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v-TRIAZOLINES—XXII[1]

CYCLOADDITION REACTIONS OF CYCLOPENTADIENONES TO 5-AMINO-4-METHYLENE-v-TRIAZOLINES

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Abstract—Tetraphenylcyclopentadienone **2a** and 2,5-dimethyl-3,4-diphenylcyclopentadienone **2b** were reacted with 5-amino-4-methylene-v-triazolines **1a–c**. A single cycloadduct, namely the correspondingly substituted spiro[bicyclo[2.2.1]hept-2-en-7-one[5.4']-1',2',3'-triazole] derivative **3a–c**, was formed in all cases. Compounds **3a–c** are not stable in solution and rearrange even at room temperature into the corresponding 5-amino-1-aryl-4-[cyclopent-3-en-1-one-2-yl]methyl-1',2',3'-triazoles **4a–e**. The structures of the products are clarified on the basis of spectroscopical data and the reaction pathways are discussed.

As a part of our studies on the chemical behaviour of spiranic v-triazoline derivatives, in a previous paper[1] we described some derivatives, of a spiro-[bicyclo[2.2.1]hept-2-en[2.4']-1',2',3'-triazole] ring which were formed both by [4+2]π-cycloaddition of cyclopentadiene to 1-aryl-5-amino-4-methylene-v-triazolines and by [3+2]π-cycloaddition of arylazides to enamines of 5-norbornene-2-carboxaldehyde.

It was shown that these compounds are easily cleaved on heating to amidine derivatives with nitrogen elimination, thus showing a behaviour which parallels that of simpler and less strained 5-amino-v-triazolines.[2]

In this paper we report our results on the cycloaddition products derived from 5-amino-4-methylene-v-triazolines and substituted cyclopentadienones; the latter are known to exhibit a high dienic reactivity with unsubstituted and substituted ene compounds.[3]

RESULTS

Tetraphenylcyclopentadienone (**2a**) reacted smoothly with 4-methylene-v-triazolines (**1a, b**) in dichloromethane solution at 0–10° affording in about 70 hr a mixture of products **3a + 4a** and **3b + 4b**, respectively, in a satisfactory yield.

By monitoring the reaction course by TLC it was shown that the amount of **3** initially increased and then decreased very slowly while the amount of **4** increased. At longer times (four days) **4** was practically the sole reaction product. As a general rule, the reactions were quenched when the starting materials had been totally consumed and an approximately equimolar mixture of **3** and **4** was present. This mixture was separated and purified by column chromatography.

Similarly, reaction of **1a** at 0° with the dimerization product of 3,4-diphenyl-2,5-dimethylcyclopentadienone **2b** (which is known to exist in equilibrium with the monomeric form[4]) resulted in the formation of cycloadduct **3c** as the main reaction product. At higher reaction temperatures (30–80°) an increasing amount of **4c** was formed together with **3c**.

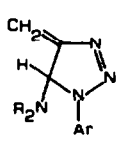
Compounds **3a–c** have been identified as the cycloaddition products of the dienone to the exocyclic double bond of the v-triazolines **1a, b** on the basis of analytical data and spectroscopic evidence. The IR spectra of **3a–c** are characterized by a strong carbonyl absorption in the 1780 cm^{-1} range, which suggests the presence of a strained carbonyl group of the norbornene-7-one structure.[5] This structure is further substantiated by the presence in ^{1}H-NMR of an AB pattern for the 6-CH_2 diastereotopic group and of a singlet in the range δ 4.6–4.9 for 5'-H.

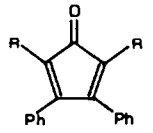
Mass spectra of **3a** and **b** show molecular ions of very low abundance. This behaviour depends on their low chemical stability. The main fragmentation pattern is represented by the *retro*-Diels–Alder cleavage, which originates tetraphenylcyclopentadienone (*m/z* 384) and other fragments derived from it (*m/z* 356, 276, 178, 152). The other ion derived from the *retro*-Diels–Alder cleavage corresponding to the starting methylene triazoline is of much lower abundance. Quite similar is the behaviour of **3c** which originates 2,5-dimethyl-3,4-diphenylcyclopentadienone (*m/z* 260) and related fragments (*m/z* 232, 178, 116).

