The differing mechanisms of photo-formation of 7-cyanobenzocyclooctatetraene from 7- and 6-cyano-2,3-benzobicyclo[4.2.0]octa-2,4,7-triene

Christopher Owen Bender, Douglas Dolman, Jeremy Christian Foesier, Sherry Lee Lawson, and Kathryn Elvia Preuss

Abstract: It is known that 7-cyanobenzocyclooctatetraene (COT **2**) is a product of the thermolysis and direct photolysis of 7- and 6-cyano-2,3-benzobicyclo[4.2.0]octa-2,4,7-triene (**1** and **5**), though the mechanisms of these rearrangements have not been reported. In the present study experiments have been carried out using the deuterium-labelled trienes **1***a* (93%-d_1 at C-6) and **5***a* (93%-d_1 at C-8), which were formed from $2\pi + 2\pi$ photo-closure (direct irradiation) of COT **2***a* labelled at C-8. The results reveal that whereas the thermolysis of **1***a* and **5***a* and the direct irradiation of **5***a* reform COT **2***a*, probably via cleavage of the strained cyclobutene C-1—C-6 bond, the direct irradiation of triene **1***a* gives a differently labelled COT product, containing the deuterium exclusively at C-9. The mechanism proposed for the latter phototransformation is a modification of the Zimmerman di-π-methane rearrangement.

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

Résumé : Il est connu que le cyano-7 benzocyclooctatétraène (COT **2**) est un produit soit lorsqu'on chauffe des solutions des composés cyano-7 et -6 benzo-2,3 bicyclo[4.2.0]octatriènes-2,4,7 (**1** et **5**) ou lorsqu'on les photolyses directement, mais les mécanismes pour les transpositions n'étaient pas données. Ces transpositions ont été réétudiées avec des triènes marqués au deutérium: le triène **1***a* contient 93 %-d_1 à C-6, tandis que le triène **5***a* contient 93 %-d_1 à C-8. Des triènes **1***a* et **5***a* sont issus de l'irradiation directe du COT **2***a* marqué au deutérium à C-8 (93 %). Des études de marquages démontrent que le COT **2***a* se formant thermiquement du **1***a* et du **5***a*, et photochimiquement du **5***a*, dérive vraisemblablement d'une ouverture de la liaison C-1—C-6 des triènes. Par contre, l'irradiation directe du triène **1***a* conduit à COT **2***b* marqué au deutérium uniquement à C-9 (93 %). Un mécanisme modifié de Zimmerman est suggéré pour cette dernière transposition, **1***a* → **2***b*.

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

Introduction

Routes to cyclooctanoids continue to be of interest because of their wide occurrence in natural products, many of which exhibit potent biological activity, with the anti-cancer drug paclitaxel being a notable example (1). Some time ago (2) we reported that 7-cyanobenzocyclooctatetraene (i.e., 7-cyano-COT, **2**) is the unique product from the thermolysis of 7- and 6-cyano-2,3-benzobicyclo[4.2.0]octa-2,4,7-triene (**1** and **5**; note Scheme 1), and the major product from the direct irradiation of **1**. Other products from the direct irradiation of **1** are 7-cyanobenzosemibullvalene (**3**), 4-cyano-7,8-benzotetracyclo[3.3.0.$0^{2,4}$.$0^{3,6}$]oct-7-ene (**4**), and naphthalene. The COT **2** is also formed from the direct photolysis of triene **5**, though only in meager amounts; the main products are 1-cyanobenzosemibullvalene (**6**) and 2-cyanonaphthalene (note Scheme 1). Triplet-sensitized irradiations of either triene **1** or **5** yield semibullvalenes and naphthalenes but do not generate COT products (2). We now report results from the study of deuterium-labelled derivatives of the trienes (viz. **1***a* and **5***a*, Scheme 2) which show that the skeletal reorganization that occurs in the photoformation of COT **2** from triene **5,** and the thermolyses of **1** and **5**, is different to that observed in the **1** → **2** photoisomerization.

Results

The deuterium-labelled trienes **1***a* and **5***a* (93%-d_1 at C-6 and C-7, respectively) were obtained as outlined in Scheme 2 (yields given in the Schemes are based on amounts of starting materials consumed) from a multistep procedure starting with the readily available 3,4-dibromobenzobarrelene **7** (3). All compounds in the synthetic sequence are either known or are deuterium-labelled derivatives of known compounds. Incorporation of deuterium at C-3 of barrelene **8** was achieved by treating dibromide **7** with 1 equiv of butyllithium, followed by quenching the resulting mono-anion with deuterium oxide. Crude **8** was then converted to the cyanolated derivative **9***a* (52% overall yield from **7**) using cuprous cyanide according to established methodology (4). The final two synthetic steps are known photorearrangements.

