Intriguing modes of addition of 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene to bicyclopropylidene

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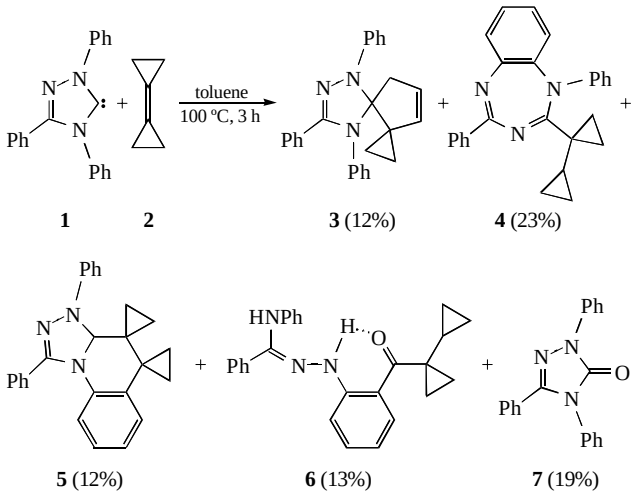
1,3,4-Triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene **1** reacts with bicyclopropylidene **2** to yield four unexpected products **3**–**6**, none of which resembles the typical [2+1] mode of cycloaddition observed for **1** with electron-deficient alkenes.

Bicyclopropylidene **2** is a uniquely strained and reactive tetrasubstituted alkene which has been shown to readily add electrophiles including organometallics[1] and undergo various cycloadditions[2] including [2+1] cycloadditions even of nucleophilic carbenes such as dimethoxycarbene.[3] We have now tested the reactivity of **2** towards the stable carbene 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene **1**[4] and found four unexpected products **3**–**6** resembling four unusual modes of addition (Scheme 1).†

The structures of all new compounds **3**–**6** were unequivocally established by X-ray crystal structure analyses (Figure 1).‡

No mechanistic details of these additions and cycloadditions have been proved as yet and even the rationalisation of their formation is difficult except for compounds **3** and **5**. Most probably, the nucleophilic carbene **1**[4] first attacks the double bond in **2** to give the 1,3-zwitterion **8** which may be in an equilibrium with the ring-closed form, the dispiro[2.0.2.1]heptane derivative **11**. For some reason, possibly due to considerable ring strain inherent in the sterically congested skeleton, **11** must be unstable under the employed conditions (100 °C)§ and prefer to open the central ring either back to **8** or with the reverse polarity to give the 1,3-zwitterion **10**. The latter can close a six-membered ring by electrophilic attack of the cationic end on one of the vicinal phenyl groups to give the product **5**. The triazaspiro[4.4]octadiene **3** can only arise by ring closure of a 1,5-zwitterion like **9** which must have formed from **8** by opening of the anionic cyclopropyl group going along with a 1,2-hydrogen shift (Scheme 2).

The formation of the benzotriazepine derivative **4** is particularly obscure as the connectivity of the atoms is changed on



1 **2** **3** (12%) **4** (23%) **5** (12%) **6** (13%) **7** (19%)

Scheme 1

† Compounds **3**–**7** were obtained by heating a solution of the heterocycle **1**[4] (183 mg, 0.615 mmol) and bicyclopropylidene **2**[5] (246 mg, 288 µl, 3.075 mmol) in anhydrous toluene (10 ml) at 100 °C under argon for 3 h in a sealed tube. The resulting mixture was concentrated under reduced pressure and chromatographed (3×15 cm column, 40 g of silica gel, CH_2Cl_2–hexane, 5:1) to give 28 mg (12%) of 5,7,8-triphenyl-5,6,8-triazadispiro[2.0.4.3]undeca-6,10-diene **3**, 53 mg (23%) of 1,4-diphenyl-2-(1-cyclopropylcyclopropyl)-6,7-benzo-1,3,5-triazepine **4**, 37 mg (19%) of 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one **7** and 60 mg (25%) of the non-separable mixture of 4,5-dihydro-1,3-diphenyl[4,1′:5,1″]bis-(spirocyclopropane)[3a-*H*][1,2,4]triazolo[4,3-*a*]quinoline **5** and *N*(3)-[2-(1-cyclopropylcyclopropylcarbonyl)phenyl]-*N*(1)-phenylbenzamidrazone **6**. Their relative ratio was determined from the ^{1}H NMR spectrum of the mixture in comparison to the spectra of the individual compounds obtained by the selection of the crystals in accordance with their shape.

