Mechanistic variations in the formation of benzocyclooctatetraene from benzobicyclo[4.2.0]octa-2,4,7-triene

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Abstract: Benzocyclooctatetraene (i.e., COT, 2) is the major product from the thermolysis and direct photolysis of 2,3-benzobicyclo[4.2.0]octa-2,4,7-triene (i.e., triene 1). It is also a minor product from the sensitized irradiation of 1. The mechanism of the reaction $1\rightarrow 2$ was investigated using deuterium-labelled triene (i.e., 1a/b), which was prepared in a two-step procedure from a known triene mixture (1*a*) containing deuterium at both C-4 (43%) and C-5 (97%): the thermolysis of 1*a* led to labelled COT 2*a*, which upon direct irradiation ($\lambda \ge 310$ nm) gave the deuterated triene mixture 1a/b in good chemical yield (61%) but in low quantum efficiency ($\Phi \approx 0.0001$). The COT produced from the direct irradiation (Corex filter) of 1a/b possessed different deuterium distributions than when generated thermally or from triplet sensitization (*p*-dimethylaminobenzophenone), as determined by ¹H NMR integration. The observed deuterium-labelling patterns are in accord with a Zimmerman di- π -methane rearrangement being involved in formation of the COT from S₁ of triene 1, while a mechanism proceeding by initial cleavage of the cyclobutene C₁—C₆ bond appears to operate during the thermal or sensitized (T₁) generations of 2.

Key words: mechanisms, rearrangements, photochemistry, di- π -methane.

Résumé: Le benzocyclooctatétraène (soit, le COT, 2) est le principal produit soit lorsqu'on chauffe des solutions du composé 2,3-benzobicyclo[4.2.0]octa-2,4,7-triène (1), ou lorsqu'on le photolyse directement. Le composé COT 2 est aussi un produit mineur des irradiations sensibilisées du triène 1. Le mécanisme pour la réaction $1\rightarrow 2$ a été étudié à l'aide du triène marqué au deutérium (1*a/b*). On a préparé le mélange 1*a/b* en deux étapes à partir du triène 1*a* contenant des atomes de deutérium à C-4 (43%) et à C-5 (97%) : la thermolyse du triène 1*a* conduit au COT 2*a* qui ensuite se transforme en 1*a/b* par irradiation directe, en bon rendement (61%) mais faible efficacité ($\Phi \approx 0,0001$). Les distributions de deutérium dans le COT obtenu par irradiation directe (filtre de Corex), par thermolyse ou par irradiation sensibilisée (*p*-diméthylaminobenzophénone), du 1*a/b* sont différentes. Des études de marquage suggèrent qu'une transposition di- π -méthane de Zimmerman est le mécanisme qui produit le COT à partir du S₁ du triène 1, tandis que la voie suivie pendant la thermolyse ou l'irradiation sensibilisée (T₁) est une ouverture de la liaison C₁—C₆ du composé 1.

Mots clés : mécanismes, transpositions, photochimie, di- π -méthane.

Introduction

There is current interest in the synthesis of benzocyclooctenes due to their demonstrated potential for conversion, via Birch reduction, to derivatives of the anti-cancer drug Taxol (1). Recently, we reported (2) that unsubstituted benzocyclooctatetraene (2) is the major product from both the thermolysis and the direct photolysis of 2,3-benzobicyclo[4.2.0]octa-2,4,7-triene (1). It is also a very minor product from sensitized irradiations of the triene. Details of the ground and excitedstate products of triene 1 are summarized in Scheme 1. It was noted that a simple $2\sigma_s+2\pi_s$ electrocyclic opening (3) of the cyclobutene ring of triene 1 could account for the COT formation in each case, and experiments using deuterium-labelled starting material $(1-d_2)$ gave results consistent with this mechanistic view, viz $1-d_2 \rightarrow 2-d_2$ (Scheme 1). We now report fur-

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Scheme 1. Triene thermolysis and photolyses products.



ther results based on a new labelling pattern that indicate that the pathways used in the formation of COT 2 from triene 1 involve different carbon reorganizations when formed from the singlet excited state than when generated from sensitization (T_1) or from thermolysis.

