nected to a mercury pressure valve was washed with argon and charged with an appropriate amount of catalyst beads containing 1.78×10^{-2} mequiv of transition metal. The flask was placed in a thermostated bath at 97 ± 0.2 °C. The substrate (2.5 mmol) in 1.9 mL of toluene and the formic acid (50 mmol) were injected into the reaction vessel and the mixture was stirred at 97 °C for 8 h. After cooling to room temperature the liquid was withdrawn with a syringe and the solid beads were washed three times with 5-mL portions of toluene. The combined solutions were concentrated and analyzed by gas chromatography on a FID equipped Hewlett-Packard Model 7620 A instrument on either OV-17 or carbowax 20 M columns. The used catalyst beads were washed repeatedly with toluene, dried at 0.05 mm, and stored under argon to await recycling.

The kinetic measurements were carried out in modified reaction flasks in which the catalyst and reactants could be preheated separately in a thermostat oil bath (accuracy ±0.1 °C). After thermal equilibration the solid catalyst and the liquid reactants were mixed. Samples were withdrawn with an air tight syringe at intervals ranging from 10 to 60 min during 5 h. The initial rate was calculated in each case from the average of at least three experiments.

Acknowledgment. We are grateful to the United States-Israel Binational Science Foundation (BSF), Jerusalem, for financial support of this study.

Registry No. $C_6H_5CH{=}CHCOC_6H_5$, 94-41-7; $C_6H_5CH{=}CHCOC_6H_4$-4-CH_3, 4224-96-8; $C_6H_5CH{=}CHCOC_6H_4$-4-F, 399-10-0; $C_6H_5CH{=}CHCOC_6H_4$-4-Cl, 956-02-5; 4-$CH_3OC_6H_4CH{=}CHCOC_6H_5$, 959-33-1; 4-$CH_3C_6H_4CH{=}CHCOC_6H_5$, 4224-87-7; 4-$ClC_6H_4CH{=}CHCOC_6H_5$, 956-04-7; $C_6H_5CH{=}CHCOCH_3$, 122-57-6; $C_6H_5CH{=}CHCOC(CH_3)_3$, 538-44-3; $(C_6H_5)_2C{=}CHCOC_6H_5$, 849-01-4; $C_6H_5CH{=}C(C_6H_5)COC_6H_5$, 4023-77-2; $C_6H_5CH{=}CHCOOC_2H_5$, 103-36-6; $C_6H_5CH_2CH{=}CH_2$, 300-57-2; 4-$FC_6H_4CH{=}CHCOC_6H_5$, 1608-51-1; $IrCl(CO)(PPh_3)_2$, 14871-41-1; formic acid, 64-18-6; cyclooctene, 931-88-4; 2,3-dimethylcyclohex-2-enone, 1122-20-9; 3,5-diphenylcyclohex-2-enone, 10346-08-4.

Singlet Oxygenation and Triazolinedione Addition to Spirofluorene-1,3,5-cycloheptatriene

