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[4 + 2]-Cycloaddition of Singlet Oxygen and Phenyltriazolinedione with Bicyclo[6.1.0]nona-2,4,6-triene and Derivatives

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The dienic reactivity of the bicyclononatrienes **1a** ([4.3.0]-isomer) and **1b** ([6.1.0]-isomer) and its oxa-derivative **6** (cyclooctatetraene epoxide) as well as 1,3,5-cyclooctatrienone (**7**), towards singlet oxygen ($^1O_2$) and phenyl-1,2,4-triazoline-3,5-dione (PTAD) as dienophiles has been investigated. Except for **1a**, which affords the endoperoxide **9a** in 60% yield, the remaining substrates **1b**, **6**, and **7** do not react with $^1O_2$. With PTAD **1a**, **1b**, **6**, and **7** afford the urazoles **10a**, **8b**, **12c**, and **11**, respectively. Unusual is the fact that the bicyclo[6.1.0]triene **1b** leads only to the tricyclic urazole **8b**, the first example of this type of [4 + 2]-cycloadduct of **1b**, while the oxa-analog **6** affords only the tetracyclic urazole **12c**. Moreover, **6** reacts with PTAD considerably more sluggishly than **1b**.

[4 + 2]-Cycloaddition von Singulett-Sauerstoff und Phenyltriazolindion an Bicyclo[6.1.0]nona-2,4,6-trien und seine Derivate

Die Dienreaktivität der Bicyclotriene **1a** ([4.3.0]-Isomeres) und **1b** ([6.1.0]-Isomeres), von dessen Oxaderivat **6** (Cyclooctatetraenepoxid) sowie von 1,3,5-Cyclooctatrienon (**7**) gegenüber Singulett-Sauerstoff ($^1O_2$) und Phenyl-1,2,4-triazolin-3,5-dion (PTAD) als Dienophile wurde untersucht. Bicyclononatrien **1a** liefert das Endoperoxid **9a** in 60proz. Ausbeute. Die anderen Substrate **1b**, **6** und **7** reagieren nicht mit $^1O_2$. Mit PTAD dagegen wurden aus **1a**, **1b**, **6** und **7** die Urazole **10a**, **8b**, **12c** und **11** gebildet. Ungewöhnlich ist, daß das Bicyclo[6.1.0]trien **1b** nur zum tricyclischen Urazol **8b** führt, dem ersten Beispiel solcher [4 + 2]-Cycloaddukte von **1b**, während die analoge Oxaverbindung **6** nur tetracyclisches Urazol **12c** gibt. Dabei ist zu bemerken, daß **6** mit PTAD beträchtlich träger reagiert als **1b**.

The three established thermal valence isomers of the C_9H_{10} cyclopolyene, namely bicyclo[4.3.0]nona-2,4,7-triene (**1a**), bicyclo[6.1.0]nona-2,4,6-triene (**1b**) and tricyclo[4.3.0.$0^{7,9}$]-nona-2,4-diene (**1c**), constitute an interesting set of dienic substrates in regard to their reactivity towards dienophiles. Thus, the most likely allowed [4 + 2]-cycloaddition modes are the respective products **2a–c** (Eq. 1). The valence isomer **1b** has been prepared some time ago[1]; its dienic reactivity has been investigated to some extent. For example, it was reported[2a–c] that tetracyanoethylene gave the [2 + 2]-cycloadduct **3** and the [4 + 2]-cycloadduct **3c**, while maleic anhydride afforded a mixture of the products **4a** and **4c** in 33% and 67%, respectively. Clearly, the [4 + 2]-cycloadduct **4a** must be derived from the valence isomer **1a** and the [4 + 2]-cycloadducts **3c** and **4c** from **1c** in order to rationalize these results. Other dienophiles that have been employed include dimethyl acetylenedicarboxylate[2d], chlorosulfonylisocyanate[2e], and