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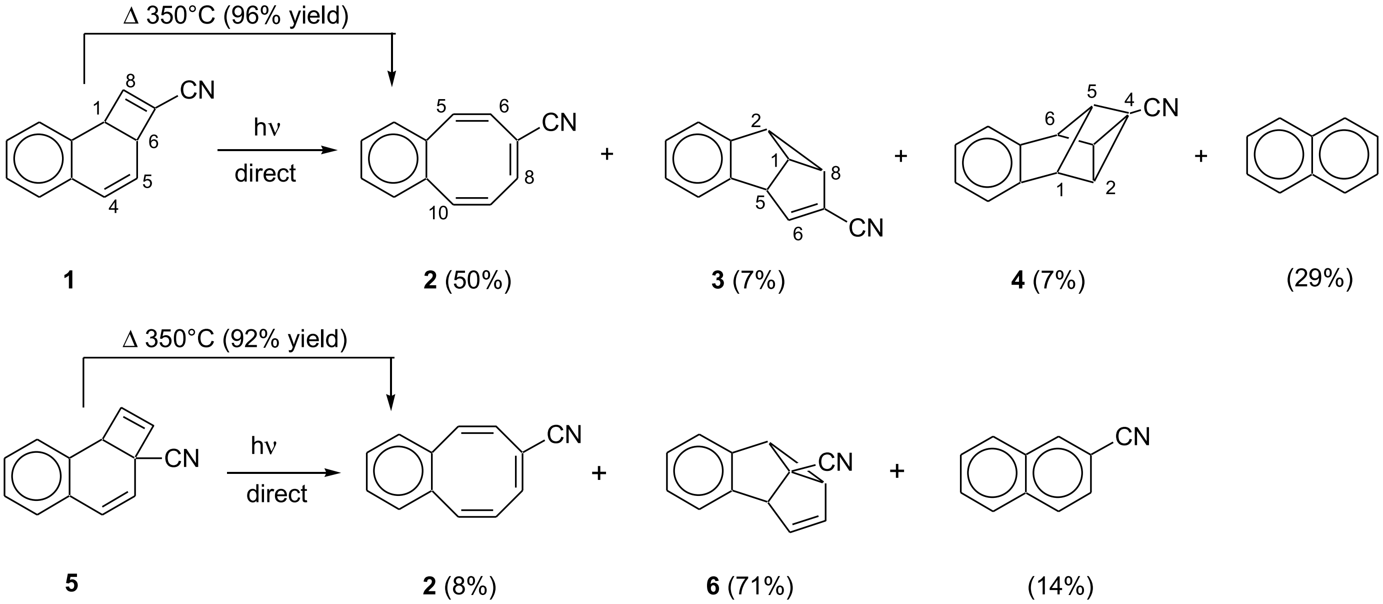
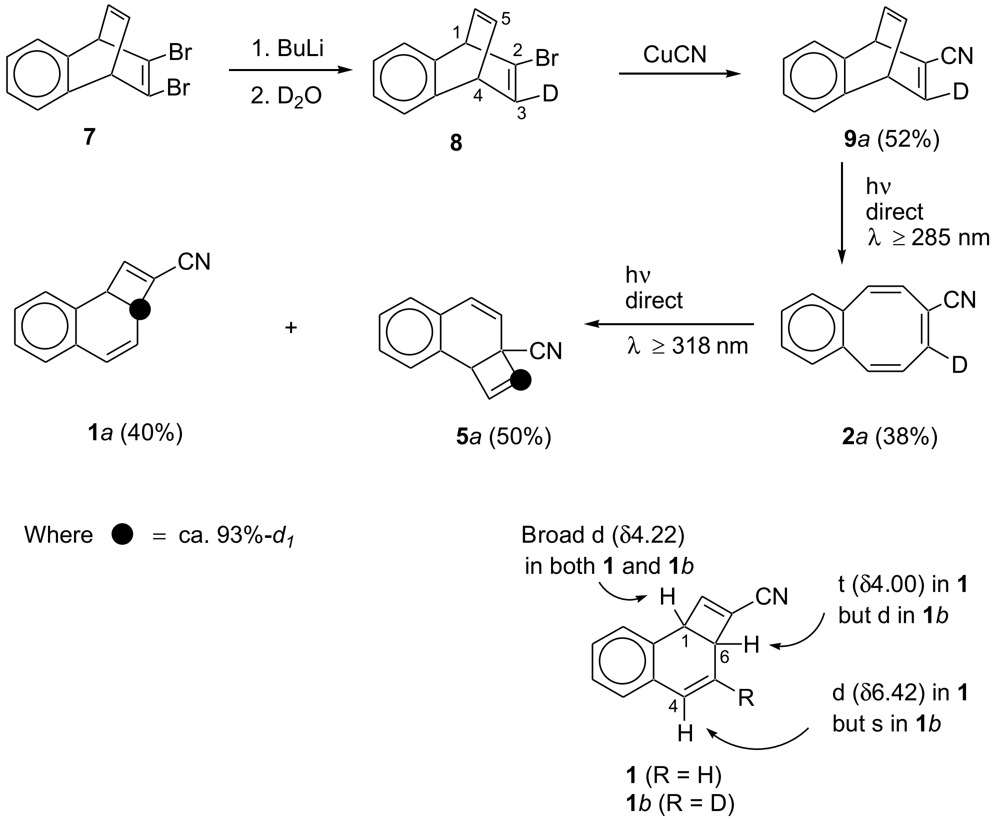
Scheme 1. Thermolysis and direct photolysis products from trienes **1** and **5**.



Scheme 2. Preparation of deuterium-labelled trienes **1***a* and **5***a*.



The first involves the direct irradiation (Corex filter) of barrelene **9***a* to give the labelled COT **2***a* as the major product (4). In the second step, the COT was photocyclized (direct irradiation at λ ≥ 318 nm, conditions under which the photolabile products absorb no light) to the desired triene **1***a*, along with the alternate closure isomer **5***a* (2).

The assignment of the deuterium attachment at C-6 of **1***a* follows from the reduction in integration signal of the lower-field bridgehead signal in the proton NMR spectrum. Differentiation between the two bridgehead hydrogens (i.e., H-1 at δ 4.22 and H-6 at δ 4.00) was previously established (2) from spin decoupling results and the observation that the triplet H-6 signal in nonlabelled triene **1** collapses to a doublet in the spectrum of the deuterium-labelled compound **1***b*. As expected, the signal due to H-1 (broad doublet) is essentially unchanged upon replacement of H-5 with deuterium.

