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5-TETRACYCLO[3.3.0.$0^{2,4}$.$0^{3,6}$]OCT-7-ENYL CARBENE; AN ATTEMPTED SYNTHESIS OF A [4.4.4.4]FENESTRANE DERIVATIVE

PROPERTIES OF DELTACYCLENYLIDENE AND BARBARALYLIDENE

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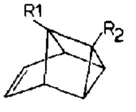
Abstract—The title carbene was generated at low temperature with the objective to effect intramolecular cyclopropanation of its double bond. Labelling studies showed intramolecular C–C bond insertion followed by intramolecular reverse Diels Alder reaction to be the major pathway to the products.

5-Tetracyclo[3.3.0.$0^{2,4}$.$0^{3,6}$]oct-7-enyl carbene **1a** was of interest to us for one main reason: would it lead to compound **2a** (isolable or as a transient) by intramolecular cyclopropanation?



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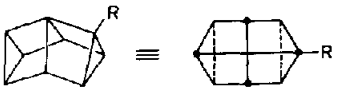
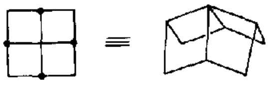


2

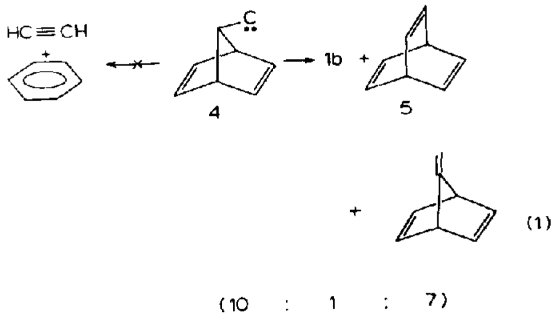
a: R_1=CH; R_2=H
b: R_1=R_2=H
c: R_1=$CHNNHSO_2C_7H_7$; R_2=H
d: R_1=CHN_2; R_2=H
e: R_1=CO_2CH_3; R_2=D
f: R_1=CHO; R_2=D
g: R_1=$CHNNHSO_2C_7H_7$; R_2=D
h: R_1=CH; R_2=D
i: R_1=CH_2OH; R_2=D
j: R_1=OLi; R_2=H

a: R=H
b: R=D



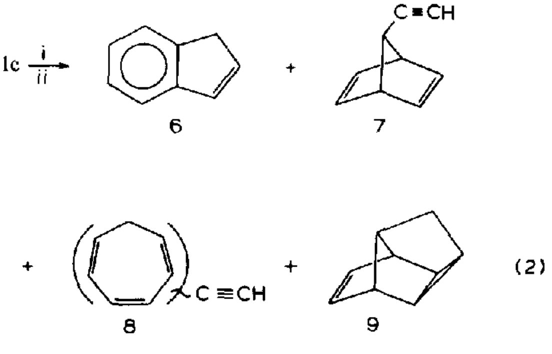
3

Compound **2a** (hexacyclo[3.3.1.$0^{2,4}$.$0^{3,9}$$0^{6,8}$.$0^{7,9}$]nonane) is the 2,4;6,8-*bis*-dehydro derivative of all-*cis*[4.4.4.4]fenestrane **3**. Although **3** has recently been calculated[1] to contain about 170 kcal/mol of strain and **2** may be more strained than **3** by at least the sum of the strain energies of two additional three-membered rings,[2] the heats of formation of **1a** and **2a** may be rather similar.[3] Encouragement to attempt the envisaged generation of **2a** was also taken from our findings with the related carbene **4**.[4] Least motion transformation of **4** into **1b** (encompassing a strain increase by 60–70 kcal/mol) is greatly favoured over alternative reactions leading to much more stable products (e.g. barrelene **5**, benzene plus acetylene, see eqn 1).[5]



RESULTS

Carbene **1a** was generated by photolysis at −78° of the sodium salt of the tosylhydrazone **1c**, the synthesis of which is described elsewhere.[4a] These conditions were chosen because they are known to work best in the synthesis of **1b** and its derivatives.[4] Ordinary work-up of the reaction mixture afforded indene **6** (15%) as the major product, together with 7-ethynylnorbornadiene **7** (2%), 7-ethynylcyclohepta-1,3,5-triene **8a** (1%), a *ca* 3 : 1 mixture of 2 and 3-ethynyl-cyclohepta-1,3,5-triene **8b** and **8c** (1%) and deltacyclene **9** (1%), with only traces of other products detectable (eqn 2).[6] By GCMS no other low molecular compounds, in particular no dimers, were found in the distillation residue of the photolysis mixture. The identity of **7** was derived from its spectral data; the identity of all other products was established by comparison of their spectroscopic properties and GLC retention volumes with those of authentic samples.



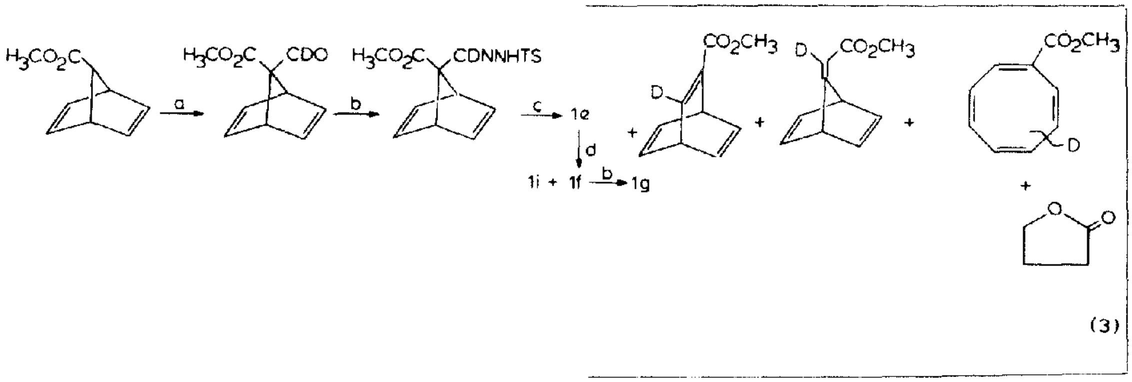
i: NaH, THF, rt
ii: $h\nu$(Duran 50), THF, −78°

a: 7-C≡CH
b: 2-C≡CH
c: 3-C≡CH

The desired *bis*-dehydro fenestrane **2a** could not be detected among the products. In view of the possibility that low thermal stability had prevented detection of 2a, the reaction described above was repeated in THF-d_8 in order to enable low temperature NMR analysis. After 5 h irradiation in a Rayonet photoreactor, equipped with eight 300- and eight 350-nm lamps, an aliquot was removed from the mixture and the remainder was concentrated at