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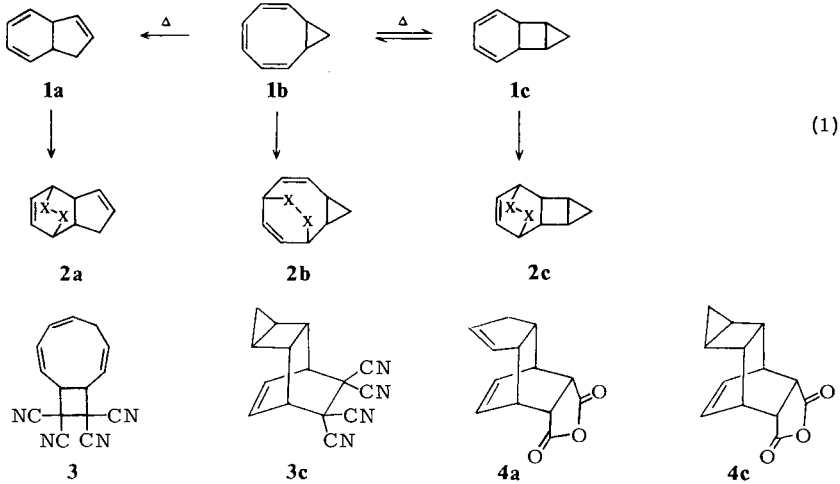
benzyne[2f]. Also the cycloaddition of **1b** with a number of dienes has been investigated, e.g. 2,5-dimethyl-3,4-diphenylcyclopentadienone[2g], 3,6-diphenyl-1,2,4,5-tetrazine[2h], α-pyrone[2i] and 1,3-diphenylbenzoisofuran[2j].



(1)

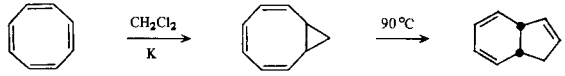
3 3c 4a 4c

It is surprising, however, that no cycloaddition reactions of the bicyclononatriene **1b** with the reactive dienophiles triazolinedione (TAD) and singlet oxygen ($^1O_2$) have been reported. Furthermore, since the dienic reactivity of the related 9-oxabicyclo[6.1.0]nona-2,4,6-triene (**6**), or cyclooctatetraene epoxide, had not been previously examined, for comparison we decided to explore its cycloaddition behavior as well as that of its oxo-derivative (**7**) with the TAD and $^1O_2$ dienophiles.

6 7

Cycloaddition with Bicyclononatrienes 1a, b

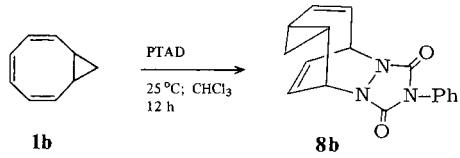
The bicyclo[6.1.0]nona-2,4,6-triene (**1b**) was prepared[1] from cyclooctatetraene (COT) in 42% yield by cyclopropanation with methylene chloride and potassium metal (Eq. 2). On thermolysis[2] at 90°C for 9 h the dihydroindene **1a** was obtained in 80% yield.



(2)

5 1b 1a

Attempted photosensitized oxygenation of **1b** in chloroform at 25°C, using tetraphenylporphyrin as sensitizer and a 150-W sodium street lamp[3] as light source, revealed that the bicyclononatriene isomer **1b** was completely inert towards $^1O_2$. Even after 12 h of irradiation no traces of peroxidic product had been formed. On the other hand, with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) the bicyclononatriene **1b** reacted smoothly at 25°C in chloroform, leading after 12 h to the urazole **8b** in 60% yield (Eq. 3).

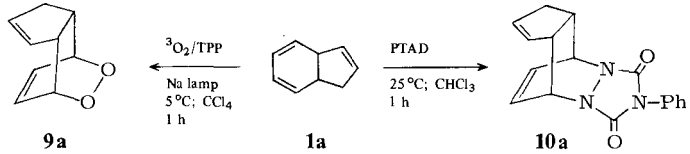


(3)

1b **8b**

The structure assignment of urazole **8b** rests on a satisfactory elemental analysis and spectral data (cf. Experimental Part). Thus, the ^{1}H NMR exhibits the characteristic cyclopropane protons as a complex multiplet at 0.53 – 2.26 ppm, the bridgehead protons as a multiplet at 4.93 – 5.63 ppm, and the olefinic protons as a multiplet at 5.92 – 6.60, besides the phenyl protons at 7.23 – 7.77, in relative intensities 4 : 2 : 4 : 5, respectively. These data are only consistent with the proposed structure **8b**.

Consequently, urazole **8b** is the first [4 + 2]-cycloaddition product derived from the valence isomer **1b** which retains the bicyclo[6.1.0]nona-2,4,6-triene skeleton.