Table 1. Hydrogen atom distributions of the nonaromatic positions in deuterium-labelled 7-cyanobenzocyclooctatetraene.

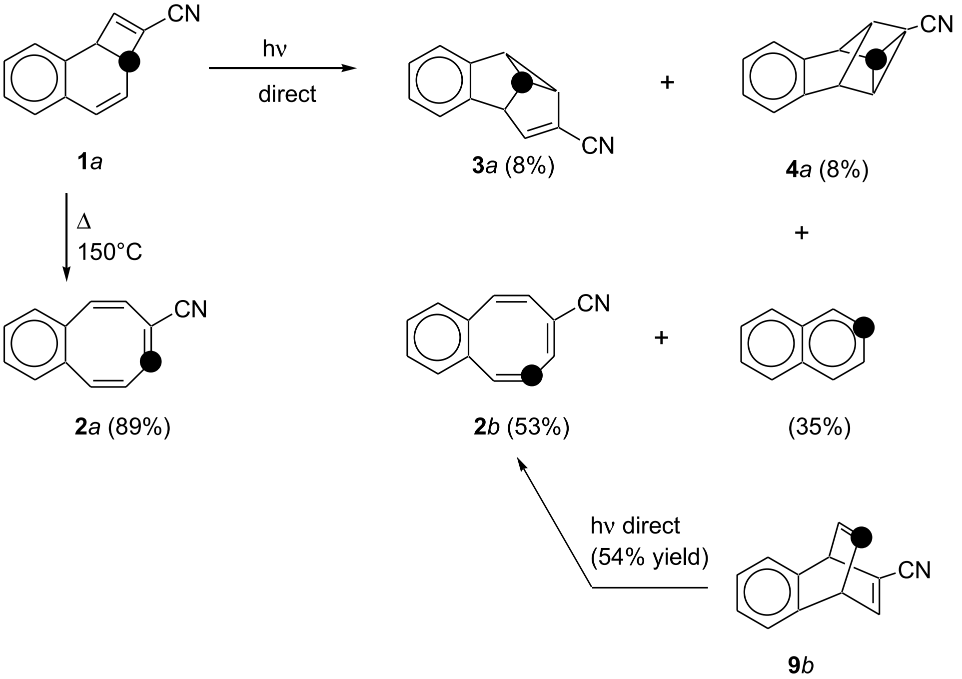
		Hydrogen atom distributions at:[a]			
Entry no.	Origin of 7-cyano-COT	C-5 and C-10 δ6.75 and δ6.73	C-6 δ5.95	C-8 δ6.66	C-9 δ6.07
1	Observed for direct hν of barrelene **9***a*[b]	2.04H	0.99H	0.07H	0.98H
2	Observed for thermolysis of triene **1***a*[c]	1.98H	0.97H	0.08H	0.95H
3	Observed for direct hν of triene **1***a*[b]	1.98H	1.02H	0.98H	0.10H
4	Calcd. for direct hν of triene **1***a* via route A	2.00H	1.00H	0.07H	1.00H
5	Calcd. for direct hν of triene **1***a* via routes B or C	2.00H	1.00H	0.54H	0.54H
6	Calcd. for direct hν of triene **1***a* via route D	2.00H	1.00H	1.00H	0.07H
7	Observed for thermolysis of triene **5***a*[c]	2.00H	0.99H	0.08H	0.99H
8	Observed for direct hν of triene **5***a*[c]	1.98H	0.98H	0.11H	0.95H

[a] In each case the aromatic multiplet at δ6.95–7.06 was set as the normalized integration standard of 2.00H; the other aromatic multiplet at δ7.22–7.31 gave variable integration values due to the presence of residual $CHCl_3$.

[b] See the experimental section for complete NMR details.

[c] The signal multiplicities were identical to those reported for 8-deuterio-COT (**2***a*).

Scheme 3. Observed label locations in products from triene **1***a* thermolysis and direct photolysis.



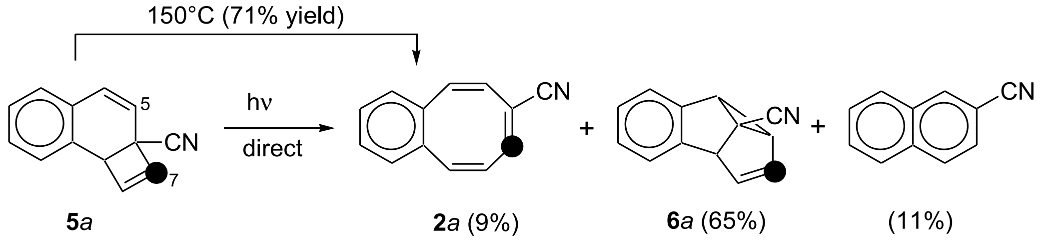
The NMR details are given at the triene structures **1**/**1***b*, in Scheme 2. In the case of triene **5***a*, the assignment of the deuterium attachment at C-7 is based on the signal designations previously given to nonlabelled **5** (2).

