# 156. Polar Substituents in Benzobarrelene Photochemistry; The Photoreactivities of Dimethyl 10-methoxy- and Dimethyl 10,11-dimethoxy-2,3-benzobicyclo[2.2.2]octatetraene-5,6-dicarboxylate

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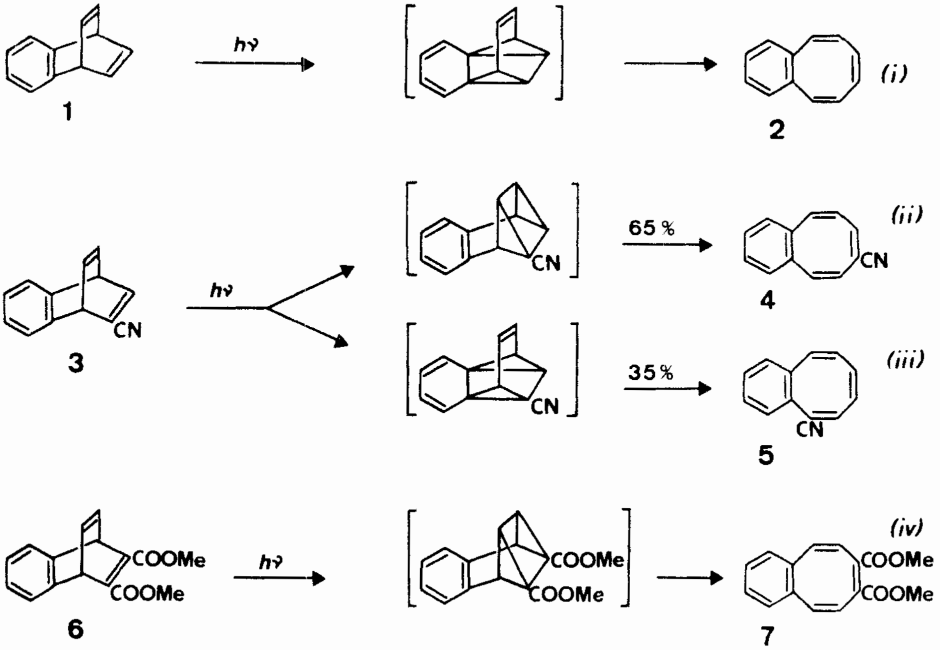
*Summary.* The direct irradiation of the monomethoxybarrelene **8** gives cyclooctatetraene product **18** ($\Phi = 0.07$) *via* the *anti*-Epiotis aromatic-vinyldiester $[2\pi + 2\pi]$ bridging route, and two semibullvalenes **16** ($\Phi = 0.075$) and **17** ($\Phi = 0.075$) from di-$\pi$-methane rearrangements initiating from vinyl-vinyldiester bridging. Benzophenone sensitization yields **16** ($\Phi = 0.11$) and **17** ($\Phi = 0.11$). The dimethoxybarrelene **9** gives only semibullvalene **10**, this resulting from di-$\pi$-methane rearrangement involving the vinyl and vinyldiester bridges, upon direct ($\Phi = 0.009$) or benzophenone sensitized irradiations ($\Phi = 0.38$). **10** undergoes a vinylcyclopropane rearrangement to give semibullvalene **11** upon direct or acetone sensitized irradiations ($\Phi = 0.008$).

On the basis of deuterium labelling studies *Zimmerman* [1] rationalized the photoconversion of benzobarrelene to benzocyclooctatetraene (benzo-COT, **2**) by process i (*Scheme 1*) which proceeds by benzo-vinyl bridging [1]. However, alternative $[2\pi + 2\pi]$ cycloaddition modes must predominate when one of the olefinic bridges is polarly substituted. Thus the cyano derivative **3** gives benzo-COT products **4** (65%) and **5** (35%) *via* vinyl-vinylcyano bridging (route ii) in the former case and by benzo-vinylcyano bridging (route iii) in the latter [2]. For the dicarbomethoxy derivative **6** the sole benzo-COT product is **7**, obtained uniquely *via* the vinyl-vinyldiester route (route iv) [3].

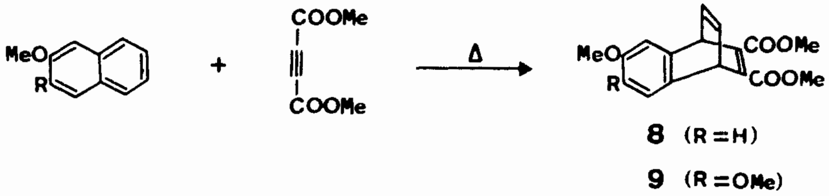
In order to examine further this polar dependency of the initial bonding process we have undertaken a study of substituent effects in the aromatic ring of **6**. In this paper we report our results with the two methoxylated derivatives **8** and **9**. These compounds were selected because the aromatic substituents are of opposing polar nature to those on the vinyl bridge and might therefore provide an opportunity to test the predictive ability of the *Epiotis* pericyclic theory [4] in a constrained, multi-choiced $[2\pi + 2\pi]$ photocyclo-adding system containing genuine *AX* (or 'push-pull') character. Furthermore, the positioning of the aromatic substituents is such that steric interactions near the cyclo-adding centres are minimized.

**Results.** – The barrelenes **8** and **9** were synthesized by *Diels-Alder* addition of dimethyl acetylene dicarboxylate to 2-methoxynaphthalene and 2,3-dimethoxynaphthalene respectively (*Scheme 2*). The structures assigned to **8** and **9** rest on the mode of preparation and on the similarity of the bridgehead hydrogen NMR. pattern with that of **6** [3].

