43. The Synthesis and Photoisomerization of 5-Methyl-5-vinyl-1,3-cyclopentadiene

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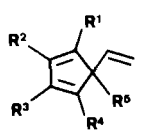
(27.I.88)

A versatile scheme for the synthesis of geminally disubstituted cyclopentadienes is used to prepare the title compound **4**. This remarkably stable vinyl-cyclopentadiene, distinguished by its C_s symmetry, undergoes exclusively electrocyclic ring closure upon direct π–π^* excitation at 254 nm. The epimeric vinyl-housenes **11** and **12**, which, for geometric reasons, are insensitive to the walk rearrangement, are suggested to be the primary photoproducts. One of them, **12**, due to its *syn*-oriented vinyl group, undergoes spontaneous *Cope* rearrangement to give 2-methylbicyclo[3.2.1]hepta-2,6-diene (**13**). The other, **11**, having an *anti*-oriented vinyl group, can only undergo thermal return to the starting material **4**. Whereas no leakage to a 1,5-vinyl migration is discernible for the S_1 state of **4**, the benzophenone-sensitized photolysis at 350 nm is shown to be governed by this rearrangement. 1-Methyl-5-vinylcyclopenta-1,3-diene (**14**), the unstable primary product of the sensitized photoreaction, is trapped by 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione (PTAD).

Introduction. – Some time ago, *Zimmerman* and *Ramsden* [1], and our laboratory [2] independently reported on the photochemical transformations of highly substituted 5-vinyl-1,3-cyclopentadienes. It was concluded that the bicyclo[3.2.0]hepta-2,6-dienes ensuing from irradiation of **1**[1], **2**[1], and **3**[2] are the result of a complex sequence of photochemical and thermal pericyclic reactions. Substituted 5-vinyl-housenes[1]) are believed to be the manifolds for scrambling, recycling, and product formation.



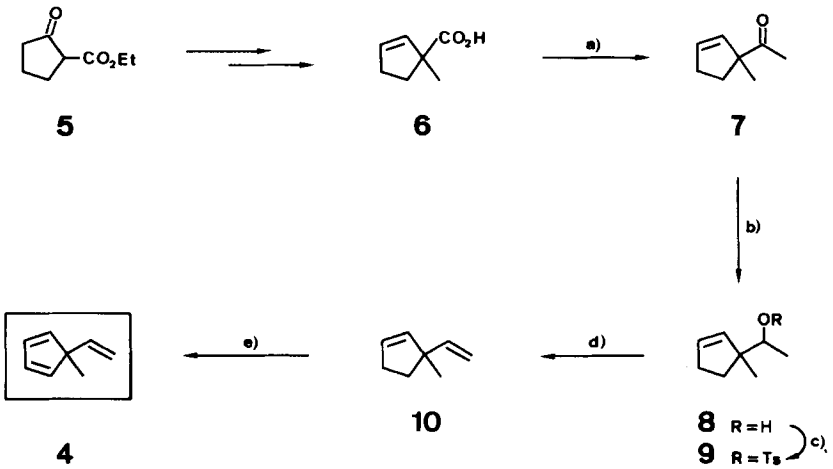
1 $R^1 = R^4 = R^5 = CH_3$, $R^2 = R^3 = Ph$
2 $R^1 = R^2 = R^5 = CH_3$, $R^3 = R^4 = Ph$
3 $R^1 = R^2 = R^3 = R^4 = R^5 = CH_3$
4 $R^1 = R^2 = R^3 = R^4 = H$, $R^5 = CH_3$

To distinguish between the inherent photochemical properties of the unperturbed 5-vinyl-cyclopentadiene chromophore and those due to substituents, we have now synthesized and examined the simplest member of the series that can be easily handled, *i.e.* the title compound **4**. The Me group at C(5) anchors the molecule in its C_s symmetry and prevents it from dimerizing or undergoing rapid thermal rearrangement to a conjugated triene. For a discussion of thermal vinyl shifts, see [3].

Results. – Starting from the commmercially available β-oxo ester **5**, the protecting Me group and the first endocyclic double bond of the target molecule **4** were introduced in early steps according to established procedures [4] [5]. Transformation of the functional side chain into a vinyl group was achieved in a few straightforward steps (**6**→**10**; *Scheme*

[1]) Housene is a widely used trivial name for bicyclo[2.1.0]pentene.