Results

The deuterium-labelled triene used in the present study was

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Entry no.	Origin	% Hydrogen atom distributions at:		
		C-5,10 (s:d) δ 6.55	C-6,9 (s:d) δ 6.03	C-7,8 ^a δ 5.88
1	Observed for thermolysis of 1a	1.56 (1:2.1)	1.04 (<0.05:1.0)	2.01
2	Calcd. for $1a \rightarrow 2a$ or $1a/b \rightarrow 2a$	1.57 (1:1.9)	1.03 (0:1.0)	2.00
3	Observed for thermolysis of 1a/b	1.51 (1:1.9)	1.01 (<0.02:1.0)	2.01
4	Calcd. for $1a/b \rightarrow 2c$	1.57 (1:0.6)	1.03 (0.7:1.0)	2.00
5	Observed for sensit. hv of 1a/b	1.54 (1:1.9)	0.96 (<0.05:1.0)	1.96
6	Observed for direct hv of $1a/b$	1.54 (1:3.2)	1.33 (0.1:1.0)	1.72
7	Calcd. for $1a/b \rightarrow 2a/b$ or $\rightarrow 2a/d$	1.57 (1:3.0)	1.30 (0.1:1.0)	1.73
8	Calcd. for $1a/b \rightarrow 2c/b$	1.57 (1:1.3)	1.30 (0.5:1.0)	1.73

Table 1. Hydrogen atom distributions of the nonaromatic positions in deuterated benzocyclooctatetraenes.

"In each case the aromatic multiplet at δ 6.93–6.99 was set as the normalized integration standard of 2.00H; the other aromatic multiplet at δ 7.17–7.24 gave integral values within the range 2.00–2.04H.



prepared in a two-step procedure from the known (2) triene mixture 1*a*, which contained deuterium at both C-4 (43%) and C-5 (97%) (Scheme 2). Thus, the thermolysis of 1*a* led to the labelled COT 2*a* (see Table 1, entry 1, for the ¹H NMR integrations of the aliphatic hydrogens), which upon direct irradiation ($\lambda \ge 310$ nm) gave the deuterated triene mixture 1*a* and 1*b* in good chemical yield (61%, based on 35% conversion), but in low quantum efficiency ($\Phi \approx 0.0001$). The inefficiency of the rearrangement may provide an explanation for a previous report that found COT 2 to be unreactive (4). The label distributions in the isotopic triene mixture 1*a,b* were determined by proton NMR analysis (see Experimental); a small isotope effect ($k_{1b}/k_{1a} \le 1.2$) in favour of the formation of 1*b* was observed in the $2\pi + 2\pi$ photoclosure step.

A solution of the mixture 1a,b in *n*-nonane, when heated to reflux (150°C) for 12 h, gave a 75% yield of COT product, which showed no deuterium attachment to C-7 and C-8 (i.e., the γ carbons) and corresponded uniquely to the presence of the mixture 2a (note Scheme 3). The observed and calculated ¹H NMR integration values are listed in Table 1 (see entries 3 and 2, respectively). Although in principle the isotopic mixture 2c (note structure in Scheme 3) would also lead to the same overall proton integrations as 2a, we were able to rule out the formation of 2c on the basis of the NMR peak ratios of

Scheme 3. Observed and possible label locations in COT product from triene thermolysis and photolyses.



the two types of signal (a singlet and a doublet)² observed for the COT α hydrogens (i.e., for H-5 and H-10), and also those found for the β hydrogens (i.e., H-6 and H-9). If **2***c* were present, the anticipated ratio of the singlet to doublet peaks would then be 1(s):0.6(d) for the α hydrogens, and 0.7(s):1.0(d) for the β hydrogens (see entry 4, Table 1). The observed ratios were 1(s):1.9(d) and <0.02(s):1.0(d), respectively, which agrees with the ratios required for **2***a* (see entry 2, Table 1).

