Cycloaddition Behavior of 2-Substituted Norbornadienes towards 4-Phenyl-4*H*-1,2,4-triazole-3,5-dione (PTAD): Homo Diels-Alder Reactivity versus Insertion, Rearrangement, and [2 + 2] Cycloaddition

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Received October 20, 1986

The reaction of PTAD with 2-trimethylsilyl-, 2-chloro-, 2-cyano-, and 2-methoxycarbonylnorbornadienes **1a–d**, respectively, was investigated. In all cases homo Diels-Alder adducts were obtained, for **1a** the unexpected regioisomer, the 1-trimethylsilyl derivative **2a**, and for other norbornadienes **1b–d** the usual cyclopropane-substituted products **2b–d**. Except for the trimethylsilyl system **1a**, for which also the dicarboximides **4a** and **4'a**, respectively, (rearrangement urazoles) were obtained, the other norbornadienes **1b–d** afforded the insertion products **5b–d**. With increasing electron-withdrawal by the 2-substituents the insertion products **5b–d** increased at the expense of the homo Diels-Alder adducts **2b–d**. These results are mechanistically rationalized in terms of stepwise cycloaddition via 1,5-dipolar intermediates. In the case of 2-chloronorbornadiene (**1b**), besides the homo Diels-Alder **2b**, the rearrangement urazole **4b** and the insertion product **5b**, also the [2 + 2] cycloadduct **3b** was formed.

Cycloadditionsverhalten von 2-substituierten Norbornadienen mit 4-Phenyl-4*H*-1,2,4-triazol-3,5-dion (PTAD): Homo-Diels-Alder-Reaktivität gegenüber Einschiebung, Umlagerung und [2 + 2]-Cycloaddition

Die Reaktion von PTAD mit den 2-Trimethylsilyl-, 2-Chlor-, 2-Cyan- oder 2-Methoxycarbonylnorbornadienen **1a–d** wurde untersucht. In allen Fällen wurden Homo-Diels-Alder-Addukte erhalten, von **1a** das unerwartete Regioisomere 1-Trimethylsilylderivat **2a** und von **1b–d** die gewöhnlichen cyclopropansubstituierten Produkte **2b–d**. Zusätzlich führte das Trimethylsilylsystem **1a** zu den Dicarboximiden **4a** bzw. **4'a** (Umlagerungsurazole). Die Norbornadiene **1b–d** bildeten die Insertionsprodukte **5b–d**. Mit steigendem Elektronenzug der 2-Substituenten werden die Einschiebungsprodukte **5b–d** auf Kosten der Homo-Diels-Alder-Addukte **2b–d** in steigendem Maß gebildet. Diese Ergebnisse erklären wir unter der Annahme eines mehrstufigen Cycloadditionsmechanismus über 1,5-dipolare Zwischenstufen. Im Fall von 2-Chlornorbornadien (**1b**) wurde neben dem Homo-Diels-Alder-Addukt **2b**, dem Umlagerungsurazol **4b** und dem Einschiebungsprodukt **5b** auch das [2 + 2]-Cycloaddukt **3b** erhalten.

The usual cycloaddition of dienophiles with norbornadienes is the homo Diels-Alder reaction[1]. In the case of carbenes and singlet oxygen, such electrophilic species lead besides homo Diels-Alder products also to [2 + 2] cycloadducts[2]. In fact, with difluorocarbene [2 + 2] cycloaddition predominates; but with increasing electron-withdrawing substituents at the 2-position of the norbornadiene, the proportion of homo Diels-Alder reaction decreases. This interesting reactivity pattern has been rationalized[2] in terms of LUMO carbene – HOMO diene interaction and polarization of the π bonds by the 2-substituents, suggesting that other electrophilic dienophiles should portray this cycloaddition behavior.

Previously we reported[3] our preliminary results on the reaction of PTAD with 2-chloronorbornadiene, which exhibits most unusual cycloaddition behavior (Eq. 1; X = Cl). While precedents for homo Diels-Alder, [2 + 2], and rearrangement products **2**, **3**, and **4** (X = Cl), respectively, are documented[4], the unusual insertion product **5** (X = Cl) was new.

Since in the difluorocarbene reaction 2-substituents in the norbornadiene markedly influence the cycloaddition mode (homo Diels-Alder versus [2 + 1] reactivity)[2], it was our interest to explore such substituent effects on the product distribution for the PTAD reaction. The results are summarized in Table 1. Before entering into the discussion of these results, it should be mentioned that also 2-methoxy- and 2-(trimethylsilyloxy)norbornadienes were examined, but both led to intractable and complex reaction mixtures and work on these derivatives was abandoned.

For comparison purposes, the data of the previously reported[3] 2-chloronorbornadiene (**1b**) are also included in Table 1. Clearly, this substrate exhibits the most diversified and complex product pattern of the 2-substituted norbornadienes examined here. Moreover, the poor product balance (ca. 30%; Table 1) must be kept in mind. Most of the 2-chloronorbornadienes lead to undefined, high-molecular-weight material, which is retained on the silica gel column during chromatography of the crude reaction mixture. While the spectral data, especially ^{1}H- and ^{13}C-NMR and ^{1}H-NMR decoupling experiments, permitted unequivocal characterization of the cycloadducts **2b**, **3b**, and **4b** (cf. Experimental), an X-ray analysis was essential in determining the structure of the unprecedented insertion product **5b**[5]. The structures of the remaining insertion products **5c** and **5d**, as well as the other cycloadducts, were arrived at by

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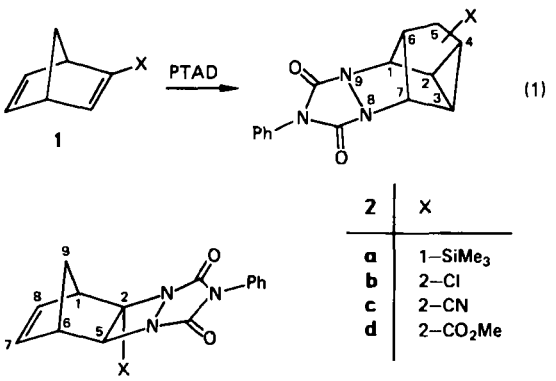
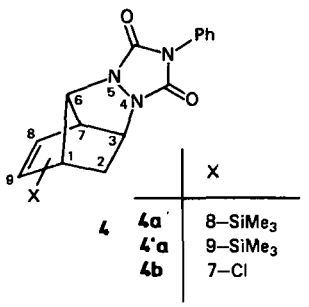
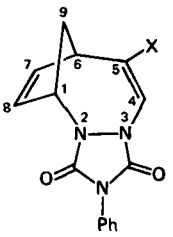
comparison of the spectral data with those of the 2-chloronorbornadiene products (cf. Experimental).







