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Unusual Rearrangement Products in the Cycloaddition of 4-Phenyl-4*H*-1,2,4-triazole-3,5-dione (PTAD) to Substituted 7-Methylenenorbornenes

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Cycloaddition of PTAD to 7-methylenenorbornene (**1a**) afforded the rearrangement urazole **2a**, but not with 7-(phenylmethylene)norbornene (**1b**) and 7-(chloromethylene)norbornene (**1c**). Instead, besides the [2 + 2] cycloadducts **3b** and **3c**, respectively, **1b** gave the double [4 + 2] adduct **4b** and **1c** the novel urazole **5c** (major product). ^{1}H NMR spectroscopy (NOE) was helpful in defining the stereochemistry of the cycloadducts **3b,c** and **4b**, while X-ray analysis was essential in determining the structure of the unusual rearrangement product **5c**.

Ungewöhnliche Umlagerungsprodukte bei der Cycloaddition von 4-Phenyl-4*H*-1,2,4-triazol-3,5-dion (PTAD) an substituierte 7-Methylennorbornene

Cycloaddition von PTAD an 7-Methylennorbornen (**1a**) führt zum Urazol **2a**. Dagegen wird mit 7-(Phenylmethylen)norbornen (**1b**) und 7-(Chlormethylen)norbornen (**1c**) neben den [2 + 2]-Cycloaddukten **3b** bzw. **3c** das zweifache [4 + 2]-Addukt **4b** bzw. das neuartige Urazol **5c** (Hauptprodukt) gebildet. ^{1}H-NMR-Spektroskopie (NOE) ergab die Stereochemie der Cycloaddukte **3b,c** und **4b**, während eine Röntgenstrukturanalyse notwendig war, um das ungewöhnliche Umlagerungsprodukt **5c** aufzuklären.

Cycloaddition of 4-phenyl-4*H*-1,2,4-triazole-3,5-dione (PTAD) to 7-methylenenorbornene (**1a**) afforded the rearrangement urazole **2a** in ca. 27% yield. Such urazoles can readily be converted into the corresponding azoalkanes via hydrolysis–oxidation[1].

Since we required for our mechanistic studies on the photodenitrogenation of azoalkanes derivatives with (*Z,E*) stereolabels, we investigated the PTAD cycloaddition of 7-(phenylmethylene) and 7-(chloromethylene)norbornenes (**1b** and **1c**),

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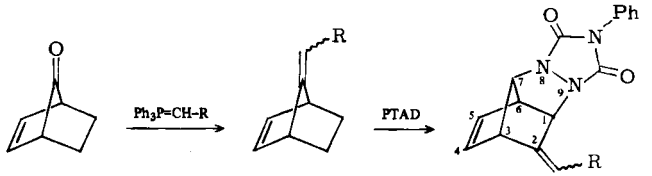
respectively. These substrates were conveniently prepared by Wittig reaction[2] with 7-norbornenone.



1a: R = H
1b: R = Ph
1c: R = Cl

2a: R = H

Contrary to our expectations, the reaction of PTAD with **1b** resulted in the [2 + 2] cycloadduct **3b** and the double [4 + 2] cycloadduct **4b**, isolated after silica gel chromatography with dichloromethane as eluant in 13% and 8% yield, respectively. Similarly, with **1c** the [2 + 2] cycloadduct **3c** was obtained in ca. 1% yield, but the major product (17%) was the unusual rearrangement urazole **5c**, as confirmed by X-ray analysis (cf. Figure 1 and Tables 1 and 2)[3]. The remainder of the crude product mixture for both cases was undefined material of higher molecular weight.

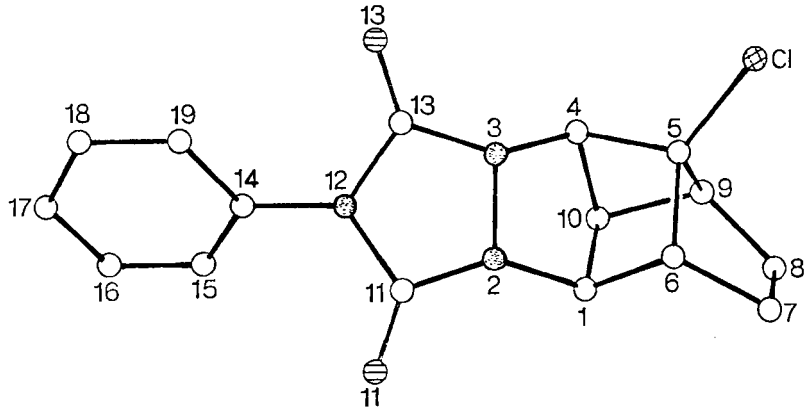
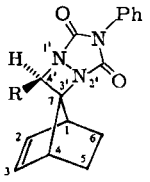