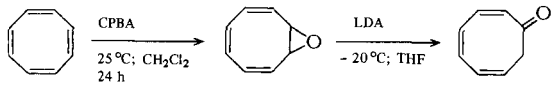
(4)

9a **1a** **10a**

The dihydroindene valence isomer **1a** reacted smoothly with both singlet oxygen and PTAD to give the expected [4 + 2]-cycloadducts **9a** and **10a**, respectively (Eq. 4). Thus, photosensitized singlet oxygenation of **1a** in carbon tetrachloride at 5 °C, using tetraphenylporphyrin (TPP) as sensitizer and a 150-W sodium street lamp as light source[3], gave endoperoxide **9a** in 61% yield. A satisfactory elemental analysis and the spectral data (cf. Experimental Part) confirm the proposed **9a** structure. The urazole **10a** was obtained in 60% yield. Again, a satisfactory elemental analysis and the spectral data support the assigned structure of **10a**. It is surprising that neither $^1O_2$ nor PTAD lead to ene-reaction of the cyclopentene allylic hydrogens. Presumably the activation energies for ene-reaction of the $^1O_2$[4] and PTAD[5] dienophiles are larger than for [4 + 2]-cycloaddition.

Cycloaddition with Oxabicyclononatriene 6 and 1,3,5-Cyclooctatrienone (7)

The cyclooctatetraene epoxide (**6**) was prepared in 30% yield[6] via *m*-chloroperbenzoic acid (CPBA) epoxidation of COT in methylene chloride at 25 °C for 24 h (Eq. 5). On base-catalyzed isomerization with LDA in THF at – 20 °C the epoxide **6** was transformed into trienone **7** in 53% yield.

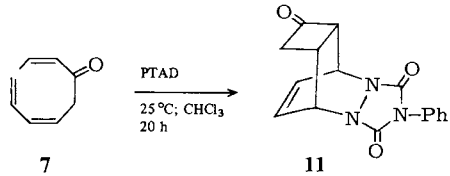


(5)

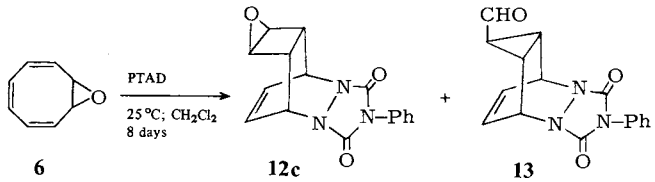
6 **7**

Both the epoxide **6** as well as the trienone **7** were inert towards photosensitized singlet oxygenation under the conditions described for bicyclononatriene **1a** even after prolonged (> 30 h) irradiation. While the trienone **7** reacted readily with PTAD, affording the bicyclic urazole **11** (Eq. 6) at 25 °C in $CHCl_3$ after 20 h in 63% yield (cf. Experimen-

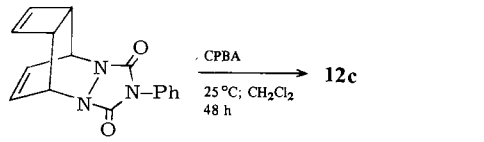
tal Part for details), the epoxide **6** was considerably more sluggish in its dienic reactivity. For example, PTAD at 25 °C, in CH_2Cl_2 gave after 8 days only 20% conversion, affording 6% [4 + 2]-cycloadduct **12c** and 14% of its rearranged urazole **13** (Eq. 7). However, in tetrachloroethane at 80 °C epoxide **6** gave ca. 70% conversion with PTAD, leading to 10% urazole **12c** and 26% of rearranged urazole **13**, along with ca. 30% phenylacetaldehyde. Urazole **12c** was independently synthesized as shown in eq. (8). Since CBPA attack must come from above, the *anti*-stereochemistry of the epoxide ring in **12c** is established.



(6)



(7)



(8)

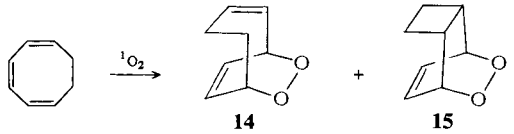
The structure of the rearranged urazole **13** could be easily confirmed by comparison with authentic material obtained by cycloaddition of cycloheptatriene-7-carboxaldehyde with PTAD. Spectral data and physical constants were identical to those reported[7a]. The most likely precursor to this PTAD adduct is cycloheptatriene-7-carboxaldehyde, formed by rearrangement of cyclooctatetraene epoxide[7b]. The possible route via epoxide ring opening and rearrangement with ring contraction of the urazole **12c** is unlikely because **12c** is stable under the conditions of the cycloaddition reaction of **6** with PTAD. Furthermore, the unstable cycloheptatriene-7-carboxaldehyde is also the source of phenylacetaldehyde[7c].