*Scheme 1*



*Scheme 2*



Photochemically the barrelenes **8** and **9** exhibit distinctly different reactivities. Most surprisingly **9** does not yield COT product: it gives solely the semibullvalene **10** upon direct or benzophenone-sensitized irradiation (*Scheme 3*).

The structure of dimethyl 10,11-dimethoxy-3,4-benzotricyclo[3.3.0.$0^{2,8}$]octa-3,6-diene-1,8-dicarboxylate (**10**) was deduced from comparison of its NMR. spectrum with that of benzosemibullvalene (**12**) [1] (see *Table 1*). As expected, the two carbomethoxy groups of **10** strongly deshield H–C(2): the downfield shift of 1.36 ppm relative to H–C(2) of **12** is comparable to 1.59 ppm found for H–C(2) in **13** [6] relative to H–C(2) in **14** [7].

Spin decoupling experiments confirmed the *ABX* spin relationship between protons at C(5), C(6) and C(7) (see Experimental Part). Furthermore, **10** was converted into the semibullvalene **11** upon direct or acetone-sensitized irradiations.

*Scheme 3*

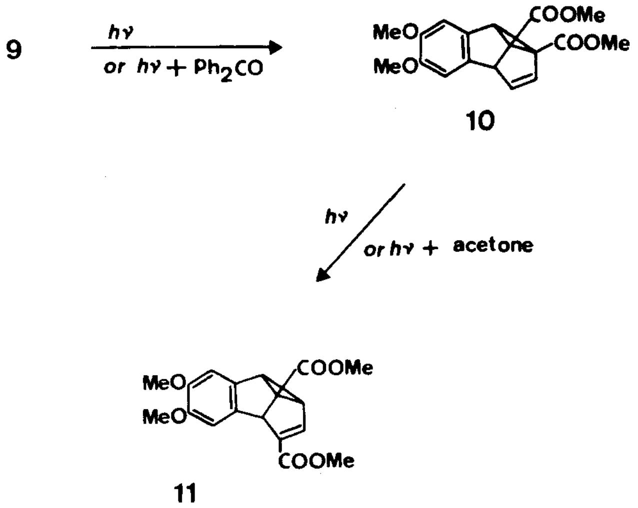


Table 1. *The NMR. data of olefinic-aliphatic protons of semibullvalenes*[a] [b]

| | Description and signal positions, τ | | | | |
|---|---|---|---|---|---|
| Assignment | **10** | **11** | **16** | **17** | **12**[c] |
| H—C(1) | none | none | none | none | 6.86 *d*×*d* |
| H—C(2) | 5.79 *s* | 6.25 *d*[d] | 5,79 *s* | 5.76 *s* | 7.14 *t* |
| H—C(5) | 5.75 *d*×*d* | 5.57 *s* | 5.75 *d* | 5.68 *d* | 6.19 *d*×*d* |
| H—C(6) | 4.38 *d*×*d* | none | 4.39 *d*×*d* | 4.36 *d*×*d* | 4.53 *d*×*d* |
| H—C(7) | 4.80 *d* | 4.08 *d* | 4.83 *d* | 4.76 *d* | 4.92 *d*×*d* |
| H—C(8) | none | 6.75 *d*×*d* | none | none | 7.40 *d*×*t* |

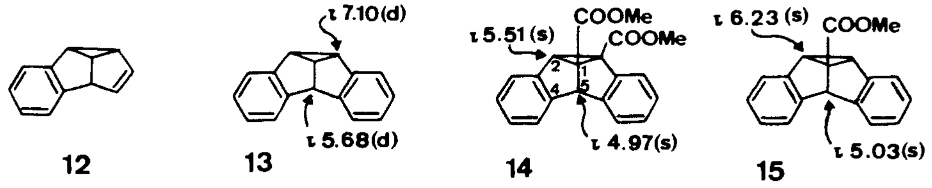
[a] Run on 60 MHz NMR. in $CCl_4$ solvent with TMS as internal standard.

[b] Corresponding coupling constants, where applicable, were within 0.5 Hz; typically, $J_{1,2} = J_{1,5} = J_{2,8} = 6.5$, $J_{5,6} = J_{7,8} = 2.0$, and $J_{6,7} = 5.0$ Hz.

[c] Run on 100-MHz-NMR.

[d] Right-hand limb hidden under $H_3CO$—C(arom) but observed in $C_6D_6$ solvent; see Experimental Part.