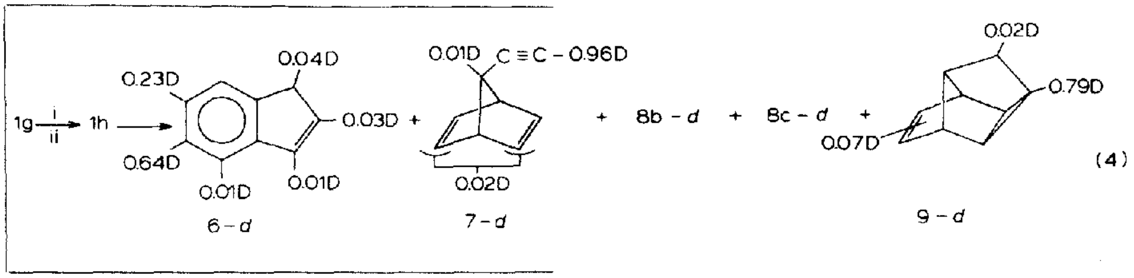
– 50° in high vacuum (*ca* 3×10^{-6} torr). The yellow liquid distilling at –30° was diluted with CDCl$_3$. The ^{1}H NMR spectrum of both the crude photolysate and the yellow distillate showed the characteristics of a 5-substituted tetracyclo[3.3.0.0^{2,4}.0^{3,6}]oct-7-ene.[4a] The substituent had a singulet accounting for one proton, which in CDCl$_3$ coincided with the absorption of H-1 and H-6 at 3.45 ppm but was clearly separated from this absorption in THF-d$_8$, now occurring at 3.81 ppm. The IR spectrum (CDCl$_3$, room temp.) showed a very strong absorption at 2048 cm^{-1}, which disappeared within 50 min. These findings point to the formation of the diazo compound **1d**. Further irradiation of **1d** in THF-d$_8$ caused the decomposition of **1d** with only the formation of indene being detected by low temperature ^{1}H NMR spectroscopy: no indication of the presence of **2a** was found.

In order to probe for the intermediacy of short-lived **2a** a D label was introduced at C-4 of the starting material. The synthesis of the tosylhydrazone **1g** is outlined in eqn (3) and is equal to the one of **1c**,[4a] except for the formylation in the first step which was carried out with DMF-d$_7$ instead of DMF.



a: i: LDA; ii: DMF-d$_7$; iii: H$^+$
b: $H_3N_2SO_2C_7H_7$
c: i: NaH, THF, rt; ii: *hν*(Duran 50), THF, –78°
d: DIBAH

All compounds showed more than 95% incorporation of D at the positions indicated, as determined by ^{1}H NMR spectroscopy. Mass spectrometrical analysis of **1f** established a D content of 97.5% d$_1$. Generation of the carbene **1h** as in the case of **1a** afforded the products shown in eqn 2 except for **8a**: in this experiment **8a** probably is converted completely into **8b** and **8c** because of a longer duration of the photolysis.[13] The distribution of the label in the products was determined by ^{1}H NMR spectroscopy and is given in eqn 4. Mass spectrometry gave D contents of 96.2% d$_1$ (**6-d**), 98.9% d$_1$ (**7-d**), 96.6% d$_1$ (**8b-d**), 97.4% d$_1$ (**8c-d**) and 88.3% d$_1$ (**9-d**). The D distribution in **8b-d** and **8c-d** could not be determined due to overlap of signals in the ^{1}H NMR spectrum of the mixture; however, it is clear that, at the most, only traces of the label could be located at the acetylenic positions.



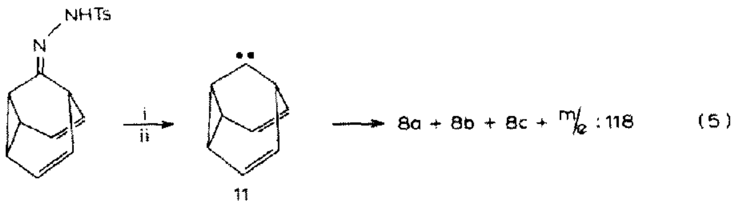
i : NaH, THF, rt
ii: *hν*(Duran 50), THF, –78°

At one point of our investigation it was considered possible that **2a**, if formed, might have rearranged to barbaralylidene **11** by the reverse of an intramolecular linear homocheletropic carbene addition.[7] Barbaralylidene had been reported to furnish—under thermal conditions—ethynylcycloheptatrienes, which were also formed from **1a**.[8] In order to test for the intermediacy of **11** in the transformations of **1a**, **11** was generated under our reaction conditions. Ordinary work-up of the reaction mixture afforded **8a** (4%), a *ca* 3 : 1 mixture of **8b** and **8c** (8%) and a very reactive unidentified compound with mass 118 (4%, eqn 5). The latter showed an allene absorption (1930 cm^{-1}) in its IR spectrum.