As indicated above, trienes **1** and **5** are known to revert to COT **2** upon heating (2). In the present study, the NMR spectra of the COT material isolated from the thermolyses (in *n*-nonane at 150°C) of the labelled trienes **1***a* and **5***a* revealed the same label distributions as were found in COT **2***a* originally prepared from barrelene **9***a* (i.e., deuterium exclusively at C-8; note the observed ^{1}H NMR integration values given in Table 1, entries 1, 2, and 7). These findings are consistent with the operation of a mechanism involving cleavage of the strained C-1—C-6 bridging bond of the trienes (see Schemes 3 and 4), and is a ground-state reaction common to other benzobicyclo[4.2.0]octa-2,4,7-trienes (5).

In contrast to the thermal results, NMR analysis of the COT product isolated as the major component from the direct irradiation of labelled triene **1***a* shows the deuterium to be uniquely located at C-9 (Scheme 3; note Table 1, entry 3), i.e., the observed COT product is identical to the known β-labelled compound **2***b* previously obtained (4) as the major product from the direct irradiation of the C-5 labelled barrelene **9***b* (note Scheme 3). Thus mechanistically, the photoformation of COT **2** from triene **1** is not a simple reversal of the 2π + 2π photoclosure process proposed in the generation of triene **1** from COT **2**. The other isomeric products (semibullvalene **3***a* and tetracycle **4***a*) isolated from the direct irradiation of triene **1***a* contain deuterium distributions that are unexceptional and fully compatible with those anticipated by previously described mechanistic routes (2), viz. via a Zimmerman di-π-methane (DPM) rearrangement (6) in the case of **3***a*, and a $2\pi_s + 2\pi_s$ cycloaddition in the case of **4***a* (4).

Interestingly, the photochemical (direct irradiation) behaviour of triene isomer **5***a* differs from that of **1***a* in giving COT product (Scheme 4) in which the deuterium distribution corresponds to **2***a*, within experimental uncertainty (note

Scheme 4. Observed label locations in products from triene **5***a* thermolysis and direct photolysis.



Scheme 5. Mechanisms that do not account for photoformation of COT from triene **1***a*.

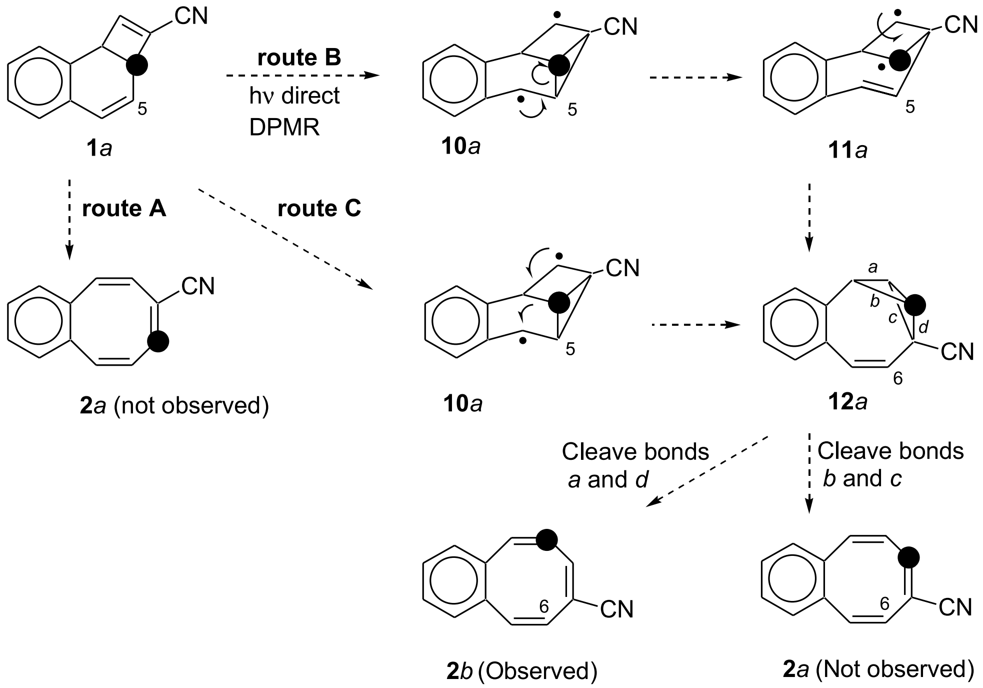


Table 1, entry 8). The major product from the direct irradiation of **5***a* is semibullvalene **6***a* labelled at C-7, which is considered to form from a Zimmerman DPM rearrangement (6) involving initial bridging between C-5 and C-7, as proposed in the earlier investigation of triene **5** (2).

Discussion

Previous studies of deuterium-labelled 2,3-benzobicyclo[4.2.0]octa-2,4,7-trienes have led to the postulation of at least three mechanistic pathways which may operate in the photogeneration of COTs (7–12). However, none of these pathways (depicted as routes A, B, and C in Scheme 5) can account for the labelling pattern observed in the photoconversion of **1***a* to **2***b*. Thus, operation of a route A-type mechanism (7–9), which is formally equivalent to a $2\sigma_s + 2\pi_s$ electrocyclic opening (13), would lead to **2***a* (not observed). Operation of a route B-type (10–12) or a route C-type mechanism (11), both of which involve the initial formation of a Zimmerman DPM rearrangement diradical **10***a*, should give approximately equal amounts of **2***a* (not observed) and **2***b* (observed) from the thermal reorganization of the proposed octavalene intermediate **12***a*, assuming minor deuterium isotope effects (14, 15).