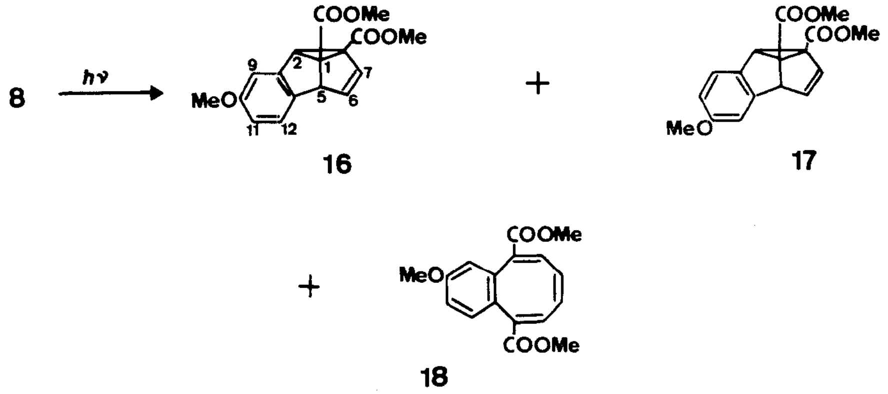
*Scheme 4*



The structure of **11** is also derived from NMR. spectral comparison with benzosemibullvalene (**12**) (see *Table 1*): the downfield shifts of 0.89 ppm for H–C(2) and 0.65 ppm for H–C(8) relative to H–C(2) and H–C(8) of **11** due to the cyclopropyl-carbomethoxy group appear to be reasonable (*cf.* 0.87 ppm for H–C(2) in **15** [7] relative to H–C(2) in **13**). Additionally, the deshielding effect of the carbomethoxy group at C(6) on the adjacent C(7) vinyl proton amounts to 0.84 ppm and this is comparable to the substituent constant of 1.02 ppm found for the *cis* proton of methyl acrylate [8]. Finally, spin decoupling experiments confirmed the *ABX* spin relationship between protons at C(2), C(8) and C(7).

The direct irradiation of monomethoxybarrelene **8** is more complex than the case of the dimethoxy analogue (**9**) in that it leads to the formation of three primary photoproducts: the two semibullvalenes **16** (34%) and **17** (34%), and the benzo-COT **18** (32%) (*Scheme 5*).

*Scheme 5*



The structures assigned to **16** and **17** were deduced from the similarity of the NMR. spectra to those of benzosemibullvalenes **10** and **12** (see *Table 1*). Distinction between the isomers, which differ only in the position of the methoxy group in the benzene ring, was tentatively established from examination of the relative shifts of the C(9) and C(12) protons. In both isomers the aromatic protons appear as *ABC* spin systems, and by virtue of the closer proximity of the deshielding dicarbomethoxy groups, $H_A$ [$\tau$ 2.80, H–C(9)] in **17** is further downfield shifted than $H_A$ [$\tau$ 3.15, H–C(12)] in **16**, as is $H_C$ [$\tau$ 3.20, H–C(9)] in **16** relative to $H_C$ [$\tau$ 3.46, H–C(12)] in **17**.

Unlike **10** the semibullvalenes **16** and **17** do not appear to undergo further isomerizations upon irradiation, but they do slowly disappear to give polymeric material.

The structural assignment of the third photoproduct **18** was deduced from both NMR. spectral evidence and hydrogenation data. The NMR. spectrum shows three singlets for the methoxyl and carbomethoxyl protons but otherwise contains only absorptions in the olefinic-aromatic region. The aromatic protons occur as an *ABC* spin system and were readily identified by spin decoupling experiments (see Experimental Part). For the olefinic protons, which appear as two narrow envelopes of peaks, the NMR. data is summarized in *Table 2*; for the purposes of comparison the data for the benzo-COT's **2** and **7** are also shown. From the *Table* it can be seen that the C(6) and C(9) protons of **18** are downfield shifted by 1.27 ppm relative to those of **2**. This displacement is in reasonable agreement with 1.02 ppm found for the *cis*

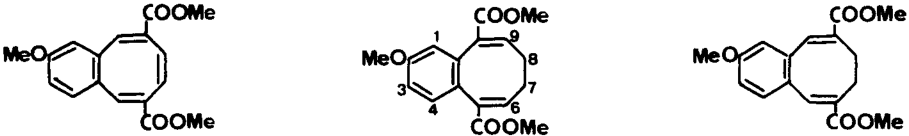
Table 2. *The NMR. data of aromatic and vinyl protons of benzo-cyclooctatetraenes*[a])

| | Description and signal positions, $\tau$ | | |
|---|---|---|---|
| Assignment | **12** | **6** | **18** |
| H–C(1) | 2.72–3.27 *m* | 3.02 *m* | 3.54 *d*<br>$J_{1,3} = 2.5$ |
| H–C(2) | | 2.85 *m* | none |
| H–C(3) | | 2.85 *m* | 3.22 *d*×*d*<br>$J_{3,4} = 8.5$ and $J_{1,3} = 2.5$ |
| H–C(4) | | 3.02 *m* | 3.01 *d*<br>$J_{3,4} = 8.5$ |
| H–C(5) and H–C(10) | 3.53 *d*<br>$J_{5,6} = J_{9,10} = 10.5$ | 3.34 *d*<br>$J_{5,6} = J_{9,10} = 11.5$ | none |
| H–C(6) and H–C(9) | 4.08 *d*<br>$J_{5,6} = J_{9,10} = 10.5$ | 3.87 *d*<br>$J_{5,6} = J_{9,10} = 11.5$ | 2.77–2.86 *m* |
| H–C(7) and H–C(8) | 4.19 *s* | none | 3.90–3.95 *m* |

[a]) $CCl_4$ solutions run on 100 MHz NMR. with TMS as internal standard; coupling constants are given in Hz.

proton of methyl acrylate [8]. However, it is evident that a structure such as **19** might also fit these NMR. data.

*Scheme 6*



**19** **20** **21**

The critical information ruling out this latter alternative was obtained from examination of the NMR. spectrum of the dihydro product **20** resulting from partial hydrogenation of **18** with *Wilkinson*'s catalyst. The NMR. spectrum of **20** reveals strong coupling (6.5 Hz) between the methylene protons and the olefinic protons at C(6) and C(9). These couplings were confirmed by spin decoupling experiments: irradiation at the centre of the methylene multiplet collapsed the H–C(6) and H–C(9) triplets to singlets (see Experimental Part). Clearly, product **21** anticipated from the partial reduction of **19** does not accord with this observation since here only allylic coupling between the olefinic and methylene protons is available and this is well known not to exceed 3 Hz [9]. Thus **18** alone remains consistent with all the information at hand for the structure of the third photoproduct of **8**.