Scheme 1



a) MeLi, Et_2O; b) $NaBH_4$, EtOH; c) TsCl, Py;
d) **9**→**10**: *t*-BuOK, DMSO; e) NBS, CCl_4; *t*-BuOK, DMSO.

1). Finally, the endocyclic diene part was completed by allylic bromination of 3-methyl-3-vinylcyclopentene (**10**), followed by HBr elimination. The resulting vinyl-cyclopentadiene **4** is remarkably stable. Neat, it can be stored in a freezer (−20°) for several weeks. In acid-free solution, it was found to be stable at r.t. for at least 24 h. However, **4** is very volatile and difficult to separate from hexane, the solvent used in our previous studies. For that reason, and for spectroscopic convenience, the photolysis experiments described below, are performed in CD_3OD.

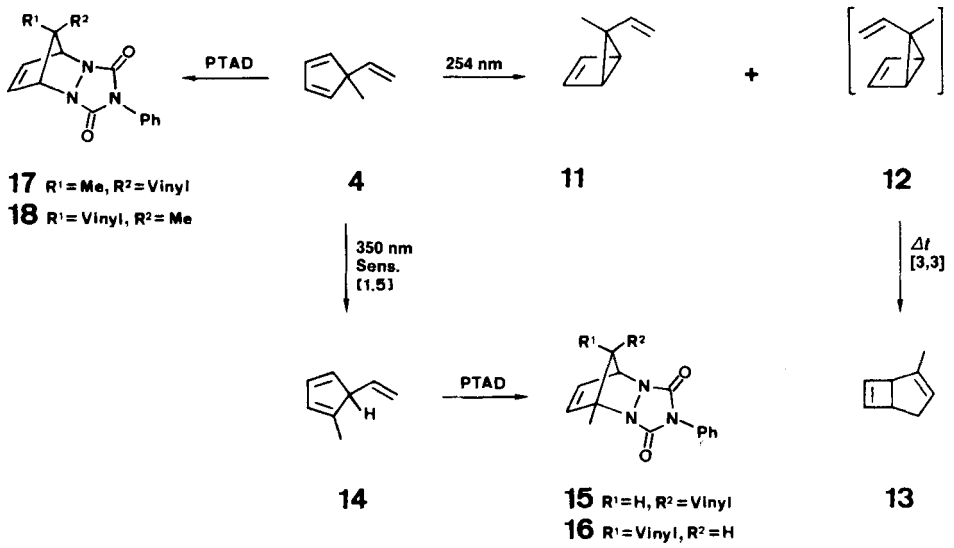
When we irradiated compound **4** at 0° in CD_3OD with light of wavelength 254 nm, we obtained two isomeric hydrocarbons, namely 5-*syn*-methyl-5-*anti*-vinylbicyclo-[2.1.0]pent-2-ene (**11**) and 2-methylbicyclo[3.2.0]hepta-2,6-diene (**13**) in a 1:1.8 ratio.

This transformation is very clean, and on the basis of a careful ^{1}H-NMR analysis at 360 MHz, no other products are formed (limit of detection 0.5%). Compound **13** was readily isolated by preparative GC and fully characterized by standard spectroscopic methods. The vinyl-housene **11**, however, is too labile for efficient GC separation. Its identification is based on the straightforward ^{1}H-NMR spectrum, which shows the expected *AA'MM'* spin pattern for the protons attached to the four-membered ring, and an isolated *ABM* system for the vinyl group. The configuration at C(5) *(Scheme 2)* follows from the low-field shift of the Me *singlet* (δ[ppm] = 1.5, *cf.* [6]). The epimer **12** is not detected in the ^{1}H-NMR spectrum recorded at 0°, it undoubtedly had undergone a fast *Cope* rearrangement to give **13**.

When a 1:2 mixture of **11** and **13** in CD_3OD was heated to 50°, the former underwent re-opening to the starting material **4**. This reaction unlike that of the parent housene[2])

[2]) In the case of the unsubstituted housene, the deviation of the decay kinetics from first-order is due to a *Diels-Alder* reaction of the cyclopentadiene product with the starting material [7].