Urazole **12c** was isolated from the **6** + PTAD reaction mixture by first treating it with dimedone (5,5-dimethyldihydroresorcinol) to remove the aldehydic products, followed by silicagel chromatography at 25 °C eluting with methylene chloride and subsequent recrystallization from ethanol. The structure assignment of urazole **12c** rests on a satisfactory elemental analysis and spectral data. For example, the ^1H NMR ($CDCl_3$) shows besides the phenyl proton multiplet at 7.40 ppm, four equally intense multiplets at 2.93, 3.70, 5.10 and 6.55 ppm, respectively, for the cyclobutane, epoxide, bridgehead and olefin protons. These spectral data are consistent with the symmetric structure proposed for **12c**.

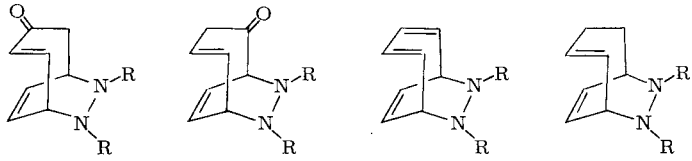
Discussion of the Results

The reactivity of singlet oxygen with the dienic substrates investigated herein is quite disappointing, since only the dihydroindene valence isomer **1a** underwent cycloaddi-

tion. That **1a** reacts readily with $^1O_2$ is not surprising since a planar diene moiety is present; however, the complete lack of dienic reactivity of the bicyclononatriene **1b**, of cyclooctatetraene epoxide (**6**) and trienone **7** with $^1O_2$ is surprising. Dreiding models show that none of the double bonds assume the optimal planar arrangement necessary for [4 + 2]-cycloaddition. Besides these stereochemical reasons, in the case of epoxide **6** the −I-effect of the epoxide ring must additionally deactivate the trienic system towards cycloaddition with the "electrophilic" dienophile singlet oxygen. Such electronic deactivation, but instead of the epoxide ring caused by the carbonyl group, is presumably the prevalent reason why the trienone **7** fails to cycloadd singlet oxygen. For example, we showed previously[8] that 1,3,5-cyclooctatriene affords with singlet oxygen the endoperoxides **14** and **15** (Eq. 9) in ca. 4:1 ratio, respectively. Thus, in analogy, no stereochemical impediment is expected in the attempted cycloaddition of trienone **7** with $^1O_2$.



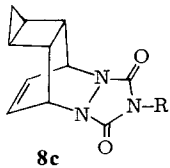
14 **15** (9)



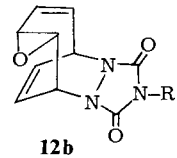
16 **17** **18** **19**

The situation is, however, quite different with PTAD as dienophile, since it is sufficiently reactive to cycloadd with all substrates investigated here. Thus, the trienone **7** gives only the bicyclic adduct **11** with PTAD. It is surprising that the urazoles **16** or **17** are not formed, especially since cyclooctatetraene[9] and cyclooctatriene[8] afford the analogous urazoles **18** and **19**. The supposition that the equilibrium of the trienone **7** lies appreciably on the side of its bicyclic valence isomer so that only the urazole **11** is formed cannot apply because in that case singlet oxygenation should have taken place to yield the bicyclic endoperoxide corresponding to the urazole **11**. It is not obvious at this stage what stereoelectronic factors operate to rationalize these divergent results.

