Tetrahedron Vol 40, No 20, pp 4025 to 4032, 1984
Printed in the U.S.A.

0040-4020/84 $3.00 + .00
Pergamon Press Ltd

v-TRIAZOLINES. Part XXI.[1]
SPIRO[BICYCLO[2.2.1]HEPT-2-ENE[5.4']1',2',3'-TRIAZOLE]DERIVATIVES FROM CYCLOPENTADIENE AND 5-AMINO-4-METHYLENE-v-TRIAZOLINES

MARIA LUISA GELMI, DONATO POCAR, PASQUALINA TRIMARCO,* MARIELLA VALSECCHI

Istituto di Chimica Organica - Facoltà di Farmacia dell'Università,
Via Venezian 21, 20133 Milano, Italy

RICCARDO DESTRO

Dipartimento di Chimica Fisica ed Elettrochimica dell'Università,
Via Golgi 19, 20133 Milano, Italy

and

MARZIA BALLABIO

Farmitalia-C. Erba S.p.A., Ricerca e Sviluppo Chimico,
Via Dei Gracchi 35, 20146 Milano, Italy

(*Received in UK 4 June* 1984)

Abstract - 1R*, 4R*, 5S*, 5'S*-5'-Amino-1'-(4-nitrophenyl)-4',5'-dihydro-spiro[bicyclo[2.2.1]hept-2-ene[5.4']-1',2',3'-triazoles] 2 have been obtained both by [4 + 2]-cycloaddition of cyclopentadiene to 5-amino-4-methylene-1-(4-nitrophenyl)-4,5-dihydro-v-triazoles 1 and by [3 + 2]-cycloaddition of 4-nitrophenylazide to 5-aminomethylene-2-norbornenes 4. The configuration has been fully established by X-ray crystallographic analysis. The course of the cycloaddition and the thermal behaviour of 2 are discussed.

5-Amino-1-aryl-4-methylene-4,5-dihydro-v-triazoles have been extensively tested as reactive substrates in cycloaddition reactions of 1,3-dipoles to their exocyclic double bond.

In some instances they afforded stable cycloadducts, whereas in other cases the primary addition products rearranged quickly according to various pathways.[1-3]

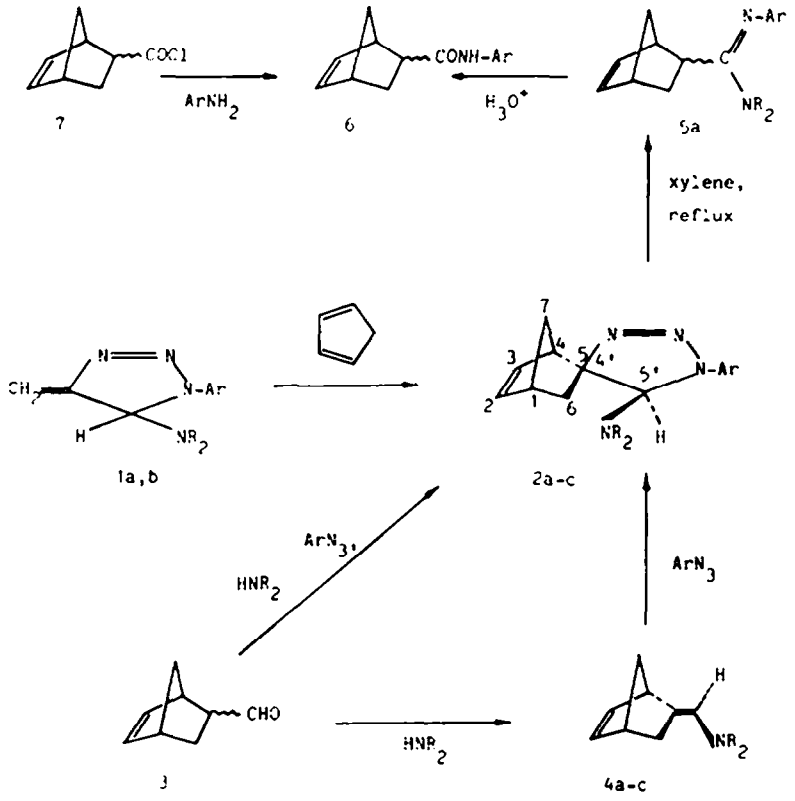
We were also interested in testing the reactivity of such substrates in [4 + 2]-cycloaddition reactions both as an access to new heterocyclic systems and as a part of our general research program on the reactivity of methylene azoles.

