The Di-π-methane Photorearrangement of 2,3-Disubstituted Benzobarrelenes and Benzonorbornadiene − Substituent Effects in Regioselectivity

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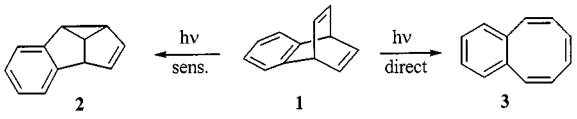
2,3-Disubstituted benzobarrelene and benzonorbornadiene derivatives **16**, **17**, and **18**, containing electron-withdrawing and electron-donating substituents, have been synthesized and subjected to triplet-sensitized photoisomerization. Methyl 3-methyl-2-benzobarrelenecarboxylate (**16**) gave two di-π-methane rearrangement products. However, methyl 3-cyano-2-benzobarrelenecarboxylate (**17**) underwent an intramolecular $[2_\pi + 2_\pi]$ cycloaddition reaction, whilst methyl 3-cyano-2-benzonorbornadienecarboxylate (**18**) formed dimer **40**. The formation of these products is discussed in terms of the radical stabilizing effect of the substituents and the destabilizing effect on the formation of cyclopropane ring.

Introduction

Benzobarrelene (**1**) is a molecule of considerable potential mechanistic interest. Zimmerman et al.[1−5] have reported that benzobarrelene undergoes two types of photochemical rearrangements to the corresponding semibullvalenes **2** and/or cyclooctatetraenes **3**, depending upon the reaction conditions (Scheme 1). The semibullvalenes are known to arise from the triplet excited state through a di-π-methane rearrangement, whereas cyclooctatetraene derivatives originate from the singlet excited state by a $[2_\pi + 2_\pi]$ cycloaddition. Zimmerman et al.[1−5] have shown that vinyl−vinyl bridging is the main pathway in the photorearrangement of benzobarrelenes.



Scheme 1

Introduction of a substituent on the vinylene group destroys the symmetry of the benzobarrelene skeleton, increasing the number of possible initial bonding modes to six different di-π-methane rearrangements. Nevertheless, the reaction generally shows great site- and regioselectivity, especially for polar substituents. The effect of one or two substituents on the bridging and the regioselectivity of the di-π-methane rearrangement has been intensively investigated by Bender et al.,[6−8] Paquette et al.,[9] Hemmetsberger et al.[10] and George et al.[11] For example, the sensitized di-π-methane rearrangement of cyanobenzobarrelene **4** furnishes only benzosemibullvalene **6**.[7,12,13] Mechanistic studies have revealed that this reaction proceeds through vinyl−cyanovinyl bridging between the less substituted carbon atoms (Scheme 2). This observed regioselectivity has been explained on the basis of favorable stabilization of the diradical intermediate **5** by the cyano group. However, destabilization of the intermediate **7** by the substituents has not been considered. It is well known that a cyano group on a cyclopropane ring lengthens the C1−C3 and C1−C2 vicinal bonds, which will result in the destabilizing of the formed intermediate **7** (Scheme 2).[14−17] This prediction has been confirmed by experiments. X-ray crystallographic data for cyclopropanes with electron-withdrawing substituents indicate the generality of this effect.[18,19]

To support this hypothesis, we have recently synthesized the disubstituted benzobarrelene derivatives **8** and **9** and studied their photochemical behavior (Scheme 3).[20] In spite of the relatively equal radical stabilizing effects[21] of cyano and methyl groups, we observed products **12** and **13**, arising from vinyl−cyano(aldehyde)−vinyl bridging **10** and **11**. The diradical intermediates **14** and **15** were not formed. We assumed that the electron-withdrawing cyano and aldehyde groups destabilize the adjacent bonds in the intermediates, such as **14** and **15**, and prevent their formation.

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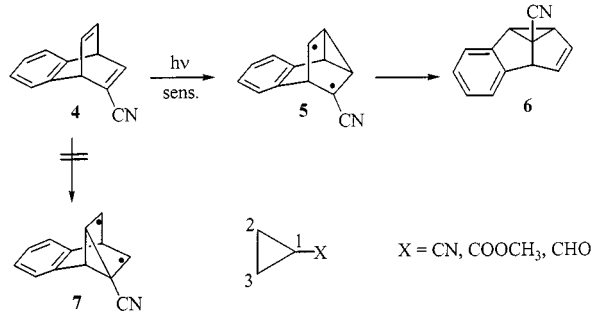
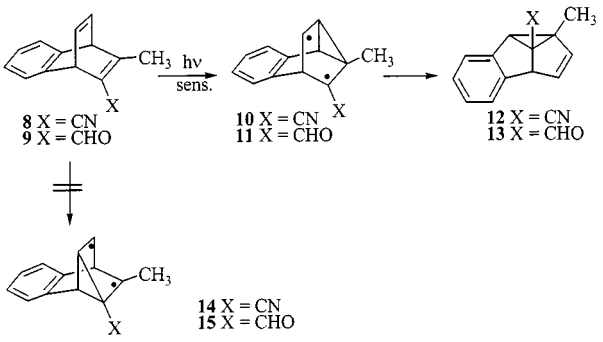
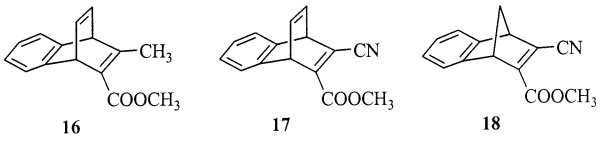


Scheme 2



Scheme 3

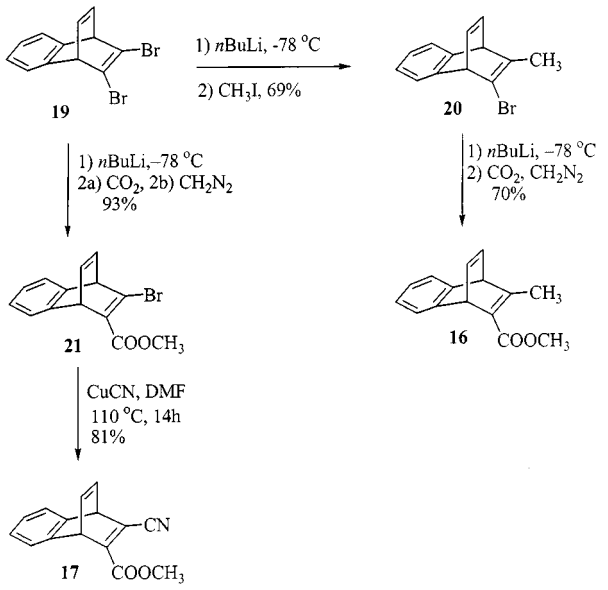
In this paper we describe further experiments, which support the view that the radical-stabilizing effect of the substituent is not the sole effect that determines the mode of the di-π-methane rearrangements. For that reason, we synthesized further disubstituted benzobarrelenes **16** and **17** and benzonorbornadiene derivative **18** and studied their photochemical behavior.



