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PHOTOREARRANGEMENT OF HOMOBENZOBARRELENES, INTERFERENCE OF CYCLOPROPYL RINGS IN THE DI-π-METHANE REARRANGEMENT

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Abstract—Acetone-sensitized irradiation of homobenzobarrelenes, exo- and endo-**4a** causes the di-π-methane rearrangement ($\Phi = 3.9 \times 10^{-1}$ and 9.5×10^{-2} respectively), whereas direct irradiation was ineffective. The products formed were exo- and endo-homobenzosemibullvalenes. On the other hand, irradiation of the dicarbomethoxy derivatives exo- and endo-**4b** leads (directly or acetone-sensitized) to dimethyl 7,8-benzotricyclo [4.3.0.0.^{2,9}] nona-4,7-diene-2,4-dicarboxylate **12** by cyclopropylcarbinyl-homoallyl isomerization (exo-**4b**: $\Phi_{dir.} = 1.8 \times 10^{-2}$, $\Phi_{sens.} = 6.9 \times 10^{-2}$). Herkstroeter-Hammond plots make probable that the same triplet state is photoreactive in all cases.

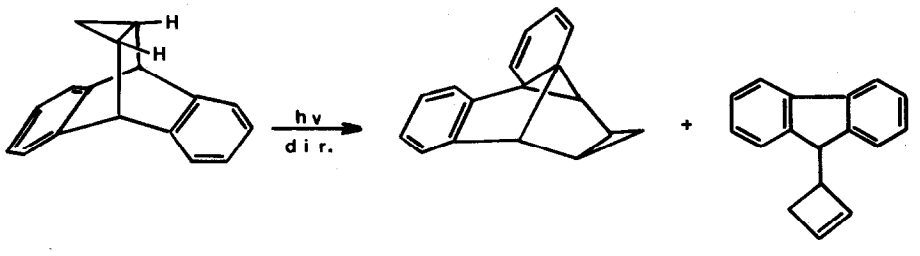
UV-irradiation of triptycenes[1] and dibenzonorbornadienes[2] effects the formation of photoproducts by a reaction path which involves a carbene intermediate. Although possible, the reaction does not follow the di-π-methane rearrangement route. On the other hand, direct irradiation of 9, 10 - cyclopropano - 9, 10 - dihydroanthracene (homodibenzobarrelene) **1** mainly yields a di-π-methane rearrangement product **2** and only a minor amount of 3-(9-fluorenyl)cyclobutene **3**, which was formed most likely via a carbene intermediate, while sensitized irradiation was not effective[3] (Scheme 1). Zimmerman[4,5] reported on a photorearrangement which was induced by vinylcyclopropyl bridging. To determine the effects of structure on the photochemical pathways in rigid molecules, and to gain knowledge of how vinyl–aryl, vinyl–cyclopropyl and aryl–cyclopropyl bridging will compete, the photochemical behaviour of exo- and endo-1,4 - cyclopropano - 1, 4 - dihydronaphthalene (**4a**) and the dicarbomethoxy derivatives **4b** was studied. These compounds could react either by a di-π-methane rearrangement, by vinyl- or aryl-cyclopropyl bridging or could show vinyl- or aryl-cyclopropyl interaction depending on the endo- or exo-configuration.

RESULTS

Synthesis of reactants

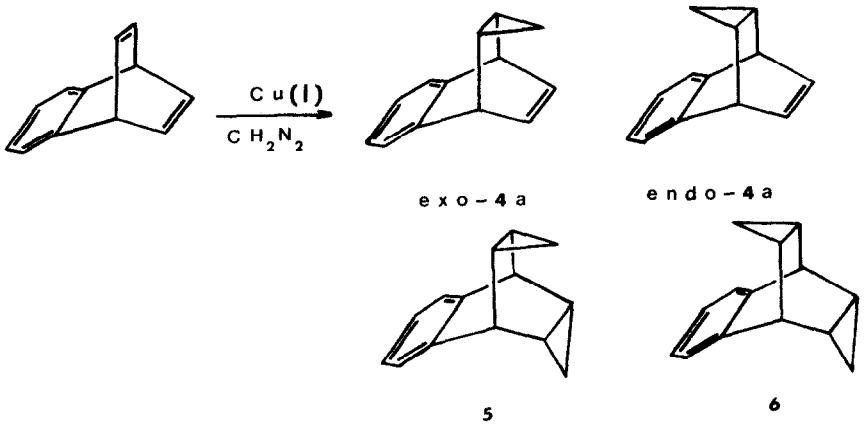
The exo- and endo-homobenzobarrelenes **4a** were synthesized as outlined in Scheme 2. The separation of the product mixture was achieved by preparative HPLC. This procedure yielded exo-**4a** as the main product in 65% and endo-**4a** in about 20% yield and was advantageous over the Simmons-Smith reaction used by Tori, since only traces of endo-**4a** were formed by this method[6] (Scheme 2).

Exo- and endo-dicarbomethoxyhomodibenzobarrelenes **4b** were synthesized as shown in Scheme 3; they could easily be separated by preparative HPLC. Prolonged reaction times of diazomethane with **7** led to addition to the unsubstituted double bond. The configurations of exo- and endo-**4b** were deduced by ^{1}H NMR. The cyclopropyl hydrogen atom of endo-**4b** experiences a strong shielding by the magnetic anisotropy of the benzene ring. As a consequence the signal appears at $\delta = 0.3$ ppm, whereas the signal of the exo-hydrogen atom is found at $\delta = 1.73$ ppm. The aromatic hydrogen atoms of the exo-**4b** show a AA'BB' spectrum,

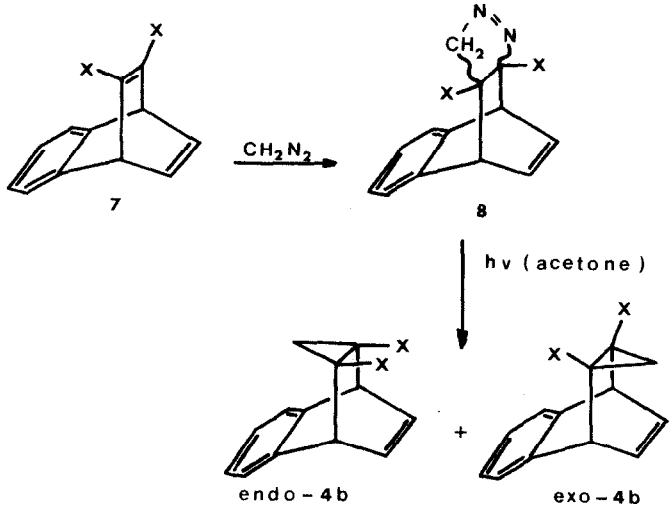


1 **2** **3**

Scheme 1.