The product composition in Table 1 for the 2-trimethylsilyl-, 2-chloro-, 2-cyano- and 2-methoxycarbonylnorbornadienes **1a–d** is mechanistically perplexing. Thus, all norbornadienes give the homo Diels-Alder adducts **2a–d**. However, while the 2-chloro-, 2-cyano- and 2-methoxycarbonyl substituents lead to the expected[2b] regioisomers **2b–d** with the substituents on the cyclopropane ring, the 2-trimethylsilyl group gives the other regioisomeric product **2a**. Moreover, the trimethylsilyl system **1a** additionally affords the rearrangement urazoles **4a** and **4'a** (1:1 mixture of 8- and 9-trimethylsilyl regioisomers), the cyano and methoxycarbonyl derivatives **1c** and **1d**, respectively, the insertion products **5c** and **5d**, and only the 2-chloronorbornadiene (**1b**) yields both the rearrangement urazole **4b** and the insertion product **5b**, together with the [2 + 2] adduct **3b**. For the norbornadienes **1a**, **1c**, and **1d** the cycloadditions proceed with more than 95% product balance (Table 1), but **1b** leads predominantly to undefined high-molecular-weight material. Furthermore, the qualitative reactivity order is that the silyl derivative reacts faster than the cyano and methoxycarbonyl cases, as one would expect for the electrophilic PTAD[6].

In terms of frontier molecular orbital theory[2b] it is difficult to rationalize the product data of Table 1 for the cycloaddition of PTAD and the norbornadienes **1**. The only trend of the difluorocarbene reactivity pattern that is paralleled by PTAD is that with increasing electron-withdrawing character of the 2-substituent the degree of homo Diels-Alder cycloaddition is diminished. While for the difluorocarbene reaction the diminution of the homo Diels-Alder product **2** is offset by an increase in the [2 + 2] cycloadduct **3**[2], for PTAD the amount of insertion product **5** augments, except for the 2-trimethylsilyl system **1a**, which instead generates the rearrangement product **4a**.

These divergent reaction paths complicate of course the mechanistic interpretation. However, interesting is the fact that the electron-withdrawing substituents 2-chloro, 2-cyano, and 2-methoxycarbonyl give with PTAD cyclopropane-substituted regioisomers of the homo Diels-Alder adducts **2b–d**, while the electron-donating 2-trimethylsilyl group leads to the other regioisomer **2a**.

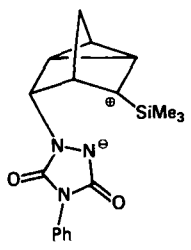
Assuming that the PTAD reaction with these substituted norbornadienes proceeds stepwise through dipolar ions[2b], for the 2-trimethylsilyl case the 1,5-dipole **6a** should be preferred in view of additional stabilization of the positive pole by the α-trimethylsilyl group. This stabilized cyclopropylcarbinyl cation would have less incentive to open the ring to give the dipole **7a**, a potential precursor of a regioisomeric insertion product of **5a**. Consequently, cyclization of the dipole **6a** leads to the homo Diels-Alder adduct and not to an insertion product. On the other hand, taking the 2-methoxycarbonyl case as example, the preferred 1,5-dipole should be **6d**, with the electron-withdrawing group as remote from the positive pole as is feasible. Cyclization of dipole **6d** to the homo Diels-Alder adduct **2d** is competed by ring-ope-

Table 1. Product composition of the cycloaddition of the norbornadienes **1a–d** and PTAD

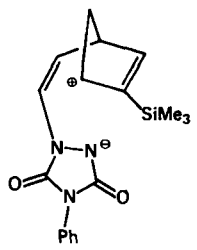
Norbornadiene	Reaction time [h][a]	Product balance (%)[b]	Relative product yields (%)[c] Homo Diels-Alder **2**	[2 + 2] **3**	Rearrangement **4**	Insertion **5**
1a (2-$SiMe_3$)	36	>95	77[d]	–	23[e]	–
1b (2-Cl)	48	29[f]	73	12	4.5	10.5
1c (2-CN)	96	>95	67	–	–	33
1d (2-CO_2Me)	48	>95	41	–	–	59

[a] For complete consumption of **1**, addition of excess PTAD is required. – [b] Total yield of isolated product by gravimetry. – [c] Obtained by quantitative ^{1}H-NMR (400 MHz) analysis of the crude reaction mixture prior to workup; normalized to 100%; values accurate within ca. 5% of stated values. – [d] Instead of the expected 2-trimethylsilyl, the 1-trimethylsilyl regioisomer was formed. – [e] A 1:1 mixture of 8- and 9-trimethylsilyl derivatives was obtained. – [f] Large quantities of intractable high molecular weight material were formed.

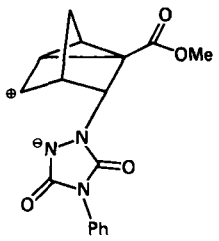
ning to the stabilized dipole **7d** (conjugated α,β-unsaturated ester) and subsequent collapse to the corresponding insertion product **5d**.



