1,3-Dipolar Cycloadditions with the Keto- and Spirocyclopropane-Substituted Norbornenes Bicyclo[2.2.1]hept-5-en-2-one and Spiro[bicyclo[2.2.1]hept-5-ene-2,1′-cyclopropane]

Waldemar Adam*[a], Nestor Carballeira[a], Elisabeth Crämer[a], Vittorio Lucchini[b], Eva-Maria Peters[c], Karl Peters[c], and Hans Georg von Schnering[c]

Institut für Organische Chemie, Universität Würzburg[a],
Am Hubland, D-8700 Würzburg, FRG

Centro Meccanismi di Reazioni Organiche, Dipartimento di Chimica Organica, Università di Padova[b],
Via Marzolo 1, I-35131 Padova, Italy

Dipartimento di Scienze Ambientali, Università di Venezia[b],
Dorsoduro 2137, I-30123 Venezia, Italy

Max-Planck-Institut für Festkörperforschung[c],
Heisenbergstraße 1, D-7000 Stuttgart 80 (FRG)

Received October 21, 1986

The keto- and spirocyclopropane-substituted norbornenes **K** and **S**, respectively, were submitted to 1,3-dipolar cycloaddition with diazomethane (**1**), diphenyldiazomethane (**2**), phenyl azide (**3**), and benzonitrile oxide (**4**) leading in equal proportions to the corresponding regioisomers of the cycloadducts **K-2a,b** through **K-4a,b** and **S-1a,b** through **S-4a,b**. The keto and spirocyclopropane substituents perturb the π systems of these norbornenes too weakly to sense any significant regioselectivity for the 1,3-dipoles employed here. A combination of NOE differential ^{1}H-NMR spectroscopy and X-ray analysis was essential to assign the structures of these regioisomers.

1,3-Dipolare Cycloadditionen mit den keto- und spirocyclopropansubstituierten Norbornenen Bicyclo[2.2.1]hept-5-en-2-on und Spiro[bicyclo[2.2.1]hept-5-en-2,1′-cyclopropan]

Die keto- und spirocyclopropansubstituierten Norbornene **K** und **S** wurden mit Diazomethan (**1**), Diphenyldiazomethan (**2**), Phenylazid (**3**) und Benzonitriloxid (**4**) umgesetzt und führten zu den korrespondierenden regioisomeren 1,3-Cycloaddukten **K-2a,b** bis **K-4a,b** und **S-1a,b** bis **S-4a,b**, die in ca. 1:1-Verhältnissen vorlagen. Die Keto- bzw. Spirocyclopropansubstituenten beeinflussen die π-Systeme dieser Norbornene nur schwach, so daß die Regioselektivität in der Cycloaddition mit den hier untersuchten 1,3-Dipolen nicht nachweisbar war. Kombination von NOE- und ^{1}H-NMR-Spektroskopie sowie Röntgenstrukturanalyse war notwendig zur Strukturzuordnung der Regioisomeren.

The extensive experimental and theoretical studies on 1,3-dipolar cycloaddition permit making quite accurate predictions on the reactivity and regioselectivity of these reactions in terms of frontier orbital theory[1]. One of the most reactive dipolarophiles is norbornene; however, little has been reported on the regioselectivity of unsymmetrically substituted norbornenes, e.g. the keto derivative bicyclo[2.2.1]hept-5-en-2-one (**K**) or the spirocyclopropane derivative spiro[bicyclo[2.2.1]hept-5-ene-2,1′-cyclopropane] (**S**). For the keto norbornene **K**, 1,3-dipolar cycloaddition with diazomethane led to a mixture of the regioisomers **K-1a,b**[2]. The regioisomer **K-1a** was formed in ca. twofold preference, as expected for HOMO-controlled diazoalkanes with electron-deficient dipolarophiles[3].

It was, therefore, of interest to assess whether this weak perturbation on the electron density of the C=C bond of norbornene caused by the transannular keto and spirocyclopropane substituents could be sensed in terms of the regioselectivity in the cycloaddition of typical 1,3-dipoles such as diazomethane (**1**), diphenyldiazomethane (**2**), phenyl azide (**3**), and benzonitrile oxide (**4**) to these norbornenes. Presently we report the results of this investigation.

The expected pairs of regioisomers **a,b** for the norbornenes **K** and **S** with the 1,3-dipoles **1**–**4** are given in Scheme 1. The regioisomer designated by **a** has the X-terminal of the 1,3-dipole proximate to the transannular substituent, while for the **b** regioisomer it is remote. The structures **K-1a,b** derived from norbornene **K** and diazomethane, as stated in the beginning, have already been reported[2].

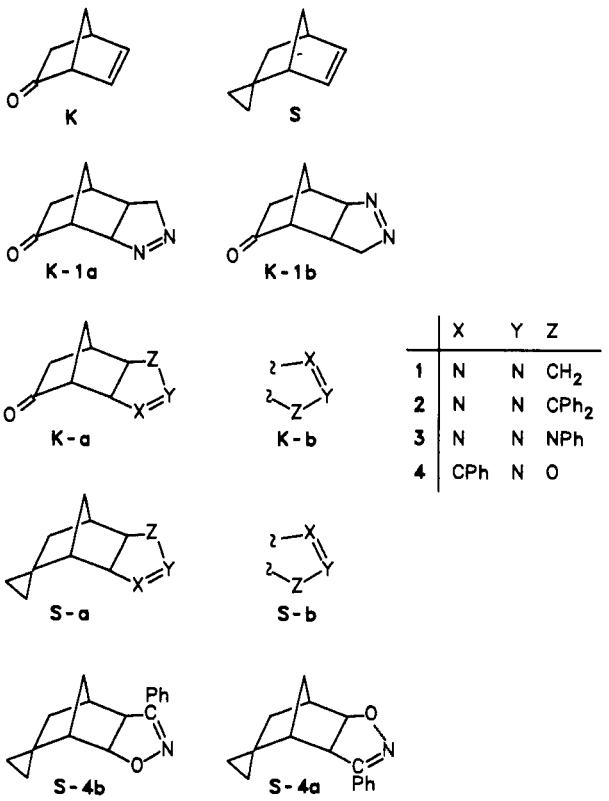
The 1,3-dipolar cycloaddition of the 1,3-dipoles **1**–**4** to the norbornenes **K** and **S** proceeded smoothly at ambient temperatures (ca. 20°C) in ethyl ether (for **1** and **4**) and carbon tetrachloride (for **2** and **3**), leading to the corresponding adducts in yields over 80%. Examination of the crude product mixtures in $CDCl_3$ by ^{1}H NMR (400 MHz) revealed that for each case both regioisomers were produced in approximately equal amounts within experimental error. This lack of regioselectivity in the formation of the cycloadducts **K-1a,b** through **K-4a,b** and **S-1a,b** through **S-4a,b** indicates that the unsymmetrical norbornenes **K** and **S** are non-discriminating dipolarophiles towards the 1,3-dipoles **1** through **4** employed here.

On the basis of the ^{1}H-NMR (Table 1) and ^{13}C-NMR (cf. Experimental) data alone it was not possible to assign the structures of the regioisomers; merely these spectral data enabled observing that both regioisomers were formed in equal proportion. For rigorous structural assignment it was necessary to employ a combination of NOE differential ^{1}H-NMR spectroscopy[4] and X-ray analysis.

In the case of the spirocyclopropane-substituted norbornene **S**, the diazomethane-derived regioisomers **S-1a,b** were

  0009–2940/87/0505–0695 $ 02.50/0

Scheme 1



	X	Y	Z
1	N	N	CH_2
2	N	N	CPh_2
3	N	N	NPh
4	CPh	N	O

obtained as an oil, which could not be separated by HPLC. However, with the help of NOE experiments, both isomers could be rigorously identified directly in the 1:1 mixture. In CCl_4 or in $CDCl_3$ the adducts tautomerized to give the corresponding hydrazones during the long runs. The NOE study was, therefore, carried out in C_6D_6. The spectral assignments (Table 1) were confirmed on the basis of vicinal and geminal interactions. The low-field resonances at δ = 4.61 and 4.40 were easily assigned to the norbornene protons next to the azo linkage. Irradiation at δ = 4.61 caused weak enhancement of some spirocyclopropane resonances, so that the multiplet was attributed to the 3-H in isomer **S-1a**. In the same experiment also the resonances of 4-H and 2-H at δ = 1.88 and 1.28 could be identified. Saturation of 2-H could not reveal the almost isochronous resonance of 1-H, but allowed the assignment of 6n-H at δ = 0.78. Irradiation in this region revealed 1-H at δ = 1.52. On the other hand, irradiation at δ = 4.40 resulted in appreciable enhancements of the broad doublet at δ = 2.75 and the doublet of doublets at δ = 0.98. Saturation of the former resonance caused enhancement of the latter one and of another doublet of doublets at δ = 1.29. The interaction pattern is consistent with the spatial arrangement of the 1-H, 2-H, 6n-H, and 6x-H protons proposed for the structure of **S-1b**.