Scheme 2.



Scheme 3.

Scheme 4.

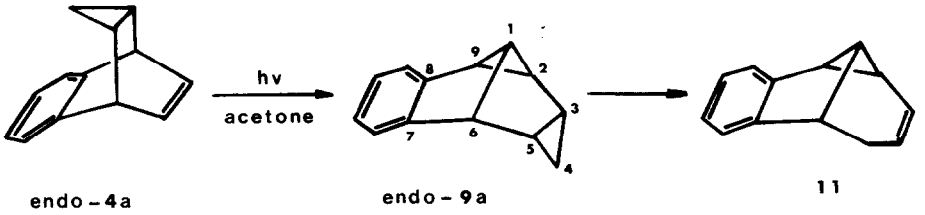
whereas those of endo-**4b** give rise to a singlet, which lends further evidence to the configurations assigned by comparison of the ^{1}H NMR spectra of exo- and endo-**4a**.

Photorearrangement—overall reaction course

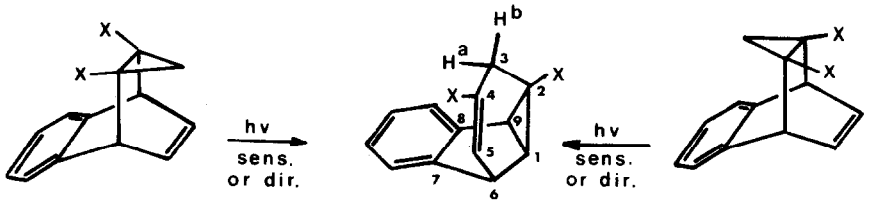
Acetone sensitized irradiation of exo-**4a** yielded as the sole product the exo-benzohomosemibullvalene (**9a**) in a di-π-methane rearrangement. The structure elucidation of **9** was accomplished by NMR analysis and by synthesis. Reaction of benzosemibullvalene **10** with diazomethane and Cu_2Cl_2 gave exo-**9a** as the only product which is less sterically hindered than the endo-isomere (Scheme 4).

In the direct irradiation of the exo-**4a** at 250 nm after extended periods of time only a complex mixture of undefined products was formed.

The irradiation of endo-**4a** in acetone produced as the primary photoproduct endo-**9a**, which was converted to **11** in a secondary photoreaction. The structure of endo-**9a**, which was isolated followed from the analysis of 270 MHz spectra and spin decoupling results and from the structure of **11**. Comparison of the positions of the resonance signals of endo-**9a** with those of benzobarrelene reveal the magnetic anisotropy effect of the additional cyclopropyl-ring. The signal of H(1) is shifted downfield by 0.25 ppm, whereas H(2) and H(5) are shifted upfield in accord with the results found with exo- and endo-**4a**[6] (Scheme 5).



Scheme 5.



Scheme 6.

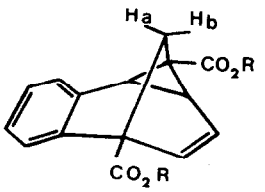
Direct photolysis of endo-**4a** in n-hexane at 254 nm led to a slow decomposition of the educt. No defined product could be observed.

In contrast to the photochemistry of exo- and endo-**4a** performing a di-π-methane rearrangement, irradiation of exo- and endo-**4b** in acetone at 310 nm through a Pyrex filter to a conversion of 40–50%, determined by the recovery of starting material, delivered as the only product dimethyl 7, 8 - benzotricyclo[4.3.0.0^{2,9}]4 - nonene-2, 4 - dicarboxylate (**12**) (Scheme 6).

The structure of **12** followed from ^{1}H- and ^{13}C NMR-spectra and from spin-decoupling experiments. The signal of H_{3a} appeared strongly shielded by the magnetic anisotropy effect of the benzene ring at $\delta = 1.14$ ppm[10] as a doublet of doublet with the coupling constants $^2J_{3a,3b} = 18$ Hz, typical for geminal coupling, and $^4J_{3,5} = 3.5$ Hz. The magnitude of the allylic coupling is in accord with a geometry placing the C-H_{3a} σ-bond approximately parallel to the π-orbital of the adjacent double bond.[11] The signal of the H_{3b} appeared as a doublet at $\delta = 3.78$ ppm with the corresponding coupling constant. The signal of the vinyl proton H(5) was shifted downfield by the carbomethoxy group and presumably by the paramagnetic anisotropic effect of the benzene ring to $\delta = 7.48$ ppm and appeared as a doublet with $J_{5,6} = 7.8$ Hz and $J_{3a,5} = 3.5$ Hz. As can be seen from molecular models the dihedral angle between the C-H_{3b} σ-bond and the π-orbital is about 120° and the coupling constant $J_{3b,5}$ is zero as expected.[11] H(1) gave rise to a triplet at $\delta = 2.74$ ppm with coupling constants $J_{1,6} = J_{1,9} = 6.6$ Hz, H(9) to a doublet at $\delta = 3.29$ ppm and H(6) to a doublet of doublets with $J_{1,6} = 6.6$ Hz and $J_{5,6} = 7.8$ Hz. The ^{13}C NMR-spectrum confirms the proposed structure. The ^{13}C NMR signals and ^{13}C–^{1}H coupling constants are listed in Table 1. The ^{13}C–^{1}H coupling constants found for carbons 1 and 9 are in accord with the presence of a cyclopropane ring.[12]

An alternative structure of a barbaralane derivative **13** must be rejected for several reasons. (i) As can be seen from molecular models the hydrogen atom H_a is not placed closely enough above the benzene ring to allow a magnetic shielding as was observed. (ii) The vinyl hydrogen atoms of **13** should give rise to signals in the region typical for vinyl-protons. (iii) The ^{13}C NMR spectrum of **13** should show two singlets, two doublets and one triplet with other ten signals in the olefinic-aromatic-carbonyl region.

n = a : X = H ; n = b : X = CO_2Me



13

Direct irradiation of exo- and endo-**4b** in cyclohexane at 254 nm to a conversion of 50% afforded as the only product **12**, as was obtained by the sensitized irradiation. No exo-/endo-isomerization or cyclopropyl-allyl rearrangement could be observed in either sensitized or direct irradiation.