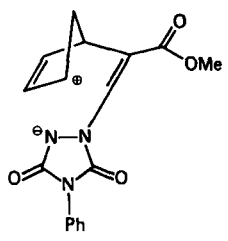
6a



7a



6d



7d

It would have been important to substantiate these mechanistic arguments by employing 2-phenyl- and 2-benzenesulfonyl-substituted norbornadienes. Unfortunately, the latter does not react with PTAD and the former undergoes preferentially Diels-Alder cycloadditions with the styryl moiety.

We are grateful to the *Deutsche Forschungsgemeinschaft*, the *Fonds der Chemischen Industrie*, and the *Italian Consiglio Nazionale delle Ricerche* for generous financial support. For spectral services we thank Dr. *G. Lange* (MS) and Dr. *D. Scheutzow* (NMR).

Experimental

IR spectra were run on the Perkin-Elmer Models 1420 and 157G. – ^{1}H-NMR and ^{13}C-NMR data were obtained with the following spectrometers: 60 and 22.6 MHz, Hitachi-Perkin-Elmer R-24B; 90 MHz, Varian EM 390; 200 and 50.3 MHz, Bruker AS-200; and 400 and 100 MHz, Bruker WM-400. Chemical shifts (δ values) are given relative to tetramethylsilane for protons and deuteriochloroform for carbons. – Melting points were taken with a Reichert Thermovar Kofler apparatus and are uncorrected. – Combustion analyses for elemental composition were run in-house. – For thin-layer chromatography (TLC) Polygram SIL/G/UV (40 × 80 mm, Macherey, Nagel & Co.) and for column chromatography silica gel (70–230 mesh or 32–63 μm, activity grade I, Merck) were employed.

Commercial reagents and solvents were purified to match the reported physical and spectral data. Unless otherwise stated, rotoevaporation was carried out at 20–25°C (room temperature, abbrev. R. T.) and 10–20 Torr (water aspirator).

2-(Trimethylsilyl)bicyclo[2.2.1]hepta-2,5-diene[7] (**1a**): Starting from 3.69 g (40.0 mmol) of norbornadiene in 10 ml of dry THF, 2.47 g (22.0 mmol) of tBuOK in 20 ml of dry THF, 17 ml of 1.3 M (22.1 mmol) n-BuLi in hexane, and 3.04 g (28.0 mmol) of trimethylsilyl chloride in 5 ml of THF was obtained 2.60 g (72%) of **1a** as colorless liquid, b.p. 58–60°C at 18 Torr (ref.[7] 53°C at 15 Torr). – ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 0.08 (s; 9H, CH_3), 1.90 (d, $J_{7s,7a}$ = 5.9 Hz; 2H, 7s-H and 7a-H), 3.66 (m; 1H, 1-H or 4-H), 3.73 (m; 1H, 1-H or 4-H), 6.70 (m; 2H, 5-H and 6-H), 7.04 (d, $J_{3,4}$ = 2.7 Hz; 1H, 3-H). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = –2.08 (q; CH_3), 51.97 (d), 53.32 (d), 74.06 (t; C-7), 142.33 (d), 143.16 (d), 153.29 (d; C-3), 155.72 (s; C-2).

2-Chlorobicyclo[2.2.1]hepta-2,5-diene[1] (**1b**): From 20.0 g (0.124 mol) of 5,6-dichloronorbornene and 10.0 g (0.178 mol) of potassium hydroxide in 40 ml of ethylene glycol was obtained after distillation 5.60 g (36%) of **1b**, b.p. 94–96°C at 14 Torr (ref.[1] 140°C at 769 Torr), n_D^{22} = 1.4960. – The product polymerizes on standing at R. T. – IR (CCl_4): 3040 cm^{-1}, 2980, 2950, 2875, 1585, 1550, 1450, 1420, 1335, 1300, 1245, 1150, 1095, 1035, 1005, 910, 860, 835, 700. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.10 (dt, $J_{7s,7a}$ = 6.0 Hz, $J_{1,7s}$ = $J_{4,7s}$ = 1.5 Hz; 1H, 7s-H), 2.26 (dt, $J_{7s,7a}$ = 6.0 Hz; $J_{1,7a}$ = $J_{4,7a}$ = 1.5 Hz; 1H, 7a-H), 3.37 (m; 1H, 4-H), 3.61 (dm, $J_{1,6}$ = 2.6 Hz; 1H, 1-H), 6.39 (d, $J_{3,4}$ = 3.3 Hz; 1H, 3-H), 6.79 (dd, $J_{5,6}$ = 5.0 Hz, $J_{1,6}$ = 2.8 Hz; 1H, 6-H), 6.89 (dd, $J_{5,6}$ = 5.0 Hz, $J_{4,5}$ = 3.0 Hz; 1H, 5-H).

Bicyclo[2.2.1]hepta-2,5-diene-2-carbonitrile[8] (**1c**): To a solution of cyanoacetylene[9] (2.80 g, 54.9 mmol) in 30 ml of methylene chloride, was added monomeric cyclopentadiene (5.5 ml, 66.8 mmol) at 0°C while stirring. The mixture was stirred for about 12 h at R. T. and the solvent roto-evaporated. The residue was purified by silica gel chromatography [1:30 substrate/adsorbent ratio, 2:8 methylene chloride/petroleum ether (30–50) as eluent], resulting in 5.70 g (90%) of **1c** as colorless liquid. The product decomposes at R. T. – IR (CCl_4): 3080 cm^{-1}, 3010, 2990, 2950, 2875, 2210, 1750, 1580, 1450, 1230, 1210, 1175, 1015, 920, 910, 885, 875, 855, 710, 610. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.16 (dt, $J_{7s,7a}$ = 6.7 Hz, $J_{1,7s}$ = $J_{4,7s}$ = 1.2 Hz; 1H, 7s-H), 2.19 (dt, $J_{7s,7a}$ = 6.7 Hz, $J_{1,7a}$ = $J_{4,7a}$ = 1.5 Hz; 1H, 7a-H), 3.84 (m; 2H, 1-H and 4-H), 6.75 (ddd, $J_{5,6}$ = 5.0 Hz, $J_{4,5}$ = 3.2 Hz, $J_{3,5}$ = 0.6 Hz; 1H, 5-H), 6.90 (dd, $J_{5,6}$ = 5.6 Hz, $J_{1,6}$ = 3.0 Hz; 1H, 6-H), 7.66 (d, $J_{3,4}$ = 3.1 Hz; 1H, 3-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 51.77 (d), 53.58 (d), 74.75 (t; C-7), 117.04 (s; C-2), 141.60 (d), 142.75 (d), 161.17 (d), 193.29 (s; CN). – MS (70 eV): *m/z* (%) = 118 (8, M^+ + 1), 117 (100, M^+), 116 (88), 104 (11), 91 (66), 90 (65), 89 (41), 77 (13), 66 (98, $C_6H_5^+$), 51(24). [The *m/z* = 117 peak overlaps with ca. 8% $^{13}C\,^{12}C_7H_7N$ (M – 1).]