The resonances of **S-1a** and **S-1b** in $CDCl_3$ were assigned by careful comparison of the signals of the mixture obtained in this solvent with those in C_6D_6.

For cycloadducts **K-2a,b** and **S-2a,b**, derived from the norbornenes **K** and **S** with diphenyldiazomethane (**2**) as 1,3-dipole, also NOE differential spectroscopy was definitive in assigning the structures of the regioisomers. Although in both cases 1:1 proportions of the regioisomers were obtained, fortunately a single pure isomer crystallized out of each mixture. For both pure regioisomers the most low-field nonaromatic resonance (a doublet) was assigned to the norbornane *endo* proton next to the azo linkage. Saturation of

Table 1. Proton chemical shifts[a] of the regioisomeric keto- and spirocyclopropane-substituted norbornene cycloadducts investigated by NOE spectroscopy[b,d]

Cyclo-adduct	1-H	2-H	3-H	4-H	6n-H	6x-H	7s-H	7a-H	Others
S-1a	2.08	1.98	4.90	2.06	1.20	1.59	0.62	1.45	4.05 (4n-H), 4.60 (4″x-H), 0.27–0.71 (cyclopropane)
S-1a[c]	1.52	1.28	4.61	1.88	0.78	1.21	0.48	1.08	3.66 (4″n-H), 4.11 (4″x-H), 0.05–0.35 (cyclopropane)
S-1b	2.93	4.75	2.18	1.21	1.41	1.71	0.62	1.45	3.98 (4″n-H), 4.57 (4″x-H), 0.27–0.71 (cyclopropane)
S-1b[c]	2.75	4.40	1.54	0.58	0.98	1.29	0.48	1.08	3.61 (4″n-H), 4.08 (4″x-H), 0.05–0.35 (cyclopropane)
K-2a	2.07	2.85	5.21	3.41	— 2.04, 1.97 —		0.98	1.29	7.27–7.41 (Ph)
S-2b	3.09	5.09	2.98	0.81	1.49	1.70	0.64	1.20	7.29–7.31 (Ph) 0.27–0.54 (cyclopropane)
K-4a	3.06	4.92	3.92	2.84	—— 1.79 ——		2.31 ——		7.72 (*o*-Ph), 7.42 (*m,p*-Ph)
K-4b	3.03	3.87	4.92	3.10	—— 1.79 ——		2.31 ——		7.74 (*o*-Ph), 7.42 (*m,p*-Ph)
S-4a	2.72	4.80	3.86	1.73	1.23	——— 1.62 ———			7.64 (*o*-Ph), 7.39 (*m,p*-Ph), 0.31–0.64 (cyclopropane)
S-4b	2.62	3.68	4.91	1.88	1.35	1.73	—— 1.62 ——		7.73 (*o*-Ph), 7.39 (*m,p*-Ph), 0.31–0.64 (cyclopropane)

[a] For ease of comparison, instead of using the IUPAC convention, the numbering refers to that of the norbornane skeleton with the bridgehead proton remote to the keto or spirocyclopropane substituents being 1-H and the proximate one 4-H, the six-membered ring methylene protons being 6n-H (*endo*) and 6x-H (*exo*) and the methylene bridge protons being 7s-H (*syn*) and 7a-H (*anti*) for all adducts. — [b] Unless otherwise stated, the spectra were taken at 200 MHz in $CDCl_3$ with $CHCl_3$ as internal standard. — [c] In [D_6]benzene with TMS as internal standard. — [d] For further ^{1}H-NMR data cf. Experimental.

this resonance at δ = 5.21 in **K-2** led to enhancement of the other *endo* proton doublet at δ = 2.85. Irradiation in this region enhanced the multiplet at about δ = 2.00 (two protons) and was attributed to the practically isochronous 6x-H and 6n-H protons. These and the other NOE results are consistent with structure **K-2a**. Once the structure of this regioisomer was known, the NMR resonances of the **K-2b** isomer could be extracted directly from the spectrum of the **K-2a,b** mixture (Table 1 and Experimental).

Analogous NOE experiments permitted us to elucidate the structure of the pure **S-2** isomer. On saturation of the low-field doublet at δ = 5.09, positive and negative enhancements were observed for the resonances at δ = 1.49 and 1.70, respectively, mutually split by a large coupling constant. The three multiplets were assigned to the quasi linearly arranged 2-H, 6n-H, and 6x-H protons in structure **S-2b**. All other interactions are consistent with this structure. The assignment of the NMR spectra for the other isomer **S-2a** (Experimental) was made on the isomeric mixture of **S-2a,b**.

X-ray analysis was helpful in assessing the structures of the cycloadducts **K-3a,b** and **S-3a,b**. Again, both pairs of regioisomers were obtained as 1:1 mixtures; but fortunately the **K-3a** and **S-3a** isomers preferentially crystallized. The X-ray structures are exhibited in Figure 1 for **K-3a** and for **S-3a** and the structural data in Tables 2, 3, and 4 and Tables 2, 5, and 6, respectively. Once this structural information and the ^{1}H-NMR data of the pure regioisomers **K-3a** and **S-3a** were available, the NMR data of the other regioisomers **K-3b** and **S-3b** could be extracted from the spectra on the respective isomeric mixtures (cf. Experimental).

Finally, the most cumbersome case was the pair of regioisomeric cycloadducts **K-4a,b** and **S-4a,b**. All attempts to separate the 1:1 mixtures proved futile; even analytical HPLC revealed insufficient separation of the respective regioisomers. A most lucky circumstance enabled obtaining the crystal structure of the regioisomer **S-4b** (cf. Figure 1 and Tables 2, 7, and 8), although the 1:1 mixture of the crystalline **S-4a,b** was submitted to X-ray analysis. Presumably, by chance a crystal of the pure regioisomer **S-4b** was picked out of the mixture. NMR spectra of this crystalline sample in $CDCl_3$ solution showed clearly that a 1:1 mixture of regioisomers **S-4a,b** was on hand.

NOE analysis was also in these cases essential for the assignment of the majority of the resonances to the individual regioisomers. In the case of the **K-4a,b** pair, the corresponding signals of the two isomers show considerable overlapping, which prevented assigning the 6-H and 7-H resonances with certainity. As a further consequence of this, the bridgehead signals of 1-H and 4-H could not be recognized by perturbations in the 6-H region, but rather from the fact that couplings with the 6-H protons broaden the 1-H singlet compared to the 4-H singlet. Irradiation of the *endo* protons next to the iminoether linkage, which resonate isochronously at δ = 4.92 ppm, singled out the sharp 4-H singlet at δ = 3.10 for **K-4b** and the broad 1-H singlet at δ = 3.06 for **K-4a**. Saturation of the other broad singlet at δ = 3.03, attributed to the 1-H proton in **K-4b**, revealed the 2-H resonance at δ = 3.87 of **K-4b**, while saturation of the remaining sharp singlet at δ = 2.84 for **K-4a** enhanced the 3-H resonance at δ = 3.92 of **K-4a**.

