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Reaction of 4-Phenyl-1,2,4-triazoline-3,5-dione (PTAD) with Bicyclic Monoterpenes

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The cycloaddition of the bicyclic monoterpenes camphene (**4**), α-pinene (**5**), β-pinene (**6**), 2-carene (**7**), bornene (**8**), and tricyclane **9** with PTAD was investigated. Only camphene and α-pinene gave rearranged urazoles (**11**, **14**) via dipolar cycloaddition. Ene-reaction was the predominant reaction course for α-pinene (→ **15**) and the exclusive route for β-pinene (→ **16**) and 2-carene (→ **17**). Steric hindrance by the *gem*-dimethyl group prevents cycloaddition of bornene. The cyclopropane rings in the tricyclane **9** and 2-carene are not sufficiently strained to undergo $[2_\pi + 2_\sigma]$-cycloaddition with PTAD. None of the monoterpenes gave $[2_\pi + 2_\pi]$-cycloaddition.

Reaktion von 4-Phenyl-1,2,4-triazolin-3,5-dion (PTAD) mit bicyclischen Monoterpenen

Die Cycloaddition der bicyclischen Monoterpene Camphen (**4**), α-Pinen (**5**), β-Pinen (**6**), 2-Caren (**7**), Bornen (**8**) und des Tricyclans **9** mit PTAD wurde untersucht. Nur Camphen und α-Pinen gaben über eine dipolare Cycloaddition umgelagerte Urazole (**11**, **14**). α-Pinen gab hauptsächlich eine En-Reaktion zu **15**, während β-Pinen und 2-Caren ausschließlich unter En-Reaktion **16** bzw. **17** bildeten. Sterische Hinderung durch die geminale Dimethylgruppe verhinderte eine Cycloaddition von Bornen. Die Cyclopropanringe im Tricyclan **9** und in 2-Caren sind nicht gespannt genug, um mit PTAD eine $[2_\pi + 2_\sigma]$-Cycloaddition einzugehen. Keines der Monoterpene gab eine $[2_\pi + 2_\pi]$-Cycloaddition.

The great reactivity of 4-substituted 1,2,4-triazoline-3,5-dione (TAD) in cycloaddition reactions has long been recognized[1] and a recent review[2] covers the important synthetic utilizations of this useful reagent. The more important cycloaddition routes of TAD are illustrated in Eq. (1). While the $[4_\pi + 2_\pi]$-cycloaddition, the homo-Diels-Alder and ene-reaction of TAD are known for some time, $[2_\pi + 2_\pi]$-cycloadditions with alkenes, e.g. adamantylideneadamantane[3], substituted norbornenes, and dibenzobarrelenes[4], or $[2_\pi + 2_\sigma]$-cycloaddition with strained cyclopropanes, e.g. bicyclo[2.1.0]pentane[5], are of recent vintage. One of the more fascinating cycloaddition reactions of TAD, however, is the recently discovered reaction with strained bicycloalkenes[6], e.g. norbornene, benzonorbornadiene, etc., leading to skeletal rearrangement products via dipolar intermediates. Particularly the latter cycloaddition process is of synthetic potential for the preparation of unusually strained molecules **3** via the azo compounds **2**, that are derived from the rearranged urazoles **1** (Eq. 2)[2].