Result and Discussion

Synthesis of the Starting Materials

The key compound for the synthesis of the other disubstituted benzobarrelene derivatives was 2,3-dibromobenzobarrelene (**19**).[22,23] Monolithium/halide exchange between 2,3-dibromobenzobarrelene (**19**) and *n*BuLi produces 2-bromo-3-lithiobenzobarrelene (Scheme 4). Trapping of this organolithium compound with MeI afforded the corresponding bromomethylbenzobarrelene (**20**).[23] A second lithium/halide exchange with bromide **20** followed by carboxylation afforded the corresponding acid, which gave methyl 3-methyl-2-benzobarrelenecarboxylate (**16**) upon esterification.[20]



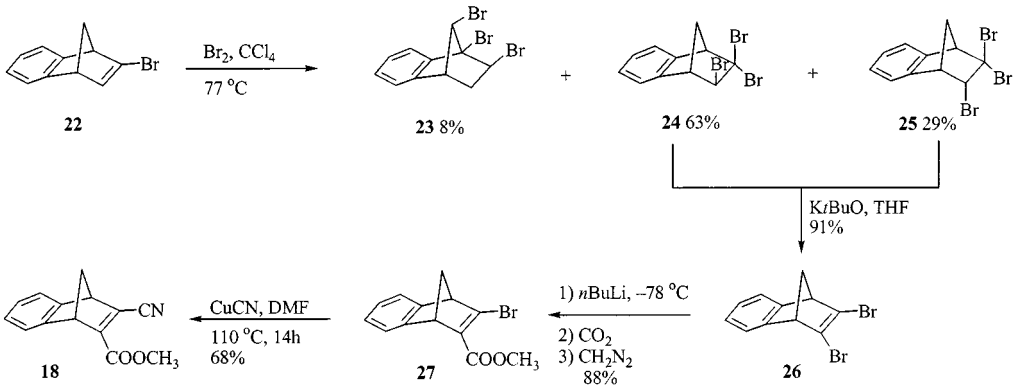
Scheme 4

The second target compound **17** was synthesized by successive replacement of bromine atoms in 2,3-dibromobenzobarrelene (**19**). Firstly, bromine atom was replaced by methoxycarbonyl group to give the bromo ester **21**, which was allowed to react with cuprous cyanide in dimethylformamide under reflux for 14 h. The substitution product **17** was isolated in 81% yield (Scheme 4).

For the synthesis of the last molecule **18** we designed a synthetic approach similar to that used in the case of the synthesis of the benzobarrelene derivatives **16** and **17**. For that reason, we at first prepared the corresponding starting material, 2,3-dibromobenzonorbornadiene (**26**), by addition of bromine to **22**[24] at 77 °C followed by dehydrobromination. However, the addition of bromine to the carbon−carbon double bond in **22** at room temperatures or lower resulted in the formation of rearranged tribromide **23** in quantitative yield as a result of Wagner−Meerwein rearrangement (Scheme 5).

The high-temperature bromination[25] of **22** at 77 °C in carbon tetrachloride gave a mixture consisting of three chromatographically separable tribromides **23**, **24**, and **25** in 8, 63, and 29% yields, respectively. The *exo*,*exo*,*endo* configuration of **24** and the *exo*,*endo*,*endo* configuration of **25** were assigned by analysis of C*H*Br resonances and bridgehead proton resonances. Since in **24** this C*H*Br proton resonance does not show any coupling to the neighboring bridgehead proton, it indicates an *endo* orientation of this proton (*exo* orientation of bromine). Furthermore, the *endo* orientation of the C*H*Br proton is supported by its doublet nature, reflecting long-range coupling (W or M orientation) with the *endo* bridge proton.

Dehydrobromination of **24** and **25**, or of a mixture, with 1 equiv. of potassium *tert*-butoxide gave the expected 2,3-dibromobenzonorbornadiene (**26**)[26] in 91% yield. Again,

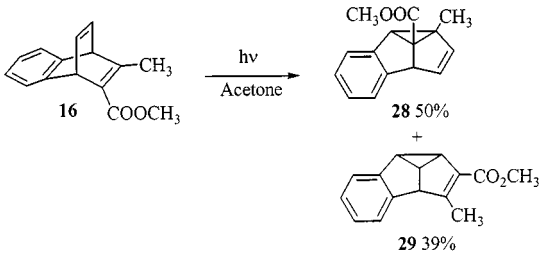


Scheme 5

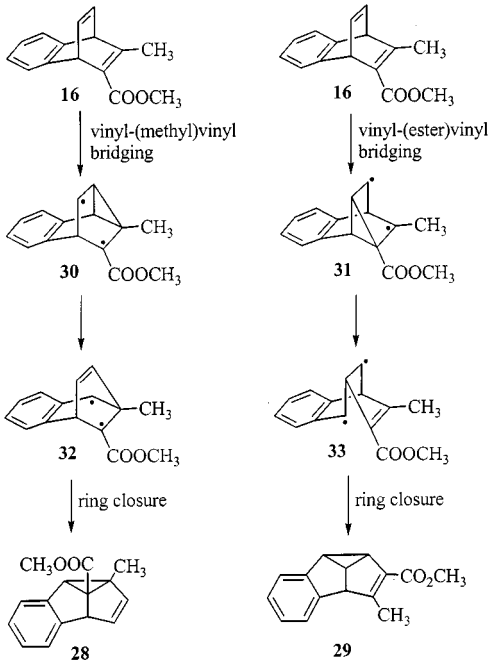
successive replacement of bromine atoms in **26**, as described for the synthesis of **17**, gave the desired compound **18** in 48% overall yield (Scheme 5).

Photochemistry of 16, 17, and 18

Our interest lays primarily in the triplet-sensitized photochemistry of **16**, **17**, and **18**. Photochemical reactions were conducted in acetone. The apparatus consisted of a 254-nm mercury arc lamp, surrounded by a water-cooled quartz immersion vessel. Irradiation of **16** gave a mixture of two photoproducts **28** and **29** in 50 and 39% yields, respectively (Scheme 6).