As for the regioisomeric mixture **S-4a,b**, the *endo* protons next to the iminoether group were assigned to the most low-

Table 2. X-ray operations and results of the cycloadducts **K-3a**, **S-3a**, and **S-4b**

Compound	**K-3a**	**S-3a**	**S-4b**
Empirical formula	$C_{13}H_{13}N_3O$	$C_{15}H_{17}N_3$	$C_{16}H_{17}NO$
Crystal size [mm]	0.6 × 0.6 × 0.3	0.6 × 0.6 × 0.3	1.0 × 1.2 × 0.15
No. of measd. intensities	7629	2361	2897
No. of obsd. reflections	6753	2256	2514
R_{aniso}	0.048	0.046	0.055
Space group (no.)	$P\bar{1}$(2)	$P\bar{1}$(2)	$P\bar{1}$(2)
a [pm]	1202.7(2)	981.0(2)	986.0(7)
b [pm]	1860.6(2)	1104.1(2)	1101.6(20)
c [pm]	1085.9(3)	660.5(2)	659.7(9)
α [deg]	107.26(2)	94.20(2)	95.20(12)
β [deg]	90.44(2)	82.67(2)	82.39(9)
γ [deg]	100.66(2)	115.9(2)	116.07(11)
No. of formular units per cell	8	2	2
Calcd. density [g·cm^{-3}]	1.327	1.251	1.246

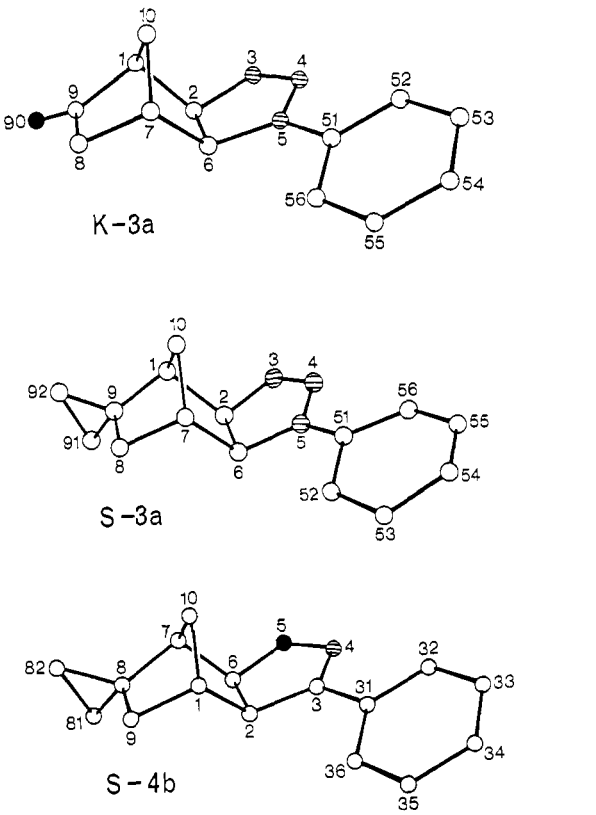


Figure 1. Perspective drawings of the crystal structures of the cycloadducts **K-3a**, **S-3a**, and **S-4b**; the numbering of the atoms corresponds to that in Tables 2–8; solid circles are oxygens, hatched circles are nitrogens, and open circles are carbons

Table 3. Positional (× 10^4) and thermal [pm^2 10^{-1}] parameters of **K-3a** for four independent molecules[a]

Atom	x	y	z	U_{eq}	Atom	x	y	z	U_{eq}
Molecule I					**Molecule III**				
C(1)	587(2)	3676(1)	1784(2)	44(1)	C(1)	4329(2)	1246(1)	-1908(2)	46(1)
C(2)	897(2)	4533(1)	2570(2)	42(1)	C(2)	4046(2)	383(1)	-2035(2)	46(1)
N(3)	118(1)	4976(1)	2195(2)	54(1)	N(3)	4833(2)	-41(1)	-2867(2)	59(1)
N(4)	639(1)	5421(1)	1619(2)	55(1)	N(4)	4307(2)	-484(1)	-3904(2)	58(1)
N(5)	1750(1)	5370(1)	1514(2)	51(1)	N(5)	3190(1)	-450(1)	-3956(2)	50(1)
C(6)	2057(2)	4813(1)	2100(2)	41(1)	C(6)	2885(2)	99(1)	-2795(2)	42(1)
C(7)	2300(2)	4083(1)	1118(2)	46(1)	C(7)	2621(2)	829(1)	-3023(2)	49(1)
C(8)	2554(2)	3554(1)	1887(2)	54(1)	C(8)	2355(2)	1338(1)	-1710(2)	53(1)
C(9)	1406(2)	3310(1)	2357(2)	46(1)	C(9)	3500(2)	1584(1)	-975(2)	47(1)
C(10)	1106(2)	3679(1)	503(2)	50(1)	C(10)	3803(2)	1254(1)	-3191(2)	55(1)
C(51)	2472(2)	5848(1)	945(2)	41(1)	C(51)	2462(2)	-926(1)	-5014(2)	47(1)
C(52)	2036(2)	6273(1)	274(2)	52(1)	C(52)	2885(2)	-1328(1)	-6141(2)	58(1)
C(53)	2757(2)	6733(1)	-285(2)	59(1)	C(53)	2151(3)	-1787(2)	-7167(2)	68(1)
C(54)	3909(2)	6782(1)	-191(2)	58(1)	C(54)	1001(3)	-1854(2)	-7101(2)	69(1)
C(55)	4340(2)	6363(1)	486(3)	61(1)	C(55)	581(2)	-1454(2)	-5989(3)	67(1)
C(56)	3631(2)	5892(1)	1049(2)	55(1)	C(56)	1300(2)	-989(1)	-4947(2)	56(1)
O(90)	1181(1)	2916(1)	3063(2)	66(1)	O(90)	3711(1)	1961(1)	150(2)	59(1)
Molecule II					**Molecule IV**				
C(1)	-1314(2)	-1187(1)	-3027(2)	47(1)	C(1)	3703(2)	3827(1)	-3203(2)	47(1)
C(2)	-1197(2)	-341(1)	-2993(2)	45(1)	C(2)	3846(2)	4679(1)	-2397(2)	47(1)
N(3)	-164(2)	137(1)	-2206(2)	56(1)	N(3)	4872(2)	5149(1)	-2721(2)	59(1)
N(4)	-426(1)	591(1)	-1188(2)	55(1)	N(4)	4594(1)	5594(1)	-3292(2)	56(1)
N(5)	-1565(1)	522(1)	-1115(2)	44(1)	N(5)	3454(1)	5529(1)	-3425(2)	49(1)
C(6)	-2196(2)	-83(1)	-2216(2)	41(1)	C(6)	2837(2)	4937(1)	-2913(2)	42(1)
C(7)	-2768(2)	-803(1)	-1874(2)	45(1)	C(7)	2238(2)	4210(1)	-3961(2)	44(1)
C(8)	-3361(2)	-1382(1)	-3123(2)	56(1)	C(8)	1661(2)	3645(1)	-3274(2)	41(1)
C(9)	-2360(2)	-1589(1)	-3904(2)	52(1)	C(9)	2665(2)	3443(1)	-2699(2)	48(1)
C(10)	-1745(2)	-1158(1)	-1695(2)	53(1)	C(10)	3238(2)	3843(1)	-4507(2)	48(1)
C(51)	-2017(2)	963(1)	-27(2)	42(1)	C(51)	2978(2)	5954(1)	-4090(2)	43(1)
C(52)	-1323(2)	1420(1)	1057(2)	54(1)	C(52)	3647(2)	6385(1)	-4753(2)	59(1)
C(53)	-1794(2)	1833(1)	2119(2)	63(1)	C(53)	3143(2)	6783(1)	-5418(2)	73(1)
C(54)	-2952(2)	1804(1)	2126(2)	66(1)	C(54)	1993(2)	6762(1)	-5427(2)	71(1)
C(55)	-3631(2)	1365(1)	1049(2)	60(1)	C(55)	1341(2)	6340(1)	-4759(2)	62(1)
C(56)	-3175(2)	941(1)	-29(2)	48(1)	C(56)	1824(2)	5935(1)	-4085(2)	51(1)
O(90)	-2404(2)	-1977(1)	-5021(2)	68(1)	O(90)	2653(2)	3078(1)	-1944(2)	70(1)

[a] U_{ij} is defined for $\exp[-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{12}hka^*b^*)]$; equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor; the standard deviations are given in parentheses; for numbering of the atoms cf. Figure 1

field nonaromatic resonances. Irradiation of the doublet at δ = 4.91 enhanced a multiplet in the spirocyclopropane region. This doublet, therefore, pertains to the **S-4b** regioisomer. Other protons revealed by this experiment were 4-H at δ = 1.88 and 2-H at δ = 3.68. On saturation of the latter, the resonances of the 6n-H proton at δ = 1.35 and of the bridgehead 1-H proton at δ = 2.62 confirmed the structural assignment. The recognition of the resonances of

Table 4. Averaged bond lengths [pm] and angles [deg] for **K-3a** from four independent molecules; the standard deviations are given in parentheses. For numbering of the atoms cf. Figure 1

C(1) - C(2)	154.3(1)	N(3) - N(4)	126.0(1)	C(6) - C(7)	153.7(1)	C(51) - C(52)	138.7(1)
C(1) - C(9)	151.1(1)	N(4) - N(5)	135.8(1)	C(7) - C(8)	153.3(1)	C(51) - C(56)	138.5(1)
C(1) - C(10)	153.0(1)	N(5) - C(6)	146.4(1)	C(7) - C(10)	153.5(1)	C(52) - C(53)	137.5(2)
C(2) - N(3)	148.3(1)	N(5) - C(51)	140.3(1)	C(8) - C(9)	151.3(1)	C(53) - C(54)	137.6(2)
C(2) - C(6)	154.3(1)			C(9) - O(90)	120.9(3)	C(54) - C(55)	137.2(2)
						C(55) - C(56)	138.4(2)