While the assigned structures for **3a–c** are well confirmed the assignment of the stereochemistry is only tentative since there is not sufficient data to establish the configuration at both chiral centres 4'-C and 5'-C of the v-triazoline moiety. Four diastereoisomeric structures are possible and, as a further complication, comparative considerations were not possible since only one diastereoisomer was formed in the reaction.† Tentatively, the 1*S**, 4*R**, 4'(5)*S**, 5'*S** configuration for **3a** and **b**‡ can be proposed on the mechanistic ground exposed in the Discussion.

† An X-ray crystallographic study was considered, but the solution instability of **3** prevented the formation of suitable crystals.

‡ For **3c** the same structure must be named 1*R**, 4*R**, 4'(5)*S**, 5'*S**.

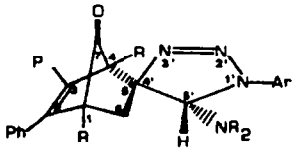




1a: NR_2 = morpholino; Ar = $C_6H_4NO_2$-4 2a: R=Ph

1b: NR_2 = pyrrolidino; Ar = $C_6H_4NO_2$-4 2b: R=Me

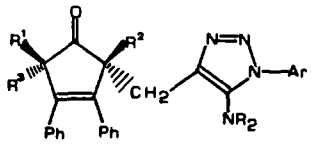
1c: NR_2 = morpholino; Ar = C_6H_4OMe-4



3a : R = Ph, NR_2 = morpholino; Ar = $C_6H_4NO_2$-4

3b : R = Ph, NR_2 = pyrrolidino; Ar = $C_6H_4NO_2$-4

3c : R = Me, NR_2 = morpholino; Ar = $C_6H_4NO_2$-4



4a : R^1=R^2=Ph; R^3=H; NR_2 = morpholino; Ar = $C_6H_4NO_2$-4

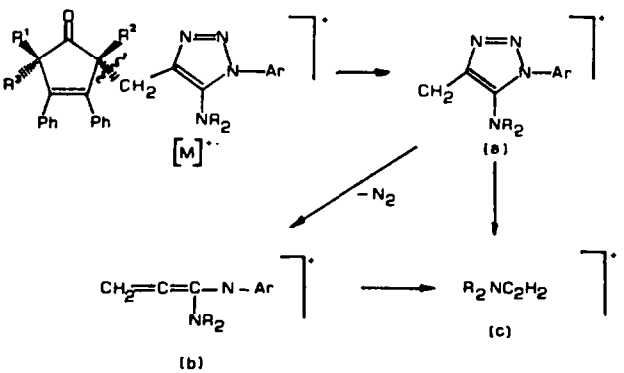
4b : R^1=R^2=Ph; R^3=H; NR_2 = pyrrolidino; Ar = $C_6H_4NO_2$-4

4c : R^1=R^2=Me; R^3=H; NR_2 = morpholino; Ar = $C_6H_4NO_2$-4

4d : R^1=R^2=Ph; R^3=H; NR_2 = morpholino; Ar = C_6H_4OMe-4

4d : R^1=H; R^2=R^3=Ph, NR_2 = morpholino; Ar = C_6H_4OMe-4

In the mass spectra of **4a–c** molecular ions are much more intense than those of **3a–c**, owing to the higher stability of these products. Fragments derived from the cyclopentadienone moiety (*m/z* 384 or 260, etc.) are present also in the mass spectra of these compounds, but with lower abundance. A new fragmentation pathway becomes evident as shown in Scheme 1. Ion **a** derived directly from the molecular ion loses N_2 giving ion **b**; both ions **a** and **b** subsequently originate ion **c**, which is the base peak in the spectra of all compounds except **4a**. The rather unusual rearrangement which gives rise to ion **c** is confirmed by



Scheme 1.

metastable analysis using the linked scan technique (B/E = const.) and by high-resolution mass spectra measurements made on ions **a–c** of **4e**.