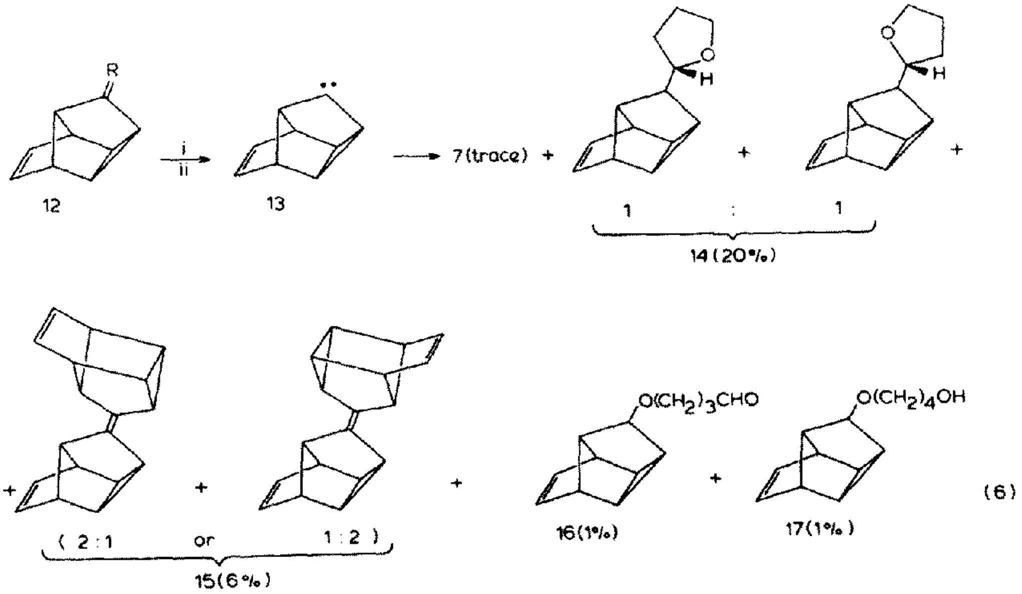
In similar vein, 5-deltacyclenylidene **13**, a possible precursor of **7** and of **9**, was generated under our reaction conditions. To our surprise the photolysis at –78° of the sodium salt of the tosylhydrazone **12b** of deltacyclenone **12a** did not lead to **7** as a major product. Only traces of this compound were detected, the major products being dimers **15** and products resulting from insertion of the carbene in the α-CH bond of the solvent instead (eqn 6).

DISCUSSION

Carbene **1a** constitutes a new entry into the C$_9$H$_8$ manifold, parts of which have been investigated before. Bicyclo[4.2.1]nona-2,4,7-trien-9-ylidene **18**,[9] bicyclo[3.2.2]nona-3,6,8-trien-2-ylidene **19**,[10] bicyclo[8.1.0]nona-2,4,6-trien-9-ylidene **20**[11] and barbaralylidene **11**[8] have been reported to yield indene **6** and/or 7-ethynylcyclohepta-1,3,5-triene **8a** in variable amounts



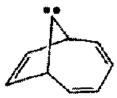
i : NaH, THF, rt
ii: hν(Duran 50), THF, −78°



a: R=O
b: R=NNHSO$_2$C$_7$H$_7$

i : NaH, THF, rt
II: hν(Duran 50), THF, −78°

as the major products. On the other hand, cyclononatetraenylidene **21** *dimerizes* via its triplet state.[12]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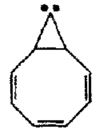
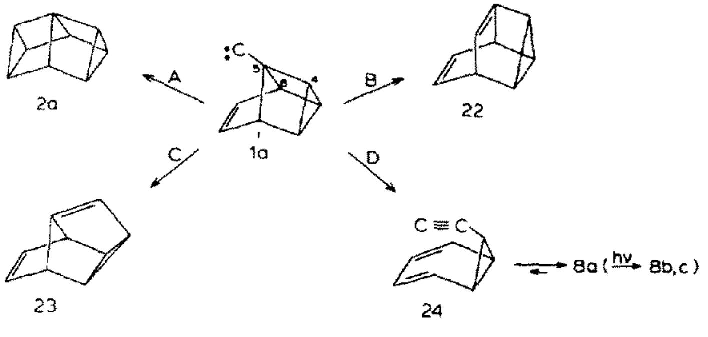

20

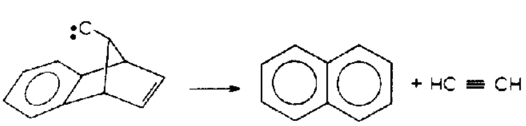

21

For **1a** four intramolecular processes can be envisaged as the respective first steps of sequences leading to the final products (Scheme 1).

Processes A, B and C, intramolecular cyclopropanation and intramolecular insertions into neighbouring C–C bonds, respectively, are well known in singlet carbene chemistry whereas, to our knowledge, only one example of process D is reported in the lit. (eqn 7).[5]

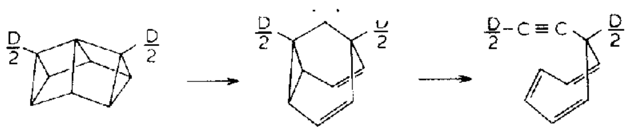


Scheme 1. Possible intramolecular reactions of **1a**.



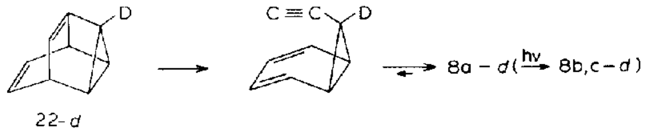
(7)

Considering **2a** first, this molecule either processes a low thermal stability or does not occur at all. The possibility that part of **2a** is converted into barbaralylidene **11**[7] and from there into **8a** (→ **8b, c**) can be neglected since it would lead to a 1 : 1 distribution of D over the ring positions and the terminal acetylenic position of the latter in the case of **2b** (eqn 8).



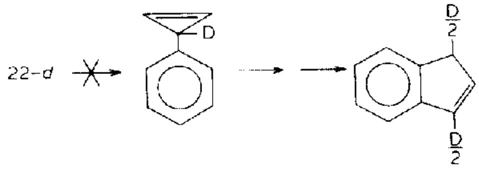
(8)

Exclusive ring deuteration of the ethynylcycloheptatrienes as actually found is in accord with pathways D and B. In the latter case **22** is to undergo a reverse Diels Alder reaction (eqn 9).



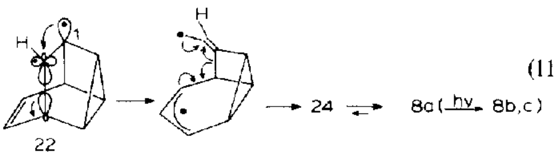
(9)

The alternative (thermodynamically more favourable) mode of reverse Diels Alder reaction of **22**, leading to 3-phenylcyclopropene and from there in a known photochemical reaction[14] to indene **6** can be discounted, since it leads to a distribution of deuterium in **6** different from the one observed (*cf* eqn 10).



