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Cycloaddition of Singlet Oxygen and 4-Methyl-4*H*-1,2,4-triazole-3,5-dione to 7-Adamantylidene-1,3,5-cycloheptatriene and Derivatives

Waldemar Adam *[a], *Eva-Maria Peters*[b], *Karl Peters*[b], *Héctor Rebollo* *)[a], *Robert J. Rosenthal* **)[a], and *Hans Georg von Schnering*[b]

Institut für Organische Chemie der Universität Würzburg[a], Am Hubland, D-8700 Würzburg (FRG),

Departamento de Quimica, Universidad de Puerto Rico[a], Rio Piedras, Puerto Rico 00931 (USA), and

Max-Planck-Institut für Festkörperforschung[b], Postfach 800655, D-7000 Stuttgart 80 (FRG)

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7-Adamantylidene-1,3,5-cycloheptatriene (**18**) was prepared via thermolysis of the thietane **22**, produced in the cycloaddition of 2-adamantanethione with 8-oxoheptafulvene (**1**). The latter reaction also afforded the thiophene **23**, presumably via [8 + 2]-cycloaddition. Reaction of singlet oxygen ($^1O_2$) with heptafulvene **18** gave the [4 + 2]-tropilidene endoperoxide **24**, while 4-methyl-4*H*-1,2,4-triazole-3,5-dione (MTAD) led to the [8 + 2]-urazole **26**. Singlet oxygenation of thietane **22** produced the [4 + 2]-tropilidene endoperoxide **27**, but with MTAD the strained [4 + 2]-norcaradiene urazole **28** was obtained. The thiophene **23** gave with $^1O_2$ and MTAD the [4 + 2]-norcaradiene products **29** and **30**, respectively. X-ray analysis confirmed the urazole **30** structure.

Cycloaddition von Singulettsauerstoff und 4-Methyl-4*H*-1,2,4-triazol-3,5-dion an 7-Adamantyliden-1,3,5-cycloheptatrien und Derivate

7-Adamantyliden-1,3,5-cycloheptatrien (**18**) wurde mittels Thermolyse des Thietans **22** hergestellt, welches wiederum durch Cycloaddition von 2-Adamantanthion mit 8-Oxoheptafulven (**1**) erhalten wurde. In dieser Reaktion wurde zusätzlich das Thiophen **23** erzeugt, anscheinend durch [8 + 2]-Cycloaddition. Die Addition von Singulettsauerstoff ($^1O_2$) an Heptafulven **18** führte zum [4 + 2]-Tropiliden-endoperoxid **24**, während mit 4-Methyl-4*H*-1,2,4-triazol-3,5-dion (MTAD) das [8 + 2]-Urazol **26** gebildet wurde. Singulettsauerstoff-Addition an Thietan **22** ergab das [4 + 2]-Tropiliden-endoperoxid **27**, aber mit MTAD wurde das gespannte [4 + 2]-Norcaradien-urazol **28** erhalten. Das Thiophen **23** führte mit $^1O_2$ und mit MTAD zu den [4 + 2]-Norcaradienprodukten **29** bzw. **30**, wovon die Struktur von **30** durch Röntgenstrukturanalyse ermittelt wurde.

Four cycloaddition modes are in principle possible with heptafulvenes, namely [2 + 2]-, [4 + 2]-, [6 + 2]-, and [8 + 2]-addition, leading to the five cycloadduct types shown in Eq. (1).

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**) Alexander von Humboldt Fellow (1982 – 83).

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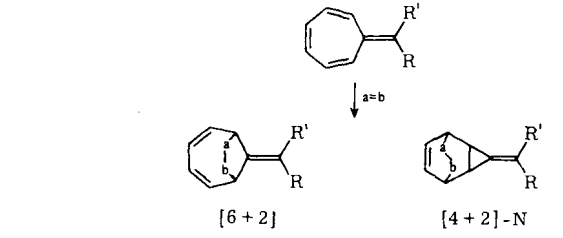
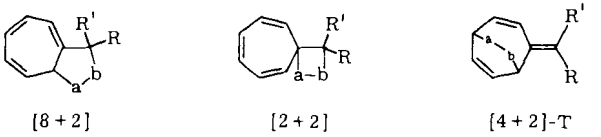
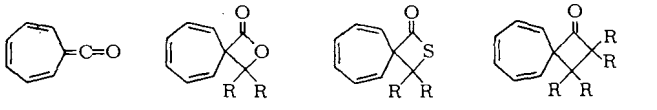
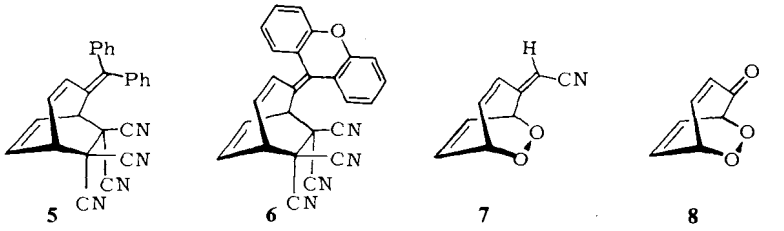
Examples of [2 + 2]-cycloaddition have been reported for 8-oxoheptafulvene (**1**) with ketones leading to β-lactones **2**[1], with thiones affording β-thiolactones **3**[2], and with alkenes giving cyclobutanones **4**[3]. [4 + 2]-Cycloadducts of the tropilidene type, i.e. the [4 + 2]-T mode, have been reported for tetracyanoethylene (TCNE), e.g. **5**[4] and **6**[3], and for singlet oxygen, e.g. **7**[5] and **8**[6].



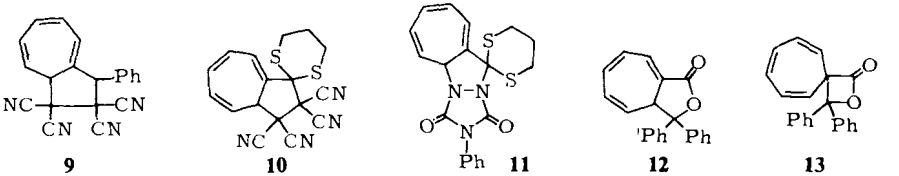
(1)

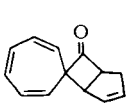






Examples of [4 + 2]-cycloadducts of the norcaradiene type, i.e. the [4 + 2]-N mode, and [6 + 2]-cycloadducts appear not to have been reported, while the [8 + 2]-cycloaddition is the most common route. For example, TCNE leads to the [8 + 2]-cycloadducts **9**[4] and **10**[7], 4-phenyl-4*H*-1,2,4-triazole-3,5-dione (PTAD) to urazole **11**[7], and ketones to the γ-lactone **12** and β-lactone **13**[1]. However, in the case of **12**, which derives from cycloaddition of benzophenone to the ketene **1**, β-lactone **13** has been proposed as primary product, which subsequently rearranges via 1,7-shift[1]. The rearrangement of the cyclobutanone **14** into cyclopentanone **15**[3] was taken as support.





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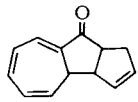
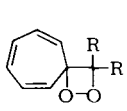


15

This literature coverage reveals the inadequate situation concerning our present day understanding of the cycloaddition behavior of heptafulvenes towards dienophiles. Our specific interest concerns the [2 + 2]-cycloaddition mode, which with singlet oxygen as dienophile would afford the much wanted 1,2-dioxetanes **16**[8]. Such dioxetanes could on thermal cleavage electronically generate excited tropone, which is of considerable interest in view of the fact that its excited state is of the π,π^*-type[9]. Consequently, we decided to undertake a more systematic study of the cycloaddition of $^1O_2$ to heptafulvenes, in the hope of obtaining 1,2-dioxetanes **16**. For comparison also triazoledione was to be used as dienophile. For this purpose the heptafvulenes **17** and **18** were chosen as model substrates. Practical reasons guided our choice since the 7-(9-fluorenylidene)-1,3,5-cycloheptatriene (**17**) was already reported in the literature[1]. However, spirofluorene-substituted 1,2-dioxetanes are notoriously labile and difficult to handle, so that in case of failure, the 7-adamantylidene-1,3,5-cycloheptatriene (**18**) was to be prepared since the spiroadamantane moiety stabilizes 1,2-dioxetanes[10].



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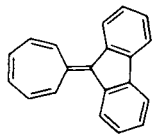

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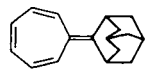
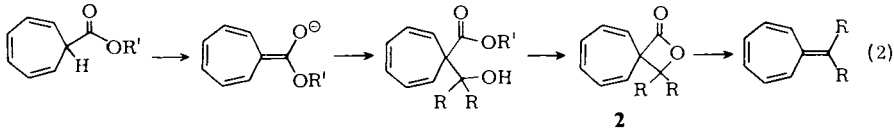


18

For the preparation of the heptafulvenes two synthetic routes were considered. In the route of Eq. (2) heptafulvenes were to be made via thermolysis of the β-lactones **2**[11]. In the alternative route of Eq. (3) thermolysis of the β-thiolactones **3** was to be employed[1]. Presently we report our results of this investigation.