As already stated, all spiranic compounds **3a–c** were unstable in solution and slowly evolved into the corresponding triazole derivatives **4a–c**. The rearrangement occurred partially during the reaction between **1** and **2**. Obviously, the same behaviour was observed by dissolving **3** in a solvent, e.g. chloroform, and keeping the solution at room temperature for several days. A higher rearrangement rate was observed for the cycloaddition product of **1c** and **2a**. In fact, this cycloadduct was detected in the reaction mixture by TLC but could not be isolated since it rearranged nearly at the same rate at which it formed from the reactants. Two main products were isolated in this case, namely the diastereoisomeric cyclopentenone derivatives **4d** and **e**. Though sufficiently stable to allow for their separation, both **4d** and **e** partially isomerized into the corresponding diastereoisomer when kept in solution for several days. IR spectra of structures **4** showed a carbonyl absorption (about 1740 cm^{-1}) indicative of the 3-cyclopentenone structure **6**, which was moreover confirmed by an X-ray crystallographic study on **4a** establishing also the configuration at the two residual chiral centres as 2*S**, 5*R**.[7] ^{1}H-NMR of **4** showed an AB pattern for the methylene bridge hydrogens, with geminal coupling constants more negative than in the case of the corresponding methylene in **3** (−15.0 Hz vs −12.5 to 13.0 Hz, respectively) due to the hyperconjugative effect of the aromatic substituent.[8] The signals belonging to the amine substituent were shifted downfield with respect to **3** reflecting the sp^2 character of the substitution site. Carbons α and β to the amine nitrogen were found in ^{13}C-NMR spectra as strongly diastereotopic in structures **3**, because of the highly anisotropic environment. In **4** instead, only one signal (for α and β carbons, respectively) was observed, pointing to a less crowded structure in which moreover two neighbouring chiral centres had been removed, e.g. **3a**, C-α-morpholino 45.36, 53.21 δ; C-β-morpholino 66.06, 67.48 δ; **4a**, C-α 50.05 δ; C-β 66.62 δ). Compound **4e** showed a mass spectrum which was identical with that of **4d** and a carbonyl absorption in the IR spectrum at slightly lower frequency (1740 cm^{-1}). The *S**-stereochemistry at C-5 was inferred from the ^{13}C-NMR shift at lower field ($\Delta\delta$ = +7 ppm) of the methylene bridge carbon in **4e** compared to **4b, d**: with the *trans* arrangement of the phenyl groups of a 2*S**, 5*S**-stereochemistry, the phenyl at C-5 strongly deshields on the whole the CH_2 group, while H-5 probably feels yet another effect, since it shows a relative shielding of about −0.5 ppm.

DISCUSSION

The cyclopentadienone derivatives **2a, b** showed good reactivity with the methylene-v-triazolines **1**. On the basis of FMO theory, this cycloaddition reaction can be rationalized in principle as a "neutral"

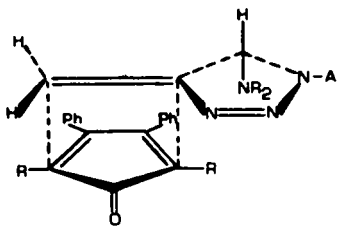


Fig. 1.

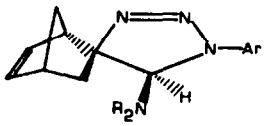
one since the $LUMO_{diene}-HOMO_{dienophile}$ and the $LUMO_{dienophile}-HOMO_{diene}$ energy gaps are nearly the same. This conclusion is supported by considering for the diene the values reported by Harano *et al.*[9] and estimating the corresponding numerical values for the dienophile—for which no exact calculations are available at present—on the basis of its general chemical behaviour which parallels that of an alkene bearing a moderately electron-withdrawing substituent. This view is supported by a spectroscopic study.[10]

The stereoselectivity of the above cycloaddition reaction is high since only one product is formed in detectable amounts. Figure 1 shows the transition state which should be involved in the process. Accordingly, the dienone approaches the methylene-v-triazoline from the diastereotopic side bearing the amino group, i.e. from the more crowded side. This is at first sight inconsistent with the behaviour of cyclopentadiene with the same substrates **1**. In that case only cycloadducts **5** derived from the addition to the less hindered side were formed.[1] However, it must be pointed out, that in the present reaction favorable secondary interactions between the dienone system and the basic amino substituent may play an important part.