C_8H_7N Calcd. 117.0579 Found 117.0575

Methyl Bicyclo[2.2.1]hepta-2,5-diene-2-carboxylate[10] (**1d**): A 25-ml three-necked flask provided with nitrogen inlet, outlet tubes, and a magnetic spinbar was flame-dried under a stream of nitrogen and charged with methyl acetylenecarboxylate (2.00 g, 23.8 mmol) and freshly distilled cyclopentadiene (1.57 g, 23.8 mmol). The reaction mixture was allowed to stir for about 12 h at 50°C, and distillation gave 2.50 g (70%) of **1d**, b.p. 80–85°C at 12 Torr (ref.[10] 28°C at 0.1 Torr). – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.14 (d, $J_{7s,7a}$ = 6.0 Hz; 2H, 7-H), 3.75 (br. s; 4H, CH_3 and 4-H), 6.76 (dd, $J_{5,6}$ = 5.1 Hz, J = 3.1 Hz; 1H, 5-H or 6-H), 6.93 (dd, $J_{5,6}$ = 5.1 Hz, J = 3.1 Hz; 1H, 6-H or 5-H), 7.71 (d, $J_{3,4}$ = 3.2 Hz; 1H, 3H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 49.73 (d), 50.19 (q; CH_3), 51.40 (d), 74.33 (t; C-7), 141.66 (d), 143.52 (d), 148.95 (s; C-2), 156.31 (d), 165.50 (s; C=O).

General Procedure for the Cycloaddition of PTAD to the Norbornadienes **1**: To a solution of the particular norbornadiene **1** in CH_2Cl_2 was added at once, while stirring magnetically, at 0°C a stoichiometric amount of PTAD. The reaction mixture was allowed to stir at R. T. The reaction progress was monitored by TLC (silica

gel, CH_2Cl_2 as eluent).The reactive norbornadienes **1a** and **1b** were consumed within 48–72 h, while for the less reactive **1c** and **1d** the PTAD was in part consumed via decomposition. Accordingly, each day another ca. 0.50 g of PTAD was added until all of the norbornadiene had been consumed. The dark-brown reaction mixture was concentrated by roto-evaporation and the residue submitted to silica gel chromatography (1:30 substrate/adsorbent ratio), affording the corresponding cycloadducts. Final purification entailed recrystallization. The experimental details for each particular case are given below.

2-(Trimethylsilyl)norbornadiene (**1a**): From 1.00 g (6.09 mmol) of **1a** and 1.02 g (6.11 mmol) of PTAD in 50 ml of CH_2Cl_2 were obtained the cycloadducts **2a**, **4a**, and **4'a** after 36 h of reaction time and silica gel chromatography using petroleum ether (30–50)/ethyl acetate as eluent. **4a** and **4'a** were eluated as first fraction and separated by fractional crystallization using AcOEt as solvent.

N-Phenyl-8-(trimethylsilyl)-4,5-diazatricyclo[4.3.0.0^{3,7}]non-8-ene-4,5-dicarboximide (**4a**): 310 mg (15%) of colorless plates, m.p. 160–161°C (AcOEt). – IR (KBr): 3035 cm^{-1}, 3020, 2960, 2950, 1720, 1655, 1595, 1410, 1320, 1290, 1260, 1250, 1240, 1130, 1090, 875, 840, 830, 770, 760, 725, 690, 645. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.10 (s; 9H, CH_3), 1.31 (ddd, $J_{2n,2x}$ = 12.6 Hz, $J_{3,2n}$ = 5.0 Hz, $J_{2n,1}$ = 1.5 Hz; 1H, 2n-H), 1.90 (dd, $J_{2n,2x}$ = 12.6 Hz, $J_{2x,1}$ = 5.1 Hz; 1H, 2x-H), 3.23 (m; 2H, 1-H and 7-H), 4.35 (dd, $J_{3,2n}$ = 5.0 Hz, $J_{3,6}$ = 1.9 Hz; 1H, 3-H), 4.38 (m; 1H, 6-H), 6.59 (d, J = 3.8 Hz; 1H, 9-H), 7.34–7.54 (m; 5H, Ph). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = –2.12 (q; CH_3), 33.39 (t; C-2), 46.05 (d), 54.98 (d), 57.07 (d), 77.19 (d), 125.44 (d), 128.25 (d), 129.14 (d), 141.67 (s), 148.44 (d), 156.07 (s; C=O), 156.35 (s; C=O). – MS (70 eV): *m/z* (%) = 340 (8, M^+ + 1), 339 (29, M^+), 324 (3), 220 (4), 192 (7), 163 (4), 119 (17), 105 (18), 100 (23), 91 (10), 78 (19), 73 [100, $Si(CH_3)_3^+$], 59 (10).