(2)

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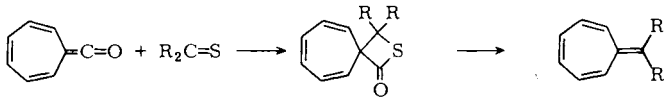


(3)

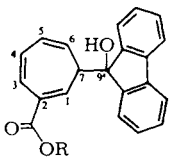
1 **3**

Results

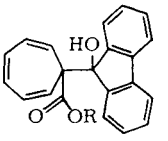
Preparation of 7-Alkylidene-1,3,5-cycloheptatrienes

7-(9-Fluorenylidene)-1,3,5-cycloheptatrienes: Utilization of the synthetic sequence outlined in Eq. (2) gave with fluorenone the γ-addition products **19a** (R = H) and **19b**

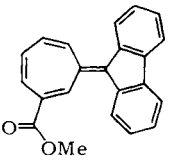
(R = Me), instead of the desired α-products **20a** (R = H) and **20b** (R = Me). Although a recent study[12] demonstrated the electrophilic attack can be directed to give selectively α-product, no efforts were expended in this direction because such heptafulvenes turned out to be problematic both for singlet oxygenation as well as triazoledione addition, as experienced with methyl 7-(9-fluorenylidene)-1,3,5-cycloheptatriene-2-carboxylate (**17b**). The latter was prepared in 75% yield from **19b** by means of dehydration in 85% H_3PO_4. Unfortunately, singlet oxygen failed to react with this heptafulvene and triazoledione gave an undefined amorphous solid. Presumably the strong polarization of this heptafulvene discouraged $^1O_2$ addition and promoted polymerization with TAD. Therefore, work on the fluorenylidene substrate **17** was abandoned.



19a: R = H
b: R = Me



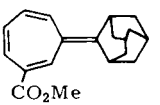
20a: R = H
b: R = Me



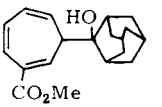
17b

7-Adamantylidene-1,3,5-cycloheptatrienes

Quite similarly, also with adamantanone the γ-product **21b** was obtained in 26% yield instead of the desired α-product when the synthetic sequence of Eq. (2) was employed. Dehydration with 85% H_3PO_4 gave the heptafulvene **18b** in 79% yield.



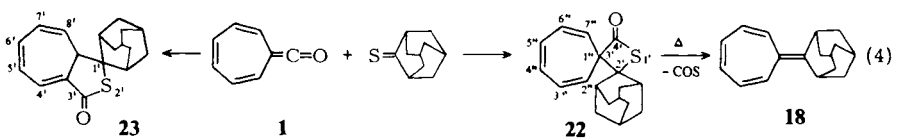
18b



21b

Since also with heptafulvene **18b** cycloaddition of $^1O_2$ and TAD turned out to be problematic, it was necessary to prepare the parent 7-adamantylidene-1,3,5-cycloheptatriene (**18**). In view of the fact that the parent 7-(9-fluorenylidene)-1,3,5-cycloheptatriene (**17**) could be prepared[1] according to the alternative synthetic sequence outlined in Eq. (3), this route was followed to synthesize the adamantylidene derivative **18**.

Addition of 2-adamantanethione to in situ generated 8-oxoheptafulvene (**1**) led to the thietane **22** and thiophene **23** in 80% and 20% relative yields, respectively via [2 + 2]- and [8 + 2]-cycloaddition, as shown in Eq. (4). On heating at ca. 165 °C, the thietane **22** lost carbon oxide sulfide to give the desired adamantylidenecycloheptatriene **18** quantitatively.



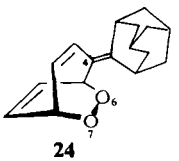
23 **1** **22** **18** (4)

Clean separation of the thietane and thiophene was possible by means of silica gel chromatography, eluting with 1:4 CH_2Cl_2/C_6H_{14}. The thietane **22** eluted first. It exhibited the expected carbonyl band at 1760 cm^{-1}. The 2''-, 7''-hydrogens appeared at $\delta = 5.36-5.39$ and the 3''-, 4''-, 5''-, 6''-hydrogens at $\delta = 6.15-6.22$ as complex multiplets. The ^{13}C NMR spectrum revealed the singlet carbonyl carbon at $\delta = 197.48$, the three doublet olefinic carbons at $\delta = 122.99$, 129.07, and 129.92, the singlet thietane carbons at $\delta = 70.91$ and 79.41, and the remaining adamantyl carbons in the expected $\delta = 25-40$ region.

The thiophene **23** was obtained as second eluate. It exhibited a carbonyl band at 1680 cm^{-1}, indicating that it is conjugated. The ^1H NMR spectrum revealed a doublet of doublets for the 8'-proton at $\delta = 5.34$, arising from coupling by the adjacent 7'- and 8a'-protons. The 4'-proton showed up as a doublet at $\delta = 7.17$, the 5'-H as a doublet of doublets at $\delta = 6.64$, the 6'-H as a doublet of doublets of doublets at $\delta = 6.53$, and 7'-H as a doublet of doublets of doublets at $\delta = 6.13$. The singlet carbonyl carbon resonated at $\delta = 192.61$, the quaternary olefinic carbon as a singlet at $\delta = 131.43$, and the remaining five olefinic carbons as doublets in the $\delta = 121-134$ region. The quaternary thiophene carbon was located at $\delta = 65.40$ as a singlet, the remaining resonances in the $\delta = 26-47$ region pertained to the adamantyl carbons.

Cycloadditions

7-Adamantylidene-1,3,5-cycloheptatriene (**18**): With singlet oxygen at −78 °C this heptafulvene gave the stable endoperoxide **24** in 37% yield after silica gel chromatography, besides 2-adamantanone and benzaldehyde.



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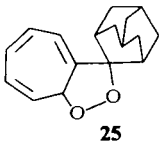

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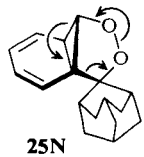
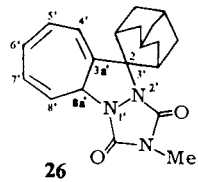


25N



26

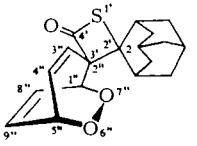
NMR inspection at −78 °C indicated that besides endoperoxide **24**, 2-adamantanone, and benzaldehyde, a very labile peroxide was also present, which with time decomposed even at −78 °C into 2-adamantanone and benzaldehyde. All attempts to isolate or at least spectroscopically characterize this labile peroxide failed. The fact that no chemiluminescence could be detected when the singlet oxygenated reaction mixture was allowed to decompose in the photometer, speaks against the 1,2-dioxetane **16** as plausible structure for this labile peroxide. Besides, dioxetane decomposition should lead to tropone rather than benzaldehyde. We suspect that the labile peroxide was the [8 + 2]-endoperoxide **25**, which via its norcaradiene tautomer **25N** decomposed to 2-adamantanone and benzaldehyde.

The stable endoperoxide **24** exhibited, besides the complex adamantyl protons, the bridgehead protons 1-H and 5-H, respectively, as a broad triplet at $\delta = 4.70$ and a broad doublet at $\delta = 5.60$ due to coupling by the adjacent 2- and 8-protons for 1-H and the 9-proton for 5-H. The 9-proton showed up as a doublet of doublets at

δ = 5.97 due to coupling from 5-H and 8-H, the 2-proton as a doublet of doublets of doublets at δ = 6.33 due to coupling from 1-H, 3-H, and 8-H. Finally, the 8-proton appeared as a broad doublet of doublets at δ = 6.60 and the 3-proton at δ = 6.71. Decoupling experiments confirmed this assignment. The ^{13}C NMR spectrum indicated the characteristic bridghead carbons as doublets at δ = 74.22 and 76.41. The four doublet olefinic carbons came as expected in the δ = 124–132 region and the two singlet olefinic carbons were located at δ = 124.84 and 153.09.