For **3**: mp 166–168 °C (decomp.) (hexane–ether), R_f 0.57. ^{1}H NMR (250 MHz, $CDCl_3$) δ: 0.86–0.97 (m, 1H, cyclopropyl), 1.04–1.12 (m, 1H, cyclopropyl), 1.24–1.26 (m, 1H, cyclopropyl), 1.39–1.46 (m, 1H, cyclopropyl), 2.46 (dt, 1H, CH_2, *J* 19.3 Hz, 2.0 Hz), 3.24 (dt, 1H, CH_2, *J* 19.3 Hz, 2.3 Hz), 5.53 (dt, 1H, =CH, *J* 6.5 Hz, 2.0 Hz), 5.70 (dt, 1H, =CH, *J* 6.5 Hz, 2.3 Hz), 6.77–6.83 (m, 1H, Ph), 7.05–7.19 (m, 3H, Ph), 7.23–7.27 (m, 9H, Ph), 7.43–7.47 (m, 2H, Ph). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ: 12.79, 14.61, 39.38 (CH_2), 125.61, 127.54, 128.15, 128.52, 128.67, 128.75 (2CH), 113.23, 117.93, 125.09, 125.87, 136.28 (CH), 38.96, 94.09, 129.07, 139.02, 142.04, 145.60 (C). HRMS (EI, 70 eV) *m*/*z*: 377.1891 $[M]^+$.

For **4**: mp 136–138 °C (decomp.) (hexane–ether), R_f 0.51. ^{1}H NMR (250 MHz, $CDCl_3$) δ: 0.08–0.12 (m, 2H, cyclopropyl), 0.40–0.55 (m, 2H, cyclopropyl), 0.65–0.88 (m, 2H, cyclopropyl), 1.41–1.43 (m, 2H, cyclopropyl), 1.71–1.80 (m, 1H, cyclopropyl), 6.59 (d, 2H, *J* 8.0 Hz), 6.72 (t, 1H, *J* 7.8 Hz), 7.02 (t, 2H, *J* 7.8 Hz), 7.26–7.88 (m, 7H, Ph), 8.04 (dd, 2H, Ph, *J* 7.2 Hz, 1.8 Hz). ^{13}C NMR (75.5 MHz, 100 °C, $C_2D_2Cl_4$) δ: 2.82, 15.11 ($2CH_2$), 127.70 (4CH), 112.43, 128.57 (2CH), 12.51, 119.84, 126.81, 128.35, 129.33, 129.64, 130.04 (CH), 27.62, 134.52, 137.15, 144.40, 145.56, 159.07, 169.51 (C). HRMS (EI, 70 eV) *m*/*z*: 377.1891 $[M]^+$.

For **5**: R_f 0.40. ^{1}H NMR (250 MHz, $CDCl_3$) δ: 0.62–0.66 (m, 4H, cyclopropyl), 0.92–1.02 (m, 4H, cyclopropyl), 5.95 (s, 1H, CH), 6.95–7.52 (m, 12H, Ph), 7.85 (d, 2H, Ph, *J* 7.5 Hz). HRMS (EI, 70 eV) *m*/*z*: 377.1891 $[M]^+$.

For **6**: ^{1}H NMR (250 MHz, $CDCl_3$) δ: 0.12–0.15 (m, 2H, cyclopropyl), 0.33–0.39 (m, 2H, cyclopropyl), 0.90–0.99 (m, 2H, cyclopropyl), 1.04–1.10 (m, 2H, cyclopropyl), 1.38–1.46 (m, 1H, cyclopropyl), 6.09 (s, 1H, NH), 6.33 (d, 1H, *J* 7.5 Hz), 6.90–7.53 (m, 11H, Ph), 8.24 (d, 2H, Ph, *J* 7.5 Hz, 1.8 Hz), 11.37 (s, 1H, NH). MS (EI, 70 eV) *m*/*z*: 395 $[M]^+$.

Compound **7** is known,[4] R_f 0.23.