C(2) - C(1) - C(9)	103.7(1)	C(2) - C(6) - N(5)	99.7(1)	N(5) - C(51) - C(52)	121.0(1)
C(2) - C(1) - C(10)	101.4(1)	C(2) - C(6) - C(7)	103.3(1)	N(5) - C(51) - C(56)	119.6(1)
C(9) - C(1) - C(10)	101.6(1)	N(5) - C(6) - C(7)	113.8(1)	C(52) - C(51) - C(56)	119.5(1)
C(1) - C(2) - N(3)	111.2(1)	C(6) - C(7) - C(8)	107.0(1)	C(51) - C(52) - C(53)	119.7(1)
C(1) - C(2) - C(6)	103.7(1)	C(6) - C(7) - C(10)	101.8(1)	C(52) - C(53) - C(54)	121.2(1)
N(3) - C(2) - C(6)	105.3(1)	C(8) - C(7) - C(10)	101.4(1)	C(53) - C(54) - C(55)	119.1(1)
C(2) - N(3) - N(4)	110.2(1)	C(7) - C(8) - C(9)	102.1(1)	C(54) - C(55) - C(56)	120.9(1)
N(3) - N(4) - N(5)	112.5(1)	C(1) - C(9) - C(8)	106.2(1)	C(51) - C(56) - C(55)	119.8(1)
N(4) - N(5) - C(6)	112.2(1)	C(1) - C(9) - O(90)	126.8(1)		
N(4) - N(5) - C(51)	120.6(1)	C(8) - C(9) - O(90)	127.1(1)		
C(6) - N(5) - C(51)	127.0(1)	C(1) - C(10) - C(7)	94.9(1)		

Table 5. Bond lengths [pm] and angles [deg] for **S-3a**; the standard deviations are given in parentheses. For numbering of the atoms cf. Figure 1

C(1) - C(2)	152.9(3)	N(3) - N(4)	125.6(2)	C(7) - C(8)	154.3(2)	C(51) - C(52)	138.7(2)
C(1) - C(9)	151.9(2)	N(4) - N(5)	137.0(2)	C(7) - C(10)	152.2(2)	C(51) - C(56)	139.0(2)
C(1) - C(10)	152.6(3)	N(5) - C(6)	146.0(2)	C(8) - C(9)	153.1(2)	C(52) - C(53)	138.4(2)
C(2) - N(3)	148.3(2)	N(5) - C(51)	139.6(2)	C(9) - C(91)	149.4(3)	C(53) - C(54)	137.4(3)
C(2) - C(6)	154.2(2)	C(6) - C(7)	153.1(3)	C(9) - C(92)	148.9(2)	C(54) - C(55)	137.1(3)
				C(91)- C(92)	148.9(4)	C(55) - C(56)	138.0(3)

C(2) - C(1) - C(9)	107.1(2)	C(2) - C(6) - N(5)	100.1(1)	C(1) - C(10) - C(7)	94.8(2)
C(2) - C(1) - C(10)	101.5(1)	C(2) - C(6) - C(7)	103.2(1)	N(5) - C(51) - C(52)	119.6(1)
C(9) - C(1) - C(10)	100.9(2)	N(5) - C(6) - C(7)	113.4(2)	N(5) - C(51) - C(56)	121.2(2)
C(1) - C(2) - N(3)	112.5(2)	C(6) - C(7) - C(8)	106.4(2)	C(52) - C(51) - C(56)	119.2(1)
C(1) - C(2) - C(6)	103.3(2)	C(6) - C(7) - C(10)	101.9(1)	C(51) - C(52) - C(53)	119.8(2)
N(3) - C(2) - C(6)	104.8(1)	C(8) - C(7) - C(10)	102.3(1)	C(52) - C(53) - C(54)	121.0(2)
C(2) - N(3) - N(4)	111.0(1)	C(7) - C(8) - C(9)	101.7(1)	C(53) - C(54) - C(55)	119.1(2)
N(3) - N(4) - N(5)	111.9(1)	C(1) - C(9) - C(8)	105.2(1)	C(54) - C(55) - C(56)	121.1(2)
N(4) - N(5) - C(6)	112.2(1)	C(1) - C(9) - C(91)	122.1(2)	C(51) - C(56) - C(55)	119.8(2)
N(4) - N(5) - C(51)	120.7(1)	C(1) - C(9) - C(92)	121.3(1)	C(9) - C(91) - C(92)	59.9(1)
C(6) - N(5) - C(51)	127.1(1)	C(8) - C(9) - C(91)	122.9(2)	C(9) - C(92) - C(91)	60.2(1)
		C(8) - C(9) - C(92)	120.6(2)		
		C(91) - C(9) - C(92)	59.9(2)		

the **S-4a** regioisomer was complicated by the fact that it was present in the **S-4a, b** mixture as minor component. Irradiations of the *ortho* aromatic protons at δ = 7.64 and of a selected multiplet in the spirocyclopropane region led to the enhancement of the sharp 4-H singlet at δ = 1.73 in **S-4a**. Its saturation enhanced the 3-H doublet at δ = 3.86. The same doublet was affected by irradiation of the low-field 2-H resonance at δ = 4.80. This latter experiment also revealed the 6n-H resonance at δ = 1.23.

Table 6. Positional (× 10^4) and thermal [$pm^2 \cdot 10^{-1}$] parameters of **S-3a**. U_{eq} as in Table 3; the standard deviations are given in parentheses. For numbering of the atoms cf. Figure 1

Atom	x	y	z	U_{eq}
C(1)	4099(2)	-3393(2)	6384(3)	50(1)
C(2)	5786(2)	-3097(2)	6017(3)	50(1)
N(3)	6299(2)	-3198(2)	3826(2)	61(1)
N(4)	7203(2)	-2062(2)	3136(2)	61(1)
N(5)	7462(2)	-1065(1)	4604(2)	52(1)
C(6)	6606(2)	-1586(2)	6571(2)	46(1)
C(7)	5292(2)	-1189(2)	7156(3)	52(1)
C(8)	4525(2)	-1817(2)	9251(3)	59(1)
C(9)	3708(2)	-3313(2)	8675(3)	51(1)
C(10)	4137(2)	-2082(2)	5721(3)	61(1)
C(51)	8466(2)	269(2)	4155(3)	50(1)
C(52)	8897(2)	1221(2)	5727(3)	55(1)
C(53)	9878(2)	2547(2)	5287(3)	64(1)
C(54)	436(2)	2941(2)	3309(4)	71(1)
C(55)	18(3)	1995(2)	1761(3)	73(1)
C(56)	9036(2)	667(2)	2156(3)	63(1)
C(91)	3485(3)	-4411(2)	58(3)	65(1)
C(92)	2161(2)	-4169(2)	9677(3)	70(1)

Table 7. Positional (× 10^4) and thermal [$pm^2 \cdot 10^{-1}$] parameters of **S-4b**. U_{eq} as in Table 3; the standard deviations are given in parentheses; for numbering of the atoms cf. Figure 1

Atom	x	y	z	U_{eq}
C(1)	282(2)	3793(2)	7107(3)	51(1)
C(2)	1573(2)	3355(2)	6479(3)	46(1)
C(3)	2434(2)	3852(2)	4432(3)	49(1)
N(4)	2195(2)	2940(2)	3019(2)	59(1)
O(5)	1160(2)	1667(1)	3808(2)	60(1)
C(6)	718(2)	1836(2)	5971(3)	50(1)
C(7)	-953(2)	1564(2)	6366(3)	49(1)
C(8)	-1293(2)	1691(2)	8665(3)	49(1)
C(9)	-473(2)	3206(2)	9207(3)	57(1)
C(10)	-902(2)	2878(2)	5685(3)	59(1)
C(31)	3483(2)	5283(2)	4021(3)	51(1)
C(32)	4014(2)	5697(2)	2019(3)	63(1)
C(33)	5011(2)	7036(2)	1649(4)	73(1)
C(34)	5460(2)	7962(2)	3240(4)	70(1)
C(35)	4951(2)	7570(2)	5225(4)	65(1)
C(36)	3951(2)	6226(2)	5608(3)	56(1)
C(81)	-1495(2)	613(2)	64(3)	63(1)
C(82)	-2833(2)	848(2)	9722(3)	66(1)