(10)

A possible reason for the preference[15] of the thermodynamically less favourable process of eqn (9) may be rehybridization at C-1 of **22** which minimizes distortion of the σ-skeleton.[16] Such rehybridization may trigger (stepwise?) rearrangement to **24** (eqn 11).



(11)

Rearrangement of **22** to **13** (by an 1,2 alkyl shift) does not occur as is shown by the absence of the products characteristic of **13** (*cf* eqn 6). The fact that **13** yields only traces of **7** is remarkable in view of the general fragmentation of cyclopropyl carbenes into an ethylenic and an acetylenic part.[17]

Bridgehead olefin **23** is recognized as an intermediate that can lead to **6**, **7** and **9** in ways that yield the observed distributions of deuterium in these compounds if **23-4-d** were produced from **1h**.[19] Two modes of reverse Diels Alder reaction of **23** can lead to **25** and from there to indene by a 1,5 H shift[20] (Scheme 2).

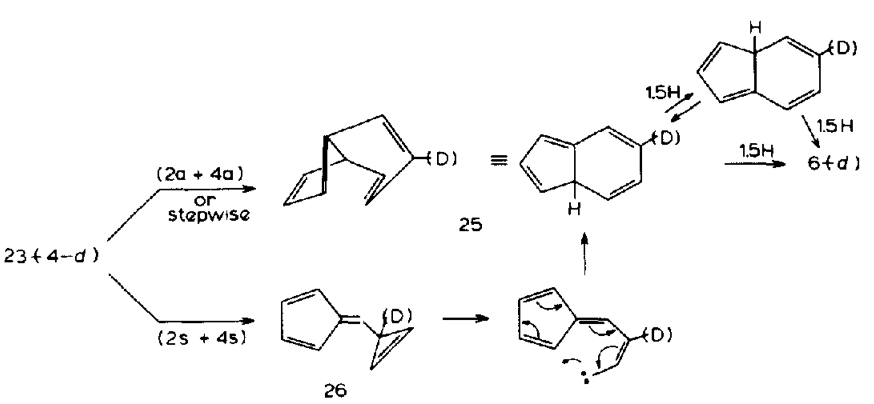
A (2a + 4a) mode or its stepwise variant (possibly favoured by rehybridization of C-6 of **23**[16]) yields **25**.[21] A (2s + 4s) process would first lead to a 6-(3-cyclopropenyl)fulvene **26** and from there to **25** by electrocyclic reaction.[14] Rehybridization at C-6 of **23**[16] seems also favourable for the latter type of reverse Diels Alder reaction, since it would induce some additional aromatic character into the transition state through contribution of canonical structure **27**.

The intermediacy of **23** is supported by the finding in the reaction of **1a** of deltacyclene **9**, in which the carbon skeleton of **23** is present. Formation of dihydro products from unstable bridgehead olefins is known.[22] Rearrangement of **23** in a way reminiscent of the rearrangement of the 5-deltacyclenyl anion[23] may explain both the partial label scrambling observed in **9-d** and the formation of **7-d** specifically deuterated at the acetylenic position[24] (Scheme 3). The loss of label in **9-d** as compared with the starting material is puzzling.

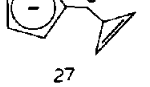
CONCLUSION

The behaviour of some C_9H_8 carbenes at low temperature in solution has been studied. The main objective, intramolecular cyclopropanation of **1a** to **2a** could not be effected, as shown by labelling studies. In particular the deuterium in the major product formed from **1a**, indene, is located at C-5 and C-6 within the limits of error of the NMR technique. This finding would be very hard to explain if **2b** would be an intermediate. Apart from the possibility that the reaction **1a**→**2a** may be "energetically uphill",[2,3] the reason for the contrast between **1a** and **4** (*cf* eqn 1) may be geometrical: bridging the norbornadiene skeleton (see **4**) as in **1a** tilts the C-1, C-5, C-6 bridge towards C-2, C-4 and causes the substituent at C-5 to point more upward.[25] Interaction between the double bond in **1a** and the carbene centre therefore is certainly less than in **4**.

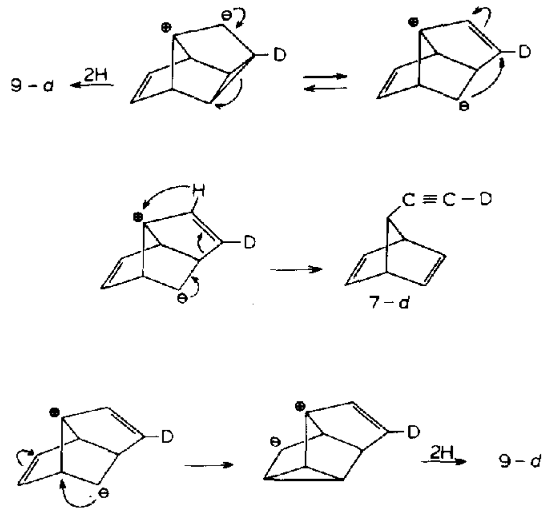
The intermediacy of barbaralylidene **11** and deltacyclenylidene **13** could be ruled out in the conversion of **1a** into the products. Though it cannot be excluded that part of **6(6-d)** is formed from **2a(2b)** in an as yet unrecognized way, the formation of the products can be rationalized



Scheme 2. Possible modes of formation of **6(d)** from **23(4-d)**.