‡ *Crystal data*: some details of the single-crystal X-ray experiments for compounds **3**–**6** and crystal data are given in Table 1. All the data were collected using MoKα radiation (λ = 0.71073 Å) on a 'Nonius KAPPA-CCD' and a 'SMART-CCD' diffractometers for compounds **3** and **4**–**6**, respectively. The structures were solved by direct methods and refined by full-matrix least-square against F^2 with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms in molecules **3**–**5** were located in the difference Fourier maps and refined isotropically. For compound **6** the positions of H atoms were calculated. For all compounds the maximum features on the final residual maps do not exceed 0.3 e/Å^3. Full lists of bond angles, bons lengths, atomic coordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Notice to Authors', *Mendeleev Communications*, 1999, Issue 1. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/36.

§ Essentially the same distribution of products **3**–**6**, yet with lower total yield (47%), was observed when carbene **1** was exposed to bicyclopropylidene **2** in THF solution under a pressure of 10 kbar at 20 °C for 24 h. Under the same conditions, but at ambient pressure, only 7% conversion of **1** to **3**–**6** was observed.

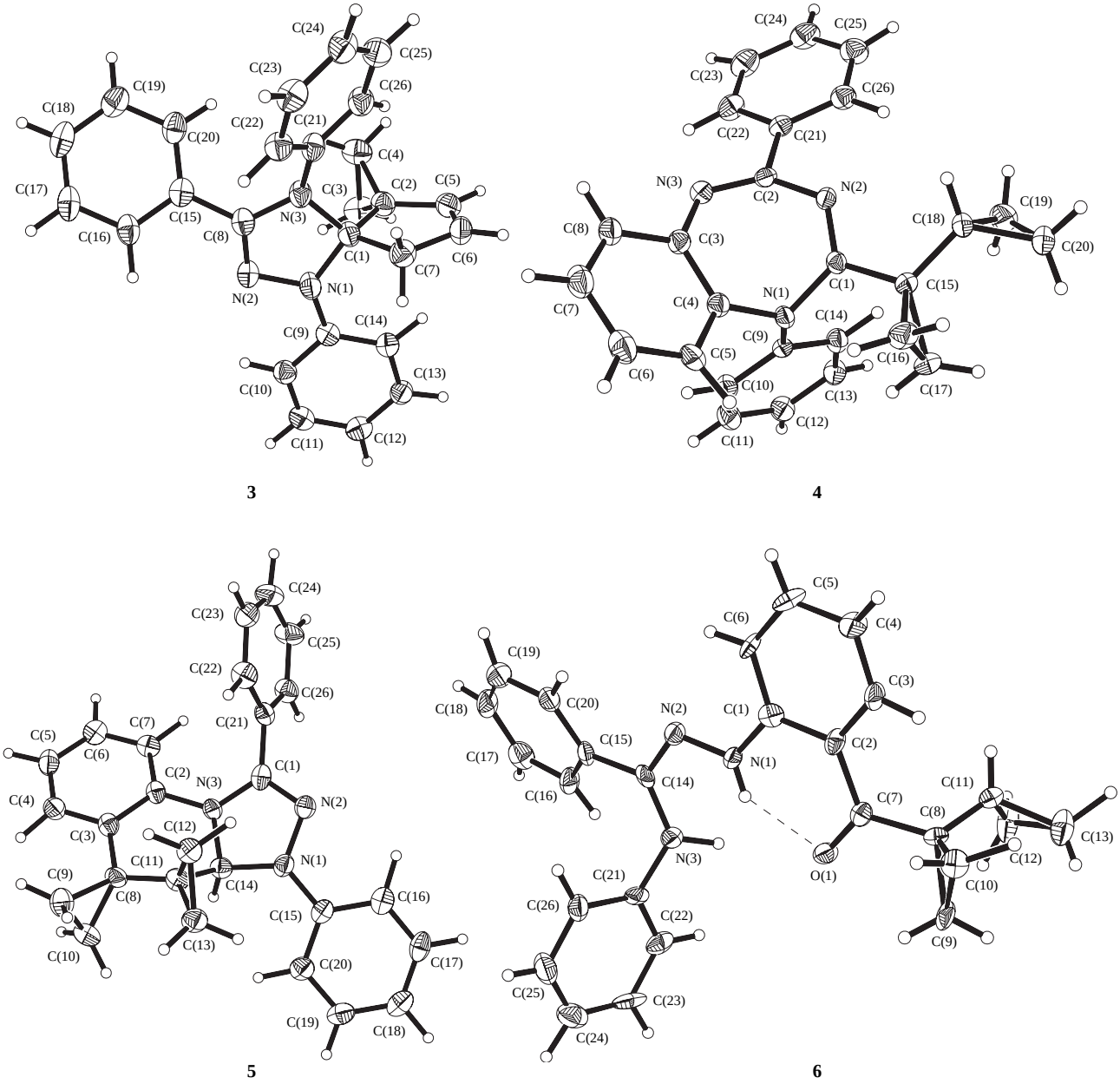
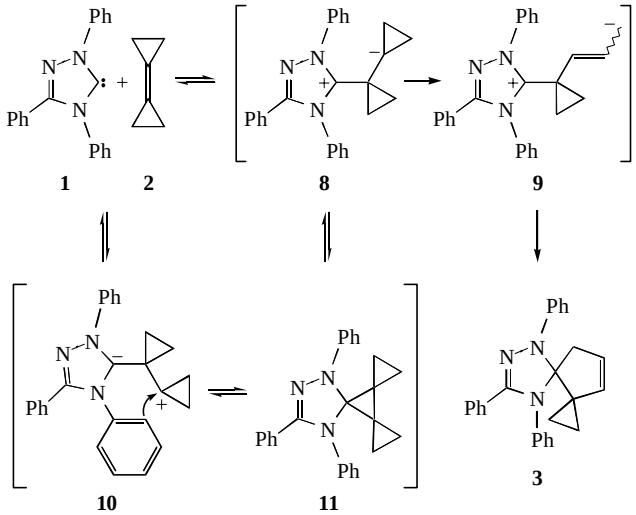