Table 8. Bond lengths [pm] and angles [deg] for **S-4b**; the standard deviations are given in parentheses. For numbering of the atoms cf. Figure 1

C(1) - C(2)	154.5(3)	C(3) - N(4)	127.0(2)	C(7) - C(8)	151.7(2)	C(31) - C(32)	139.3(3)
C(1) - C(9)	153.9(2)	C(3) - C(31)	148.3(2)	C(7) - C(10)	153.3(3)	C(31) - C(36)	137.8(2)
C(1) - C(10)	152.9(2)	N(4) - O(5)	141.9(2)	C(8) - C(9)	153.2(2)	C(32) - C(33)	138.9(3)
C(2) - C(3)	150.5(2)	O(5) - C(6)	145.6(2)	C(8) - C(81)	149.8(3)	C(33) - C(34)	136.7(3)
C(2) - C(6)	153.5(2)	C(6) - C(7)	152.9(3)	C(8) - C(82)	150.1(2)	C(34) - C(35)	137.5(3)
				C(81) - C(82)	150.0(4)	C(35) - C(36)	139.5(2)
C(2) - C(1) - C(9)	106.9(2)	C(2) - C(6) - O(5)	105.3(1)	C(1) - C(9) - C(8)	101.9(1)		
C(2) - C(1) - C(10)	101.6(1)	C(2) - C(6) - C(7)	103.7(2)	C(1) - C(10) - C(7)	94.6(2)		
C(9) - C(1) - C(10)	102.0(1)	O(5) - C(6) - C(7)	111.6(1)	C(3) - C(31) - C(32)	120.5(2)		
C(1) - C(2) - C(3)	113.7(2)	C(6) - C(7) - C(8)	106.5(1)	C(3) - C(31) - C(36)	120.6(2)		
C(1) - C(2) - C(6)	103.2(1)	C(6) - C(7) - C(10)	101.7(1)	C(32) - C(31) - C(36)	118.8(2)		
C(3) - C(2) - C(6)	100.6(1)	C(8) - C(7) - C(10)	101.1(1)	C(31) - C(32) - C(33)	120.1(2)		
C(2) - C(3) - N(4)	114.8(1)	C(7) - C(8) - C(9)	105.3(1)	C(32) - C(33) - C(34)	120.4(2)		
C(2) - C(3) - C(31)	124.4(1)	C(7) - C(8) - C(81)	122.1(2)	C(33) - C(34) - C(35)	120.2(2)		
N(4) - C(3) - C(31)	120.8(1)	C(7) - C(8) - C(82)	121.1(1)	C(34) - C(35) - C(36)	119.7(2)		
C(3) - N/4) - O(5)	109.7(1)	C(9) - C(8) - C(81)	123.2(2)	C(31) - C(36) - C(35)	120.7(2)		
N(4) - O(5) - C(6)	109.5(1)	C(9) - C(8) - C(82)	120.2(2)	C(8) - C(81) - C(82)	60.1(1)		
		C(81) - C(8) - C(82)	60.0(1)	C(8) - C(82) - C(81)	59.9(1)		

We thank the *Deutsche Forschungsgemeinschaft*, the *Fonds der Chemischen Industrie* and the *Italian Consiglio Nazionale delle Ricerche* for generous financial support of this work. N. C. appreciates a travel grant from the *Fritz-Thyssen-Stiftung*. We are grateful to Dr. *G. Lange* (MS) and Dr. *D. Scheutzow* (NMR) for spectral services.

Experimental

UV spectra: Varian Cary 17. – IR spectra: Beckman Acculab 4. – ^{1}H-NMR spectra: Varian EM-390 (90 MHz), Bruker WP 200 S4 (200 MHz). – ^{13}C-NMR spectra: Bruker WM-400 (100 MHz); chemical shifts (δ values) relative to TMS or $CHCl_3$ for protons and $CDCl_3$ for carbons. – Combustion analyses: Run in-house.

Commercial reagents and solvents were purchased from standard chemical suppliers and used as such, if not mentioned otherwise. Known compounds were prepared according to literature procedures and purified to match the reported physical and spectral data. After aqueous workup, organic layers were dried with $MgSO_4$ or Na_2SO_4.

Nuclear Overhauser Spectroscopy of the Cycloadducts **S-1a,b**, **K-2a**, **S-2b**, **K-4a,b**, *and* **S-4a,b**: The NOE experiments were carried out with a Bruker WP 200 SY instrument. The samples (in $CDCl_3$ or C_6D_6) were freed from oxygen through sonication under N_2 gas purging. The usual procedure for gated irradiation experiments was modified[5] and the selected resonance was saturated by an 8-s cyclic perturbation of all lines with a 38–40-dB attenuation of a nominal 0.2-W decoupling power. The enhancements (in %) were obtained from the multiplier of the reference spectrum by bringing the observed multiplet to exact matching with the corresponding multiplet in the perturbed spectrum. Errors are ca. 0.3%. By careful choice of the multiplier, in most cases it was possible in the differential mode to single out a pure multiplet from a bunch of overlapping signals. The pertinent chemical shifts are given in Table 1. The NOE results are available on request from the author in the form of structural interaction diagrams.

X-ray Crystallography of the Cycloadducts **K-3a**, **S-3a**, *and* **S-4b**: The orientation matrix and the cell parameters were determined from transparent colorless crystals of given dimensions on a Syntex-P3 four-circle diffractometer. Measurement of intensities: ω-scan, 1° range, Mo-K_α, 2Θ maximum = 55°. All reflections with $F \geq 3\sigma(F)$ were applied for the structure determination. For the evaluation the SHELXTL[6] program system on an Eclipse S/250 was employed. All structures could be refined by anisotropic least-squares cycles to the given R values. The positions of the hydrogen atoms were calculated geometrically and considered isotropically in all refinements. The special X-ray operations and results are listed in Table 2, the positional and thermal parameters in Tables 3, 6, and 7, and the bond lengths and angles in Tables 4, 5, and 8, respectively, for the cycloadducts **K-3a**, **S-3a**, and **S-4b**. The perspective drawings of the crystal structures are shown in Figure 1.

Further details of the structure determination are deposited at the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2 (FRG). These data are available with quotation of the registry number CSD 52165, the authors, and the reference to this publication.

Cycloadducts **S-1a,b** *of Diazomethane* (**1**) *and Spironorbornene* **S**: A mixture of 5.00 g of KOH in 8 ml of water and 25 ml of ethanol was stirred at 65°C in a 50-ml flask, especially adapted for the preparation of diazomethane[7]. A solution of 21.5 g (100 mmol) of "Diazald" in 200 ml of ether was added dropwise into the 50-ml flask at such a rate that the distilling and dropping rate were equal (ca. 25 min). After all diazomethane had distilled (until colorless distillate), the yellow solution was cooled to 0°C, 2.00 g (16.7 mmol) of spiroolefin **S** in 10 ml of ether was added and stirred at 20°C for 3 d in the dark. Rotoevaporation of the solvent (30°C at 20 Torr) and kugelrohr distillation (95–100°C at 0.1 Torr) of the yellow-brown oil afforded 1.70 g (63%) of a ca. 1:1 mixture of **S-1a,b**.

Spiro[cyclopropane-1,9′-[3,4]diazatricyclo[5.2.1.0^{2,6}]dec[3]ene] (**S-1a**): ^{1}H NMR (C_6D_6, 400 MHz): δ = 0.0–0.4 (m; 2H, 2a-H, 3a-H), 0.40 (mc; 2H, 2s-H, 3s-H), 0.48 (br. dd, $J_{10s,10a}$ = 10.4 Hz, $J_{10s,8n}$ = 2.4 Hz; 1H, 10′s-H), 0.78 (dd, $J_{8n,8x}$ = 11.6 Hz, $J_{8n,10s}$ = 2.4 Hz; 1H, 8′n-H), 1.08 (ddd, $J_{10a,10s}$ = 10.4 Hz, $J_{10a,7}$ = $J_{10a,1}$ = 1.5 Hz; 1H, 10′a-H), 1.21 (dd, $J_{8x,8n}$ = 11.6 Hz, $J_{8x,7}$ = 4.3 Hz; 1H, 8′x-H), 1.28 (ddd, $J_{6,2}$ = 7.3 Hz, $J_{6,5x}$ = 3.7 Hz, $J_{6,5n}$ = 9.8 Hz; 1H, 6′-H), 1.52 (mc; 1H, 7′-H), 1.88 (br. s; 1H, 1′-H), 3.66 (ddd, $J_{5x,5n}$ = 18.2 Hz, $J_{5x,6}$ = 3.7 Hz, J' = 3.1 Hz; 1H, 5′x-H), 4.11 (ddd, $J_{5x,5n}$ = 18.2 Hz, $J_{5n,6}$ = 9.8 Hz, J' = 1.5 Hz; 1H, 5′n-H), 4.61 (br. d, $J_{2,6}$ = 7.3 Hz; 1H, 2′-H). – These spectroscopic data were retrieved from the regioisomeric mixture of **S-1a,b**.