Scheme 6



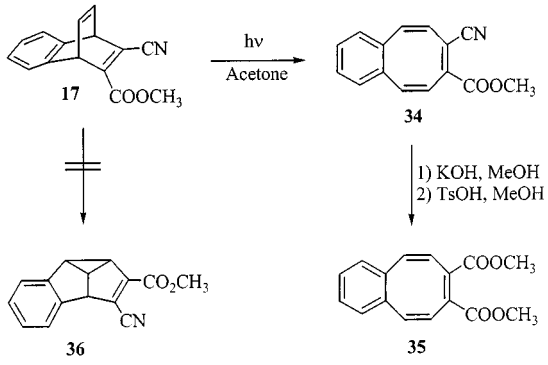
Scheme 7

The products were separated and characterized. A series of NOE experiments confirmed the exact positions of the substituents. From the structures of these isolated products we can propose that the operating mechanism involves vinyl−vinyl bridging. Unsymmetrical substitution in the starting material results in two possible vinyl−vinyl bridging modes: (i) vinyl−(methyl)vinyl bridging and (ii) vinyl−(ester)vinyl bridging, as shown in Scheme 7.

The formation of the product **28** arising from vinyl−(methyl)vinyl bridging **30** can be explained by the electron-withdrawing effect of the ester group, which can stabilize the radical. Bordwell and Lynch[21] have calculated the relative radical stabilizing effects of the ester and methyl groups and have shown that the resonance stabilization energies are of comparable size. We can therefore easily understand the formation of the second product **29**, arising from vinyl−(ester)vinyl bridging. However, if we compare these results with those obtained by photoisomerization of **8** and **9**, we notice that products with structures like that of **29,** arising from vinyl−(cyano or aldehyde)vinyl bridging, were not formed in the photoisomerization reaction of **8** and **9**. This has been attributed to the destabilization effect of the adjacent bond in cyclopropane rings **14** and **15**. Now, we may raise the question of why aldehyde and cyano groups destabilize cyclopropane formation and ester groups do not. Actually, ester groups also interact with the Walsh orbitals of the cyclopropane ring.[14−17] However, this interaction is not so effective as in the case of formyl and cyano groups. For efficient interaction between the ester group and the cyclopropane ring, a perpendicular conformation of the carbonyl group relative to the cyclopropane ring is desired, in order to achieve maximum interaction between the cyclopropane Walsh orbital and the π* orbital of the carbonyl group. We assume that the carbonyl group of an aldehyde can adopt the desired conformation much better than the carboxylate group can, due to the increased steric repulsion present between the cyclopropane ring and the

bulky −OR group. Furthermore, it has been demonstrated experimentally[16,27] and theoretically[28] that the interaction between a cyclopropane ring and an aldehyde group is much stronger than that between the cyclopropane ring and an ester group. At this stage, we assume that the destabilizing effect of cyano and formyl groups on cyclopropane ring formation is more pronounced than that of the ester group.

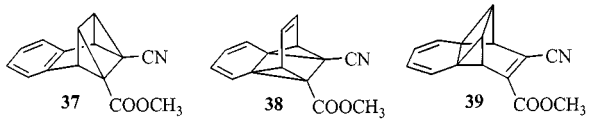
We next conducted triplet-sensitized photolysis of **17** in order to study the effects of two different polar groups on the regioselectivity. Interestingly, irradiation of **17** under analogous conditions yielded benzocyclooctatetraene derivative **34**, along with 41% of the unchanged starting material (Scheme 8).



Scheme 8

For further characterization of **34** it was converted into the symmetrical and known benzocyclooctatetraene derivative **35**.[29] Unfortunately, the expected photoproduct **36**, which should be formed by vinyl−(ester)vinyl bridging, was not observed in this case.

Generally, direct irradiation of benzobarrelene derivatives results in exclusive formation of benzocyclooctatetraene.[30,31] This transformation occurs through an excited state of benzobarrelene. However, a small amount of cyclooctatetraene was also observed upon photosensitized irradiation of benzobarrelene.[32] The photochemical behavior of **17** shows that cyclic di-π-methane systems have competing pericyclic processes available. For the formation of **34** there are three possible initial $[2_\pi+2_\pi]$ cycloadditions modes: (i) benzo−vinyl, (ii) benzo−(substituted)vinyl, and (iii) vinyl−vinyl cycloadditions. All three possible intermediates are given below.

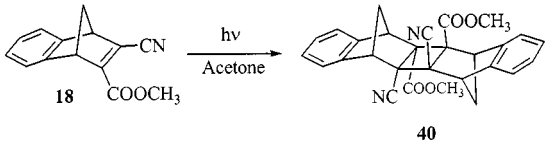


Zimmerman et al.[30] elegantly used deuterated benzobarrelene to distinguish between the possible modes; the results indicated that an initial benzo−vinyl bridging prevails. On the basis of this finding and our observations that electron-withdrawing groups such as cyano and formyl groups destabilize the formation of the cyclopropane ring, we propose that the intermediate **39** is formed initially, followed by a retrocycloaddition to give **34**.

At this stage, we cannot determine the effects of the substituents in **17** on the regioselectivity in the di-π-methane rearrangement. Furthermore, we cannot address the question of why no di-π-methane rearrangement product is observed in the photolysis of **17**. It is possible that the substituents in **17** slow the rate of intersystem crossing to such an extent that singlet chemistry plays the dominant role. It is well known that such electrocyclic processes, $[2_\pi + 2_\pi]$ cycloadditions, tend to be exceptionally rapid. There are certain systems described in the literature in which $[2_\pi+2_\pi]$ cycloaddition reactions occur even in cases of sensitized irradiation. For example, when a solution of 2,3-dicyanobarrelene in *n*-hexane containing 10% of acetone was irradiated, 1,2-dicyanocyclooctatetraene was obtained in quantitative yield.[33] However, the irradiation of 2,3-dicyanobarrelene in acetone gave a mixture of 1,2-dicyanocyclooctatetraene and di-π-methane rearrangement products. Furthermore, Klärner et al.[34] have shown that the photolysis of a dicyanobarrelene derivative substituted by norbornene units produces only the cyclooctatetraene derivative upon sensitized photolysis.

In the case of the sensitized irradiation of **17**, we assume that there is competition between the di-π-methane rearrangement and the $[2_\pi + 2_\pi]$ cycloaddition reaction, in which the latter dominates. To eliminate this competition and to force the system to undergo only di-π-methane rearrangement, we synthesized the corresponding benzonorbornadiene derivative **18** and studied its photochemical behavior. This system can undergo di-π-methane rearrangement as well as the intramolecular electrocyclic addition. In both cases, however, intermediates in which the electron-withdrawing groups (such as ester and/or cyano groups) are attached to the cyclopropane ring will be formed, which will further destabilize the formation of the cyclopropane ring.