Figure 1 Structures of compounds **3**–**6** in the crystals.

Table 1 Crystal data for compounds **3**–**6**.

	3	**4**	**5**	**6**
Chemical formula	$C_{26}H_{23}N_3$	$C_{26}H_{23}N_3$	$C_{26}H_{23}N_3$	$C_{26}H_{25}N_3O$
Formula weight	377.47	377.47	377.47	395.49
T/K	100	150	120	150
Crystal system	monoclinic	triclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
Z	4	2	2	4
a/Å	14.607(2)	9.583(1)	8.870(1)	10.715(1)
b/Å	9.031(1)	10.053(1)	10.509(1)	19.578(1)
c/Å	15.936(2)	12.805(1)	11.889(1)	10.415(1)
α/°	90	98.12(1)	78.24(1)	90
β/°	110.05(1)	105.96(1)	70.70(1)	105.43(1)
γ/°	90	116.99(1)	72.67(1)	90
V/Å^3	1974.9(5)	1004.6(1)	991.6(1)	2106.2(1)
D_c/g cm^{-3}	1.270	1.248	1.264	1.247
μ/mm^{-1}	0.075	0.074	0.075	0.077
Reflections measured	7471	8406	9014	11941
Unique reflections	3872	5241	4506	2748
R_1 ($I = 2\sigma$)	0.0575	0.0553	0.0863	0.0973
wR_2	0.1654	0.1305	0.2299	0.1643
GOOF	0.990	1.076	0.972	1.196



Scheme 2

going from **8** or **10** to **4**. Formally, this could be brought about by opening of the five-membered heterocycle in **10** between the two adjacent nitrogens, a subsequent 1,3-shift of a phenyl group from the central to the terminal nitrogen and ring closure by intramolecular nucleophilic aromatic substitution. Similarly difficult to explain is the formation of compound **6**. Formally, an intramolecular electrophilically assisted nucleophilic aromatic substitution in **10** could lead to a tricyclic benzazepine derivative which due to its ring strain might undergo hydrolysis to give **6** during column chromatography.

Without any further evidence, all these mechanistic considerations, especially the last ones, are highly speculative. None the less, the observed reactivity of the stable carbene **1**, which so far has been reported to react only with acceptor-activated C=C double bonds,[4] towards the strained tetrasubstituted alkene **2** is quite remarkable, and so are the products **3**–**6**.

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