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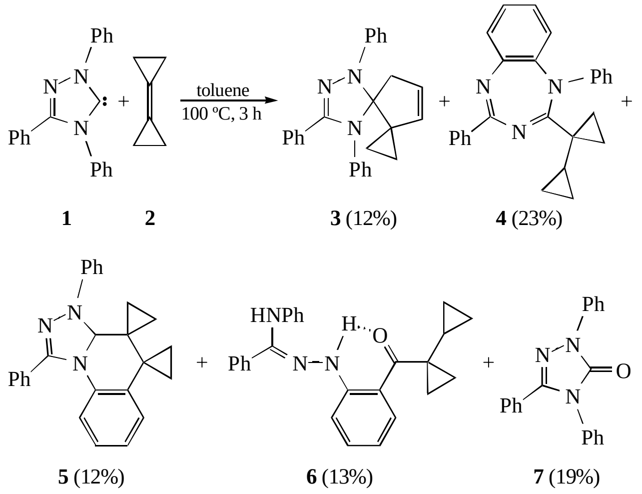
1,3,4-Triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene 1 reacts with bicyclopropylidene 2 to yield four unexpected products 3–6, none of which resembles the typical [2+1] mode of cycloaddition observed for 1 with electron-deficient alkenes.

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 $[M]^+$.

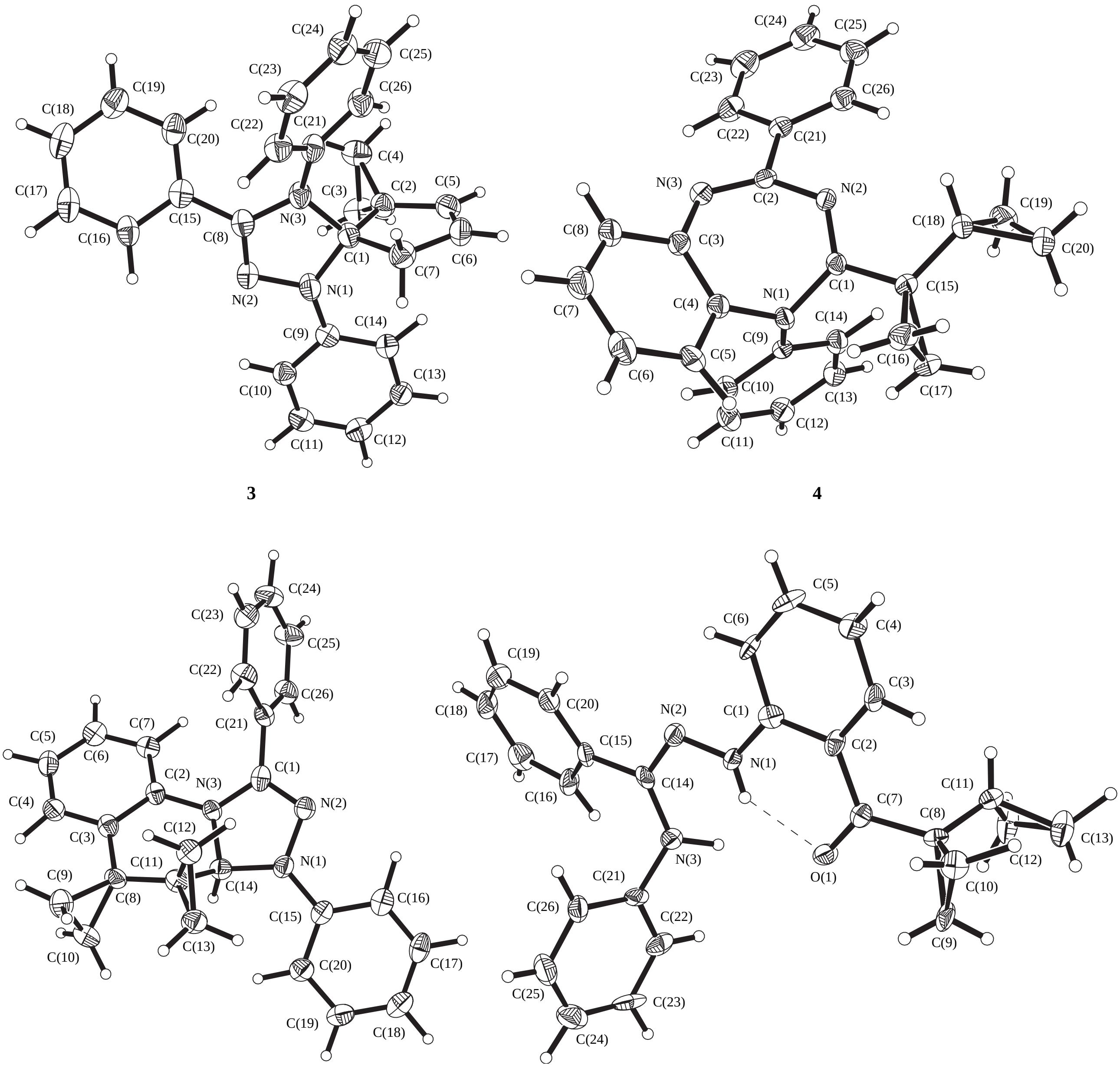
For **5**: R_f 0.40. ^{1}H NMR (250 MHz, $CDCl_3$) δ: 0.62–0.66 (m, 4H, cyclopropyl), 0.92–1.02 (m, 4H, cyclopropyl), 5.95 (s, 1H, CH), 6.95–7.52 (m, 12H, Ph), 7.85 (d, 2H, Ph, *J* 7.5 Hz). HRMS (EI, 70 eV) *m*/*z*: 377.1891 $[M]^+$.

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.



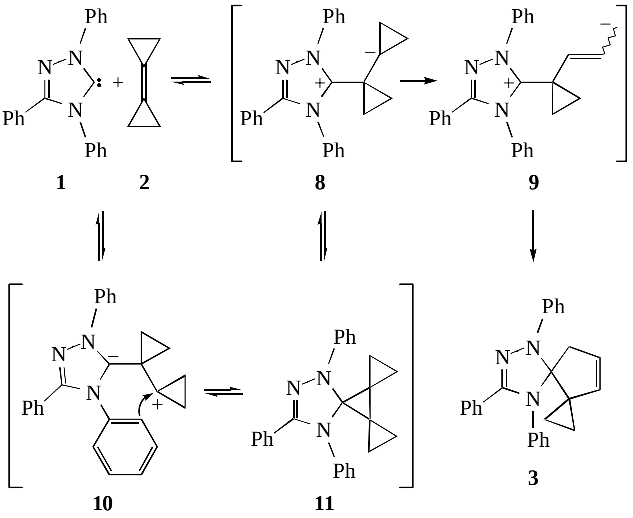
3 **4**

5 **6**

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	$P2_1/n$	$P1$	$P1$	$P2_1/c$
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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