27



Scheme 3. Possible modes of formation of **7(d)** and **9(d)** from **23(4-d)**.

from well known carbene and bridgehead olefin reactions:[26] the most likely mechanism for the formation of the major product, indene, and **7** and **9** from **1a** is intramolecular carbene insertion into the C-4, C-5 bond of **1a** yielding tetracyclo(4.3.0.0^{2,4}.0^{3,7})nona-5(6), 8-diene **23** which undergoes reverse Diels Alder reaction to **25**, rearrangement to **7** and H-abstraction giving **9**. The isomeric bridgehead olefin **22** could be the precursor of **8a**, however, least motion transformation of **1a** directly into **24**, tautomer of **8a**, may also be put forward as an explanation for the formation of **8a, b, c**. Predominance of products ascribable to **23** is in line with earlier observations showing that ring expansion involving carbenes attached to a bridgehead position preferably takes place through migration of the shorter bridge.[21,27]

EXPERIMENTAL

General and analytical procedures. IR spectra were recorded as solns in CCl_4 or $CDCl_3$ or as KBr disks on a Perkin-Elmer 580B spectrophotometer. Only strong and medium absorptions are given (cm^{-1}) with a precision of 5 cm^{-1}. Mps are uncorrected. UV spectra were recorded on a Cary 118 spectrophotometer. Mass spectra were obtained from a Finnigan 4000 mass spectrometer (70 eV). For GCMS column D was used. Deuterium analyses were performed under chemical ionisation conditions if necessary. Peak heights of fragments are given in brackets relative to the base peak (100%). Gaschromatographic analyses were performed on a Varian 90-P or on an Intersmat GC 120. H_2 was used as carrier gas. Columns used: A: 15% SE 30 on Chromosorb WAW-DMCS, 60–80 mesh (stainless steel; 0.4 × 180 cm); B: 10% Carbowax 20 M on Chromosorb W-HP, 80–100 mesh (glass; 0.4 × 150 cm); C: 10% SE 30 on Chromosorb WAW-DMCS, 60–80 mesh (glass; 0.4 × 150 cm); D: micro packed Cp^{sil}-5 (fused silica; 0.2 mm × 25 m). Chromatograms were integrated with a Pye Unicam DP 101. Routinely, GLC analyses were performed by subjecting the samples first to GLC on a non-polar column, collecting the peak(s) and then resubjecting any individual peak to GLC on a polar column. NMR spectra were recorded on a Bruker WH-90 (90 MHz) or WH-250 (250 MHz) spectrometer in $CDCl_3$ with $CHCl_3$ as internal standard or in THF-d_8 with TMS as internal standard; chemical shifts (δ_{TMS}) are given in ppm with a precision of 0.01 ppm; coupling constants have an accuracy of 0.4 Hz. The ^1H NMR assignments of new compounds were checked by double resonance experiments: the results of these experiments were in accordance with the proposed structures. Abbreviations used: b = broad, p = pseudo, d = doublet, t = triplet, qa = quartet, sx = sextet, m = multiplet, rrv = relative retention volume, ltp = linear temperature programme. All compounds are colourless liquids unless stated otherwise. Solvents were distilled shortly before use: *n*-pentane was washed twice with concentrated H_2SO_4, twice with brine, dried over $CaCl_2$, distilled from LAH and stored over Na-wire; THF was dried by distillation from LAH and stored over Na-wire, THF-d_8 was dried by distillation from LAH and used immediately and DMF-d_7 (99% d, Gold Label) was used as purchased from Aldrich.

Starting materials. Compound **1c**[4a] and the tosylhydrazone of barbaralone[29] were prepared according to published procedures.

Tosylhydrazone of 4-deuterio-5-tetracyclo[3.3.0.0^{2,4}.0^{3,6}]*oct-7-ene carbaldehyde* (**1g**). The synthesis of **1g** was carried out as reported for **1c**[4a] except that the formylation of 7-carbomethoxy-norbornadiene was carried out with DMF-d_7 instead of DMF. All compounds showed more than 95% D incorporation at the positions indicated in eqn (5), as determined by ^1H NMR spectroscopy. The other products[4a] in the synthesis of **1a** showed more than 95% D incorporation at the positions indicated in eqn (5), as determined by ^1H NMR spectroscopy or mass spectroscopy. The position of D in carbomethoxy-cyclooctatetraene was not determined. Butyrolacton showed less than 1% D incorporation. Compound **1i** showed more than 95% D incorporation located at C-4, as determined by ^{1}H NMR spectroscopy. Mass spectroscopical analysis of **1f** established its D content as 97.5 ± 1% d_1.

Tosylhydrazone of deltacyclenone (**12b**). Compound **12b** was prepared according to the reported procedure for the preparation of the tosylhydrazone of barbaralone,[29] Yield: 68% pale yellow needles, mp. 135.5–136.5° (dec). *m/e*: 300 (4), 145 (51), 116 (63), 115 (100). (Found: 300.0932. Calc. for $C_{16}H_{16}N_2SO_2$, 300.0940).

Preparation of the sodium salt of tosylhydrazone **1c** *and subsequent photolysis in THF*. In an inert argon atmosphere 1.9 mmol NaH (55–60% dispersion in oil) was washed twice with dry *n*-pentane. The solvent was removed and 25 ml dry THF was added. To this suspension a soln of 464.5 mg (1.55 mmol) **1c** in 5 ml dry THF was added with a syringe (gas evolution). The mixture was stirred for 2 h in the dark. With the aid of an additional amount of 425 ml dry THF the white suspension was transferred into the photolysis apparatus which is essentially equal to the one described in ref. 30. The mixture was cooled in dry ice/i-PrOH for 30 min and then photolyzed under N_2 for 5 h at −78° (400 medium pressure Hg: Applied Photophysics Ltd, 400 LQ; Duran 50 filter). After warming to room temp the mixture was diluted with 500 ml *n*-pentane and washed first with 10 portions of 500 ml H_2O, then twice with 100 ml brine and dried ($MgSO_4$). After filtration the mixture was carefully concentrated through a 20-cm vacuum-jacketed vigreux column. The remaining volatile components were collected under reduced pressure (*ca* 5×10^{-2} torr) in a trap maintained at −196°. By GCMS no low molecular compounds, in particular no dimers, were found in the distillation residue. The contents of the cold trap were subject to preparative GLC (A, 72°) to afford toluene[31] (rrv: 0.14), 3,4 mg (0.03 mmol, 2%) **7** (rrv: 0.34; melts just below room temp), 1.7 mg **9** + **10**[6] (rrv: 0.40), 1.0 mg (0.01 mmol, 1%) **8a** (rrv: 0.48), 1.7 mg (0.02 mmol, 1%) **8b** + **8c** (rrv: 0.72) and 27.0 mg (0.23 mmol, 15%) **6** (rrv: 1.00). The mixture of **9** and **10**[6] was separated on column B (60°; ltp: 4°/min) affording 1.6 mg (0.01 mmol, 1%) **9** (rrv: 1.00) and **10**[6] (trace; rrv: 1.15). The mixture of **8b** and **8c** could only be separated on column D, **8b** eluting first. The identity of **7** (^{1}H NMR (90 MHz; $CDCl_3$): 6.77 (pqa, 4H, H-2,3,5,6), 3.68 (psx, 2H, H-1,4) 3.06 (pqa, 1 h, H-7), 1.82 (d, 2.0 Hz, 1H, C≡CH); IR (CCl_4): 3310, 2995, 2115, 1545, 1317, 1304, 645; *m/e*: 116 (16), 115 (100), 89 (15); found: 116.0625, calc. for C_9H_8: 116.0626), was derived from its spectral data. Compounds, **8a**, **b**, **c** were identical with the compounds obtained from the reaction of the tosylhydrazone of barbaralone. The other compounds were identified by comparison of their spectral data with those of authentic samples.