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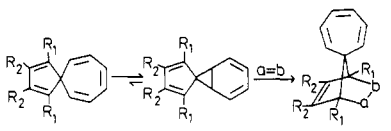
Spirocyclopentadiene-, 1,4-diphenylspirocyclopentadiene-, and 1,2,3,4-tetrachlorospirocyclopentadiene-1,3,5-cycloheptatrienes (**1a–c**) all afford urazoles **3a–c** with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) in which cycloaddition takes place at the cyclopentadiene moiety. For spirofluorene-1,3,5-cycloheptatriene (**1d**), however, cycloaddition with 4-methyl-1,2,4-triazoline-3,5-dione (MTAD) is forced to take place at the cycloheptatriene site, leading initially to the norcaradiene adduct *N*-methyl-3-spirofluorene-6,7-diazatricyclo[3.2.2.$0^{2,4}$]non-8-ene-6,7-dicarboximide (**6**), which rearranges above 0 °C into the urazole *N*-methyl-9-spirofluorene-7,8-diazabicyclo[4.3.0]nona-2,4-diene-7,8-dicarboximide (**7**). On the other hand, singlet oxygenation produces the tropilidene endoperoxide 2-spirofluorene-6,7-dioxabicyclo[3.2.2]nona-3,8-diene (**8**). Endoperoxide **8** was converted into the diepoxide *syn*-3,4:5,6-diepoxy-7-spirofluorenecycloheptene (**9**) on thermal rearrangement into a mixture of bicyclic peroxides 4-spirofluorene-6,7-dioxabicyclo[3.2.2]non-2-ene (**10**) and 4-spirofluorene-6,7-dioxabicyclo[3.2.2]nonane (**11**) via diimide reduction, into a mixture of epoxy endoperoxides *syn*- and *anti*-2,3-epoxy-4-spirofluorene-6,7-dioxabicyclo[3.2.2]non-8-enes (**12a,b**) via epoxidation with *m*-chloroperbenzoic acid, and into the epoxy enone 6,7-epoxy-3-spirofluorenecyclohepten-4-one (**13**) on triethylamine treatment. X-ray analyses of urazoles **3b** and **7** and endoperoxides **8** and **12b** confirm these structure assignments. The mechanistic implications are discussed.

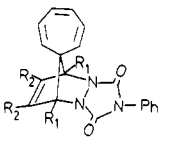
Spirocyclopentadiene-1,3,5-cycloheptatriene (**1**) exists at room temperature as the norcaradiene valence isomer **N-1**.[5] Although both 1,2-diene moieties are perfectly planar, (4 + 2) cycloaddition takes place preferentially at the cyclopentadiene site (eq 1), despite electronic or steric factors. For example, with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) the respective urazoles **3a–c** are produced.



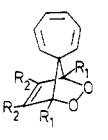
(1)

T-1 N-1 **2**

a, $R_1 = R_2 = H$
b, $R_1 = Ph$; $R_2 = H$
c, $R_1 = R_2 = Cl$
d, $R_1 + R_2$ = benzo



3



4

Attempted singlet oxygenation also proceeds via preferential attack at the cyclopentadiene moiety, but the resulting endoperoxides **4a–c** are too unstable even for spectral characterization at −60 °C.

Benzo annelation, as in the spirofluorene derivative **1d**, encumbers a (4 + 2) reaction at the cyclopentadiene site,

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(2) Universität des Saarlandes.
(3) Max-Planck-Institut für Festkörperforschung.
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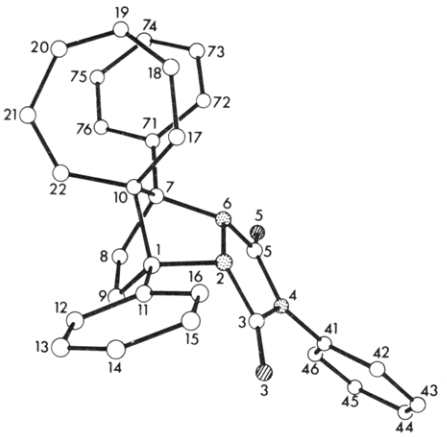
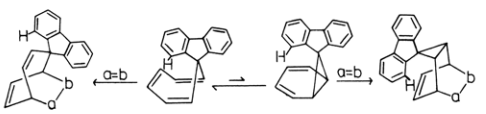


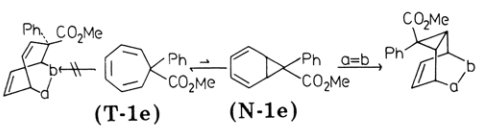
Figure 1. Perspective drawing of **3b** with the labeling of the atoms corresponding to Tables II and VI in supplementary material. White, dotted, and hatched spheres represent carbon, nitrogen, and oxygen atoms, respectively.

obliging cycloaddition to take place at the cycloheptatriene ring. In view of the tropilidene–norcaradiene valence isomerization (eq 2), in principle two cycloadducts may