In contrast to the direct irradiation of **8** sensitization with benzophenone leads only to the semibullvalenes **16** and **17**. The quantum yield for this and all other transformations observed in this study are shown in *Table 3*.

**Discussion.** – Firstly we can conclude that the benzo-COT **18** formed in the direct irradiation of **8** derives from the singlet excited state since only the semibull-

Table 3. *Quantum yield data*[a])

| Compound | Light wavelength (nm) | Sensitizer | Products | Quantum yields |
|---|---|---|---|---|
| **8** | 313 | None | **16**, **17**, and **18** | 0.075, 0.075, and 0.07 |
| **8** | 366 | Benzophenone[b]) | **16** and **17** | 0.11 and 0.11 |
| **9** | 313 | None | **6** | 0.009 |
| **9** | 366 | Benzophenone[b]) | **6** | 0.38 |
| **10** | 313 | None | **11** | 0.008 |
| **10** | 313 | Acetone (neat)[c]) | **11** | 0.008 |

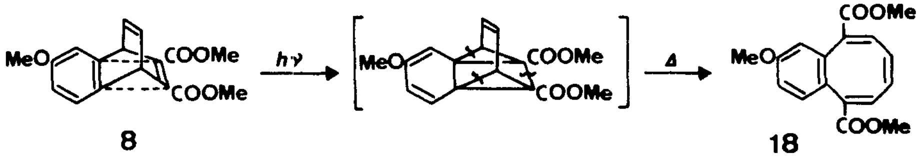
[a]) Benzene solvent.
[b]) Sensitizer absorbing >95% of light.
[c]) Sensitizer absorbing >90% of light.

valenes **16** and **17** are produced during sensitized runs. Also, the intersystem crossing from singlet excited **8** to its triplet must be relatively efficient since these same semibullvalenes result from direct irradiation with only *ca.* 30% lowering of quantum efficiency.

The situation regarding singlet excited **9** is quite different. It gives no benzo-COT product and intersystem crosses less than 4% as efficiently as **8** (note *Table 3*). Since no fluorescence was observed for **9** radiationless decay appears to be the principal deactivation process. Presently we are unable to reasonably account for this observation.

With respect to the singlet cycloaddition of barrelene **8**, it is evident that despite the *a priori* availability of three different [$2\pi + 2\pi$] initial bridging options, only the aromatic-vinyldiester route is utilized in benzo-COT formation (*Scheme 7*). Thus, the presence of one methoxy group in the aromatic nucleus of **6** dramatically changes the bonding preference.

*Scheme 7*

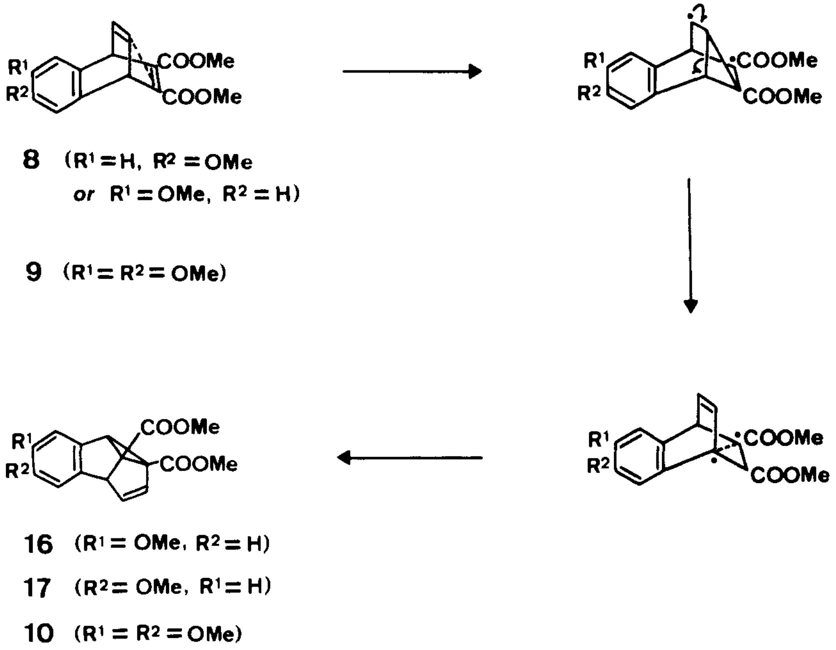


Interestingly this new route involves the [$2\pi + 2\pi$] cycloaddition of greatest charge transfer character and is therefore precisely the one not anticipated on the basis of the *Epiotis* formulations [4]. The general theory of pericyclic processes outlined by *Epiotis* predicts an [$s + a$] mode of closure for polar-concerted [$2\pi + 2\pi$] photocycloadditions. Consequently, for the constrained barrelene system, where [$2\pi_s + 2\pi_a$] processes are precluded by geometry, one is led to predict preferred bridging between the least polar [$2\pi + 2\pi$] units, *i.e.*, between the aromatic and vinyl groups, and/or between the vinyl and vinyldiester units. We therefore conclude that if the cyclization step is product controlling, then either the *Epiotis* approach is invalid for this constrained system or non-concerted processes are involved in the benzo-COT formation.