$C_{18}H_{21}N_3O_2Si$ (339.5) Calcd. C 63.69 H 6.24 N 12.38
Found C 63.93 H 6.28 N 12.53

N-Phenyl-9-(trimethylsilyl)-4,5-diazatricyclo[4.3.0.0^{3,7}]non-8-ene-4,5-dibarboximide (**4'a**): 150 mg (8%), colorless powder, m.p. 146–148°C (AcOEt). – IR (KBr): 3100 cm^{-1}, 3000, 2960, 1800, 1750, 1510, 1440, 1330, 1300, 1260, 1250, 1140, 1095, 870, 845, 780, 760, 715, 700, 640. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.11 (s; 9H, CH_3), 1.19 (ddd, $J_{2n,2x}$ = 12.6 Hz, $J_{2n,3}$ = 5.0 Hz, $J_{2n,1}$ = 1.5 Hz; 1H, 2n-H), 1.88 (dd, $J_{2n,2x}$ = 12.6 Hz, $J_{1,2x}$ = 4.9 Hz; 1H, 2x-H), 3.23 (m; 1H, 7-H), 3.28 (m; 1H, 1-H), 4.38 (m; 1H, 6-H), 4.43 (dd, $J_{2n,3}$ = 4.9 Hz, $J_{3,7}$ = 2.0 Hz; 1H, 3-H), 6.13 (dd, $J_{7,8}$ = 3.0 Hz, $J_{1,8}$ = 1.1 Hz; 1H, 8-H), 7.32–7.56 (m; 5H, Ph). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = –2.11 (q; CH_3), 33.11 (t; C-2), 47.21 (d), 53.59 (d), 57.32 (d), 77.76 (d), 125.43 (d), 128.24 (d), 129.14 (d), 131.75 (s), 135.21 (d), 148.44 (d), 155.53 (s; C=O), 156.17 (s; C=O). – MS (70 eV): *m/z* (%) = 341 (1, M^+ + 2), 340 (6, M^+ + 1), 340 (26, M^+), 220 (3), 219 (2), 205 (3), 192 (6), 178 (3), 163 (3), 135 (7), 132 (5), 119 (16), 105 (18), 100 (24), 91 (11), 78 (20), 59 (10).

$C_{18}H_{21}N_3O_2Si$ (339.5) Calcd. C 63.69 H 6.24 N 12.38
Found C 63.93 H 6.28 N 12.53

1-(Trimethylsilyl)-N-phenyl-8,9-diazatetracyclo[4.3.0.0^{2,4}.0^{3,7}]-nonane-8,9-dicarboximide (**2a**) was isolated as second fraction, 1.36 g (66%), colorless plates, m.p. 155–156°C (AcOEt). – IR (KBr): 3080 cm^{-1}, 3000, 2960, 2890, 1760, 1700, 1600, 1595, 1505, 1490, 1455, 1400, 1325, 1270, 1245, 1215, 1135, 1125, 1110, 1085, 1075, 1025, 935, 895, 855, 840, 800, 770, 745, 700, 690, 660, 645, 630. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.29 (s; 9H, CH_3), 1.52–1.64 (m; 3H, 2-H, 3-H and 4-H), 1.76 (dt, $J_{5s,5a}$ = 11.8 Hz, J = 1.3 Hz; 1H, 5-H), 1.83 (dt, $J_{5s,5a}$ = 11.8 Hz, J = 1.4 Hz; 1H, 5-H), 2.56 (m; 1H, 6-H), 4.46 (t, J = 2.1 Hz; 1H, 7-H), 7.31–7.54 (m; 5H, Ph). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = –1.94 (q; CH_3), 13.18 (d), 15.85 (d), 28.81 (t; C-5), 46.70 (d), 65.60 (d; C-7), 67.51 (s; C-1), 125.41 (d), 127.89 (d), 132.09 (s), 156.32 (s; C=O), 156.53 (s; C=O). – MS (70 eV): *m/z* (%) = 340 (11, M^+ + 1), 339 (47, M^+), 324 (18), 234 (16), 205 (5), 192 (8), 178 (4), 163 (6), 149 (6), 119 (10), 105 (7), 100 (20), 91 (10), 83 (6), 73 [100, $Si(CH_3)_3^+$], 66 (12), 59 (7).

$C_{18}H_{21}N_3O_2Si$ (339.5) Calcd. C 63.69 H 6.24 N 12.38
Found C 63.84 H 6.61 N 12.10

2-Chloronorbornadiene (**1b**): From 6.30 g (49.8 mmol) of **1b** and 9.15 g (52.2 mmol) of PTAD in 10 ml of CH_2Cl_2 were obtained the cycloadducts **2b**, **3b**, **4b**, and **5b** after 48 h reaction time and silica gel chromatography using methylene chloride as eluent.

2-Chloro-N-phenyl-3,4-diazatricyclo[4.2.1.0^{2,5}]non-7-ene-3,4-dicarboximide (**3b**) was isolated as first fraction, 300 mg (2%), colorless needles, m.p. 202–203°C (ethanol). – IR (KBr): 3000 cm^{-1}, 1790, 1730, 1600, 1500, 1405, 1320, 1240, 1140, 1025, 970, 780, 755, 720, 690. – ^{1}H NMR (90 MHz, $CDCl_3$): δ = AB system (δ_A = 2.10, δ_B = 2.65, $J_{A,B}$ = 10.2 Hz; 2H, 9-H), 3.38 (m; 2H, 1-H and 6-H), 4.32 (t, $J_{1,5}$ = $J_{5,9a}$ = 1.6 Hz; 1H, 5-H), 6.25 (m; 2H, 7-H and 8-H), 7.50 (m; 5H, C_6H_5). – ^{13}C NMR (22.6 MHz, $CDCl_3$): δ = 44.42 (t; C-9), 45.46 (d), 51.92 (d), 74.89 (d), 92.73 (s; C-2), 125.59 (d), 128.81 (d), 129.33 (d), 131.40 (s), 134.94 (d), 137.27 (d), 156.84 (s), 161.14 (s).