Preparation of the sodium salt of tosylhydrazone **1c** *and subsequent photolysis in THF-d_8*. In a previously dried 10 ml cylindrical pyrex vessel equipped with an argon inlet and a serum cap 0.18 mmol NaH (55–60% dispersion in oil) was washed twice with 0.5 ml dry THF-d_8 in an inert argon atmosphere. Then 1.0 ml dry THF-d_8 was added, followed by the addition of 31.7 mg (0.11 mmol) **1c** dissolved in 1.0 ml dry THF-d_8 with a syringe (gas evolution). The mixture was stirred for 2 h at room temp in the dark. The white suspension was then diluted with 2.5 ml dry THF-d_8. The argon inlet was removed and the vessel was equipped with a syringe needle reaching to the bottom of the mixture (serving as N_2 inlet and stirring device) and a second syringe needle serving as N_2 outlet. N_2 was bubbled through the mixture during the reaction. The vessel was placed concentrically in a cylindrical vacuum-jacketed quartz vessel, which was kept at −73 ± 2° by injection of cold N_2 gas (Cryoson Type 19–98/1 temp controller). The whole was placed in a Rayonet photochemical reactor equipped with eight 300 and eight 350 nm lamps. After 5 h irridiation an aliquot was removed from the mixture for NMR analysis and the remainder was distilled in a bulb to bulb fashion at *ca* 3×10^{-6} torr in an all glass apparatus consisting of the distillation vessel connected in series with two traps. First the last trap was kept at 196° and the mixture was allowed to warm to −51 − 2° and kept at this temp for 1.5 h. Then the first trap was also cooled to −196° and the distillation vessel was warmed to −30 ± 1° and kept at that temp for 6 h. Under N_2 the yellow contents of the first trap were diluted with cold $CDCl_3$ and subjected to ^{1}H NMR analysis, which indicated the presence of toluene[31] and a tetracyclo$[3.3.0.0^{2,4}.0^{3,6}]$oct-7-ene substituted at C-5:[4a] (90 MHz; −46°C; $CDCl_3$) 6.10 (bt, 1.7 Hz, 2H, H-7,8), 3.45 (s, 3H, H-1,6 and CHN_2), 2.73 (bt, 3.6 Hz, 1H, H-4), 2.09 (m, 2H, H-2,3). The same substance was found to be present in the aliquot taken from the THF-d_8 solution: (90 MHz; −46°C; THF-d_8) 6.03 (t, 1.7 HZ, 2H, H-7,8), 3.81 (s, 1H, CHN_2), 3.42 (bs, 2H, H-1,6) 2.73 (t. 3.6 Hz, 1H, H-4), 2.06 (m, 2H, H-2,3). The IR spectrum of the yellow distillate ($CDCl_3$, room temp) showed a strong absorption at 2048 cm^{-1} which disappeared in the IR cell within 50 min. When the yellow distillate was redistilled as described above and dissolved in dry THF-d_8, the ^{1}H NMR spectrum of the solution showed the same absorption as seen in the spectrum of the crude photolysate. A sealed NMR tube containing the THF-d_8 solution of the diazo compound **1d** was attached to the cooler of the photolysis apparatus used in the other photolyses (*vide supra*) and photolyzed for $4\frac{1}{4}$ h at −78°. The mixture was distilled at high vacuum as described above and the colourless contents of the first trap (distilling at −35°) were dissolved in dry THF-d_8. The ^{1}H NMR spectrum (90 MHz; −43°) showed the disappearance of **1d** and the presence of indene, **6**; other products were not detected, probably due to their low concentration.

Preparation of the sodium salt of tosylhydrazone **1g** *and subsequent photolysis*. The preparation of the sodium salt of **1g**, its subsequent photolysis (6 h) and the work-up of the mixture were carried out as described in the case of **1c** (THF, *vide supra*). In this case **8a** was detected in such low quantities that its analysis was not possible. Mass spectroscopy gave deuterium contents of 96.2 ± 1% d_1 (**6-d**), 98.9 ± 1% d_1 (**7-d**), 96.6 ± 1% d_1 (**8b-d**), 97.4 ± 1% d_1 (**8c-d**) and 88.3 ± 1% d_1 (**9-d**). D distribution determinations were carried out under full relaxation conditions (30 sec relaxation delay after each scan) and are averages of at least 4 runs. The determinations were straightforward in the cases of **7-d** and **9-d**. The D distribution in **8b-d** and **8c-d** could not be determined due to overlap of signals in the ^{1}H NMR spectrum of the mixture; however, it was clear that only traces of the label were located at the acetylenic positions. The determination of the label distribution in **6-d** required the analysis of the 250 MHz spectrum of **6**, as the reported computational analysis obviously was wrong with respect to the assignment of the aromatic protons.[32] It was checked by double resonance experiments that absorptions retained their positions on going from $CDCl_3$ to THF-d_8. The ^{1}H NMR spectrum of **6** [(250 MHz; THF-d_8); 7.46 (bd, 7.0 Hz, 1H, H-7), 7.38 (d, 6.9 Hz. 1H, H-4), 7.21 (bdt, *ca* 1 Hz. 7.0 Hz, 1H, H-5), 7.15 (dt, *ca* 1.2 Hz, 7.0 Hz, 1H, H-6), 6.89 (m, 1H, H-3), 6.53 (td, 1.9 Hz, 5.0 Hz, 1H, H-2), 3.41 (bs, 2H, H-1)] can be analyzed in first order. Assignments in the aromatic region were based on the long range coupling between H-3 and H-7[33] and were checked by double resonance. In **6** the same numbering of hydrogen is used as in ref. 32.