In the case of the COT product isolated from the direct irradiation of the triene mixture 1a, b, the NMR hydrogen distributions were distinctly different from those found for the

² There are two types of signal observed for the α hydrogens: besides the doublet centred at $\delta 6.55 (J_{5(10),6(9)} = 12 \text{ Hz})$ there is a singlet at $\delta 6.55$ that results from the absence of coupling when a β carbon is partially deuterated. The integration ratio of the singlet to doublet signals indicates the relative amount of deuterium at the β positions. The situation is similar for the β hydrogens, which occur as a doublet of triplets centred at $\delta 6.03$ $(J_{6(9),5(10)} = 12 \text{ Hz}, J_{6(9),7(8)} = J_{6(9),8(7)} = 2 \text{ Hz})$, and which are accompanied by a broad singlet at $\delta 6.03$ when an α carbon is partially deuterated.

Scheme 4. Mechanisms that operate in semibullvalene photoformation.

thermally generated COT.³ Importantly, the integrations for the β hydrogens were heavy, while those for the γ hydrogens were light (note entry 6, Table 1), and accord well with a composite of 72.5% 2a and 27.5% 2b (note entry 7, Table 1). Although the formation of mixture 2c in place of 2a can be discounted, since this would have led to significantly different s:d ratios for the α and for the β hydrogen signals (see entry 8, Table 1), we are not able to eliminate the possibility that isotope mixture 2d (see structure in Scheme 3) forms part of the COT product in place of 2b: both 2b and 2d would give the same gross proton integrations and also the same s:d ratios for the α and for the β signal peaks (see entry 7, Table 1). Similar difficulties in interpretation of the proton distributions for related deuterated benzocyclooctatetraenes were encountered by Zimmerman, Givens, and Pagni (4), and arise from the C_{2y} symmetry of the benzo-COT system.

In contrast to the direct irradiation results, the COT material obtained from the sensitized irradiation of the triene mixture 1a,b showed NMR spectral details that were the same as those observed for the thermally generated COT 2a product (cf. Table 1, entries 5 and 3, respectively).³

The direct and sensitized photolyses of the deuterated triene also gave the labelled semibullvalenes (i.e., SB) 3a-c. The observed SB deuterium distributions (see Experimental) depend on the mode of excitation and fully confirm conclusions from a previous report (2) that the semibullvalene product from direct irradiation derives from two reaction pathways (note Scheme 4, route A (17%) and route B (83%)), whereas that from triplet senistization is provided uniquely by a Zimmerman di- π -methane (DPM) rearrangement (5) (Scheme 4, route B). **Scheme 5.** Mechanisms that account for COT formation from triene thermolysis and sensitized irradiation.



Discussion

The thermal rearrangement of the parent aliphatic triene 7 to COT 8 (Scheme 5) is a facile reaction (6) that is formally a $2\pi_s + 2\pi_s + 2\sigma_s$ electrocyclic opening of the six-membered ring (3). The concerted process, however, would be expected to be more demanding in the case of the benzo derivative 1 since the initial loss of aromaticity (note route C and structure 9a, Scheme 5) is required before bond reorganization can occur to give the boat structure of COT 2a. It is therefore not surprising that benzo-triene 1 has a half-life of ca. 1 h at 150°C whereas the parent triene 7 has a $t_{1/2}$ of 14 min at 0°C (6). An alternative explanation for the thermal rearrangement of triene 1 to COT 2 is that the reaction proceeds via a stepwise process (route D, Scheme 5) involving the initial cleavage of the strained C_1 — C_6 bond of 1a,b. The observed deuterium labelling in 2a is in accord with operation of either route C or route D (Scheme 5).

The photochemical generation of COT from triene **1** is more complex. The previous study (2) of the excited-state reactivity of **1** showed that \geq 98% of the COT produced from the direct irradiation originates from the S₁ state of the triene; the COT from sensitized runs is triplet derived (T₁). The present results now reveal that S₁ and T₁ engage different pathways when forming the COT. In the case of T₁, the observed COT deuterium-labelling pattern (entry 5, Table 1) is consistent with a process that proceeds with a simple opening of the cyclobutene ring of triene **1**, similar to the stepwise thermal pathway to COT **2***a* (cf. route D, Scheme 5).