The reaction of heptafulvene **18** with 4-methyl-4*H*-1,2,4-triazole-3,5-dione (MTAD) gave the urazole **26** in 50% yield as only isolable product. ^1H NMR decoupling experiments confirmed the proposed structure of this [8 + 2]-cycloadduct. Thus, the 8a′-proton appeared as a multiplet at δ = 3.59 due to coupling by 8′-H and 7′-H, the 8′-proton as a broad doublet of doublets at δ = 5.65, coupled with the adjacent 7′-H and 8a′-H. The 4′- and 5′-, 6′-, 7′-protons constituted complex multiplets at δ = 6.19–6.28 and 6.50–6.78, respectively. Besides the two carbonyl singlets at δ = 152.26 and 159.27, the ^{13}C NMR spectrum exhibited the C-3a′ as a singlet at δ = 141.74 and the remaining C-4′, -5′, -6′, -7′, -8′ as distinct doublets in the δ = 117 to 132 region. The quaternary adamantyl carbon C-2 resonated as a singlet at δ = 75.37 and the C-8a′ as a doublet at δ = 64.85. Of course, the expected quartet for the *N*-CH_3 carbon occurred at δ = 25.48 and the remaining resonances in the δ = 26–41 region pertained to the various adamantyl carbons.

Thietane **22**: On photooxygenation this substance afforded the tropilidene-type endoperoxide **27** in 72% yield. Its complex ^1H NMR spectrum implicated a rather unsymmetrical structure, so that a norcaradiene-type endoperoxide could be safely ruled out. The tropilidene structure of this endoperoxide was deduced from ^1H NMR decoupling experiments. Also the ^{13}C NMR spectrum corroborated this structure assignment. Thus, the singlet carbonyl resonance occurred at δ = 162.09 and the four doublet olefinic carbons in the expected δ = 126–134 region. The bridgehead doublets C-5″ and C-1″ resonated at δ = 73.07 and 80.10 and the quaternary carbons C-2′ and C-2″ at δ = 65.91 and 83.05. The remaining resonances in the δ = 25–38 region pertained to the adamantyl carbons.



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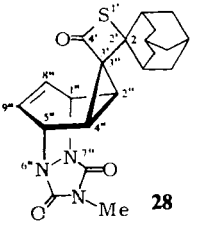


28

As expected for triazoledione cycloaddition[13], the norcaradiene-type urazole **28** was formed in 83% yield when the thietane **22** was allowed to react with MTAD. ^1H NMR decoupling experiments of this AA′MM′XX′ spectrum permitted this structure assignment. Thus, the cyclopropyl 2″- and 4″-protons occurred at δ = 2.60–2.80 as a multiplet. The bridgehead protons 1″-H and 5″-H resonated at δ = 5.20–5.40 as a multiplet and the olefinic protons 8″-H and 9″-H at δ = 6.10–6.30 as a multiplet.

The ^{13}C NMR spectrum corroborated this assignment. The singlet carbonyl resonances were visible at δ = 158.46 and 190.03, the olefinic C-8'' and C-9'' as a doublet at δ = 127.70 and the C-1'' and C-5'' bridgehead carbons at δ = 52.47 as doublets. The singlet spiro-carbons C-3'' and C-2' were located at δ = 59.11 and 60.45.

Thiophene **23**: Both with $^1O_2$ and with MTAD the respective norcaradiene-type adducts **29** and **30** were formed in 45% and 70% yields. An X-ray analysis rigorously established the urazole **30** structure (Figure 1). By comparison of the ^1H and ^{13}C NMR

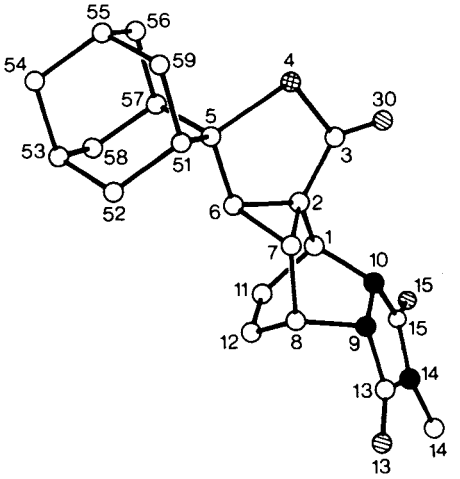
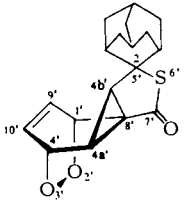
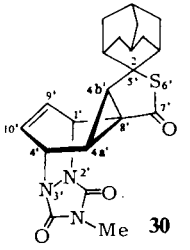


Figure 1. X-ray perspective drawing of urazole **30** with the labeling of the atoms corresponding to Table 1; white, black, hatched, and dotted spheres represent carbon, nitrogen, oxygen, and sulfur atoms, respectively

spectra the endoperoxide **29** structure could be deduced. Definitive in this assignment were the olefinic protons 9'-H and 10'-H which manifested themselves as two doublets of doublets of doublets at δ = 6.32 and 6.53 for urazole **29** and at δ = 6.10 and 6.34 for endoperoxide **30**.



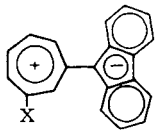
29



30

Discussion

As already mentioned in the Results Section, the 7-(9-fluorenylidene)-1,3,5-cycloheptatriene (**17**) proved useless in this study because it failed to react with $^1O_2$ and with TAD it afforded intractable material. Presumably, charge polarization as shown in the dipolar resonance structure **17'** precluded normal dienic behavior toward dienophiles.



17'

Consequently, this model substrate was abandoned and subsequent work concentrated on the 7-adamantylidene-1,3,5-cycloheptatriene (**18**) and its derivatives **22** and **23**, respectively. Although an investigation of the $^1O_2$ and TAD cycloaddition with these compounds was initially not contemplated, the results were nevertheless quite informative with respect to cycloaddition to spiro-substituted cycloheptatrienes[13].

The differentiation between the dienophiles $^1O_2$ and TAD was again clearly brought out by the exomethylenic cycloheptatriene **18**. With few exceptions[14], TAD avoids formation of tropilidene-type products, while $^1O_2$ can form such products exclusively depending on the electronic and steric nature of the cycloheptatriene substrate[15]. Thus, MTAD afforded with heptafulvene **18** exclusively the [8 + 2]-urazole **26**, while $^1O_2$ led to the [4 + 2]-T endoperoxide **24**. Presumably the [8 + 2]-endoperoxide **25** was formed as well, but it decomposed via its norcaradiene valence isomer **25N** into benzaldehyde and 2-adamantanone. However, the emphasis here lies in the finding that the [4 + 2]-T endoperoxide was formed with $^1O_2$, but the corresponding urazole was not formed with MTAD.

The present results convincingly demonstrated that [2 + 2]-cycloaddition with $^1O_2$ does not take place to give the desired 1,2-dioxetanes **16**. This is disappointing, especially since it was hoped that the spiroadamantane moiety would stabilize the resulting 1,2-dioxetane[10], had it been formed. Since spiroadamantane-substituted[10] and cycloheptatriene-derived[15b] dioxetanes have been reported, steric factors can hardly be the reason that [2 + 2]-cycloaddition between $^1O_2$ and heptafulvene **18** did not take place. Presumably electronic factors are at play.

More rewarding turned out to be the cycloaddition of $^1O_2$ and TAD to the thietane **22** and thiophene **23**, respectively. Analogous to the 7-spirofluorenyl-1,3,5-cycloheptatriene[13], the spiro-annelated thietane **22** gave exclusively the [4 + 2]-T endoperoxide **27** with $^1O_2$, while MTAD afforded exclusively the [4 + 2]-N urazole **28**. The preference of TAD for norcaradiene-type products[15] is dramatically displayed here in the formation of the highly strained but stable urazole **28**. However, the fused-annelated thiophene **23** gave with $^1O_2$ and MTAD the [4 + 2]-N products **29** and **30**, respectively. In view of the fact that 7,7-disubstitution in cycloheptatrienes promotes displacement of the valence tautomeric equilibrium (T $\rightleftharpoons$ N) towards the N-isomer[16], the formation of these strained norcaradiene products is not overly surprising, especially since the spiro-ring acts as a vice by holding the three-membered ring in place. It is important in this context to mention that no norcaradiene valence isomer for thiophene **23** can be detected by ^1H NMR even at low temperatures. Thus, while the spiro-ring vice shifts the T $\rightleftharpoons$ N equilibrium towards the N-isomer, the effect is not sufficient to observe the latter, but it is sufficient to form exclusively the [4 + 2]-N-products **29** and **30**.

We thank the *Deutsche Forschungsgemeinschaft,* the *Fonds der Chemischen Industrie* and the *Alexander von Humboldt-Stiftung* for generous financial support of this work. Dr. *D. Scheutzow*

(University of Würzburg) ran for us the NMR spectra and Dr. *G. Lange* the mass spectra, for which we are grateful. We thank Professor *G. Maier's* staff (University of Gießen) for running the elemental analyses for us.