Still more puzzling is the cycloaddition behavior of bicyclononatriene **1b** versus its oxa-derivative **6** with PTAD. Thus, while **1b** reacts with PTAD exclusively through its monocyclic valence isomer to afford urazole **8b** and no **8c**, the oxa-derivative **6** gives only **12c** and no **12b**. It is difficult to rationalize this dichotomy in cycloaddition behavior of these cyclotrienic substrates on the basis of their valence tautomeric equilibria (Eq. 1), since no experimental nor theoretical data have been reported. However, our observation that the oxa-derivative **6** reacts considerably more sluggishly than **1b**, a fact that has been recognized in other diene substrates[10], could imply that the tautomeric equilibrium of **6** is shifted to the more reactive tricyclodiene valence isomer because more drastic reaction conditions must be employed to force cycloaddition of PTAD with **6** than with **1b**. This cannot be realized with **1b** because at elevated temperatures it irreversibly isomerizes to the dihydroindene tautomer **1a** (Eq. 1).



8c



12b

We are grateful to the *Deutsche Forschungsgemeinschaft,* the *Fonds der Chemischen Industrie,* the *National Institutes of Health,* the *National Science Foundation* and the *Petroleum Research Fund* for generous financial support of our research work.

Experimental Part

Boiling points and melting points are uncorrected. Infrared spectra were taken on a Beckman Acculab 4 or on a Perkin-Elmer 157G spectrophotometer and ^1H NMR spectra on a Varian T-60, Hitachi-Perkin-Elmer R-24B or on a 90 MHz Bruker HFX 10 instrument. The elemental analyses of all new substances were performed in house and were within accepted limits, i. e. ±0.3 for C, N and H. Commercial reagents and solvents were purified according to literature procedures to match reported physical and spectral data. Known compounds used in this research were either purchased from standard suppliers or prepared according to the literature procedures and purified to match the reported physical and spectral data.

1. *Bicyclo[4.3.0]nona-2,4,7-triene* (**1a**): Thermolysis[2a] of nonatriene **1b** at 90°C for 9 h afforded the dihydroindene **1a** in 80% yield; b.p. 46–48°C/16 Torr (lit.[2a] 47–49°C/18 Torr). – IR (CCl_4): 3020, 2890, 2830 cm^{-1}. – ^1H NMR (CCl_4): δ = 1.97–3.78 (m, 4H), 5.08–6.05 (m, 6H).

2. *Bicyclo[6.1.0]nona-2,4,6-triene* (**1b**) was prepared in 42% yield starting from cyclooctatetraene according to the procedure of *Katz*[1]; b.p. 56°C/16 Torr (lit.[1] 51°C/7 Torr). – IR (CCl_4): 3070, 2995, 1125, 1025, 845 cm^{-1}. – ^1H NMR (CCl_4): δ = −0.17–0.20 (m, 1H), 0.79–1.60 (m, 3H), 5.92 (m, 6H).

3. *9-Oxabicyclo[6.1.0]nona-2,4,6-triene* (**6**): Reaction of cyclooctatetraene with *m*-CPBA in CH_2Cl_2 at 25°C for 24 h afforded the epoxide **6** in 30% yield; b.p. 71–73°C/15 Torr (lit.[6] 72°C/12 Torr). – IR (CCl_4): 3010, 2980, 1070, 1010, 900, 830 cm^{-1}. – ^1H NMR (CCl_4): δ = 3.30 (s, 2H), 5.62–6.10 (m, 6H).

4. *2,4,6-Cyclooctatrien-1-one* (**7**) was prepared in 53% yield according to the procedure of *Cope*[6]; b.p. 50°C/1.5 Torr (lit.[6] 75–105°C/13 Torr). – IR (CCl_4): 3020, 2920, 1665 cm^{-1}. – ^1H NMR (CCl_4): δ = 3.00 (d, 2H, *J* = 8 Hz), 5.56–6.90 (m, 6H).

5. *N-Phenyl-8,9-diazatricyclo[5.2.2.0^{2,4}]undeca-5,10-diene-8,9-dicarboximide* (Urazole **8b**): A solution of 0.20 g (1.69 mmol) of bicyclononatriene **1b** and 0.30 g (1.71 mmol) of PTAD in 5 ml of $CHCl_3$ was stirred at 25°C for 12 h. After roto-evaporation of the solvent (25°C/15 Torr) the residue was submitted to silicagel column chromatography at 25°C eluting with CH_2Cl_2. Subsequent recrystallization from ethanol gave 0.30 g of pure urazole **8b** (60% yield), m.p. 205–206°C. – IR ($CHCl_3$): 2060, 3000, 1760, 1700, 1420 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 0.53–2.26 (m, 4H), 4.93–5.63 (m, 2H), 5.92–6.60 (m, 4H), 7.23–7.77 (m, 5H). – ^{13}C NMR ($CDCl_3$): δ = 10.10 (t), 16.71 (d), 27.91 (d), 48.89 (d), 50.62 (d), 125.45 (d), 125.54 (d), 127.75 (d), 129.00 (d), 129.11 (s), 129.45 (d), 130.68 (d), 132.55 (d), 148.29 (s), 148.82 (s).