Another interesting difference among cycloadducts **3** and their simpler analogues **5** is the greater thermal unstability of the former, which are easily isomerized even at room temperature to **4**. Instead **5** becomes thermally labile only at higher temperatures and when heated, undergoes cleavage of the triazoline ring and nitrogen elimination affording 5-norbornene-2-carboxamidines.[1] Three main facts may be responsible for the behaviour of **3**, (i) a greater strain of the 7-oxonorbornene ring resulting both from the crowding of the bulky phenyl substituents and the presence of the carbonyl bridge;† (ii) the different configuration about the C-4′—C-5′ bond and (iii) the electronic effect of the C-7 carbonyl group β to the spiranic carbon. The reaction can be interpreted as a base-catalyzed elimination as depicted in Scheme 2. Although this reaction apparently occurs without added catalyst the basic character of the reactants themselves should not be overlooked. The driving force of this rearrangement should be the relieving of the ring strain and the very high stability of the aromatic triazole product. According to the suggested mechanism the presence of the carbonyl group should be critical. To check this, the spiranic compound **8** was prepared by reaction of 4-nitrophenylazide with morpholine and the aldehyde **6**, via the enamine **7**.‡ This cycloadduct was found to be quite stable in solution, even for long periods.

† This feature is also evidenced by crystallographic studies[7] on **5** and stereoisomers of **3**.

‡ We were not able to obtain **8** by cycloaddition of 1,2,3,4-tetraphenylcyclopentadiene to **1a** because it did not react at an appreciable rate.



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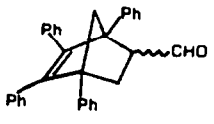

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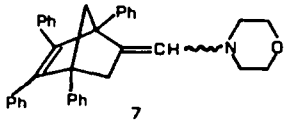

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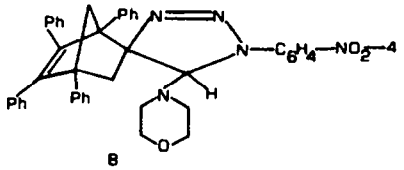


8

EXPERIMENTAL

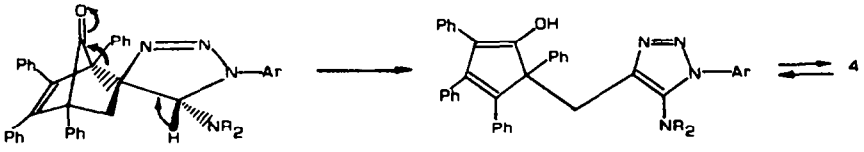
M.ps are not corrected and were taken with a Tottoli instrument. ^{1}H-NMR spectra were recorded on Varian 360 A and XL-200 spectrometers at 60 and 200 MHz, respectively (TMS as internal standard). ^{13}C-NMR spectra were obtained at 50.3 MHz on a Varian XL-200 instrument. Chemical shifts are given in ppm from TMS. MS were obtained on a Varian MAT-311-A instrument by using the direct inlet technique (probe temp 130–160°, electron energy 70 eV). High-resolution mass measurements were made on the same instrument at a resolution of 10,000 by using the peak matching technique and perfluorokerosine as reference compound. IR spectra were recorded with a 197 Perkin–Elmer spectrophotometer (nujol mull). Column chromatography was run on silica gel with the eluent indicated and ready-to-use silica gel plates were employed for TLC.

Materials. The methylene-v-triazolines **1a–c** were prepared as described previously.[10,11] Tetraphenylcyclopentadienone was a commercial product and 2,5-dimethyl-3,4-diphenyl-cyclopentadiene-1-one was prepared according to the literature.[12] The preparation of 1,2,3,4-tetraphenyl-cyclopentadiene is also known.[13]