Experimental Part

Boiling points and melting points are uncorrected. Commercial reagents and solvents were purified according to literature procedures until reported physical constants or spectral data matched. Known compounds used in this study were either prepared according to known literature procedures or purchased from standard suppliers and purified to match the reported physical and spectral data.

IR spectra: Beckman Acculab 4 or Perkin-Elmer 157 G spectrophotometer. – ^{1}H NMR spectra: Varian EM 390 at 90 MHz or Bruker WH 400 at 400 MHz. – ^{13}C NMR spectra: At 100.61 MHz on the latter spectrometer. Unless specified, the carbon resonances pertain to one carbon atom. In those cases in which two carbon atoms are given in brackets, the NOE was eliminated and the relative intensity of the specific carbon remeasured. – Mass spectra: Varian MAT CH-7. – The elemental analyses of all new compounds were kindly run for us by Prof. Dr. *G. Maier's* staff at the University of Gießen.

Unless stated, roto-evaporation of the solvent was carried out at 15 – 20 °C/10 – 20 Torr. Column chromatography was run on silica gel, using a substrate-adsorbant ratio of ca. 1 : 20. The eluant mixture is specified for each particular case. Drying of the reaction mixtures after aqueous work-up was conducted over anhydrous magnesium sulfate. Stirring was performed magnetically by means of a spinbar. Peroxide tests were run with potassium iodide in acetic acid, affording the characteristic brown iodine color.

7-(9-Hydroxy-9-fluorenyl)-1,3,5-cycloheptatriene-2-carboxylic acid (**19a**): A 250-ml, round-bottomed flask, provided with a magnetic spinbar, a rubber septum and nitrogen inlet and outlet, was flame-dried under vacuum. The flask was charged with 70 ml of anhydrous THF (freshly distilled from benzophenone ketyl radical) and 1.02 g (10 mmol) of diisopropylamine (freshly distilled from NaH) was introduced through the rubber septum by means of a syringe. The THF solution was cooled to – 60 °C by means of a dry ice-acetone bath and while stirring 6 ml (10.2 mmol) of 1.7 N *n*-BuLi (in hexane) were added dropwise. After 30 min at – 60 °C the pale yellow reaction mixture was allowed to warm up to room temperature and stirred for another 30 min. The LDA solution was then cooled to – 78 °C by means of a dry ice-acetone bath and while stirring was added dropwise 5 ml of a solution of 1.01 g (7.4 mmol) of 1,3,5-cycloheptatriene-7-carboxylic acid in anhydrous THF by means of a syringe. The dianion solution was stirred for 30 min at – 78 °C and a solution of 1.30 g (7.40 mmol) of 9-fluorenone in 5 ml of THF was added. After stirring the reaction mixture at – 78 °C for 1 h, it was allowed to warm up slowly to room temperature and at reduced pressure (ca. 10 – 15 Torr) as much THF as possible was evaporated. The residue was diluted with 25 ml of water, transferred to a separatory funnel, adjusted to pH $\leqslant$ 3 with HCl, and extracted with 3 × 20 ml of ether. The combined ether extracts were washed with 10 ml of water, dried and the solvent roto-evaporated. Recrystallization of the crude product from CH_2Cl_2/C_6H_{14} afforded 1.90 g (83%) of **19a**, m.p. 161 – 162 °C as colorless plates. – IR (KBr): 3530 (m), 3480 (m), 3050 (w), 3010 (w), 2910 (w), 1680 (s), 1600 (m), 1475 (w), 1450 (s), 1420 (m), 1360 (w), 1325 (w), 1300 (s), 1215 (m), 1085 (w), 1068 (w), 1040 (m), 985 (m), 940 (m), 900 cm^{-1} (m). – ^{1}H NMR ([D$_6$]DMSO) at 90 MHz: δ = 2.25 (dd, J = 6.6, 6.0 Hz; 1 H, 7-H), 5.35 (dd, J = 9.8, 6.0 Hz; 1 H, 6-H), 6.15 (b. dd, J = 9.8, 6.0 Hz; 1 H, 5-H), 6.18 (b. s; 1 H, OH), 6.48 (d, J = 6.6 Hz; 1 H, 1-H), 6.76 (dd, J = 12.0, 6.0 Hz; 1 H, 4-H), 7.16

(d, J = 12.0 Hz; 1H, 3-H), 7.35–8.05 (m; 8H, Ar), 11.5 (b. s; 1H, CO_2H). – ^{13}C NMR ([D_6]DMSO) at 100 MHz: δ = 40.08 (d), 80.82 (s), 119.66 (d), 122.93 (d), 122.99 (d), 123.68 (d), 124.09 (d), 124.30 (d), 125.50 (d), 127.60 (d), 128.21 (d) (2 carbons), 128.65 (d), 129.04 (d) (2 carbons), 130.66 (s), 130.87 (s), 139.51 (s), 148.46 (s), 148.76 (s), 167.40 (s).

$C_{21}H_{16}O_3$ (316.4) Calc. C 79.72 H 5.10 Found C 79.91 H 5.04

Methyl 7-(9-hydroxy-9-fluorenyl)-1,3,5-cycloheptatriene-2-carboxylate (**19b**): 2.41 g (50%) of **19b**, m.p. 144.5–145.5°C (granular solid from CH_2Cl_2/C_6H_{14}), were obtained following the above procedure by starting from ca. 16 mmol of LDA solution, 2.00 g (13.3 mmol) of methyl 1,3,5-cycloheptatriene-7-carboxylate, and 2.40 g (13.3 mmol) of 9-fluorenone in 10 ml of dry THF. – IR (KBr): 3450 (s), 3050 (w), 3020 (w), 2950 (w), 1700 (s), 1520 (w), 1480 (w), 1450 (s), 1440 (m), 1395 (w), 1360 (m), 1325 (w), 1290 (s), 1250 (m), 1075 (m), 990 (m), 900 cm^{-1} (w). – ^1H NMR ($CDCl_3$) at 400 MHz: δ = 2.35 (ddd, J = 7.0, 5.5, 1.3 Hz; 1H, 7-H), 2.55 (b. s; 1H, OH), 3.70 (s; 3H, OCH_3), 5.08 (dd, J = 9.5, 5.5 Hz; 1H, 6-H), 6.08 (ddd, J = 9.5, 5.5, 1.3 Hz; 1H, 5-H), 6.69 (d, J = 7.0 Hz; 1H, 1-H), 6.73 (dd, J = 11.4, 5.5 Hz; 1H, 4-H), 7.13 (d, J = 11.4 Hz; 1H, 3-H), 7.2–7.6 (m; 8H, Ar). – ^{13}C NMR ($CDCl_3$) at 100 MHz: δ = 47.95 (d), 51.80 (q), 81.97 (s), 120.02 (d), 120.07 (d), 121.58 (d), 124.05 (d) (2 carbons), 124.60 (d), 126.30 (d), 128.15 (d), 128.28 (d), 128.77 (s), 129.45 (d) (2 carbons), 129.86 (d), 131.49 (d), 139.88 (s), 140.05 (s), 147.40 (s), 147.91 (s), 166.98 (s). – MS (70 eV): m/e = 330 (2%, M^+), 180 (100), 165 (20, $C_{13}H_8^+$), 90 (50, $C_7H_7^+$).

$C_{22}H_{18}O_3$ (330.4) Calc. C 79.97 H 5.50 Found C 79.64 H 5.35

Methyl 7-(2-hydroxy-2-adamantyl)-1,3,5-cycloheptatriene-2-carboxylate (**21b**): 1.03 g (26%) of **21b**, m.p. 170–171.5°C (plates from CH_2Cl_2/C_6H_{14}), were prepared following the above procedure by starting from ca. 20 mmol of LDA solution, 2.55 g (17.0 mmol) of methyl 1,3,5-cycloheptatriene-7-carboxylate, and 2.79 g (17.0 mmol) of 2-adamantanone in 10 ml of dry THF. – IR (KBr): 3500 (s), 3020 (s), 3000 (s), 2940 (m), 1700 (s), 1600 (w), 1450 (s), 1390 (w), 1355 (m), 1340 (m), 1315 (s), 1304 (s), 1275 (s), 1247 (s), 1204 (s), 1150 (m), 1105 (w), 1085 (s), 1060 (m), 1045 cm^{-1} (m). – ^1H NMR ($CDCl_3$) at 90 MHz: δ = 1.43–2.60 (m; 16H, Ad, OH, 7-H), 3.75 (s; 3H, OCH_3), 5.48 (dd, J = 9.6, 5.4 Hz; 1H, 6-H), 6.30 (dd, J = 9.6, 5.4 Hz; 1H, 5-H), 6.56 (d, J = 6.9 Hz; 1H, 1-H), 6.80 (dd, J = 11.8, 5.4 Hz; 1H, 4-H), 7.29 (d, J = 11.8 Hz; 1H, 3-H). – ^{13}C NMR ($CDCl_3$) at 100 MHz: δ = 26.62 (d), 27.31 (d), 32.90 (t) (2 carbons), 33.90 (t), 34.00 (t), 34.85 (d), 35.50 (d), 38.22 (t), 43.86 (d), 51.79 (q), 74.32 (s), 121.08 (d), 126.18 (d), 128.16 (d), 128.37 (s), 129.42 (d), 131.51 (d), 167.37 (s). – MS (70 eV): m/e = 300 (0.2%, M^+), 283 (2, M^+ – OH), 241 (0.3, M^+ – CO_2Me), 164 (17, M^+ – Ad), 150 (100, M^+ – $C_9H_9O_2$), 135 (43, $C_{10}H_{15}^+$), 90 (41, $C_7H_7^+$).