To rationalize the photoconversion of **1***a* → **2***b*, we propose a novel mechanism (route D, Scheme 6) which is a modification of the Zimmerman DPM pathway identified as route B in Scheme 5. The modification allows for the rearrangement of the initially formed diradical **10***a* to the more stabilized species **13***a* (Scheme 6). The transformation of **10***a* to **13***a* can be viewed as an interconversion between two housane-type species, i.e., **14** → **15**. Interestingly, the diradical **13**, in which favorable stabilization is afforded the radical centres by the cyano and benzo groups, was invoked previously by us (4) to explain the formation of COT **2***b* from the direct irradiation of barrelene **9***b* (note Scheme 7)[2]. However, lest it be thought that barrelene **9***b* is involved in the present case through a two-step process (viz., **1***a* → **9***b* → 2b, the primary step would be an excited-state allowed 1,3-shift), we point out that the subsequent photolysis of **9***b* would have led not only to COT **2***b* but also to the co-formation of semibullvalene **6***a* and COT **16***b* (note Scheme 7) (2). Since neither the barrelene **9***b* nor **6***a* nor **16***b* are observed in photolysates of triene **1***a*, at any conversion

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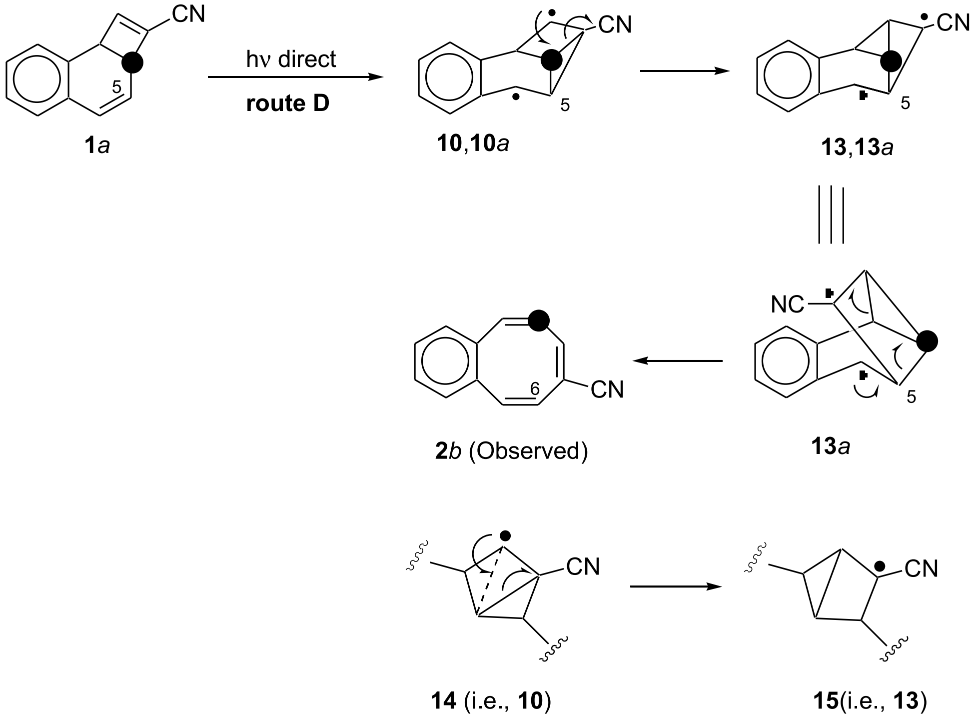
[2] Following the suggestion of a referee, we note that the same overall skeletal organization of COT **2***b* would result from two 1,2-shifts of the cyanovinyl group of triene **1***a* via the mechanism given in Fig. 1.

Scheme 6. Suggested mechanism for photoformation of COT **2***b* from triene **1***a*.



Scheme 7. Pathway not observed from triene **1***a* to COT **2***b*.

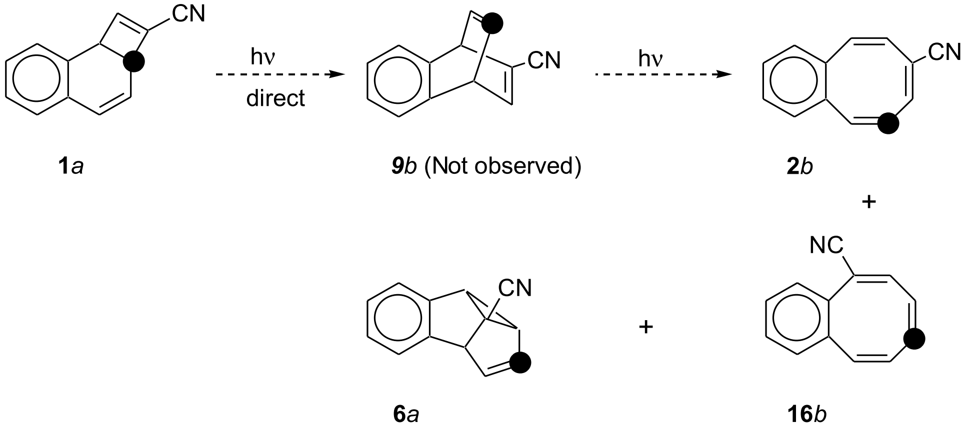
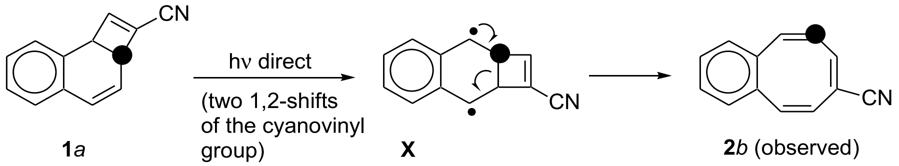


Fig. 1. Alternative mechanism for photoformation of COT **2***b* from triene **1***a*.