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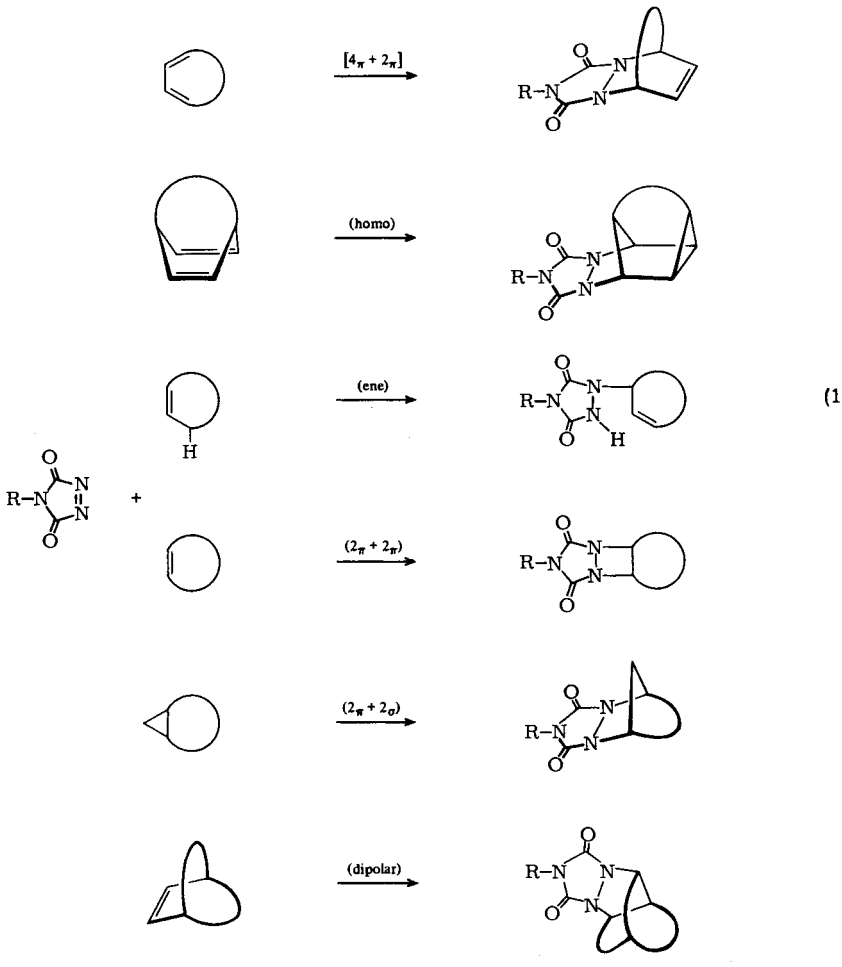
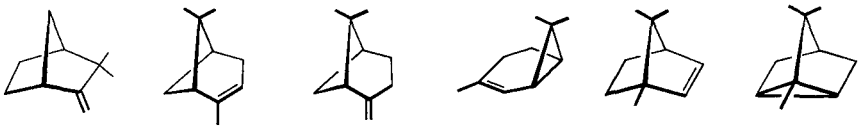


With this in mind, we felt it worthwhile to investigate the cycloaddition reactivity of PTAD towards the bicyclic monoterpenes **4**–**9**. Except [4 + 2]- and homo-Diels-Alder reactions, since none of these natural products possess, respectively, the necessary conjugated and isolated dienic moieties, all the other cycloaddition modes, i.e. the dipolar, the ene-, and the [2 + 2]-reactions are viable with these substrates. Again, if dipolar cycloaddition were to occur, leading to skeletal rearranged urazoles **1**, a variety of interesting isomeric structures **3** from these naturally occuring



4 5 6 7 8 9

bicyclic monoterpenes would become available through thermal or photochemical denitrogenation of the respective azoalkanes **2** (Eq. 2). Thus, we posed the following questions concerning the reactivity of PTAD towards these terpenic substrates:

(i) What structural element in these bicyclic monoterpenes is essential to promote dipolar cycloaddition with skeletal rearrangement?

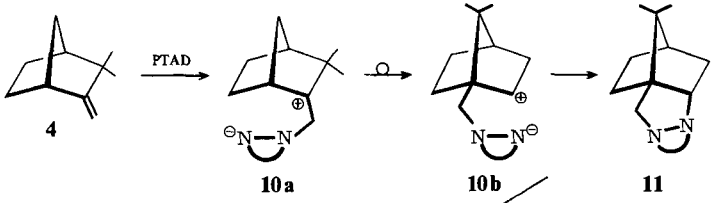
(ii) How effective does this dipolar cycloaddition route compete with the ene- and [2 + 2]-modes?

(iii) Whas is the steric influence of the *gem*-dimethyl moiety?

Herein we report the results of this investigation.

