems even more likely than from S_1.

glc of the resulting oil showed the presence of 7 (70%), 8 (26%) and an unknown (2%). Preparative glc (6 ft column, 155°) yielded 7 (532 mg) and 8 (167 mg). The glc waste trap was now much richer in the unknown component whose retention time was too close to that of 7 to allow separation on the first run. A second run on the waste trap contents enabled isolation of 6 (3 mg). The NMR (Table 2) and glc characteristics of this material were identical to those of a specimen synthesised as described in experiments 8–11.

7. 2-*Ethoxycarbonylquadricyclene* (13). A N_2 purged benzene soln of 1 (50 mg) in benzene (25 ml) was irradiated through quartz for 5 hr. After removal of solvent distillation (0.05 Torr, 60°, air bath) gave 13 (35 mg) as a colourless oil, ν_{max} 3160, 1711. $\tau(CDCl_3)$ 5.91 (2H; q; 7 Hz; $-C\underline{H}_2CH_3$), 7.61 (1H; d with fine coupling), 7.76 (1H; d with fine coupling), 7.89 (2H; s with fine coupling), 8.01 (1H; t with fine coupling), 8.38 (2H; m), 8.78 (3H; t; 7 Hz; $-CH_2C\underline{H}_3$). *m/e* 164 (M^+, 9), 91 (100), 66 (35), 65 (39), 43 (25).

8. *Ethyl* 2 - *oxobicyclo*(3.2.0)*hept* - 6 - *ene* - 3 - *carboxylate* (10). A soln of methyl magnesium carbonate was prepared as described[32] using Mg (2.02 g) and DMF (40 ml). Five degassed tubes each containing bicyclo(3.2.0)hept-6-ene-2-one[15,33] (150 mg) and methyl magnesium carbonate soln (2.5 ml) were heated at 116° for 50 min. The combined contents were added to a mixture of conc H_2SO_4 (25 ml) and abs EtOH (125 ml), left overnight and then the whole poured into water (600 ml) and ether extracted. After washing with sat $NaHCO_3$ aq, water and sat NaCl aq, the dried solvent was removed under vacuum. Distillation of the residue (0.1 Torr, 85°, air bath) gave 10 (745 mg) which exists as a keto-enol mixture, ~4:1 in chloroform, λ_{max} 260 (2340), λ_{sh} 305 (99). ν_{max} 3140–2700, 1750, 1725, 1657, 1615. $\tau(CDCl_3)$ 3.60–4.14 (2H; H(6) and H(7)), 5.73 (2H; q, 7 Hz; $-C\underline{H}_2CH_3$), 5.98–6.90 (3H; H(1), H(3) and H(5)), 7.40–8.30 (2H; H(4)), 8.75 (3H; t; 7 Hz; $-CH_2C\underline{H}_3$). *m/e* 180 (M^+, 28), 149 (43), 134 (37), 107 (35), 103 (56), 79 (100), 78 (56), 77 (58), 77 (25), 58 (96), 57 (45), 55 (56), 43 (94). The 2,4-dinitrophenylhydrazone of 10 was prepared, m.p. 122.5–126° (H_2O/EtOH) (Found: C, 53.7; H, 4.4; N, 15.6. Calc. for $C_{16}H_{16}H_4O_6$: C, 53.3; H, 4.4; N, 15.6%).