$C_{19}H_{24}O_3$ (300.4) Calc. C 76.17 H 7.97 Found C 76.13 H 7.97

Methyl 7-(9-fluorenylidene)-1,3,5-cycloheptatriene-2-carboxylate (**17b**): A 50-ml, round-bottomed flask was charged with 990 mg (3.00 mmol) of **19b** and 10 ml of 85% H_3PO_4. While stirring, the reaction was heated up to 110°C within a period of 4 h. The resulting dark solution was poured into a separatory funnel, 20 ml of distilled water were added and the reaction mixture extracted with 4 × 20 ml of CH_2Cl_2. The organic layer was washed with 20 ml of a 10% aqueous $NaHCO_3$, dried and the solvent roto-evaporated. The solid residue was chromatographed on silica gel, using CH_2Cl_2 as eluant. Recrystallization from CH_2Cl_2/C_6H_{14} gave analytically pure product in 75% yield (700 mg, 2.24 mmol), m.p. 99–100°C (yellow needles). – IR (CCl_4): 3040 (w), 3000 (w), 2925 (m), 2900 (w), 2820 (w), 1725 (s), 1448 (m), 1295 (s), 1265 (m), 1240 (m), 1100 (m), 1085 (w), 1020 cm^{-1} (w). – ^1H NMR ($CDCl_3$) at 400 MHz: δ = 3.92 (s; 3H, OCH_3), 7.06–7.73 (m; 11H, Ar, 3-H, 4-H, 5-H), 8.10 (d, J = 7.5 Hz; 1H, 6-H), 8.30 (b. s; 1H, 1-H). – ^{13}C NMR ($CDCl_3$) at 100 MHz: δ = 52.02 (q), 119.55 (d), 119.79 (d), 120.31 (d), 124.18 (d),

125.64 (d), 126.70 (d), 127.01 (d), 127.39 (s), 128.40 (d), 128.50 (d), 128.77 (d), 128.98 (d), 130.34 (d), 130.54 (s), 133.60 (d), 136.22 (s), 137.14 (s), 137.31 (s), 139.23 (s), 141.41 (s), 166.59 (s). – MS (70 eV): *m/e* = 313 (15%, $M^+ + 1$), 312 (64, M^+), 279 (14), 252 (100, $C_{19}H_{13}^+$), 126 (32), 113 (14), 91 (1, $C_7H_7^+$).

$C_{22}H_{16}O_2$ (312.4) Calc. C 84.58 H 5.17 Found C 84.75 H 5.15

Methyl 7-(2-adamantylidene)-1,3,5-cycloheptatriene-2-carboxylate (**18b**): 734 mg (79%) of **18b**, purified by bulb-to-bulb distillation, b.p. 125°C/0.01 Torr (colorless oil), were obtained, following the above procedure by starting with 991 mg (3.30 mmol) of **21b**. – IR (CCl_4): 3090 (w), 3050 (w), 3000 (w), 2970 (m), 2925 (s), 2870 (s), 1740 (s), 1660 (m), 1460 (m), 1450 (m), 1300 (s), 1225 (s), 1210 (s), 1115 (s), 1095 cm^{-1} (m). – ^1H NMR ($CDCl_3$) at 400 MHz: δ = 1.26–2.50 (m; 14H, Ad), 3.89 (s; 3H, OCH_3), 6.19 (s; 1H, 1-H), 7.29–7.37 (m; 2H, 5-, 6-H), 7.82–7.87 (m; 2H, 4-, 3-H). – ^{13}C NMR ($CDCl_3$) at 100 MHz: δ = 28.41 (d) (2 carbons), 32.38 (d), 37.16 (t), 39.02 (t) (2 carbons), 39.93 (t) (2 carbons), 41.03 (d), 51.83 (q), 116.25 (d), 126.81 (d), 127.99 (d), 129.84 (d), 130.08 (s), 133.09 (d), 138.64 (s), 152.62 (s), 167.15 (s). – MS (70 eV): *m/e* = 282 (25%, M^+), 168 (48), 167 (61), 165 (31), 152 (24), 91 (29, $C_7H_7^+$), 32 (100).

$C_{19}H_{22}O_2$ (282.4) Calc. C 80.80 H 7.86 Found C 80.68 H 7.73

Dispiro[adamantane-2,2'-thietane-3',1''-[2,4,6]cycloheptatrien]-4'-one (**22**) *and 3',8a'-dihydrospiro[adamantane-2,1'-[1H]cyclohepta[c]thiophen]-3'-one* (**23**): A 100-ml, 3-necked, round-bottomed flask, provided with magnetic spinbar, rubber septum, reflux condenser and nitrogen inlet and outlet, was charged with 60 ml of dry benzene, 507 mg (3.30 mmol) of 1,3,5-cycloheptatriene-7-carbonyl chloride, and 540 mg (3.25 mmol) of 2-adamantanethione. While stirring and heating at 40°C, 607 mg (6.00 mmol) of triethylamine (freshly distilled over sodium metal) were added dropwise by means of a syringe over a period of 30 min. The brown solution was stirred for 1 h at 40°C and then allowed to cool to ca. 25°C, poured into a separatory funnel together with 20 ml of water and extracted with 3 × 10 ml of CH_2Cl_2. The combined extracts were dried and the solvent roto-evaporated, affording a brown solid, which was chromatographed on silica gel eluting with 1:4 CH_2Cl_2/C_6H_{14}. Two isomers were obtained in 80:20 ratio (by ^1H NMR), the first corresponded to β-thiolactone **22** and the second to the γ-thiolactone **23**.

Thietane **22**, 654 mg (69%), m.p. 121–123°C (needles from Et_2O/C_5H_{12}), were obtained. – IR (CCl_4): 3025 (w), 2910 (s), 2860 (m), 1760 (s), 1720 (m), 1455 (m), 1250 (w), 1220 (w), 1103 (m), 1005 (w), 980 (w), 930 (w), 915 cm^{-1} (w). – ^1H NMR ($CDCl_3$) at 400 MHz: δ = 1.45–2.15 (m; 14H, Ad), 5.36–5.39 (m; 2H, 2''-, 7''-H), 6.15–6.22 (m; 4H, 3''-, 4''-, 5''-, 6''-H). – ^{13}C NMR ($CDCl_3$) at 100 MHz: δ = 25.48 (d), 27.67 (d), 34.09 (t), 35.55 (t), 36.97 (t), 37.43 (d), 70.91 (s), 79.41 (s), 122.99 (s), 129.07 (d), 129.92 (d), 197.48 (s). – MS (70 eV): *m/e* = 285 (0.1%, M^+), 224 (40, $M^+ - COS$), 167 (12), 128 (11), 118 (87), 115 (11), 90 (100, $C_7H_7^+$), 77 (11, $C_6H_5^+$).

$C_{18}H_{20}OS$ (284.4) Calc. C 76.00 H 7.09 Found C 76.01 H 7.00

Thiophene **23**, 185 mg (20%), m.p. 183–185°C (plates from CH_2Cl_2/C_5H_{12}), were obtained. – IR (CCl_4): 3050 (w), 2920 (s), 2860 (m), 1680 (s), 1550 (w), 1460 (w), 1360 (w), 1325 (w), 1250 (m), 1210 (m), 1170 (s), 1100 (w), 1090 (w), 1005 (m), 980 (m), 955 (m), 945 (m), 915 (s), 860 cm^{-1} (m). – ^1H NMR (90% C_6D_6 – 10% $CDCl_3$) at 400 MHz: δ = 1.41–1.89 (m; 12H, Ad), 2.39–2.47 (m; 3H, Ad, 8a'-H), 5.34 (dd, *J* = 9.3, 5.5 Hz; 1H, 8'-H), 6.13 (ddd, *J* = 9.3, 5.5, 1.0 Hz; 1H, 7'-H), 6.53 (ddd, *J* = 10.8, 5.5, 1.0 Hz; 1H, 6'-H), 6.64 (dd, *J* = 10.8, 5.5 Hz; 1H, 5'-H), 7.17 (d, *J* = 5.5 Hz; 1H, 4'-H). – ^{13}C NMR (90% C_6D_6 – 10% $CDCl_3$) at 100 MHz: δ = 25.95 (d), 27.27 (d), 32.94 (d), 34.31 (d), 34.50 (t) (2 carbons), 36.89 (t), 37.86 (t), 40.17 (d), 47.08 (d), 65.40 (s), 121.27 (d), 122.45 (d), 125.58 (d), 130.01 (d), 131.43 (s), 134.43 (d),

192.61 (s). – MS (70 eV): *m/e* = 285 (1%, M^+), 284 (6, $M^+ - 1$), 224 (7, $M^+ - COS$), 118 (100), 105 (28), 90 (48, $C_7H_7^+$).