Cycloaddition with Camphene (4)

Camphene was quite sluggish in its reaction with PTAD and drastic conditions were essential. For example, heating in 1,1,2,2-tetrachloroethane as solvent in a stainless steel autoclave at 70–75 °C overnight was necessary to promote reaction. After silica gel chromatography the rearranged urazole **11** was isolated in 6% yield. The structure



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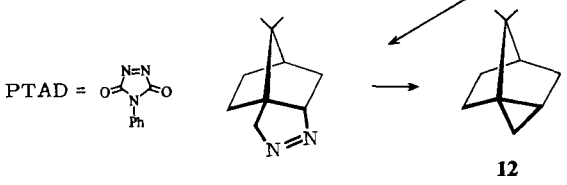


(4)

assignment of **11** rests mainly on spectral evidence. For example, neither the IR nor the NMR show olefinic protons. The ten ^{13}C NMR resonances (cf. Exp. Section) are observed at the expected chemical shifts, but it is difficult to assign each of the resonances to the specific carbons. The ^1H NMR (90 MHz) was most definitive. Thus, the methylene protons adjacent to the urazolyl nitrogen appears as an AB-pattern at $\delta_A = 3.78$ and $\delta_B = 3.52$ with $J_{AB} = 10.5$ Hz. The skeletal ring proton next to the other urazolyl nitrogen occurs at $\delta = 3.80$ as a doublet of doublets, coupled to the adjacent ring methylene protons with $J = 4.5$ and 8.7 Hz. The remaining seven skeletal ring protons form a complex multiplet at $\delta = 1.20-2.70$. The *gem*-dimethyl protons resonate at $\delta = 1.00$ and 1.10 as a sharp singlets. The MS shows a molecular ion peak at *m/e* 311.

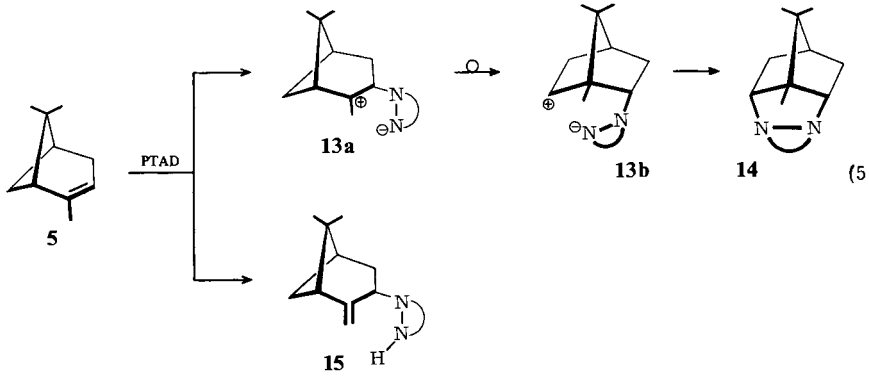
The mechanism of formation of the rearranged urazole **11** is given in Eq. (3). Whether the dipolar intermediate **10a** is formed directly or via an aziridinium ion[3] is not clear at this point; however, for skeletal rearrangement into the dipolar intermediate **10b** to take place, cationic charge must accumulate at the carbon adjacent to the bridgehead. Cyclization of dipole **10b** affords the rearranged urazole **11**.

Although the yield of **11** is very low (6%), it represents an interesting structure for further investigation. For example, oxidative hydrolysis to the corresponding azoalkane and denitrogenation could afford the as yet unknown and unusual bridgehead cyclopropane derivative **12** (Eq. 4). Work is in progress along these lines.

With respect to the other cycloaddition modes, the ene-reaction is blocked out since no allylic, non-bridgehead hydrogens are present. (2 + 2)-Reaction via collapse of dipole **10a** must be unfeasible energetically.

Cycloaddition with α-Pinene (5)

The reactivity of α-pinene towards PTAD was considerably greater than that of camphene (**4**). Thus, methylene chloride solutions of **5** at room temperature led to decoloration of the intense red PTAD color in ca. 24 h. Silica gel chromatography afforded as first eluate the rearranged urazole **14** in 14% yield. The structure assignment of **14** rests again mainly on spectral data. The IR spectrum shows the urazolyl carbonyls at 1770 and 1710 cm^{-1}, but no olefinic bonds. The ^{13}C NMR (cf. Exp. Section) reveals two methyl carbon resonances (bridgehead methyl and *gem*-dimethyl) and the expected five skeletal carbon resonances, which can only be reconciled with the proposed symmetrical structure for the rearranged urazole **14**. The ^1H NMR (90 Hz) shows the three methyl groups as a singlet at $\delta = 0.97$, the skeletal protons adjacent to the urazolyl nitrogens as a doublet at $\delta = 4.20$ ($J = 8.7$ Hz), the bridgehead proton as a multiplet at $\delta = 1.88$, and the remaining four skeletal protons as two multiplets at 1.23 – 1.67 and 2.40 ppm. The mechanism of formation of **14** is rationalized in Eq. (5).