$C_{15}H_{12}ClN_3O_2$ (301.7) Calcd. C 59.71 H 4.01 N 13.93
Found C 59.47 H 4.17 N 13.77

5-Chloro-N-phenyl-2,3-diazabicyclo[4.2.1]nona-4,7-diene-2,3-dicarboximide (**5b**) was isolated as second fraction, 300 mg (2%), colorless plates, m.p. 153–154°C (ethanol). – IR (KBr): 3080 cm^{-1}, 2990, 2930, 2860, 1775, 1720, 1655, 1590, 1500, 1490, 1410, 1305, 1275, 1145, 1065, 830, 755, 735. – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 2.15 (d, $J_{9s,9a}$ = 13.2 Hz; 1H, 9s-H), 2.43 (dt, $J_{9s,9a}$ = 13.2 Hz, $J_{1,9a}$ = $J_{6,9a}$ = 6.3 Hz; 1H, 9a-H), 3.58 (br. d; 1H, 6-H), 5.38 (dd, $J_{1,9}$ = 6.3 Hz, $J_{1,8}$ = 2.7 Hz; 1H, 1-H), AB system (δ_A = 6.20, δ_B = 6.24, $J_{A,B}$ = 5.4 Hz, $J_{6,7}$ = 3.0 Hz, $J_{1,8}$ = 2.7 Hz; 2H, 7-H and 8-H), 6.98 (d, $J_{4,6}$ = 1.5 Hz; 1H, 4-H), 7.48 (m; 5H, C_6H_5). – ^{13}C NMR (22.6 MHz, $CDCl_3$): δ = 39.45 (t; C-9), 51.40 (d), 60.17 (d), 119.32 (d), 122.32 (s), 125.39 (d), 128.29 (d), 129.11 (d), 130.11 (d), 131.14 (s), 136.51 (d), 147.89 (s), 150.01 (s).

$C_{15}H_{12}ClN_3O_2$ (301.7) Calcd. C 59.71 H 4.01 N 13.93
Found C 59.71 H 4.20 N 13.76

7-Chloro-N-phenyl-4,5-diazatricyclo[4.3.0.0^{3,7}]non-8-ene-4,5-dicarboximide (**4b**) was isolated as third fraction, 300 mg (2%), colorless prisms, m.p. 214–215°C (ethanol). – IR (KBr): 3090 cm^{-1}, 3040, 2990, 2940, 1770, 1710, 1590, 1500, 1400, 1290, 1260, 1230, 1125, 1095, 820, 735, 700, 690. – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 1.67 (ddd, $J_{2x,2n}$ = 12.3 Hz, $J_{3,2n}$ = 5.4 Hz, $J_{2n,1}$ = 1.5 Hz; 1H, 2n-H), 2.23 (dd, $J_{2n,2x}$ = 12.3 Hz, $J_{2x,1}$ = 5.4 Hz; 1H, 2x-H), 3.20 (br. s; 1H, 1-H), 4.55 (m; 2H, 3-H and 6-H), 6.00 (dd, $J_{8,9}$ = 6.0 Hz, $J_{1,8}$ = 1.4 Hz; 1H, 8-H), 6.45 (dd, $J_{8,9}$ = 6.0 Hz, $J_{1,9}$ = 3.6 Hz; 1H, 9-H), 7.45 (m; 5H, C_6H_5). – ^{13}C NMR (22.6 MHz, $CDCl_3$): δ = 37.31 (t; C-2), 43.44 (d), 62.15 (d), 78.74 (s), 84.14 (d), 125.85 (d), 128.45 (d), 129.21 (d), 130.58 (d), 131.70 (s), 138.67 (d), 156.78 (s), 157.49 (s).

$C_{15}H_{12}ClN_3O_2$ (301.7) Calcd. C 59.71 H 4.01 N 13.93
Found C 59.86 H 3.88 N 13.80

2-Chloro-N-phenyl-8,9-diazatetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonane-8,9-dicarboximide (**2b**) was isolated as fourth fraction, 3.00 g (20%), colorless prisms, m.p. 220–221°C (ethanol). – IR (KBr): 3060 cm^{-1}, 2940, 1765, 1700, 1490, 1410, 1330, 1270, 1220, 1130, 865, 815, 770, 700, 650. – ^{1}H NMR (90 MHz, $CDCl_3$): δ = AB system (δ_A = 1.86, δ_B = 2.11, $J_{A,B}$ = 12.3 Hz; 2H, 5-H), 2.07 (m; 2H, 3-H and

4-H), 2.53 (m; 1H, 6-H), 4.62 (ddm, $J_{6,7}$ = 2.7 Hz, $J_{3,7}$ = 1.5 Hz; 1H, 7-H), 4.68 (d, $J_{1,6}$ = 2.7 Hz; 1H, 1-H), 7.46 (m; 5H, C_6H_5). – ^{13}C NMR (22.6 MHz, $CDCl_3$): δ = 24.16, 26.23, 28.84, 43.04, 44.93, 66.24, 70.30, 125.79, 128.52, 129.31, 131.68.

$C_{15}H_{12}ClN_3O_2$ (301.7) Calcd. C 59.71 H 4.01 N 13.93
Found C 59.42 H 4.16 N 13.81

2-Norbornadienecarbonitrile (**1c**): From 6.42 g (54.9 mmol) of **1c** and 14.4 g (82.3 mmol) of PTAD in 100 ml of CH_2Cl_2 were obtained the cycloadducts **2c** and **5c** after 8 d reaction time and silica gel chromatography using methylene chloride as eluent.