The COT formed from S_1 , on the other hand, must involve another mechanism, at least in part, since deuterium occurs also at the γ carbon(s) (note entry 6, Table 1). One possible rationale that does account for the observed label distribution involves the formation of the COT products 2a and $2d^4$ via a 1:1 competition between the pathways depicted in Scheme 6 (routes E and F): 2a may derive in part (50%) from the $2\sigma_s +$ $2\pi_s$ electrocyclic process (route F) or stepwise, whereas 2d(27.5%) and additional 2a (22.5%) may arise from the initial C_5 – C_8 diagonal bridging shown as route E. However, a point of concern with this rationale is that the latter mechanism has not been reported in derivatives of bicyclo[4.2.0]octatriene,



³ To minimize complications due to possible kinetic isotope effects in the photolyses of triene mixture 1a,b, the runs were carried out to almost complete conversion of the starting material: $\geq 97\%$ in the direct irradiation, and 96% in the case of sensitization.

⁴ We are unable to differentiate between isomer mixture 2*d* and 2*b* with the NMR data at hand, vide supra.

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Scheme 6. Possible mechanism for COT formation from direct irradiation of triene.



and diagonal bridging of this kind is unknown in other di- π -methane systems.⁵

A more simple explanation of the labelling results, and one that has literature precedence, involves the coformation of the COTs 2a and 2b from a single mechanistic pathway. This pathway proceeds by Zimmerman DPM rearrangement (5) of triene 1 and entails the initial formation and subsequent thermal reorganization of the symmetrical octavalene intermediate 12 (note Scheme 7). The final step is assumed to occur with equal facility via rupture of alternate pairs of allylic (b and d) and benzylic (a and c) bonds of 12, i.e., 50% by cleavage of bonds a and b, and 50% by cleavage of bonds c and d. A similar mechanism was previously invoked by us (7) to account for the photochemical conversion of the 8-cyano triene 13 to equal amounts of the labelled cyano COTs 17 and 18 (see route G, Scheme 8). Interestingly, and as required by the present proposal for 1, in the case of 8-cyano triene 13 the $2\sigma_s + 2\pi_s$ electrocyclic opening (route H, Scheme 8) was totally avoided, i.e., COT 19 was not detected. We have not obtained physical evidence for the formation of the octavalene 12 during the direct photolysis of 1, but this may be due to the rate of rearrangement of $12 \rightarrow 2$ being much higher than the rate of formation of the octavalene at the photolysis temperature employed (ca. 20°C). The 1,4-diradical 5 is thus viewed to be a common species on the pathways to the major products observed in the photochemistry of triene 1, and rearranges to give alternative vinylcyclopropanes, i.e., SB $3b_{,c}$ (route B, Scheme 4) and the thermally unstable octavalene 12 (Scheme 7).

A referee has suggested an additional route that might account for the label distributions in the COT product obtained from the triene direct irradiation, viz. rearrangement of 1a,b to benzobarrelene (a photochemically allowed 1,3-shift), which then undergoes the well-known singlet-mediated transformation to COT (4). Evidence against this proposal exists from a previous study (2) based on the labelled triene $1-d_2$ (note structure in Scheme 1). If the benzobarrelene 20 (note Fig. 1 below) were formed from $1-d_2$ its subsequent photolysis would have led to the COT mixture $2a_{,b}$ d_2 through a pathway that involves initial $2\pi + 2\pi$ bridging, mainly $(94 \pm 3\%)$ between the benzo-vinyl portions of 20 (4). The NMR spectrum of the COT product therefore would have revealed a low hydrogen integration for the γ hydrogens. The reported (2) integration value was 1.97H, which indicates that within experimental error no deuterium was attached to the COT C-7 or C-8 positions. Hence the COT $2a \cdot d_2$ is not formed, and consequently (assuming reasonable isotope effects) the pathway depicted in Fig. 1 does not operate. Furthermore, careful

Scheme 7. Suggested mechanism for COT formation from direct irradiation of triene.



Structures denoted by "a" and "b" represent compounds labelled with deuterium at the positions marked by \triangle and \bullet . For structures denoted by a number only (e.g.,12) \triangle and $\bullet = H$.