As second eluate the ene-product **15** was obtained in 37% yield. Besides the urazolyl carbonyls at 1780 and 1690 cm^{-1}, the IR spectrum shows the presence of the N–H stretching at 3120 cm^{-1} and the expected resonances for the exomethylenic moiety. The ^{13}C NMR shows, as expected, eight aliphatic and two olefinic resonances, besides those

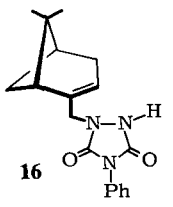
of the urazole ring. The ^1H NMR (90 MHz) exhibits the NH proton (exchanged with D_2O) at $\delta = 8.15$, two distinct methyl proton singlets at $\delta = 0.85$ and 1.27, the skeletal proton adjacent to nitrogen as multiplet at $\delta = 5.30$, the methylenic protons at $\delta = 5.00$ as a doublet of multiplets ($J = 6.9$ Hz), and the remaining skeletal protons as multiplets at $\delta = 1.35$ (1H), 1.67–2.17 (2H) and 2.28–2.70 (3H).

Pinene shows, therefore, as substrate greater diversity in its reaction with PTAD, since both the ene-product **15** and the rearranged urazole **14** are formed, the latter as minor product. The fact that the *gem*-dimethyl group is located at the methylene bridge carbon of the resulting bicyclo[2.2.1]heptane skeleton of **14** implies that PTAD attacks from the *endo*-side of the double bond in α-pinene, affording the dipolar intermediate **13a**. Migration of the *gem*-dimethyl bearing methylene bridge is predisposed for stereoelectronic reasons, i.e. it has the antiperiplanar geometry with respect to the incoming PTAD and the *gem*-dimethyl groups stabilize the transition state for this cationic 1,2-shift.

Cycloaddition with β-Pinene (6) and 2-Carene (7)

While β-pinene reacted with PTAD in CH_2Cl_2 at room temperature within 30 min to completion, 2-carene was sufficiently more reactive so that only 0 °C was necessary. In both cases only the ene-products **16** and **17**, respectively, in 62 and 91% yields, were isolated by silica gel chromatography. The ^1H NMR spectra of the crude reaction mixtures showed no evidence for other types of cycloaddition products. The structure assignments of **16** and **17** rest on IR and ^1H and ^{13}C NMR spectral data (cf. Exp. Section).

It is unfortunate that the β-pinene (**6**) and 2-carene (**7**) substrates did not undergo dipolar cycloaddition with PTAD. In the case of β-pinene we should have obtained the rearranged urazole **11**. Since this product was on hand from the reaction of camphene with PTAD (Eq. 3), it was easy to confirm that not even traces of **11** had been formed in the reaction of β-pinene with PTAD. In the case of 2-carene dipolar cycloaddition with PTAD would have enabled an entry into the bicyclo[3.1.1]-skeleton of pinene, leading to the rearranged urazole **18**. Presumably for both substrates **6** and **7** ene-reaction is the energetically prefered cycloaddition route. This is indeed surprising, especially for the α- and β-pinenes, since *a priori* one would have thought that α-pinene (**5**) should be more ene-active than β-pinene, because the freely rotating methyl group in the α-isomer can provide more readily the essential ene-transition state **19**[7].



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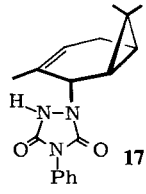

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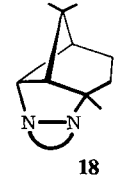

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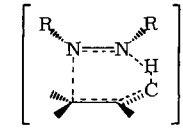

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Similarly surprising is the fact that with 2-carene only the ring hydrogens are ene-active towards PTAD, but not the methyl group. For example, towards singlet oxygen 2-carene gives predominantly the ene-product with the allylic hydrogen from the methyl group[8].