Surprisingly, irradiation of **18** under similar reaction conditions gave the $[2_\pi + 2_\pi]$ cycloaddition product **40** in 68% yield (Scheme 9). The mass spectrum (MW = 450) indicated the formation of a dimer. The ^{1}H NMR spectrum of **40** showed broad singlets of two bridgehead protons resonating separately at δ = 3.92 and 3.80, while the bridge protons appeared as an AB system (J = 11.7 Hz) centered at δ = 2.42 and 1.96. The ^{13}C NMR spectrum of **40** showed signals of six carbon atoms in the sp^3 region and of eight carbon atoms in the sp^2 region. These spectroscopic data were in complete agreement with a symmetrical structure. The exact configuration of this dimer **40** was further confirmed by X-ray crystallographic analysis (Figure 1).



Scheme 9

The observed different behavior in the photoisomerization of benzobarrelene and benzonorbornadiene derivatives **16**, **17**, and **18** may be attributable to the stabilities of

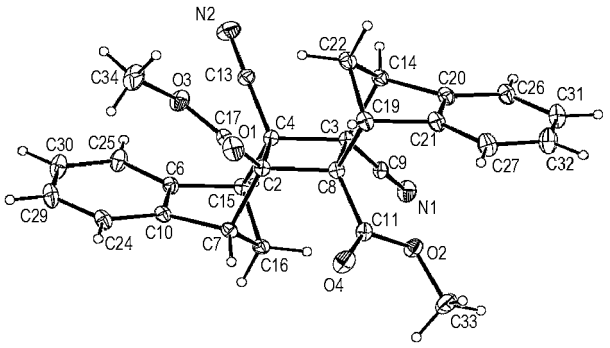


Figure 1. X-ray structure of the dimer **40**

the initially formed substituted cyclopropane derivatives. Of course, the relative stabilities of the radical intermediates also determine the mode of the di-π-methane rearrangement. However, in cases in which the system can initially form cyclopropane rings attached to the electron-withdrawing substituents, the destabilizing effect of the substituent should be taken into account in determining the mode of the di-π-methane rearrangement. Further experiments, with different substituents, to support our findings further are currently in progress.

Experimental Section

General: All solvents were dried and distilled by standard procedures. Melting points were determined by using a capillary melting point apparatus (Thomas−Hoover) and are uncorrected. IR: Perkin−Elmer 377 Infrared recording spectrophotometer. NMR: Varian Gemini 200 at 200 MHz (^{1}H). Data are reported in δ units with TMS as internal standard. All column chromatography was performed on silica gel (60 mesh, Merck). All substances reported in this paper are in their racemic forms.

Synthesis of Methyl [1*R*(*S*),8*S*(*R*)]-10-Bromotricyclo[6.2.2.0^{2,7}]dodeca-2,4,6,9,11-pentaene-9-carboxylate (21): BuLi (2 M, 3.84 mL) was added by syringe, under N_2 at −78 °C, to a magnetically stirred solution of 2,3-dibromobenzobarrelene (**19**) (2.0 g, 6.41 mmol) in tetrahydrofuran (150 mL). The reaction mixture was stirred for 2 h at the given temperature, and dry ice (CO_2) (2 g) was then added. The reaction mixture was allowed to warm to 0 °C over 1 h, and stirred at 0 °C for an additional 2 h. Tetrahydrofuran was removed under reduced pressure and water (50 mL) was added to the residue. The resulting mixture was acidified (pH = 1) with 1 M HCl, and the organic phase was extracted with ether (3 × 100 mL). The combined extract were washed with water, and dried ($MgSO_4$). Removal of the solvent and chromatography of the residue on a short silica gel column, with $CHCl_3$/acetone (5:1) as eluent, gave the corresponding acid (1.65 g, 93%, white solid, m.p. 167−168 °C). IR (neat): ṽ = 3080, 2500, 1660, 1580 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.10 (m, 1 H, 1-H), 5.70 (m, 1 H, 8-H), 6.98−6.92 (m, 4 H, olefinic and aromatic), 7.32−7.00 (m, 2 H, aromatic). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 51.1, 62.3, 123.4, 123.7, 125.0, 125.6, 138.1, 138.4, 139.8, 144.0, 145.0, 146.3, 169.5. A solution of diazomethane in ether was added at −5 °C to a solution of the carboxylic acid (1.65 g, 5.95 mmol) in dry ether (70 mL). Removal of the solvent and chromatography of the residue on a short silica gel column, with hexane/ether (9:1) as eluent, quantitatively gave ester **21** as a colorless, oily residue. IR (neat): ṽ = 3060, 2830, 1790, 1740, 1700, 1610, 1590 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.79 (s, 3 H, methyl), 5.06 (m, 1 H, 1-H), 5.54 (m, 1 H, 8-H), 7.01−6.92 (m, 4 H, olefinic and aromatic), 7.31−7.26 (m, 2 H, aromatic). ^{13}C NMR (50 MHz, $CDCl_3$) 52.4, 61.9, 123.3, 123.6, 124.9, 125.4, 138.3, 138.9, 139.7, 143.2, 144.4, 145.1, 164.7. $C_{14}H_{11}BrO_2$ (291.14): calcd. C 57.76, H 3.81; found C 57.61, H 3.75.

Methyl [1*R*(*S*),8*S*(*R*)]-10-Cyanotricyclo[6.2.2.0^{2,7}]dodeca-2,4,6,9,11-pentaene-9-carboxylate (17): Compound **21** (6 g, 20.61 mmol) and cuprous cyanide (4.45 g, 24.86 mmol) were dissolved in dry dimethylformamide (100 mL). The solution was magnetically stirred at 100−110 °C for 14 h. The reaction mixture was cooled to room temperature, benzene (750 mL) was added, and the organic phase was washed with 2 × 200 mL of $FeCl_3$ solution, 2 × 200 mL of 10% aqueous NaOH, and 2 × 200 mL of water, and dried with $CaCl_2$. The solvent was removed. After chromatography of the residue on a short silica gel column with hexane/ether (8:2) as eluent, the residue was recrystallized from chloroform/hexane (1:3) to give **17** (3.93 g, 81%, white crystals, m.p. 107−109 °C). IR (neat): ṽ = 3060, 3040, 2220, 1730, 1700, 1620, 1580 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.86 (s, 3 H, methyl), 5.17 (m, 1 H, 1-H), 5.57 (m, 1 H, 8-H), 7.06−6.94 (m, 4 H, olefinic and aromatic), 7.34−7.26 (m, 2 H, aromatic). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 50.0, 53.3, 53.5, 116.3, 124.0, 124.2, 125.5, 125.8, 131.4, 138.6, 139.4, 144.0, 143.6, 155.6, 162.9. $C_{15}H_{11}NO_2$ (237.25): calcd. C 75.94, H 4.67, N 5.90; found C 75.86, H 4.71, N 5.83.