Multiplicity studies

Only sensitized irradiation of endo- and exo-**4a** afforded the photoproducts exo- and endo-**9a**. Consequently, it seems reasonable to assume that the triplet state is solely photoreactive as was found for the benzobarrelene itself.[8] Benzobarrelene delivered benzocyclooctatetraene by direct irradiation, which was formed to 94 ± 3% by aryl–vinyl and to 6 ± 3% by vinyl–

Table 1. ^{13}C NMR-signals and ^{13}C-H coupling constants of **12**, obtained on a Bruker WM 250 MHz

Carbon	(ppm)	Multiplicity	$J_{^{13}C-H}$	
3	19.787	t	130.56	
2	34.653	s	-	
1	35.167	d	180.56	
9	39.674	d	175.00	
6	42.073	d	138.89	
$-OCH_3$	51.838	q	138.15	
$-OCH_3$	52.538	q	138.15	
	124.484	d		a)
	124.787	d		a)
Aromat	127.132	d		a)
	127.759	d		a)
	134.447	s		
	141.027	s		
Vinyl	141.696	d		a)
Vinyl	143.103	s		
C=O	166.848	s		
C=O	173.071	s		

a) Coupling constants not determined

vinyl bridging. Similar results were obtained by direct irradiations of substituted benzobarrelenes.[7,9]

It is remarkable therefore that direct irradiations of exo- and endo-**4a** are totally inefficient. These results imply that in the barrelene-cyclooctatetraene rearrangement all π-bonds, aryl- or vinyl, are involved.

In contrast to these results exo- and endo-**4b** are equally reactive in the direct and sensitized irradiations. Quench experiments with piperylene revealed that the photoreactions of exo- and endo-**4b** could be quenched. A linear Stern–Vollmer plot was obtained in the reaction of exo-**4b** in the range of piperylene concentration of 1×10^{-3} to 5×10^{-3} M.

Quantum yield determination

The quantum yields were obtained with an apparatus consisting of a HBO 200 lamp, Bausch & Lomb high intensity monochromator. The light intensity was measured by a unit described by Amrein *et al.*[13] and was calibrated by ferrioxalate actinometry.[14] The photochemical conversions were monitored by HPLC. Table 2 lists the quantum yields by extrapolation to zero conversion.

It is noticeable that with the compounds studied in this work the quantum yields of the exo-compounds exceed those of the endo-. Triplet decay to the ground state seems to be more efficient with the endo-compounds. Intersystem crossing from singlet excited exo- and endo-**4b** is moderately efficient, since the photoproducts are formed in the direct irradiations with a reduction of the quantum yields to about a third of the sensitized irradiations.

The quantum yields listed in Table 2 compare rather well with those obtained with carbomethoxy substituted benzobarrelenes,[7] but care has to be taken, since different sensitizers with different triplet energies were used (*vide infra*).

To gain information on the triplet energies of the photoreactive states exo- and endo-**4a** and -**4b** Herkstroeter–Hammond plots[15] of the quantum yields *vs* sensitizer energies were drawn (Fig. 1). As can be seen an increase in the quantum yields up to *ca* 80 kcal/mol was observed in all cases. These results imply that E_T of all compounds is larger than 75 kcal/mol, and most probably, the triplet excitation energies are localized in

Table 2. Quantum yields

	dir.[a]	sens.[b] [c]
exo-4a	-	0.37
		0.41
endo-4a	-	0.09
		0.10
exo-4b	0.031	0.090
	0.03	0.090
endo-4b	0.018	0.069
	0.017	0.069

a) λ irradiation was 250 nm, b) acetone was used as sensitizer, c) λ irradiation was 316 nm.