Attempted Cycloaddition with Bornene (8) and Tricyclane 9

Even after heating in an autoclave for three days at 75 °C and tetrachloroethane as solvent no cycloaddition could be achieved with bornene (**8**) and tricyclane **9**. In the case of **8**, it must be the *gem*-dimethyl substituent which blocks out dipolar cycloaddition, because norbornene reacts readily with PTAD to give the corresponding rearranged urazole[6]. For **9**, besides such steric inhibition, the cyclopropane ring is apparently not strained enough, as is the case with bicyclo[2.1.0]pentane[5], to undergo $[2_\pi + 2_\sigma]$-cycloaddition.

Considering the three questions that we initially posed about the cycloaddition of PTAD with the bicyclic monoterpenes **4** through **9**, our results allow us to provide the following answers:

(i) Since only camphene (**4**) and α-pinene (**5**) gave rearranged urazoles, namely **11** and **14**, it is difficult from these examples to recognize a structural element which dictates dipolar cycloaddition. A particularly illustrative example is α-pinene (**5**) and β-pinene (**6**). Thus, while α-pinene gives some dipolar addition and mainly ene-reaction, for β-pinene only ene-reaction takes place.

(ii) Given the possibility for ene-reaction, e.g. α- and β-pinenes and 2-carene (**7**), this will be the predominant if not exclusive course of action. Only α-camphene (**4**) gives exclusively, albeit in low yield, dipolar cycloaddition since no allylic hydrogens for ene-reaction are available. None of these monoterpenes give either $[2_\pi + 2_\pi]$- or $[2_\pi + 2_\sigma]$-cycloaddition.

(iii) Steric blocking by the *gem*-dimethyl group is brought out in the dipolar cycloaddition process since bornene (**8**) does not react while norbornene does. Steric blocking appears not to be serious for the ene-reaction since the monoterpenes **5** – **7** all react with PTAD, but quantitative kinetic experiments would be necessary to differentiate their relative reactivity.

We are grateful to the *Deutsche Forschungsgemeinschaft,* the *Fonds der Chemischen Industrie,* the *National Institutes of Health,* the *National Science Foundation,* and the *Petroleum Research Fund,* administered by the *American Chemical Society,* for financial support of this work.

Experimental Part

Melting points: Reichert Thermovar Kofler apparatus, uncorrected. – Infrared spectra: Beckman Acculab 4 or Perkin-Elmer 157 G spectrophotometer. – ^{1}H NMR spectra: Perkin-Elmer R-24 B or Varian EM-390. – ^{13}C NMR spectra were kindly run for us by Dr. *D. Scheutzow* on a Bruker WM-400 at 100 MHz or by Dipl.-Chem. *O. Brüchner* on a Bruker WH-90 at 22.6 MHz, TMS as internal standard. – Combustion analyses were run in house. – Commercial reagents and solvents were purified to match reported physical and spectral data. Known compounds used were either purchased or prepared according to literature procedures and purified to match the reported physical and spectral data.

1. *10,10-Dimethyl-N-phenyl-3,4-diazatricyclo[5.2.1.0^{1,5}]decan-3,4-dicarboximide* (**11**): A solution of 1.00 g (7.43 mmol) of camphene (**4**) and 2.50 g (14.5 mmol) of 4-Phenyl-1,2,4-triazoline-3,5-dione (PTAD) in ca. 20 ml of freshly distilled 1,1,2,2-tetrachloroethane was placed into a 100-ml stainless steel autoclave and heated with mechanical stirring at 70 – 75 °C overnight. After cooling, the resulting clear brown mixture was filtered and the filtrate concentrated in the roto-

evaporator (25 °C, 15 Torr). The residue was chromatographed on silica gel (ca. 10:1 ratio of adsorbant to substrate) eluting with CH_2Cl_2, to afford colorless crystals, 0.11 g (6%), m.p. 158–160 °C (prisms from ethanol). – IR (KBr): 3080, 2990, 2970, 2900, 1780, 1710, 1610, 1510, 1500, 1475, 1420, 1400, 1385, 1295, 1210, 1130, 1110, 775, 700 cm^{-1}. – ^{1}H-NMR ($CDCl_3$): δ = 1.00 (s, 3H, CH_3), 1.10 (s, 3H, CH_3), 1.20–2.70 (m, 7H), AB-pattern (δ_A = 3.78, δ_B = 3.52, J = 10.5 Hz; 2H, NCH_2), 3.80 (dd, J = 4.5 and 8.7 Hz; 1H, NCH), 7.25–7.55 (m, 5H, Ph). – ^{13}C-NMR ($CDCl_3$): δ = 19.84, 20.23, 26.73, 29.33, 35.19, 44.56, 46.34, 46.98, 62.36, 66.42, 125.54, 127.85, 129.03, 132.20, 152.05, 152.41. – MS (70 eV): *m/e* = 311 (41%, M^+), 135 (33, $M^+ - PhN_3C_2O_2H$), 119 (49, $PhNCO^+$), 93 (51), 79 (36), 69 (15), 41 (100).