5-Cyano-N-phenyl-2,3-diazabicyclo[4.2.1]nona-4,7-diene-2,3-dicarboximide (**5c**) was obtained as first fraction, 170 mg (5%), m.p. 88–90°C (ethanol). – IR (KBr): 3060 cm^{-1}, 2200, 1780, 1720, 1625, 1500, 1415, 1310, 1150, 1050, 1020, 935, 830, 750, 690, 645. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.11 (d, $J_{9s,9a}$ = 13.0 Hz; 1H, 9s-H), 2.54 (ddd, $J_{9s,9a}$ = 13.0 Hz, $J_{1,9a}$ = 6.4 Hz, $J_{6,9a}$ = 6.7 Hz; 1H, 9a-H), 3.63 (dd, $J_{6,9a}$ = 6.7 Hz, $J_{2,6}$ = 2.9 Hz; 1H, 6-H), 5.51 (dd, $J_{1,9a}$ = 6.4 Hz, $J_{1,8}$ = 2.8 Hz; 1H, 1-H), 6.20 (dd, $J_{7,8}$ = 5.4 Hz, $J_{1,8}$ = 2.8 Hz; 1H, 8-H), 6.29 (dd, $J_{7,8}$ = 5.4 Hz, $J_{6,7}$ = 2.9 Hz; 1H, 7-H), 7.49 (m; 6H, 5-H and C_6H_5). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 40.67 (t; C-9), 45.12 (d), 59.16 (d), 96.26 (s), 118.54 (s), 125.44 (d), 128.78 (d), 129.29 (d), 129.62 (d), 130.59 (s), 131.40 (d), 138.72 (d), 147.12 (s), 148.31 (s). – MS (70 eV): *m/z* (%) = 292 (100, M^+), 241 (3), 173 (51, M^+ – PhNCO), 146 (18), 145 (24), 144 (15), 131 (27), 130 (44), 129 (14), 120 (12), 119 (88, PhNCO), 117 (16), 116 (15), 104 (23), 103 (48), 91 (49), 90 (23), 77 (20).

$C_{16}H_{12}N_4O_2$ (292.1) Calcd. C 65.75 H 4.14 N 19.17
Found C 66.16 H 4.27 N 19.26

2-Cyano-N-phenyl-8,9-diazatetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonane-8,9-dicarboximide (**2c**) was isolated as second fraction, 1.35 g (40%), colorless powder, m.p. 239–241°C (methylene chloride/ether). – IR (KBr): 3065 cm^{-1}, 2980, 2885, 2240 (CN), 1790, 1705, 1500, 1460, 1425, 1385, 1220, 1165, 1140, 1085, 870, 780, 700, 660. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.01 (br. d, $J_{5s,5a}$ = 12.3 Hz; 1H, 5-H), 2.12 (br. d, $J_{5s,5a}$ = 12.3 Hz; 1H, 5-H), 2.40 (ddt, $J_{3,4}$ = 5.2 Hz, $J_{4,6}$ = 1.2 Hz, $J_{4,5s}$ = $J_{4,5a}$ = 1.4 Hz; 1H, 4-H), 2.48 (dd, $J_{3,4}$ = 5.1 Hz, $J_{3,7}$ = 1.8 Hz; 1H, 3-H), 2.56 (m; 1H, 6-H), 4.71 (dd, $J_{3,7}$ = $J_{6,7}$ = 2.3 Hz; 1H, 7-H), 4.84 (d, $J_{1,6}$ = 2.6 Hz; 1H, 1-H), 7.5 (m; 5H, C_6H_5). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.55 (s; C-2), 24.77 (d), 26.48 (d), 28.83 (t; C-5), 41.96 (d), 65.50 (d), 66.72 (d), 117.41 (s; CN), 125.56 (d), 128.66 (d), 129.29 (d), 131.85 (s), 157.63 (s). – MS (70 eV): *m/z* (%) = 292 (100, M^+), 173 (1), 119 (13, $PhNCO^+$), 117 (9), 116 (5), 91 (9), 66 (6).

$C_{16}H_{12}N_4O_2$ (292.1) Calcd. C 65.75 H 4.14 N 19.17
Found C 65.43 H 3.87 N 19.45

Methyl 2-Norbornadienecarboxylate (**1d**): From 2.50 g (16.7 mmol) of **1d** and 4.50 g (25.7 mmol) of PTAD in 40 ml of CH_2Cl_2 were obtained the cycloadducts **2d** and **5d** after 4 d reaction time and silica gel chromatography using methylene chloride as eluent.

5-Methoxycarbonyl-N-phenyl-2,3-diazabicyclo[4.2.1]nona-4,7-diene-2,3-dicarboximide (**5d**) was isolated as first fraction, 3.00 g (55%), colorless powder, m.p. 163–164°C (methylene chloride/ether). – IR (KBr): 3490 cm^{-1}, 3380, 3085, 2960, 1780, 1730, 1695, 1635, 1605, 1510, 1425, 1345, 1315, 1290, 1265, 1215, 1190, 1175, 1170, 1120, 1080, 1050, 1025, 1000, 980, 955, 930, 900, 880, 830, 770, 750, 690, 645, 620. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.01 (d, $J_{9s,9a}$ = 12.8 Hz; 1H, 9s-H), 2.52 (ddd, $J_{9s,9a}$ = 12.8 Hz, $J_{6,9a}$ = $J_{4,9a}$ = 6.7 Hz; 1H, 9a-H), 3.80 (s; 3H, CH_3), 4.21 (dd, $J_{6,9a}$ = 6.9 Hz, $J_{6,7}$ = 3.0 Hz; 1H, 6-H), 5.50 (dd, $J_{1,9a}$ = 6.5 Hz, $J_{1,8}$ = 2.7 Hz; 1H, 1-H), 6.11 (dd, $J_{7,8}$ = 5.4 Hz, $J_{1,8}$ = 2.7 Hz; 1H, 8-H), 6.24 (dd, $J_{7,8}$ = 5.4 Hz, $J_{6,7}$ = 3 Hz; 1H, 7-H), 7.48–7.53 (m; 5H, C_6H_5), 8.01 (d, $J_{4,6}$ = 0.9 Hz; 1H, 6-H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 39.78 (t; C-9), 41.24 (d; C-6), 52.07 (q; CH_3), 59.29 (d; C-1), 115.16 (s; C-4), 125.39 (d), 128.11 (d), 128.38 (d), 128.63 (d), 129.05 (d), 140.33 (d), 147.55 (s; CO), 148.19 (s; CO), 166.66 (s; COO). – MS (70 eV): *m/z* (%) = 325 (100, M^+), 206 (21, M^+ – PhNCO), 175 (11, $PTAD^+$), 174 (81), 149 (12), 147 (20), 146 (14), 132 (26), 131 (15), 119 (42, $PhNCO^+$), 118 (13), 105 (16), 104 (38), 103 (12), 92 (17), 91 (49), 90 (15), 77 (26), 66 (17), 65 (27), 64 (12), 59 (14), 51 (10).