Scheme 2



PTAD = 4-Phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione

follows first-order kinetics ($k_1(50°/CD_3OD) = 1.5 \cdot 10^{-4}$ s^{-1}), and, within the limits of NMR detection, it is quantitative; there is no detectable leakage from **11** to **13**.

Irradiation of **4** at 0° in CD_3OD with light of wavelength of 350 nm and in presence of benzophenone as sensitizer ($hc/E_T = 413$ nm [8]) gave 1-methyl-5-vinyl-1,3-cyclopentadiene (**14**) as primary product. Monitoring this reaction by ^{1}H-NMR at 0° showed that the concentration of **14** builds up and passes through a maximum (*ca.* 38% at 50% photoconversion of **4**). Prolonged irradiation brought about destruction of **14** by photochemical and presumably also by thermal transformation into a multitude of unidentified compounds. Both, the photochemical and the thermal lability of **14** are expected, since this primary photoproduct has virtually the same chromophore as the starting material **4**; moreover, it has a mobile H-atom capable of undergoing a [1,5] shift [9]. The structure of **14** was first deduced from a careful ^{1}H-NMR analysis with appropriate spin decoupling. To secure this assignment, we intercepted, after 25% photoconversion of **4**, the primary product **14** with the powerful dienophile, 4-phenyl-3*H*-1,2,4-triazol-3,5(4*H*)-dione (PTAD). From this experiment, we isolated a 1:1 mixture of the urazoles **15** and **16** besides the *Diels-Alder* adducts **17** and **18** of the unconverted starting material **4**.

Discussion. – From the clean course of the unsensitized photolysis of **4**, it is obvious that the electrocyclization of the S_1 state is by far the most efficient and probably the only chemical process occurring upon direct π–π^* excitation. It is well documented, that the three-membered ring of the housene can move around the four-membered base, both upon thermal and photochemical activation [10]. However, the vinyl-housenes **11** and **12**, resulting from electrocyclization of **4**, are insensitive to this circumambulation. This is also true for the pentamethylated compound **3** [2], and consequently, **3** and **4** behave very similarly on direct irradiation at 254 nm. The circumambulation at the housene level results for geometric reasons in an automerization without further consequence. Substit-

uent scrambling, as had been encountered with the Ph-substituted compounds **1** and **2**, is avoided, and the essential phototransformations of the virtually unperturbed vinyl-cyclopentadiene chromophore emerge in more transparent fashion. A 1,5-vinyl shift, which is also allowed in the S_1 state [1], is not observed in the direct photolysis of **4** and had not been observed in our previous work with isotopically labelled **3**. This contrasts with the behaviour of the Ph-substituted derivative **2** [1], where the sigmatropic rearrangement was found to compete with the electrocyclization process.

The benzophenone-sensitized reaction of **4**, on the other hand, is obviously governed by a vinyl migration. A corresponding vinyl shift in the sensitized photolysis of labelled **3**, thus, accounts for the scrambling observed in our earlier study [2]. As the triplet energies of cyclopentadiene (58.0 kcal/mol [11]) and symmetrical vinyl-cyclopentadiene ($\leqslant$ 58.0 kcal/mol [1]) are roughly 11 kcal/mol below that of benzophenone, we may be dealing with T_1-state chemistry of **4**. Alternatively, as was suggested by a referee, the excited sensitizer may oxidize the diene to its radical cation, which then could isomerize before undergoing back electron transfer. For 1,2,3,4,5-pentamethyl-cyclopentadiene, photooxidation in CF_3COOH has been reported to give a persistent pentamethyl-cyclopentadiene radical cation [12]. For a recent discussion of charge transfer and the implication of radical ions in photochemical transformations, see *e.g.* [13].

The authors wish to express their gratitude to Mr. *J.-P. Saulnier* (NMR), Mrs. *D. Clément* (MS), and Dr. *H.-J. Eder* (elementary analysis). Financial support was provided by the *Swiss National Science Foundation* (grant No. 2.864-0.85).