$C_{18}H_{21}N_3O_2$ (311.4) Calcd. C 69.43 H 6.80 N 13.49 Found C 69.07 H 6.74 N 13.43

2. *7,8,8-Trimethyl-N-phenyl-4,5-diazatricyclo[4.2.1.0^{3,7}]nonan-4,5-dicarboximide* (**14**) *and 1-(6,6-Dimethyl-2-methylenebicyclo[3.1.1]hept-3-yl)-4-phenyl-1,2,4-triazolidine-3,5-dione* (**15**): To 0.50 g (3.68 mmol) of α-pinene (**5**), dissolved in ca. 15 ml of CH_2Cl_2, PTAD (0.64 g, 3.68 mmol) was added in one portion. The solution was stirred magnetically at room temperature under protection from light until the red colour of the PTAD had completely faded (ca. 24 h), resulting in a light yellow solution. The reaction mixture was concentrated by rotoevaporation (25 °C/15 torr) and chromatographed on a silica gel column (ca. 20:1 ratio adsorbant to substrate) eluting with CH_2Cl_2 to afford two products, each pure by TLC (silica gel/CH_2Cl_2/UV detection). The first eluate was cycloadduct **14**, 0.15 g (14%), m.p. 187–188 °C (needles from ethanol). – IR (KBr): 2980, 2940, 2920, 2860, 1770, 1710, 1500, 1490, 1450, 1410, 1290, 1270, 1125, 755, 690, 640 cm^{-1}. – ^{1}H-NMR ($CDCl_3$): δ = 0.97 (s, 9H, CH_3), 1.23–1.67 (m, 2H), 1.88 (m, 1H), 2.40 (m, 2H), 4.20 (d, J = 8.7 Hz; 2H, CHN), 7.47 (m, 5H, Ph). – ^{13}C-NMR ($CDCl_3$): δ = 11.37, 20.46, 36.04, 43.61, 48.24, 62.24, 64.32, 125.57, 128.12, 129.16, 131.97, 155.13.

$C_{18}H_{21}N_3O_2$ (311.4) Calcd. C 69.43 H 6.80 N 13.49 Found C 69.63 H 6.51 N 13.49

As second eluate the ene-reaction product **15** was obtained, 0.42 g (37%), m.p. 185–186 °C (prisms from methanol). – IR (KBr): 3120, 2990, 2970, 2940, 1780, 1690, 1600, 1510, 1495, 1450, 1420, 1300, 1150, 1140, 1020, 910, 810, 780, 710, 635 cm^{-1}. – ^{1}H-NMR ($CDCl_3$): δ = 0.85 (s, 3H, CH_3), 1.27 (s, 3H, CH_3), 1.35 (m, 1H), 1.67–2.17 (m, 2H), 2.28–2.70 (m, 3H), 5.00 (d of m, J_{gem} = 6.9 Hz; $=CH_2$), 5.30 (m, 1H, CHN); 7.45 (m, 5H, Ph), 8.15 (br. s, 1H, NH). – ^{13}C-NMR ($CDCl_3$): δ = 22.38, 26.05, 30.37, 30.80, 39.67, 40.44, 50.91, 51.75, 111.53, 125.30, 128.00, 128.94, 131.31, 148.37, 153.17, 154.02.