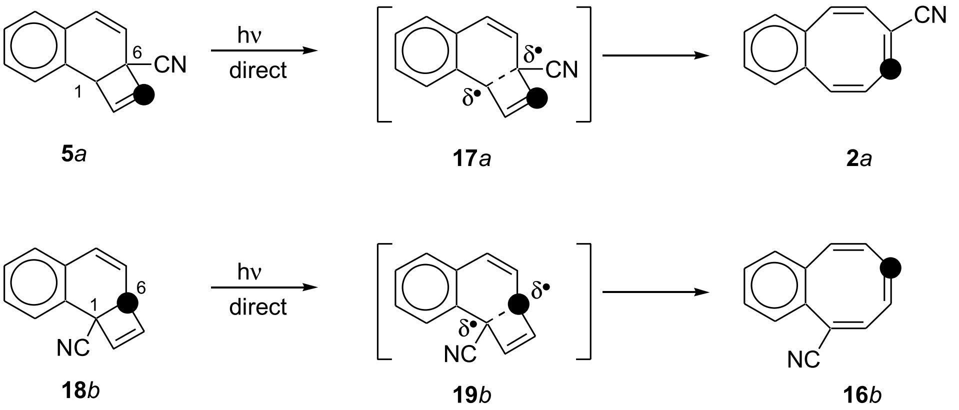


level (GC and NMR monitoring), it follows that **9***b* does not feature in the production of COT **2** from triene **1**.

For triene **5***a*, the deuterium results are most readily interpreted in terms of a route A-type mechanism, wherein cleavage of the strained C-1—C-6 bond would be particularly favorable due to the extensive stabilization of the "diradical-like" centres in the proposed transition state, approximated by structure **17***a* (Scheme 8). A similar explanation was given to account for the facile photoformation of COT **16***b* in the case of triene **18***b*, which also contains a cyano group at a bridgehead location (C-1) (8).

A last point of interest is that the deuterium-labelled triene **1***b* (i.e., deuterium attached to C-5; note structure **1***b* in Scheme 2), which was initially prepared in 1986 to delineate the mechanistic details of the photoformations of semibullvalene **3** and **6** from trienes **1** and **5**, respectively (2), is

Scheme 8. Possible mechanism for photoformation of COT **2***a* from triene **5***a*.



not appropriately labelled to distinguish between operation of the route B- (or C-) type mechanisms (Scheme 5) and the novel pathway proposed here (route D, Scheme 6). Thus, according to either route B (or C) in Scheme 5, or the modified mechanism (route D) shown in Scheme 6, a label at C-5 of the triene becomes a label at C-6 in the COT product.[3]

Experimental

Instrumentation and general procedures

The NMR spectra were recorded on a Bruker 250-MHz instrument in $CDCl_3$ solvent with TMS as the internal standard; 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. The photolysis 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 glass, or an aqueous lead nitrate solution (1 g of $Pb(NO_3)_2$ 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 (A, B, or C) were used. Cell A (250 mL sample volume) consisted of a cylindrical vessel (Pyrex) which surrounded the immersion well. Cell B (200 mL sample volume) consisted of a cylindrical collar (Pyrex) which surrounded the aqueous filter jacket. Both Cells A and B were fitted with gas inlet and outlet ports, and sample solutions were deoxygenated by flushing with argon, before and during irradiations. Cell C (40 mL sample volume) was a test tube-like vessel (quartz), and sample solutions were deoxygenated by flushing with argon and sealed under a positive pressure; the solutions were magnetically stirred throughout the course of the irradiations. Column chromatography was carried out on Lobar (Merck; size B, LiChroprep Si 60) or on Silica Gel 60/$AgNO_3$ columns (10:1 by weight). All compounds described in this study are either known or are deuterium-labelled derivatives of known compounds; their purities were estimated to be ≥98% by a combination of NMR and GC analyses.

*3-Deuteriocyanobarrelene (9*a*) from 2,3-dibromo-1,4-dihydro-1,4-ethenonaphthalene (7)*

To a magnetically stirred solution of 3.62 g (12 mmol) of 2,3-dibromobenzobarrelene **7** (3) in 90 mL of dry, freshly distilled THF at –70°C was added dropwise 8.90 mL (14 mmol) of 1.6 M butyllithium in hexane over a 15 min period under a nitrogen atmosphere. Stirring was continued for an additional 25 min followed by the dropwise addition of 1.8 mL (99 mmol) of deuterium oxide during 5 min at –70°C. After stirring for 10 min, the cooling was removed and the reaction mixture allowed to warm to room temperature. The mixture was concentrated on the rotovap and distilled water (200 mL) and hexane (200 mL) were added. The aqueous layer was removed and extracted with hexane (100 mL). The combined organic layers were washed with distilled water (2 × 100 mL) and dried ($MgSO_4$). The solvent was removed via the rotovap and the crude 3-deuteriobromobenzobarrelene **8** was converted without purification to 3-deuterio-2-cyano-1,4-dihydro-1,4-ethenonaphthalene (**9***a*) using 2.10 g (23 mmol) of cuprous cyanide, according to the method previously described (4) for the conversion of unlabelled 2-bromo-1,4-dihydro-1,4-ethenonaphthalene to 2-cyano-1,4-dihydro-1,4-ethenonaphthalene. Crystallization of the crude product from 95% ethanol yielded 1.09 g (52%) of **9***a*, mp 65–67°C (lit. (4) value 66 to 67°C for the nondeuterated parent). ^{1}H NMR: 7.61 (dd, 0.06H, residual H-3, $J_{3,4} = 6$, $J_{1,3} = 2$), 7.19–7.3 (m, 2.21H, 2 aromatics and residual $CHCl_3$), 6.86–7.01 (m, 4.04H, 2 aromatics, H-5 and H-6), 5.00–5.10 (m, 2.00H, H-1 and H-4), corresponding to 94%-d_1 at C-3; uncertainties from NMR signal integrations are within ±0.05H for **9***a* and for all subsequent integrations of deuterated compounds.