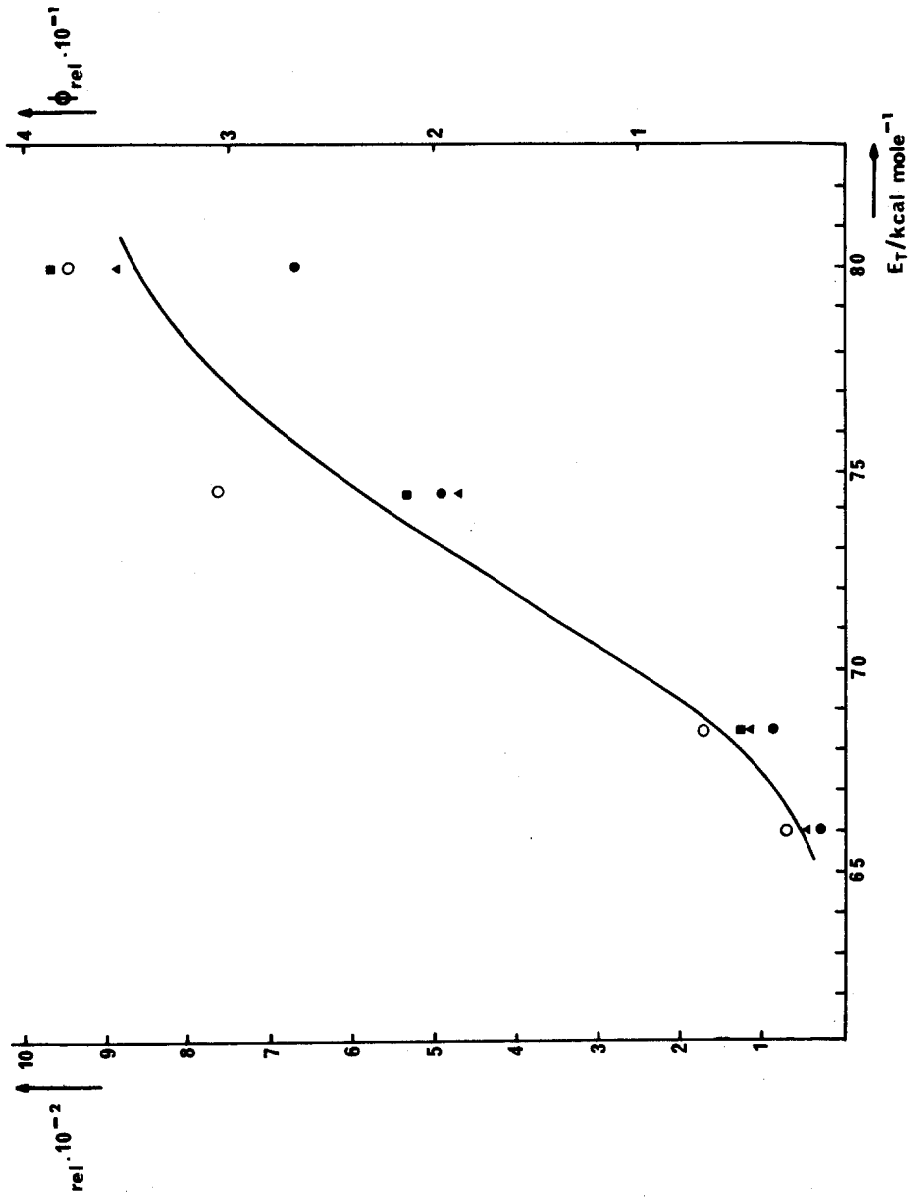


Fig. 1. Herkstroeter-Hammond plots for: (a) exo-**4a** ■; (b) endo-**4a** ○, (c) endo-**4b** ●, (d) exo-**4b** ▲. Left scale for b, c and d; right scale for a.

the benzene chromophore. The excellent correspondence of the plots of exo- and endo-**4a** and -**4b** confirms the assumption that in all cases the same photoreactive triplet state was involved.

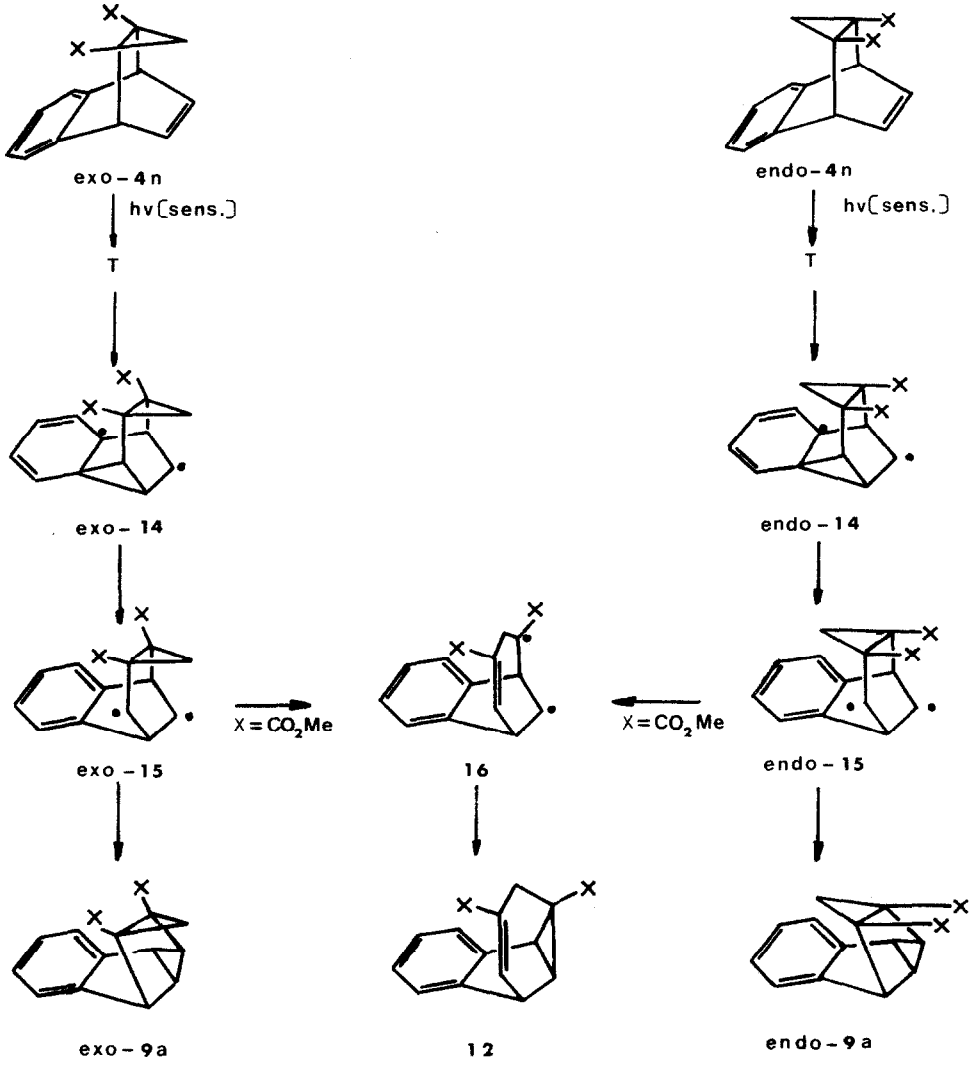
DISCUSSION

Reaction path of the photorearrangement

Irradiations of endo- and exo-**4a** only afford a di-π-methane rearrangement. The mechanism of this rearrangement was studied in an impressive systematic way by Zimmerman.[16] Barrelene-type compounds were found to rearrange via their triplet excited states and a cyclopropyl-dicarbinyl diradical was shown to be a possible intermediate by independent generation. Schaffner demonstrated that in di-π-methane rearrangement of benzoylnaphthobarrelene two ground state triplet diradical intermediates intervene consecutively.[17] Consequently, it seems reasonable to assume that a cyclopropyldicarbinyl diradical is also formed in the excited triplet state from exo- and endo-**4a**. Bond dissociation leads to the back-formation of the aromatic system and to the formation of a new triplet diradical. The bond dissociation step **14**→**15** should get assistance by radical stabilization. The orbital on the radical centre of exo-**14** is oriented to allow maximum overlap with the Walsh π-orbitals of the cyclopropyl ring.