In this paper we report our results on the preparation and chemistry of some derivatives of the spiro[bicyclo[2.2.1]hept-2-ene[5.4']-1',2',3'-triazole] ring.

RESULTS

The triazolines 1a, b[4] were reacted with pure cyclopentadiene at 0°C for 70 h with a conversion of about 50%. Longer reaction times did not increase appreciably the yield, partly owing to the

dimerization of cyclopentadiene and partly owing to decomposition of the substrate which is unstable in solution. The crude reaction mixtures were analyzed both by TLC and ^{1}H-NMR and showed the formation of a single cycloadduct. The pure products 2a, b were isolated by chromatography and recrystallization.



	NR_2
a	morpholino
b	dimethylamino
c	pyrrolidino

Ar = C_6H_4-NO_2-4

The structure of the cycloadducts 2a, b was inferred from their spectroscopical data. In the MS the molecular ion is lacking and the largest fragment (m/z = M-28) corresponds to the typical loss of N_2 from the triazoline ring.[5] The ^{1}H-NMR spectrum is characterized by a sharp singlet at δ 4.34-4.37 (H-5') and by two multiplets at δ 6.16-6.20 and 6.58-6.67 (-CH=CH-). The ^{13}C-NMR spectrum was taken for compound 2a and showed the following significant signals: δ 80.09 (C-5') which is in good agreement with the shielding of C-5 in 5-amino-v-triazoline 1a;[4,6] δ 90.28 (spiranic carbon); δ 48.38 (C-6); δ 32.85 (C-7) (for the other signals see experimental). Clearly, the above data, though sufficient to establish the structure of compounds 2a, b did not allow to assign the configuration of the single diastereoisomer obtained. In fact, structure 2 is characterized by four asymmetric carbon atoms. Taking into account the restraint imposed by the methylene bridge in the norbornene moiety, four diastereomeric pairs are possible. To assign unequivocally the configuration to 2a an X-ray crystallographic study was undertaken, allowing to assess the configuration of 2a, b as 1R*, 4R*, 5S*, 5'S*.

The derived molecular model, and hence the position of the morpholino group relative to the nor-

bornene system, is illustrated in Figure 1, which shows also the atom numbering scheme adopted for the X-ray analysis.

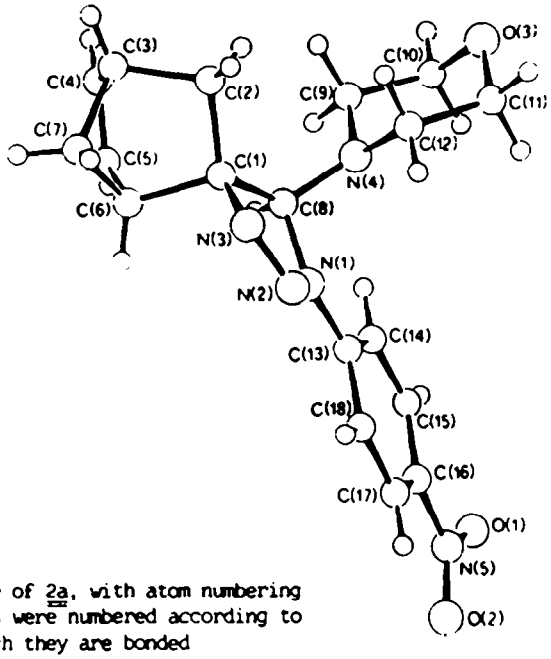


Figure 1. Perspective view of the molecule of 2a, with atom numbering scheme. The non-labelled H atoms were numbered according to the carbon atom to which they are bonded

Table 1. Final positional parameters for the non-H atoms of 2a, with estimated standard deviations in parentheses

