Chem. Ber. **118**, 3357–3379 (1985)

Cycloaddition of Singlet Oxygen and 4-Phenyl-4*H*-1,2,4-triazole-3,5-dione to 7-Substituted 1,3,5-Cyclooctatrienes

*Waldemar Adam**[a], *Nanette Gretzke**)[a], *Ludwig Hasemann***)[a], *Günter Klug****)[a], *Eva-Maria Peters*[b], *Karl Peters*[b], *Hans Georg von Schnering*[b], and *Bernd Will*[a]

Institut für Organische Chemie, Universität Würzburg[a],
Am Hubland, D-8700 Würzburg, and
Max-Planck-Institut für Festkörperforschung[b],
Heisenbergstr. 1, D-7000 Stuttgart 80

Received September 25, 1984

The cycloaddition of the 7-substituted (X; Y) 1,3,5-cyclooctatrienes **3** (N_3; H), **4** (OAc; H), **5** (OEt; OEt), **6** (Me; H), and **7** (*i*Pr; H) with singlet oxygen ($^1O_2$) and 4-phenyl-4*H*-1,2,4-triazole-3,5-dione (PTAD) was investigated. Singlet oxygen gave with all cyclooctatrienes the corresponding tricyclic endoperoxides derived from the bicyclic valence isomers (bicyclo[4.2.0]octa-2,4-dienes). The corresponding bicyclic endoperoxides derived from the monocyclic valence isomers (1,3,5-cyclooctatriene) were only obtained for the alkyl-substituted derivatives **6** (Me; H) and **7** (*i*Pr; H). PTAD cycloaddition led to both the bicyclic and tricyclic urazoles, except with the acetal **5** which gave only tricyclic product. The bromo derivative **2** did not react with $^1O_2$ nor PTAD. Control experiments with the parent cyclooctatriene showed that the cycloaddition products were derived from the "static" amounts of the monocyclic and bicyclic valence isomers in the substrate mixture.

Cycloaddition von Singulettsauerstoff und 4-Phenyl-4*H*-1,2,4-triazol-3,5-dion mit 7-substituierten 1,3,5-Cyclooctatrienen

Die Cycloadditionen von 7-substituierten (X; Y) 1,3,5-Cyclooctatrienen **3** (N_3; H), **4** (OAc; H), **5** (OEt; OEt), **6** (Me; H) und **7** (*i*Pr; H) mit Singulettsauerstoff ($^1O_2$) und 4-Phenyl-4*H*-1,2,4-triazol-3,5-dion (PTAD) wurden untersucht. Singulettsauerstoff reagierte mit diesen Cyclooctatrienen aus dem bicyclischen Valenzisomeren (Bicyclo[4.2.0]octa-2,4-dien) heraus zu den entsprechenden tricyclischen Endoperoxiden. Bicyclische Endoperoxide, ausgehend von monocyclischen Valenzisomeren (1,3,5-Cyclooctatrien), wurden lediglich bei den alkylsubstituierten Derivaten **6** (Me; H) und **7** (*i*Pr; H) erhalten. Die Cyclcoaddition mit PTAD führte zu den bicyclischen und tricyclischen Urazolen, mit Ausnahme des Acetals **5** (OEt; OEt), welches nur das tricyclische Produkt gab. Das Bromderivat **2** reagierte weder mit $^1O_2$ noch mit PTAD. Kontrollexperimente mit der Stammverbindung zeigten, daß die Cycloadditionsprodukte entsprechend den mono- und bicyclischen Valenzisomerenanteilen des Eduktgemisches erhalten wurden.

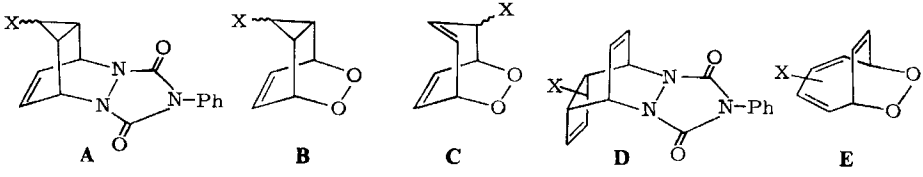
4-Phenyl-4*H*-1,2,4-triazole-3,5-dione (PTAD) affords with few exceptions[1] exclusively norcaradiene-type urazoles with 7-substituted cycloheptatrienes (**A**)[2]. On the other hand,

*) Research participant in the science teachers program.
**) Undergraduate research participant, Fall 1983.
***) Doctoral Dissertation, University of Würzburg, July 1984.

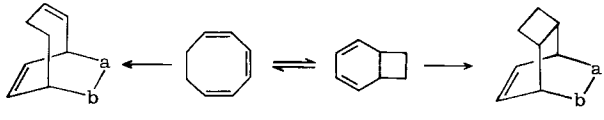
0009–2940/85/0808–3357 $ 02.50/0

singlet oxygen ($^1O_2$) leads to both norcaradiene-type and tropilidene-type endoperoxides (**B** and **C**), the relative proportions depending on substituent, solvent, and temperature[3]. Presumably the more reactive $^1O_2$ is capable of intervening in the valence-tautomeric equilibrium of cycloheptatriene. Consequently, the proportion of norcaradiene versus tropilidene endoperoxides reflects the relative amounts of the bicyclic and monocyclic valence isomers of cycloheptatriene in solution. Unfortunately, the more sluggish PTAD selects to cycloadd only with the much more reactive norcaradiene isomer. Thus, the cycloheptatriene substrate does not permit to probe substituent, solvent, and temperature effects on such valence isomerizations with PTAD as was possible for $^1O_2$[3]. This precludes comparing and contrasting the cyclophilic nature of these two reagents[4].

An attempt to use cyclooctatetraene derivatives for this purpose proved difficult for several reasons. While PTAD gave the tricyclic urazoles derived from the bicyclic valence tautomer of cyclooctatetraene (**D**)[5], with $^1O_2$ the bicyclic endoperoxides (**E**) were produced preferentially[6]. Besides, extensive formation of undefined high-molecular-weight peroxides and the lack of reactivity of cyclooctatetraenes bearing electron-withdrawing substituents obliged us to search for a more suitable dienic substrate.



Some time ago we reported[7] our preliminary results on the cycloaddition of PTAD and $^1O_2$ to 1,3,5-cyclooctatriene, showing that both reagents gave essentially the same ratios (ca. 4:1) of the bicyclic and tricyclic cycloadducts [Eq. (1)]. It seemed, therefore, opportune to examine the cycloaddition of PTAD and $^1O_2$ with a variety of 7-substituted 1,3,5-cyclooctatrienes, with the purpose of comparing the dienophilic behavior of these two reagents. Herein we describe the full details of this investigation.



(1)

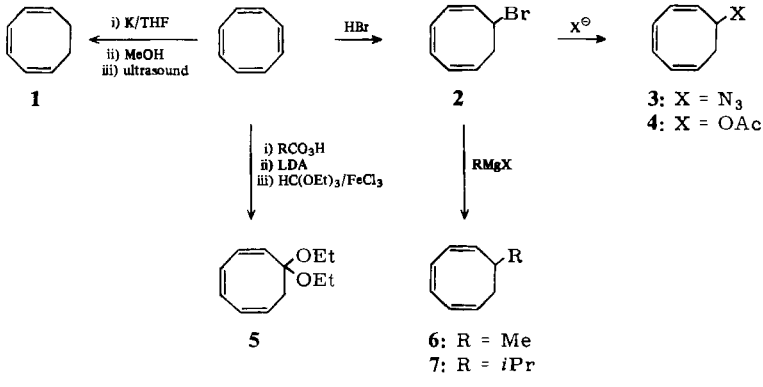
Results

Preparation of 7-Substituted 1,3,5-Cyclooctatrienes 1–7

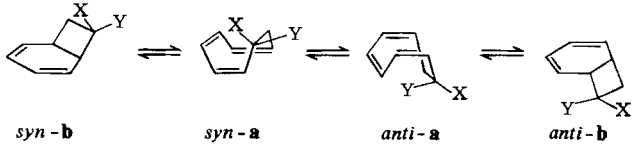
These substrates were prepared according to reported or adapted procedures as summarized in Scheme 1. Thus, the 1,3,5-cyclooctatriene (**1**) was obtained in 80% yield via a one-pot synthesis by potassium metal reduction of cyclooctatetraene in THF, protonation with methanol and subsequent ultrasound treatment at 60°C of the reaction mixture to isomerize the 1,3,6-isomer into the fully conjugated 1,3,5-isomer[8]. The 7-bromo-1,3,5-cyclooctatriene (**2**) was prepared by HBr addition to cyclooctatetraene[9]. Treatment of the bromide **2** with sodium azide or

with sodium acetate gave the azide **3** and acetate **4**, respectively[9]. The reaction of methyl- and isopropylmagnesium bromides with cyclooctatriene **2** afforded the 7-methyl and 7-isopropyl derivatives **6** and **7**, respectively[10]. Finally, the acetal **5** was obtained from cyclooctatetraene via epoxidation with CPBA, isomerization of the epoxide with LDA and transacetalation with triethyl orthoformate, catalyzed with anhydrous $FeCl_3$[11].

Scheme 1



Except for the two alkyl derivatives **6** (R = Me) and **7** (R = *i*Pr), all the other 7-substituted 1,3,5-cyclooctatrienes in Scheme 1 are known and our physical constants and spectral data matched those reported. The hitherto unknown 7-methyl- and 7-isopropyl-1,3,5-cyclooctatrienes **6** and **7** were fully characterized on the basis of ^1H and ^{13}C NMR data (Experimental Part). It suffices to say here that the 400 MHz ^1H NMR and 100 MHz ^{13}C NMR spectra were rather complex in view of the mixture of stereoisomers of the monocyclic and bicyclic forms **6a,b** (X = Me; Y = H) and **7a,b** (X = *i*Pr; Y = H) due to the valence isomerization[9] shown in Eq. (2). Indeed at elevated temperatures (50–60°C) the proportion of the bicyclic valence tautomers **6b** and **7b** increased, but a great deal of undefined high-molecular-weight material was formed as well. In view of this facile valence isomerization, all derivatives investigated consisted of a mixture of their monocyclic and bicyclic valence isomers. The proportion of valence isomers, as determined by ^1H NMR, is given in Table 1.



syn-**b** *syn*-**a** *anti*-**a** *anti*-**b** (2)

(*syn,anti* designations refer to X-substituent)

Furthermore, for both the methyl and isopropyl derivatives appreciable (ca. 10–50%) amounts of the 5-alkyl-1,3,6-cyclooctatrienes (**6c,7c**) were present as

well. Attempts to isomerize the latter by means of MeONa in MeOH into their conjugated 7-alkyl-1,3,5-cyclooctatriene (**6a**, **7a**), as was possible in the preparation of the parent 1,3,6-cyclooctatriene (**1c**), led unfortunately to a complex mixture of intractable products. In view of the thermal lability of these alkylcyclooctatrienes, it was not possible to free completely the desired conjugated 1,3,5-isomer from its 1,3,6-isomer by fractional distillation and chromatography. The amounts of the 1,3,6-isomers in the cyclooctatrienes **6** and **7**, as determined by ^{1}H NMR, are given in Table 1.

Table 1. Relative amounts (%) of monocyclic and bicyclic valence tautomers of 1,3,5-cyclooctatriene and of the 1,3,6-isomer

	Substituents[a] X	Y	 a	 b	 c
1	H	H	80[b]	20[b]	–
2	Br	H	65[c]	35[c]	–
3	N_3	H	25[c]	75[c]	–
4	OAc	H	47[c]	53[c]	–
5	OEt	OEt	<5[c]	>95[c]	–
6	Me	H	55[b]	35[b]	≈10[b]
7	*i*Pr	H	26[b]	23[b]	≈51[b]

[a] No stereochemistry specified here. – [b] Determined by 400 MHz ^{1}H NMR in $CDCl_3$ at 35°C after distillation at 50°C. – [c] See Ref.[9].

Singlet Oxygenations

As already reported[7], the singlet oxygenation of the parent 1,3,5-cyclooctatriene (**1**) afforded a mixture of the endoperoxides **1d** (80%) and **1g** (20%), derived from the cycloaddition of $^1O_2$ to the monocyclic and bicyclic valence isomers **1a** and **1b**, respectively (Table 2). This 4:1 ratio of the endoperoxides **1d** and **1g** was within experimental error equal to the ratio of the valence tautomers **1a** and **1b**, respectively (Table 1). However, control experiments revealed that pure monocyclic **1a** and pure bicyclic **1b** valence isomers, isolated by subambient silica gel chromatography, gave on singlet oxygenation at room temperature (ca. 20°C) exclusively the respective endoperoxides **1d** and **1g**. Since at ca. 20°C the valence isomerization **1a** ⇄ **1b** is kinetically frozen in[8a], the yields of endoperoxides **1d** and **1g** reflect merely the „static" amounts of the valence isomers **1a** and **1b**. Indeed, raising the temperatures to 70°C, the singlet oxygenation of cyclooctatriene **1** gave only the endoperoxide **1g**, besides extensive decomposition products. The latter fact precluded a quantitative analysis of the products. No convenient intermediate temperature for the singlet oxygenation of the parent 1,3,5-cyclooctatriene (**1a**, **b**) could be achieved to ascertain the dynamic effects of the **1a** ⇄ **1b** valence isomerization in terms of the proportion of endoperoxides **1d** and **1g**.