The same orbital in endo-**14** is twisted about 90°. Accordingly, the stabilization of the radical centre is greater in exo-**14**, than in endo-**14**. These differences in radical stabilization[18] might be the reason for the lower quantum yields of the endo-compounds, if it is assumed that partitioning between the pathways **14**→**15** or return to starting material is the determining factor of the reaction efficiency (Scheme 7).

The triplet diradicals will either proceed to the di-π-methane photoproduct, if X = H or will undergo a cyclopropylcarbinyl-homoallyl rearrangement, if X = CO_2Me, and form a diradical **16**, in which one radical centre is stabilized by a carbomethoxy group. The driving force for the conversion from **15** to **16** will derive from the removal of the diester strain energy. Further the cyclopropyl bond C(2)–C(4) is predicted to be weak on the basis of ground state electronic arguments, since electron withdrawing groups weaken the adjacent cyclopropyl bond.[19] In the case the photorearrangement proceeds along the proposed pathway, it can simply be explained that either exo- or endo-**15** forms the same diradical **16** and, ultimately, the same photoproduct **12**.



Scheme 7.

Other mechanisms can be formulated. A photoinduced bond dissociation of C(2)–C(4) in exo- and endo-**4b** is very unlikely, since no exo-/endo-isomerization could be observed. Cyclopropyl–vinyl- or cyclopropyl–aryl-bridging as the primary photochemical steps seem to be unprobable. Exo- and endo-**4b** form the same photoproduct and high energetic intermediates would have to be passed along the reaction coordinate with endo-**4b**. A strong argument for the reaction pathway proposed is that the same photoreactive electronic state for the rearrangement of exo- and endo-**4a** and -**4b** gives rise to the same primary photochemical step. The total missing of a di-π-methane rearrangement product in the photoisomerization of exo- and endo-**4b** can be explained by the interference of the cyclopropyl ring in a later step along the reaction coordinate.

EXPERIMENTAL

Proton NMR-spectra were determined on a Varian T-60-D, Bruker WP 80, 1 FX-90 and ^{13}C NMR on a Bruker WP 80 and WM 250. Mass-spectra were obtained using a Varian MAT-CH-5. UV-spectra were recorded on a Varian Cary 17, IR-spectra on Perkin–Elmer 257 and 325.

Preparative irradiations were performed in a Rayonet-Photochemical Reactor, RPC 100 of the Southern New England Ultraviolet Co. equipped with RPR 2537 or RPR 3000 lamps respectively.

Analytical and semipreparative separations were performed with HPLC apparatus consisting of a Waters M6000 pump, Waters UK 6 injector and LDC UV III detector at 254 nm. Peak height and peak area determinations were performed with LDC 308 computing integrator.

Silica gel used for column chromatography was Merck, Kieselgel 60, <0.063 and 0.063–0.200 mm. Column chromatography was performed using quartz columns. 2% fluorescence indicator F_{254}, Merck, were mixed with the packing, thus allowing the bands to be monitored by a UV-fluorescence lamp.

Acetone used for photolysis was purified by refluxing over $CaCl_2$ and distillation through a Vigreux column. The photolysis solns were purged prior and during photolysis using vanadous-purified N_2 to remove O_2.[20]

Endo- and exo-1, 4 - *cyclopropano* - 1, 4 - *dihydro* - *naphthalene* (**4a**)

Benzobarrelene[21] (2 g) was dissolved in 100 cm^3 dry ether. 0.2 g $(CuCl)_2$ was added and the mixture was stirred and cooled in an icebath. CH_2N_2 was transfered by a N_2 stream into the reaction flask. CH_2N_2 was prepared from N-nitroso-N-methylurea by repeated addition of KOH 6 times 1 g in 10 min intervals. After completion of the addition the reaction mixture was stirred and purged another 45 min. Filtration of the catalyst and distillation of the ether give 2.1 g of a yellow oil. To remove polymeric byproducts the oil was filtered through a 2 cm layer of silica gel using n-hexane as solvent. The semipreparative separation was conducted with HPLC, using two columns 28 cm × 7.6 mm i.d., packed with Li Chrosorb Si 100, 10 μm. n-Hexane, dried and purified over H_2SO_4, was used as mobile phase; flow rate 6 $cm^3 \cdot min^{-1}$, RI-detector.

Peak 1, endo, endo - 9, 10 - benzotetracyclo[3.3.2.0^{2,4}.0^{6,8}]dec - 9 - ene; retention time 8.5 min, 3% yield. m.p. 132–133° (131–132° lit[6]). Peak 2, exo, endo - 9, 10 - benzotetracyclo[3.3.2.0^{2,4}.0^{6,8}]dec - 9 - ene; retention time 10 min; 4% yield. m.p. 91.5–92.5° (92–93° lit[6]). Peak 3, endo - 6, 7 - benzotricyclo[3.2.2.0^{2,4}]nona - 6, 8 - diene (**4a**); retention time 11.5 min; yield 15%; m.p. 25° (43° lit[6]). Peak 4, exo - 6, 7 - benzotricyclo[3.2.2.0^{2,4}]nona - 6, 8 - diene **4a**, retention time 12.5 min; yield 25%; m.p. 48–49° (47–48.5° lit[6]). Peak 5, benzobarrelene; retention time 22.5 min; 20% recovery.

Exo - 7, 8 - *benzotetracyclo* [4.3.0.0^{2,9}.0^{3,5}]*non* - 7 - *ene* (**9a**) *from benzobarrelene*

Benzobarrelene (1.1 g) was reacted with CH_2N_2 and $(CuCl)_2$ as described above. 15 g N - nitroso - N - methylurea were used. After removal of the ether by distillation, the oil was distilled in a microdistillation apparatus to yield 1.1 g exo-**9a** (92%). No endo-**9a** could be detected using analytical HPLC.