We have noted previously that preferred bridging in benzobarrelenes seems to occur between the [2π + 2π] partners of greatest charge transfer character [3], and in the present cases we rationalize the differing abilities of **8** and **9** to yield benzo-COT product in terms of electron donation from alternative HOMO's of the benzene-like nuclei.

As concerns the semibullvalene formations from triplet excited **8** and **9**, these can readily be rationalized in terms of di-π-methane rearrangements proceeding exclusively *via* vinyl-vinyldiester bridging routes (*Scheme 8*; note that the two routes available to **8** are equally utilized).

*Scheme 8*



**8** (R¹ = H, R² = OMe *or* R¹ = OMe, R² = H)

**9** (R¹ = R² = OMe)

**16** (R¹ = OMe, R² = H)

**17** (R² = OMe, R¹ = H)

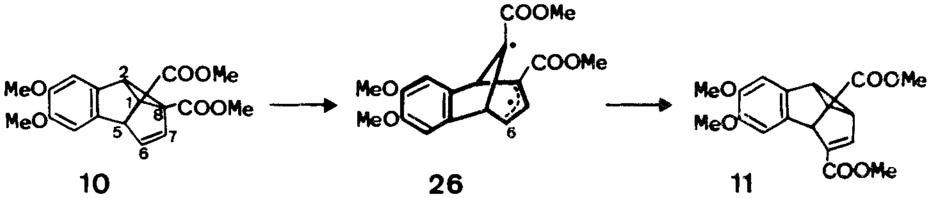
**10** (R¹ = R² = OMe)

Finally, the conversion of the semibullvalene **10** to **11** is deserving of comment. Since the quantum yields for both the direct and sensitized irradiations of **10** are the same (within experimental error), it is feasible that **11** derives from the same triplet excited state, providing we assume an efficient intersystem crossing. The absence of fluorescence from **10** is consistent with this view.

The formation of **11** can be envisaged as proceeding concertedly ($[2\pi_s + 2\sigma_s]$ sigmatropic 1,3-shift) or *via* a stepwise process involving an initial cleavage of the C(1)–C(8) cyclopropyl bond to yield the stabilized biradical species **26**, which then closes at C(6) to yield the more conjugated and less sterically crowded isomer **11** (*Scheme 9*).

Occasionally semibullvalenes photoisomerize, but only to give benzo-COT products *via* cleavage of the C(1)–C(5) and C(2)–C(8) bonds [1] [2] [10]. Thus the vinyl-

*Scheme 9*



cyclopropane interconversion found here for **10** is without precedent in the semibullvalene series, and the driving force for its occurrence probably derives from removal of the diester strain energy. We note also that the C(1)–C(8) bond of **10** is predicted to be weak on the basis of ground-state electronic arguments, since in cyclopropanes electron withdrawing substituents (here the carbomethoxy groups) strengthen the bond opposite and weaken the bonds adjacent, while electron donating groups (here the dimethoxy benzo group) weaken the bond opposite and strengthen the bonds adjacent, *i.e.*, cumulatively the C(1)–C(8) bond of **10** suffers three bond weakening effects [11].

Overall then, we conclude that the occurrence and the direction of the initial $[2\pi + 2\pi]$ bonding in barrelene system **6** is dramatically sensitive to the presence of methoxy substituents in the aromatic ring, and once again find that the *Epiotis* pericyclic theory is not helpful in predicting the preferred mode of photoclosure leading to benzo-COT product [2] [3].

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## Experimental Part

*General methods.* UV. spectra are given as absorption maxima in nm with $\varepsilon$ values in parentheses; sh = shoulder. IR. band positions are given in $cm^{-1}$; br. = broad. NMR. spectra are given in $\tau$ units relative to TMS as internal reference, and coupling constants ($J$) in Hz; $s$ = singlet, $d$ = doublet, $t$ = triplet, and $m$ = multiplet. Benzene solvent for photolyses was shaken three times with 20% fuming sulfuric acid, washed with 10% aqueous NaOH, dried ($MgSO_4$), and distilled from calcium hydride. Benzophenone sensitizer was recrystallized three times from ethanol, m.p. 47–49°. Acetone sensitizer was *Fluka* UV. grade and was used without further purification. All m.p. are uncorrected. Silicic acid for chromatography was *Mallenckrodt* CC-7 grade, 100–200 mesh.

*Synthesis of dimethyl 10-methoxy-2,3-benzobicyclo[2.2.2]octatetraene-5,6-dicarboxylate* (**8**). A mixture of 3.0 g (19.0 mmol) of 2-methoxynaphthalene and 2.7 g (19.0 mmol) of dimethyl acetylene dicarboxylate was sealed in a 250 ml pressure bottle (*Fisher*) and heated on an oil bath at 155–160° for 72 h. The cooled mixture was dissolved in 10 ml of benzene and chromatographed on 100 g of silicic acid. Elution with 1 l of 1% acetone in hexane removed the unreacted starting materials; elution with 4% acetone in hexane gave 620 mg of an oil. The oil was re-chromatographed on 400 g of silicic acid with 4% acetone in hexane as eluting agent; 40 ml fractions were collected. Short-path distillation (140°/0.1 mm Hg) of fractions 78–108 gave 307.4 mg (5%) of **8** as a colourless oil. – UV. (cyclohexane): 229 sh (5900), 280 (2200), 285 (2000), and 304 sh (640). – IR. ($CCl_4$): 1720 br. – NMR. (60 MHz, $CCl_4$): 3.00/*d*, $J$ = 8, H—C(12); 3.09–3.25/*m*, H—C(7, 8, 9); 3,71/*d*×*d*, $J$ = 2.5 and 8, H—C(11); 4.86–5.05/*m*, H—C(1,4); 6.34/*s*, $H_3CO$—C(arom.) and two $H_3COCO$.