Atom	x	y	z
C(1)	0.5423(3)	-0.0716(1)	0.6982(1)
C(2)	0.4875(4)	-0.0816(2)	0.6067(1)
C(3)	0.4911(5)	-0.1784(2)	0.5940(1)
C(4)	0.7082(5)	-0.2053(2)	0.6082(2)
C(5)	0.7531(4)	-0.1991(2)	0.6865(2)
C(6)	0.5690(4)	-0.1671(2)	0.7254(1)
C(7)	0.3989(5)	-0.2079(2)	0.6728(2)
C(8)	0.7230(3)	-0.0164(1)	0.7264(1)
C(9)	0.9407(3)	0.0423(2)	0.6227(1)
C(10)	1.0268(4)	0.1265(2)	0.5995(1)
C(11)	0.7264(4)	0.1956(1)	0.6255(1)
C(12)	0.6284(3)	0.1143(1)	0.6500(1)
C(13)	0.7521(3)	0.0500(1)	0.8677(1)
C(14)	0.9568(3)	0.0685(1)	0.8621(1)
C(15)	1.0659(3)	0.1014(1)	0.9274(1)
C(16)	0.9725(3)	0.1147(1)	0.9990(1)
C(17)	0.7686(3)	0.0981(1)	1.0057(1)
C(18)	0.6583(3)	0.0661(1)	0.9402(1)
N(1)	0.6447(2)	0.0120(1)	0.8034(1)
N(2)	0.4367(3)	0.0044(1)	0.8032(1)
N(3)	0.3704(3)	-0.0374(1)	0.7432(1)
N(4)	0.7838(2)	0.0559(1)	0.6800(1)
N(5)	1.0935(3)	0.1441(1)	1.0693(1)
O(1)	1.2701(2)	0.1659(1)	1.0602(1)
O(2)	1.0147(3)	0.1439(1)	1.1353(1)
O(3)	0.8742(2)	0.1814(1)	0.5668(1)

Table 2. Selected portion of the molecular geometry of 2a, with estimated standard deviations in parentheses

a) Bond lengths (Å)

C(1)-C(2)	1.548(3)	C(5)-C(6)	1.487(4)
C(1)-C(6)	1.582(3)	C(6)-C(7)	1.531(4)
C(1)-C(8)	1.533(3)	C(8)-N(1)	1.465(2)
C(1)-N(3)	1.485(3)	C(8)-N(4)	1.442(2)
C(2)-C(3)	1.546(4)	N(1)-N(2)	1.376(2)
C(3)-C(4)	1.501(5)	N(1)-C(13)	1.388(2)
C(3)-C(7)	1.535(4)	N(2)-N(3)	1.255(2)
C(4)-C(5)	1.320(4)		

b) Bond angles (deg)

C(2)-C(1)-C(6)	101.5(2)	C(5)-C(6)-C(1)	106.5(2)
C(2)-C(1)-C(8)	120.0(2)	C(5)-C(6)-C(7)	101.6(3)
C(2)-C(1)-N(3)	112.1(2)	C(1)-C(6)-C(7)	99.9(2)
C(6)-C(1)-C(8)	112.5(2)	C(3)-C(7)-C(6)	92.7(3)
C(6)-C(1)-N(3)	106.4(2)	C(1)-C(8)-N(1)	98.1(2)
C(8)-C(1)-N(3)	103.8(2)	C(1)-C(8)-N(4)	121.3(2)
C(1)-C(2)-C(3)	103.3(2)	N(1)-C(8)-N(4)	109.7(2)
C(2)-C(3)-C(4)	106.2(3)	C(8)-N(1)-C(13)	127.7(2)
C(2)-C(3)-C(7)	100.2(3)	C(8)-N(1)-N(2)	111.1(2)
C(4)-C(3)-C(7)	101.1(3)	C(13)-N(1)-N(2)	120.9(2)
C(3)-C(4)-C(5)	107.6(3)	N(1)-N(2)-N(3)	111.1(2)
C(4)-C(5)-C(6)	107.3(3)	N(2)-N(3)-C(1)	110.0(2)

c) Torsion angles (deg)

C(2)-C(1)-C(8)-N(4)	29.9(2)	C(14)-C(13)-N(1)-N(2)	-170.5(2)
C(6)-C(1)-C(8)-N(4)	149.1(2)	C(18)-C(13)-N(1)-C(8)	-173.9(2)
N(3)-C(1)-C(8)-N(1)	22.8(2)	C(18)-C(13)-N(1)-N(2)	12.7(2)
C(8)-C(1)-C(2)-C(3)	124.3(2)	C(1)-C(8)-N(1)-N(2)	-21.1(2)
N(3)-C(1)-C(2)-C(3)	-113.5(2)	C(8)-N(1)-N(2)-N(3)	10.9(2)
C(5)-C(6)-C(1)-C(8)	-61.7(3)	N(1)-N(2)-N(3)-C(1)	6.0(2)
C(5)-C(6)-C(1)-N(3)	-174.8(3)	C(8)-C(1)-N(3)-N(2)	-19.3(2)
C(14)-C(13)-N(1)-C(8)	3.0(2)		

d) Short intramolecular contacts (Å)

C(2)...C(12)	3.302(4)	H(2A)...H(9B)	2.25(3)
C(2)...H(12A)	2.76(2)	H(8)...H(9A)	2.17(2)
H(2A)...C(9)	2.87(2)	H(8)...C(5)	2.56(2)
H(2A)...H(12A)	2.36(3)		

As described below, the results of the X-ray investigation indicate that 2a qualifies as a highly strained molecule, whose geometry displays numerous severe distortions. Since a close inspection of the intermolecular contacts revealed that the crystal packing is rather loose, the geometrical and conformational features shown by the molecule in the solid state can be assumed as mainly, if not totally, dictated by intramolecular energy effects.