Experimental Part

General. Photolyses: *Srinivasan-Griffin* reactor *(Rayonet-RPR-100)* with *RPR* lamps, 2537 Å; quartz vessels; and *RPR* lamps, 3500 Å; *Pyrex* vessels. GC: *Perkin-Elmer-900;* glass columns. IR spectra [cm^{-1}]: *Polaris-Mattson* FT-IR spectrometer. UV spectra (λ [nm] (log ε)): *Kontron-Uvikon-860*. NMR spectra: *Bruker WM-360* (8.46 Tesla) or *Varian XL-200* (4.7 Tesla); chemical shifts in δ[ppm] relative to internal TMS; apparent scalar coupling constants J in Hz; multiplicities for ^{13}C under off-resonance decoupling or according to attached proton test (APT). MS: (*m/z* (% relative to base peak)): *Finnigan-4023* with *INCOS* data system; electron impact, 70 eV.

5-Methyl-5-vinyl-1,3-cyclopentadiene (**4**). A soln. of **10** *(vide infra)* (620 mg, 5.74 mmol) in 45 ml of CCl_4 with *N*-bromosuccinimide (1.03 g, 6.3 mmol) and *ca.* 15 mg of dibenzoyl peroxide was refluxed for 45 min. The succinimide was filtered off and the solvent removed *i.v.* The remaining crude allylic bromination products (isomers, including those with shifted endocyclic double bond) were dissolved without further purification in 4.5 ml of DMSO. This soln. was added slowly at 20° to a soln. of *t*-BuOK (1.2 g, 10.6 mmol) in 5 ml of DMSO. The black mixture was stirred for 30 min at 20°. Et_2O (5 ml) was added, and the mixture was hydrolyzed with ice-water. The combined Et_2O extracts (total 50 ml) were washed with sat. brine and dried ($MgSO_4$). The volume was reduced to 1/10 by careful distillation of Et_2O through a *Vigreux* column (25 cm). GC on silicon oil *SE-30* at 70° showed **4** to be the principal product (*ca.* 350 mg, 57%). Pure samples were isolated by prep. GC (*SE-30* on *Chromosorb-W*, 3 m, 70°). Compound **4** is a volatile colorless liquid. UV (EtOH): 203 (4.95), 252 (4.44). IR ($CDCl_3$): 3095*m*, 2980*s*, 1630*s*. ^{1}H-NMR (360 MHz, $CDCl_3$): 1.27 (*s*, 3 H); 4.96 (*dd*, J = 10.7, 1.3, 1 H); 5.18 (*dd*, J = 17.3, 1.3, 1 H); 5.62 (*dd*, J = 17.3, 10.7, 1 H); 6.27 (narrow *AA'BB'*, 4 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 18.14 (CH_3); 58.84 (C); 111.8 (CH_2); 129.2 (CH); 139.3 (CH); 144.2 (CH). MS: 106 (51, C_6H_{10}), 105 (28), 91 (100), 79 (19), 78 (22).

Methyl 1-Methyl-2-cyclopentenyl Ketone (**7**). A soln. of MeLi (60 ml, 1.5M; 96 mmol) in Et_2O was added slowly to an ice-cold soln. of **6** (6.0 g, 47.6 mmol) [5] in 320 ml of Et_2O. The mixture was stirred for 3 h at r.t. and then hydrolyzed with 96 ml of 1M HCl. The product was extracted with Et_2O, washed with sat. $NaHCO_3$ soln., and dried ($MgSO_4$). Removal of Et_2O left **7** as a colorless liquid which was distilled *i.v.* (5.48 g, 93%). B.p. 51–52°/12 Torr. GC on silicon oil *SE-30* at 130° shows purity of > 97%. IR (NaCl): 3055*w*, 2980*m*, 1720*s*, 1455*w*, 1355*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.2 (*s*, 3 H); 2,11 (*s*, 3 H); 1.4–2.8 (*m*, 4 H); 5.5–5.9 (*m*, 2 H). Anal. calc. for $C_8H_{12}O$ (124.18): C 77.38, H 9.74; found: C 77.15, H 9.89.