$C_{18}H_{20}OS$ (284.4) Calc. C 76.00 H 7.09 Found C 76.09 H 7.12

7-(2-Adamantylidene)-1,3,5-cycloheptatriene (**18**): 404 mg (100%) of **18** were obtained as colorless oil, b.p. 145°C/0.01 Torr, by heating 512 mg (1.80 mmol) of **22** up to 170°C for 15 min. – IR (CCl_4): 3020 (m), 2990 (s), 2840 (s), 1550 (w), 1450 (m), 1100 (m), 1080 (w), 1035 (w), 975 cm^{-1} (m). – ^1H NMR ($CDCl_3$) at 90 MHz: δ = 1.50–2.10 (m; 12H, Ad), 2.94 (br. s; 2H, Ad), 5.69–6.19 (m; 6H). – ^{13}C NMR ($CDCl_3$) at 100 MHz: δ = 28.38 (d), 32.17 (d), 32.99 (d), 37.05 (t), 38.80 (t) (2 carbons), 125.99 (d), 128.66 (s), 130.69 (d), 130.99 (d), 144.33 (s).

All efforts to obtain an analytical sample of **18** by chromatography and fractional distillation failed.

4-(2-Adamantylidene)-6,7-dioxabicyclo[3.2.2]nona-2,8-diene (**24**): 184 mg (37%) of **24**, m.p. 73–75°C (needles from CH_2Cl_2/C_5H_{12}), were obtained on photosensitized oxygenation of 431 mg (1.92 mmol) of **18** at –30°C in CH_2Cl_2 according to the above procedure. Benzaldehyde and 2-adamantanone were also isolated in the silica gel chromatography. – IR (CCl_4): 3060 (m), 2905 (s), 2850 (s), 1620 (s), 1465 (m), 1450 (s), 1400 (m), 1365 (m), 1340 (w), 1260 (m), 1220 (m), 1165 (m), 1110 (s), 1060 (w), 1000 (m), 975 (s), 900 cm^{-1} (s). – ^1H NMR ($CDCl_3$) at 90 MHz: δ = 1.5–2.1 (m; 12H, Ad), 3.10 (m; 2H, Ad), 4.70 (br. t, *J* = 7.2, 2.7 Hz; 1H, 1-H), 5.60 (br. d, *J* = 7.2 Hz; 1H, 5-H), 5.97 (dd, *J* = 11.4, 7.2 Hz; 1H, 9-H), 6.33 (ddd, *J* = 9.6, 7.2, 1.2 Hz; 1H, 2-H), 6.60 (br. dd, *J* = 11.4, 2.7 Hz; 1H, 8-H), 6.71 (br. d, *J* = 9.6 Hz; 1H, 3-H). – ^{13}C NMR ($CDCl_3$) at 100 MHz: δ = 27.92 (d) (2 carbons), 33.27 (d), 33.82 (d), 36.82 (t), 39.00 (t), 39.16 (t), 39.28 (t), 40.60 (t), 74.22 (d), 76.41 (d), 124.24 (d), 124.30 (d), 124.84 (s), 128.00 (d), 132.24 (d), 153.09 (s).

$C_{17}H_{20}O_2$ (256.3) Calc. C 79.65 H 7.86 Found C 79.82 H 7.95

1',8a'-Dihydro-N-methylspiro[adamantane-2,3'(2'H)-cycloheptapyrazole]-1',2'-dicarboximide (**26**): 75.0 mg (50%) of **26**, m.p. 186–188°C (cubes from CH_2Cl_2/Et_2O), were obtained by allowing 144 mg (0.64 mmol) of **18** to react with 73.5 mg (0.65 mmol) of MTAD in 10 ml of CH_2Cl_2. – IR (KBr): 2900 (m), 2840 (w), 1780 (m), 1710 (s), 1450 (s), 1380 (m), 1305 (w), 1265 (w), 1250 (w), 1240 (w), 1200 (w), 1160 (w), 1100 (w), 1020 (m), 975 cm^{-1} (m). – ^1H NMR ($CDCl_3$) at 90 MHz: δ = 1.58–3.20 (m; 14H, Ad), 3.05 (s; 3H, Me), 3.59 (br. m; 1H, 8a'-H), 5.65 (br. dd, *J* = 9.0, 4.5 Hz; 1H, 8'-H), 6.19–6.28 (m; 1H, 4'-H), 6.50–6.78 (m; 3H, 5'-, 6', 7'-H). – ^{13}C NMR ($CDCl_3$) at 100 MHz: δ = 25.48 (q), 26.76 (d), 26.81 (d), 32.26 (d or t), 33.52 (t or d), 34.73 (t) (2 carbons), 37.00 (t), 38.09 (t), 41.59 (d), 64.85 (d), 75.37 (s), 117.47 (d), 123.39 (d), 126.57 (d), 129.91 (d), 132.09 (d), 141.74 (s), 152.26 (s), 159.27 (s).

$C_{20}H_{23}N_3O_2$ (337.4) Calc. C 71.19 H 6.87 N 12.45 Found C 71.21 H 7.03 N 12.52

Dispiro[adamantane-2,2'-thietane-3',2''-(6,7-dioxabicyclo[3.2.2]nona-3,8-dien)]-4'-one (**27**): A 50-ml test tube, provided with a rubber septum, was charged with 400 mg (1.41 mmol) of **22** in 25 ml of CH_2Cl_2 (freshly distilled from EDTA) and 6.5 mg of tetraphenylporphine (TPP). The violet solution was cooled to –20°C by means of a dry ice-acetone bath and externally irradiated with a 150-Watt sodium street lamp while passing a vivid stream of dry oxygen gas, introduced through the rubber septum to the bottom of the test tube by means of Teflon tubing. The reaction progress was monitored by ^1H NMR, silica gel TLC or peroxide test (KI-HOAc). After total consumption of the starting material, the solvent was roto-evaporated and the residue chromatographed on silica gel (activity grade III) at ca. 25°C, using 2:1 CH_2Cl_2/C_6H_{14} mixture as eluant. Recrystallization from CH_2Cl_2/C_6H_{14} afforded 315 mg (72%) of the pure product, m.p. 178–180°C (needles). – IR (KBr): 3050 (m), 3000 (s), 2980 (m), 1750 (s), 1450 (m), 1350 (w), 1265 (w), 1210 (w), 1160 (w), 1145 (w), 1100 (w), 1090 (w), 1065 (m), 1035 (m),

1005 (w), 970 (m), 955 (m), 905 (m), 865 cm^{-1} (m). – ^1H NMR ($CDCl_3$) at 90 MHz: δ = 1.51 – 2.40 (m; 14H, Ad), 4.78 (dd, *J* = 7.8, 7.0 Hz; 1H, 5''-H), 5.48 (br. d, *J* = 7.5 Hz; 1H, 1''-H), 5.98 (br. d, *J* = 11.3 Hz; 1H, 3''-H), 6.31 (dd, *J* = 11.3, 7.0 Hz; 1H, 4''-H), 6.40 (dd, *J* = 9.0, 7.5 Hz; 1H, 8''-H), 6.82 (dd, *J* = 9.0, 7.8 Hz; 1H, 9''-H). – ^{13}C NMR ($CDCl_3$) at 100 MHz: δ = 25.48 (d), 26.78 (d), 35.09 (t), 35.43 (t), 36.54 (t) (2 carbons), 37.12 (d), 37.52 (d), 38.64 (d), 65.91 (s), 73.07 (d), 80.10 (d), 83.05 (s), 126.88 (d), 128.15 (d), 131.94 (d), 134.13 (d), 162.09 (s). – MS (70 eV): *m/e* = 316 (2%, M^+), 284 (2, $M^+ - O_2$), 256 (22, $M^+ - COS$), 228 (28), 227 (56), 224 (48), 211 (24), 183 (5), 134 (20), 117 (29), 115 (38), 107 (35), 105 (31), 91 (100, $C_7H_7^+$), 77 (58, $C_6H_5^+$), 67 (32), 60 (30), 41 (71), 39 (48).