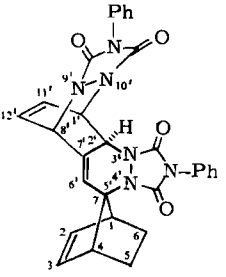
Figure 1. Perspective drawing of the crystal structure of **5c**; the numbering of the atoms corresponds to that of Tables 1 and 2; solid circles are nitrogens, hatched circles are oxygens, and open circles are carbons

While the proposed structures for the cycloadducts **3b,c** and **4b** were consistent with the observed spectroscopic and analytical data (cf. Experimental Section), the elucidation of the stereochemical features of these products required more rigorous proof. For this purpose NOE differential ^{1}H NMR spectroscopy[4] was helpful and definitive. For example, in the case of the [2 + 2] cycloadduct **3b**, irradiation of the *ortho* protons (δ = 7.44) of the phenyl group at C-4′ resulted in small (1.3%) enhancements of the olefinic protons 2-H (δ = 5.43) and 3-H (δ = 6.01), an

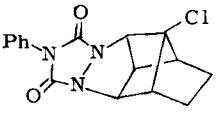
appreciable (5.2%) enhancement of the bridgehead proton 4-H (δ = 2.80), and a large (14.2%) enhancement of the adjacent proton 4′-H (δ = 5.40). No detectable enhancement of the ethano bridge *exo* protons 5-H and 6-H was observed. This clearly places the phenyl group at C-4′ above the olefinic bridge. Irradiation of 4′-H caused a moderate (5.8%) enhancement for the signal of the bridgehead proton 1-H (δ = 3.06). Furthermore, all the expected vicinal enhancements could be confirmed. By analogy the same stereochemistry of the [2 + 2] cycloadduct **3c** was assigned.



3b: R = Ph
3c: R = Cl



4b



5c

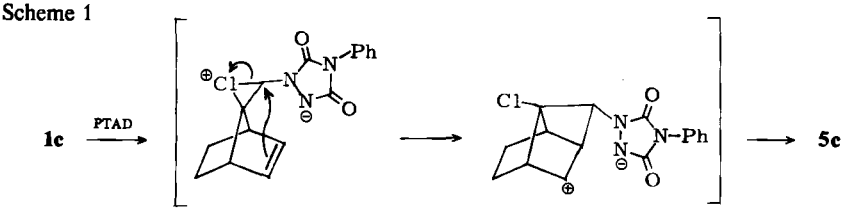
More involved was the elucidation of the double PTAD adduct **4b**, but NOE differential ^{1}H NMR spectroscopy permitted an unequivocal confirmation of the proposed stereochemistry. The crucial protons for this purpose are 2′-H and 6′-H. Since the bridgehead protons adjacent to the urazole nitrogens (1′-H, 2′-H, and 8′-H) resonate at low field, and thus the signals are located in the region of the olefinic protons 2-H, 3-H, 6′-H, 11′-H, and 12′-H, first an unequivocal assignment of the 2′-H and 6′-H protons was necessary. This assignment was further complicated by the fact that in $CDCl_3$ the ^{1}H NMR spectrum (200 MHz) shows the 1′-H, 6′-H, 11′-H, and 12′-H signals bunched together as a complex signal at δ = 6.58–6.69. Fortunately, in C_6D_6 these signals are separated sufficiently to permit a rigorous NOE analysis. By means of the large and mutual vicinal enhancements within the diazacyclooctene system, 2′-H and 6′-H could be assigned to either resonance at δ = 3.75 or 5.98. Their absolute assignment could not be obtained from quantitative considerations of the dipolar enhancements between these resonances and those of the bridgeheads 1-H and 4-H at δ = 2.52 and 3.47 since the relative distances are determined by the preferred conformation of the "lower" dihydropyrazine ring. The following qualitative analysis is more definitive. From the resonance at δ = 5.98 positive interaction of this proton with both olefinic protons 2-H and 3-H can be concluded and it is, therefore, to be assigned to the olefinic 6′-H, while the resonance at δ = 3.75 displays a negative interaction with the olefinic resonance at δ = 5.47 only. Inspection of a molecular model reveals a quasi colinear alignment of protons 2′-H (δ = 3.75), 1′-H (δ = 2.52), and 2-H (δ = 5.47), which is particularly prominent when the dihydropyrazine ring acquires the boat conformation. The other bridgehead proton (4-H) resonates at δ = 3.47.

With this analysis all protons could be characterized rigorously. The stereochemistry of the urazole ring (3′,4′-N) is implicit in the analysis. Irradiation of proton 6′-H caused unequivocal enhancements of the signals of the olefinic protons 2,3-H, but not for the methylenic protons 5,6-H. This places the urazole ring above the ethano bridge. Furthermore, the mutual appreciable interactions between protons 2′-H and 11′-H imply that the 2′-H proton is *exo* to the second urazole ring (9′,10′-N). Consequently, both PTAD moieties are located *anti* to the double bond of the norbornene ring.