Steric hindrance between the morpholino ring and the methylene group at C(2) is substantially relieved by several angular deformations; among them, of particular note is the relevant enlargement -- with respect to the tetrahedral value - of the bond angles C(2)-C(1)-C(8) [120.0(2)°] and C(1)-C(8)-N(4) [121.3(2)°]. As a result, only few intramolecular contacts involving atoms of the methylene group at C(2) are less than the sum of van der Waals radii, and then only slightly (see Table 2). On the other hand, such deformations bring atom H(9A) into close contact with atom H(8), their distance being 0.23 Å shorter than a normal H...H contact. The same atom H(8) is involved in the strongest non-bonded interaction occurring in the molecule, namely H(8)...C(5), 2.56(2) Å. Such a

contact is prevented from being even more severe by the significant lengthening, to 1.582(3) Å, of the bond distance C(1)–C(6), 0.042 Å longer than the average value of the other four $C(sp^3)$–$C(sp^3)$ bonds of the norbornene moiety. (In this fragment of molecule, no other unusual values were found for interatomic distances and bond angles).

Bond distances and angles of the morpholino group are in agreement with the values found in other strained molecules,[7] where relief from overcrowding is achieved, among other factors, by a substantial flattening at the N atom, as in the present case.

In the triazoline ring, a torsion angle of 6° around the formally double bond N(2)–N(3) is observed, and individual atoms are displaced by up to 0.14 Å from the least-squares plane of the heterocycle. Its conformation can be defined[8] by a puckering amplitude q_2 of 0.24 Å and a phase angle ϕ_2 of -131°, close to the value (126°) appropriate to one of the T forms with twist axis through atom N(2). Indeed, atoms C(1) and C(8) lie on opposite sides of the plane defined by atoms N(1), N(2), and N(3), with displacements of -0.15 and 0.26 Å, respectively. By contrast, a pure envelope conformation is shown[9] by 1,4-dimethyl-5-ethyl-5-hydroxy-Δ^2-1,2,3-triazoline, where the torsion angle around the N(2)–N(3) bond is 0°. Clearly, the conformation of the five-membered ring is strongly dependent on the possible interactions of its side groups: for the highly symmetrically substituted triazoline moiety of syn-sesquinorbornene-phenyl azide, a planar conformation within experimental uncertainty was found[10] in two crystallographically independent molecules. The large difference between the two angles at N(1) external to the ring, 120.9(2)° for N(2)–N(1)–C(13) *vs.* 127.7(2)° for C(8)–N(1)–C(13), is partly dictated by the need of easing the interaction between atoms C(8) and H(14), that are 2.66(2) Å apart. Virtually identical values for these two angles were found[10] in the above mentioned molecules of syn-sesquinorbornene-phenyl azide, where the same interaction between a phenyl system and a triazoline ring occurs.

Since compounds of structure 2 should be also accessible by 1,3-dipolar cycloaddition of 4-nitrophenylazide to the enamines derived from 5-norbornene-2-carboxaldehyde 3, compounds 4a–c were prepared from an *exo*–*endo* mixture of 3 by a known procedure.[11] The pure enamine 4a was carefully analyzed by NMR and proved to be substantially a single isomer to which the *E*-configuration was tentatively assigned, mainly resting on the results of the cycloaddition reaction.

The enamines 4a–c reacted smoothly with 4-nitrophenylazide and afforded the cycloadducts 2a–c which were in all respects identical with the Diels–Alder adducts obtained from 1 and cyclopentadiene. The yields were good (80–90%). A trace amount of another cycloadduct with a different configuration at the chiral centers was detected both by TLC and ^{1}H-NMR in the crude reaction mixtures. However, this minor product could not be isolated in a pure condition, owing to its instability to chromatographic separations. As expected, compounds 2b, c were also obtained by direct reaction of the aldehyde 3 with dimethylamine or pyrrolidine, respectively, and 4-nitrophenylazide.[12] Compound 2a was readily decomposed by heating in boiling xylene for about 30 minutes into the corresponding amidine 5a consisting of a mixture of the *exo* and *endo* isomers. Their separation was not attempted and their identity was confirmed by acidic hydrolysis to the corresponding anilides 6 which were obtained independently from commercial 7.