Spiro[cyclopropane-1,8′-[3,4]diazatricyclo[5.2.1.0^{2,6}]dec[3]ene] (**S-1b**): ^{1}H NMR (C_6D_6, 400 MHz): δ = 0.0–0.4 (m; 2H, 2a-H, 3a-H), 0.40 (mc; 2H, 2s-H, 3s-H), 0.48 (br. dd, $J_{10s,10a}$ = 10.4 Hz, $J_{10s,9n}$ = 2.4 Hz; 1H, 10′s-H), 0.58 (br. s; 1H, 7′-H), 0.98 (dd, $J_{9n,9x}$ = 11.9 Hz, $J_{9n,10s}$ = 2.4 Hz; 1H, 9′n-H), 1.08 (ddd, $J_{10a,10s}$ = 10.4 Hz, $J_{10a,1}$ = $J_{10a,7}$ = 1.5 Hz; 1H, 10′a-H), 1.29 (dd, $J_{9x,9n}$ = 11.9 Hz, $J_{9x,1}$ = 4.9 Hz; 1H, 9′x-H), 1.54 (mc; 1H, 6′-H), 2.75 (br. d, $J_{1,9x}$ = 4.9 Hz; 1H, 1′-H), 3.61 (ddd, $J_{5x,5n}$ = 18.2 Hz, $J_{5x,6}$ = 3.7 Hz, J' = 3.1 Hz; 1H, 5′x-H), 4.08 (ddd, $J_{5n,5x}$ = 18.2 Hz, $J_{5n,6}$ = 9.8 Hz, J' = 1.5 Hz; 1H, 5′n-H), 4.40 (br. d, $J_{2,6}$ = 7.3 Hz; 1H, 2′-H). – These spectral data were retrieved from the regioisomeric mixture of **S-1a,b**. For additional ^{1}H-NMR data (200 MHz) of **S-1a,b** cf. Table 1. – IR (CCl_4) of **S-1a,b**: 3060 cm^{-1}, 2960, 2860, 1540, 1460, 1450, 1435, 1310, 1280, 1250, 1220, 1050, 1015, 950, 930, 910. – UV (CH_2Cl_2) of **S-1a,b**: λ_{max} (lg ε) = 325 nm (2.17). – ^{13}C NMR ($CDCl_3$, 100 MHz) of **S-1a,b**: δ = 8.92, 9.14, 14.72 and 14.85 (four t; C-2, C-3), 23.09 and 24.69 (two s; C-1), 31.82 (t), 36.04 (t), 37.37 (t), 37.91 (d), 40.13 (d), 41.04 (d), 43.05 (d), 47.57 (d), 49.60 (d), 81.97 and 82.26 (two t; C-5′), 95.61 and 96.40 (two d; C-2′). – MS (70 eV) of **S-1a,b**: m/z (%) = 162 (12; M^+), 91 (45), 80 (40), 79 (100), 53 (13). $C_{10}H_{14}N_2$ (162.2) Calcd. C 73.98 H 8.69 N 17.33 Found C 73.92 H 8.72 N 17.28

General Procedure for the 1,3-Dipolar Cycloadditions of Diphenyldiazomethane (**2**) *and Phenyl Azide* (**3**): To a solution of the olefin (8.00–17.0 mmol) in 20–50 ml of dry CCl_4 were added equimolar amounts of the norbornenes **K** or **S**. The reaction progress was monitored by ^{1}H NMR. After stirring for 5–15 d at ca. 20°C in the dark, the solvent was rotoevaporated (40°C at 20 Torr) and the brown residue repeatedly recrystallized from ethanol.

Cycloadducts **K-2a,b** *of Diphenyldiazomethane* (**2**) *and Ketonorbornene* **K**: A mixture of 1.00 g (9.25 mmol) of ketonorbornene **K** and 1.79 g (9.25 mmol) of diphenyldiazomethane (**2**) in 30 ml of dry CCl_4 afforded after 4 d reaction time 992 mg (35%) of a ca. 1:1 isomeric mixture of **K-2a,b**. Recrystallization from ethanol yielded colorless prisms of **K-2a**, m.p. 179–181°C.

5,5-Diphenyl-3,4-diazatricyclo[5.2.1.0^{2,6}]dec-3-en-9-one (**K-2a**): IR (CCl_4): 3080 cm^{-1}, 3040, 3000, 2920, 1770, 1600, 1500, 1450, 1420, 1170, 980, 710, 640. – UV (CH_2Cl_2): λ_{max} (lg ε) = 336 nm (2.68). – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = AB signal (δ_{10a} = 1.29, δ_{10s} = 0.98, $J_{10s,10a}$ = 11.0 Hz; 2H, 10-H), 1.97 (m; 2H, 8-H), 2.07 (br. s; 1H, 7-H), 2.85 (d, $J_{6,2}$ = 7.0 Hz; 1H, 6-H), 3.41 (mc; 1H, 1-H), 5.21 (d, $J_{2,6}$ = 7.0 Hz; 1H, 2-H), 7.3–7.4 (m; 10H, C_6H_5). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 31.53 (t; C-8), 37.87 (d; C-7), 45.07 (t; C-10), 48.09 (d; C-1), 51.31 (d; C-6), 86.70 (d; C-2), 104.00 (s; C-5), 126.54, 126.66, 126.77, 126.87, 127.31, 127.48, 127.56, 127.79, 128.14, 128.50, 129.35, 129.47, 156.00 (s), 156.50 (s), 214.0 (s). – MS

(70 eV): *m/z* (%) = 274 (31; $M^+ - N_2$), 230 (100), 205 (78), 191 (32), 165 (49), 91 (35), 77 (21).

$C_{20}H_{18}N_2O$ (302.4) Calcd. C 79.44 H 6.00 N 9.26
Found C 79.69 H 6.13 N 8.95

5,5-Diphenyl-3,4-diazatricyclo[5.2.1.0^{2,6}]dec-3-en-8-one (**K-2b**): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.91 (br. d; $J_{6,2}$ = 7.0 Hz; 1H, 6-H), 3.35 (br. s; 1H, 7-H), 5.25 (br. d, $J_{2,6}$ = 7.0 Hz; 1H, 2-H). – For additional ^{1}H-NMR data (200 MHz) on **K-2a,b** cf. Table 1. – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 31.83 (t; C-9), 38.15 (d; C-1), 46.23 (t; C-10), 47.66 (d; C-7), 52.93 (d; C-6), 92.94 (d; C-2), 103.95 (s; C-5), 127.13 (d), 127.61 (d), 127.76 (d), 128.10 (d), 128.43 (d), 128.76 (d), 140.85 (s), 142.57 (s), 214.11 (s). – These spectroscopic data were retrieved from the regioisomeric mixture of **K-2a,b**.

Cycloadducts **S-2a,b** *of Diphenyldiazomethane* (**2**) *and Spironorbornene* **S**: A mixture of 960 mg (8.00 mmol) of spironorbornene **S** and 1.75 g (9.00 mmol) of diphenyldiazomethane in 30 ml of dry CCl_4 afforded after 10 d reaction time 950 mg (38%) of a ca. 1:1 isomeric mixture of **S-2a,b**. Recrystallization from ethanol yielded colorless prisms, m.p. 155–157°C, of regioisomer **S-2b**.