Spin decoupling (60 MHz, $CCl_4$): irradiation of H–C(12) collapsed H–C(11) to a *d* ($J$ = 2.5). – MS.: Calc. 300.0991 ($C_{17}H_{16}O_5^+$), found 300.0994 (100%).

*Synthesis of dimethyl 10,11-dimethoxy-2,3-benzobicyclo[2.2.2]octatetraene-5,6-dicarboxylate* (**9**). A mixture of 3.0 g (16.0 mmol) of 2,3-dimethoxynaphthalene and 2.3 g (16.2 mmol) of dimethyl acetylene dicarboxylate was sealed in a 250 ml pressure bottle (*Fisher*) and heated on an oil bath at 155–160° for 72 h. The cooled mixture was dissolved in 10 ml of benzene and chromatographed on 100 g of silicic acid. Elution with 1 l of 2% acetone in hexane removed the unreacted starting materials; elution with 7% acetone in hexane gave 580.7 mg of an oil. The oil was re-chromatographed on 400 g of silicic acid with 7% acetone in hexane as eluting agent; 40 ml fractions were collected. Crystallization of fractions 64–83 from methanol gave 217.3 mg (4%) of **9** as a colourless solid, m.p. 123–125°. – UV. (cyclohexane): 212 (35000), 242 (5200), 288 (3900), 292 (3900), 297 sh (3000), 319 sh (860). – IR. ($CCl_4$): 1720 br. – NMR. (60 MHz, $CCl_4$): 3.05–3.23/*m*, H–C(7), H–C(8), H–C(9), H–C(12); 4.85–5.05/*m*, H–C(1), H–C(4); 6.25+6.30/2*s*, two $H_3CO$ each. – MS.: Calc. 330.1109 ($C_{18}H_{18}O_6^+$), found 330.1106 (100%).

*Preparative photolyses.* The apparatus consisted of a 125 W high-pressure Hg lamp (*Philips*) surrounded by a water-cooled pyrex immersion well. For benzophenone-sensitized irradiations at wavelengths >340 nm the light was passed through an aqueous filter jacket (10 mm thick), prepared from a solution of 750 g NaBr and 8 g $Pb(NO_3)_2$ per 1 l of water. Prior to irradiations, the solutions were deoxygenated by argon flushing. A positive pressure of argon was maintained over the solutions throughout the course of the photolyses.

*Direct irradiation of dimethoxybarrelene* **9**. A solution of 155.4 mg (0.47 mmol) of **9** in 250 ml of benzene was photolysed for 1 h. The solvent was removed *in vacuo* and the residue was chromatographed on 400 g of silicic acid and eluted with 7% acetone in hexane. The first band contained 49.7 mg (32%) of semibullvalene **10**, a colourless solid, m.p. 118–120° (from methanol). – UV. (cyclohexane): 247 sh (6100), 287 sh (5300), 292 (6200), 295 (6300), and 300 sh (5000). – IR. ($CCl_4$): 1730 br. – NMR. (60 MHz, $CCl_4$): 3.20/*s*, H–C(9); 3.48/*s*, H–C(12); 4.38/*d*×*d*, $J_{5,6}$ = 2.5 and $J_{6,7}$ = 6, H–C(6); 4.80/*d*, $J_{6,7}$ = 6, H–C(7); 5.75/*d*, $J_{5,6}$ = 2.5, H–C(5); 5.79/*s*, H–C(2); 6.28/*s*, three $H_3CO$; 3.61/*s*, $H_3CO$. Spin decoupling (60 MHz, $CCl_4$): irradiation of H–C(6) collapsed H–C(7) and H–C(5) to singlets; irradiation of H–C(7) collapsed H–C(6) to a *d* ($J$ = 2.5); irradiation of H–C(5) collapsed H–C(6) to a *d* ($J$ = 6). – MS.: 330 ($C_{18}H_{18}O_6^+$, 95%), 271 (100%).

Unreacted starting material (91.2 mg, 59%, m.p. 122–124°) was recovered from the second band off the column.

*Direct irradiation of semibullvalene* **10**. A solution of 59.9 mg (0.18 mmol) of **10** in 250 ml of benzene was photolysed for 6.5 h. The solvent was removed *in vacuo* and the residue was chromatographed on 200 g of silicic acid and eluted with 7% acetone in hexane. The first band contained 28.6 mg (48%) of dimethyl 10,11-dimethoxy-3,4-benzotricyclo[3.3.0.$0^{2,8}$]octa-3,6-diene-1,6-dicarboxylate (**11**), a colourless solid, m.p. 130–132° (from methanol). – UV. (cyclohexane): 235 (12700) and 299 (3600). – IR. ($CCl_4$): 1715 and 1725. – NMR. (60 MHz, $CCl_4$): 3.25/*s*, H–C(9), 3.33/*s*, H–C(12), 4.08/*d*, $J_{7,8}$ = 2.5, H–C(7); 5.57/*s*, H–C(5); 6.25/*d*, one limb hidden, but see following spectrum, H–C(1); 6.28/*s*, $H_3CO$; 6.31/*s*, $H_3CO$; 6.39/*s*, two $H_3CO$ and 6.75/*d*×*d*, $J_{7,8}$ = 2.5 and $J_{2,8}$ = 8, H–C(8). – NMR. (60 MHz, $C_6D_6$): 3.01/*s*, H–C(9); 3.21/*s*, H–C(12); 4.08/*d*, $J_{7,8}$ = 2.5, H–C(7); 5.15/*s*, H–C(5); 6.35/*d*, $J_{2,8}$ = 8, H–C(2); 6.56/*s*, $H_3$–CO; 6.60/*s*, $H_3$–CO; 6.65/*s*, $H_3CO$; 6.68/*s*, $H_3CO$; 6.87/*d*×*d*, $J_{7,8}$ = 2.5 and $J_{2,8}$ = 8, H–C(8). Spin decoupling (60 MHz, $C_6D_6$): irradiation of H–C(7) collapsed H–C(8) to a *d* ($J$ = 8); irradiation of H–C(2) collapsed H–C(8) to a *d* ($J$ = 2.5); irradiation of H–C(8) collapsed H–C(2) and H–C(7) to singlets. – MS.: 330 ($C_{18}H_{18}O_6^+$, 100%).