Similar but considerably more complex results were obtained in the singlet oxygenation of the 7-substituted 1,3,5-cyclooctatrienes **3**–**7** (Table 2). Moreover, quantitative product analyses were made difficult in view of the formation of

Table 2. Total and absolute yields of endoperoxides in the singlet oxygenation of 1,3,5-cyclooctatrienes

	Substituents X	Y	Total Yields (%)[a]	Absolute Yields (%)[b] d	e	f	g	h
1	H	H	25	20	—	—	5	
3	N_3	H	28	—	—	—	28	
4	OAc	H	29	—	—	—	22	7
5	OEt	OEt	66	—	—	—	66	
6	Me	H	48	c)	c)	c)	6	
7	*i*Pr	H	9	2	—	1	6	

[a] Remainder unidentified, high-molecular-weight peroxides; **Caution**: explosive! — [b] Unless specified, yields of products isolated by column chromatography. — [c] HPLC-analysis showed at least four peroxidic components (total ca. 42%); it was not possible to separate this mixture of products.

considerable amounts (ca. 20—100%) of intractable high-molecular-weight peroxidic materials. This obliged chromatographic isolation of the bicyclic and tricyclic endoperoxides, thereby negating acquisition of the essential quantitative product distribution as a measure of the monocyclic and bicyclic valence isomers. Besides, the formation of *exo,endo*-stereoisomeric regioisomers **d**, **e** and **f** of the bicyclic endoperoxides and *syn,anti*-isomers **g** and **h** of the tricyclic endoperoxides precluded any reasonable chance of obtaining quantitative results even for the isolated product also at the level of 400 MHz ^1H NMR analysis.

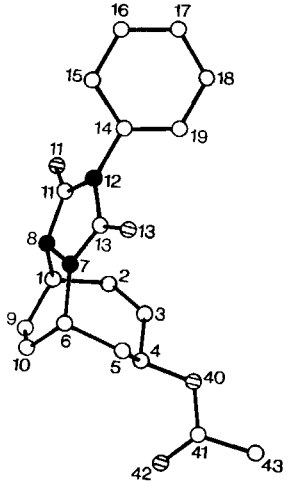


Figure 1. Perspective drawing of the urazole **4i** with the labeling of the atoms corresponding to Tables 6 and 7. White, black, and hatched spheres represent carbon, nitrogen, and oxygen atoms, respectively

Needless to say, product characterization and isomer separation was at best tedious and not in all cases achieved. Although the details are given in the Experimental Part, it is instructive to bring here some of the conclusive features. In

all cases satisfactory elemental compositions were obtained by combustion analyses. While the mass spectra were consistent with the proposed structures, definitive characterization rests on ^1H and ^{13}C NMR. Most decisive and helpful in the assignment of regio- and stereochemistry was the *X*-ray structure determination of urazole **4i**, establishing beyond doubt the *endo*-acetate substituent at the C-4 position (Fig. 1). Also the *X*-ray structure determination of the urazole **6l** was informative in that the *exo*-methyl substituent is located at the C-2 position; however, the poor quality of the diffraction data did not allow rigorous assignment of bond lengths and bond angles. The *X*-ray structural data of the urazole **4i** played a key role in the spectral assignments of the endoperoxides. The regular patterns in the ^1H and ^{13}C NMR data of the urazoles and endoperoxides will be given together and postponed after the results of the product compositions of the PTAD cycloadditions are presented.

PTAD Cycloadditions

Analogous to the singlet oxygenation of the cyclooctatrienes **1**–**7**, the reaction with PTAD afforded a complex pattern of all possible cycloadducts (Table 3).

Table 3. Total and absolute yields of urazoles in the PTAD cycloaddition of 1,3,5-cyclooctatrienes

	Substituent		Total Yield (%)	Absolute Yields (%)[a]				
	X	Y		 **i**	 **k**	 **l**	 **m**	 **n**
1	H	H	44	35	–	–	9	
3	N_3	H	49	2	–	–	47	
4	OAc	H	57	13	–	–	14	30
5	OEt	OEt	41	–	–	–	41	–
6	Me	H	52[b]	6	5	7	34	
7	*i*Pr	H	34	–	–	14	20	

} = $-CO-N(C_6H_5)-CO-$

[a] Isolated by silica gel chromatography. – [b] Does not include ca. 20% of a mixture of urazoles **6i,k,l**, which were not separated by chromatography, making the total yield of bicyclic urazoles **6i,k,l** ca. 40%.

This included the *exo,endo*-stereoisomers of the bicyclic urazoles **i,k** and **l** and the *syn,anti*-stereoisomers of the tricyclic urazoles **m** and **n**. Also here extensive formation of intractable high-molecular-weight material precluded a rigorous quantitative product analysis because preparative chromatographic separation of the complex product mixtures was essential. The details of their characterization are given in the Experimental Part and rests, besides the already mentioned *X*-ray data, on satisfactory elemental composition by means of combustion analysis, consistent mass spectral fragmentations, and ^1H and ^{13}C NMR spectra.

NMR Spectral Data of Bicyclic Endoperoxides and Urazoles

Besides the *X*-ray data for the urazole **4i** (Fig. 1), the structure assignments of the bicyclic endoperoxides and urazoles rest largely on 400 MHz ^1H and 100 MHz ^{13}C NMR spectra. Elaborate decoupling experiments were essential in these assignments. Here we shall only focus on some of the regularities of the results within and between the endoperoxide and urazole sets.

Selected ^{13}C and ^1H NMR chemical shifts and proton coupling constants are collected in Table 4 for those new bicyclic endoperoxides and urazoles for which an internally consistent spectral assignment was possible. Extensive decoupling experiments were employed to confirm these assignments. Particularly helpful in the assignment of the complex proton spectra were the known regio- and stereochemistry of the urazole **4i**, which were known with certainty from *X*-ray data (Fig. 1).

The sets of coupling constants (Table 4) for the urazole **4i** are best accommodated in terms of the confirmation given by the *X*-ray structure (Fig. 1). Thus, in solution as well as in the crystalline state the same conformational preference obtain, i.e. the acetoxy and methyl substituents assume quasi-equatorial arrangements in the urazoles **4i** and **6l**, respectively. Dreiding models confirm that the best set of dihedral angles of the vicinal protons with respect to the observed coupling constants (Table 4) correspond to the conformation of the *X*-ray structure (Fig. 1) for the urazole **4i**. Furthermore, the coupling constants of the remaining cycloadducts also correspond best with these conformations.

In the case of the urazole **6k**, the regioisomer of the PTAD adduct of the monocyclic 7-methyl-1,3,5-cyclooctatriene (**6a**), no *X*-ray structure to define the regio- and stereochemistry is available. However, in regard to the *X*-ray structure of the related urazole **4i**, the NMR spectral data is best accommodated if the 5-methyl substituent in urazole **6k** is located in the *endo*-position, assuming a quasi-equatorial conformation. In that way the relatively small coupling constant $J_{5,6}$ = 2.0 Hz, the relatively large coupling constant $J_{4n,5}$ = 11.6 Hz and the intermediate coupling constants $J_{3,4x}$ = 9.1 Hz and $J_{3,4n}$ = 5.0 Hz can be readily rationalized. Again inspection of Dreiding models shows that the experimental coupling constants match best this structure.

NMR Spectral Data of Tricyclic Endoperoxides and Urazoles

Although no *X*-ray data on any of these cycloadducts are available, a definitive assignment of the regio- and stereochemistry of the hitherto unknown tricyclic endoperoxides and urazoles derived from the bicyclic valence tautomers of the 1,3,5-cyclooctatrienes **3**–**7** was possible on the basis of the ^{13}C and ^1H NMR spectra. For this task extensive decoupling experiments were essential. Whenever possible, the stereoisomers were separated by preparative chromatography: however, even for some mixtures of stereoisomers a plausible structure assignment could be made. Selected pertinent chemical shifts and coupling constants are collected in Table 5.

Table 4. Selected ^{13}C and ^{1}H NMR chemical shifts (δ in ppm) and proton coupling constants (J in Hz) for some bicyclic endoperoxides and urazoles derived from cyclooctatrienes

Cyclo-adduct	^{13}C-Shifts (δ)			^{1}H-Shifts (δ)							Coupling Constants (Hz)						
	C-6,1(d)	C-4(d)	C-5(t)	1-H	2-H	3-H	4-H	5-H_x	5-H_n	6-H	$J_{1,2}$	$J_{2,4}$	$J_{3,4}$	$J_{4,5x}$	$J_{4,5n}$	$J_{5x,6}$	$J_{5n,6}$
3i	49.24 50.08	56.72	43.60	5.22	5.83	5.94	4.50	2.45	2.60	5.03	7.0	2.6	3.6	4.7	11.9	4.9	1.7
4i	48.99 49.89	68.75	42.71	5.22	5.77	5.88	5.76	2.46	2.57	4.98	7.0	2.5	3.1	5.0	12.1	5.1	1.5
6i	[a]	[a]	[a]	5.16	5.70	5.75	2.67– 2.79	2.07	2.30	4.95	7.0	2.1	4.1	4.9	12.0	4.5	1.5
6k	[a]	[a]	[a]	5.16	5.77	6.00	2.67– 2.79[b]	2.14[c]	2.17[d]	4.75	7.2	2.2, 2.5[e]	9.1, 5.0[f]	2.3[g]	11.6, 2.3[h]	2.0	
6l	49.65 54.32	44.52[i]	38.10	4.83– 4.86	3.20– 3.29	5.25–5.26		3.00– 3.09	2.50– 2.59	5.17	4.5	–	[k]	2	2	4.4	2.5
7d	74.43 76.77	39.89	40.46	4.76	5.78	5.97	2.43	1.81	2.00	5.05	7.1	2.5	4.4	4.3	12.2	3.6	2.5
7f	76.15 79.53	51.60[i]	35.26	4.74– 4.80	2.82– 2.88	5.29– 5.36	5.40– 5.48	2.24– 2.34	2.78– 2.88	4.90– 4.95	2.0	–	13.5[j]	7.0	2.1	3.9	2.5
7l	51.95 55.36	48.77[i]	37.64	4.98– 5.04	2.95	5.38		3.01– 3.10	2.49– 2.57	4.98– 5.04	5.0	–	[k]	2	2	4.2	2.8

[a] The resonances could not be assigned to the individual endoperoxide isomers. – [b] 5-H. – [c] 4-H_x. – [d] 4-H_n. – [e] $J_{2,4x}$, $J_{2,4n}$. – [f] $J_{3,4x}$, $J_{3,4n}$. – [g] $J_{4x,5}$. – [h] $J_{4n,5}$, $J_{4x,5}$. – [i] C-2 (d). – [j] $J_{3,4}$ represents a vinylic coupling constant in this case. – [k] Broad singlet.

Table 5. Selected ^{13}C and ^1H NMR chemical shifts (δ in ppm) and proton coupling constants (J in Hz) for some tricyclic endoperoxides and urazoles derived from cyclooctatrienes

Cyclo-adduct	^{13}C-Shifts (δ)			^1H-Shifts (δ)							Δδ	Coupling Constants (Hz)			
	C-6,1(d)	C-3	C-4(t)	1-H	6-H	3-H	4-H_s	4-H_a	9-H	10-H	9,10-H	$J_{2,3}$	$J_{2,5}$	$J_{4s,5}$	$J_{4a,5}$
3g	70.61 72.40	53.52	29.54	4.68–4.76		4.28	1.90	2.55	6.69	6.90	0.21	10.5	8.2	5.9	8.5
4g	70.27 72.47	67.48	31.50	4.73		5.05	1.88	2.54	6.83	6.66	0.17	8.5	7.5	6.5	8.5
5g	70.67 72.97	100.15	35.91	4.76		–	1.87	2.13	6.74	6.52	0.22	–	8.8	6.1	9.2
6g	[a]	[a]	[a]	4.62–4.72		2.74	1.44	2.16	6.90	6.69	0.21	9.6	8.0	6.2	8.9
7g	72.19 73.40	29.03	27.45	4.74	4.65	2.16	1.45	2.06	6.82	6.63	0.19	7.2	[b]	6.1	7.5
3h	71.18 72.76	55.11	28.75	4.81	4.68–4.76	3.47	2.03	2.24	6.77	6.85	[c]	3.9	9.5	4.9	9.8
4h	71.17 73.00	69.63	29.23	4.88	4.74	4.43	2.02–2.12	2.25	6.83		[c]	3.9	9.0	4.5	10.0
6h	[a]	[a]	[a]	4.62–4.72		1.84–1.96	1.64	1.74	6.80		[c]	4.9	8.4	5.8	9.3
7h	73.40 73.52	28.28	25.61	4.61–4.70		1.37	1.57–1.66	1.76	6.74–6.82		[c]	4.9	8.0	5.1	8.9
3m	52.92 54.29	51.84	27.79	5.02	4.92	4.25	1.82	2.50	6.69	6.46	0.23	[d]	[d]	[d]	[d]

Table 5 (*continued*)

Cyclo-adduct	^{13}C-Shifts (δ) C-6,1(d)	C-3	C-4(t)	^{1}H-Shifts (δ) 1-H	6-H	3-H	4-H_s	4-H_a	9-H	10-H	Δδ 9,10-H	Coupling Constants (Hz) $J_{2,3}$	$J_{2,5}$	$J_{4s,5}$	$J_{4a,5}$
4m	50.79 53.22	66.25	30.68	5.03	5.00	5.09	1.90	2.60	6.66	6.49	0.17	8.1	7.9	5.5	7.7
5m	51.08 53.43	99.12	34.32	5.07	4.97	–	1.86	2.17	6.56	6.33	0.23	–	8.8	6.3	8.8
6m	52.04 53.68	27.49	29.02	4.98	4.94	2.72	1.44	2.21	6.70	6.51	0.19	10.0	8.5	7.5	8.0
7m	[a]	[a]	[a]	4.91– 4.98	5.10	2.06– 2.20	1.44– 1.70	2.06– 2.20	6.59– 6.69	6.47– 6.50	0.16	8.6	[b]	6.5	9.0
3n	52.65 53.13	51.05	28.96	5.04	4.94	3.44	1.96	2.19	6.55	6.63	0.08	3.8	9.0	5.1	9.8
4n	51.74 53.12	68.68	28.25	5.20	5.02	4.45	2.02– 2.13	2.29	6.68		[c]	4.0	8.0	5.0	10.0
6n	52.89 53.37	28.22	27.96	4.98	4.96	1.90	1.64–1.79		6.63		[c]	5.0	8.1	5.6	9.5
7n	[a]	[a]	[a]	4.91–4.98		1.39	1.58– 1.71	1.80	6.59–6.69		[c]	4.9	8.2	4.5	10.0

[a] The resonance could not be assigned to the individual regioisomers. – [b] $J_{2,5}$ could not be determined because the signals for 2-H and 5-H overlap. – [c] Very narrow ABXY-system. – [d] Decoupling experiments could not be run because of too little of **3m** in the mixture.