5′,5′-Diphenylspiro[cyclopropane-1,8′-[3,4]diazatricyclo[5.2.1.0^{2,6}]-dec[3]ene] (**S-2b**): IR (CCl_4): 3050 cm^{-1}, 2960, 2910, 2840, 1590, 1480, 1440, 1270, 1030, 1000, 940, 690. – UV (CH_2Cl_2): λ_{max} (lg ε) = 345 nm (2.75) . – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.2–0.6 (m; 4H, 2-H, 3-H), 0.75 (br. s; 1H, 7′-H), AB signal (δ_{10a} = 1.16, δ_{10s} = 0.65, $J_{10a,10s}$ = 10.5 Hz; 2H, 10′-H), 1.42 (br. d, $J_{9n,9x}$ = 12.0 Hz, 1H, 9′n-H), 1.62 (dd, $J_{9x,9n}$ = 12.0 Hz, $J_{9x,1}$ = 5.0 Hz; 1H, 9′x-H), 2.95 (d, $J_{6,2}$ = 7.0 Hz; 1H, 6′-H), 3.03 (br. d, $J_{1,9x}$ = 5.0 Hz; 1H, 1′-H), 5.08 (d, $J_{2,6}$ = 7.0 Hz; 1H, 2′-H), 7.1–7.4 (m; 10H, C_6H_5). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 9.51 and 15.92 (two t; C-2, C-3), 25.70 (s; C-8′), 33.22 (t; C-10′), 37.86 (t; C-9′), 40.55 (d; C-1′), 46.87 (d; C-7′), 47.71 (d; C-6′), 99.65 (d; C-2′), 102.62 (s; C-5′), 126.91 (d), 127.25 (d), 127.58 (d), 127.91 (d), 128.09 (d), 128.49 (d), 142.04 (s), 143.66 (s). – MS (70 eV): *m/z* (%) = 315 (0.3, $M^+ + 1$), 286 (19, $M^+ - N_2$), 192 (43), 167 (58), 115 (45), 92 (13), 91 (100), 77 (28), 41 (18), 28 (21; N_2).

$C_{22}H_{22}N_2$ (314.4) Calcd. C 84.04 H 7.05 N 8.91
Found C 84.25 H 7.15 N 8.62

5′,5′-Diphenylspiro[cyclopropane-1,9′-[3,4]diazatricyclo[5.2.1.0^{2,6}]-dec[3]ene] (**S-2a**): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.81 (m; 1H, 7′-H), 2.13 (br. s; 1H, 1′-H), 2.64 (d, $J_{6,2}$ = 7.0 Hz; 1H, 6′-H), 5.19 (d, $J_{2,6}$ = 7.0 Hz; 1H, 2′-H). – For additional ^{1}H-NMR data (200 MHz) on **S-2a,b** cf. Table 1. – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 23.07 (s; C-9′), 32.93 (t; C-10′), 40.24 (t; C-8′), 40.72 (d; C-7′), 46.57 (d; C-1′), 47.40 (d; C-6′), 98.54 (d; C-2′). – These spectroscopic data were retrieved from a regioisomeric mixture of **S-2a,b**.

Cycloadducts **K-3a,b** *of Phenyl Azide* (**3**) *and Ketonorbornene* **K**: A mixture of 1.50 g (13.9 mmol) of ketonorbornene **K** and 1.65 g (13.9 mmol) of phenyl azide (**3**) in 20 ml of dry CCl_4 yielded after 5 d reaction time 1.11 g (35%) of a ca. 1:1 isomeric mixture of **K-3a,b**. Recrystallization from ethanol afforded colorless prisms, m.p. 141–145°C, of pure **K-3a**.

3-Phenyl-3,4,5-triazatricyclo[5.2.1.0^{2,6}]dec-3-en-8-one (**K-3a**): IR (CCl_4): 2980 cm^{-1}, 2960, 1760, 1600, 1500, 1480, 1360, 1300, 1280, 1120, 980. – ^{1}H NMR ($CDCl_3$, 90 MHz): δ = AB signal (δ_A = 1.70, δ_B = 1.45, J_{AB} = 11.0 Hz; 2H, 10-H), 2.1–2.2 (m; 2H, 9-H), 3.0–3.2 (m; 2H, 1-H, 7-H), 4.07 (d, $J_{2,6}$ = 9.0 Hz; 1H, 2-H), 4.87 (d, $J_{6,2}$ = 9.0 Hz; 1H, 6-H), 6.9–7.5 (m; 5H, C_6H_5). – ^{13}C NMR ($CDCl_3$): δ = 31.33 (t; C-9), 40.33 (d; C-1), 42.67 (t; C-10), 54.77 (d; C-7), 59.73 (d; C-2), 80.45 (d; C-6), 114.22 (d), 122.78 (d), 129.56 (d), 139.68 (s), 212.08 (s; C-8). – MS (70 eV): *m/z* (%) = 228 (0.3; M^+), 170 (58), 79 (36), 77 (100; $C_6H_5^+$), 51 (36), 28 (39; N_2).

$C_{13}H_{13}N_3O$ (227.3) Calcd. C 68.71 H 5.77 N 18.49
Found C 69.07 H 5.76 N 18.10

The X-ray data of **K-3a** are given in Tables 2, 3, and 4, and its structure is exhibited in Figure 1.

5-Phenyl-3,4,5-triazatricyclo[5.2.1.0^{2,6}]dec-3-en-8-one (**K-3b**): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.0 (br. s; 1H, 1-H), 3.2 (br. s; 1H, 7-H), 4.04 (d, $J_{6,2}$ = 9.0 Hz; 1H, 6-H), 4.82 (d, $J_{2,6}$ = 9.0 Hz; 1H, 2-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 30.87 (t; C-9), 40.96 (d; C-1), 42.18 (t; C-10), 53.76 (d; C-7), 55.31 (d; C-6), 84.91 (d; C-2), 211.74 (s; C-8). – These spectral data were retrieved from the regioisomeric mixture of **K-3a,b**.

Cycloadducts **S-3a,b** *of Phenyl Azide* (**3**) *and Spironorbornene* **S**: A mixture of 1.00 g (8.33 mmol) of spironorbornene **S** and 991 mg (8.33 mmol) of phenyl azide in 20 ml of dry CCl_4 yielded after 6 d reaction time 760 mg (38%) of a ca. 1:1 isomeric mixture of **S-3a,b**. Recrystallization from ethanol gave colorless prisms, m.p. 113–116°C, of pure **S-3a**.

5′-Phenylspiro[cyclopropane-1,9′-[3,4,5]triazatricyclo[5.2.1.0^{2,6}]-dec[3]ene] (**S-3a**): IR (CCl_4): 3065 cm^{-1}, 2980, 2940, 1605, 1510, 1500, 1460, 1365, 1120, 1100, 990, 910, 690. – UV (CH_2Cl_2): λ_{max} (lg ε) = 238 nm (3.85), 288 (3.88), 309 (3.89). – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.4–0.8 (m; 4H, 2-H, 3-H), 1.18 (br. dd, $J_{10s,10a}$ = 11.5 Hz, $J_{10s,7}$ = $J_{10s,1}$ = 2.0 Hz; 1H, 10′s-H), 1.35 (dd, $J_{8n,8x}$ = 12.5 Hz, $J_{8n,10s}$ = 2.0 Hz; 1H, 8′n-H), 1.62 (br. dd, $J_{10a,10s}$ = 11.5 Hz, $J_{10a,1}$ = $J_{10a,7}$ = 2.5 Hz; 1H, 10′a-H), 1.69 (dd, $J_{8x,8n}$ = 12.5 Hz, $J_{8x,7}$ = 4.5 Hz; 1H, 8′x-H), 2.01 (br. s; 1H, 1′-H), 2.74 (br. d, $J_{7,8x}$ = 4.5 Hz; 1H, 7′-H), 3.89 (br. dd, $J_{6,2}$ = 9.3 Hz, $J_{6,10a}$ = 1.3 Hz; 1H, 6′-H), 4.86 (br. d, $J_{2,6}$ = 9.3 Hz; 1H, 2′-H), 7.0–7.4 (m; 5H, C_6H_5). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 9.18 and 15.12 (two t; C-2, C-3), 22.67 (s; C-9′), 32.81 (t, C-10′), 37.08 (t; C-8′), 42.23 (d; C-7′), 49.80 (d; C-1′), 60.11 (d, C-6′), 85.24 (d; C-2′), 114.00 (d), 121.89 (d), 129.35 (d), 140.46 (s). – MS (70 eV): *m/z* (%) = 240 (0.2; M^+), 211 (11; $M^+ - N_2$), 119 (38; $M^+ - PhN_3$), 91 (49; Ph – N^+), 77 (100; $C_6H_5^+$), 28 (50; N_2).

$C_{15}H_{17}N_3$ (239.3) Calcd. C 75.28 H 7.16 N 17.56
Found C 75.37 H 7.32 N 17.59

The X-ray data of **S-3a** are given in Tables 2, 5, and 6, and its structure is exhibited in Figure 1.