9. *Ethyl* 2 - *hydroxybicyclo*(3.2.0)*hept* - 6 - *ene* - 3 - *carboxylate* (11). To a soln of 10 (600 mg) in MeOH (90 ml) was added with stirring a soln of $NaBH_4$ (380 mg) in MeOH (65 ml). After stirring for 3 hr the solvent was removed and the residue partitioned between ether (4 × 100 ml) and water (100 ml). Removal of dried solvent gave a residue which was distilled (0.1 Torr, 80°, air bath) to give crude 11 (446 mg) as a colourless liquid. This was used directly for mesylation (experiment 10) but on one occasion a pure sample of 11 was prepared by column chromatography on florisil using 2:1 hexane:ether as eluant, ν_{max} 3445 (broad), 1731. $\tau(CDCl_3)$ 3.89 (2H; q; 3 Hz; H(6) and H(7)), 5.79 (2H; q; 7 Hz; $-C\underline{H}_2CH_3$), 5.87 (1H; m; H(2)), 6.47–7.10 (3H; m; H(1), H(2) and H(5)), 7.32 (1H; broad s; OH, exchanged with D_2O), 7.84–8.52 (2H; m; H(4)), 8.74 (3H; t; Hz; $-CH_2C\underline{H}_3$). *m/e* 182 (M^+, 9), 137 (25), 129 (30), 108 (40), 107 (32), 91 (70), 82 (25), 80 (32), 79 (100), 77 (55), 66 (40), 65 (35), 58 (32), 56 (66), 54 (45), 53 (35), 52 (40), 44 (90), 41 (40). On some occasions partial transesterification took place during this reaction. Subsequent treatment with ethanolic sulphuric acid gave 11.

10. *Ethyl* 2 - *mesyloxybicyclo*(3.2.0)*hept* - 6 - *ene* - 3 - *carboxylate* (12). Methane sulphonyl chloride (250 mg) was added to an ice cooled soln of 11 (92 mg) in dry pyridine (10 ml). After standing at RT overnight the mixture was poured into water (90 ml) and ether extracted (3 × 45 ml). The ether extract was washed with water (90 ml), 0.15 N HCl (3 × 90 ml) and water 2 × 90 ml). After removal of the dried ether a pale yellow homogenous oil (113 mg) was obtained, ν_{max} 1731, 1357, 1236. $\tau(CDCl_3)$ 3.90 (2H; s; H(6) and H(7)), 5.10 (1H; dd; 9 and 7 Hz; H(2)), 5.84 (2H; q; 7 Hz; $-C\underline{H}_2CH_3$), 6.48 (1H; dd; 7 and 4 Hz; H(1)), 6.55–6.90 (2H; m; H(3) and H(5)), 6.98, (3H; s; $-SO_2CH_3$), 7.80–8.60 (2H; m; H(4)), 8.74 (3H; t; 7 Hz; $-CH_2C\underline{H}_3$). *m/e* 260 (M^+, 15), 91 (100), 79 (32).

11. 3E-BCHD (6). To sodium hydride (~170 mg) prepared by washing a 50% suspension in oil with benzene (4 × 1 ml) was added 1,2-dimethoxyethane (20 ml, freshly distilled from LAH). This and the subsequent procedure were carried out under N_2. To the stirred mixture maintained at 75° was added mesylate 12 (114 mg) in dimethoxy-ethane (9 ml) and the temp. maintained for 6 hr. To the ice-cooled mixture was added glacial AcOH (1.6 ml), the whole poured into water (200 ml) and ether extracted (3 × 100 ml). The combined extracts were washed successively with water (90 ml), satd $NaHCO_3$ aq (90 ml), water (2 × 90 ml) and satd NaCl aq (90 ml). Removal of the dried solvent gave a crude product shown to contain one major component (~77%) by glc. Purification by tlc on silica gel (1:1 chloroform:benzene) followed by distillation (0.1 Torr, 60°, air bath) gave 6 (19 mg) as a colourless oil, λ_{max} 232.5 (5300). ν_{max} 1714, 1627. NMR data Table 2. *m/e* 164 (M^+, 15), 135 (78), 91 (100), 65 (27).

12. 3E-1M-HCT (47). A N_2 purged soln of ethyl diazoacetate (10 ml) in anisole (150 ml) was refluxed for 20 hr. After removal of the anisole under reduced pressure the residue was distilled (0.25 Torr, 100–125°, air bath) to give a pale yellow oil (10.5 g). A portion of this product (2 g) was subjected to dry column chromatography on silica gel (200 g) using 10:1 hexane:ether as eluent. This gave 47 (263 mg) which was distilled (0.2 Torr, 70–75°, air bath), λ_{max} 222 (10800), 264 (4100), 321 (4100). ν_{max} 1710, 1615. NMR data Table 1. *m/e* 194 (M^+, 5), 193 (50), 165 (26), 164 (38), 148 (38), 120 (100), 91 (67), 78 (43), 77 (50).