Further corroboration of this *anti,anti* stereochemistry derives from other negative enhancements. For example, irradiation of bridgehead 1-H caused a positive enhancement of the signal of 2′-H, but also an appreciable negative enhancement in the case of 1′-H. A quasi colinear alignment of these three bridgehead protons is attained when the "lower" dihydropyrazine ring acquires a boat conformation. The latter fact (cf. molecular models) would also explain why the mutual NOE enhancements were larger (ca. 2–3-fold) for the 1-H and 2′-H interaction than for the 4-H and 6′-H interaction. A boat conformation of the "lower" dihydropyridazine ring brings the bridgehead protons 1-H and 2′-H into closer proximity. Also 4-H, 6′-H, and 8′-H must be quasi colinear since a negative NOE enhancement was observed for 8′-H when 4-H was irradiated. These structural requisites can only be satisfactorily rationalized if the *anti,anti* stereochemistry is assumed for the double PTAD adduct **4b**.

Mechanistically the preferential formation of the *anti,anti* stereoisomer out of the four possible ones can be rationalized on grounds that electrophilic reagents attack 7-alkylidenenorbornenes predominantly from the ethano bridge[5]. The *anti* π bond can in this way stabilize the incipient positive charge of the dipolar transition state through secondary orbital interactions. Thus, the first PTAD molecule attacks the styryl dienic moiety *anti* to the norbornene π bond through such stereoelectronic control. The *anti* attack of the second PTAD molecule on the resulting cyclohexadiene unit is dictated by steric reasons. The spironorbornene moiety and the 2′-H proton (*syn* approach) provide greater steric impediment towards the approaching PTAD molecule than the urazole ring (*anti* approach).

Scheme 1



Similarly, stereoelectronic factors explain the *anti* stereochemistry of the [2 + 2] cycloadducts **3b** and **3c**. The π-donating phenyl and chloro substituents activate the 7-alkylidene bond towards electrophilic attack by PTAD. The resulting dipolar species[6] is again better stabilized if the PTAD molecule approaches *anti* to the

norbornene double bond. Preferential attack of PTAD on the activated 7-alkylidene π bond also explains why no rearrangement urazoles **2b,c** were obtained from norbornenes **1b,c**.

The mechanistic origin for the unexpected rearrangement product **5c** (Figure 1) formed from **1c** as major cycloadduct with PTAD is perplexing. Clearly, some rather unconventional skeletal rearrangements must have taken place. A plausible mechanism is suggested in Scheme 1 in which PTAD approaches from the *syn* side of the norbornene double bond, the positive charge being stabilized by the neighboring chloro substituent. Double-bond attack with chlorine migration and collapse of the resulting dipolar ion would lead to the unusual urazole **5c**. Inspection of molecular models reveals that the 2p orbitals of the π bond are situated optimally for such participation. Once again the complex and diverse cycloaddition behavior of PTAD is emphasized by means of this unconventional reaction[7].

We thank the *Deutsche Forschungsgemeinschaft*, the *Fonds der Chemischen Industrie*, and the Italian *Consiglio Nazionale delle Ricerche* for generous financing. We appreciate the assistance of Dr. *G. Lange* in measuring the mass spectra and Dr. *D. Scheutzow* for the NMR spectra.

Experimental

General Methods: IR spectra were obtained on a Perkin-Elmer Model 1420 and Beckman Acculab 4 instruments. – ^{1}H NMR data were run on the Hitachi-Perkin Elmer R-24B (60 MHz), Varian EM-390 (90 MHz), Bruker WP-200SY (200 MHz), and Bruker WM-400 (400 MHz) spectrometers, the ^{13}C NMR data (100 MHz) also on the latter. Chemical shifts (δ values) are given relative to tetramethylsilane for protons and deuteriochloroform for carbons. NOE experiments were run on a Bruker WP 200SY instrument. The samples (in $CDCl_3$ or C_6D_6) were freed from oxygen through sonication under N_2 flow. In the perturbational experiments the selected multiplet was saturated in the gated mode with the least power through an 8-s cyclic irradiation of all multiplet lines[8]. The enhancements were determined from the multiplier of the reference spectrum, bringing the observed multiplet to exact matching with the corresponding multiplet in the perturbed spectrum. – Mass spectra (70 eV) were measured on a Varian MAT CH-7. – Melting points were taken on a Reichert Thermovar Kofler apparatus and are uncorrected. – Combustion analyses for elemental composition were run in-house or by Professor *G. Maier*'s staff (Gießen). – For thin-layer chromatography (TLC) Polygram SIL/G/UV (40 × 80 mm) of Macherey, Nagel & Co. were used. Preparative GC was performed on a Carlo Erba 420 (FID) instrument. Column A consisted of 3-m × 3/8-in. stainless steel tubing, packed with 20% Apiezon M on 60/80 mesh Chromosorb W/AW-DMCS and column B of 6-m × 3/8-in. stainless steel tubing, packed with 25% SE 30 on 60/80 mesh Chromosorb W/AW-DMCS.