5′-Phenylspiro[cylopropane-1,8′-[3,4,5]triazatricyclo[5.2.1.0^{2,6}]-dec[3]ene] (**S-3b**): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.84 (br. s; 1H, 1′-H), 3.96 (br. d, $J_{6,2}$ = 9.3 Hz, 1H, 6′-H), 4.65 (d, $J_{2,6}$ = 9.3 Hz; 1H, 2′-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 8.99 and 14.89 (two t; C-2, C-3), 21.96 (s; C-8′), 32.55 (t; C-10′), 37.43 (t; C-9′), 43.17 (d; C-1′), 48.23 (d, C-7′), 58.79 (d; C-6′), 85.69 (d; C-2′), 113.57 (d), 121.52 (d), 129.07 (d), 140.46 (s). – These spectroscopic data were retrieved from the regioisomeric mixture of **S-3a,b**.

General Procedure for the 1,3-Dipolar Cycloadditions of Benzonitrile Oxide (**4**): To a solution of the norbornenes **K** or **S** (8.00–9.00 mmol) in 30–50 ml of dry ether was added under nitrogen at –10 to 0°C an equimolar amount of phenylhydroxamic acid chloride in 5–10 ml of dry ether. After 10 min an equimolar amount of Et_3N in 1–5 ml of dry ether was added and the reaction mixture stirred for 3 h at –10 to 0°C and 12 h at 20°C. To the mixture was added 100 ml of H_2O, the organic layer separated, the water layer extracted with ether (3 × 50 ml), and the combined organic phases dried with Na_2SO_4. After rotoevaporation of the solvent (20°C at 20 Torr), the crude yellow-brown residue was repeatedly recrystallized from ethanol.

Cycloadducts **K-4a,b** *of Benzonitrile Oxide* (**4**) *and Ketonorbornene* **K**. – From 1.00 g (9.26 mmol) of ketonorbornene **K** and 1.44 g (9.26 mmol) of phenylhydroxamic acid chloride in 30 ml of dry ether was obtained 1.30 g (62%) of a ca. 1:1 isomeric mixture of **K-4a,b**. Recrystallization from ethanol yielded **K-4a,b** as colorless prisms, m.p. 87–91 °C. It was not possible to separate the regioisomers of *5-phenyl-3-oxa-4-azatricyclo[5.2.1.0^{2,6}]dec-4-en-8-one* and *-9-one* **K-4a,b**, respectively, by fractional recrystallization or by chromatography.

IR (CCl_4) of **K-4a,b**: 3080 cm^{-1}, 2995, 2975, 1770, 1595, 1455, 1420, 1365, 1170, 970, 935, 915, 900, 700. – ^1H NMR ($CDCl_3$, 90 MHz) of **K-4a,b**: δ = 1.5–2.4 (m; 8H), 2.8–3.2 (m; 4H, 1-H, 7-H), 3.88 (d, $J_{6,2}$ = 7.5 Hz; 1H, 6-H), 3.90 (d; 1H, 6-H), 4.88 (d, $J_{2,6}$ = 7.5 Hz, 1H, 2-H), 4.90 (d, $J_{2,6}$ = 7.5 Hz, 1H, 2-H), 7.3–7.9 (m; 10H, C_6H_5). – For additional ^1H NMR data (200 MHz) on **K-4a,b** cf. Table 1. – ^{13}C NMR ($CDCl_3$, 100 MHz) of **K-4a,b**: δ = 31.48 (t), 32.08 (t), 39.80 (t), 39.99 (d), 42.79 (d), 44.51 (t), 52.03 (d), 52.38 (d), 57.00 and 58.24 (two d; C-2), 83.00 and 86.66 (two d; C-6), 126.93 (d), 128.98 (d), 130.32 (s), 154.64 and 156.71 (two s; C-5), 212.45 and 213.18 (two s; C=O). – MS (70 eV) of **K-4a,b**: *m/z* (%) = (16; M^- + 1), 227 (100; M^+), 170 (21), 155 (24), 130 (96), 117 (30), 79 (26), 77 (74), 51 (36), 39 (44), 27 (34).

$C_{14}H_{13}NO_2$ (227.3) Calcd. C 73.99 H 5.77 N 6.16
Found C 73.69 H 5.98 N 6.16

Cycloadducts **S-4a,b** *of Benzonitrile Oxide* (**4**) *and Spironorbornene* **S**: From 1.00 g (8.32 mmol) of spironorbornene **S** and 1.29 g (8.32 mmol) of phenylhydroxamic acid chloride in 30 ml of dry ether was obtained 1.54 g (77%) of a ca. 1:1 isomeric mixture of **S-4a,b**. Recrystallization from ethanol yielded **S-4a,b** as colorless prisms, m.p. 119–123 °C. It was not possible to separate the regioisomers of *5'-phenylspiro[cyclopropane-1,8'-[3]oxa[4]azatricyclo[5.2.1.0^{2,6}]-dec[4]ene]* and *-1,9'-[3]oxa[4]azatricyclo[5.2.1.0^{2,6}]dec[4]ene]* **S-4a,b**, respectively by fractional recrystallization or by chromatography. – IR (CCl_4) of **S-4a,b**: 3060 cm^{-1}, 2980, 2930, 2860, 1590, 1500, 1450, 1355, 910, 890, 690. – ^1H NMR ($CDCl_3$, 400 MHz) of **S-4a,b**: δ = 0.2–0.7 (m; 8H, cyclopropane 2-H, 3-H), 1.1–1.9 (m; 10H), 2.58 (br. d, J = 4.5 Hz; 1H), 2.66 (br. d; 1H), 3.64 (d, $J_{2',6'}$ = 8.5 Hz; 1H, 6'-H), 3.82 (d, $J_{2',6'}$ = 8.5 Hz, 1H, 6'-H), 4.76 (d, $J_{6',2'}$ = 8.5 Hz, 1H, 2'-H), 4.87 (d, $J_{6',2'}$ = 8.5 Hz; 1H, 2'-H), 7.2–7.8 (m; 10H, C_6H_5). – ^{13}C NMR ($CDCl_3$, 100 MHz) of **S-4a,b**: δ = 8.86, 9.33, 13.78, and 15.45 (four t; C-2, C-3), 20.26 and 24.46 (two s; C-1), 32.92 (t), 33.17 (t), 34.86 (t), 39.53 (t), 41.53 (d), 45.20 (d), 48.22 (d), 51.47 (d), 55.91 and 56.81 (two d; C-2'), 86.84 and 87.67 (two d; C-6'), 126.64 (d), 126.77 (d), 128.62, 129.55, 156.40, and 156.64 (two s; C-5'). – MS (70 eV) of **S-4a,b**: *m/z* (%) = 239 (37; M^+), 146 (54), 91 (34), 79 (100), 77 (65).

$C_{16}H_{17}NO$ (239.3) Calcd. C 80.30 H 7.16 N 5.85
Found C 80.25 H 7.21 N 5.81

For additional ^1H NMR data (200 MHz) on **S-4a,b** cf. Table 1. X-ray data of **S-4b** (cf. text) are given in Tables 2, 7, and 8, and its structure is exhibited in Figure 1.

CAS Registry Numbers

S-1a: 107300-47-0 / **S-1b**: 107300-48-1 / **K-2a**: 107300-49-2 / **K-2b**: 107300-50-5 / **S-2a**: 107300-51-6 / **S-2b**: 107300-52-7 / **K-3a**: 107300-53-8 / **K-3b**: 107300-54-9 / **S-3a**: 86359-30-0 / **S-3b**: 86359-31-1 / **K-4a**: 107300-55-0 / **K-4b**: 107300-56-1 / **S-4a**: 107300-57-2 / **S-4b**: 107300-58-3 / **K**: 694-98-4 / **S**: 6572-50-5 / CH_2N_2: 334-88-3 / Ph_2CN_2: 883-40-9 / PhN_3: 622-37-7 / PhCNO: 873-67-6 / PhC(Cl)=NOH: 698-16-8

[1] A. Pawda (Editor), *1,3-Dipolar Cycloadditions*, vol. 1 and 2, John Wiley and Sons, New York 1984.
[2] R. S. Bly, B. Culp, R. K. Bly, *J. Org. Chem.* **35** (1970) 2235.
[3] I. Fleming, *Frontier Orbitals and Organic Chemical Reactions*, J. Wiley and Sons, New York 1976.
[4] J. H. Noygh, R. E. Schirmer, *The Nuclear Overhauser Effect*, Academic Press, New York 1971.
[5] M. Kinns, J. K. M. Sanders, *J. Magn. Res.* **56** (1984) 518.
[6] G. M. Sheldrick, *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*, University of Göttingen 1983.
[7] T. J. de Bar, H. J. Backer, *Org. Synth.* **IV** (1963) 250.

[264/86]