$C_{18}H_{20}O_3S$ (316.4) Calc. C 68.56 H 6.39 Found C 68.69 H 6.42

N-Methyl-4'-oxo-dispiro[adamantane-2,2'-thietane-3',3''-(6,7-diazatricyclo[3.2.2.0^{2,4}]non-8-ene)]-6'',7''-dicarboximide (**28**): 230 mg (83%) of **28**, m.p. 178 – 180 °C (plates from CH_2Cl_2/C_6H_{14}, gas evolution), were obtained by allowing 199 mg (0.70 mmol) of **22** to react with 79 mg (0.70 mmol) of 4-methyl-4*H*-1,2,4-triazole-3,5-dione (MTAD) in 10 ml of CH_2Cl_2 at room temperature for 1 h. – IR (KBr): 3040 (m), 2980 (w), 2905 (m), 2850 (w), 1775 (s), 1705 (s), 1455 (s), 1395 (m), 1185 (m), 1050 (w), 1020 (m), 965 (w), 940 (m), 875 (w), 820 cm^{-1} (w). – ^1H NMR ($CDCl_3$) at 90 MHz: δ = 1.60 – 2.30 (m; 14H, Ad), 2.60 – 2.80 (m; 2H, 2'', 4''-H), 3.95 (s; 3H, Me), 5.20 – 5.40 (m; 2H, 1''-, 5''-H), 6.10 – 6.30 (m; 2H, 8''-, 9''-H). – ^{13}C NMR ($CDCl_3$) at 100 MHz: δ = 25.33 (d), 25.51 (d), 27.17 (d), 34.97 (t), 37.89 (q), 38.77 (t), 52.47 (d), 59.11 (s), 60.45 (s), 127.70 (d), 158.46 (s), 190.03 (s). – MS (70 eV): *m/e* = 398 (0.1%, M^+), 337 (2, $M^+ - COS$), 224 (35), 167 (11), 165 (21), 141 (7), 129 (10), 119 (10), 118 (100), 90 (82, $C_7H_7^+$), 77 (10, $C_6H_5^+$).

$C_{21}H_{23}N_3O_3S$ (397.5) Calc. C 63.46 H 5.83 N 10.57 Found C 63.45 H 6.04 N 10.63

4',4a'-Dihydrospiro[adamantane-2,5'(4b'H)-(1,4-ethenothieno[3',4': 1,3]cyclopropa[1,2-d]-[1,2]dioxin)]-7'-one (**29**): 126 mg (45%) of **29**, m.p. 242 – 244 °C (plates from CH_2Cl_2/C_6H_{14}), were obtained on photosensitized oxygenation of 250 mg (0.88 mmol) of **23** at – 30 °C in 20 ml of CH_2Cl_2 according to the above procedure. – IR (KBr): 2905 (s), 2875 (m), 1690 (s), 1460 (m), 1360 (m), 1340 (m), 1215 (m), 1200 (s), 1100 (m), 1085 (m), 1075 (m), 975 (m), 890 (m), 840 (m), 820 (m), 740 cm^{-1} (s). – ^1H NMR ($CDCl_3$) at 90 MHz: δ = 1.51 – 2.34 (m; 15H, Ad, 4b'-H), 2.25 (t, *J* = 6.0 Hz; 1H, 4a'-H), 5.08 (br. dd, *J* = 7.5, 6.0 Hz; 1H, 4'-H), 5.23 (br. d, *J* = 6.0 Hz; 1H, 1'-H), 6.32 (ddd, *J* = 8.0, 6.0, 2.3 Hz; 1H, 9'-H or 10'-H), 6.53 (ddd, *J* = 7.5, 6.0, 1.5 Hz; 1H, 10'-H or 9'-H). – ^{13}C NMR ($CDCl_3$) at 100 MHz: δ = 20.59 (d), 26.04 (d), 26.79 (d), 33.26 (t), 33.56 (t), 34.74 (t), 35.75 (d), 36.51 (d), 36.92 (s), 37.66 (t), 37.72 (t), 39.81 (d), 62.86 (s), 70.20 (d), 72.24 (d), 127.89 (d), 130.49 (d), 201.20 (s). – MS (70 eV): *m/e* = 317 (13%, $M^+ + 2$), 316 (59, $M^+ + 1$), 288 (13), 271 (48), 245 (19), 227 (14), 218 (56), 167 (22), 129 (25), 118 (100), 115 (28), 105 (54), 91 (89, $C_7H_7^+$), 77 (59, $C_6H_5^+$).

$C_{18}H_{20}O_3S$ (316.4) Calc. C 68.56 H 6.39 Found C 68.58 H 6.26

1',2',3',4',4a',4b'-Hexahydro-N-methyl-7'-oxospiro[adamantane-2,5'-(1,4-etheno-5H-thieno-[3',4': 1,3]cyclopropa[1,2-d]pyridazine)]-2',3'-dicarboximide (**30**): 97 mg (70%) of **30**, m.p. 243 – 245 °C (plates from CH_2Cl_2/C_6H_{14}), were obtained by allowing 99.5 mg (0.35 mmol) of **23** to react with 40.7 mg (0.36 mmol) of MTAD in 10 ml of CH_2Cl_2 at room temperature for 1 h. – IR (KBr): 3010 (w), 2900 (s), 2850 (m), 1780 (s), 1720 (s), 1405 (s), 1400 (m), 1355 (w), 1330 (w), 1270 (m), 1240 (w), 1210 (w), 1180 (s), 1100 (w), 1080 (m), 1060 (m), 1045 (m), 1000 (w), 980 (m), 965 cm^{-1} (m). – ^1H NMR ($CDCl_3$) at 400 MHz: δ = 1.62 – 2.15 (m; 14H, Ad), 2.19 (d, *J* = 3.9 Hz; 1H, 4b'-H), 2.24 (dd, *J* = 4.0, 3.9 Hz; 1H, 4a'-H), 2.95 (s; 3H, Me), 5.27 (ddd, *J* = 6.0, 4.0, 1.6 Hz; 1H, 4'-H), 5.37 (dd, *J* = 6.0, 1.6 Hz; 1H, 8'-H), 6.10 (br. ddd, *J* = 7.6, 6.0, 1.6 Hz; 1H, 9'-H), 6.34 (ddd, *J* = 7.6, 6.0, 1.6 Hz; 1H, 10'-H). – ^{13}C NMR ($CDCl_3$) at

100 MHz: δ = 22.48 (d), 25.38 (s), 26.31 (d), 27.06 (d), 33.52 (t), 33.79 (t), 34.97 (t), 36.71 (d), 37.93 (t) (2 carbons), 38.14 (q), 38.19 (d), 40.07 (d), 51.15 (d), 53.03 (d), 63.04 (s), 125.73 (d), 128.95 (d), 157.85 (s), 158.13 (s), 199.43 (s). – MS (70 eV): *m/e* = 399 (0.7%, M^+ + 2), 398 (3, M^+ + 1), 397 (8, M^+), 337 (1, M^+ – COS), 284 (15), 198 (15), 141 (11), 134 (1, $C_{10}H_{14}^+$), 118 (100), 90 (24, $C_7H_7^+$), 77 (9, $C_6H_5^+$).

$C_{21}H_{23}N_3O_3S$ (397.5) Calc. C 63.46 H 5.83 N 10.57 Found C 63.63 H 5.92 N 10.35

X-Ray Crystallography of Urazole **30** *)

A clear colorless crystal was optically centered on a Syntex-P3 four circle diffractometer. The intensities of 2901 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 29.3 deg · min^{-1} as a function of the intensities of the reflections. In the range between 3.0° ≤ 2Θ ≤ 55.0° 2853 reflections *hkl* with $F > 3\sigma(F)$ were applied for the structure determination. For the evaluation the SHELXTL-System on an Eclipse S/250 was employed. The structure was solved by the direct