Lastly, we note that the proposed pathway in Scheme 7 is attributed to S_1 of 1. Although the occurrence of a DPM rearrangement from S_1 is uncommon in rigid molecules (5), it has precedent in other benzobicyclo[4.2.0]octa-2,4,7-trienes (8), e.g., 13 gives 17 and 18 (7).

Experimental

Instrumentation and materials

The ¹H spectra were recorded in CDCl₃ solvent at 250 MHz; the chemical shifts are in δ units and the coupling constants (*J*) in Hz. The abbreviations br, s, d, t, q, and m refer to broad, singlet, doublet, triplet, quartet, and multiplet, respectively. Cyclohexane solvent for photolyses was prepared by scrub-

monitoring of the photolysates of the direct irradiation of triene 1 revealed no trace of benzobarrelene (by NMR and GC analyses).

Fig. 1. Location of deuterium labels in COT product formed from benzobarrelene.





Scheme 8. Label locations in COT product from direct irradiation of 8-cyano triene.

bing with 20% fuming sulfuric acid, followed by washing with 10% aqueous sodium hydroxide, drying (MgSO₄), and finally distilling from calcium hydride. Column chromatography was carried out on Silica Gel 60 (Merck; 230–400 mesh), or Lobar columns (Merck; size B, LiChroprep Si 60), or on Silica Gel 60/AgNO₃ columns (10:1, by weight). The GC analyses were determined by FID on a DB-23 fused silica capillary column (30 m × 0.25 mm; J&W Scientific).

General procedures for preparative photolyses

The apparatus consisted of a 450-W Hanovia medium-pressure mercury arc surrounded by a water-cooled quartz immersion well. Unless otherwise stated, the light was filtered through either a cylindrical sleeve of Pyrex, or Corex, or an aqueous lead nitrate solution (1 g of Pb(NO₃)₂ and 100 g of NaBr in 1 L of water; transmittance was 0% below 318 nm) contained in a concentric filter jacket (10 mm path length). Three types of sample cell were used. Cell A (200 mL sample volume) consisted of a cylindrical collar (Pyrex) that surrounded the aqueous filter jacket. Cell A was fitted with gas inlet and exit ports, and sample solutions were purged with argon prior to and during irradiations. Cell B (40 mL sample volume) and Cell C (3.5 mL) were a quartz test-tube-like vessel and a quartz cuvette, respectively; sample solutions contained therein were deoxygenated by flushing with argon and sealed under a positive pressure; the solutions were magnetically stirred throughout the course of the irradiations.

Deuterium-labelled triene 1a

Deuterated triene 1a (97%- d_1 labelled at C-5 and 43%- d_1 labelled at C-4) was obtained as previously described (2); ¹H NMR: 7.00–7.17 (m, 4.35H, aromatics and residual CHCl₃), 6.26 (br s, 0.57H, H-4), 6.13 (d, 1.02H, H-7, $J_{8,7} = 2.7$), 6.02 (dd, 0.98H, H-8, $J_{7,8} = 2.7$, $J_{7,6} = 0.9$), 5.88 (dd, 0.03H, H-5, $J_{5,4} = J_{5,6} = 4.5$), 4.11 (d, 1.02H, H-1, $J_{1,6} = 4.5$), and 3.64 (d, 1.00H, H-6, $J_{6,1} = 4.5$).

Thermolysis of deuterium labelled triene 1a

A solution of 186.6 mg (1.21 mmol) of triene 1a in 4 mL of *n*nonane was refluxed (ca. 150°C) for 10 h. The thermolysis product was chromatographed on Silica Gel 60 (0.9 cm × 10 cm; hexane), to give 162.7 mg (87%) of COT 2a; mp 47–49°C (lit. (4) mp 48–50°C); ¹H NMR: 7.17–7.24 (m, 2.03H, aromatics), 6.93–6.99 (m, 2.00H, aromatics), 6.55 (d + br s, 1.56H, H-10 and H-5, $J_{10,9} = 11.8$), 6.03 (dm, 1.04H, H-6 + H-9, $J_{9,10} = 11.5$), and 5.88 (d, 2.01H, H-7 and H-8, J = 1.8); the ratio of the s:d at $\delta 6.55$ is given in entry 1, Table 1.