All known compounds used here were either purchased or prepared according to the reported methods and purified to match the reported physical and spectral data. Unless otherwise stated, roto-evaporation of the solvent was carried out at ca. 20–25°C and 10–20 Torr (water aspirator). Drying was conducted over anhydrous sodium sulfate and the adsorbant for column chromatography (CC) was silica gel (32–63 mesh), using a substrate to adsorbant ratio of ca. 1:20. Stirring was carried out magnetically by means of a spinbar. Room temperature (r.t.) was ca. 20°C.

7-(Phenylmethylene)bicyclo[2.2.1]hept-2-ene (**1b**): A suspension of 8.30 g (74.1 mmol) of potassium *tert*-butoxide in 150 ml of ether was added over a period of 2 h to a suspension of 32.0 g (73.9 mmol) of benzyltriphenylphosphonium bromide in ca. 150 ml of ether under nitrogen. After the solution was stirred for additional 2 h at r.t., a solution of 4.00 g (37.0 mmol) of 7-norbornenone was added dropwise to the mixture and stirred for about 12 h. After work-up, filtration, drying, and roto-evaporation, the oily residue was distilled under reduced pressure to afford 4.10 g (60%) of **1b**, b.p. 141–145°C/16 Torr. – IR (film): 3022, 2975, 2960, 2922, 1683, 1598, 1490, 1441, 908, 857, 750, 690 cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.15 (bd, $J_{5n,5x} = J_{6n,6x}$ = 10 Hz; 2H, 5-H_n, 6-H_n), 1.80 (m, 2H, 5-H_x, 6-H_x), 3.11 (m; 1H, 1-H), 3.66 (m; 1H, 4-H), 5.70 (s; 1H, 8-H), 6.22 (dd, $J_{2,3}$ = 6.0 Hz, $J_{2,1}$ = 3.0 Hz; 1H, 2-H), 6.26 (dd, $J_{2,3}$ = 6.0 Hz, $J_{3,4}$ = 3.0 Hz; 1H, 3-H), 7.13–7.27 (m; 5H, C_6H_5). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 24.25 (t), 24.59 (t), 41.05 (d, C-4), 46.63 (d, C-1), 107.30 (d; C-8), 125.80 (d), 127.98 (d), 128.13 (d), 135.57 (d; C-2), 135.70 (d; C-3), 137.92 (s), 157.64 (s; C-7). – MS (70 eV): *m/z* (%) = 182 (56, $M^{\oplus}$), 167 (13), 154 (100), 153 (90), 152 (45), 128 (13), 115 (15).

$C_{14}H_{14}$ (182.3) Calcd. C 92.26 H 7.74 Found C 92.14 H 7.72

7-(Chloromethylene)bicyclo[2.2.1]hept-2-ene (**1c**): To a suspension of 14.5 g (41.8 mmol) of triphenyl(chloromethyl)phosphonium chloride in 150 ml of ether was gradually added 4.60 g (41.1 mmol) of potassium *tert*-butoxide. The mixture turned yellow at once, was stirred for 4 h, and 3.00 g (27.8 mmol) of 7-norbornenone was added during 20 min by means of a dropping funnel. The solution turned gradually brown and was allowed to stir for about 12 h. After removal of the solid residues by filtration, 200 ml of water was added to the filtrate, the ether layer dried with sodium sulfate and concentrated. Distillation under reduced pressure afforded 2.50 g (64%) of **1c** as colorless liquid, b.p. 85–88°C/55 Torr. – IR (film): 3025, 2978, 2963, 2928, 1680, 1319, 1270, 853, 775, 714 cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.15 (q, $J_{5n,5x} = J_{6n,6x}$ = 10.3 Hz, $J_{5n,6n} = J_{6n,5n}$ = 2.4 Hz; 2H, 5-H_n, 6-H_n), 1.75 (m; 2H, 5-H_x, 6-H_x), 3.13 (m; 1H, 4-H), 3.52 (m; 1H, 1-H), 5.33 (s; 1H, 8-H), 6.18 (m; 2H, 2-H, 3-H). – ^{13}C NMR ($CDCl_3$, 400 MHz): δ = 23.50 (t), 25.07 (t), 41.86 (d), 44.36 (d), 95.38 (d), 134.87 (d), 135.26 (d), 156.25 (s, C-7). – MS (70 eV): *m/z* (%) = 142 (1, $M^{\oplus}$ + 2), 140 (3, $M^{\oplus}$), 112 (100), 105 (17), 103 (7).