Quite helpful in the assignment of the *syn,anti*-stereochemistry of the substituent on the four-membered ring were the corresponding protons. For this purpose the results of the ^{1}H NMR analysis of the carbocyclic analogue, i.e. tricyclo[4.2.2.0^{2,5}]-dec-7-ene[12], could be advantageously utilized. Thus, the α-proton of the substituent-bearing C-3 carbon is expectedly displaced to lower field for the *syn*-isomers **g** compared to the *anti*-isomers **h** due to the anisotropy effect of the double bond at C-9 and C-10 of the endoperoxides **3g,h**, **4g,h**, **6g,h**, **7g,h** and urazoles **3m,n**, **4m,n**, **6m,n**, **7m,n** (Table 5). This effect is also clearly visible for the *syn,anti*-4-H protons in these compounds. Furthermore, the 9,10-H protons (each appearing as pseudo-triplets) are notably differentiated in the *syn*-isomers **g** and **m** compared to the *anti*-isomers **h** and **n**. Finally, the vicinal $J_{2,3}$ coupling constants are consistently larger for the *syn*-isomers **g** and **m** (7–11 Hz) compared to those for the *anti*-isomers **h** and **n** (4–5 Hz). This spectral feature is corroborated nicely with the respective dihedral angles exhibited by Dreiding models.

Discussion

The present results (Tables 2 and 3) clearly manifest that the 1,3,5-cyclooctatrienes **1**–**7**, investigated here in regard to understand the dienophilic nature of singlet oxygen and PTAD, offer no advantages over the cycloheptatrienes[3]. On the contrary, the propensity of the cyclooctatrienes to give mixtures of monocyclic 1,3,5- and 1,3,6-isomers **a** and **c**, which are difficult to separate (as was experienced here with the methyl- and isopropyl-substituted derivatives **6a,c** and **7a,c**, respectively), presents additional complications in the quantitative product analysis. Furthermore, the complex product mixtures resulting from the $^1O_2$ and PTAD cycloaddition, including the stereoisomeric regioisomers of the endoperoxides **d,e** and of the urazoles **i,k** derived from the monocyclic valence isomers **a** and the stereoisomers of the endoperoxides **g,h** and of the urazoles **m,n** derived from the bicyclic valence isomers **b** preclude an accurate quantitative product determination even with the help of direct 400 MHz ^{1}H NMR analysis of the cycloaddition mixture. Moreover, the extensive amounts of undefined high-molecular-weight material, e.g. in the case of the bromocyclooctatriene **2** the exclusive mode of reaction, oblige tedious preparative separation of the complex product mixtures. It is, therefore, not surprising that the fragmentary product composition of Tables 2 and 3 do not permit recognizing any quantitative trend and regularities of the effect of substituents on the valence isomeric equilibrium between the monocyclic and bicyclic tautomers **a** and **b**.

Even if all these complications could be put under control, the most serious disadvantage of the 1,3,5-cyclooctatrienes is the fact that the kinetic barrier between the monocyclic and bicyclic valence isomers **a** and **b**, respectively, is too high at the temperatures of interest. Consequently, at ambient temperatures the 1,3,5-cyclooctatrienes constitute „static" equilibria, each valence isomer reacting with the dienophile independently, without being replenished through valence isomerization on the time scale of the cycloaddition. The latter fact, however, would provide the means to compare and contrast the dienophilic nature of

reagents such as $^1O_2$ and PTAD. This condition was optimally fulfilled for the tropilidene-norcaradiene valence isomerization of cycloheptatriene[2,3]. Unfortunately, for this system the cycloaddition of PTAD with the norcaradiene valence isomer is so much faster than with the tropilidene valence isomer, that exclusively the norcaradiene-type urazole is obtained.

That the bicyclic valence isomer of the cyclooctatrienes is also the more reactive towards $^1O_2$ and PTAD is evident in Tables 2 and 3. Except for the parent cyclooctatriene **1** and its methyl derivative **6**, the yields of tricyclic endoperoxides **g, h** and urazoles **m, n** derived from the bicyclic valence isomers **b** are consistently larger than the corresponding cycloadducts from the monocyclic isomers **a**. The reason that the reverse trend is obtained for the parent cyclooctatriene **1** and its methyl derivative **6** is merely a consequence of the fact that the content of the monocyclic valence tautomers **1a** and **6a**, respectively, predominate by a wide margin (4:1) at room temperature (ca. 20°C) over the bicyclic tautomers **1b** and **6b** in the „static" valence isomer equilibrium.

We are grateful to the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* for generous financial support of this work. For the assistance in measuring the mass spectra we thank Dr. *G. Lange* and for the NMR spectra Dr. *D. Scheutzow*. A generous supply of cyclooctatetraene was provided by *BASF Aktiengesellschaft*, for which we are most thankful.

Experimental Part

All melting points were taken on a Kofler hot stage and are uncorrected. – IR spectra: Beckman Acculab 4 spectrometer. – NMR spectra: Unless otherwise stated, in $CDCl_3$ with tetramethylsilane (TMS) as reference on a Varian EM 390 (90 MHz), Bruker WH 90 (22.6 MHz), Bruker WM 400 (400 MHz), or a Hitachi Perkin-Elmer R-24B spectrometer. – Mass spectra (70 eV): Varian CH-7. – Elemental analyses were performed in-house. For the TLC runs Macherey and Nagel Polygram SIL G/UV 40 × 80 mm plates were used, eluting with the appropriate solvent system, which is specified for each case. For column chromatography silica gel (70–230 mesh, activity grade I; Merck Co.) was employed. Commercial reagents and solvents were purified according to the literature procedures to match reported physical and spectral data. Known compounds used in this research were either purchased or prepared and purified according to literature procedures. Metal-free dichloromethane was obtained by first distilling from alumina (Woelm B, activity grade I) and then from ethylenediaminetetraacetate.

1,3,5-Cyclooctatriene (**1**): To a solution of 26.1 g (250 mmol) of cyclooctatetraene in 200 ml of dry THF were added at 20°C under N_2 atmosphere 21.5 g (550 mmol) of potassium and heated to 60°C, while irradiating with ultrasound. The dropwise addition of 40 ml of methanol at 0°C afforded a brown suspension which was heated for 3 h to 60°C while irradiating with ultrasound. For hydrolysis a 20% NH_4Cl solution (1 × 230 ml) was added. The aqueous layer was extracted with ether (3 × 100 ml), the combined organic layers were washed with 10% $KHCO_3$ solution (1 × 50 ml) and water (1 × 50 ml) and dried over $MgSO_4$. After removal of the solvent, the yellow oil (22.8 g) was distilled at 30 Torr between 49 and 53°C to give 21.2 g (80%) of a colourless oil. n_D^{25} = 1.5225 (lit.[1]) n_D^{25} = 1.5520). The ^1H NMR and IR spectra were in accordance with those of 1,3,5-cyclooctatriene synthesized independently.

7-Methyl-1,3,5-cyclooctatriene (**6**): To a mixture of 1.68 g (69.0 mmol) of magnesium and 9.59 g (67.6 mmol) of methyl iodide in 70 ml of ether were added dropwise 10.0 g (54.0 mmol) of 7-bromo-1,3,5-cyclooctatriene (**2**) in 40 ml of ether. The mixture was stirred at 0°C for 12 h. After addition of 60 ml of 2 N HCl, the aqueous layer was extracted with ether (3 × 30 ml). The combined organic layers were washed with 40% $Na_2S_2O_5$ solution (1 × 40 ml), 20% $KHCO_3$ solution (1 × 40 ml), and water (1 × 20 ml) and dried over $MgSO_4$. After roto-evaporation of the solvent at 20°C and 15 Torr, the yellow oily residue (6.63 g) was bulb-to-bulb distilled at 0°C and 10^{-2} Torr to give 3.64 g (56%) of a colourless oil, n_D^{25} = 1.5040. – IR (film): 3050, 3020, 3000, 2950, 2870, 1640, 1460, 1375, 775, 650 cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.04 (d; 3H, CH_3), 2.31 (ddd; 2H, 8-H, 8-H), 2.73 (mc; 1H, 7-H), 5.65–5.96 (m; 6H, 1-H, 2-H, 3-H, 4-H, 5-H, 6-H); $J_{CH_3,7}$ = 7 Hz, $J_{7,8}$ = 6 Hz. – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 22.81 (q; CH_3), 33.50 (d; C-7), 35.69 (t; C-8), 124.51 (d), 126.28 (d), 126.60 (d), 127.17 (d), 134.11 (d), 140.98 (d). – MS (70 eV): *m/e* = 120 (13%, M^+), 105 (33, M – CH_3), 78 (100, C_6H_6).

C_9H_{12} (120.2) Calcd. C 89.94 H 10.06 Found C 89.90 H 10.02

7-Isopropyl-1,3,5-cyclooctatriene (**7a**) *and 5-Isopropyl-1,3,6-cyclooctatriene* (**7c**): To a mixture of 1.68 g (69.0 mmol) of magnesium and 8.32 g (67.6 mmol) of isopropyl bromide in 70 ml of ether were added dropwise 10.0 g (54.0 mmol) of **2** in 50 ml of ether. The mixture was stirred for 12 h at 0°C. After addition of 60 ml of 2 N HCl, the aqueous layer was extracted with ether (3 × 30 ml). The combined organic layers were washed with 10% $KHCO_3$ solution (1 × 20 ml) and H_2O (1 × 20 ml) and dried over $MgSO_4$. After roto-evaporation of the solvent at 20°C and 15 Torr, the yellow oily residue (7.63 g) was bulb-to-bulb distilled at 0°C and 10^{-2} Torr to give 5.41 g (68%) of a colourless oil (n_D^{25} = 1.4990), which could not be separated into its two components by chromatographic methods. – IR (film): 3050, 3010, 2960, 2920, 2880, 1640, 1620, 1470, 1390, 1370, 780, 720, 650 cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz)[a]: δ = 0.88 (d; CH_3), 0.90 (d; CH_3), 0.928 (d; CH_3), 0.931 (d; CH_3), 1.60 (mc; 1H, C*H*CH_3), 1.72 (mc; 1H, C*H*CH_3), 2.23 (mc; 1H, 8-H), 2.40 (ddd; 1H, 8-H), 2.55–2.66 (m; 2H, 7-H, 8-H), 2.84–2.97 (m; 2H, 7-H, 8-H), 5.33–6.07 (m; 12H, olefinic H). – ^{13}C NMR*) ($CDCl_3$, 100 MHz): δ = 19.64 (q; 2CH_3), 19.73 (q; CH_3), 20.13 (q; CH_3), 28.38 (t; C-8), 31.23 (t; C-8), 31.88 (d), 33.08 (d), 43.63 (d), 43.95 (d), 125.26 (d), 126.12 (d), 126.30 (d), 126.57 (d), 126.75 (d), 129.27 (d), 131.22 (d), 131.54 (d), 134.62 (d), 138.76 (d). – MS (70 eV): *m/e* = 148 (11%, M^+), 133 (6%, M – CH_3), 105 (100, M – C_3H_7), 78 (83, C_6H_6).