13. 1E-3M-CHT (48). Early chromatographic fractions containing 47 from experiment 12 were contaminated with a minor component. These were combined and subjected to preparative tlc on alumina using 15:1 hexane:ether as eluent (6 cycles) to give 48, λ_{max} 262 (4100), 325 (300). ν_{max} 1705, 1627. NMR data Table 1. The total amount of this compound isolated from one thermal decomposition of ethyl diazoacetate in anisole (experiment 12) was ~20 mg.

14. 4E-1M-CHT (46). Preparative glc (6 ft column, 190°) of a portion (0.92 g) of the distillate from experiment 12 yielded ethyl phenoxyacetate (77 mg), 47 (67 mg) and 46 (91 mg), λ_{max} 223 (14500), 314 (9500). ν_{max} 1705, 1610. NMR data Table 1. *m/e* 194 (M^+, 6), 193 (50), 164 (32), 148 (90), 120 (100), 91 (45), 78 (73), 77 (25).

15. 1E-6M-CHT (49). A N_2 purged soln of 47 (100 mg) in benzene (100 ml) was irradiated for 3 hr with a low pressure mercury lamp. Removal of solvent and chromatography of the residue on silica gel (10 g) using 10:1 hexane:ether as eluent gave a pale yellow oil (50 mg) which was distilled (0.2 Torr, 70–75°, air bath) to give 49, λ_{max} 227 (13300), 260 (2600), 340 (3900). ν_{max} 1705, 1620. NMR data Table 1. *m/e* 194 (M^+, 20), 165 (100), 121 (25), 91 (35).

16. *Irradiation of* 3E-1M-CHT (47) *in benzene.* A N_2 purged soln of 3E-1M-CHT (70 mg) in benzene (75 ml) was irradiated through pyrex for 1 hr. After this time glc and tlc analysis showed complete loss of starting material and the formation of two products. These were separated by preparative tlc on silica gel using 95:5 hexane:acetone as eluent to give (a) 50 (38 mg), λ_{max} 218 (8000). NMR data Table 2. *m/e* 194 (M^+, 3), 166 (25), 149 (68), 121 (100), 91 (83), 79 (25), 78 (25), 77 (44). (b) 51 (19 mg), λ_{max} 224 (6800). NMR data Table 2. *m/e* 194 (M^+, 1), 166 (67), 121 (48), 105 (33), 91 (100), 78 (95), 77 (95).

17. *Irradiation of* 1E-3M-CHT (48) *in benzene.* Treatment of 48 under conditions identical to those of experiment 16 resulted in loss of starting material after 1 hr. The total product was essentially identical (glc, tlc and NMR) to that from experiment 16.

18. *Irradiation of* 1E-6M-CHT (49) *in benzene.* Treatment of 49 under conditions identical to those of experiment 16 resulted in loss of starting material after 2.0 hr. Analysis by glc, tlc and NMR showed the total product to be essentially pure 51.

19. *Thermolysis of* 7E-5M-BCHD (50). A degassed soln of 50 (23 mg) in benzene (2 ml) was heated in a sealed pyrex tube at 155° for 4 hr. The NMR spectrum of the product after solvent removal was of a mixture of 47 (40%) and 49 (60%).

20. *Thermolysis of* 3E-5M-BCHD (51). Procedure identical to that in experiment 19 converted 51 quantitatively into 49.

21. *Thermolysis of* 3E-1M-CHT (47). A series of experiments using a procedure apparently identical to that of experiment 19 resulted in varying degrees of conversion of 47 into 49. It would appear that surface catalysis is playing a role in this isomerisation process.

22. *Irradiation of* 4E-1M-CHT (46) *in benzene.* Treatment of 46 under conditions identical to those of experiment 16 resulted in extremely slow loss of starting material to give one product as monitored by NMR. Reaction was complete after 400 hr and the product was identified solely on the basis of its NMR spectrum (Table 2) as 52. On attempted analysis by glc or tlc on silica gel only 46 could be identified indicating the facile nature of the reverse reaction. On one occasion attempted preparative tlc of a product shown to be essentially homogenous 52 by NMR resulted in isolation of 46 in 75% yield.