Dimethyl exo - 8, 9 - *benzotricyclo*[5.2.2.0^{2,6}]3, 4 - *diazaundeca* - 3, 8, 10 - *trien* - 2, 6 - *dicarboxylate* (**8**)

Dicarbomethoxybenzobarrelene (8 g) **7**[22] were disolved in 200 cm^3 of an ether soln of diazomethane and stirred at 0°. After 3 h acetic acid was added dropwise until the soln was colorless. The solution was concentrated to 100 cm^3 and the crystals which had deposited were filtered. 5 g (55%) pure exo-**8** were obtained. The mother liquor, which contained endo-**8** was collected for preparation of endo-**6b**; m.p. 110–111°; Calc. C, 65.37; H, 5.16. Found C, 65.29; H, 5.05%. MS: no M^+ peak; 252 = M^+-N_2HCO_2R. UV {cyclohexane, λ_{max} (ϵ_{max})}: 320 (250), 269 (291), 262 (374), 258 (426). IR (CCl_4): 2995, 2945, 1720, 1580, 1430, 1235, 1070 cm^{-1}. ^1H NMR (90 MHz/$CDCl_3$): δ (ppm) 3.40 (s, CH_3O–, 3H); 3.55 (s, CH_3O–, 3H); 4.12 (m, H-bridgehead, 1H); 4.41-5.07 AB-system, CH_2, 2H); 5.00 (m, H-bridgehead, 1H); 5.98 (m, H-vinyl, 2H); 7.06–7.58 (m, H-arom, 4H). ^{13}C NMR ($CDCl_3$, off-resonance decoupled): δ (ppm) 45.49 (d, CH-bridgehead); 48.53 (d, CH-bridgehead); 52.02 and 52.22 (q, CH_3O–); 60.50 and 108.09 (s, C-pyrazoline ring); 85.16 (t, CH_2-pyrazoline ring); 123.41, 125.48, 125.74, 126.12 (d, C-arom.) 138.48 and 141.33 (s, C-arom.); 133.05 and 136.61 (d, C-vinyl); 166.89 and 170.77 (s, CO_2R).

Dimethyl exo - 6, 7 - *benzotricyclo*[3.2.2.0^{2,4}]*nona* - 6, 8 - *dien* - 2, 4 - *dicarboxylate* (*exo*-**4b**)

Exo-**8** (1.5 g) was dissolved in 1 l acetone and irradiated with stirring in a Pyrex vessel at 300 nm. The solution was cooled with tap-water and purged with oxygen free N_2. The solutions of five identical runs were combined and the solvent removed by distillation *in vacuo*. The residual oil was filtered through a layer of silica gel using benzene as solvent. After distillation of the solvent the product was recrystallized from methanol. 5.5 g (80.5%) yield; m.p. 127–128°; Calc. C, 71.82; H, 5.67; Found C, 71.84; H, 5.75%. MS: M^+ 284. IR (CCl_4): 2995, 2950, 1725, 1470, 1455, 1435, 1340, 1310, 1250, 1155, 1140, 1105 cm^{-1}. ^1H NMR ($CDCl_3$, 90 MHz): δ (ppm) 1.73–2.17 (AB-system, CH_2-cyclopropyl, 2H); 3.56 (s, CH_3O–, 6H); 4.32 (m, H-bridgehead, 2H); 6.34 (m, H-vinyl, 2H) and 6.99–7.37 (AA'BB', H-arom., 4H). ^{13}C NMR: ($CDCl_3$. off-resonance decoupled): δ (ppm) 24.46 (t, CH_2), 39.67 (s, C-cyclopropane), 43.42 (d, CH-bridgehead); 51.83 (q, CH_3O), 124.38, 124.51, (d, CH-arom.), 133.44 (d, CH-vinyl), 144.44 (s, C-arom.) and 170.77 (s, C=O).

Dimethyl endo - 6, 7 - *benzotricyclo*[3.2.2.0^{2,4}]*nona* - 6, 8 - *dien* - 2, 4 - *dicarboxylate* (*endo*-**4b**)

The mother liquor obtained in the preparation of **8** was concentrated and the residue dissolved in benzene. The soln was filtered through a layer of silica (5 cm; 2.5 cm i.d.) to remove polymers. The benzene was removed by distillation *in vacuo* and the residue dissolved in 1 l. acetone and irradiated through Pyrex at 300 nm under oxygen-free N_2 with stirring. Three identical runs were combined and the acetone removed. The residue was dissolved in boiling CH_3OH. After cooling, 1.1 g exo-**4b** crystallized and was filtered off. The residue was separated by semipreparative HPLC: column, C18, 10 μm; 28 cm, 7.6 mm i.d.); mobile phase: CH_3OH/H_2O = 70:30, flow rate: 7 ml min^{-1}; detection: RI; Peak 1: exo-**8**, retention time 2.1 min., Peak 2, exo-**4b**, retention time 3.1 min, Peak 3, endo-**4b** retention time 3.9 min. Fraction 3 was collected and recrystallized from CH_3OH; m.p. 67.5–68.5°, Calc. C, 71.82, H, 5.67; Found: C, 71.72, H, 5.60%. MS: M^+ 284; IR (CCl_4): 2930, 1730, 1440, 1360, 1330, 1310, 1255, 1215, 1150, 1130, 1110, 700 cm^{-1}. ^1H NMR (60 MHz. CCl_4) δ (ppm) 0.3 (d, CH_2, H_{endo}, 1H, $J_{exo,endo}$ = 10 Hz); 1.8 (d, CH_{exo}, 1H, ($J_{exo,endo}$ = 10 Hz); 3.6 (s, CH_3O, 6H); 4.3 (m, H-bridgehead, 2H); 6.8 (m, H-vinyl, 2H); 7.0 (s, H-arom., 4H).