Formation of mixture **1**a,b from direct irradiation of COT **2**a A solution of 162.0 mg (1.05 mmol) of 2a in 200 mL of cyclohexane was irradiated at >318 nm for 91 h in Cell A (ca. 35% conversion by GC). The photolysate was concentrated and chromatographed on a Silica Gel/AgNO₃ column ($1 \text{ cm} \times 11$ cm; 0.1% ethyl acetate – hexane). Two bands were observed. The first band contained 34.4 mg (21%) of the triene mixture 1a,b; ¹H NMR: 7.00–7.17 (m, 4.15H, aromatics and residual CHCl₃), 6.26 (d + br s, 0.81H, H-4), 6.13 (br s, 1.02H, H-7), 6.02 (br d, 0.46H, H-8, $J_{8,7}$ = 2.7), 5.88 (dd, 0.55H, H-5, $J_{5,4}$ = $J_{5.6} = 4.5$), 4.11 (d, 0.76H, H-1, $J_{1.6} = 4.5$), and 3.64 (br d, 1.00H, H-6, $J_{6,1} = 4.5$); the calculated integrations for a mixture of 55% 1a and 45% 1b are: 0.81 H-4, 1.00 H-7, 0.47 H-8, 0.56 H-5, 0.76 H-1, and 1.00 H-6. The second band off the column gave 105.8 mg (65%) of recovered COT 2a; ¹H NMR: 7.17-7.24 (m, 2.02H, aromatics), 6.93-6.99 (m, 2.00H, aromatics), 6.55 (d + br s, 1.60H, H-10 and H-5, $J_{10.9} = 11.8$), 6.03 (dm, 1.01H, H-6 + H-9, $J_{9,10} = 11.5$), and 5.88 (d, 1.98H, H-7 and H-8, J = 1.8).

Thermolysis of deuterium-labelled triene Ia,b

A solution of 4.0 mg (0.026 mmol) of triene 1a,b in 1 mL of *n*nonane was refluxed (ca. 150°C) for 12 h. The thermolysis product was chromatographed on Silica Gel 60 (0.9 cm × 10 cm; hexane), to give 3.0 mg (75%) of COT 2a; note Table 1, entry 3 for details of the ¹H NMR spectrum.

Direct irradiation of labelled triene mixture 1a,b

A solution of 39.4 mg (0.26 mmol) of 1a, b and ca. 40 mg of dodecane (GC standard) in 40 mL of cyclohexane was irradiated (Corex filter) for 30 min in Cell B (97% conversion by GC). The photolysate was chromatographed, first on Silica Gel 60 (0.9 cm \times 10 cm; 100 mL hexane) to remove polymeric materials, and then on a Lobar column with hexane solvent. The first band gave ca. 2 mg (5%) of naphthalene (identified by GC comparison with an authentic sample). The last band (i.e., third) gave 7.5 mg (19%) of deuterated 3,4-benzotri $cyclo[3.3.0.0^{2.8}]octa-3,6-diene$ (i.e., SB mixture 3a-c) as a colourless oil (GC purity >98%), which was identified by comparison of the chemical shifts and coupling constants of the ¹H NMR spectrum with that reported for authentic SB 3 (4); 1 H NMR: 7.31-7.35 (m, 1.00H, aromatic), 7.04-7.18 (m, 3.20H, aromatics), 5.60 (dd, 0.47H, H-6, $J_{6,7} = 5$, $J_{6,5} = 2.3$), 5.21 (m, 0.99H, H-7, $3.90 (dd, 0.77H, H-5, J_{5,1} = 6.3, J_{5,6} = 2), 3.29 (m, 10.00)$ 0.94H, H-1), 3.04 (t, 0.81H, H-2, $J_{2,1} = J_{2,8} = 6.3$), and 2.70– 2.76 (m, 0.67H, H-8); the calculated integrations for a mixture of 7.7% 3a, 55% 3b, and 37.4% 3c (as required by 17% utilization of route A and 83% of route B, Scheme 4) are 0.47 H-6, 1.00 H-7, 0.76 H-5, 0.93 H-1, 0.81 H-2, and 0.64 H-8.