C_8H_9Cl (140.6) Calcd. C 68.34 H 6.45 Found C 68.08 H 6.67

2-Methylene-N-phenyl-8,9-diazatricyclo[4.3.0.0^{3,7}]non-4-ene-8,9-dicarboximide (**2a**): A sample of PTAD (18.0 g, 103 mmol) was added in small portions to 10.6 g (100 mmol) of 7-methylenenorbornene (**1a**) in 100 ml of methylene chloride while protecting from light. An exothermic reaction ensued and the reaction mixture was allowed to stand for about 12 h. After filtration the filtrate was concentrated by roto-evaporation and the residue was chromatographed on silica gel, eluting with methylene chloride. As first eluate 7.61 g (27%) of urazole **2a** was isolated, which was recrystallized from acetone to give colorless plates, m.p. 164–165°C. – IR (KBr): 2960, 2940, 2860, 1768, 1720, 1598, 1498, 1400, 1124, 915, 770, 735 cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.60 (m; 2H), 1.86 (m; 2H), 3.04 (bs; 1H, 6-H or 3-H), 3.20 (bs; 1H, 3-H or 6-H), 4.36 (m; 1H, 1-H or 7-H), 4.58 (d, *J* = 2.0 Hz; 1H, 7-H or 1-H), 5.12 (d, *J* = 0.5 Hz; 1H, $=CH_2$), 5.31 (bs; 1H, $=CH_2$), 7.30–7.48 (m; 5H, C_6H_5). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 18.40 (t), 29.86 (t), 47.97 (d), 49.67 (d), 66.46 (d), 67.57 (d), 110.82 (t, $=CH_2$), 125.63 (d), 128.31 (d), 129.08 (d), 131.59 (s), 145.39 (s), 156.44 (s; C=O), 156.58 (s; C=O). – MS (70 eV): *m/z* (%) = 281 (100, $M^{\oplus}$), 162 (39), 134 (26), 119 (48), 107 (23), 91 (66), 78 (52).

$C_{16}H_{15}N_3O_2$ (281.3) Calcd. C 68.31 H 5.37 N 14.94 Found C 68.30 H 5.30 N 15.05

Cycloaddition of PTAD to **1b**: Following the procedure for **1a**, from the reaction of 1.00 g (5.49 mmol) of **1b** and 1.52 g (8.68 mmol) of PTAD in 15 ml of methylene chloride at ca. 20°C were obtained 260 mg (13%) of the urazole **3b** as first eluate, m.p. 128–129°C, colorless prisms (acetone) and 230 mg (8%) of diurazole **4b** as second eluate, m.p. 263–265°C, colorless prisms (acetone).

N,4'-Diphenylspiro[bicyclo[2.2.1]hept-2-ene-7,3'-[1,2]diazetidine]-1',2'-dicarboximide (**3b**): IR (KBr): 3065, 3000, 1781, 1720, 1597, 1485, 1390, 1042, 1022, 750, 700 cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.04 (ddd, $J_{6n,6x}$ = 11.5 Hz, $J_{6n,5n}$ = 10.0 Hz, $J_{6n,5x}$ = 4.5 Hz; 1H, 6-H_n), 1.15 (ddd, $J_{5n,5x}$ = 12.5 Hz, $J_{5n,6n}$ = 10.0 Hz, $J_{5n,6x}$ = 2.5 Hz; 1H, 5-H_n), 2.07 (ddd, $J_{5x,5n}$ = 12.5 Hz, $J_{5x,6x}$ = 9.0 Hz, $J_{5x,6n}$ = 4.5 Hz; 1H, 5-H_x), 2.69 (m; 1H, 6-H_x), 2.75 (m; 1H, 4-H), 2.99 (m; 1H, 1-H), 5.34 (dd, $J_{3,2}$ = 6.0 Hz, $J_{3,4}$ = 3.0 Hz; 1H, 3-H), 5.38 (s; 1H, 4'-H), 5.91 (dd, $J_{2,3}$ = 6.0 Hz, $J_{2,1}$ = 3.5 Hz; 1H, 2-H), 7.28–7.68 (m; 10H, C_6H_5). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.16 (t), 24.47 (t), 45.84 (d, C-4), 47.25 (d; C-1), 70.35 (d; C-4'), 90.56 (s; C-7), 125.17 (d), 127.75 (d), 128.11 (d), 128.16 (d), 128.35 (d), 128.96 (d), 131.45 (d), 131.60 (s), 132.90 (d), 136.24 (s), 159.00 (s), 161.02 (s). – MS (70 eV): *m/z* (%) = 357 (100, $M^{\oplus}$), 214 (56), 182 (36), 181 (39), 167 (28), 154 (67), 153 (65), 152 (28), 132 (17), 128 (13), 119 (46).

$C_{22}H_{19}N_3O_2$ (357.4) Calcd. C 73.93 H 5.36 N 11.76 Found C 74.09 H 5.24 N 11.77