1-(1-Methyl-2-cyclopentenyl)ethanol (**8**; mixture of diastereoisomers). A soln. of **7** (10.7 g, 86.3 mmol) in 40 ml of EtOH was added slowly to an ice-cold soln. of $NaBH_4$ (1.45 g, 38.3 mmol) in 40 ml of EtOH and stirred at r.t. for 15 h. The mixture was acidified with neat AcOH to pH 5.5. The colorless precipitate was filtered, dissolved in H_2O, and extracted with pentane. The ethanolic filtrate was combined with the pentane extracts, and removal of solvent gave a liquid, which was dissolved in Et_2O, washed with sat. brine, and dried ($MgSO_4$). Distillation gave **8** (9.47 g, 87%) as a colorless liquid. B.p. 55–62°/12 Torr. IR (CCl_4): 3640*m*, 2980*s*. ^{1}H-NMR (360 MHz, $CDCl_3$) 1:1 mixture of diastereoisomers: 0.97 (*s*, 3 H) and 0.99 (*s*, 3 H); 1.08 (*d*, J = 6.4, 2 × 3 H); 1,45 (*m*, 2 × 1 H); 1.9 (*m*, 2 × 1 H); 2.3 (*m*, 2 × 2 H overlapping with 2 × OH); 3.56 (*q*, J = 6.4, 1 H) and 3.60 (*q*, J = 6.4, 1 H); 5.38 (*m*, 1 H) and 5.52 (*m*, 1 H); 5.8 (*m*, 2 × 1 H). Anal. calc. for $C_8H_{10}O$ (126.20): C 76.14, H 11.18; found: C 76.02, H 11.32.

3-Methyl-3-vinyl-1-cyclopentene (**10**). A soln. of **8** (1.92 g, 15.2 mmol) and TsCl (6.2 g, 32.6 mmol) in 40 ml of pyridine was kept for 24 h at 0° and then hydrolyzed with 200 ml ice-water. The mixture was extracted (3×) with Et_2O, washed with ice-cold 2M HCl and brine, and dried ($MgSO_4$). Medium-pressure chromatography (silica gel, hexane/Et_2O 9:1) gave **9** (3.66 g, 86%) as a colorless oil (mixture of diastereoisomers). This material was used without further purification. A soln. of **9** (2.04 g, 7.28 mmol) in 7.5 ml of DMSO was added to a soln. of *t*-BuOK (1.64 g, 14.5 mmol) in 7.5 ml of DMSO and the mixture stirred for 30 min at 20°. CCl_4 (5 ml) was added under ice-cooling and the mixture was hydrolyzed. The product was extracted with CCl_4 (3 × 20 ml), washed with brine, and dried ($MgSO_4$). Distillation of this soln. at 760 Torr gave **10** (682 mg, 87% by GC) in *ca.* 50 ml of CCl_4. Contamination (10%) by an isomer of **10**, having the endocyclic double bond shifted, does not disturb the subsequent bromination reaction (see **4**). An anal. sample of **10** was obtained by prep. GC (silicon oil *SE-30*, 5% on *Chromosorb-W*, 50°), colorless volatile liq. IR (CCl_4): 3095*w*, 3060*m*, 2960*s*, 1635*w*, 910*s*. ^{1}H-NMR (360 MHz, $CDCl_3$): 1.16 (*s*, 3 H); 1.70 (*m*, 1 H); 1.86 (*m*, 1 H); 2.38 (*m*, 2 H); 4.89 (*dd*, J = 10.7, 1.6, 1 H); 4.96 (*dd*, J = 17.4, 1.6, 1 H); 5.51 (*dt*, J = 5.5, 2.2, 1 H); 5.72 (*dt*, J = 5.5, 2.3, 1 H); 5.91 (*dd*, J = 17.4, 10.7, 1 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 25.43 (CH_3); 31.46 (CH_2); 37.89 (CH_2); 50.96 (C); 109.78 (CH_2); 129.6 (CH); 138.6 (CH); 146.7 (CH).