The contents of the second band from the Lobar chromatography were rechromatographed on a Silica Gel $60/\text{AgNO}_3$ column (1 cm × 11 cm; 0.1% ethyl acetate – hexane). Two bands were observed. The first band contained 1.0 mg (2.5%) of recovered triene mixture 1a/b; ¹H NMR: 7.00–7.17 (m, 4.15H, aromatics and residual CHCl₃), 6.26 (d + br s, 0.84H, H-4), 6.13 (br s, 1.00H, H-7), 6.02 (br d, 0.38H, H-8, $J_{8,7}$ = 2.7), 5.88 (dd, 0.63H, H-5, $J_{5,4} = J_{5,6} = 4.5$), 4.11 (d, 0.71H, H-1, $J_{1,6} = 4.5$), and 3.64 (br d, 1.00H, H-6, $J_{6,1} = 4.5$). The second band off the column gave 11.8 mg (30%) of COT 2*a*,*b* (or perhaps 2*a*,*d*); note Table 1, entry 6 for details of the ¹H NMR spectrum.

Sensitized irradiation of labelled triene mixture 1a,b

A solution containing 12.9 mg (0.058 mmol) of p-dimethylaminobenzophenone, 43.5 mg (0.28 mmol) of 1a, b, and 29.3 mg of dodecane (GC standard) in 40 mL of cyclohexane was irradiated for 40 min in Cell B, with light filtered through a Pyrex and WG 345 glass (Schott) filter (95% conversion by GC). The photolysate was concentrated, chromatographed on Silica Gel 60 (0.9 cm \times 10 cm; 100 mL hexane) to remove polymeric materials and sensitizer, and then rechromatographed on a Lobar column (hexane). The first band contained a trace of naphthalene (identified by GC comparison with an authentic sample). The second band gave 1.6 mg (4%) residual triene mixture 1a/b, ¹H NMR: 7.00–7.17 (m, 4.26H, aromatics and residual CHCl₃), 6.26 (d + br s, 0.81H, H-4), 6.13(br s, 1.00H, H-7), 6.02 (br d, 0.43H, H-8, $J_{8,7}$ = 2.7), 5.88 (dd, 0.60H, H-5, $J_{5,4} = J_{5,6} = 4.5$), 4.11 (d, 0.74H, H-1, $J_{1,6} = 4.5$), and 3.64 (br d, 1.01H, H-6, $J_{6,1} = 4.5$). The third band gave ca. 1.0 mg (2%) of COT 2a: note Table 1, entry 5, for details of the ¹H NMR spectrum.

The final band gave 24.1 mg (55%) of SB mixture 3b,c (GC purity >98%); ¹H NMR: 7.31–7.35 (m, 1.00H, aromatic), 7.04–7.18 (m, 3.29H, aromatics), 5.60 (dd, 0.46H, H-6, $J_{6,7} = 5$, $J_{6,5} = 2.3$), 5.21 (m, 1.00H, H-7), 3.90 (dd, 0.76H, H-5, $J_{5,1} = 6.3$, $J_{5,6} = 2$), 3.29 (m, 1.01H, H-1), 3.04 (t, 0.80H, H-2, $J_{2,1} = J_{2,8} = 6.3$), and 2.70–2.76 (m, 0.59H, H-8); the calculated integrations for a mixture of 55% 3b, and 45% 3c (as required by 100% utilization of route B Scheme 4) are 0.47 H-6, 1.00 H-7, 0.76 H-5, 1.00 H-1, 0.81 H-2, and 0.56 H-8.

Quantum efficiencies

The quantum yield for the conversion of COT $1\rightarrow 2$ was performed on an apparatus previously described (9), which includes an optical bench arranged for beam splitting into a potassium ferrioxalate actinometer (10). Cyclohexane solutions (in Cell C, 3.5 mL) of COT 2 (8 × 10⁻₃ M) were deoxygenated prior to irradiation by flushing with argon. A positive pressure of argon was maintained over the stirred solutions throughout the course of the irradiations carried out with light of wavelength 313 nm. The quantum yield of 0.0001 was obtained from two runs extrapolated to zero conversion. Product analyses were determined by GC (internal dodecane standard).

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