$C_{11}H_{16}$ (148.2) Calcd. C 89.12 H 10.88 Found C 89.36 H 11.00

General Procedure for Photooxygenation

Through a solution of the particular cyclooctatriene (33.0–80.0 mM), hydroquinone (5.00×10^{-2}–5.00 mM), and 5–20 mg of tetraphenylporphine (TPP) in the specified solvent was bubbled a gentle stream of dry oxygen at subambient temperatures, while irradiated externally with a sodium high pressure lamp (Philips G/98/250 N). The reaction progress was monitored either by TLC or ^1H NMR until all starting material was consumed. Work-up and isolation consisted of roto-evaporation of the solvent at ca. 0°C and 15 Torr, followed by low temperature chromatography. The details are given in the specific cases (**Caution!** The crude products contain dangerous peroxidic high-molecular-weight material, which may explode spontaneously when warmed above 20°C).

syn- and anti-3-Azido-7,8-dioxatricyclo[4.2.2.0^{2,5}]dec-9-ene (**3g,h**): A solution of 1.02 g (6.93 mmol) of the mixture of azides **3** and 10 mg of TPP in 60 ml of CCl_4 was photooxy-

*) Resonances of the mixture of the isomeric trienes.

genated for 24 h at −5°C. Roto-evaporation of the solvent, followed by silica gel chromatography (50:1 adsorbent-substrate ratio) at −20°C eluting with CH_2Cl_2, afforded two fractions, which were identified as monocyclic 7-azido-1,3,5-cyclooctatriene (**3a**) and the stereoisomeric endoperoxides **3g,h**. The triene **3a** was eluted as first fraction (R_F = 0.82), affording 200 mg (20%) of a yellow oil. The endoperoxides **3g,h** were eluted as second fraction (R_F = 0.54). Roto-evaporation at 0°C and 15 Torr gave 380 mg of a colourless solid, which on recrystallizing from CH_2Cl_2/pentane (1:1) yielded 343 mg (28%) of **3g,h** in a 3:1 ratio as colourless needles, m.p. 63−72°C. − **3g,h**: IR (CCl_4): 3060, 2940, 2100, 1630, 1430, 1370, 1340, 1260, 905, 705 cm^{-1}. − MS (70 eV): *m/e* = 151 (2%, M − N_2), 122 (12, M − N_3CH), 94 (27, C_6H_6O), 67 (66, C_4H_5N), 41 (100, NC_2H_3).

$C_8H_9N_3O_2$ (179.2) Calcd. C 53.63 H 5.06 N 23.45 Found C 53.76 H 5.19 N 23.39

Endoperoxide **3g**: ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.90 (mc; 1H, 4-H_s), 2.55 (mc; 1H, 4-H_a), 2.94−3.08 (m; 1H, 5-H), 3.29 (mc; 1H, 2-H), 4.28 (mc; 1H, 3-H), 4.68−4.76 (m; 2H, 1-H, 6-H), 6.69 (ddd; 1H, 9-H), 6.90 (ddd; 1H, 10-H); $J_{1,2}$ = 5.1, $J_{1,9}$ = 6.0, $J_{1,10}$ = 1.5, $J_{2,3}$ = 10.5, $J_{2,4a}$ = 1.0, $J_{2,5}$ = 8.2, $J_{3,4s}$ = 6.9, $J_{3,4a}$ = 9.1, $J_{4s,4a}$ = 14.0, $J_{4s,5}$ = 5.9, $J_{4a,5}$ = 8.5, $J_{6,9}$ = 1.5, $J_{6,10}$ = 6.0, $J_{9,10}$ = 8.1 Hz. − ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 27.63 (d; C-5), 29.54 (t; C-4), 38.52 (d; C-2), 53.52 (d; C-3), 70.61 (d; C-6), 72.40 (d; C-1), 130.09 (d; C-10), 133.18 (d; C-9).

Endoperoxide **3h**: ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.03 (mc; 1H, 4-H_s), 2.24 (mc; 1H, 4-H_a), 2.94−3.08 (m; 1H, 5-H), 3.13 (mc; 1H, 2-H), 3.47 (mc; 1H, 3-H), 4.68−4.76 (m; 1H, 6-H), 4.81 (mc; 1H, 1-H), 6.77 (ddd; 1H, 9-H), 6.85 (ddd; 1H, 10-H); $J_{1,2}$ = 6.0, $J_{1,9}$ = 6.1, $J_{1,10}$ = 1.9, $J_{2,3}$ = 3.9, $J_{2,5}$ = 9.5, $J_{3,4s}$ = 7.5, $J_{3,4a}$ = 4.5, $J_{4s,4a}$ = 15.1, $J_{4s,5}$ = 4.9, $J_{4a,5}$ = 9.8, $J_{6,9}$ = 1.9, $J_{6,10}$ = 6.1, $J_{9,10}$ = 8.2 Hz. − ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 28.38 (d; C-5), 28.75 (t; C-4), 39.70 (d; C-2), 55.11 (d; C-3), 71.18 (d; C-6), 72.76 (d; C-1), 131.52 (d; C-10), 132.82 (d; C-9).

syn- and anti-3-Acetoxy-7,8-dioxatricyclo[4.2.2.0^{2,5}]dec-9-ene (**4g,h**): A solution of 3.00 g (18.3 mmol) of acetoxycyclooctatriene **4** and 10 mg of TPP in 40 ml of acetone was photooxygenated for 24 h at 10°C. Roto-evaporation of the solvent at 0°C and 15 Torr gave 3.30 g of a green, viscous oil which was chromatographed on silica gel (50:1 adsorbent-substrate ratio) at −20°C, eluting with CH_2Cl_2. Two fractions were obtained, which were identified as unreacted triene **4** and the stereoisomeric endoperoxides **4g,h**. The triene **4a** (1.07 g, 33%) eluted as first fraction (R_F = 0.82) as yellow, viscous oil. The endoperoxides **4g,h** eluted as second fraction (R_F = 0.49). Roto-evaporation of the solvent at 0°C and 15 Torr afforded 1.10 g (31%) of a colourless oil, which crystallized on standing at −25°C. Fractional recrystallization from CCl_4/pentane (1:3) gave 794 mg (22%) of the *syn*-endoperoxide **4g** as colourless plates, m.p. 65−66°C, and 250 mg (7%) of the *anti*-endoperoxide **4h** as a pale yellow oil after silica gel chromatography of the mother liquor (100:1 adsorbant-substrate ratio) at −20°C, eluting with CH_2Cl_2 and roto-evaporation of the solvent at 0°C and 15 Torr.

Endoperoxide **4g**: IR (KBr): 3070, 3000, 2960, 1730, 1375, 1265, 1240, 1070, 900, 700 cm^{-1}. − ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.88 (ddd; 1H, 4-H_s), 2.03 (s; 3H, CH_3), 2.54 (mc; 1H, 4-H_a), 2.96 (mc; 1H, 5-H), 3.44 (mc; 1H, 2-H), 4.73 (mc; 1H, 6-H), 5.05 (mc; 1H, 3-H), 6.66 (dd; 1H, 10-H), 6.83 (dd; 1H, 9-H); $J_{1,2}$ = 5.5, $J_{1,9}$ = 6.0, $J_{1,10}$ = 1.0, $J_{2,3}$ = 8.5, $J_{2,4a}$ = 1.3, $J_{2,5}$ = 7.5, $J_{3,4s}$ = 6.5, $J_{3,4a}$ = 8.4, $J_{4s,4a}$ = 14.0, $J_{4s,5}$ = 6.5, $J_{4a,5}$ = 8.5, $J_{5,6}$ = 6.0, $J_{6,9}$ = 1.5, $J_{6,10}$ = 6.0, $J_{9,10}$ = 8.0 Hz. − ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.88 (q; CH_3), 27.01 (d; C-5), 31.50 (t; C-4), 38.85 (d; C-2), 67.48 (d; C-3), 70.27 (d; C-6), 72.42 (d; C-1), 129.81 (d;

C-10), 132.94 (d; C-9), 170.14 (s; C=O). – MS (70 eV): *m/e* = 196 (0.2%, M^+), 164 (5, M – O_2), 136 (3, M – CH_3CO_2H), 86 (15, $C_4H_6O_2$), 43 (100, $COCH_3$).

$C_{10}H_{12}O_4$ (196.2) Calcd. C 61.22 H 6.16 Found C 60.81 H 6.04

Endoperoxide **4h**: IR (CCl_4): 3060, 2950, 1730, 1650, 1375, 1240, 1075, 1050, 905, 610 cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.07 (s; 3H, CH_3), 2.02–2.12 (m; 1H, 4-H_a), 2.25 (dddd; 1H, 4-H_a), 3.05 (dddd; 1H, 5-H), 3.10 (mc; 1H, 2-H), 4.43 (ddd; 1H, 3-H), 4.74 (mc; 1H, 6-H), 4.88 (mc; 1H, 1-H), 6.83 (mc; 2H, 9-H, 10-H); $J_{1,2}$ = 5.5, $J_{1,6}$ = 2.0, $J_{1,9}$ = 5.5, $J_{1,10}$ = 1.9, $J_{2,3}$ = 3.9, $J_{2,4a}$ = 1.0, $J_{2,5}$ = 9.0, $J_{3,4s}$ = 8.0, $J_{3,4a}$ = 4.9, $J_{4s,4a}$ = 15.0, $J_{4s,5}$ = 4.5, $J_{4a,5}$ = 10.0, $J_{5,6}$ = 4.5, $J_{6,9}$ = 1.9, $J_{6,10}$ = 5.5, $J_{9,10}$ = 6.0 Hz. – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.01 (q; CH_3), 28.59 (d; C-5), 29.23 (t; C-4), 40.83 (d; C-2), 69.63 (d; C-3), 71.17 (d; C-6), 73.00 (d; C-1), 132.16 (d; C-10), 132.44 (d; C-9), 171.15 (s; C=O). – MS (70 eV): *m/e* = 164 (2%, M – O_2), 136 (0.2, M – CH_3CO_2H), 86 (14, $C_4H_6O_2$), 43 (100, $COCH_3$).

$C_{10}H_{12}O_4$ (196.2) Calcd. C 61.22 H 6.16 Found C 60.92 H 5.94

3,3-Diethoxy-7,8-dioxatricyclo[4.2.2.0^{2,5}]dec-9-ene (**5g**): A solution of 850 mg (4.37 mmol) of the triene **5** and 10 mg of TPP in 60 ml of CCl_4 was photooxygenated for 48 h at –20°C. After roto-evaporation of the solvent at 0°C and 15 Torr and silica gel chromatography (50:1 adsorbent-substrate ratio) at –20°C eluting with CH_2Cl_2 gave after roto-evaporation of the solvent at 0°C and 15 Torr 654 mg (66%) of **5g** as yellow oil. – IR (film): 3060, 2980–2870, 1475, 1445, 1280, 1260, 1180, 1130, 1050, 960, 900, 830 cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.13 (t; 3H, OCH_2CH_3), 1.21 (t; 3H, OCH_2CH_3), 1.87 (q; 1H, 4-H_s), 2.13 (m; 1H, 4-H_a), 2.87 (mc; 1H, 5-H), 3.01 (t; 1H, 2-H), 3.63 (q; 2H, OCH_2CH_3), 3.40 (mc; 2H, OCH_2CH_3), 4.76 (mc; 2H, 1-H, 6-H), 6.52 (mc; 1H, 10-H), 6.74 (mc; 1H, 9-H); $J_{1,2}$ = 5.0, $J_{1,9}$ = 6.1, $J_{1,10}$ = 2.2, $J_{2,4a}$ = 2.0, $J_{2,4s}$ = 1.2, $J_{2,5}$ = 8.8, $J_{4s,4a}$ = 13.5, $J_{4s,5}$ = 6.1, $J_{4a,5}$ = 9.2, $J_{5,6}$ = 5.3, $J_{6,9}$ = 2.0, $J_{6,10}$ = 6.1, $J_{9,10}$ = 8.2 Hz. – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 15.10 (q; OCH_2CH_3), 15.23 (q; OCH_2CH_3), 23.74 (d; C-5), 35.91 (t; C-4), 43.46 (d; C-2), 55.77 (t; OCH_2CH_3), 56.62 (t; OCH_2CH_3), 70.67 (d; C-6), 72.97 (d; C-1), 100.15 (s; C-3), 127.63 (d; C-9), 133.34 (d; C-10). – MS (70 eV): *m/e* = 226 (0.5%, M^+), 181 (13%, M – OEt), 45 (20, OEt), 29 (100, C_2H_5).

$C_{12}H_{18}O_4$ (226.3) Calcd. C 63.70 H 8.02 Found C 63.39 H 8.00

syn- and anti-3-Methyl-7,8-dioxatricyclo[4.2.2.0^{2,5}]dec-9-ene (**6g, h**): A solution of 1.42 g (11.8 mmol) of methylcyclooctatriene **6** and 5 mg of TPP in 50 ml of CH_2Cl_2 was photooxygenated for 40 h at 0°C. The green coloured solution was evaporated at 0°C and 15 Torr, followed by silica gel chromatography (100:1 adsorbent-substrate ratio) at –20°C, eluting with CH_2Cl_2. Two fractions were obtained. The first fraction (R_F = 0.43) yielded 750 mg (42%, peroxidic titer = 87%) of a mixture of at least four compounds, which could not be separated into its individual components even by HPLC. The second fraction (R_F = 0.25) afforded 107 mg (6%) of the tricyclic endoperoxides **6g, h**, which could not be separated by chromatographic methods. – **6g, h**: IR (CCl_4): 3060, 2970, 2860, 1460, 1430, 1380, 1100, 950, 920, 650, 620 cm^{-1}. – MS (70 eV): *m/e* = 152 (2%, M^+), 137 (3, M – CH_3), 81 (87, C_5H_5O), 79 (100, C_6H_7).

$C_9H_{12}O_2$ (152.2) Calcd. C 71.03 H 7.95 Found C 71.12 H 8.21

Endoperoxide **6g**: ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.93 (d; 3H, CH_3), 1.44 (ddd; 1H, 4-H_s), 2.16 (mc; 1H, 4-H_a), 2.74 (mc; 1H, 3-H), 3.01–3.13 (m; 2H, 2-H, 5-H), 4.62–4.72 (m; 2H, 1-H, 6-H), 6.69 (ddd; 1H, 10-H), 6.90 (ddd; 1H, 9-H); $J_{CH_3,3}$ = 7.6, $J_{1,2}$ = 5.3, $J_{1,9}$ = 5.6, $J_{1,10}$ = 1.1, $J_{2,3}$ = 9.6, $J_{2,5}$ = 8.0, $J_{2,4a}$ = 1.3, $J_{3,4s}$ = 10.3, $J_{4s,4a}$ = 12.4, $J_{4s,5}$ = 6.2, $J_{4a,5}$ = 8.9 Hz.