DISCUSSION

Cyclopentadiene adds at a moderate rate to the exocyclic double bond of 1a, b. The reaction is slow and less reactive dienes (butadiene and 2,3-dimethylbutadiene) were found unreactive. This is in accord with the electronic situation of the substrates 1 in which the double bond should be described as an alkene bearing a moderately electron withdrawing substituent with small conjugative effect.[6] Ac-

cordingly, this cycloaddition should be classified as a normal Diels–Alder reaction ($HOMO_{diene}$-$LUMO_{dipolarophile}$-controlled).

The main feature of the addition reaction of cyclopentadiene to substrates 1 is its high stereoselectivity. This is confirmed by the formation of a single cycloadduct with the 1R*, 4R*, 5S*, 5'S* configuration. This may be partially rationalized by considering a transition state as represented in Figure 2 in which the diene approaches the dienophile from the less hindered face, thus affording a product in which the amino group lies cis to the CH_2-6 group of the norbornene ring.

Transition state for the reaction of 1 with cyclopentadiene

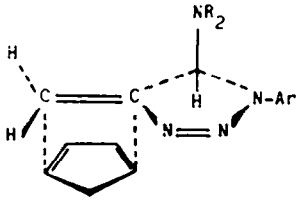


Figure 2

The relatively high bulkiness of the amino group probably makes this effect quite important. On the other hand we are not able to offer a satisfactory explanation of the experimental fact that only the transition state leading to the product in which the azo bridge is exo is operating.

Interestingly, the main product deriving from the cycloaddition of 4-nitrophenylazide to the enamines 4a–c has the same configuration as the product of the diene addition. Also in this case steric factors are probably determinant. As mentioned before, the enamines 4 consist of one geometrical isomer, with little, if not any, of the other isomer. According to molecular models, the E-isomer appears to be favoured by a lower steric hindrance and its predominance seems to be supported by the course of the 1,3-dipolar cycloaddition which is known[13] to be stereospecific. Also, the syn–anti behaviour of this cycloaddition is quite logical since the preference for the exo side by the reactants which attack the double bond of an alkylidene-norbornane or -norbornene structure has been well established.[14]

The known thermal instability of the v-triazoline ring is maintained in the spiranic structure 2, which undergoes decomposition to the amidine derivatives 5 on heating. It should be noted that this reaction is accompanied by a partial configurational inversion at the spiranic carbon in good agreement with the accepted mechanisms.[15]

EXPERIMENTAL

Melting points are uncorrected and were taken with a Tottoli instrument. ^{1}H-NMR spectra were recorded on a Varian 360 A and XL-200 spectrometers at 60 MHz and 200 MHz, respectively (Me_4Si as internal standard); ^{13}C-NMR spectra were obtained at 50.3 MHz on a Varian XL-200 instrument, chemical shifts being given in ppm from Me_4Si. Ready-to-use silica gel plates were employed for TLC.

5'-Morpholino-1'-(4-nitrophenyl)-4',5'-dihydro-spiro[bicyclo[2.2.1]hept-2-ene[5.4']-1',2',3'-triazole] 2a. – a) The morpholino-v-triazoline 1a (4.62 g, 16 mmol) was dissolved in anhyd THF (110 ml). To the solution freshly distilled cyclopentadiene (25 ml) was added. The reaction mixture was kept at 0–5° for 72 hr. The solution was then evaporated under reduced pressure leaving a yellow pasty residue (4.9 g) which was washed several times with cold diisopropyl ether. After drying the crude product was chromatographed on a silica gel column (AcOEt : C_6H_6, 3 : 2) yielding a main fraction containing pure 2a (TLC) which on evaporation yielded the product (1.65 g, 25% yield). An analytically pure sample was obtained by washing the crystals with diisopropyl ether or by recrystallization from MeCN/n-pentane, m.p. 128–130°, dec. (Found: C, 61.05; H, 6.05; N, 19.55. $C_{18}H_{21}N_5C_3$ requires C, 60.85; H, 5.95; N, 19.7%). MS: m/z 327 ($M-N_2$); ^{1}H-NMR (60 MHz, $CDCl_3$): δ 1.44–2.68 and 3.28–3.70 (2m, 14H, CH,CH_2 and morpholino; 4.34 (s, 1H, H-5'); 6.00–6.31 and 6.45–6.69 (2m, 2H,