Direct Photolysis of **4**. A deoxygenated soln. of **4** (13 mg, 0.12 mmol) in 0.6 ml of CD_3OD was irradiated at 0° in a sealed quartz NMR tube for 15 min with light of wavelength 254 nm. ^{1}H-NMR (360 MHz, CD_3OD, 0°) showed unconsumed **4** (25%), **11** (26.8%), and **13** (48.2%). ^{1}H-NMR of **11**: 1.50 (*s*, 3 H); 2.08 (narrow *AA'* of *AA'MM'*, 2 H); 4.90 (*dd*, J = 11, 1.5, 1 H); 5.03 (*dd*, J = 18, 1.5, 1 H); 5.51 (*dd*, J = 18, 11, 1 H); 6.05 (narrow *MM'* of *AA'MM'*, 2 H). *2-Methylbicyclo[3.2.0]hepta-2,6-diene* (**13**) was isolated by prep. GC (silicon oil *SE-30*, 10% on *Chromosorb-W*, 60°)[3]. UV (MeOH): 215 (end absorption). ^{1}H-NMR (360 MHz, CD_3OD): 1.70 (narrow *m*, CH_3); 2.13 (*dm*, J = 16, H–C(4) ('*endo*')); 2.31 (*ddm*, J = 16, 9, H–C(4) ('*exo*')); 3.29 (*dm*, J = 9, H–C(5)); 3.46 (*m*, H–C(1)); 5.18 (*m*, H–C(3)); 6.12 (*dm*, J = 3.2, H–C(6)); 6.45 (*dm*, J = 3.2, H–C(7)).

Benzophenone-Sensitized Photolysis of **4**. A soln. of **4** (15 mg, 0.14 mmol) and benzophenone (2.4 mg, 0.014 mmol) in 0.6 ml of CD_3OD was deoxygenated in a *Pyrex* NMR tube by a triple freeze-thaw cycle under N_2 and sealed. The tube was placed in a cylindrical *Pyrex* vessel (∅ 7.5 cm) which was equipped with an internal cooling spiral (*Haake* cryostate) and filled with 0.4M aq. soln. of $CuSO_4$ as cut-off filter for light < 320 nm. In a typical experiment, the sample was irradiated for 20 min at 0° at 350 nm, and then inserted into the pre-cooled NMR probe (–20°). The spectrum showed unconsumed **4** (*ca.* 70%), the sensitizer, which was used as integration standard, and *1-Methyl-5-vinyl-1,3-cyclopentadiene* (**14**) (*ca.* 27%). ^{1}H-NMR of **14**: 1.90 (*d*, J = 2, 3 H); 3.38 (*dm*, J = 7.8, H–C(5)); 5.1–5.3 (*m*, CH_2=CH); 6.05 (*m*, H–C(2)); 6.14 (*dm*, J = 5.6, 1 H); 6.22 (*dm*, J = 5.6, 1 H).

A multitude of unidentified new compounds appeared to the detriment of **14** upon prolonged irradiation or, when the tube was allowed to warm to r.t.

Interception of **14** *by PTAD*. A soln. of **4** (23 mg, 0.22 mmol) and benzophenone (3.7 mg, 0.02 mmol) in 0.8 ml of CD_3OD was deoxygenated and irradiated (350 nm) at 0° for 16 min as described above. ^{1}H-NMR indicated *ca.* 25% photoconversion. The sample was cooled to –20°, and a pre-cooled soln. of PTAD (41.8 mg, 0.24 mmol) in 0.5 ml of (D_6)acetone was added. The red color of PTAD disappeared rapidly. The mixture was kept for 2 h at –20° and then allowed to warm to r.t. A slight colorless precipitate, which is of no particular interest (*cf.* [15]), was filtered off and discarded. ^{1}H-NMR of the filtrate revealed the presence of **15**, **16**, **17**, and **18** in the ratio 1.0:1.05:3.2:3.3 (spectral data *vide infra*). Prep. TLC (silica gel, hexane/AcOEt 6:1, triple development) gave three fractions consisting of **16** (R_f 0.43, 5.9 mg, 9.8%), a 1:3.3 mixture **15**/**18** (R_f 0.32, total 25.3 mg, 41.5%), and **17** (R_f 0.21, 18.9 mg, 31%).

*1-Methyl-*N*-phenyl-7-*syn*-vinyl-5,6-diazabicyclo[2.2.1]hept-2-ene-5,6-dicarboximide*[4]) (**15**). ^{1}H-NMR (360 MHz, $CDCl_3$, recorded in presence of **18**): 1.83 (*s*, CH_3); 2.52 (*d*, J = 8.5, H–C(7)); 4.86 (*m*, H–C(4)); 5.29 (*dm*,

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[3]) For spectral parameters of the parent system, see [14].

[4]) The descriptors *syn* and *anti* indicate that the substituent at C(7) is oriented towards and away, respectively, from the bridge of highest priority, *i.e.* N(5)–N(6).