Preparation of the sodium salt of the tosylhydrazone of barbaralone and subsequent photolysis. The preparation of the Na salt of the tosylhydrazone of barbaralone, its subsequent photolysis and the work-up of the mixture was carried out as described in the case of **1c** (THF, *vide supra*). By GCMS no volatile compounds could be detected in the distillation residue. GLC analysis (C, ltp, 50°, 6°/min) afforded toluene[31] (rrv: 0.40), **8a** (4%; rrv: 1.00), **8b** + **8c** (*ca* 3 : 1; 8%; rrv: 1.25) and a very unstable unidentified compound [4%; rrv: 1.49; *m/e* 118 (66), 117 (65), 115 (55), 103 (25), 91 (54), 78 (100); ^{1}H NMR (90 MHz; $CDCl_3$): 6.20 − 5.50 (m, 4H), 4.81 (bs, 2H), 2.48 (m, 4H); IR (CCl_4): 3025, 1930, 1431, 847, 703; UV (cyclohexane): 283 nm)].

Preparation of the sodium salt of the tosylhydrazone of deltacyclenone (**12b**) *and subsequent photolysis*. The preparation of the Na salt of **12b**, its subsequent photolysis and the work-up of the mixture was carried out as described in the case of **1c** (THF, *vide supra*). GLC analysis (A; 61°) of the volatile components revealed the presence of toluene[31] and traces of **7**. The distillation residue was subjected to short path distillation (1.5 torr; 60–110°) and the distillate was subjected to preparative GLC (C; ltp, 125°, 4°/min) affording **14** (20%; rrv: 1.00), **16** [1%; rrv: 1.18; ^{1}H NMR (250 MHz; $CDCl_3$): 9.78 (t, 3.4 Hz, 1H, CHO), 6.15 (pqa, 1H, H-8 or H-9), 6.02 (pqa, 1H, H-8 or H-9), 3.74 (bs, 1H, H-5), 3.47 (m, 2H, OCH_2), 3.05 (m, 1H, H-1 or H-7), 2.68 (m, 1H, H-1 or H-7), 2.54 (dt, 1.5 Hz, 6.8 Hz, 2H, CH_2–CHO), 1.99 (bs, 1H, H-6), 1.91 (bt, 6.5 Hz, 2H, CH_2), 1.79 (m, 1H, H-4), 1.49 (m, 1H, H-2 or H-3), 1.41 (m, 1H, H-2 or H-3); IR (CCl_4): 3065, 2965, 2865, 2720, 1730, 1352, 1114, 703; *m*/*e*: 204 (−), 160 (8), 134 (16), 133 (22), 117 (37), 115 (42), 71 (100) (Found: 160.0891. Calc. for $C_{11}H_{12}O$ ($M^{\pm}$-C_2H_4O): 160.0888)], **17** [1%: rrv: 1.41; ^{1}H NMR (250 MHz; $CDCl_3$): 6.14 (pqa, 1H, H-8 or H-9), 6.01 (pqa, 1H, H-8 or H-9), 3.77 (bs, 1H, H-5), 3.65 (bt, 5.3 Hz, 2H, CH_2OH), 3.48 (m, 2H, OCH_2), 3.09 (m, 1H, H-1 or H-7), 2.68 (m, 1H, H-1 or H-7), 2.02 (bs, 1H, H-6), 1.82 (m, 1H, H-4), 1.68 (m, 4H, CH_2–CH_2), 1.51 (m, 1H, H-2 or H-3), 1.41 (m, 1H, H-2 or H-3), OH not found; IR (CCl_4): 3600–3150, 3065, 2945, 2870, 1352, 1105, 703 *m*/*e*: 206 (1), 134 (73), 133 (100), 117 (73), 115 (86), 105 (66), 92 (78), 91 (66) 52 (92); (Found: 133.0625, Calc. for C_9H_9O (M^+-C_4H_9O): 133.0604], and **15** (6%; rrv: 2.20) with traces of other products detectable. The 1 : 1 mixture of diastereomers **14** [^{1}H NMR (250 MHz, $CDCl_3$): 6.10 (m, 4H), 3.95–3.66 (m, 4H), 3.50 (m, 2H), 2.86 (bs, 1H), 2.78 (bs, 1H), 2.68 (bs, 2H), 2.16–1.26 (m, 18H); IR (CCl_4): 3065, 2970, 2890, 2870, 1323, 1071, 703; *m*/*e*: 188 (2), 129 (9), 117 (14), 116 (14), 115 (13), 91 (10), 71 (100); (Found (mixture): 188.1250. Calc. for $C_{13}H_{16}O$: 188.1224)] could not be separated on a variety of columns, including column D. The 2 : 1 mixture of dimers **15** (white solid, m.p. 118–133°; IR (KBr): 3065, 2985, 2965, 1562, 1315, 1262, 1205, 1045, 952, 946, 849, 841, 771, 701, 619) could only be separated on column D, the minor dimer eluting first. Major dimer [^{1}H NMR (250 MHz; $CDCl_3$): 6.13 (t, 1.8 Hz, 4H, H-8,9,8′,9′), 2.70 (bs, 4H, H-1,7,1′,7′), 2.26 (bs, 2H, H-6,6′), 2.22 (bdt, 1.5 Hz, 4.7 Hz, 2H, H-4,4′), 1.65 (md, 4.6 Hz, 4H, H-2,3,2′,3′), *m*/*e*: 232 (9), 231 (17), 215 (36), 202 (31), 153 (26), 141 (51), 128 (38), 117 (49), 116 (81), 115 (100), 91 (54)] minor dimer [^{1}H NMR (250 MHz; $CDCl_3$): 6.16 (t, 1.9 Hz, 4H, H-8,9,8′,9′), 2.74 (bs, 4H, H-1,7,1′,7′), 2.39 (bs, 2H, H-6,6′), 2.06 (bdt, 1.5 Hz, 4.8 Hz, H-4,4′), 1.59 (md, ca. 4.5 Hz, 4H, H-2,3,2′,3′), *m*/*e*: 232 (10), 231 (18), 215 (38), 202 (32), 153 (26), 141 (48), 128 (37), 117 (48), 116 (66), 115 (100), 91 (50)]. (Found: (mixture): 232,1274. Calc. for $C_{18}H_{16}$: 232.1265).