Endoperoxide **6h**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.12 (d; 3H, CH_3), 1.64 (ddd; 1H, 4-H_s), 1.74 (ddd; 1H, 4-H_a), 1.84–1.96 (m; 1H, 3-H), 2.60 (ddd; 1H, 2-H), 2.96 (mc; 1H, 5-H), 4.62–4.72 (m; 2H, 1-H, 6-H), 6.80 (mc; 2H, 9-H, 10-H); $J_{CH_3,3}$ = 7.1, $J_{1,2}$ = 4.9, $J_{2,3}$ = 4.9, $J_{2,5}$ = 8.4, $J_{3,4s}$ = 9.8, $J_{3,4a}$ = 5.5, $J_{4s,4a}$ = 13.7, $J_{4s,5}$ = 5.8, $J_{4a,5}$ = 9.3, $J_{5,6}$ = 6.5, $J_{6,10}$ = 5.0, $J_{9,10}$ = 8.1 Hz. – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 15.74 (q; CH_3), 21.81 (q; CH_3), 28.23 (t; C-4), 28.56 (t; C-4), 28.95 (d), 29.17 (d), 29.75 (d), 29.86 (d), 37.01 (d), 39.69 (d), 72.30 (d), 72.81 (d), 73.42 (d), 131.38, 131.66, 132.23, 133.99.

4-Isopropyl-7,8-dioxabicyclo[4.2.2]deca-2,9-diene (**7d**), *2-Isopropyl-7,8-dioxabicyclo[4.2.2]-deca-3,9-diene* (**7f**), *and syn- and anti-3-Isopropyl-7,8-dioxatricyclo[4.2.2.0^{2,5}]dec-9-ene* (**7g,h**): A solution of 1.50 g (10.1 mmol) of isopropylcyclooctatriene **7** and 5 mg of TPP in 50 ml of CH_2Cl_2 was photooxygenated for 24 h at 5°C. Roto-evaporation of the solvent, followed by silica gel chromatography (60:1 adsorbent-substrate ratio) at –20°C, eluting with CH_2Cl_2, afforded three fractions, which were identified as the endoperoxides **7d**, **7f**, and **7g,h**.

Of the *endoperoxide* **7d**, which eluted as first fraction (R_F = 0.56), were obtained 41 mg (2%), after roto-evaporation of the solvent at 0°C and 15 Torr, as colourless solid. Recrystallization from pentane yielded 38 mg (2%) of **7d** as colourless plates, m.p. 48–52°C. – IR (CCl_4): 3060, 3030, 2980, 2960, 1470, 1430, 1395, 1375, 1050, 1030, 930, 870, 670 cm^{-1}. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.92 (d; 3H, CH_3), 0.94 (d; 3H, CH_3), 1.79 (ddd; 1H, C*H*(CH_3)$_2$), 1.81 (ddd; 1H, 5-H_x), 2.00 (ddd; 1H, 5-H_n), 2.43 (mc; 1H, 4-H), 4.76 (ddd; 1H, 1-H), 5.05 (mc; 1H, 6-H), 5.78 (ddd; 1H, 2-H), 5.97 (dd; 1H, 3-H), 6.15 (dd; 1H, 10-H), 6.56 (dd; 1H, 9-H); $J_{CH_3,CH}$ = 6.9, $J_{CH,4}$ = 4.8, $J_{1,2}$ = 7.1, $J_{1,6}$ = 1.4, $J_{1,9}$ = 6.3, $J_{2,3}$ = 12.1, $J_{2,4}$ = 2.5, $J_{3,4}$ = 4.4, $J_{4,5x}$ = 4.3, $J_{4,5n}$ = 12.2, $J_{5x,5n}$ = 14.4, $J_{5x,6}$ = 3.6, $J_{5n,6}$ = 2.5, $J_{6,10}$ = 5.0, $J_{9,10}$ = 10.0 Hz. – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 19.31 (q; CH_3), 20.14 (q; CH_3), 32.24 (d; CH), 39.89 (d; C-4), 40.46 (t; C-5), 74.43 (d), 76.77 (d), 122.05 (d), 126.66 (d), 129.55 (d), 140.51 (d). – MS (70 eV): *m/e* = 180 (1%, M^+), 105 (100, C_8H_9), 81 (91, C_5H_5O).

$C_{11}H_{16}O_2$ (180.2) Calcd. C 73.30 H 8.95 Found C 73.49 H 9.14

Of the *endoperoxide* **7f**, which eluted as second fraction (R_F = 0.52), were obtained 25 mg (1%) after roto-evaporation of the solvent, followed by molecular distillation of the yellow, viscous oil. – IR (CCl_4): 3060, 3020, 2970, 1470, 1430, 1415, 1390, 1370, 1315, 1205, 1100, 915, 670 cm^{-1}. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.93 (d; 3H, CH_3), 1.00 (d; 3H, CH_3), 1.79 (mc; 1H, C*H*(CH_3)$_2$), 2.24–2.34 (m; 1H, 5-H_x), 2.78–2.88 (m; 1H, 5-H_n), 2.82–2.88 (m; 1H, 2-H), 4.74–4.80 (m; 1H, 1-H), 4.90–4.95 (m; 1H, 6-H), 5.29–5.36 (m; 1H, 3-H), 5.40–5.48 (m; 1H, 4-H), 6.18 (dd; 1H, 10-H), 6.27 (dd; 1H, 9-H); $J_{CH_3,CH}$ = 6.5, $J_{1,2}$ = 2.0, $J_{1,9}$ = 5.0, $J_{2,CH}$ = 5.1, $J_{2,3} \approx 1$, $J_{3,4}$ = 13.5, $J_{3,5x} \approx 1$, $J_{4,5x}$ = 7.0, $J_{4,5n}$ = 2.1, $J_{5x,5n}$ = 20.0, $J_{5x,6}$ = 3.9, $J_{5n,6}$ = 2.5, $J_{6,10}$ = 4.5, $J_{9,10}$ = 10.0 Hz. – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.20 (q; CH_3), 20.49 (q; CH_3), 31.99 (d; CH), 35.26 (t; C-5), 51.60 (d; C-2), 76.15 (d; C-6), 79.53 (d; C-1), 121.87 (d), 127.41 (d), 128.38 (d), 129.42 (d). – MS (70 eV): *m/e* = 180 (4%, M^+), 137 (8, M – C_3H_7), 81 (100, C_5H_5O).

$C_{11}H_{16}O_2$ (180.2) Calcd. C 73.30 H 8.95 Found C 72.77 H 9.20

The *endoperoxides* **7g,h** eluted as third fraction (R_F = 0.46). Roto-evaporation of the solvent at 0°C at 15 Torr afforded 120 mg (6%) of a colourless solid. Fractional recrystallization from CCl_4 yielded 30 mg (2%) of the *syn*-endoperoxide **7g** as colourless needles, m.p. 65–67°C. The *anti*-endoperoxide **7h** could only be isolated as 1:1 mixture with **7g**.

syn-Endoperoxide **7g**: IR (CCl_4): 3060, 2960, 2860, 1470, 1430, 1415, 1050, 1010, 915 cm^{-1}. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.66 (d; 3H, CH_3), 0.79 (d; 3H, CH_3), 1.45 (ddd; 1H, 4-H_s), 1.69 (dq; 1H, C*H*(CH_3)$_2$), 2.06 (mc; 1H, 4-H_a), 2.16 (mc; 1H, 3-H), 3.06 (mc; 2H,

5-H), 4.65 (mc; 1H, 6-H), 4.74 (mc; 1H, 1-H), 6.63 (ddd; 1H, 10-H), 6.82 (ddd; 1H, 9-H); $J_{1,2}$ = 6.5, $J_{1,6}$ = 1.8, $J_{1,9}$ = 6.9, $J_{1,10}$ = 1.8, $J_{2,3}$ = 7.2, $J_{2,4a}$ = 2.0, $J_{3,4s}$ = 8.6, $J_{3,4a}$ = 10.1, $J_{3,5}$ = 2.1, $J_{4s,4a}$ = 11.8, $J_{4s,5}$ = 6.1, $J_{4a,5}$ = 7.5, $J_{5,6}$ = 6.5, $J_{6,9}$ = 1.7, $J_{6,10}$ = 5.0, $J_{9,10}$ = 8.1, $J_{CH_3,CH}$ = 6.5, $J_{CH,3}$ = 11.0. – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 19.80 (q; CH_3), 21.24 (q; CH_3), 27.45 (t; C-4), 28.51 (d), 29.03 (d), 35.95 (d), 42.34 (d), 72.19 (d), 73.40 (d), 131.30 (d), 132.83 (d). – MS (70 eV): *m/e* = 180 (0.4%, M^+), 148 (5, M – O_2), 137 (3, M – C_3H_7), 78 (100, C_6H_6).

$C_{11}H_{16}O_2$ (180.2) Calcd. C 73.30 H 8.95 Found C 73.02 H 9.07

anti-Endoperoxide **7h** (the values were obtained by comparing the spectrum of the pure endoperoxide **7g** with that of the mixture of **7g** and **7h**): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.74 (d; 3H, CH_3), 0.82 (d; 3H, CH_3), 1.37 (mc; 1H, 3-H), 1.57–1.66 (m; 2H, C*H*(CH_3)$_2$, 4-H_s), 1.76 (ddd; 1H, 4-H_a), 2.70 (mc; 1H, 2-H), 2.85 (mc; 1H, 5-H), 4.61–4.70 (m; 2H, 1-H, 6-H), 6.74–6.82 (m; 2H, 9-H, 10-H); $J_{1,2}$ = 5.5, $J_{2,3}$ = 4.9, $J_{2,5}$ = 8.0, $J_{3,4s}$ = 10.1, $J_{3,4a}$ = 5.0, $J_{4s,4a}$ = 12.5, $J_{4a,5}$ = 8.9, $J_{4s,5}$ = 5.1 Hz. – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 19.98 (q; CH_3), 19.34 (q; CH_3), 25.61 (t; C-4), 28.28 (d), 32.02 (d), 36.86 (d), 42.44 (d), 73.40 (d), 73.52 (d), 131.48 (d), 132.02 (d).

General Procedure for the Reaction of the Trienes **3**–**7** *with PTAD*

A ca. 0.8 M solution of the triene (4.0–16 mmol) and of 4-phenyl-4*H*-1,2,4-triazole-3,5-dione (5.0–20 mmol) in dichloromethane (5–20 ml) was stirred for 24 h at 20°C in the dark. After filtration of the suspension over Celite, the solvent was roto-evaporated and the yellow oil was chromatographed on silica gel (100:1 adsorbent-substrate ratio) eluting with CH_2Cl_2/CH_3CO_2Et (10:1). Fractions with equal R_F-values were combined and the solvent was roto-evaporated at 20°C and 15 Torr.

4-Azido-N-phenyl-7,8-diazabicyclo[4.2.2]deca-2,9-diene-7,8-dicarboximide (**3i**) *and syn- and anti-3-Azido-N-phenyl-7,8-diazatricyclo[4.2.2.0^{2,5}]dec-9-ene-7,8-dicarboximide* (**3m, n**): Reaction of 3.03 g (20.2 mmol) of **3** with 3.90 g (22.3 mmol) of PTAD afforded after chromatography two fractions, which were identified as the urazoles **3i** and **3m, n**.

Urazoles **3m, n**: The first fraction (R_F = 0.67) afforded 2.70 g (47%) of a 1:3 mixture of the urazoles **3m, n** as colourless needles, m.p. 155°C (dec.) from ethanol. – IR (KBr): 3050, 2980, 2905, 2100, 1775, 1715, 1500, 1460, 1420, 1260, 1140, 770, 640 cm^{-1}. – MS (70 eV): *m/e* = 322 (6%, M^+), 294 (19%, M – N_2), 280 (5, M – N_3), 227 (91, M – $C_4H_5N_3$), 119 (15, PhNCO), 91 (78, PhN), 80 (100, C_5H_6N).

$C_{16}H_{14}N_6O_2$ (322.3) Calcd. C 59.67 H 4.38 N 26.07
Found C 59.57 H 4.29 N 25.90

^{1}H-NMR ($CDCl_3$, 400 MHz): **3m**: δ = 1.82 (mc; 1H, 4-H_s), 2.50 (mc; 1H, 4-H_a), 3.00 (mc; 1H, 5-H), 3.22–3.30 (m; 1H, 2-H), 4.25 (mc; 1H, 3-H), 4.92 (mc; 1H, 6-H), 5.02 (mc; 1H, 1-H), 6.46 (mc; 1H, 10-H), 6.69 (mc; 1H, 9-H), 7.2–7.3 (m; 5H, phenyl). – **3n**: δ = 1.96 (mc; 1H, 4-H_s), 2.19 (mc; 1H, 4-H_a), 3.12 (mc; 1H, 5-H), 3.18 (m; 1H, 2-H), 3.44 (mc; 1H, 3-H), 4.94 (ddd; 1H, 6-H), 5.04 (ddd; 1H, 1-H), 6.55 (mc; 1H, 9-H), 6.63 (mc; 1H, 10-H), 7.38–7.58 (m; 5H, phenyl); $J_{1,2}$ = 4.6, $J_{1,9}$ = 5.2, $J_{1,10}$ = 1.9, $J_{2,3}$ = 3.8, $J_{2,4s}$ = 1.8, $J_{2,5}$ = 9.0, $J_{2,4s}$ = 8.5, $J_{3,4a}$ = 5.1, $J_{4s,4a}$ = 14.9, $J_{4s,5}$ = 5.1, $J_{4a,5}$ = 9.8, $J_{5,6}$ = 4.4, $J_{6,9}$ = 1.9, $J_{6,10}$ = 5.2, $J_{9,10}$ = 7.9 Hz.