Unreacted starting material (27.1 mg, 45%, m.p. 117–119°) was recovered from the second band off the column.

*Sensitized irradiations of semibullvalene* (**10**).

a) *With acetone.* A solution of 76.9 mg (0.23 mmol) of **10** in 250 ml of neat acetone was photolysed for 6.0 h. The solvent was removed *in vacuo* and the residue was worked-up in the same way as for the direct irradiation (*vide supra*) of **10** to give 22.4 mg (29%) of **11**, m.p. 130–132°, and 51.2 mg (66%) of unreacted **10**, m.p. 118–120°.

b) *With benzophenone.* Irradiations (>340 nm) with benzophenone sensitizer led quickly to the formation of an intensely absorbing yellow-coloured solution, and was attended by the slow loss of **10**: no **11** was found.

*Sensitized irradiation of dimethoxybarrelene* **9**. A solution of 310.2 mg (0.94 mmol) of **9** and 5.0 g (24.3 mmol) of benzophenone in benzene was photolysed (>340 nm) for 10 min. The solvent was removed *in vacuo* and the residue was chromatographed on 400 g of silicic acid. The benzophenone was brought off the column with 1 l of 3% acetone in hexane. Elution with 7% acetone in hexane gave **10** (57.4 mg, 18%, m.p. 118–120°) followed by unreacted starting material (236.2 mg, 76%, m.p. 123–125°).

*Direct irradiation of monomethoxybarrelene* **8**. A solution of 634.2 mg (2.1 mmol) of **8** in 250 ml of benzene was photolysed for 0.5 h. The solvent was removed *in vacuo* and the residue was chromatographed on 450 g of silicic acid and eluted with 4% acetone in hexane; 40 ml fractions were collected. Shortpath distillation (140°/0.1 Torr) of fractions 61–62 yielded 16.7 mg (3%) of **16** as a colourless oil. – UV. (cyclohexane): 245 sh (7500), 287 (2300), and 293 (2200). – IR. ($CCl_4$): 1732 br. – NMR. (60 MHz, $CCl_4$): 3.15/*d*, $J_{11,12} = 8$, H—C(12); 3.20/*d*, $J_{9,11} = 2.5$, H—C(9); 3.48/*d*×*d*, $J_{11,12} = 8$ and $J_{9,11} = 2.5$, H—C(11); 4.39/*d*×*d*, $J_{5,6} = 2.5$ and $J_{6,7} = 5.5$, H—C(6); 4.83/*d*, $J_{6,7} = 5.5$, H—C(7); 5.75/*d*, $J_{5,6} = 2.5$, H—C(5); 5.79/*s*, H—C(2); 6.28/*s*, $H_3CO$; 6.31/*s*, $H_3CO$; 6.40/*s*, $H_3CO$. – MS.: 300 ($C_{17}H_{16}O_5^+$, 26%), 143 (100%).

Short-path distillation (135°/0.1 mm Hg) of fractions 63–67 yielded 41.9 mg (7%) of a mixture of **16** (42% by NMR.) and **17** (58%). Short-path distillation (140°/0.1 Torr) of fractions 68–70 yielded 21.1 mg (3%) of **17** as a colourless oil. – UV. (cyclohexane): 223 sh (13500), 252 sh (5800), 282 (2800), and 292 (2000). – IR. ($CCl_4$): 1730 br. – NMR. (60 MHz, $CCl_4$): 2.80/*d*, $J_{9,10} = 8$, H—C(9); 3.30/*d*×*d*, $J_{10,12} = 2.5$ and $J_{9,10} = 8$, H—C(10); 3.46/*d*, $J_{10,12} = 2.5$, H—C(12); 4.36/*d*×*d*, $J_{5,6} = 2.5$ and $J_{6,7} = 5$, H—C(6); 4.76/*d*, $J_{6,7} = 5$, H—C(7); 5.68/*d*, $J_{5,6} = 2.5$, H—C(5); 5.76/*s*, H—C(2); 6.26/*s*, $H_3CO$; 6.30/*s*, $H_3CO$; 6.38/*s*, $H_3CO$. – MS.: 300 ($C_{17}H_{16}O_5^+$, 27%), 157 (100%).