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[2] Models show that the 2,4 and 6,8 distances in rigid **3** are larger than those in bicyclo[3.3.1]nonane. Closing a 3-membered ring between these positions may therefore introduce more than the usual 28 kcal/mol of strain. However, it is also conceivable that in **2a** the two 3-membered rings exert a stabilizing effect similar to the one in the bisected form of cyclopropylcarbinyl cations on the electron deficient (*cf* ref. 28, Chap. 6) 1,9 and 5,9 bonds. MNDO calculations revealed the C-1, C-5 and C-5, C-9 bonds to be rather long (1.60 Å) and showed the presence of a partial negative charge (0.17 e) at C-9 in **2a**; the heat of formation of **2a** was calculated to be 208.6 kcal/mol.

[3] Hypothetical unstrained **1a** should be about 105 kcal/mol higher in energy than hypothetical unstrained **2a**: this is the heat of reaction of the addition of methylene to ethylene yielding cyclopropane [see B. Zurawski and W. Kutzelnigg, *J. Am. Chem. Soc.* **100**, 2654 (1978)]. By addition of the estimated strain energy of **1a** (110 kcal/mol) to this value one can estimate **1a** to be about 215 kcal/mol higher in energy than hypothetical unstrained **2a**. This is only 10 kcal/mol below the strain energy estimated for **2a**.

[4a] G. W. Klumpp and J. Stapersma, *Tetrahedron Lett.* 747 (1978); J. Stapersma, I. D. C. Rood and G. W. Klumpp, *Tetrahedron* **38**, 191 (1982); [b]: cf. also the reported analogous behaviour of the related 2,3-diazacarbene: B. M. Trost, R. M. Cory, P. H. Scudder and H. B. Neubold, *J. Am. Chem. Soc.* **95**, 7813 (1973).

[5] Aromatization by loss of acetylene was reported for a benzo derivative of **4**: R. N. Warrener, R. A. Russell and G. J. Collin, *Tetrahedron Lett.* 4447 (1978) (see eqn 7).

[6] One of these products presumably is 8-methylene-*exo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene **10**. Compound **10-d** [^{1}H NMR (250 MHz; $CDCl_3$): 6.58 (t, 1.8 Hz, 2H, H-6,7), 4.28 (s, 2H, H-9), 3.01 (bs, 2H, H-1,5), 1.15 (bd, 6.3 Hz, 2H, H-2,4), 0.93 (bt, 6.5 Hz, 1H, H-3-*exo*); *m*/*e*: at least 60% d_1] was detected and analyzed for the first time in the reaction of **1g**. Inspection of the GLC's of the reaction mixtures of **1c** established its presence in those cases by comparison of rrv's on columns A, B and D.

[7] *Cf* C. W. Jefford, J. Mareda, J. C. E. Gehret, T. Kabengele, W. D. Graham and U. Burger, *J. Am. Chem. Soc.* **98**, 2585 (1976); see however: G. W. Klumpp and P. M. Kwantes, *Tetrahedron Lett.* 831 (1981).

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[10] Ref. 11, footnote 15.

[11] E. E. Waali and N. T. Allison, *J. Org. Chem.* **44**, 3266 (1979).

[12] E. E. Waali and C. W. Wright, *Ibid.*, **46**, 2201 (1981).

[13] Known photochemical H-shifts in (substituted) cycloheptatrienes explain the formation of **8b,c** from **8a**: T. Tezuka, O. Kikuchi, K. N. Houk, M. N. Paddon-Row, C. M. Santiago, N. C. Rondan, J. C. Williams, Jr. and R. W. Gandour, *J. Am. Chem. Soc.* **103**, 1367 (1981) and refs. cited; the ethynyl group being a weak acceptor **8a,b,c** are expected to undergo 1,7 sigmatropic shifts instead of electrocyclization to ethynylbicyclo[3.2.0]hepta-2,6-dienes.

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[15] For a related example in which the thermodynamically less favourable reverse Diels Alder reaction is preferred, see: L. A. Paquette and R. T. Taylor, *Tetrahedron Lett.* 2745 (1976); M. Christl and M. Lechner, *Angew. Chem. Int. Ed. Engng* **14**, 765 (1975).

[16] Concerning the nature of strained bridgehead olefins, see: ref. 18; ref. 28 (chap. 3); P. Warner and R. F. Palmer, *J. Am. Chem. Soc.* **103**, 1584 (1981) and refs. cited.

[17] W. Kirmse, *Carbene Chemistry*, (2 Edn) p. 467. Academic Press, New York-London (1971); M. Jones, Jr. and R. A. Moss, *Carbenes*, Vol. 1, p. 32. Wiley, New York–London–Sydney–Toronto (1973); recent example: R. A. Moss and W. P. Wetter, *Tetrahedron Lett.* 997 (1981).

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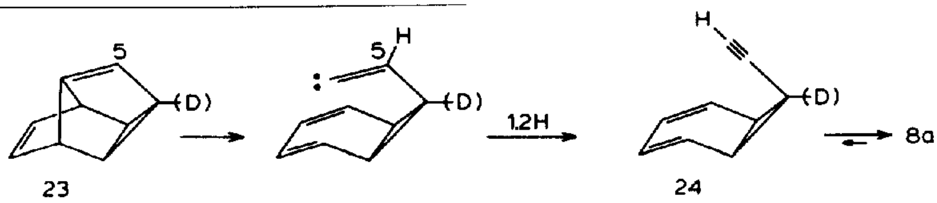

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$$\mathbf{8a,b,c} \xrightarrow{h\nu} \text{ethynylbicyclo[3.2.0]hepta-2,6-dienes} \xrightarrow{h\nu} \mathbf{7} \qquad \text{(Eqn 13)}$$

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