Sensitized photorearrangement of exo - 1, 4 - *cyclopropano* - 1, 4 - *dihydronaphthalene* (*exo*-**4a**)

Exo-**4a** (2 g) was dissolved in 900 cm^3 acetone and irradiated for 6 h at 300 nm in a quartz apparatus with stirring under N_2. The solvent was removed by distillation *in vacuo* and the residue dissolved in petrol ether (60–80°). The reaction mixture was

chromatographed on silica, 60 × 4 cm with petrol ether as mobile phase. The photoproduct, exo - 7, 8 - benzotetracyclo[4.3.0.0^{2,9}.0^{3,5}]non - 7 - ene (exo-**9a**) was eluted first. After removal of the solvent by distillation *in vacuo*, a colorless oil was obtained, which was purified further by microdistillation, to yield 1.1 g, n_D^{20} = 1.5820; Calc. C, 92.81, H, 7.19; Found C, 92.75, H, 7.22%. MS: M^+ 168; UV: {cyclohexane, λ_{max} (ϵ_{max})}: 282 (1400); 274 (1330), 267 (1040). IR (CCl_4): 3065, 3020, 2930, 1475, 1455, 1330, 1025, 1010, 690, 635, 610, 530 cm^{-1}. ^{1}H NMR (60 MHz, CCl_4): δ (ppm) 0.22 and 0.20 (2t, H(4)-exo, H(4)-endo, 2H, J = 5.0 Hz, J = 5.7 Hz; $J_{exo,endo}$ = 0); 0.9 and 1.15 (2q, H(3) and H(5), 2H, J = 5.7 Hz and 5.0 Hz, and $J_{2,9}$ and $J_{5,8}$ = 0); 1.75–2.2 (m, H(1), H(2) and H(9), 34); 3.5 (d, H(6), 1H, $J_{6,8}$ = 4 Hz). ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm) 6.60 (t, J = 160 Hz, CH_2-cyclopropane); 13.89 (d, 170 Hz, CH-cyclopropane); 26.06 (d, 170 Hz, CH-cyclopropane); 29.47 (d, 175 Hz, CH-cyclopropane; 33.31 (d, 165 Hz, CH-cyclopropane); 38.48 (d, 165 Hz, CH-cyclopropane); 50.69 (d, 140 Hz, C(6)-bridgehead); 121.53 (d, 155 Hz); 124.50 (d, 155 Hz); 125.54 (d, 160 Hz); 126.10 (d, 160 Hz), all CH-arom.; 141.79 and 153.28 (s, C-arom).

*Sensitized photorearrangement of endo - 1, 4 - cyclopropano - 1, 4 - dihydronaphthalene (endo-**4a**)*

Endo-**4a** (170 mg) was dissolved in 150 cm^3 acetone and irradiated 65 min in a quartz apparatus at 300 nm under stirring and N_2. The solvent was removed by distillation *in vacuo* and the residue separated by HPLC. Column: 2 × silica (LiChrosorb Si 100, 10 μm, Merck), 28 cm × 7.6 mm i.d. each; solvent n-hexane, flow rate 5 cm^3 min^{-1}; detector: RI. Three components could be isolated with the retention times 1.2, 2.3 and 4.3 min.

Fraction 1 was collected. After removal of the solvent by distillation *in vacuo* the residue was distilled with a microdistillation apparatus giving 70 mg endo - 7, 8 - benzo - tetracyclo[4.3.0.0^{2,9}0.^{3,5}]non - 7 - ene, n_D^{20} = 1.5872; Calc. C, 92.81, H, 7.19; Found C, 92.95, H, 7.18%. MS: M^+ = 168, UV {cyclohexane, λ_{max} (ϵ_{max})}: 270 shoulder (850); 276 (1169), 284 (1146). IR (CCl_4): 3020, 2955, 1470, 1460, 1095, 1040, 890, 865 cm^{-1}. ^{1}H NMR ($CDCl_3$, 270 MHz): δ (ppm) 0.19–0.31 (m, H_4 exo and endo, 2H); 1.74–1.89 (m, H(2) and H(3), 2H); 1.98–2.07 (t, H(9), 1H); 2.07–2.13 (t, H(5), 1H); 3.52–3.58 (m, H(1), 1H); 3.67–3.72 (t, H(6), 1H) and 6.72–7.11 (m, H-arom., 4H); $J_{3,5}$ = $J_{5,6}$ = 3 Hz, $J_{1,9}$ = $J_{2,9}$ = 3 Hz, $J_{1,6}$ = 2.2 Hz, $J_{1,2}$ = 2.2 Hz; spin-decoupling experiments revealed that irradiation at δ = 0.19–0.31 ppm leads to a decoupling of H(3) and irradiation at δ = 1.98–2.13 to a decoupling of H(1) and H(6). ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm, $J_{^{13}C-H}$ Hz) 18.18 (t, 160, CH_2-cyclopropane); 27.89 (d, 160); 34.49 (d, 160); 35.00 (d, 160); 37.98 (d, 170); 57.33 (d, 175, CH-cyclopropane); 49.05 (d, 135, CH-bridgehead); 121.59 (d, 155) 122.82 (d, 155); 2 times 125.34 (d, 160) all CH-arom; 142.77 and 148.75 (s), C-arom.

*Preparation of 7, 8 - benzotricyclo[4.3.0.0^{2,9}]nona - 3, 7 - diene (**11**)*

Endo-**4a** (140 mg) was dissolved in 150 cm^3 acetone and irradiated as described above. The irradiation time was extended to 140 min. The solvent was removed *in vacuo* and the residue chromatographed as described above. The third peak was collected. After removal of the solvent **11** was recrystallized from pentane with cooling. 45 mg pure product was obtained; m.p. 33–34°; Calc. C, 92.81, H, 7.19; Found C, 92.88, H, 7.10%. MS: M^+ 168, UV {cyclohexane, λ_{max} (ϵ_{max})}: 266 shoulder (800), 273 (1130), 280 (1125). IR (CCl_4): 3040, 2920, 2850, 1640, 1485, 1465, 1440, 1350, 1340, 1285, 1180, 1140, 1028, 942, 910 cm^{-1}. ^{1}H NMR (90 MHz, $CDCl_3$): δ (ppm) 1.4–1.6 (m, H(2), 1H); 1.8–2.05 (m, H(5)-endo, 1H); 2.05–2.88 (m, H(1)-cyclopropane, 1H); 2.45–2.77 (m, H(5)-exo and H(9), 2H); 3.38–3.55 (m, H(6), 1H); 5.33–5.66 (m, H(3) and H(4), 2H); 6.8–7.2 (m, H-arom, 4H); decoupling experiments revealed, which H-atoms coupled, but coupling constants could not be evaluated. Irradiation at H(6) led to decoupling of H(1) and H(5)-exo: at H(5)-exo to decoupling of H(6), H(3) and H(4); at H(3) and H(4) of H(2); at H(5)-endo of H(3) and H(4); at H(9) to a decoupling of H(2).