-CH=CH-); 7.27-7.60 and 8.00-8.34 (2m, 4H, arom.); ^{13}C-NMR ($CDCl_3$), δ : 32.85 (C-7); 43.46 (C-'); 48.00 (very broad, CH_2N, morpholino); 48.38 (C-6); 53.44 (C-4); 66.63 (CH_2O, morpholino); 80.09 (C-5'); 90.28 (C-5(4')); 115.56 (C-2", C-6"); 125.42 (C-3", C-5"); 132.08 (C-3); 142.26 (C-1"); 143.62 (C-2); 146.38 (C-4").

b) The enamine 4a[7] (2.0 g, 10.4 mmol) was dissolved in anhyd C_6H_6 (16 ml) and 4-nitrophenylazide (1.71 g, 10.4 mmol) dissolved in C_6H_6 (15 ml) was added dropwise at room temp. The reaction mixture was stirred at room temp. A yellow precipitate began to separate after 30 min. The mixture was further stirred for 3 hr, then the precipitate was filtered and washed twice with diisopropylether, yielding pure 2a (2.77 g, 75% yield), m.p. 128-129°, dec. A further crop (0.4 g, 10% yield) was obtained by elaborating the mother liquor.

5'-Dimethylamino-1'-(4-nitrophenyl)-4',5'-dihydro-spiro[bicyclo[2.2.1]hept-2-ene[5.4']-1',2',3'-triazole] 2b. - a) The triazoline 1b (1.1 g, 4.4 mmol) was dissolved in anhyd THF (15 ml) and reacted with pure cyclopentadiene (5 ml). The reaction mixture was kept at 5° for 100 hr and evaporated under reduced pressure. The residue (1.5 g) was chromatographed on silica gel (AcOEt : C_6H_6, 1 : 4). The main fraction yielded on evaporation a yellow solid which was recrystallized from C_6H_6/n-pentane, affording pure 2b (0.56 g, 26% yield), m.p. 127-129°, dec. (Found: C, 61.1; H, 6.3; N, 22.0. $C_{16}H_{19}N_5O_2$ requires C, 61.4; H, 6.1; N, 22;35%). ^{1}H-NMR (200 MHz, $CDCl_3$); δ : 1.61-2.20 and 3.18 (m+s, 5+1H, norbornene ring); 2.39 and 2.18 (2s, 6H, $N(CH_3)_2$); 4.37 (s, 1H, H-5'); 6.18-6.22 and 6.56-6.60 (2m, 2H, -CH=CH-); 7.46 and 8.21 (2m, 4H, arom); ^{13}C-NMR ($CDCl_3$), δ : 32.86 (C-7); 39.8 (very broad, $N(CH_3)_2$; 43.42 (C-1); 48.37 (C-6); 53.30 (C-4); 80.31 (C-5'); 90.10 (C-5(4')); 115.32 (C-2", C-6"); 125.37 (C-3", C-5"); 132.38 (C-3); 142.19 (C-1"); 143.32 (C-2); 146.50 (C-4").

b) The enamine 4b (1.49 g, 10 mmol) was reacted with an equimolecular amount of 4-nitrophenylazide as described for 4a. A small of precipitate was formed during the reaction. This was separated (m.p. 166°) and identified (Found: C, 55.0; H, 5.0; N, 25.95. $C_{22}H_{23}N_9O_4$ requires C, 55.35; H, 4.85; N, 26.4%) as an addition product of two moles of 4-nitrophenylazide both to the enamine double bond and to the alkene double bond. The filtrate was evaporated and the yellow residue was recrystallized from C_6H_6/n-pentane yielding pure 2b (1.78 g, 57% yield), m.p. 128-129°, dec.

c) 5-Norbornene-2-carboxaldehyde 3 (2.0 g, 16.3 mmol) and 4-nitrophenylazide (2.7 g, 16.3 mmol) were dissolved in anhyd C_6H_6. A solution of dimethylamine (0.75 g, 16.5 mmol) in C_6H_6 (5 ml) was added dropwise at 10°. The reaction mixture was stirred at room temperature for 4 hr, then dried (Na_2SO_4) and evaporated. The residue was purified as described under b), yielding 2.19 g (70% yield) of pure 2b, m.p. 128-129°, dec.