Short-path distillation (135°/0.1 Torr) of fractions 75–95 gave 500.6 mg (79%) of a mixture of unreacted **8** (95% by NMR.) and **18** (5%). Short-path distillation (140°/0.1 Torr) of fractions 96–100 yielded 22.3 mg (3.5%) of **18** as a colourless oil. – UV. (cyclohexane): 224 sh (14500) and 271 sh (3900). – IR. ($CCl_4$): 1725 br. – NMR. (100 MHz, $CDCl_3$): 2.69–2.76/*m*, H—C(7,9); 3.01/*d*, $J_{3,4} = 8.5$, H—C(4); 3.15/*d*×*d*, $J_{3,4} = 8.5$ and $J_{1,3} = 2.5$, H—C(3); 3.44/*d*, $J_{1,3} = 2.5$, H—C(1); 3.89–3.94/*m*, H—C(7), H—C(8); 6.23/*s*, $H_3CO$; 6.27/*s*, two $H_3COCO$. Spin decoupling (100 MHz, $CDCl_3$): irradiation of H—C(1) collapsed H—C(3) to a *d* ($J = 8.5$); irradiation of H—C(3) collapsed H—C(1) to a *s* (H—C(4) to close to centre of irradiation to see); irradiation of H—C(6) and H—C(9) multiplet simplified the *m* of H—C(7) and H—C(9) to a br. *s*; irradiation of H—C(7) and H—C(8) multiplet changed the *m* of H—C(6) and H—C(9) to a simpler *m*. For the NMR. (100 MHz) in $CCl_4$ see *Table 2*. – MS.: 300 ($C_{17}H_{16}O_5^+$, 3%), 58 (100%).

NMR. examination of the semibullvalene-C(6) and -C(7) protons in the crude photolysate residue (before chromatography) revealed **16** and **17** to be present in equal amounts.

*Sensitized irradiation of monomethoxybarrelene* **8**. A solution of 192.8 mg (0.64 mmol) of **8** and 2.0 g (9.7 mmol) of benzophenone in 250 ml of benzene was irradiated (>340 nm) during 0.75 h. The solvent was removed *in vacuo* and the residue was chromatographed on 400 g of silicic acid. Elution with 2% acetone in hexane brought off benzophenone. The column was then eluted with 4% acetone in hexane; 40 ml fractions were collected. Short-path distillation (140°/0.1 Torr) of fractions 52–53 yielded 27.1 mg (14%) of **16**. Short-path distillation (140°/0.1 Torr) of fractions 54–62 gave 76.9 mg (40%) of a mixture of **16** (45% by NMR.) and **17** (55%). Short-path distillation (140°/0.1 Torr) of fractions 63–66 gave 34.9 mg (18%) of **17**. Unreacted starting material (35.1 mg, 18%) was obtained from short-path distillation (140°/0.1 Torr) of fractions 71–76.

NMR. examination of the semibullvalene-C(6) and -C(7) protons in the crude photolysate residue (before chromatography) revealed **16** and **17** to be present in equal amounts.

*Partial hydrogenation of* **18** *with* Wilkinson*'s catalyst.* A solution of 50.8 mg (0.17 mmol) of **18** and 91.7 mg (0.1 mmol) of chlorotris (triphenylphosphine) rhodium chloride (*Wilkinson*'s catalyst) in 20 ml of benzene was stirred under a hydrogen atmosphere during 24 h. in the absence of light. The solution was concentrated to 5 ml *in vacuo* and chromatographed on 100 g of silicic acid and eluted with 4% acetone in hexane. Short-path distillation (130°/0.1 Torr) of the first band gave 40.1 mg (79%) of **20** as a colourless oil. – UV. (MeOH): 218 sh (19000) and 276 sh (2800). – IR. ($CCl_4$): 1720 br. – NMR. (100 MHz, $CDCl_3$): 2.80/*t*, $J_{6,7} = 6.5$, H—C(6); 2.84/*t*, $J_{8,9} = 6.5$, H—C(9); 2.86/*d*, $J_{3,4} = 8.5$, H—C(4); 3.09/*d*×*d*, $J_{3,4} = 8.5$ and $J_{1,3} = 2.5$, H—C(3); 3.27/*d*, $J_{1,3} = 2.5$, H—C(1); 6.16/*s*, $H_3CO$; 6.27/*s*, two $H_3CO$; 7.45–7.75/*symm. m*, 2H—C(7), 2H—C(8), see decoupling results below. Spin decoupling (100 MHz, $CDCl_3$): irradiation at the centre of the methylene *m* (7.60) collapsed H—C(6) and H—C(9) to singlets; irradiation at H—C(6) [or at H—C(9)] collapsed the methylene *m* to two triplets (7.72, 2 H—C(7), $J_{7,8} = 3.5$; 7.48, 2 H—C(8), $J_{7,8} = 3.5$). – MS.: Calc. 302.1154 ($C_{17}H_{18}O_5^+$), found 302.1153 (4%), 84 (100%).

Short-path distillation (130°/0.1 Torr) of the second band off the column gave 6.2 mg (12%) of unreacted starting material.

*Quantum yield irradiations.* Quantum yields were determined on the apparatus described by *Schaffner et al.* [12] using Rhodamine B actinometry. The bandwidth at half-height of the irradiating light was $<10$ nm. Before irradiations, the solutions of samples (*ca.* 0.06 mmol) and benzophenone (*ca.* 1.7 mmol, if any) in 3.0 ml of benzene solvent were deoxygenated by flushing with argon and sealed under a positive pressure. Photolysates were concentrated *in vacuo*, a known amount of methyl-$\beta$-naphthylketone was added as internal standard, and the product composition was determined by NMR. analysis; the peak areas were calibrated against authentic mixtures of similar constitution. Conversions were kept below 20% and the quantum yields, shown in *Table 7*, were determined from the average of two runs for each system; the mean deviations are within ± 12%.

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