T-5 T-1d N-1d N-5 (2)

result, namely the tropilidene product **T-5** or the norcaradiene adduct **N-5**. Since substantial amounts of the norcaradiene isomer **N-1d** are present even at ambient temperatures, i.e., at 37 °C 25% **N-1d** and 75% **T-1d**,[6] in view of the much greater reactivity of the planar cyclohexadiene moiety in **N-1d** vs. the puckered cycloheptatriene group in **T-1d**, exclusive formation of the norcaradiene adduct **N-5** would be expected with singlet oxygen ($^1O_2$) and triazolinedione (TAD). For example, in the case of 7-carbomethoxy-7-phenyl-1,3,5-cycloheptatriene (**1e**), for which at −81 °C both the norcaradiene and tropilidene valence isomers **N-1e** and **T-1e**, respectively, can be detected by dynamic NMR techniques,[7] exclusive formation of the norcaradiene adducts ensues with $^1O_2$ and TAD (eq 3). However, as reported in our preliminary



(T-1e) (N-1e) (3)

communication,[8] for the spirofluorene substrate **1d** singlet oxygen affords exclusively the tropilidene adduct **T-5**, while 4-methyl-1,2,4-triazoline-3,5-dione (MTAD) gives only the norcaradiene adduct **N-5**. We describe herein the full details of this divergent behavior of $^1O_2$ and TAD, together with a number of chemical transformations of the cycloadducts.

Results and Discussion

The fact that for the unsubstituted spirocyclopentadiene **1a** and its diphenyl and tetrachloro derivatives **1b** and **1c**, respectively, cycloaddition takes place at the cyclopentadiene moiety is not surprising in view of the quite general greater dienic reactivity of cyclopentadiene vs. cyclohexadiene. Since all these substrates exist in the norcaradiene form **N-1** at room temperature, cycloaddition of TAD leads to the cycloadducts **3**. The ^1H and ^{13}C NMR data (cf. Experimental Section) clearly speak for this structure assignment. In fact, an X-ray determination of the diphenyl derivative **3b** confirms rigorously that cycloaddition occurred at the cyclopentadiene ring (cf. Figure 1). Interesting to mention in this context is the fact that in the urazole **3b** the cycloheptatriene ring prefers the tropilidene form. Presumably ring strain is responsible that the norcaradiene form is energetically inaccessible.

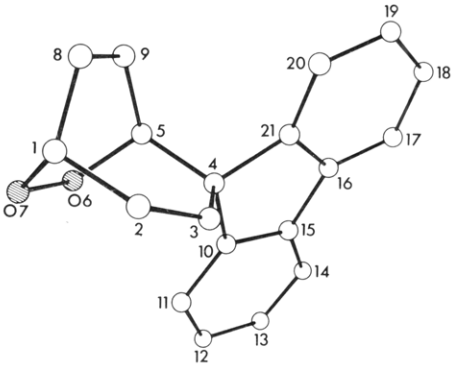


Figure 2. Perspective drawing of **8** with the labeling of the atoms corresponding to Tables III and VII in supplementary material. White and hatched spheres represent carbon and oxygen atoms, respectively.

Singlet oxygen as dienophile also attacks preferentially the cyclopentadiene moiety, although our evidence is circumstantial. Already at −78 °C, at which the photosensitized singlet oxygenations are conducted, a complex product mixture results. The infrared and ^1H NMR spectra indicate hydroxy and carbonyl groups quite analogous to the decomposition products of the endoperoxide of cyclopentadiene.[9] Attempts to convert the labile intermediary cyclopentadiene endoperoxide of the spirocyclopentadienes **1a–c** to the more stable saturated bicyclic peroxides[10] by means of diimide reduction at −60 °C failed. Again only decomposition products could be detected, indicating that already prior to reduction by diimide the extremely reactive endoperoxide rearranged.