23. *Prolonged irradiation of* 3E-1M-CHT (47). An experiment identical to 16 was performed except that irradiation was continued for 80 hr. Analysis by glc indicated the expected rapid production fo 50 and 51 followed by slow disappearance of the peaks due to these products and their replacement by a single major peak. The NMR spectrum of the final product indicated the presence of traces of 50 and 51 and two major products in approximately equal amounts. The products could not be separated due to their identical glc characteristics and instability with respect to hydrolysis. They were identified as 55 and 56 from the NMR spectrum of the mixture (Table 2) and their hydrolysis to the ketone 57 (experiment 25).

24. *Prolonged irradiation of* 1E-6M-CHT (49). An experiment identical to 18 was performed except that irradiation was continued for 80 hr. The NMR spectrum of the final product was very similar to that obtained in experiment 23. On repetition of experiments 23 and 24 some variation in the 55:56 ratio was observed.

25. *Ethyl 2-oxobicyclo*(3.2.0)*hepta-2,6-diene-1-carboxylate* (57). The product from experiment 23 (20 mg) was refluxed in 50% aq EtOH (15 ml) containing 2 N HCl (0.5 ml) for 30 min. The mixture was poured into water (100 ml) and the whole ether extracted. Removal of the dried solvent and distillation of the residue (0.1 Torr, 85°, air bath) gave 57 (18 mg), λ_{max} 303 (94). IR and NMR data theoretical section. *m/e* 180 (M^+, 29), 152 (96), 151 (57), 135 (43), 134 (43), 124 (38), 123 (100), 108 (34), 107 (83), 106 (30), 105 (30), 80 (38), 79 (61), 78 (50), 77 (50).

Similar treatment of the product from experiment 24 gave an essentially identical result.

26. *Irradiation of benzene solutions of* 3E-1M-CHT (47) *and* 1E-6M-CHT (49) *in the presence and absence of oxygen.* Each cycloheptatriene (20 mg) in benzene (15 ml) was sealed in both a non-degassed and a freeze-thaw degassed (6 cycles) pyrex tube. The tubes were irradiated on a merry-go-round apparatus for 95 hr and the products analysed by NMR spectroscopy (Table 6).

27. *Irradiation of a* 1E-3M-BCHD (55): 5E-2M-BCHD (56 *mixture in air saturated benzene.* Two sealed pyrex tubes each containing a mixture of the enol ethers 55 and 56 (24 mg) in air saturated benzene (17 ml) were irradiated on a merry-go-round apparatus for 27 and 46 hr respectively. The NMR analysis showed progressive loss of the enol ethers to the extent of 60% after 46 hr. New signals in the spectra were not present in the NMR spectra of the products of the non-degassed reactions described in experiment 26. This also applied to the respective glc chromatograms.

28. *Irradiation of a cyclohexane solution of* 3E-1M-CHT (47) *at* 313 nm. A N_2 purged soln of 47 (372 mg) in cyclohexane (350 ml) was irradiated through a filter solution consisting of 0.02 M potassium chromate in 1% potassium carbonate.[29] Conversion to a single product was complete after 80 hr. It was identified as 50 by glc and NMR.

29. *Irradiation of a cyclohexane solution of* 1E-6M-CHT (49) *at* 313 nm. A N_2 purged soln of 49 (122 mg) in cyclohexane (200 ml) was irradiated as in experiment 28. Conversion to a single product had occurred to the extent of 35% after 90 hr. It was identified as 51 by glc and NMR.

30. *Irradiation of a cyclohexane solution of* 1E-6M-CHT (49) *at* 254 nm. A N_2 purged soln of 1E-6M-CHT (51 mg) in cyclohexane (50 ml) was irradiated with a low pressure mercury lamp through glass which transmits above 200 nm and the reaction monitored for 5 hr by glc. The observed products were 51 and 56 (see Fig. 2), identified by glc and NMR.

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