$C_{17}H_{15}N_3O_2$ (293.3) Calc. C 69.61 H 5.15 N 14.33 Found C 69.51 H 5.42 N 14.15

6. *8,9-Dioxatricyclo[5.2.2.0^{2,6}]undeca-3,10-diene* (Endoperoxide **9a**): A solution of 0.20 g (1.69 mmol) of bicyclononatriene **1a** and 2 mg of tetraphenylporphyrin (TPP) in 8 ml of CCl_4

was irradiated with a General Electric 150-W sodium street lamp at 5 °C, while bubbling oxygen gas continuously through it. The reaction was complete after 1 h, as monitored by ^{1}H NMR. Column chromatography of the crude endoperoxide **9a** on silicagel at −5 °C eluting with a 3:1 mixture of methylene chloride and pentane and subsequent recrystallization from pentane afforded the pure product, 0.16 g (61% yield), m.p. 63 – 64 °C. – IR (CCl_4): 3040, 2940, 2900, 2840, 1440, 1370, 945, 930, 715 cm^{-1}. – ^{1}H NMR (CCl_4): δ = 1.53 – 3.57 (m, 4H), 4.55 (m, 2H), 5.53 (m, 2H), 6.50 (m, 2H). – ^{13}C NMR ($CDCl_3$): δ = 35.43 (d), 36.12 (t), 47.68 (d), 73.07 (d), 74.08 (d), 129.41 (d), 129.70 (d), 132.71 (d), 132.97 (d).

$C_9H_{10}O_2$ (150.2) Calc. C 71.98 H 6.71 Found C 72.04 H 6.60

7. *N-Phenyl-8,9-diazatricyclo[5.2.2.0^{2,6}]undeca-3,10-diene-8,9-dicarboximide* (Urazole **10a**): A solution of 0.20 g (1.69 mmol) of bicyclononatriene **1a** and 0.30 g (1.71 mmol) of PTAD in 5 ml of $CHCl_3$ was stirred at 25 °C for 1 h. After roto-evaporation of the solvent (25 °C/15 Torr) the residue was submitted to silicagel column chromatography at 25 °C eluting with CH_2Cl_2. Subsequent recrystallization from ethanol gave the pure urazole, 0.30 g (60% yield), m.p. 216 – 217 °C. – IR ($CHCl_3$): 3050, 2900, 1760, 1700, 1410 cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 1.6 – 3.7 (m, 4H), 4.97 (m, 2H), 5.59 (m, 2H), 6.39 (m, 2H), 7.40 (m, 5H). – ^{13}C NMR ($CDCl_3$): δ = 36.25 (t), 36.76 (d), 49.17 (d), 52.72 (d), 53.96 (d), 125.51 (d), 128.09 (d), 128.86 (d), 128.96 (d), 129.04 (d), 131.00 (d), 131.76 (s), 133.82 (d), 155.88 (s), 155.95 (s).

$C_{17}H_{15}N_3O_2$ (293.3) Calc. C 69.61 H 5.15 N 14.33 Found C 69.63 H 5.29 N 14.26

8. *3-Oxo-N-phenyl-7,8-diazatricyclo[4.2.2.0^{2,5}]dec-9-ene-7,8-dicarboximide* (Urazole **11**): A solution of 0.40 g (3.33 mmol) of trienone **7** and 0.59 g (3.37 mmol) of PTAD in 10 ml of $CHCl_3$ was stirred at 25 °C for 20 h. After roto-evaporation of the solvent (25 °C/15 Torr) the residue was submitted to silicagel column chromatography at 25 °C eluting with CH_2Cl_2. Subsequent recrystallization from ethanol gave 0.61 g of pure urazole **11** (63% yield), m.p. 230 – 232 °C. – IR (KBr): 3050, 3000, 1770, 1700, 1500, 1412, 1140, 770 cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 2.43 – 2.93 (m, 1H), 3.00 – 3.40 (m, 2H), 3.90 – 4.17 (m, 1H), 5.07 – 5.40 (m, 2H), 6.54 (m, 2H), 7.47 (m, 5H). – ^{13}C NMR ($CDCl_3$): δ = 22.87 (d), 49.32 (t), 49.92 (d), 52.53 (d), 60.33 (d), 125.51 (d), 128.24 (d), 128.44 (d), 129.18 (d), 130.27 (d), 131.33 (s), 156.01 (s), 156.15 (s), 202.56 (s).