*Acetone sensitized photorearrangement of dimethyl exo - 1, 4 - cyclopropano - 1, 4 - dihydronaphthalene - 9, 10 - dicarboxylate (exo-**4b**)*

Exo-**4b** (1.5 g) was dissolved in 1 l. acetone and irradiated 2.5 h through Pyrex at 300 nm. The reaction mixture was stirred and purged with N_2. Five runs were combined and the solvent was removed *in vacuo*. The residue was crystallized from methanol and 3.15 g (42%) starting material recovered. The mother liquor was concentrated and separated by HPLC. Column: C-18, 28 cm × 7.6 cm i.d., 10 μm; methanol/H_2O = 7:3 was used as mobile phase: RI. Peak 1, retention time 3.4 min, exo-**4b**; peak 2, retention time 5.0 min, dimethyl 7, 8 - benzotricyclo[4.3.0.0^{2,9}]nona - 4, 7 - diene - 2, 4 - dicarboxylate (**12**). Fraction 2 was collected and **12** was isolated by extraction with benzene to yield 1.15 g (15%) after recrystallisation from methanol; m.p. 110.5–111°; Calc. C, 71.82, H, 5.67; Found C, 71.86, H, 5.76%. MS: M^+ 284; UV {(cyclohexane, λ_{max} (ϵ_{max})}: 271 (1096), 278 (996). IR (CCl_4): 2930, 1720, 1645, 1440, 1290, 1250, 1215, 1120, 1100, 1090 cm^{-1}, ^{1}H NMR ($CDCl_3$, 80 MHz): δ (ppm) 1.03 (d, d(3)-endo, 1H, $J_{3,gem}$ = 18 Hz); 2.74 (t, H(1)-cyclopropane, 1H, $J_{1,6}$ = 6.6 Hz, $J_{1,9}$ = 6.6 Hz); 3.29 (d, H(9), 1H, $J_{1,9}$ = 6.6 Hz); 3.72 (s, CH_3O–, 6H) 3.81 (d, H(3)-exo, 1H, $J_{3,gem}$ = 18 Hz); 4.40 (d,d H(6), 1H, $J_{5,6}$ = 7.8 Hz, $J_{1,6}$ = 6.6 Hz); 6.85–7.3 (m, H-arom, 4H); 7.45 (d, d, H(5), $J_{5,6}$ = 7.8 Hz, $J_{3\text{-endo},5}$ = 3.5 Hz). ^{13}C NMR data are given in Table 1.

Photolysis equipment and procedure for quantum yield determination

Quantum yield irradiations were performed using a microbench apparatus similar to that described by Zimmerman.[23] Light from an Osram HBO 200 W high pressure mercury lamp was passed through a Bausch and Lomb Model 33-86-75 high intensity monochromator, entrance slit 5.4 mm and exit slit 3.0 mm, giving a band pass of 20 nm at half peak height (wavelength setting given below). Samples were irradiated in 1 cm quartz cells in an electronic actinometer[13] calibrated by ferrioxalate actinometry.[14] Solutions used cyclohexane, benzene or acetone as solvent and were degassed 15 min prior to and during photolysis using deoxygenated nitrogen. After irradiations of the solutions an aliquot of a solution with a standard was added. Analysis was performed with HPLC. All runs were to a conversion of less than 3% and may be taken to be kinetic. All quantum yields were determined by two independent runs.

Summary of quantum yield determinations

The results are listed in the order: photoadduct, concentration mole/l., λ-irradiation nm, irradiation time min, solvent, internal standard, quantum yields. *exo*-**4a**, 1.15×10^{-2}, 316, 8, acetone, 1, 2, 3, 4 - tetrachlorobenzene, $\Phi = 3.7 \times 10^{-1}/4.1 \times 10^{-1}$. *endo*-**4a**, 1.10×10^{-2}, 316, 8, acetone, 1, 2, 3, 4 - tetrachlorobenzene, $\Phi = 9.0 \times 10^{-2}/10.10^{-2}$. *exo*-**4b**, 9.9×10^{-3}, 316, 10, acetone, 1, 2, 3-trichlorobenzene, $\Phi = 9.0 \times 10^{-2}/9.0 \times 10^{-2}$. *exo*-**4b**, 5.72×10^{-3}, 251, 40, cyclohexane, diphenyl, $\Phi = 3.1 \times 10^{-2}/3.0 \times 10^{-2}$. *endo*-**4b**, 6.05×10^{-3}, 316, 10, acetone *trans*-stilbene, $\Phi = 6.9 \times 10^{-2}/6.3 \times 10^{-2}$. *endo*-**4b**, 7.29×10^{-3}, 251, 30, cyclohexane, *trans*-stilbene, $\Phi = 1.8 \times 10^{-2}/1.7 \times 10^{-2}$.

The conditions for the photolysis using sensitizer of different triplet energy were the following: propiophenone (8.02×10^{-3} M), E_T = 74.6 kcal/mol;[26] triphenylene (9.58 M), E_T = 66.5 kcal/mol[24] The sensitizers were dissolved in benzene and all concentrations were adjusted that the sensitizer adsorbed more than 99% of the incident light. The quantum yields were determined relative to those found in the acetone-sensitized runs and are given in Table 3.

Quench experiments

Five solutions of exo-**4b** (9.30×10^{-3} M) in cyclohexane in presence of differing concentrations of trans-piperylene were irradiated at 254 nm. The quantum yields were determined as described above using trans-stilbene as internal standard for HPLC-analysis. Quantum yields Φ were determined relatively to an unquenched sample Φ_0. The data are listed in the order: trans-piperylene concentration, Φ_0/Φ; (1) 1.84×10^{-3}, 1.52; (2) 2.76×10^{-3}, 1.75; (3) 3.68×10^{-3}, 1.96; (4) 4.60×10^{-3}, 2.54.

Table 3. Quantum yields for sensitized irradiations using sensitizer of different triplet energy

educt	acetone	proprio-phenone	benzo-phenone	triphenylene
exo-4a (8.56×10^{-3})	0.39	0.22	0.05	-
endo-4a (1.07×10^{-2})	0.095	0.079	0.018	0.0076
exo-4b (8.82×10^{-3})	0.090	0.047	0.012	0.0049
endo-4b (1.05×10^{-2})	0.066	0.0497	0.0061	0.0042

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