Table 1. Positional (× 10^4) and thermal (× 10^3) parameters (Å^2) of urazole **30** [a]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	9624(2)	5394(2)	1915(2)	35(1)	33(1)	35(1)	3(1)	10(1)	-2(1)
C(2)	8438(2)	5358(2)	1220(2)	34(1)	33(1)	38(1)	-1(1)	13(1)	-0(1)
C(3)	7786(2)	6376(2)	1152(2)	43(1)	43(2)	42(1)	3(1)	16(1)	5(1)
S(4)	6523(1)	6220(1)	9980(1)	40(1)	65(1)	54(1)	-8(1)	11(1)	17(1)
C(5)	6859(2)	4977(2)	9288(2)	30(1)	44(1)	43(1)	-3(1)	11(1)	1(1)
C(6)	7908(2)	4550(2)	210(2)	34(1)	37(1)	37(1)	-4(1)	11(1)	-2(1)
C(7)	8002(2)	4213(2)	1394(2)	35(1)	37(1)	44(1)	1(1)	16(1)	-4(1)
C(8)	8921(2)	3459(2)	2157(2)	43(1)	31(1)	40(1)	0(1)	16(1)	-2(1)
N(9)	9398(2)	4071(2)	3312(2)	48(1)	35(1)	37(1)	2(1)	18(1)	1(1)
N(10)	9794(2)	5180(2)	3174(2)	41(1)	34(1)	35(1)	0(1)	13(1)	-0(1)
C(11)	117(2)	4409(2)	1549(2)	31(1)	47(2)	33(1)	2(1)	11(1)	3(1)
C(12)	9751(2)	3405(2)	1676(2)	37(1)	37(1)	34(1)	-2(1)	12(1)	5(1)
C(13)	208(2)	3506(2)	4215(2)	58(2)	42(2)	35(1)	2(1)	25(1)	9(1)
O(13)	186(2)	2539(2)	4532(2)	81(1)	42(1)	45(1)	10(1)	30(1)	7(1)
N(14)	1008(2)	4284(2)	4693(2)	50(1)	44(1)	32(1)	2(1)	12(1)	9(1)
C(14)	1993(2)	4043(3)	5683(3)	57(2)	65(2)	43(2)	5(2)	9(1)	19(2)
C(15)	835(2)	5254(2)	4018(2)	44(1)	43(2)	33(1)	-5(1)	13(1)	8(1)
O(15)	1432(1)	6034(2)	4140(2)	45(1)	47(1)	49(1)	-4(1)	10(1)	-4(1)
O(30)	8033(2)	7201(2)	1770(2)	61(1)	45(1)	57(1)	-10(1)	12(1)	9(1)
C(51)	5986(2)	4071(3)	8953(3)	35(1)	63(2)	60(2)	6(2)	12(1)	-11(1)
C(52)	6308(3)	3053(3)	8408(3)	50(2)	51(2)	87(3)	-5(2)	-0(2)	-15(2)
C(53)	6429(3)	3412(3)	7292(3)	60(2)	65(2)	65(2)	-27(2)	2(2)	5(2)
C(54)	5393(3)	3902(4)	6402(3)	56(2)	90(3)	60(2)	-19(2)	-1(2)	-7(2)
C(55)	5091(2)	4937(3)	6946(3)	35(1)	78(2)	56(2)	-3(2)	-1(1)	2(2)
C(56)	5954(2)	5842(3)	7263(3)	43(2)	63(2)	49(2)	5(2)	9(1)	5(1)
C(57)	6990(2)	5344(2)	8166(2)	32(1)	50(2)	45(1)	-0(1)	10(1)	-2(1)
C(58)	7278(2)	4317(3)	7597(3)	44(2)	74(2)	46(2)	-9(2)	13(1)	7(2)
C(59)	4952(2)	4574(3)	8055(3)	31(1)	85(3)	72(2)	0(2)	9(1)	-10(2)

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

*) 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 50594, the authors, and the reference to this publication.

phase determination. The parameters of the complete structure could be refined by anisotropic least-squares cycles to $R = 0.041$. The positions of the hydrogen atoms were calculated geometrically and considered isotropically in all refinements. Special X-ray operations and results are listed below:

Space group (no.) = $P2_1/c$ (14), $a = 1396.7(9)$, $b = 1177.7(6)$, $c = 1246.1(7)$ pm, $\beta = 113.82(5)°$, no. of formula units/cell = 4, calc. density = 1.408 g · cm^{-3}.

The positional and thermal parameters of the atoms of urazole **30** are given in Table 1 and the bond lengths and angles in Table 2. The perspective drawing of urazole **30** is shown in Figure 1.

Table 2. Bond lengths (pm) and bond angles (°) of urazole **30**; standard deviations are given in parentheses

C(1) - C(2)	152.9(3)	S(4) - C(5)	185.4(3)	N(9) - N(10)	145.5(3)	C(51) - C(52)	153.2(5)
C(1) - N(10)	151.1(3)	C(5) - C(6)	153.5(3)	N(9) - C(13)	140.0(3)	C(51) - C(59)	154.4(4)
C(1) - C(11)	151.0(4)	C(5) - C(51)	154.5(4)	N(10) - C(15)	141.2(3)	C(52) - C(53)	152.7(6)
C(2) - C(3)	148.8(4)	C(5) - C(57)	154.4(4)	C(11) - C(12)	132.2(4)	C(53) - C(54)	153.7(4)
C(2) - C(6)	151.1(3)	C(6) - C(7)	148.2(4)	C(13) - N(14)	138.1(3)	C(53) - C(58)	152.3(5)
C(2) - C(7)	153.0(4)	C(7) - C(8)	153.5(3)	C(13) - O(13)	120.9(3)	C(54) - C(55)	153.4(6)
C(3) - S(4)	178.8(2)	C(8) - N(9)	150.3(3)	N(14) - C(15)	138.1(3)	C(55) - C(56)	153.6(5)
C(3) - O(30)	120.0(3)	C(8) - C(12)	150.6(4)	N(14) - C(14)	145.8(3)	C(55) - C(59)	153.1(5)
				C(15) - O(15)	120.9(3)	C(56) - C(57)	154.6(3)
						C(57) - C(58)	153.5(5)

C(2) - C(1) - N(10)	105.3(2)	C(2) - C(7) - C(6)	60.2(2)	N(10) - C(15) - N(14)	106.1(2)
C(2) - C(1) - C(11)	109.2(2)	C(2) - C(7) - C(8)	108.5(2)	N(10) - C(15) - O(15)	126.3(2)
N(10) - C(1) - C(11)	106.6(2)	C(6) - C(7) - C(8)	119.2(3)	N(14) - C(15) - O(15)	127.6(2)
C(1) - C(2) - C(3)	120.5(2)	C(7) - C(8) - N(9)	104.6(2)	C(5) - C(51) - C(52)	108.6(3)
C(1) - C(2) - C(6)	122.9(2)	C(7) - C(8) - C(12)	111.3(2)	C(5) - C(51) - C(59)	109.7(3)
C(1) - C(2) - C(7)	110.3(2)	N(9) - C(8) - C(12)	106.7(2)	C(52) - C(51) - C(59)	109.6(3)
C(3) - C(2) - C(6)	112.2(2)	C(8) - N(9) - N(10)	111.1(2)	C(51) - C(52) - C(53)	110.3(3)
C(3) - C(2) - C(7)	116.7(2)	C(8) - N(9) - C(13)	116.3(2)	C(52) - C(53) - C(54)	110.0(3)
C(6) - C(2) - C(7)	58.3(2)	N(10) - N(9) - C(13)	107.4(2)	C(52) - C(53) - C(58)	109.1(3)
C(2) - C(3) - S(4)	110.0(2)	C(1) - N(10) - N(9)	111.4(2)	C(54) - C(53) - C(58)	109.2(3)
C(2) - C(3) - O(30)	127.3(2)	C(1) - N(10) - C(15)	116.5(2)	C(53) - C(54) - C(55)	109.0(3)
S(4) - C(3) - O(30)	122.7(2)	N(9) - N(10) - C(15)	107.1(2)	C(54) - C(55) - C(56)	109.8(3)
C(3) - S(4) - C(5)	96.3(1)	C(1) - C(11) - C(12)	114.0(3)	C(54) - C(55) - C(59)	109.5(3)
S(4) - C(5) - C(6)	104.8(2)	C(8) - C(12) - C(11)	114.0(2)	C(56) - C(55) - C(59)	109.5(2)
S(4) - C(5) - C(51)	110.5(2)	N(9) - C(13) - O(13)	126.2(2)	C(55) - C(56) - C(57)	109.3(2)
S(4) - C(5) - C(57)	110.2(2)	N(9) - C(13) - N(14)	106.4(2)	C(5) - C(57) - C(56)	110.3(2)
C(6) - C(5) - C(51)	112.8(2)	O(13) - C(13) - N(14)	127.4(2)	C(5) - C(57) - C(58)	110.2(2)
C(6) - C(5) - C(57)	110.1(2)	C(13) - N(14) - C(14)	124.0(2)	C(56) - C(57) - C(58)	107.8(2)
C(51) - C(5) - C(57)	108.5(2)	C(13) - N(14) - C(15)	111.9(2)	C(53) - C(58) - C(57)	110.1(3)
C(2) - C(6) - C(5)	114.6(2)	C(14) - N(14) - C(15)	123.4(2)	C(51) - C(59) - C(55)	109.8(3)
C(2) - C(6) - C(7)	61.5(2)				
C(5) - C(6) - C(7)	120.5(3)				

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