Reaction of **1a** *and* **2a.** The methylene-v-triazoline **1a** (4 g, 13.8 mmol) was dissolved in anhyd CH_2Cl_2 (60 ml). To this soln **2a** (5.3 g, 13.8 mmol) dissolved in CH_2Cl_2 (20 ml) was added at room temp. The mixture was kept at 5° for 72 hr and occasionally stirred. The solvent was then evaporated under reduced pressure and the residue was directly chromatographed on a silica gel column (400 g) using CH_2Cl_2–AcOEt, 95 : 5 as eluent. From the main fractions pure **3a** (2.25 g), pure **4a** (1.6 g) and a mixture of **3a** and **4a** (2.7 g) were isolated. This mixture was chromatographed a second time to obtain another crop of pure **3a** (0.9 g) and **4a** (1.2 g), respectively. Product **3a** was purified by dissolving in CH_2Cl_2 at room temp and precipitation with n-pentane, affording 2.8 g (30% yield), m.p. 145°, dec. (Found: C, 74.55; H, 5.15; N, 10.15. $C_{42}H_{35}N_5O_4$ requires: C, 74.85; H, 5.25; N, 10.4%.) IR: 1780 cm^{-1} (C=O). ^{1}H-NMR δ: 3.01, 3.87 (dd, J = −12.5 Hz, 2H, CH_2-6), 4.57 (s, 1H, H-5'). ^{13}C-NMR δ: 32.12 (C-6), 45.36, 53.21 (C—α-morpholino), 66.06, 67.48 (C—β-morpholino), 78.21 (C-5'), 92.20 (C-4'), 198.50 (C-7). MS: *m/z* 673 (0.2, $M^{+\cdot}$), 384 (27), 356 (24), 289 (3), 276 (10), 178 (100), 176 (25), 152 (15), 129 (12), 105 (13), 86 (18). Product **4a** was purified by dissolving it in CH_2Cl_2 and precipitation with n-pentane, yielding 2.45 g (26.4% yield), m.p. 210–211°, dec. (Found: C, 67.8; H, 4.95; N, 9.25. $C_{42}H_{35}N_5O_4 \cdot CH_2Cl_2$ requires: C, 68.05; H, 4.9; N, 9.1%.) Several solvents can be trapped in the crystal lattice of **4a**, e.g. THF and MeCN. IR: 1747 cm^{-1} (C=O). ^{1}H-NMR δ: 3.20, 4.08 (dd, J = −15.0 Hz, 2H, CH_2), 5.53 (s, 1H, H-5). ^{13}C-NMR δ: 30.34 (CH_2), 50.05 (C—α-morpholino), 61.78 (C-5), 65.27 (C-2), 66.62 (C—β-morpholino), 212.98 (C-1). MS: *m/z* 673 (12, $M^{+\cdot}$), 400 (8), 384 (33), 356 (23), 289 (7), 276 (11), 260 (7), 214 (14), 178 (100), 152 (16), 112 (81).

Reaction of **1b** *and* **2a.** The dienone **2a** (2.1 g, 5.5 mmol) and the v-triazoline **1b** (1.5 g, 5.5 mmol) were dissolved in anhyd C_6H_6 (80 ml). The mixture was stirred at room temp for 3 hr and then kept at 0° with occasional shaking. After 6 hr a small amount of precipitate began to separate (**3b**). After 24 hr at 0° the mixture was evaporated to 25 ml and the precipitate was filtered with suction. The solid was washed with diisopropyl ether and n-pentane affording pure **3b**, m.p. 157–158°, dec. (1.7 g, 47% yield). (Found: C, 76.3; H, 5.5; N, 10.4. $C_{42}H_{35}N_5O_3$ requires: C, 76.7; H, 5.35; N, 10.65%.) IR: 1775 cm^{-1} (C=O). ^{1}H-NMR δ: 2.99, 3.50 (dd, J = −12.5 Hz, 2H, CH_2-6), 4.89 (s, 1H, H-5'). ^{13}C-NMR δ: 24.56 (C—β-pyrrolidino), 32.47 (C-6), 74.20 (C-5'), 91.71 (C-4), 198.28 (C-7). MS: *m/z* 657 (0.03, $M^{+\cdot}$), 384 (41), 356 (24), 276 (8), 273 (7), 178 (100), 176 (18), 152 (12), 129 (22), 108 (26), 70 (38). In the mother liquors, **4b** was identified on TLC by comparison with an authentic sample prepared from pure **3b** (see below).

Rearrangement of **3b** *to* **4b.** The spiranic cycloadduct **3b** (0.5 g, 0.76 mmol) was dissolved in $CHCl_3$ (40 ml) and kept at room temp for a week until practically complete transformation of the starting material was achieved (TLC). The mixture was evaporated to dryness and the residue was chromatographed on a silica gel column with CH_2Cl_2 as eluent. The main fraction was evaporated and the residue was purified by dissolving in CH_2Cl_2 and reprecipitating with n-pentane. Pure **4b** (0.12 g, 24% yield) was collected, m.p. 209–213°. (Found: C, 69.8; H, 5.25; N, 9.7. $C_{42}H_{35}N_5O_3 \cdot CH_2Cl_2$ requires: C, 69.7; H, 5.15; N, 9.45%.) IR: 1750 cm^{-1} (C=O).