Bromination of [1*R*(*S*),8*R*(*S*)]-9-Bromotricyclo[6.2.1.0^{2,7}]undeca-2,4,6,9-tetraene (22) at −10 °C: A solution of bromine (150 mg, 0.93 mmol) in 2 mL of chloroform was added dropwise over 2 min to a magnetically stirred solution of **22**[12] (200 mg, 0.90 mmol) in dry chloroform, cooled to −10 °C. After having been stirred for 10 min, the solution was allowed to warm to 20 °C. The solvent was removed under reduced pressure. The oily residue was crystallized from dichloromethane/hexane (1:3) to give 345 mg (100%) of rearranged tribromide **23** (m.p. 92−93 °C, colorless crystals).

[1*S*(*R*),8*R*(*S*),10*S*(*R*),11*R*(*S*)]-1,10,11-Tribromotricyclo[6.2.1.0^{2,7}]-undeca-2,4,6-triene (23): IR (neat): ṽ = 3080, 3055, 3004, 2978, 1472, 1293, 1268, 1140, 987, 910, 885, 782 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.38 (bdd, $J_{9endo,9exo}$ = 13.2, $J_{10,9endo}$ = 7.6, 9*endo*-H), 3.08 (dt, $J_{9endo,9exo}$ = 13.2, $J_{8,9exo}$ = $J_{9exo,10}$ = 4.4, 1 H, 9*exo*-H), 3.55 (d, $J_{8,9exo}$ = 4.4 Hz, 1 H, 8-H), 3.95 (bdd, $J_{10,9endo}$ = 7.6, $J_{10,9exo}$ = 4.4 Hz, 1 H, 10-H), 4.25 (m, 1 H, 11-H), 7.47−7.17 (m, 4 H, aromatic). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 40.8, 50.8, 53.4, 65.1, 70.9, 123.3, 124.1, 130.0, 131.1, 144.1, 144.8. $C_{11}H_9Br_3$ (380.90): calcd. C 34.69, H 2.38; found C 34.61, H 2.45.

Bromination of [1*R*(*S*),8*R*(*S*)]-9-Bromotricyclo[6.2.1.0^{2,7}]undeca-2,4,6,9-tetraene (22) at 77 °C: Compound **22** (200 mg, 0.90 mmol) was dissolved in carbon tetrachloride (80 mL) in a 100-mL two-necked flask, equipped with a reflux condenser and an inlet glass tube touching the bottom of the reaction flask. The inlet glass tube was connected to a 2-mL round-bottomed flask, which contained bromine (160 mg, 1.0 mmol). Bromine vapor obtained by heating of the flask to 100 °C was transferred directly to the refluxing solution of **22** in CCl_4 at 77 °C over 2 min, while stirring magnetically. After the mixture had been stirred at that reaction temperature for 2 min, the solvent was removed under reduced pressure. The oily residue was chromatographed on silica gel (90 g), eluting with hexane, and three products were obtained: **24** (217 mg, 63%), **25** (100 mg, 29%), and **23** (28 mg, 8%), in that order.

[1*S*(*R*),8*R*(*S*),10*S*(*R*)]-9,9,10-Tribromotricyclo[6.2.1.0^{2,7}]undeca-2,4,6-triene (24): Colorless liquid. IR (neat): ṽ = 3080, 3055, 3029,

3004, 2978, 1472, 1293, 1265, 1165, 1114, 987 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.25 (ddt, B part of AB system, $J_{11anti,11syn}$ = 10.4, $J_{10,11syn}$ = 2.7, $J_{1,11syn}$ = $J_{8,11syn}$ = 1.7 Hz, 1 H, 11*syn*-H), 2.77 (dt, A part of AB system, $J_{11anti,11syn}$ = 10.4, $J_{1,11anti}$ = $J_{8,11anti}$ = 1.4 Hz, 1 H, 11*anti*-H), 3.59 (dd, $J_{1,11syn}$ = 1.7, $J_{1,11anti}$ = 1.4 Hz, 1 H, 1-H), 4.14 (dd, $J_{8,11syn}$ = 1.7, $J_{8,11anti}$ = 1.4 Hz, 1 H, 8-H), 4.47 (d, $J_{10,11syn}$ = 2.7 Hz, 1 H, 10-H), 7.42−7.20 (m, 4 H, aromatic). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 48.4, 57.5, 66.5, 67.3, 71.4, 123.4, 127.0, 129.2, 130.1, 145.6, 146.4. $C_{11}H_9Br_3$ (380.90): calcd. C 34.69, H 2.38; found C 34.55, H 2.41.

[1*S*(*R*),8*R*(*S*),10*R*(*S*)]-9,9,10-Tribromotricyclo[6.2.1.0^{2,7}]undeca-2,4,6-triene (25): Colorless crystals from ether/hexane (1:3), m.p. 84−85 °C. IR (neat): ṽ = 3029, 3004, 2953, 1472, 1293, 1268, 1191, 1063, 987, 910 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.37 (dt, B part of AB system, $J_{11anti,11syn}$ = 10.4, $J_{1,11syn}$ = $J_{8,11syn}$ = 1.9 Hz, 1 H, 11*syn*-H), 2.66 (dt, A part of AB system, $J_{11anti,11syn}$ = 10.4, $J_{1,11anti}$ = 1.4 = $J_{8,11anti}$ = 1.4 Hz, 1 H, 11*anti*-H), 3.59 (ddd, $J_{1,10}$ = 3.6, $J_{1,11syn}$ = 1.9, $J_{1,11anti}$ = 1.4, Hz, 1 H, 1-H), 4.16 (dd, $J_{8,11syn}$ = 1.9, $J_{8,11anti}$ = 1.4, Hz, 1 H, 8-H), 5.33 (d, $J_{10,1}$ = 3.6, 1 H, 10-H), 7.37−7.21 (m, 4 H, aromatic), − ^{13}C NMR (APT) (50 MHz, $CDCl_3$): δ = 49.0, 54.4(−), 65.9(−), 66.5(−), 71.13, 126.4(−), 126.7(−), 128.9(−), 129.2(−),144.0, 145.25. $C_{11}H_9Br_3$ (380.90): calcd. C 34.69, H 2.38; found C 34.83, H 2.42.