The situation is, however, quite distinct in the case of the spirofluorene derivative **1d**. In view of the dibenzo annelation of the spirocyclopentadiene moiety, the valence isomerization equilibrium (eq 2) lies on the side of the tropilidene form **T-1d**. Electronic factors seem to be principally responsible.[6] Steric factors, as suggested by Dreiding models, seem to play a minor role. For example, the *peri*-hydrogen of the benzo ring on the endo side of the cycloheptatriene (eq 2) is in close proximity to the C_3 and C_4 atoms of the tropilidene form **T-1d**; this interaction of the corresponding atoms is also severe for the norcaradiene form **N-1d**. However, more significantly, in the activated complex of the dienophile addition this unfavorable *peri*-hydrogen interaction is still further aggrevated for the norcaradiene adduct **N-5** but relieved for the tropilidene adduct **T-5** (eq 2). Consequently, one would expect preferential dienophile addition leading to the less strained **T-5** adduct. In fact, for singlet oxygen the exclusive addition is formation of the tropilidene-type endoperoxide **8**, as confirmed by ^1H and ^{13}C NMR spectra

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(10) Adam, W.; Eggelte, H. J. *J. Org. Chem.* **1977**, *42*, 3987.

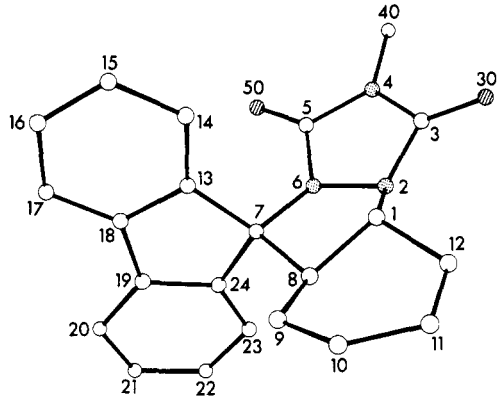
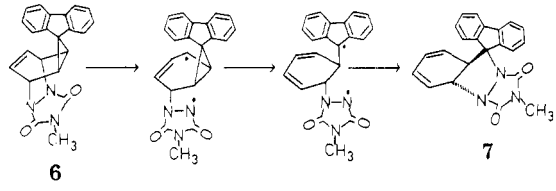


Figure 3. Perspective drawing of **7** with the labeling of the atoms corresponding to Tables IV and VIII in supplementary material. White, dotted, and hatched spheres represent carbon, nitrogen, and oxygen atoms, respectively.

(cf. Experimental Section) and X-ray analysis (Figure 2).

Surprisingly, the course of action is quite contrary with TAD as dienophile. Above 0 °C the product that is isolated is the cycloadduct **7**. While ^1H and ^{13}C NMR spectra (cf. Experimental Section) are consistent with this structure, they do not provide a definitive assignment. An X-ray determination (Figure 3) was absolutely essential for rigorous structure proof.

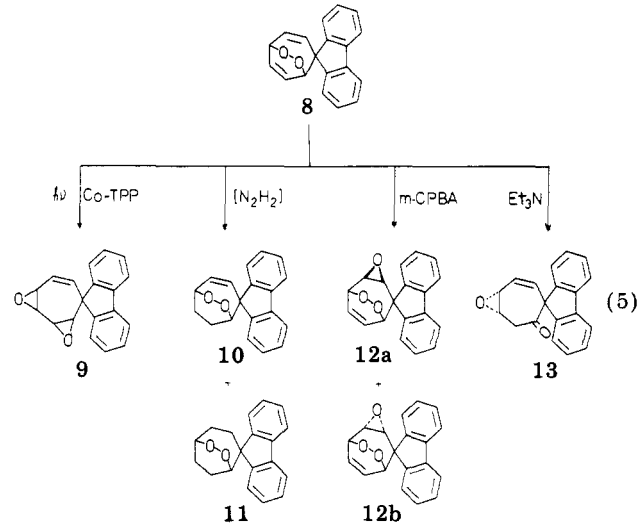
In regard to the mode of formation of urazole **7**, the low-temperature cycloaddition of 4-methyl-1,2,4-triazoline-3,5-dione (MTAD) to **1d** is important. At 0 °C in methylene chloride as solvent the ^1H NMR detects an intermediate product which exhibits the characteristic cyclopropyl resonances at δ 2.55 (complex triplet, J = 2.0 Hz), the bridgehead protons at δ 5.35 (m), and the olefinic protons at δ 6.53 (complex triplet, J = 4.0 Hz). Also the ^{13}C NMR spectrum (cf. Experimental Section) confirmed that the norcaradiene adduct **6** was formed. Efforts to isolate this labile product by low-temperature silica gel chromatography or conversion to a more stable entity by means of diimide reduction of the double bond met with failure. Only the rearranged urazole **7** could be isolated. A reasonable mechanism for the **6** → **7** rearrangement is displayed in eq 4, but it is uncertain whether diradical or dipolar intermediates are involved.