^{13}C NMR ($CDCl_3$, 100 MHz): **3m**: δ = 27.79 (t; C-4), 30.48 (d; C-5), 41.50 (d; C-2), 51.84 (d), 52.92 (d), 54.29 (d), 154.5 (s; C=O). – **3n**: δ = 28.96 (t; C-4), 29.33 (d; C-5), 40.58 (d; C-2), 51.05 (d), 52.65 (d), 53.13 (d), 151.5 (s; C=O). – **3m, n** (these resonances could not be assigned to the individual urazoles because of severe overlapping): δ = 125.61 (d), 128.74

(d), 128.78 (d), 129.64 (d), 130.12 (d), 131.31 (d), 131.41 (s; aromatic C), 131.49 (s; aromatic C).

Urazole **3i**: The second fraction afforded 157 mg (2%) of the urazole **3i** as colourless needles, m.p. 158–160°C (from ethanol). – IR (KBr): 3060, 2960, 2100, 1775, 1710, 1500, 1400, 1245, 1030, 760 cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.45 (ddd; 1H, 5-H_x), 2.60 (ddd; 1H, 5-H_n), 4.50 (mc; 1H, 4-H), 5.03 (ddd; 1H, 6-H), 5.22 (dd; 1H, 1-H), 5.83 (ddd; 1H, 2-H), 5.94 (dd; 1H, 3-H), 6.37 (dd; 1H, 10-H), 6.44 (dd; 1H, 9-H), 7.32–7.58 (m; 5-H, phenyl); $J_{1,2}$ = 7.0, $J_{1,9}$ = 6.9, $J_{2,3}$ = 12.2, $J_{2,4}$ = 2.6, $J_{3,4}$ = 3.6, $J_{4,5x}$ = 4.7, $J_{4,5n}$ = 11.9, $J_{5x,5n}$ = 14.3, $J_{5x,6}$ = 4.9, $J_{5n,6}$ = 1.7, $J_{6,10}$ = 6.0, $J_{9,10}$ = 9.6 Hz. – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 43.60 (t; C-5), 49.24 (d), 50.08 (d), 56.72 (d; C-4), 122.76 (d), 126.20 (d), 126.40 (d), 127.52 (d), 128.36 (d), 129.52 (d), 131.64 (s, aromatic C), 137.16 (d), 148.81 (s; C=O), 149.39 (s; C=O). – MS (70 eV): *m/e* = 322 (28%, M^+), 294 (21, M – N_2), 119 (100, PhNCO), 91 (98, PhN).

$C_{16}H_{14}N_6O_2$ (322.3) Calcd. C 59.62 H 4.38 N 26.07
Found C 60.04 H 4.42 N 25.67

4-Acetoxy-N-phenyl-7,8-diazabicyclo[4.2.2]deca-2,9-diene-7,8-dicarboximide (**4i**) *and syn- and anti-3-Acetoxy-N-phenyl-7,8-diazatricyclo[4.2.2.0^{2,5}]dec-9-ene-7,8-dicarboximide* (**4m,n**): Reaction of 700 mg (4.27 mmol) of **4** with 790 mg (4.51 mmol) of PTAD gave after chromatography two fractions, which were identified as the urazoles **4i** and **4m,n**.

Urazoles **4m,n**: The first fraction (R_F = 0.75) yielded 726 mg (50%) of **4m,n** as colourless solid, m.p. 150–170°C. Fractional recrystallization from ethanol gave 204 mg (14%) of **4m** (m.p. 165–167°C) and 435 mg (30%) of **4n** (m.p. 176–178°C) as colourless needles.

Urazole **4m**: IR (KBr): 3060, 3020, 2980, 2940, 1780, 1740, 1720, 1650, 1600, 1500, 1420, 1240, 1145, 750 cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.90 (mc; 1H, 4-H_s), 2.04 (s; 3H, CH_3), 2.60 (mc; 1H, 4-H_a), 2.97 (ddd; 1H, 5-H), 3.42 (mc; 1H, 2-H), 5.00 (ddd; 1H, 6-H), 5.03 (ddd; 1H, 1-H), 5.09 (ddd; 1H, 3-H), 6.49 (ddd; 1H, 10-H), 6.66 (ddd; 1H, 9-H), 7.23–7.54 (m; 5H, phenyl); $J_{1,2}$ = 4.3, $J_{1,6} \approx 1$, $J_{1,9}$ = 5.5, $J_{1,10}$ = 1.7, $J_{2,3}$ = 8.1, $J_{2,4s} \approx 1$, $J_{2,4a}$ = 1.5, $J_{2,5}$ = 7.9, $J_{3,4s}$ = 6.0, $J_{3,4a}$ = 7.7, $J_{4s,4a}$ = 14.3, $J_{4s,5}$ = 5.5, $J_{4a,5}$ = 7.7, $J_{5,6}$ = 4.5, $J_{6,9}$ = 1.7, $J_{6,10}$ = 5.7, $J_{9,10}$ = 7.4 Hz. – ^{13}C NMR ($CDCl_3$, MHz): δ = 20.69 (q; CH_3), 28.70 (d; C-5), 30.68 (t; C-4), 40.95 (d; C-2), 50.79 (d; C-6), 53.22 (d; C-1), 66.25 (d; C-3), 125.51 (d), 128.15 (d), 128.21 (d), 129.06 (d), 131.47 (d), 131.80 (s), 156.3 (s; C=O), 156.54 (s; C=O), 169.82 (s; $OCOCH_3$). – MS (70 eV): *m/e* = 339 (12%, M^+), 279 (4, M – CH_3CO_2H), 177 (73, $C_9H_9N_2O_2$), 119 (24, PhNCO), 91 (17, PhN), 43 (100, CH_3CO).

$C_{18}H_{17}N_3O_4$ (339.4) Calcd. C 63.71 H 5.05 N 12.38
Found C 63.44 H 5.16 N 11.92

Urazole **4n**: IR (KBr): 3070, 2980, 2930, 1780, 1740, 1710, 1600, 1505, 1420, 1245, 1140, 1075, 770 cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.07 (s; 3H, CH_3), 2.02–2.13 (m; 1H, 4-H_s), 2.29 (ddd; 1H, 4-H_a), 3.04–3.15 (m; 2H, 2-H, 5-H), 4.45 (ddd; 1H, 3-H), 5.02 (ddd; 1H, 6-H), 5.20 (ddd; 1H, 1-H), 6.68 (mc; 2H, 9-H, 10-H), 7.32–7.47 (m; 5H, phenyl); $J_{1,2}$ = 4.5, $J_{1,9}$ = 4.8, $J_{1,10}$ = 2.5, $J_{2,3}$ = 4.0, $J_{2,4a}$ = 1.5, $J_{2,5}$ = 8.0, $J_{3,4s}$ = 8.5, $J_{3,4a}$ = 5.0, $J_{4s,4a}$ = 13.5, $J_{4s,5}$ = 5.0, $J_{4,5}$ = 10.0, $J_{5,6}$ = 4.0, $J_{6,10}$ = 5.0 Hz. – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.79 (q; CH_3), 28.25 (t; C-4), 30.85 (d; C-5), 42.77 (d; C-2), 51.74 (d; C-6), 53.12 (d; C-1), 68.68 (d; C-3), 125.49 (d), 128.18 (d), 129.05 (d), 130.65 (d), 130.77 (d), 131.52 (s; aromatic C), 156.21 (s; C=O), 170.20 (s; OCO). – MS (70 eV): *m/e* = 339 (14%, M^+), 279 (3, M – CH_3CO_2H), 177 (60, $C_9H_9N_2O_2$), 119 (20, PhNCO), 91 (15, PhN), 43 (100, CH_3CO).

$C_{18}H_{17}N_3O_4$ (339.4) Calcd. C 63.71 H 5.05 N 12.38
Found C 64.00 H 4.97 N 11.90

Urazole **4i**: The second fraction (R_F = 0.41) gave 185 mg (13%) of **4i** as colourless plates, m.p. 193–195°C from ethanol. – IR (KBr): 3060, 2950, 1765, 1735, 1705, 1650, 1600, 1500, 1435, 1370, 1250, 1230, 1035, 735 cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.08 (s; 3H, CH_3), 2.46 (ddd; 1H, 5-H_x), 2.57 (ddd; 1H, 5-H_n), 4.98 (mc; 1H, 6-H), 5.22 (mc; 1H, 1-H), 5.76 (mc; 1H, 4-H), 5.77 (ddd; 1H, 2-H), 5.88 (dd; 1H, 3-H), 6.43 (mc; 2H, 9-H, 10-H), 7.32–7.57 (m; 5H, phenyl); $J_{1,2}$ = 7.0, $J_{1,6}$ = 3.0, $J_{1,9}$ = 5.0, $J_{2,3}$ = 12.7, $J_{2,4}$ = 2.5, $J_{3,4}$ = 3.1, $J_{4,5x}$ = 5.0, $J_{4,5n}$ = 12.1, $J_{5x,5n}$ = 14.5, $J_{5n,6}$ = 1.5, $J_{5x,6}$ = 5.1 Hz. – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.08 (q; CH_3), 42.71 (t; C-5), 48.99 (d; C-6), 49.89 (d; C-1), 68.75 (d; C-4), 121.11 (d), 125.48 (d), 126.03 (d), 127.21 (d), 128.00 (d), 129.09 (d), 132 (s; aromatic C), 138.13 (d), 148.80 (s; NCO), 149.66 (s; NCO), 170.20 (s; OCO). – MS (70 eV): *m/e* = 339 (33%, M^+), 279 (7, M – CH_3CO_2H), 177 (16, $C_9H_9N_2O_2$), 119 (34, PhNCO), 91 (30, PhN), 43 (100, $COCH_3$).

$C_{18}H_{17}N_3O_4$ (339.4)	Calcd.	C 63.71	H 5.05 N 12.38
	Found	C 63.59	H 5.13 N 11.86

X-Ray Analysis of the Urazole **4i***)

A clear, colourless crystal was optically centered on a Syntex four-circle diffractometer. The intensities of all reflections were measured according to the ω-technique (Mo-K_α, graphite monochromator) using a scan-range of 1° and a scan-speed between 0.5 and 24.0 degrees min^{-1} as a function of the intensities of the reflections. In the range between 3.0° ≦ 2Θ ≦ 55.0° all reflections *hkl* with $F > 3\sigma(F)$ were applied for the structure determination. For the evaluation the SHELXTL-System on an Eclipse S/250 at the Max-Planck-Institut für Festkörperforschung was employed. The structure was solved by the direct phase determination. The parameters of the complete structure could be refined by anisotropic least squares cycles to the given *R*-value. The positions of the hydrogen atoms were calculated geometrically and considered isotropically in all refinements. Details of the measurements and the crystallographic results, positional and thermal parameters of the atoms of the urazole **4i** and bond lengths and angles are given in Tables 6 and 7, respectively. A perspective drawing of the urazole **4i** is shown in Figure 1 (see Page 3361).

Empirical formula = $C_{18}H_{17}N_3O_4$ (339.4); crystal size = 0.31 × 0.79 × 0.19 mm; number of measured intensities = 3233; number of observed reflections = 2967; number of structure factors of the direct phase determinations = 200; R_{aniso} = 0.046; space group = $P\bar{1}(2)$; cell parameters: *a* = 826.2 (8), *b* = 1330.3 (19), *c* = 812.3 (6) pm, α = 101.03 (9)°, β = 97.67 (7)°, γ = 104.16 (9)°; *Z* = 2; d_r = 1.351 g·cm^{-3}.

3,3-Diethoxy-N-phenyl-7,8-diazatricyclo[4.2.2.0^{2,5}]dec-9-ene-7,8-dicarboximide (**5m**): The reaction of 2.54 g (13.1 mmol) of **5** with 2.50 g (14.3 mmol) of PTAD afforded 1.93 g (41%) of **5m** as colourless needles, m.p. 179–180°C (from ethanol). – IR (KBr): 3080, 2990, 2900, 1775, 1715, 1610, 1510, 1420, 1140, 960, 770 cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.12 (t; 3H, OCH_2CH_3), 1.20 (t; 3H, OCH_2CH_3), 1.86 (mc; 1H, 4-H_s), 2.17 (mc; 1H, 4-H_a), 2.85–2.93 (m; 1H, 5-H), 3.06–3.11 (mc; 1H, 2-H), 3.22–3.34 (m; 2H, OCH_2CH_3), 3.42 (mc; 2H, OCH_2CH_3), 4.97 (mc; 1H, 6-H), 5.07 (ddd; 1H, 1-H), 6.33 (mc; 1H, 10-H), 6.56 (ddd; 1H, 9-H), 7.30–7.44 (m; 5H, phenyl); $J_{1,2}$ = 4.3, $J_{1,5}$ = 5.5, $J_{1,10}$ = 1.5, $J_{2,4s}$ = 1, $J_{2,4a}$ = 2.1, $J_{2,5}$ = 8.8, $J_{4s,4a}$ = 13.1, $J_{4s,5}$ = 6.3, $J_{4a,5}$ = 8.8, $J_{5,6}$ = 4.5, $J_{6,9}$ = 1.5, $J_{6,10}$ = 5.5, $J_{9,10}$ = 8.2 Hz. – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 15.17 (q; CH_3), 15.31 (q; CH_3), 25.72 (d; C-5), 34.32 (t; C-4), 45.58 (d; C-2), 51.08 (d; C-6), 53.43 (d; C-1), 56.12 (t; OCH_2), 56.78 (t; OCH_2),

*) Further details of the structure determination are deposited at the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen (West Germany). These data are available with quotation of the registry number CSD 51079, the authors, and the reference to this publication.