5'-Pyrrolidino-1'-(4-nitrophenyl)-4',5'-dihydro-spiro[bicyclo[2.2.1]hept-2-ene[5.4']-1',2',3'-triazole] 2c. - a) The cycloaddition of 4-nitrophenylazide (1.86 g, 11 mmol) to the enamine 4c[7] (2.0 g, 11 mmol) was performed as described for 2b (method b). The reaction mixture was worked up after 60 min and the product 2c was obtained by direct addition of n-pentane. The precipitate was recrystallized from C_6H_6/n-pentane yielding pure 2c (1.0 g, 28% yield), m.p. 163-164°, dec. (Found: C, 63.9; H, 6.05; N, 20.3. $C_{18}H_{21}N_5O_2$ requires C, 63.7; H, 6.25; N, 20.65%). ^{1}H-NMR (60 MHz, $CDCl_3$); δ : 1.20-3.30 (m, 14H, norbornene ring and pyrrolidino; 4.67 (s, 1H, H-5'); 6.11-6.32 and 6.45-6.68 (2m, 2H, -CH=CH-); 7.35-7.55 and 8.10-8.35 (2m, 4H, arom).

b) 5-Norbornene-2-carboxaldehyde 3 (1.27 g, 10.4 mmol), pyrrolidine (0.74 g, 10.4 mmol) and 4-nitrophenylazide (1.7 g, 10.4 mmol) were reacted in C_6H_6 (25 ml) as described for 2b yielding 2c (1.87 g, 53% yield), m.p. 162-164°, dec.

5-Morpholino-methylene-2-norbornene 4a. - This compound was prepared as described.[7] Its ^{13}C-NMR spectrum was as follows: 31.68 (C-7); 42.49 (C-6); 49.45 (C-1); 50.07 (C-4); 51.22 (CH_2N, morpholino); 66.58 (CH_2O, morpholino); 118.85 (C-5); 129.72 (C-α); 134.41 (C-2); 134.72 (C-3).

5-Dimethylaminomethylene-2-norbornene 4b. - 5-Norbornene-2-carboxaldehyde 3 (6 g, 49 mmol) was dissolved in anhyd Et_2O (200 ml) containing K_2CO_3 (13.5 g, 98 mmol). Under vigorous stirring a solution of Me_2NH (6.6 g, 147 mmol) in Et_2O (50 ml) was added dropwise at -5°. The reaction mixture was stirred for 2 hr and filtered. The filtrate was evaporated and the oily residue distilled (N_2) under reduced pressure, using a Vigreux column. The enamine 4b was obtained as a pale yellow liquid (2.25 g, 31% yield), b.p. 60-62°/0.2 torr. ^{1}H-NMR (60 MHz, $CDCl_3$), δ : 1.2-3.3 (m, 6H, norbornene ring); 2.45 and 2.61 (2s, 6H, $N(CH_3)_2$); 5.70-6.30 (m, 3H, -CH=).

N-(4-Nitrophenyl)-N',N'-(3-oxapentamethylene)-5-norbornene-2-carboxamidine 5a. - The triazoline 2a (1.0 g, 2.8 mmol) was dissolved in xylene (50 ml) and refluxed for 30 min. The solvent was evaporated and the residue was recrystallized twice from EtOH yielding pure 5a (0.5 g, 58% yield), m.p. 137-139°. (Found: C, 66.05; H, 6.55; N, 12.85. $C_{18}H_{21}N_3O_3$ requires C, 66.05; H, 6.45; N, 12.85%). ^{1}H-NMR (60 MHz, $CDCl_3$), δ : 1.20-3.08 (m, 7H, norbornene ring); 3.05-3.35 and 3.36-3.70 (2m, 8H, morpholino); 6.04-6.10 (m, 2H, -CH=CH-); 6.50-8.20 (m, 4H, arom).