*8-Deuterio-7-CN-COT (2*a*) from 3-deuteriocyanobarrelene (9*a*)*

A solution containing 1.039 g (5.77 mmol) of labelled cyanobarrelene (**9***a*) in 1 L of cyclohexane was irradiated in four equal aliquots in Cell A (Corex filter) for 40 min each. The photolysates were combined and chromatographed as described previously (4) for the preparation of COT **2** from unlabelled cyanobarrelene, to give 395.1 mg (38%) of 8-deuterio-COT (**2***a*) as the major product, mp 99–101° C (lit.

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[3] Triene **1***b* does in fact give 7-cyanobenzocyclooctatetraene exclusively labelled with deuterium at C-6 upon direct photolysis (C.O. Bender, P.D. England, and K.E. Preuss. Unpublished results).

(4) value 102 to 103° C for non-deuterated **2**) after recrystallization from 95% ethanol. ^{1}H NMR: 7.22–7.31 (m, 2.67H, 2 aromatics + residual $CHCl_3$), 6.95–7.06 (m, 2.00H, 2 aromatics), 6.75 and 6.73 (d and d, 2.04H, H-5 and H-10, $J_{5,6} = J_{9,10} = 11.5$), 6.66 (d, 0.07H, residual H-8, $J_{8,9} = 4.5$), 6.07 (d, 0.98H, H-9, $J_{9,10} = 11.5$), and 5.95 (d, 0.99H, H-6, $J_{6,5} = 11.5$). Also note ^{1}H NMR data given in entry number 1 in Table 1.

Direct irradiation of 8-deuterio-COT (2a)

A solution containing 366.5 mg (2.04 mmol) of **2**_a_ in 200 mL of cyclohexane was irradiated directly in Cell B ($Pb(NO_3)_2$ filter) for 96 h. The photolysate was concentrated to 8 mL and chromatographed (in four 2 mL aliquots) on a Lobar column with 1% ethyl acetate – hexane solvent; the eluant was monitored by UV spectroscopy at λ = 300 nm. The last band from the column contained 116.6 mg (32%) of labelled 6-cyano-2,3-benzobicyclo[4.2.0]octa-2,4,7-triene (**5**_a_). ^{1}H NMR: 7.10–7.30 (m, 4.28H, 4 aromatics + residual $CHCl_3$), 6.46 (d, 1.00H, H-4, $J_{4,5} = 10$), 6.19 (dd, 0.06H, residual H-7, $J_{7,8} = 2.8$, $J_{7,1} = 1$), 6.07 (d, 0.95H, H-8, $J_{8,1} = 1$), 5.85 (d, 0.98H, H-5, $J_{5,4} = 10$), and 4.46 (br s, 0.97H, H-1). The first band from the column contained COT **2**_a_ and triene **1**_a_, and was rechromatographed in three equal aliquots on a Silica Gel 60/$AgNO_3$ column (0.9 cm × 11 cm; 0.5% ethyl acetate – hexane). The first band gave 93.8 mg (26%) of triene **1**_a_. ^{1}H NMR: 7.16–7.22 (m, 2.05H, 2 aromatics), 7.06–7.13 (m, 2.07H, 2 aromatics), 6.71 (d, 1.00H, H-8, $J_{8,1} = 1$), 6.42 (d, 1.00H, H-4, $J_{4,5} = 10$), 5.93 (d, 0.98H, H-5, $J_{5,4} = 10$), 4.22 (br s, 1.01H, H-1), and 4.00 (t, 0.07H, residual H-6, $J_{6,1} = J_{6,5} = 4.5$). The second band gave 133.8 mg (37%) of recovered COT starting material (**2**_a_). ^{1}H NMR: 7.22–7.31 (m, 2.08H, 2 aromatics + residual $CHCl_3$), 6.95–7.06 (m, 2.00H, 2 aromatics), 6.75 and 6.73 (d and d, 1.95H, H-5 and H-10, $J_{5,6} = J_{9,10} = 11.5$), 6.66 (d, 0.08H, residual H-8, $J_{8,9} = 4.5$), 6.07 (d, 0.94H, H-9, $J_{9,10} = 11.5$), and 5.95 (d, 0.96H, H-6, $J_{6,5} = 11.5$).

*Thermolysis of triene 1*a

A solution of 8.0 mg (0.044 mmol) of **1**_a_ in 4 mL of _n_-nonane was refluxed (ca. 150°C) under a nitrogen atmosphere for 8 h. The thermolysis product was chromatographed on Silica Gel 60 (0.9 cm × 10 cm) with 3% ethyl acetate – hexane to give 7.1 mg (89%) of 8-deuterio-COT (**2**_a_) (the ^{1}H NMR data are given in entry 2, Table 1).