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Scheme 2.

^{1}H-NMR δ: 3.11, 4.01 (dd, J = −15.0 Hz, 2H, CH_2), 5.47 (s, 1H, H-5). ^{13}C-NMR δ: 25.29 (C—β-pyrrolidino), 30.47 (CH_2), 50.63 (C—α-pyrrolidino), 61.82 (C-5), 65.57 (C-2), 212.43 (C-1). MS: *m/z* 657 (9, $M^{+\cdot}$), 400 (5), 384 (11), 356 (8), 272 (19), 244 (9), 197 (11), 178 (45), 169 (25), 105 (32), 96 (100).

Reaction of **1a** *and* **2b**. A CH_2Cl_2 soln (60 ml) of triazoline **1a** (2.89 g, 10 mmol) was mixed at room temp with a CH_2Cl_2 soln (60 ml) of the dimerization product of **2b** (3.12 g, 6 mmol). The mixture was kept at 5° for 90 hr. The solvent was evaporated to dryness and the residue was chromatographed on a silica gel column with CH_2Cl_2–AcOEt, 95:5, as eluent. Two main fractions (i) and (ii) were obtained. Fraction (i) afforded on evaporation nearly pure **3c** (0.6 g, 18.2% yield) and fraction (ii) was an almost equimolar mixture of **3c** and **4c**. Compound **3c** was purified by dissolving in anhyd C_6H_6 and adding n-pentane, m.p. 139–141°, dec. (Found: C, 69.55; H, 6.1; N, 12.3. $C_{32}H_{31}N_5O_4$ requires: C, 69.95; H, 5.7; N, 12.75%.) IR: 1770 cm^{-1} (C=O). ^{1}H-NMR δ: 0.87, 1.38 (s, 6H, CH_3), 2.49, 2.75 (dd, J = −13.0 Hz, 2H, CH_2-6), 4.80 (s, 1H, H-5'). ^{13}C-NMR δ: 7.28 (CH_3-1), 12.14 (CH_3-4), 37.40 (C-6), 44.97, 53.23 (C—α-morpholino), 65.69, 67.44 (C—β-morpholino), 77.12 (C-5'), 88.63 (C-4'). MS: *m/z* 549 (0.7, $M^{+\cdot}$), 289 (10), 260 (88), 245 (39), 232 (67), 215 (49), 202 (55), 189 (32), 178 (45), 116 (100), 115 (89), 87 (98). Fraction (ii) was used to prepare pure **4c** as described below.

Rearrangement of **3c** *to* **4c**. The mixture of **3c** and **4c** (0.4 g, 0.7 mmol) obtained from the reaction of **1a** and **2b** was dissolved in MeCN (20 ml) and refluxed for 5 hr. The solvent was then evaporated and the residue was chromatographed on a silica gel column using AcOEt–C_6H_6, 1:9, as eluent. The main fraction containing **4c** was evaporated and the residue was recrystallized from EtOH affording pure **4c** (0.17 g, 44% yield), m.p. 185–186°. (Found: C, 69.9; H, 5.55; N, 12.5. $C_{32}H_{31}N_5O_4$ requires: C, 69.95; H, 5.7; N, 12.75%.) IR: 1738 cm^{-1} (C=O). ^{1}H-NMR δ: 1.25 (d, J = 8.0 Hz, 3H, CH_3-5), 1.62 (s, 3H, CH_3-2), 2.66, 3.16 (dd, J = −15.5 Hz, 2H, CH_2), 3.92 (q, J = 8.0 Hz, 1H, H-5). ^{13}C-NMR δ: 15.83 (CH_3-5), 27.01 (CH_3-2), 31.67 (CH_2), 49.70 (C-5), 50.24 (C—α-morpholino), 57.14 (C-2), 66.69 (C—β-morpholino). MS: *m/z* 549 (17, $M^{+\cdot}$), 288 (7), 261 (11), 260 (17), 232 (10), 214 (23), 213 (12), 203 (7), 157 (9), 112 (100), 91 (9).