Synthesis of [1*R*(*S*),8*S*(*R*)]-9,10-Dibromotricyclo[6.2.1.0^{2,7}]undeca-2,4,6,9-tetraene (26): A potassium *tert*-butoxide (680 mg, 6.04 mmol) solution in THF (10 mL) was added to a stirred solution of dibromides **24/25** (2.0 g, 5.24 mmol) in dry and freshly distilled THF (40 mL) at 0 °C. The resulting reaction mixture was stirred at room temp. for 12 h. After the solvent had been evaporated, the mixture was diluted with water and the aqueous solution was extracted with ether (3 × 50 mL), washed with water, and dried with $MgSO_4$. After removal of the solvent, the residue was filtered through a short silica gel column (5 g) eluted with hexane to give 1.43 g (91%) of dibromide **26** as the sole product. Colorless crystals from ether/hexane (1:3), m.p. 74 °C. IR (neat): ṽ = 3080, 3055, 3004, 2953, 2876, 1574, 1472, 1393, 1012, 859, 757 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.40 (dt, B part of AB system, $J_{11syn,11anti}$ = 7.4, $J_{1,11syn}$ = $J_{8,11syn}$ = 1.8 Hz, 1 H, 11*syn*-H), 2.77 (dt, A part of AB system, $J_{11syn,11anti}$ = 7.4, $J_{1,11anti}$ = $J_{8,11anti}$ = 1.6 Hz, 1 H, 11*anti*-H), 3.94 (dd, $J_{1,11syn}$ = $J_{8,11syn}$ = 1.8, $J_{1,11anti}$ = $J_{8,11anti}$ = 1.6, 2 H, 1-H and 8-H), 7.38−6.99 (AA′BB′ system, 4 H, aromatic). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 60.8. 69.2, 124.1, 127.5, 135.8, 149.85. $C_{11}H_8Br_2$ (299.99): calcd. C 44.04, H 2.69; found C 43.94, H 2.76.

Methyl [1*S*(*R*),8*R*(*S*)]-10-Bromotricyclo[6.2.1.0^{2,7}]undeca-2,4,6,9-tetraene-9-carboxylate (27): BuLi (2 M, 3.66 mL) was added by syringe under N_2 at −78 °C to a magnetically stirred solution of 2,3-dibromobenzobarrelene (**26**) (2.0 g, 6.67 mmol) in tetrahydrofuran (150 mL). The reaction mixture was stirred for 2 h at the given temperature, and dry ice (CO_2) (2 g) was then added. The reaction mixture was allowed to warm to 0 °C over 1 h, and stirred at 0 °C for an additional 2 h. Tetrahydrofuran was removed under reduced pressure, and water (50 mL) was added to the residue. The resulting mixture was acidified (pH = 1) with 1 M HCl, and the organic phase was extracted with ether (3 × 100 mL). The combined extracts were washed with water, and dried ($MgSO_4$). After removal of the solvent, the residue was crystallized from ether/hexane (1:3) to give the corresponding acid (1.55 g, 88%, white solids, m.p. 196−197 °C). IR (neat): ṽ = 3540, 3489, 3412, 3080, 3004, 2978, 2902, 1676, 1600, 1574, 1446, 1344, 1319, 1268, 1242, 1165, 1012 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.37 dt (B part of AB system, $J_{11syn,11anti}$ = 7.8 Hz, $J_{1,11syn}$ = $J_{8,11syn}$ = 1.6 Hz, 1 H, 11*syn*-H), 2.65 (dt, A part of AB system, $J_{11syn,11anti}$ = 7.8, $J_{1,11anti}$ = $J_{8,11anti}$ = 1.6 Hz, 1 H, 11*anti*-H), 4.33 (m, 1 H, 1-H), 4.04 (m, 1 H, 8-H), 7.04 (m, 2 H, aromatic), 7.33 (m, 2 H, aromatic). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 54.1, 64.1, 124.3, 69.0, 124.6, 127.2, 128.0, 143.9, 148.9, 150.5, 152.7, 170.1. *p*-Toluenesulfonic acid (catalytic amount) was added to a solution of the carboxylic acid (1.5 g, 5.6 mmol) in dry methanol (50 mL). The reaction mixture was refluxed for 4 d. After removal of the solvent, the mixture was extracted with ether (2 × 100 mL) and **27** was obtained as a yellow, oily residue (1.27 g, 80%). IR (neat): ṽ = 3080, 3004, 2953, 2876, 1727, 1600, 1472, 1319, 1268, 1217, 1110, 1012 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.35 dt (B part of AB system, $J_{11syn,11anti}$ = 7.8 Hz, $J_{1,11syn}$ = $J_{8,11syn}$ = 1.6 Hz, 1 H, 11*syn*-H), 2.63 (dt, A part of AB system, $J_{11syn,11anti}$ = 7.8 Hz, $J_{1,11anti}$ = $J_{8,11anti}$ = 1.6 Hz, 1 H, 11*anti*-H), 3.76 (s, 3 H, methoxy), 4.01 (m, 1 H, 8-H), 7.04 (m, 2 H, aromatic), 4.32 (m, 1 H, 1-H), 7.34 (m, 2 H, aromatic), − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 53.5, 54.3, 63.7, 69.0, 124.2, 124.5, 127.1, 127.8, 144.3, 149.3, 149.4, 150.7, 165.9. $C_{13}H_{11}BrO_2$ (279.13): calcd. C 55.94, H 3.97; found C 56.08, H 4.03.

Methyl [1*S*(*R*),8*R*(*S*)]-10-Cyanotricyclo[6.2.1.0^{2,7}]undeca-2,4,6,9-tetraene-9-carboxylate (18): Monobromide **27** (1.59 g, 5.70 mmol) and cuprous cyanide (1.22 g, 6.84 mmol) were dissolved in dry dimethylformamide (100 mL). The solution was magnetically stirred at 100−110 °C for 14 h. The reaction mixture was cooled to room temperature, benzene (200 mL) was added, and the organic phase was washed with 2 × 200 mL of $FeCl_3$ solution, 2 × 200 mL of 10% aqueous NaOH, and 2 × 200 mL of water, and dried with $CaCl_2$. The solvent was removed. After chromatography of the residue on a silica gel column (110 g), with hexane/ethyl acetate (8:2) as eluent, the residue was recrystallized from dichloromethane/hexane (1:3) to give **18** (873 mg, 68%, white crystals, m.p 71−78 °C). IR (neat): ṽ = 3080, 3055, 3029, 2978, 2953, 2902, 2238, 1727, 1600, 1472, 1446, 1344, 1268, 1242, 1140, 1114, 1089 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.44 (dt, B part of AB system, $J_{11syn,11anti}$ = 8.2 Hz, $J_{1,11syn}$ = $J_{8,11syn}$ = 1.6 Hz, 1 H, 11*syn*-H), 2.63 (dt, A part of AB system, $J_{11syn,11anti}$ = 8.2, $J_{1,11anti}$ = $J_{8,11anti}$ = 1.6 Hz, 1 H, 11*anti*-H), 3.83 (s, 3 H, methyl), 4.25 (m, 1 H, 1-H), 4.41 (m, 1 H, 8-H), 7.06 (m, 2 H, aromatic), 7.40 (m, 2 H, aromatic). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 53.8, 54.4, 57.5, 71.1, 116.4, 125.1, 125.3, 127.8, 128.2, 135.8, 148.5, 148.7, 161.9, 164.1. $C_{14}H_{11}NO_2$ (225.24): calcd. C 74.65, H 4.92, N 6.22; found C 74.53, H 4.99, N 6.18.