J = 17.2, 1 H, vinyl); 5.35 (*dm*, J = 10.2, 1 H, vinyl); 5.90 (*ddd*, J = 17.2, 10.2, 8.5, 1 H, vinyl); 6.39 (*dm*, J = 5.8, 1 H, H–C(3)); spin saturation of H–C(7) shows NOE (8%) for H–C(3); 6.45 (*dm*, J = 5.8, H–C(2)); 7.3–7.5 (*m*, 5 arom. H).

*1-Methyl-*N*-phenyl-7-*anti*-vinyl-5,6-diazabicyclo[2.2.1]hept-2-ene-5,6-dicarboximide*[4]) (**16**). Colorless oil. UV (EtOH): 202 (4.86), 218 (sh), 252 (sh). IR ($CHCl_3$): 1780*w*, 1720*s*, 1400*m*. ^{1}H-NMR (360 MHz, $CDCl_3$): 1.86 (*s*, CH_3); 3.06 (*dm*, J = 7.5, H–C(7)); 4.92 (*m*, H–C(4)); 5.26 (*dm*, J = 10, 1 H, vinyl); 5.30 (*dm*, J = 17, 1 H, vinyl); 5.44 (*ddd*, J = 17, 10, 7.5, 1 H, vinyl); 6.20 (*dd*, J = 5, 1, 1 H); 6.38 (*dd*, J = 5, 2, 1 H); 7.3–7.5 (*m*, 5 arom. H). ^{13}C-NMR (50 MHz, $CDCl_3$): 14.63 (CH_3); 67.79 (CH); 67.91 (CH); 78.11 (C(1)); 121.8 (CH_2); 125.5, 128.3, 129.0, 129.2, 130.4 (5 × CH); 131.2 (C); 133.4 (CH); 2 × CO uncertain. MS: 281 (14, M^+, $C_{16}H_{15}N_3O_2$), 162 (19), 147 (20), 133 (14), 119 (22), 105 (27), 91 (100).

*7-*anti*-Methyl-*N*-phenyl-7-*syn*-vinyl-5,6-diazabicyclo[2.2.1]hept-2-ene-5,6-dicarboximide*[4]) (**17**). Colorless oil. UV (EtOH): 202 (4.34), 217 (sh), 252 (sh). IR ($CHCl_3$): 1755*w*, 1720*s*, 1400*m*. ^{1}H-NMR (360 MHz, $CDCl_3$): 1.18 (*s*, CH_3); 4.76 (*AA'* of *AA'MM'*, 2 H); 5.32 (*dd*, J = 9.8, 1, 1 H, vinyl): 5.36 (*dd*, J = 16.8, 1, 1 H, vinyl); 6.21 (*dd*, J = 16.8, 9.8, 1 H, vinyl); 6.46 (*MM'* of *AA'MM'*, 2 H); 7.3–7.5 (*m*, 5 arom. H). ^{13}C-NMR (50 MHz, $CDCl_3$): 18.27 (CH_3); 63.67 (C); 71.12 (CH); 116.5 (CH_2); 125.5, 128.4, 129.1, 130.6 (4 × CH); 131.3 (C); 138.1 (CH); 158.6 (CO). MS: 281 (36, M^+, $C_{16}H_{15}N_3O_2$), 162 (35), 147 (40), 135 (43), 135 (45), 120 (47), 119 (60), 105 (53), 91 (100).

*7-*syn*-Methyl-*N*-phenyl-7-*anti*-vinyl-5,6-diazabicyclo[2.2.1]hept-2-ene-5,6-dicarboximide*[4]) (**18**). ^{1}H-NMR (360 MHz, $CDCl_3$, recorded in presence of **15**): 1.46 (*s*, CH_3); 4.72 (*AA'* of *AA'MM'*, 2 H); 5.03 (*dd*, J = 17.6, 0.4, 1 H, vinyl); 5.16 (*dd*, J = 10.4, 0.4, 1 H, vinyl); 5.74 (*dd*, J = 17.6, 10.4,1 H, vinyl); 6.38 (*MM'* of *AA'MM'*, 2 H); 7.3–7.5 (*m*, 5 arom. H).

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