*Direct irradiation of triene 1*a

A solution containing 42.3 mg (0.24 mmol) of **1**_a_ in 40 mL of cyclohexane was irradiated directly in Cell C (Pyrex filter) for 3.2 h. The photolysate was concentrated and chromatographed on Silica Gel 60 (0.9 cm × 7 cm) with 4% ethyl acetate – hexane to remove polymeric materials, and then rechromatographed on a Lobar column with 2% ethyl acetate – hexane solvent; the eluant was monitored by UV spectroscopy at λ = 265 nm. The first band off the column gave 3.3 mg (11%) of naphthalene-d_1. The second band contained a mixture of the triene starting material and COT product. The third band contained ca. 1 mg (2%) of semibullvalene **3**_a_. ^{1}H NMR: 7.22–7.31 (m, 1.00H, 1 aromatic), 7.03–7.26 (m, 5.14H, 3 aromatics + residual $CHCl_3$), 6.30 (d, 1.03H, H-6, $J_{6,5} = 2.5$), 4.04 (d, 1.02H, H-5, $J_{5,6} = 2.5$), 3.38 (q, 0.09H, residual H-1, $J_{1,2} = J_{1,5} = J_{1,8} = 6.5$), 3.19 (d, 1.03H, H-2, $J_{2,8} = 6.5$), and 2.94 (d, 1.01H, H-8, $J_{2,8} = 6.5$). The last band gave ca. 1 mg (2%) of tetracycle **4**_a_. ^{1}H NMR: 7.16–7.28 (m, 4.38H, 4 aromatics and residual $CHCl_3$), 4.32–4.36 (m, 2.00H, H-1 and H-6), 3.28 (q, 1.01H, H-5, $J_{5,1} = J_{5,2} = J_{5,6} = 4.5$), and 2.91–2.98 (m, 1.00H, H-2 and residual H-3).

The second band containing the triene starting material and COT product was rechromatographed on a Silica Gel 60/$AgNO_3$ column (0.9 cm × 11 cm; 0.25% ethyl acetate – hexane), monitored by UV spectroscopy at λ = 300 nm. The first band gave 29.0 mg (69%) of recovered triene starting material **1**_a_. ^{1}H NMR: 7.16–7.22 (m, 1.99H, 2 aromatics), 7.06–7.13 (m, 2.03H, 2 aromatics), 6.71 (d, 1.00H, H-8, $J_{8,1} = 1$), 6.42 (d, 1.00H, H-4, $J_{4,5} = 10$), 5.93 (d, 0.97H, H-5, $J_{5,4} = 10$), 4.22 (br s, 0.99H, H-1), and 4.00 (t, 0.07H, residual H-6, $J_{6,1} = J_{6,5} = 4.5$). The second band gave 7.0 mg (17%) of COT product **2**_b_. ^{1}H NMR: 7.22–7.31 (m, 2.07H, 2 aromatics + residual $CHCl_3$), 6.95–7.06 (m, 2.00H, 2 aromatics), 6.75 and 6.73 (d and br s, 1.98H, H-5 and H-10, $J_{5,6} = 11.5$), 6.66 (br s, 0.98H, H-8), 6.07 (dd, 0.10H, residual H-9, $J_{9,8} = 4.5$, $J_{9,10} = 11.5$), and 5.95 (d, 1.02H, H-6, $J_{6,5} = 11.5$); also note the ^{1}H NMR data given in entry number 3, Table 1.

Thermolysis of triene 5a

A solution of 8.5 mg (0.047 mmol) of **5**_a_ in 5 mL of _n_-nonane was refluxed (ca. 150°C) under a nitrogen atmosphere for 5.2 h. The thermolysis product was chromatographed on Silica Gel 60 (0.9 cm × 10 cm) with 3% ethyl acetate – hexane to give 6.0 mg (71%) of 8-deuterio-COT (**2**_a_); for ^{1}H NMR details note entry 7, Table 1.

Direct irradiation of 7-deuterio-6-cyano-triene (i.e., triene 5a)

A solution containing 20.2 mg (0.09 mmol) of **5**_a_ in 40 mL of cyclohexane was irradiated directly in Cell C (Pyrex filter) for 1.5 h. The photolysate was worked up as in the case of the direct irradiation of unlabelled triene **5** (2) to give ca. 1 mg (5%) of 2-cyanonaphthalene and ca. 1 mg (5%) of 8-deuterio-COT (**2**_a_); for the ^{1}H NMR details note entry number 8, Table 1; 8.5 mg (42%) of recovered triene **5**_a_ (^{1}H NMR: 7.10–7.30 (m, 4.50H, 4 aromatics + residual $CHCl_3$), 6.46 (d, 1.00H, H-4, $J_{4,5} = 10$), 6.19 (dd, 0.06H, residual H-7, $J_{7,8} = 2.8$, $J_{7,1} = 1$), 6.07 (d, 0.98H, H-8, $J_{8,1} = 1$), 5.85 (d, 1.00H, H-5, $J_{5,4} = 10$), and 4.46 (br s, 1.00H, H-1)); and 7.5 mg (37%) of semibullvalene **6**_a_ (^{1}H NMR: 7.32–7.40 (m, 1.00H, 1 aromatic), 7.06–7.25 (m, 3.10H, 3 aromatics + residual $CHCl_3$), 5.70 (d, 0.95H, H-6, $J_{6,5} = 2.5$), 5.20 (dd, 0.06H, residual H-7, $J_{7,6} = 5.0$, $J_{7,8} = 2.5$), 4.22 (d, 1.01H, H-5, $J_{5,6} = 2.5$), 3.68 (d, 1.01H, H-2, $J_{2,8} = 7.0$), and 3.35 (d, 1.02H, H-8, $J_{8,2} = 7$)).

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