N,N'-Diphenylspiro[bicyclo[2.2.1]hept-2-ene-7,5'-[3,4,9,10]tetraazatricyclo[6.2.2.0^{2,7}]dodeca[6,11]diene]-anti-3',4',anti-9',10'-bis(dicarboximide) (**4b**): IR (KBr): 3070, 2950, 1781, 1760, 1718, 1701, 1501, 1415, 1397, 768, 744 cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.23 (m; 2H, 5-H_n, 6-H_n), 1.84 (m; 1H, 6-H_x), 2.58 (m; 1H, 5-H_x), 3.07 (m; 1H, 1-H), 3.59 (m; 1H, 4-H), 4.48 (dd, $J_{2',6'}$ = 3.0 Hz. $J_{2',1'}$ = 2.0 Hz; 1H, 2'-H), 5.29 (dd, $J_{8',12'}$ = 5.5 Hz, $J_{8',11'}$ = 1.5 Hz; 1H, 8'-H), 5.98 (ddd, $J_{2,3}$ = 5.7 Hz, $J_{2,1}$ = 3.3 Hz, $J_{2,4}$ = 1.0 Hz; 1H, 2-H), 6.28 (ddd, $J_{3,2}$ = 5.7 Hz, $J_{3,4}$ ≈ 3.3 Hz, $J_{3,1}$ = 1.0 Hz; 1H, 3-H), 6.58 (dm, $J_{1',11'}$ = 5.5 Hz; 1H, 1'-H), 6.64 (td, $J_{12',11'}$ = $J_{12',8'}$ = 5.5 Hz, $J_{12',1'}$ = 1.5 Hz; 1H, 12'-H), 6.69 (d, $J_{6',2'}$ = 3.0 Hz; 1H, 6'-H), 6.70 (dt, $J_{11',12'}$ = $J_{11',1'}$ = 5.5 Hz; 1H, 11'-H), 7.32–7.76 (m; 10H, C_6H_5). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 22.68 (t), 24.20 (t), 46.92 (d; C-1), 49.64 (d; C-4), 51.88 (d), 54.04 (d), 56.96 (d), 75.24 (s; C-7), 125.44 (d), 125.92 (d), 127.92 (d), 128.32 (d), 129.92 (d), 129.04 (d), 129.52 (d), 130.92 (d), 131.24 (s), 131.60 (s), 132.68 (d), 132.88 (d), 136.32 (d), 146.80 (s; C-7'), 150.80 (s), 154.72 (s), 155.64 (s). – MS (70 eV): *m/z* (%) = 532 (28, $M^{\oplus}$), 357 (34), 356 (100), 355 (70), 329 (30), 328 (23), 237 (16), 207 (17), 182 (34), 177 (41), 153 (39), 132 (48), 119 (98).

$C_{30}H_{24}N_6O_4$ (532.6) Calcd. C 67.66 H 4.54 N 15.78 Found C 68.15 H 4.38 N 15.99

Cycloaddition of PTAD to **1c**: Following the above procedure for **1a**, from the reaction of 9.00 g (64.0 mmol) of **1c** and 16.0 g (91.4 mmol) of PTAD in 40 ml of methylene chloride at ca. 20°C were obtained as first eluate 150 mg (0.6%) of urazole **3c**, m.p. 122–123°C, colorless prisms (acetone) and 4.07 g (17%) of urazole **5c** as second eluate, m.p. 230–232°C, colorless powder (acetone). As third eluate was isolated 10 mg (0.1%) of a product, m.p. 282–284°C (acetone), which could not be characterized until now.

4'-Chloro-N-phenylspiro[bicyclo[2.2.1]hept-2-ene-7,3'-[1,2]diazetidine]-1',2'-dicarboximide (**3c**): IR (KBr): 2945, 1774, 1732, 1715, 1496, 1399, 1382, 1268, 782, 720 cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.28 (ddd, $J_{6n,6x}$ = 11.5 Hz, $J_{6n,5n}$ = 9.5 Hz, $J_{6n,5x}$ = 4.0 Hz; 1H, 6-H_n), 1.33 (ddd, $J_{5n,5x}$ = 11.5 Hz, $J_{5n,6n}$ = 9.5 Hz, $J_{5n,6x}$ = 4.0 Hz; 1H, 5-H_n), 2.32 (ddt, $J_{5x,6x}$ = 9.5 Hz, $J_{5x,6n}$ = $J_{5x,4}$ = 4.0 Hz; 1H, 5-H_x), 2.51 (ddt, $J_{6x,6n}$ = 11.5 Hz, $J_{5x,6x}$ = 9.5 Hz, $J_{6x,5n}$ = $J_{6x,1}$ = 4.0 Hz; 1H, 6-H_x), 3.16 (m; 1H, 4-H), 3.29 (m; 1H, 1-H), 5.86 (s; 1H, 4'-H), 5.99 (dd, $J_{2,3}$ = 6 Hz, $J_{2,1}$ = 3.5 Hz; 1H, 2-H), 6.14 (dd, $J_{2,3}$ = 6 Hz, $J_{3,4}$ = 3.5 Hz; 1H, 3-H), 7.45 (m; 5H, C_6H_5). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.31 (t), 23.04 (t), 44.94 (d,

C-4), 48.12 (d, C-1), 78.70 (d, C-3'), 89.54 (s, C-7), 125.59 (d), 128.78 (d), 129.23 (d), 130.32 (d), 131.13 (s), 134.29 (d), 157.70 (s), 159.14 (s). – MS (70 eV): *m/z* (%) = 317 (7, $M^{\oplus}$ + 2), 315 (21, $M^{\oplus}$), 280 (4), 237 (4), 214 (35), 161 (15), 119 (100), 91 (31).