Acetone-Sensitized Photolsis of 16: A solution of **16** (1.0 g, 4.42 mmol) in acetone (105 mL) was placed in a quartz phototube. The magnetically stirred solution was flushed with N_2 gas and irradiated at 254 nm for 2 h. The acetone was evaporated and NMR analysis of the resulting mixture showed the formation of **28** as a major product (50%), together with semibullvalene derivatives **29** (39%). Chromatography of the mixture on a silica gel column (80 g) with ether/benzene/hexane (3:8:89) gave two photoproducts: **28** and **29**.

Methyl 2a-Methyl-2b,6b-dihydrobenzo[*a*]cyclopropa[*cd*]pentalene-6c(2a*H*)-carboxylate (28): IR (neat): ṽ = 3060, 2940, 2860, 1720, 1470 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.80 (s, 3 H, methyl), 3.63 (s, 1 H, 2b-H), 3.77 (s, 3 H, ester protons), 4.53 (d, $J_{1,6b}$ = 2.4, 6b-H), 5.16 (d, $J_{1,2}$ = 5.3 Hz, 1 H, 2-H), 5.74 (dd, $J_{1,2}$ = 5.3, $J_{1,6b}$ = 2.4 Hz, 1 H, 1-H), 7.39−7.17 (m, 4 H, aromatic). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 171.68, 149.44, 137.62, 135.03, 126.74, 126.57, 125.56, 125.36, 121.84, 65.16, 56.21, 56.11, 52.18, 52.03, 17.23. $C_{15}H_{14}O_2$ (226.27): calcd. C 79.62, H 6.24; found C 79.33, H 6.12.

Methyl 1-Methyl-2a,2b,6b,6c-tetrahydrobenzo[*a*]cyclopropa[*cd*]pentalene-2-carboxylate (29): IR (neat): $\tilde{\nu}$ = 3040, 2940, 1800, 1710, 1620, 1470 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.32−7.07 (m, 4 H, aromatic), 3.77 (d, $J_{6b,6c}$ = 6.2 Hz, 1 H, 6b-H), 3.66 (s, 3 H, ester protons), 3.24 (dt, $J_{2b,6c} = J_{2a,6c}$ = 7.0, $J_{6b,6c}$ = 6.2 Hz, 1 H, 6c-H), 3.03 (m, 2 H, 2a-H and 2b-H), 2.11 (s, 3 H, methyl). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 166.52, 159.18, 148.13, 139.82, 127.38, 126.07, 125.99, 121.56, 120.36, 60.82, 51.49, 46.65, 39.23, 37.26, 14.76. $C_{15}H_{14}O_2$ (226.27): calcd. C 79.62, H 6.24; found C 79.55, H 6.17.

Acetone-Sensitized Photolsis of 17: A solution of **17** (1.5 g, 6.32 mmol) in acetone (105 mL) was placed in a quartz phototube. The magnetically stirred solution was flushed with N_2 gas and irradiated at 254 nm for 90 min. The acetone was evaporated and NMR analysis of the resulting mixture showed the formation of **34** as the product (37%), besides the unchanged starting material (41%). Prolonged irradiation caused decomposition of the formed product. Chromatography of the mixture on a silica gel column (70 g) with ether/benzene/hexane (5:8:87) gave methyl 8-cyanobenzo[*a*]cyclooctene-7-carboxylate (**34**) (195 mg, 13%), which was crystallized from same solvent system, to give pale yellow crystals (m.p. 88−90 °C). IR (neat): $\tilde{\nu}$ = 3040, 3000, 2940, 2200, 1730, 1720, 1630, 1600 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.31−7.24 (m, 2 H, aromatic), 7.12−7.03 (m, 2 H, aromatic), 6.85 (d, $J_{9,10}$ = 11.5 Hz, 1 H, 10-H), 6.74 (d, $J_{5,6}$ = 11.9 1 H, 5-H), 6.37 (dd, $J_{5,6}$ = 11.9, $J_{6,9}$ = 1.1 Hz, 1 H, 6-H), 6.10 (dd, $J_{9,10}$ = 11.5, $J_{6,9}$ = 1.1 Hz, 1 H, 9-H) 3.82 (s, 3 H, methyl). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 164.02, 144.59, 139.27, 135.95, 135.38, 129.99, 129.93, 128.56, 128.41, 128.27, 127.72, 120.27, 116.31, 53.32. $C_{15}H_{11}NO_2$ (237.25): calcd. C 75.94, H 4.67, N 5.90; found C 76.08, H 4.58, N 5.85.

Dimethyl Benzo[*a*]cyclooctene-7,8-dicarboxylate (35):[29] A solution of KOH (10%, 15 mL) was added to a solution of **34** (180 mg, 0.76 mmol) in MeOH (3 mL). The resulting mixture was refluxed for 5 h. The reaction mixture was cooled to room temperature and treated with 1 N HCl solution until pH = 1. The aqueous layer was extracted with ether (2 × 75 mL). The combined organic extracts were washed with water (2 × 50 mL) and dried with $CaCl_2$. The solvent was evaporated to give the corresponding dicarboxylic acid (150 mg, 82%, yellow crystals from chloroform/ether/*n*-hexane, m.p. 201−203 °C). ^1H NMR (200 MHz, $CDCl_3$): δ = 7.31−7.26 (AA′BB′ system, 4 H, aromatic), 6.75 (d, A part of AB system, $J_{5,6} = J_{9,10}$ = 11.5 Hz, 2 H, olefinic), 2.20 (d, B part of AB system, $J_{5,6} = J_{9,10}$ = 11.5 Hz, 2 H, olefinic), 3.74 (s, 6 H, methyl).