Reaction of **1c** *and* **2a**. The v-triazoline **1c** (1.7 g, 6.2 mmol) was dissolved in anhyd C_6H_6 (40 ml) and the diene **2a** (2.38 g, 6.2 mmol) in C_6H_6 (40 ml) was added. The mixture was stirred at room temp for 2 hr and then kept at 0° for 48 hr. The mixture was then evaporated and the solid residue chromatographed on a silica gel column with C_6H_6–AcOEt, 7:3, as eluent. The main fraction containing both **4d** and **e** was evaporated and chromatographed on silica gel using CH_2Cl_2–AcOEt, 95:5, as eluent, affording two main fractions containing **4d** and **e**, respectively. Product **4d** was purified by dissolving in CH_2Cl_2 and adding n-pentane (2 g, 49% yield), m.p. 219–221°. (Found: C, 78.2; H, 5.9; N, 8.15. $C_{43}H_{38}N_4O_3$ requires: C, 78.4; H, 5.8; N, 8.5%.) IR: 1750 cm^{-1} (C=O). ^{1}H-NMR δ: 3.14, 4.02 (dd, J = −15.0 Hz, 2H, CH_2), 3.84 (s, 3H, OCH_3), 5.55 (s, 1H, H-5). ^{13}C-NMR δ: 28.59 (CH_2), 49.90 (C—α-morpholino), 55.50 (OCH_3), 61.48 (C-5), 66.90 (C—β-morpholino), 213.64 (C-1). MS: *m/z* 658 (49, $M^{+\cdot}$), 384 (6), 356 (4), 273 (28), 245 (51), 217 (14), 178 (17), 174 (20), 161 (37), 153 (17), 112 (100). Product **4e** was purified by dissolving in CH_2Cl_2 and adding n-pentane (90 mg, 2.2% yield), m.p. 170°, dec. (Found: C, 78.1; H, 5.95; N, 8.15. $C_{43}H_{38}N_4O_3$ requires: C, 78.4; H, 5.8; N, 8.5%.) IR: 1740 cm^{-1} (C=O). ^{1}H-NMR δ: 3.48, 3.86 (dd, J = −14.5 Hz, 2H, CH_2), 3.85 (s, 3H, OCH_3), 4.86 (s, 1H, H-5). ^{13}C-NMR δ: 36.70 (CH_2), 49.91 (C—α-morpholino), 55.25 (OCH_3), 59.61 (C-5), 62.23 (C-2), 66.74 (C—β-morpholino), 208.28 (C-1). MS: *m/z* 658 (50, $M^{+\cdot}$), 384 (11), 356 (7), 273 (44), 245 (68), 217 (18), 178 (28), 174 (25), 161 (45), 153 (19), 112 (100).

1,4,5,6 - *Tetraphenylbicyclo*[2.2.1]*hept* - 5 - *en* - 2 - *carboxaldehyde* **6**. 1,2,3,4-Tetraphenylcyclopentadiene (1.2 g, 3.24 mmol) was dissolved in acrolein (10 ml) and refluxed for 24 hr. The mixture was evaporated and the residue chromatographed on a silica gel column affording as a main fraction a mixture of the *endo* and *exo* isomers of **6** which were not separated. The mixture was purified by recrystallization from diisopropyl ether yielding pure **6** (0.9 g, 65% yield), m.p. 90–105°. (Found: C, 90.4; H, 6.3. $C_{32}H_{26}O$ requires: C, 90.15; H, 6.1%.) IR: 1710 cm^{-1} (C=O). ^{1}H-NMR δ: 1.9–2.95 (m, 4H, CH_2), 3.71–4.1 (m, 1H, CH), 6.4–7.7 (m, 20H, arom.), 9.4 and 9.85 (d, J = 4 Hz, 1H, CHO, *exo* + *endo*).

Reaction of **6** *with morpholine and 4-nitrophenylazide*. The aldehyde **6** (2.0 g, 4.7 mmol) was dissolved in anhyd C_6H_6 (10 ml). 4-Nitrophenylazide (0.77 g, 4.7 mmol) and morpholine (0.41 g, 4.7 mmol) were added to the soln and the mixture was stirred at room temp for 26 hr. The solvent was then evaporated and the residue chromatographed on a silica gel column using AcOEt–C_6H_6, 1:9, as eluent. The main fraction afforded nearly pure **8** which was purified by washing twice with diisopropyl ether, m.p. 159° (2.07 g, 67% yield). (Found: C, 76.35; H, 5.75; N, 10.6. $C_{42}H_{37}N_5O_3$ requires: C, 76.5; H, 5.6; N, 10.6%.)

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