Table 6. Positional and thermal parameters[a] (Å^2) of the atoms of the urazole **4i**

Atom	x	y	z	U_{11}	U_{22}	U_{22}	U_{23}	U_{13}	U_{12}
C(1)	8075(2)	6789(2)	2873(2)	31(1)	58(1)	45(1)	19(1)	4(1)	12(1)
C(2)	8232(3)	7967(2)	3382(3)	48(1)	57(1)	45(1)	11(1)	-1(1)	8(1)
C(3)	7848(3)	8597(2)	2392(3)	60(1)	49(1)	51(1)	10(1)	5(1)	12(1)
C(4)	7374(3)	8381(2)	465(3)	57(1)	47(1)	52(1)	21(1)	14(1)	21(1)
C(5)	5699(3)	7553(2)	-422(2)	49(1)	59(1)	37(1)	18(1)	10(1)	22(1)
C(6)	5561(2)	6433(2)	-123(2)	40(1)	53(1)	31(1)	11(1)	6(1)	13(1)
N(7)	5139(2)	6379(1)	1572(2)	34(1)	60(1)	34(1)	17(1)	6(1)	16(1)
N(8)	6293(2)	6184(1)	2845(2)	36(1)	56(1)	36(1)	18(1)	6(1)	15(1)
C(9)	8422(2)	6381(2)	1117(3)	40(1)	60(1)	54(1)	24(1)	17(1)	21(1)
C(10)	7220(3)	6167(2)	-243(2)	48(1)	48(1)	45(1)	15(1)	18(1)	18(1)
C(11)	5632(2)	6337(2)	4352(2)	41(1)	51(1)	38(1)	16(1)	9(1)	17(1)
O(11)	6324(2)	6300(1)	5742(2)	53(1)	81(1)	39(1)	25(1)	8(1)	29(1)
N(12)	4065(2)	6501(1)	3898(2)	39(1)	63(1)	38(1)	20(1)	12(1)	21(1)
C(13)	3770(2)	6563(2)	2174(2)	37(1)	57(1)	38(1)	16(1)	8(1)	14(1)
O(13)	2524(2)	6722(1)	1409(2)	40(1)	92(1)	49(1)	27(1)	8(1)	29(1)
C(14)	2974(2)	6724(2)	5080(2)	38(1)	58(1)	37(1)	16(1)	10(1)	19(1)
C(15)	2207(3)	5934(2)	5827(3)	51(1)	56(1)	54(1)	21(1)	18(1)	17(1)
C(16)	1182(3)	6167(2)	6994(3)	55(1)	79(2)	60(1)	28(1)	25(1)	14(1)
C(17)	922(3)	7155(2)	7373(3)	53(1)	90(2)	48(1)	10(1)	19(1)	26(1)
C(18)	1687(3)	7936(2)	6619(3)	71(2)	68(1)	59(1)	11(1)	18(1)	36(1)
C(19)	2736(3)	7725(2)	5467(3)	63(1)	57(1)	57(1)	23(1)	20(1)	24(1)
O(40)	7206(2)	9386(1)	90(2)	77(1)	54(1)	62(1)	27(1)	25(1)	29(1)
C(41)	7823(3)	9652(2)	-1267(3)	80(2)	59(1)	57(1)	26(1)	18(1)	20(1)
O(42)	8604(3)	9163(2)	-2074(3)	144(2)	87(1)	93(1)	47(1)	72(1)	58(1)
C(43)	7383(4)	623(2)	-1619(4)	119(2)	73(2)	86(2)	44(2)	25(2)	38(2)

[a] U_{ij} is defined for $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots U_{12}hka^*b^*)]$; numbers in parentheses represent standard deviations.

Table 7. Bond lengths (pm) and angles (deg) for urazole **4i**[a]

C(1) - C(2)	151.1(3)	C(5) - C(6)	153.3(3)	C(11) - O(11)	121.1(2)	C(15) - C(16)	139.4(3)
C(1) - N(8)	149.0(2)	C(6) - N(7)	147.5(2)	C(11) - N(12)	137.9(3)	C(16) - C(17)	136.7(4)
C(1) - C(9)	151.7(3)	C(6) - C(10)	150.7(3)	N(12) - C(13)	141.1(2)	C(17) - C(18)	137.2(4)
C(2) - C(3)	133.1(3)	N(7) - N(8)	141.6(2)	N(12) - C(14)	144.1(3)	C(18) - C(19)	139.3(4)
C(3) - C(4)	151.4(3)	N(7) - C(13)	134.8(3)	C(13) - O(13)	121.5(3)	O(40) - C(41)	134.6(3)
C(4) - C(5)	152.8(2)	N(8) - C(11)	140.5(2)	C(14) - C(15)	137.7(3)	C(41) - O(42)	119.3(4)
C(4) - O(40)	146.1(3)	C(9) - C(10)	131.8(3)	C(14) - C(19)	137.6(3)	C(41) - C(43)	149.2(4)

C(2) - C(1) - N(8)	108.6(2)	C(1) - N(8) - N(7)	111.1(2)	N(12) - C(14) - C(15)	119.3(2)
C(2) - C(1) - C(9)	116.3(2)	C(1) - N(8) - C(11)	118.7(1)	N(12) - C(14) - C(19)	119.7(2)
N(8) - C(1) - C(9)	105.3(1)	N(7) - N(8) - C(11)	106.1(2)	C(15) - C(14) - C(19)	121.0(2)
C(1) - C(2) - C(3)	128.1(2)	C(1) - C(9) - C(10)	119.8(2)	C(14) - C(15) - C(16)	118.7(2)
C(2) - C(3) - C(4)	130.1(2)	C(6) - C(10) - C(9)	121.4(2)	C(15) - C(16) - C(17)	120.8(2)
C(3) - C(4) - C(5)	118.0(2)	N(8) - C(11) - O(11)	125.2(2)	C(16) - C(17) - C(18)	120.2(2)
C(3) - C(4) - O(40)	105.9(2)	N(8) - C(11) - N(12)	106.2(2)	C(17) - C(18) - C(19)	120.0(2)
C(5) - C(4) - O(40)	105.5(2)	O(11) - C(11) - N(12)	128.6(2)	C(14) - C(19) - C(18)	119.4(2)
C(4) - C(5) - C(6)	114.4(2)	C(11) - N(12) - C(13)	111.1(2)	C(4) - O(40) - C(41)	116.8(2)
C(5) - C(6) - N(7)	110.2(2)	C(11) - N(12) - C(14)	124.4(2)	O(40) - C(41) - O(42)	123.8(3)
C(5) - C(6) - C(10)	109.7(2)	C(13) - N(12) - C(14)	124.0(2)	O(40) - C(41) - C(43)	110.9(2)
N(7) - C(6) - C(10)	109.9(2)	N(7) - C(13) - N(12)	104.9(2)	O(42) - C(41) - C(43)	125.3(3)
C(6) - N(7) - N(8)	120.6(2)	N(7) - C(13) - O(13)	128.3(2)		
C(6) - N(7) - C(13)	128.0(2)	N(12) - C(13) - O(13)	126.7(2)		
N(8) - N(7) - C(13)	111.3(1)				

[a] Numbers in parentheses represent standard deviations.

99.12 (s; C-3), 129.59 (d), 125.70 (d), 129.09 (d), 129.64 (d), 131.02 (s; aromatic C), 131.22 (d), 156.42 (s; C=O), 156.57 (s; C=O). – MS (70 eV): *m/e* = 369 (32%, M^+), 340 (6, M – Et), 324 (5, M – OEt), 194 (14, M – PTAD), 119 (50, PhNCO), 91 (100, PhN).

$C_{20}H_{23}N_3O_4$ (369.5) Calcd. C 65.03 H 6.28 N 11.38
Found C 65.21 H 6.47 N 11.21

2-Methyl-N-phenyl-7,8-diazabicyclo[4.2.2]deca-3,9-diene-7,8-dicarboximide (**6l**), *4-Methyl- and 5-Methyl-N-phenyl-7,8-diazabicyclo[4.2.2]deca-2,9-diene-7,8-dicarboximide* (**6i,k**), *and syn- and anti-3-Methyl-N-phenyl-7,8-diazatricyclo[4.2.2.0^{2,5}]dec-9-ene-7,8-dicarboximide* (**6m,n**): The reaction of 500 mg (4.16 mmol) of **6** with 802 mg (4.58 mmol) of PTAD afforded after chromatography three fractions, which were identified as the urazoles **6i,k**, **6l** und **6m,n**.

Urazoles **6m,n**: The first fraction (R_F = 0.75) gave 464 mg of a colourless solid which on recrystallization from ethanol afforded 405 mg (34%) of **6m,n** in relative ratio of 1.8 as colourless needles, m.p. 150–155°C. – IR (KBr): 3080, 3045, 2970, 2930, 2870, 1775, 1715, 1600, 1500, 1420, 1040, 770 cm^{-1}. – MS (70 eV): *m/e* = 295 (45%, M^+), 227 (24, M – C_5H_8), 119 (82, PhNCO), 120 (19, M – PTAD), 78 (100, C_6H_6).

$C_{17}H_{17}N_3O_2$ (295.3) Calcd. C 69.14 H 5.80 N 14.23
Found C 68.96 H 5.73 N 14.02

Urazole **6m**: ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.95 (d; 3H, CH_3), 1.44 (ddd; 1H, 4-H_s), 2.21 (ddd; 1H, 4-H_a), 2.72 (mc; 1H, 3-H), 3.03 (ddd; 1H, 2-H), 3.11 (mc; 1H, 5-H), 4.94 (mc; 1H, 6-H), 4.98 (mc; 1H, 1-H), 6.51 (mc; 1H, 10-H), 6.70 (ddd; 1H, 9-H), 7.30–7.46 (m; 5H, phenyl); $J_{1,2}$ = 4.0, $J_{1,9}$ = 7.8, $J_{1,10}$ = 1.6, $J_{2,3}$ = 10.0, $J_{2,4a}$ = 1.2, $J_{2,5}$ = 8.5, $J_{3,4s}$ = 8.8, $J_{3,4a}$ = 10.0, J_{3,CH_3} = 7.0, $J_{4s,4a}$ = 12.0, $J_{4s,5}$ = 7.5, $J_{4a,5}$ = 8.0, $J_{5,6} \approx 6$, $J_{6,9} \approx 2$, $J_{6,10} \approx$ 8 Hz.

Urazole **6n**: ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.15 (d; 3H, CH_3), 1.64–1.79 (m; 2H, 4-H_s, 4-H_a), 1.90 (mc; 1H, 3-H), 2.62 (ddd; 1H, 2-H), 2.98 (mc; 1H, 5-H), 4.96 (mc; 1H, 6-H), 4.98 (mc; 1H, 1-H), 6.63 (mc; 2H, 9-H, 10-H), 7.30–7.46 (m; 5H, phenyl); $J_{1,2}$ = 4.8, $J_{2,3}$ = 5.0, $J_{2,5}$ = 8.1, $J_{3,4s}$ = 9.5, $J_{3,4a}$ = 6.0, J_{3,CH_3} = 6.8, $J_{4s,4a}$ = 13.0, $J_{4s,5}$ = 5.6, $J_{4a,5}$ = 9.5, $J_{5,6}$ = 4.3 Hz.

^{13}C NMR ($CDCl_3$, 100 MHz): **6m**: δ = 15.43 (q; CH_3), 27.49 (d), 29.02 (t; C-4), 31.29 (d), 39.05 (d), 52.04 (d), 53.68 (d). – **6n**: δ = 21.49 (q; CH_3), 27.96 (t; C-4), 28.22 (d), 30.22 (d), 41.57 (d), 52.89 (d), 53.37 (d). – **6m,n** (the olefinic and aromatic C-atoms could not be assigned to the individual urazoles because of severe overlapping): δ = 125.42 (d), 127.73 (d), 127.99 (d), 128.93 (d), 129.99 (d), 130.32 (d), 131.41 (d), 131.50 (d), 156.01 (s; C=O), 156.41 (s; C=O).

Urazoles **6i,k**: The urazoles **6i,k** were eluted as second fraction (R_F = 0.48). Recrystallization from ethanol gave 150 mg (11%) of **6i,k** in a relative ratio of 1.2 as colourless needles, m.p. 158–173°C. – IR (KBr): 3060, 3040, 3000, 2950, 2920, 1750, 1700, 1490, 1420, 1120 cm^{-1}. – MS (70 eV): *m/e* = 295 (92%, M^+), 119 (93, PhNCO), 91 (100, M – Ph).