$C_{18}H_{21}N_3O_2$ (311.4) Calcd. C 69.43 H 6.80 N 13.49 Found C 69.39 H 6.98 N 13.54

3. *1-(6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-ylmethyl)-4-phenyl-1,2,4-triazolidine-3,5-dione* (**16**): β-Pinene (**6**) (0.50 g, 3.68 mmol) was dissolved in 15 ml of CH_2Cl_2 and while stirring PTAD (0.64 g, 3.68 mmol) was added. The reaction mixture, protected from light, was stirred 30 min at room temperature, at which point the color of the reaction mixture turned from dark red to light yellow. The solution was concentrated in the rotoevaporator (25 °C, 15 torr). TLC analysis (silica gel/CH_2Cl_2/UV-detection) showed the formation of only one product. Recrystallization from ethyl acetate/ethanol (1:1) afforded colorless prisms, 0.70 g (62%), m.p. 137–139 °C. – IR (KBr): 3200, 1775, 1715, 1680, 1505 cm^{-1}. – ^{1}H-NMR ($CDCl_3$): δ = 0.82 (s, 3H, CH_3), 1.16 (d, J = 9 Hz, 1H), 1.26 (s, 3H, CH_3), 1.90–2.50 (m, 5H), 3.80–4.40 (m, 2H, NCH_2), 5.50–5.70 (m, 1H, vinyl H), 7.30–7.70 (m, 5H, Ph), 7.50–8.50 (br. s, 1H, NH). – ^{13}C-NMR ($CDCl_3$): δ = 20.99, 26.05, 31.12, 31.22, 38.11, 40.41, 43.69, 50.87, 123.29, 141.19, 128.03, 128.94, 131.31, 141.19, 152.23, 152.88. – MS (70 eV): *m/e* = 311 (1%, M^+), 135 (63, $M - PhN_3C_2O_2H$), 119 (45, $PhNCO^+$), 91 (100, PhN^+).

$C_{18}H_{21}N_3O_2$ (311.4) Calcd. C 69.43 H 6.80 N 13.49 **16**: Found C 69.35 H 6.84 N 13.40
17: Found C 69.19 H 7.06 N 13.28

4. *4-Phenyl-1-(3,7,7-trimethylbicyclo[4.1.0]hept-3-en-2-yl)-1,2,4-triazolidine-3,5-dione* (**17**): To 2-carene (**7**) (0.78 g, 5.72 mmol), dissolved in ca. 13 ml of CH_2Cl_2 and cooled at 0 °C by means of an ice bath, PTAD (1.00 g, 5.71 mmol) was added in one portion and the solution was stirred magnetically for 30 min at 0 °C. The resulting clear yellow solution was concentrated in the rotoevaporator (25 °C, 15 torr) and chromatographed on a silica gel column (ca. 10:1 ratio adsorbant to substrate) eluting with CH_2Cl_2 to afford the crystalline product, 1.63 g (91%), m.p. 198 – 200 °C (needles from ethanol). – IR (KBr): 3200, 3010, 2980, 2920, 2880, 2820, 1775, 1700, 1600, 1500, 1490, 1430, 1410, 1265, 1130, 870, 770, 710 cm^{-1}. – ^{1}H-NMR ($CDCl_3$): δ = 0.50 – 1.30 (m, 2H, 1,6-H), 0.93 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 1.67 (br. s, 3H, CH_3), AB-pattern (δ_A = 2.50, δ_B = 2.07, J = 19.8 Hz; 2H, 5-H), 4.67 (br. s, 1H, CHN), 5.62 (br. s, 1H, 4-H), 7.33 – 7.75 (m, 5H, Ph). – ^{13}C-NMR ($CDCl_3$): δ = 13.45, 15.53, 17.38, 20.79, 21.18, 23.58, 28.49, 51.55, 125.30, 127.57, 127.90, 128.29, 128.91, 131.63, 151.68, 153.11.

5. *Attempted Reaction of Bornene* (**8**) *and Tricyclane* **9** *with PTAD:* A solution of **8** or **9** (1.00 g, 7.35 mmol) in 30 ml of 1,1,2,2-tetrachloroethane was placed into a 100-ml stainless steel autoclave. PTAD (2.00 g, 11.4 mmol) was added in one portion and the reaction mixture was heated by means of an oil bath at 75 °C for 3 days. After cooling, the solution was filtered, the filtrate was concentrated in the rotoevaporator (25 °C, 15 torr) and chromatographed on silica gel (ca. 10:1 ratio adsorbant to substrate), eluting wich CH_2Cl_2. Only unreacted **8** or **9** were recovered.

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[363/81]