$C_{16}H_{14}ClN_3O_2$ (315.6) Calcd. C 60.86 H 4.47 N 13.91 Found C 61.13 H 4.40 N 12.91

5-Chloro-N-phenyl-2,3-diazatetracyclo[4.4.0.0^{4,10}.0^{5,9}]decane-2,3-dicarboximide (**5c**): IR (KBr): 1775, 1712, 1498, 1410, 1272, 1130, 1039, 775 cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.64 (ddd, $J_{8x,8n}$ = 14 Hz, $J_{8n,7n}$ = 9.2 Hz, $J_{8n,7x}$ = 7.5 Hz; 1H, 8-H_n), 1.91 (m; 2H, 8-H_x, 7-H_n), 2.20 (dddd, $J_{7x,7n}$ = 13 Hz, $J_{7x,8x}$ = 11 Hz, $J_{7x,8n}$ = 7.5 Hz, $J_{7x,6}$ = 3.5 Hz; 1H, 7-H_x), 2.47 (dm; 1H, 6-H), 2.54 (ddd, $J_{8x,9}$ = 6.1 Hz, $J_{9,10}$ = 3.5 Hz, $J_{6,9}$ = 1.2 Hz; 1H, 9-H), 3.08 (qd, $J_{1,10}$ = $J_{4,10}$ = $J_{9,10}$ = 3.5 Hz, $J_{6,10}$ = 1.5 Hz; 1H, 10-H), 4.32 (d, $J_{1,10}$ = 3.5 Hz; 1H, 1-H), 4.67 (d, $J_{4,10}$ = 3.5 Hz; 1H, 4-H), 7.38–7.46 (m; 5H, C_6H_5). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 22.71 (t, C-8), 27.94 (t, C-7), 46.43 (d), 47.67 (d), 51.09 (d, C-10), 62.20 (d, C-1), 68.72 (d, C-4), 71.87 (s, C-5), 125.40 (d), 128.40 (d), 129.19 (d), 131.44 (s), 156.22 (s), 156.37

Table 1. Positional [× 10^4] and isotropic thermal [$pm^2 \times 10^{-1}$] parameters of **5c**[a]

	x	y	z	U
Cl	906(1)	-4047(1)	1274(1)	69(1)
C(1)	498(2)	-1774(2)	3867(2)	37(1)
N(2)	1285(2)	-1038(1)	3493(2)	37(1)
N(3)	1199(2)	-1236(1)	1982(2)	35(1)
C(4)	199(2)	-1930(2)	1450(2)	36(1)
C(5)	397(2)	-3021(2)	2117(2)	39(1)
C(6)	986(2)	-2869(2)	3782(3)	39(1)
C(7)	426(2)	-3668(2)	4535(3)	49(1)
C(8)	-874(2)	-3635(2)	3557(3)	55(1)
C(9)	-848(2)	-2993(2)	2234(3)	46(1)
C(10)	-564(2)	-1822(2)	2471(3)	41(1)
C(11)	1389(2)	11(2)	3752(2)	38(1)
O(11)	1418(2)	464(1)	4864(2)	52(1)
N(12)	1526(2)	437(1)	2457(2)	35(1)
C(13)	1297(2)	-297(2)	1330(2)	35(1)
O(13)	1240(2)	-158(1)	60(2)	45(1)
C(14)	1859(2)	1484(2)	2322(2)	35(1)
C(15)	1352(2)	2284(2)	2861(3)	45(1)
C(16)	1704(3)	3295(2)	2753(3)	60(1)
C(17)	2543(3)	3501(2)	2095(3)	61(1)
C(18)	3027(2)	2701(2)	1529(3)	53(1)
C(19)	2697(2)	1682(2)	1645(3)	43(1)

[a] The standard deviations are given in parentheses. Equivalent isotropic *U* is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. Bond lengths [pm] and angles [deg] of **5c**; the standard deviations are given in parentheses