$C_{17}H_{17}N_3O_2$ (295.3) Calcd. C 69.14 H 5.80 N 14.23 Found C 68.94 H 5.41 N 13.88

Urazole **6i**: ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.10 (d; 3H, CH_3), 2.07 (ddd; 1H, 5-H_x), 2.30 (ddd; 1H, 5-H_n), 2.67–2.79 (m; 1H, 4-H), 4.95 (ddd; 1H, 6-H), 5.16 (dd; 1H, 1-H), 5.70 (ddd; 1H, 2-H), 5.75 (dd; 1H, 3-H), 6.28 (dd; 1H, 10-H), 6.44 (dd; 1H, 9-H), 7.30–7.55 (m; 5H, phenyl); $J_{1,2}$ = 7.0, $J_{1,9}$ = 7.0, $J_{2,3}$ = 12.0, $J_{2,4}$ = 2.1, $J_{3,4}$ = 4.1, J_{4,CH_3} = 7.0, $J_{4,5x}$ = 4.9, $J_{4,5n}$ = 12.0, $J_{5x,5n}$ = 14.8, $J_{5x,6}$ = 4.5, $J_{5n,6}$ = 1.5, $J_{6,10}$ = 6.1, $J_{9,10}$ = 9.9 Hz.

Urazole **6k**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.07 (d; 3H, CH_3), 2.14 (mc; 1H, 4-H_x), 2.17 (mc; 1H, 4-H_n), 2.67–2.79 (m; 1H, 5-H), 4.75 (dd; 1H, 6-H), 5.16 (dd; 1H, 1-H), 5.77 (ddd; 1H, 2-H), 6.00 (ddd; 1H, 3-H), 6.30 (dd; 1H, 10-H), 6.48 (dd; 1H, 9-H), 7.30–7.55 (m; 5H, phenyl); $J_{1,2}$ = 7.2, $J_{1,9}$ = 7.0, $J_{2,3}$ = 11.5, $J_{2,4x}$ = 2.2, $J_{2,4n}$ = 2.5, $J_{3,4x}$ = 9.1, $J_{3,4n}$ = 5.0, $J_{4x,4n}$ = 11.6, $J_{4x,5}$ = 2.3, $J_{4n,5}$ = 11.6, J_{5,CH_3} = 7.0, $J_{5,6}$ = 2.0, $J_{6,10}$ = 6.1, $J_{9,10}$ = 9.9 Hz.

^{13}C NMR ($CDCl_3$, 100 MHz) of **6i,k** (the resonances could not be assigned to the individual urazoles): δ = 18.62 (s; CH_3), 22.62 (s; CH_3), 27.64 (d), 31.26 (t), 44.31 (d), 46.26 (t), 50.46 (d; two C-atoms), 51.36 (d), 56.51 (d), 121.51 (d), 124.09 (d), 125.27 (d), 125.36 (d), 125.42 (d), 125.96 (d), 126.87 (d), 127.63 (d), 127.70 (d), 128.92 (d), 131.86 (s), 132.51 (d), 134.54 (d), 142.69 (d), 148.37 (s; two C=O), 149.43 (s; two C=O).

Urazole **6l**: The third fraction (R_F = 0.46) yielded 85.6 mg (7%) of **6l** as colourless prisms, m.p. 222–224°C from ethanol. – IR (KBr): 3040, 2960, 2910, 2880, 1750, 1690, 1600, 1500, 1450, 1420, 1330, 1255, 850, 765 cm^{-1}. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.50 (d; 3H, CH_3), 2.50–2.59 (m; 1H, 5-H_n), 3.00–3.09 (m; 1H, 5-H_x), 3.20–3.29 (m; 1H, 2-H), 4.83–4.86 (m; 1H, 1-H), 5.17 (mc; 1H, 6-H), 5.25–5.26 (m; 2H, 3-H, 4-H), 6.34 (mc; 2H, 9-H, 10-H), 7.32–7.58 (m; 5H, phenyl); $J_{CH_3,2}$ = 7.5, $J_{1,2}$ = 4.5, $J_{1,9}$ = 3.8, $J_{1,10}$ = 1.8, $J_{2,3}$ = 1.5, $J_{2,5n} \approx$ 2, $J_{4,5x} \approx$ 2, $J_{4,5n} \approx$ 2, $J_{5x,5n}$ = 18.5, $J_{5x,6}$ = 4.4, $J_{5n,6}$ = 2.5, $J_{6,10}$ = 3.5 Hz. – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 19.45 (q; CH_3), 38.10 (t; C-5), 44.52 (d; C-2), 49.65 (d), 54.32 (d), 120.20 (d), 125.75 (d), 125.97 (d; two C-atoms), 128.41 (d), 129.60 (d; two C-atoms), 132.20 (s; aromat C), 138.04 (s; C=O), 138.08 (s; C=O). – MS (70 eV): *m/e* = 295 (13%, M^+), 227 (85, M – C_5H_8), 119 (45, PhNCO), 88 (100, C_6H_8).

$C_{17}H_{17}N_3O_2$ (295.3)	Calcd.	C 69.14	H 5.80 N 14.23
	Found	C 69.13	H 5.94 N 13.68

2-Isopropyl-N-phenyl-7,8-diazabicyclo[4.2.2]deca-3,9-diene-7,8-dicarboximide (**7l**) *and syn- and anti-3-Isopropyl-N-phenyl-7,8-diazatricyclo[4.2.2.0^{2,5}]dec-9-ene-7,8-dicarboximide* (**7m,n**): Reaction of 600 mg (4.05 mmol) of **7** and 780 mg (4.45 mmol) of PTAD gave two fractions after chromatography, which were identified as the urazoles **7l** and **7m,n**.

Urazoles **7m,n**: The first fraction (R_F = 0.78) gave 270 mg of a yellow crystalline solid, which on recrystallizing from ethanol afforded 260 mg (20%) of colourless needles of **7m,n** in a 1:1 ratio, m.p. 155–165°C. – IR (KBr): 3060, 3040, 3000, 2950, 2925, 2885, 1780, 1720, 1500, 1420, 1240, 1140, 770, 680 cm^{-1}. – MS (70 eV): *m/e* = 323 (74%, M^+), 280 (10, M – C_3H_7), 119 (66, PhNCO), 91 (100, NPh), 78 (99, C_6H_6).

$C_{19}H_{21}N_3O_2$ (323.4)	Calcd.	C 70.57	H 6.55 N 12.99
	Found	C 70.78	H 6.41 N 12.70

Urazole **7m**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.68 (d; 3H, CH_3), 0.86 (d; 3H, CH_3), 1.44–1.70 (m; 2H, 4-H_s, C*H*(CH_3)$_2$), 2.06–2.20 (m; 2H, 3-H, 4-H_a), 3.00–3.13 (m; 2H, 2-H, 5-H), 4.91–4.98 (m; 1H, 1-H), 5.10 (mc; 1H, 6-H), 6.47–6.50 (mc; 1H, 10-H), 6.59–6.69 (m; 1H, 9-H), 7.31–7.48 (m; 5-H, phenyl); $J_{1,2}$ = 5.0, $J_{2,3}$ = 8.6, $J_{3,4s}$ = 5.0, $J_{3,4a}$ = 7.4, $J_{4s,4a}$ = 12.9, $J_{4s,5}$ = 6.5, $J_{4a,5}$ = 9.0, $J_{5,6}$ = 4.7 Hz.

Urazole **7n**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.78 (d; 3H, CH_3), 0.86 (d; 3H, CH_3), 1.39 (mc; 1H, 3-H), 1.58–1.71 (m; 2H, 4-H_s, C*H*(CH_3)$_2$), 1.80 (mc; 1H, 4-H_a), 2.71 (mc; 1H, 2-H), 2.86 (mc; 1H, 5-H), 4.91–4.98 (m; 2H, 1-H, 6-H), 6.59–6.69 (m; 2H, 9-H, 10-H), 7.31–7.48 (m; 5H, phenyl); $J_{1,2}$ = 4.8, $J_{2,3}$ = 4.9, $J_{2,5}$ = 8.2, $J_{3,4s}$ = 10.1, $J_{3,4a}$ = 6.5, $J_{4s,4a}$ = 13.0, $J_{4s,5}$ = 4.5, $J_{4a,5}$ = 10.0, $J_{5,6}$ = 4.6 Hz.

^{13}C NMR ($CDCl_3$, 100 MHz) of **6m,n** (the resonances could not be assigned to the individual urazoles): δ = 19.13 (q; CH_3), 19.28 (q; CH_3), 19.83 (q; CH_3), 20.04 (q; CH_3), 24.69

(t; C-4), 26.68 (t; C-4), 29.01 (d), 30.33 (d), 33.02 (d), 33.69 (d), 38.16 (d), 38.65 (d), 41.44 (d), 41.52 (d), 52.20 (d), 53.45 (d), 53.55 (d), 53.71 (d), 125.51 (d), 128.08 (d), 129.00 (d), 129.75 (d), 129.90 (d), 129.96 (s), 130.48 (d), 131.15 (d), 131.54 (s), 156.12 (s; C=O).

Urazole **7l**: Roto-evaporation of the second fraction (R_F = 0.47) and recrystallization from ethanol yielded 187 mg (14%) of **7l** as colourless needles, m.p. 185–187°C. – IR (KBr): 3050, 2950, 2900, 1750, 1690, 1490, 1425, 1330, 840, 800, 770 cm^{-1}. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.05 (d; 3H, CH_3), 1.07 (d; 3H, CH_3), 1.73–1.85 (m; 1H, $CH(CH_3)_2$), 2.49–2.57 (m; 1H, 5-H_n), 2.95 (mc; 1H, 2-H), 3.01–3.10 (m; 1H, 5-H_x), 4.98–5.04 (m; 2H, 1-H, 6-H), 5.38 (br. s; 2H, 3-H, 4-H), 6.25–6.32 (m; 2H, 9-H, 10-H), 7.31–7.57 (m; 5H, phenyl); $J_{CH_3,CH}$ = 6.5, $J_{1,2}$ = 5.0, $J_{2,CH}$ = 7.0, $J_{2,3} \approx 1$, $J_{2,5x} \approx 1$, $J_{2,5n}$ = 3.0, $J_{4,5x} \approx 2$, $J_{4,5n} \approx 2$, $J_{5x,5n}$ = 19.0, $J_{5x,6}$ = 4.2, $J_{5n,6}$ = 2.8 Hz. – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.78 (q; CH_3), 21.29 (q; CH_3), 31.48 (d; $CHCH_3$), 37.64 (t; C-5), 48.77 (d; C-2), 51.95 (d; C-6), 55.36 (d; C-1), 122.29 (d), 125.42 (d), 126.12 (d), 126.84 (d), 127.00 (d), 127.70 (d), 131.97 (s; aromatic C), 147.56 (s; C=O), 147.62 (s; C=O). – MS (70 eV): *m/e* = 323 (5%, M^+), 227 (94, M – C_7H_{12}), 119 (34, PhNCO), 80 (100, C_5H_6N).

$C_{19}H_{21}N_3O_2$ (323.4) Calcd. C 70.57 H 6.55 N 12.99
Found C 70.75 H 6.75 N 12.77

[1] *G. Welt, E. Wolf, P. Fischer,* and *B. Föhlisch,* Chem. Ber. **115**, 3427 (1982).
[2] *W. Adam, M. Balci,* and *B. Pietrzak,* J. Am. Chem. Soc. **101**, 6285 (1979).
[3] *W. Adam* and *H. Rebollo,* Isr. J. Chem. **23**, 399 (1984).
[4] *F. D. Greene,* in Stereochemistry and Reactivity of Systems Containing π-Electrons, *W. H. Watson,* (Ed.), pp. 197–240, Verlag Chemie International, Deerfield Beach, Florida 1983.
[5] *L. A. Paquette, D. R. James,* and *G. H. Birnberg,* J. Am. Chem. Soc. **96**, 7454 (1974).
[6] *W. Adam* and *G. Klug,* Tetrahedron, in press.
[7] *W. Adam* and *I. Erden,* Tetrahedron Lett. **1979**, 2781.
[8] [8a] *A. C. Cope* and *F. A. Hochstein,* J. Am. Chem. Soc. **72**, 2515 (1950). – [8b] *A. C. Cope, L. C. Stevens,* and *F. A. Hochstein,* J. Am. Chem. Soc. **72**, 2510 (1950). – [8c] *A. C. Cope* and *C. G. Overberger,* J. Am. Chem. Soc. **70**, 1433 (1948). – [8d] *T. Kauffmann, C. Kosel,* and *W. Schoeneck,* Chem. Ber. **96**, 999 (1963). – [8e] *T. J. Katz, C. R. Nicholson,* and *C. A. Reilly,* J. Am. Chem. Soc. **88**, 3832 (1966). – [8f] *W. R. Roth,* Liebigs Ann. Chem. **671**, 25 (1964).
[9] [9a] *M. Kröner,* Chem. Ber. **100**, 3162 (1967). – [9b] *R. Huisgen, G. Boche, A. Dahmen,* and *W. Hechtel,* Tetrahedron Lett. **1968**, 5215.
[10] *H. Straub, J. M. Rao,* and *E. Müller,* Liebigs Ann. Chem. **1973**, 1352.
[11] [11a] *W. Reppe, O. Schlichting, K. Klager,* and *T. Toepel,* Liebigs Ann. Chem. **550**, 1 (1948). – [11b] *A. C. Cope* and *B. D. Tiffany,* J. Am. Chem. Soc. **73**, 4158 (1951). – [11c] *A. C. Cope, S. F. Schaeren,* and *E. R. Trumbull,* J. Am. Chem. Soc. **76**, 1096 (1954).
[12] *J. P. Snyder* and *D. G. Farnum,* J. Org. Chem. **31**, 1699 (1966). – [12b] *D. G. Farnum* and *J. P. Snyder,* Tetrahedron Lett. **1965**, 3861.

[288/84]