Acetone-Sensitized Photolysis of (18): A solution of **18** (1.0 g, 4.40 mmol) in acetone (110 mL) was placed in a quartz phototube. The magnetically stirred solution was flushed with N_2 gas and irradiated at 254 nm for 8 h. The acetone was evaporated, and NMR analysis of the resulting mixture showed the formation of **67**, which was crystallized from dichloromethane/hexane. Colorless crystals were obtained (680 mg, 68%, m.p 297−298 °C). IR (neat): $\tilde{\nu}$ = 3106, 3055, 3029, 3004, 2953, 2263, 1753, 1497, 1472, 1446, 1293, 1114, 1089, 1012. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.53−7.11 (m, 8 H, aromatic), 3.92 (m, 2 H), 3.80 (m, 2 H), 3.55 (s, 6 H, methyl), 2.42 (dt, A part of AB system, J = 11.7, J = 1.5, 2 H), 1.96 (dt, B part of AB system, J = 11.7, J = 1.5, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 170.54, 145.04, 143.96, 130.16, 129.85, 126.16, 124.12, 65.36, 54.40, 54.14, 52.95, 49.66, 46.26. MS: *m*/*z* = 450 [M^+], 419 [$M^+ - OCH_3$], 391 [$M^+ - OCH_3$, CO], 386, 359, 335, 116 (indenyl cation).

X-ray Structural Analysis of $C_{28}H_{22}N_2O_4$: MW = 450.49, colorless, thin plate (0.21 mm × 0.16 mm × 0.7 mm), a = 7.691 (3) Å, b = 23.144 (3) Å, c = 12.444 (3) Å, V = 2209.0(9) $Å^3$, β = 94.224(9), T = 293(2) K, monoclinic, space group $P2_1/n$ (no. 14), Z = 4, μ (Mo-K_α) = 0.91 cm^{-1}. Intensity data were collected with a RIGAKU AFC7S diffractometer with graphite-monochromated Mo-K_α radiation (0.71069 Å). The structure was solved by direct methods with SHELXS-97 and refinement (full-matrix least squares) was performed against F^2 with the program SHELXL-97.[35] 8689 reflections were measured in the range of 2.41−32.5°. 8185 of them were unique reflections and 2881 with $F_o > 2\sigma(F_o)$. $R1$ [$F_o > 2\sigma(F_o)$] = 0.0626, $wR2$ for all data = 0.2072, GoF = 0.970, residual electron density: 0.32 $e^-/Å^3$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-173661 Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] H. E. Zimmerman, D. Armesto, *Chem. Rev.* **1996**, *96*, 3065−3112.
[2] H. E. Zimmerman, *CRC Handbook of Organic Chemistry and Photobiology*(Eds.: W. M. Horspool, P. S. Song), CRC Press, New York, **1995**.
[3] H. E. Zimmerman, *Rearrangement in Ground and Excited States* (Ed.: P. de Mayo), Academic Press, New York, **1980**, vol. III.
[4] S. S. Hixon, P. S. Mariano, H. E. Zimmerman, *Chem. Rev.* **1973**, *73*, 531−551.
[5] H. E. Zimmerman, R. S. Givens, R. M. Pagni, *J. Am. Chem. Soc.* **1968**, *90*, 6096−6108.
[6] C. O. Bender, D. W. Brooks, W. Cheng, D. Dolman, S. F. O'Shea, S. S. Shugarman, *Can. J. Chem.* **1978**, *56*, 3027−3037.
[7] C. O. Bender, E. H. King-Brown, *J. Chem. Soc., Chem. Commun.* **1976**, 878−879.
[8] C. O. Bender, J. Wilson, *Helv. Chim. Acta* **1976**, *59*, 1469−1479.
[9] L. A. Paquette, A. Y. Ku, C. Santiago, M. D. Rozeboom, K. N. Houk, *J. Am. Chem. Soc.* **1979**, *101*, 5981−5985.
[10] H. Hemmetsberger, M. Nobbe, *Tetrahedron* **1988**, *44*, 67−80.
[11] M. C. Sajimon, D. Ramaiah, S. A. Kumar, N. P. Rath, M. V. George, *Tetrahedron* **2000**, *56*, 5421−5428.
[12] C. O. Bender, S. F. O'Shea, S. S. Shugarman, *Can. J. Chem.* **1979**, *57*, 2804−2811.
[13] C. O. Bender, H. D. Burgess, *Can. J. Chem.* **1973**, *51*, 3486−3493.
[14] R. Hoffmann, *Tetrahedron Lett.* **1970**, 2907−2909.
[15] H. Günther, *Tetrahedron Lett.* **1970**, 5173−5176.
[16] M. Balci, H. Fischer, H. Günther, *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 301−303.
[17] M. Balci, *Turk. J. Chem.* **1992**, *16*, 42−90.
[18] F. H. Allen, *Acta Crystallogr., Sect. B* **1980**, *36*, 81−96.
[19] A. Greenberg, T. A. Stevenson, *Molecular Structure and Energetics* (Eds.: J. F. Liebman, A. Greenberg), Verlag Chemie, Florida, **1986**, vol. 5.
[20] R. Altundas, M. Balci, *Aust. J. Chem.* **1997**, *50*, 787−793.

[21] F. G. Bordwell, T. Y. Lynch, *J. Am. Chem. Soc.* **1989**, *111*, 7558−7562.
[22] M. Balci, O. Cakmak, T. Hökelek, *Tetrahedron* **1992**, *48*, 3163−3182.
[23] O. Cakmak, M. Balci, *J. Org. Chem.* **1989**, *54*, 181−187.
[24] J. W. Wilt, R. J. Chenier, *J. Org. Chem.* **1970**, *35*, 1562−1570.
[25] A. Dastan, M. Balci, T. Hökelek, D. Ulku, O. Buyukgungor, *Tetrahedron* **1994**, *50*, 10555−10578.
[26] S. Cossu, O. De Lucchi, V. Lucchini, G. Vallec, M. Balci, A. Dastan, B. Demirci, *Tetrahedron Lett.* **1997**, *38*, 5319−5322.
[27] R. Wehner, H. Gunther, *J. Am. Chem. Soc.* **1975**, *97*, 923−924.
[28] R. Hoffmann, W. D. Stohrer, *J. Am. Chem. Soc.* **1971**, *93*, 6941−6948.
[29] E. Grovenstein, Jr., T. C. Campbell, T. Shibata, *J. Org. Chem.* **1969**, *34*, 1198−1203.
[30] H. E. Zimmerman, R. S. Givens, M. R. Pagni, *J. Am. Chem. Soc.* **1968**, *90*, 4191−4193.
[31] P. W. Rabideau, J. B. Hamilton, L. Friedman, *J. Am. Chem. Soc.* **1968**, *90*, 4465−4466.
[32] H. E. Zimmerman, R. S. Givens, M. R. Pagni, *J. Am. Chem. Soc.* **1968**, *90*, 6096−6108.
[33] K. Saito, T. Mukai, *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2334−2335.
[34] F. K. Klärner, R. Ehrfardt, H. Bandmann, R. Boesse, D. Blaser, K. N. Houk, B. R. Beno, *Chem. Eur. J.* **1999**, *5*, 2119−2132.
[35] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467; G. M. Sheldrick, *SHELXL-97, Program for Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.

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