Bond lengths			
Cl-C(5)	175.4(3)	C(1)-N(2)	146.5(3)
C(1)-C(6)	154.1(3)	C(1)-C(10)	154.2(3)
N(2)-N(3)	143.7(3)	N(2)-C(11)	137.3(3)
N(3)-C(4)	146.4(3)	N(3)-C(13)	138.2(3)
C(4)-C(5)	153.2(3)	C(4)-C(10)	154.1(4)
C(5)-C(6)	154.1(3)	C(5)-C(9)	154.7(4)
C(6)-C(7)	152.8(4)	C(7)-C(8)	156.4(3)
C(8)-C(9)	151.7(4)	C(9)-C(10)	154.9(3)
C(11)-O(11)	120.2(3)	C(11)-N(12)	140.8(3)
N(12)-C(13)	139.5(3)	N(12)-C(14)	142.5(3)
C(13)-O(13)	120.6(3)		
Bond angles			
N(2)-C(1)-C(6)	106.9(2)	N(2)-C(1)-C(10)	104.3(2)
C(6)-C(1)-C(10)	98.6(2)	C(1)-N(2)-N(3)	106.1(2)
C(1)-N(2)-C(11)	128.6(2)	N(3)-N(2)-C(11)	109.3(2)
N(2)-N(3)-C(4)	104.7(2)	N(2)-N(3)-C(13)	107.8(2)
C(4)-N(3)-C(13)	123.7(2)	N(3)-C(4)-C(5)	114.1(2)
N(3)-C(4)-C(10)	108.6(2)	C(5)-C(4)-C(10)	82.4(2)
Cl-C(5)-C(4)	122.2(2)	Cl-C(5)-C(6)	116.9(2)
C(4)-C(5)-C(6)	106.0(2)	Cl-C(5)-C(9)	122.6(2)
C(4)-C(5)-C(9)	88.7(2)	C(6)-C(5)-C(9)	94.3(2)
C(1)-C(6)-C(5)	96.2(2)	C(1)-C(6)-C(7)	111.0(2)
C(5)-C(6)-C(7)	105.5(2)	C(6)-C(7)-C(8)	102.3(2)
C(7)-C(8)-C(9)	103.7(2)	C(5)-C(9)-C(8)	108.5(2)
C(5)-C(9)-C(10)	81.7(2)	C(8)-C(9)-C(10)	118.0(2)
C(1)-C(10)-C(4)	92.7(2)	C(1)-C(10)-C(9)	104.7(2)
C(4)-C(10)-C(9)	88.3(2)	N(2)-C(11)-O(11)	127.8(2)
N(2)-C(11)-N(12)	104.7(2)	O(11)-C(11)-N(12)	127.3(2)
C(11)-N(12)-C(13)	111.3(2)	C(11)-N(12)-C(14)	124.2(2)
C(13)-N(12)-C(14)	124.5(2)	N(3)-C(13)-N(12)	105.7(2)
N(3)-C(13)-O(13)	126.6(2)	N(12)-C(13)-O(13)	127.6(2)
N(12)-C(14)-C(15)	120.2(2)	N(12)-C(14)-C(19)	119.0(2)

(s). – MS (70 eV): *m/z* (%) = 317 (6, $M^{\oplus}$ + 2), 315 (18, $M^{\oplus}$), 214 (100), 146 (9), 119 (19), 95 (51).

$C_{16}H_{14}ClN_3O_2$ (315.6) Calcd. C 60.86 H 4.47 N 13.31 Found C 60.92 H 4.31 N 13.46

X-Ray Analysis of 5c[9]

The orientation matrix and the cell parameters were determined from a clear colorless crystal of dimensions 0.4 × 0.6 × 0.2 mm on a Syntex-P3 four-circle diffractometer. Measurement of intensities: ω-scan, 1° range, MoK_α, 2Θ maximum = 55°. The intensities of 2659 reflections were measured. 2322 of them with $F > 3\sigma(F)$ were applied for the structure determination. The structure was solved by direct phase determination. The phases of 426 strong reflections were determined and from the resulting *E*-map approximate postitions of all non-hydrogen atoms could be refined by anisotropic least squares cycles to $R = 0.044$. The positions of the hydrogen atoms were calculated geometrically and considered isotropically in all refinements.

5c crystallizes monoclinically in the space group $P2_1/3$ (No. 14) with $a = 1211.0(8)$, $b = 1288.1(8)$, $c = 954.4(6)$ pm and $\beta = 107.92(5)°$. The unit cell contains $Z = 4$ formula units, the density was calculated to be 1.480 g·cm^{-3}. Selected atomic parameters are listed in Table 1. The labeling of the atoms is given in Figure 1. Selected bond distances and angles are summarized in Table 2.

CAS Registry Numbers

1a: 694-69-9 / **1b**: 103850-97-1 / **1c**: 103834-95-3 / **2a**: 103834-96-4 / **3b**: 103834-97-5 / **3c**: 103834-99-7 / **4b**: 103834-98-6 / **5c**: 103835-00-3 / PTAD: 4233-33-4 / 7-norbornenone: 694-71-3 / benzyltriphenylphosphonium bromide: 1449-46-3 / triphenyl(chloromethyl)-phosphonium chloride: 5293-84-5

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[3] Remarkable is the deviation of the tetrahedral configuration about C-5 (cf. Table 2). For an ideal tetrahedron the sum of angles amounts to 12 × arctan $\sqrt{2}$ = 656.83°. Is the tetrahedron, however, distorted such that three bonds form a cube vertex and the fourth is parallel to the space diagonal of that cube, then the sum of angles amounts to 3 × 90° + 3 (180° − arctan $\sqrt{2}$) = 645.79°. In the case of C-5, the sum of angles is 650.7° and consequently lies almost exactly between the sums of angles of the ideal tetrahedron and the cube configurations.

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[9] Further details and basic data concerning the X-ray analysis may be obtained from Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen 2 (W. Germany) by specifying registry number CSD 51857, author, and the reference to this publication.

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