$C_{16}H_{13}N_3O_3$ (295.3) Calc. C 65.08 H 4.44 N 14.22 Found C 64.66 H 4.70 N 14.41

9. *Reaction of Oxabicyclononatriene* **6** *with PTAD*

a) *In methylene chloride at 25 °C:* To a stirred solution of 1.37 g (11.4 mmol) of epoxide **6** in 30 ml of CH_2Cl_2, were added 2.00 g (11.4 mmol) of PTAD in portions and stirred at 25 °C for 8 days. After roto-evaporation of the solvent (25 °C/15 Torr) the residue was submitted to silicagel column chromatography at 25 °C eluting with CH_2Cl_2. As first fraction the starting material, i.e. epoxide **6**, was reisolated, 1.10 g (80% yield). The second fraction consisted of a mixture of urazoles **12c** and **13** in a total yield of 0.67 g (20% yield, ca. 6% and 14%, respectively, by NMR analysis).

The spectral data of rearranged urazole **13** matched perfectly with those of an authentic sample prepared by reaction of cycloheptatriene-7-carboxaldehyde with PTAD[7]. The isolation of urazole **12c** was achieved by treatment of the urazole mixture with dimedone (5,5-dimethyldihydroresorcinol) to remove the aldehydic urazole **13**. Column chromatography on silicagel at 25 °C eluting with CH_2Cl_2 and subsequent recrystallization from ethanol afforded the pure urazole **12c**, m.p. 204 – 205 °C. – IR (KBr): 3070, 2950, 1760, 1710, 1590, 1490, 1400, 1235, 1135, 1060, 770 cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 2.93 (m, 2H), 3.70 (m, 2H), 5.10 (m, 2H), 6.55

(m, 2H), 7.40 (m, 5H). – ^{13}C NMR ($CDCl_3$): δ = 42.08 (d), 50.91 (d), 55.39 (d), 125.53 (d), 156.34 and phenyl resonances.

$C_{16}H_{11}N_3O_3$ (293.3) Calc. C 65.53 H 3.78 N 14.32 Found C 65.61 H 3.96 N 14.15

b) *In tetrachloroethane at 80 °C:* A solution of 0.58 g (4.83 mmol) of epoxide **6** and 0.85 g (4.86 mmol) of PTAD in 25 ml of 1,1,2,2-tetrachloroethane was heated at 80 °C for 2 h. After rotoevaporation of the solvent (25 °C/15 Torr), the residue was submitted to silicagel column chromatography at 25 °C eluting with CH_2Cl_2. Urazoles **12c** and **13** were obtained, 0.14 g and 0.37 g, respectively (10% and 26% yield), besides 0.18 g (31% yield) starting epoxide **6** and 0.19 g (33% yield) phenylacetaldehyde. These compounds were characterized by comparison of their spectral data with authentic samples.

c) *Preparation of N-Phenyl-4-oxa-8,9-diazatetracyclo[5.2.2.$0^{2,6}$.$0^{3,5}$]undeca-10-ene-8,9-dicarboximide* (Urazole **12c**): 200 mg (0.7 mmol) of the cycloadduct of cyclooctatetraene and PTAD[11] were treated with 250 mg (1.4 mmol) of *m*-CPBA in 10 ml of methylene chloride at room temperature with continuous magnetic stirring in the presence of solid $NaHCO_3$. After 48 h the white suspension was poured into a solution of saturated aqueous sodium sulfite, washed with water (3 × 70 ml), and dried over anhydrous Na_2SO_4. After silicagel column chromatography (ca. 10:1 ratio of adsorbant to substrate), eluting with CH_2Cl_2 130 mg (62% yield) of the urazole **12c** was obtained, m.p. 204–205 °C (from ethanol) as colorless plates, which was identical to the sample isolated in the cycloaddition of **6** with PTAD.

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