$C_{17}H_{15}N_3O_4$ (325.2) Calcd. C 62.79 H 4.61 N 12.92
Found C 62.80 H 4.62 N 13.02

2-Methoxycarbonyl-N-phenyl-8,9-diazatetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonane-8,9-dicarboximide (**2d**) was isolated as second fraction, 2.20 g (40%), colorless powder, m.p. 167–168°C (methylene chloride/ether). – IR (KBr): 3475 cm^{-1}, 3075, 3070, 3020, 3010, 2980, 2960, 2940, 2880, 1770, 1730, 1720, 1600, 1590, 1500, 1455, 1435, 1415, 1335, 1300, 1285, 1260, 1230, 1215, 1195, 1160, 1130, 1120, 1095, 1070, 970, 870, 825, 770, 760, 750, 700, 650, 645. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.96 (d, $J_{5s,5a}$ = 12.0 Hz; 1H, 5-H), 2.03 (dt, δ_B = 2.05, $J_{5s,5a}$ = 12.0 Hz, $J_{4,5}$ = $J_{5,6}$ = 1.4 Hz; 1H, 5-H), 2.35 (ddt, $J_{3,4}$ = 5.1 Hz, $J_{4,6}$ = 1.4 Hz, $J_{4,5s}$ = $J_{4,5a}$ = 1.2 Hz; 1H, 4-H), 2.42 (m; 1H, 6-H), 2.44 (ddd, $J_{3,4}$ = 5.1 Hz, $J_{3,7}$ = 2.1 Hz, J = 0.7 Hz; 1H, 3-H), 3.76 (s; 3H, CH_3), 4.71 (t, $J_{3,7}$ = $J_{6,7}$ = 2.3 Hz; 1H, 7-H), 4.90 (d, $J_{1,6}$ = 2.5 Hz; 1H, 1-H), 7.45 (m; 5H, C_6H_5). – ^{13}C NMR (22.6 MHz, $CDCl_3$): δ = 26.22, 27.94, 28.49, 29.46, 42.82 (d), 51.98 (d), 65.49 (d), 66.27 (d), 125.24, 128.06 (s), 128.91, 131.24, 157.10 (s; C=O), 157.40 (s; C=O), 169.87 (s; COO). – MS (70 eV): *m/z* (%) = 327 (3), 326 (18), 325 (100, M^+), 226 (9, M^+ – CH_3CO_2), 206 (3), 175 (5, $PTAD^+$), 174 (28), 149 (12), 147 (17), 135 (8), 132 (10), 119 (39, $PhNCO^+$), 105 (15), 104 (12), 91 (68), 77 (19), 66 (16), 65 (20), 59 (24).

$C_{17}H_{15}N_3O_4$ (325.2) Calcd. C 62.79 H 4.61 N 12.92
Found C 63.05 H 4.60 N 13.01

CAS Registry Numbers

1a: 16205-92-8 / **1b**: 2294-41-9 / **1c**: 39863-20-2 / **1d**: 3604-36-2 / **2a**: 106567-08-2 / **2b**: 82204-55-5 / **2c**: 106567-10-6 / **2d**: 106567-12-8 / **3b**: 106624-48-0 / **4a**: 106567-06-0 / **4'a**: 106567-07-1 / **4b**: 82204-57-7 / **5b**: 82204-58-8 / **5c**: 106567-09-3 / **5d**: 106567-11-7 / HC≡CCN: 1070-71-9 / HC≡CCO$_2$Me: 922-67-8 / PTAD: 4233-33-4 / norbornadiene: 121-46-0 / 2,6-dichloronorbornene: 59975-41-6 / cyclopentadiene:

[1] D. I. Davies, *J. Chem. Soc.* **1960**, 3669.
[2] [2a] C. W. Jefford, P. T. Huy, *Tetrahedron Lett.* **21** (1980) 755. – [2b] K. N. Houk, N. G. Rondan, M. N. Paddon-Row, C. W. Jefford, P. T. Huy, P. D. Burrow, K. D. Jordan, *J. Am. Chem. Soc.* **105** (1983) 5563.
[3] W. Adam, L. A. Arias, O. De Lucchi, *Tetrahedron Lett.* **23** (1982) 399.
[4] W. Adam, O. De Lucchi, *Angew. Chem.* **92** (1980) 815; *Angew. Chem. Int. Ed. Engl.* **19** (1980) 762.
[5] K. Peters, E.-M. Peters, H. G. von Schnering, *Z. Kristal.* **168** (1984) 145.
[6] W. Adam, N. Carballeira, *J. Am. Chem. Soc.* **106** (1984) 2874.
[7] H. D. Verkruijsse, L. Braudsma, *Recl. Trav. Chim. Pays-Bas* **105** (1986) 66.
[8] C. D. Buchecker, D. Martina, M. F. Neumann, *J. Chem. Res. (S)* **1978**, 78.
[9] S. Murahashi, T. Takizawa, S. Kurioka, S. Maekawa, *Nippon Kagaku Zasshi* 77 (1956) 1689 [*Chem. Abstr.* **53** (1959) 5163f].
[10] O. Baumgärtel, G. Szeimies, *Chem. Ber.* **116** (1983) 2180.

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