N-(4-Nitrophenyl)-norbornene-2-carboxamide 6. - a) The amidine 5a (0.5 g, 1.5 mmol) was dissolved in MeOH (10 ml) and diluted with H_2O (5 ml). Conc HCl (0.3 ml) was added and the mixture was refluxed for 30 min, then evaporated under reduced pressure. The aqueous residue was then extracted with $CHCl_3$. The organic layer was evaporated and the residue purified by column chromatography on silica gel (cyclohexane-AcOEt, 3 : 2), yielding pure 6 (0.41 g, 79% yield), m.p. 153-155°. (Found: C, 64.85; H, 5.35; N, 10.65. $C_{14}H_{14}N_2O_3$ requires C, 65.1; H, 5.45; N, 10.85%). ^{1}H-NMR (60 MHz, $CDCl_3$ +

DMSO, 1 : 1), δ : 1.20-3.50 (m, 7H, norbornene ring); 5.82-6.39 (m, 2H, -CH=CH-); 7.60-8.32 δ (m, 4H, arom); 9.15 (bs, 1H, exchangeable, NH); IR ($CHCl_3$), cm^{-1}: 3430 (NH); 1700 (CO).

b) 4-Nitroaniline (0.44 g, 3.2 mmol) was dissolved in pyridine (7 ml). The solution was heated at 100° and 5-norbornene-2-carbonyl chloride 7 (0.5 g, 3.2 mmol) was added dropwise. The solution was refluxed for 15 min and poured into H_2O, made acidic (pH = 2) with HCl and extracted with $CHCl_3$.

After evaporation the residue was purified as described under a), yielding 6, (0.6 g, 73% yield), m.p. 149-152°.

The products obtained under a) and b) are slightly different in their ratio of exo and endo isomers in the mixture and this accounts for the differences found in their melting points.

X-Ray analysis of 2a. - Crystals in form of yellowish prisms were obtained by slow evaporation of a THF solution of 2a.

Crystal Data. For $C_{18}H_{21}N_5O_3$: Mol wt 355.4; monoclinic, a = 6.590(2) Å, b = 15.805(3) Å, c = 16.541(3) Å, β = 92.53(1)°, U = 1721(1) $Å^3$, Z = 4, ρ_{obs} = 1.37 g cm^{-3} (flotation in a dilute K_2HgI_4 solution), ρ_{calcd} = 1.371 g cm^{-3}, F(000) = 752; space group $P2_1/c$ (C_{2h}^5, No. 14); MoKα radiation (graphite monochromator, λ = 0.7107 Å), μ(MoKα) = 0.9 cm^{-1}; room temp (293 ± 2K).

Data collection and reduction. A crystal of approximate dimensions 0.27 x 0.17 x 0.10 mm was accurately centred on an Enraf-Nonius CAD-4 diffractometer. The orientation matrix for data collection and the unit cell parameters reported above were obtained from a least-squares treatment of the automatically determined setting angles of 25 reflections with 2θ values in the range 15<2θ<25°. The space group $P2_1/c$ was indicated by the absences of reflections 0k0 with k odd and h0l with l odd.

The intensities of all accessible reflections with 2θ<50° were measured by the variable rate ω-scan technique. The periodic monitoring of three standard reflections showed no appreciable trend. Out of 3009 independent reflections measured, 618 having I<0 were given zero weight; all other reflections were assigned variances $\sigma^2(I)$ based on counting statistics plus the additional term $(0.03S)^2$, where S is the scan count. Diffraction data were corrected for Lorentz and polarization factors, but not for absorption.

The structure was solved by direct methods using the program MULTAN[16] and refined by least-squares techniques. The 21 H atoms were located in difference maps during the course of the refinement, which was by minimization of the quantity $\Sigma w(\Delta F)^2$, with weights $w = 4F_o^2/\sigma^2(F_o^2)$ for the 2391 reflections classified as observed. In the final cycles 320 parameters were simultaneously adjusted: coordinates and anisotropic temperature coefficients for 26 non-H atoms, coordinates and isotropic temperature factors for 21 H atoms, a scale factor, and a secondary extinction coefficient g. The final results are R = 0.063 and Rw = 0.041 for the 2391 reflections included in the refinement [R = 0.040 and Rw = 0.039 for the 1784 reflections with $F^2 > 2\sigma(F^2)$]. The goodness-of-fit, defined as $[\Sigma w(\Delta F)^2/(m-s)]^{1/2}$, where m is the number of observations and s the number of parameters, is 1.17. Atomic scattering factors were from ref[17]. Final atomic parameters are given in Table 1;* the final value of the extinction parameter g is 8.03(5) x 10^{-6}. A portion of the molecular geometry is reported in Table 2; a drawing of the molecule is shown in Figure 1.

Acknowledgment. This work has been supported by the Italian Ministero della Pubblica Istruzione.

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* Lists of coordinates and B's of the H atoms, thermal parameters for the non-H atoms, and calculated structure factors have been deposited with Cambridge Crystallographic Data Centre, Lensfield Road, Cambridge CB2 1EW, England