(4)

As to the mechanistic reasons for this divergent dienic reactivity of **1d** toward TAD and $^1O_2$, i.e., norcaradiene adduct **6** with TAD and tropilidene adduct **8** with $^1O_2$, one can only speculate at this time. While it is an empirical fact that TAD avoids formation of tropilidene-type adducts such as **T-5**, recently[11] a few examples have been reported. Certainly all the simple 7-substituted cycloheptatrienes, irrespective of the steric and electronic nature of the 7-substituent, lead exclusively to the norcaradiene adducts with TAD.[12] On the other hand, singlet oxygen does lead to tropilidene adducts, especially if the 7-substituent is an electron donor. Whether this differentiation in the behavior of these two dienophiles toward cycloheptatriene results from distinct cycloaddition mechanisms, e.g., concerted for TAD and dipolar intermediates for $^1O_2$,[13] cannot be answered at this stage. Speaking against this possibility is our finding[12d] that for both reactions solvent polarity is of no consequence on the product distribution. Obviously, more experimentation will be essential to understand this perplexing mechanistic problem.

The chemical transformations of the endoperoxide **8** are summarized in eq 5. Photolysis in the presence of cobalt



(5)

complex of TPP (Co–TPP) in methylene chloride at 0 °C for 2 h affords the *syn*-diepoxide **9** in ca. 100% yield. The 90-MHz ^1H NMR spectrum (cf. Experimental Section) clearly defines the proposed structure **9**. The four epoxide protons H_1–H_4 are located at δ 2.80 (m), 3.45 (m), 3.60 (m), and 3.75 (m), respectively, and the olefinic protons H_5 and H_6 at δ 6.10 (m) and 5.50 (m), respectively. The 100.61-MHz ^{13}C NMR corroborates the assignment, showing doublets at δ 51.29, 52.53, 54.54, and 62.12 for the epoxide carbons C_1–C_4 and a singlet for the quarternary C_7 carbon at δ 56.84. The olefinic carbons C_5 and C_6 are buried as doublets in the complex region of the aromatic carbons.

It is of interest to mention that the diepoxide **9** can be formed directly from **1d** by means of singlet oxygenation in the presence of Co–TPP complex.[14] Thus, at 0 °C in CH_2Cl_2 in the presence of Co–TPP the diepoxide **9** was obtained in 30% yield, providing thus a convenient direct access to such complex oxygen-functionalized derivatives of spirofluorene **1d**.

The diimide reduction[10] of **8** at 0 °C in methylene chloride, generating the diimide by treating the sodium azodicarboxylate salt with acetic acid, gave a mixture of the dihydro and tetrahydro derivatives **10** and **11**, respectively, in a total yield of 90%. Even use of a large excess of diimide reductant and repeated cycles did not lead to complete reduction of both double bonds. Fortunately, by means of silica gel chromatography the two products could be separated. Recrystallization afforded the pure substances. Elemental analyses and the ^1H and ^{13}C NMR spectra support the structure assignment of the peroxides **10** and **11**.

Epoxidation with *m*-chloroperbenzoic acid transformed **8** into a mixture of epoxyendoperoxides **12a,b** in a total

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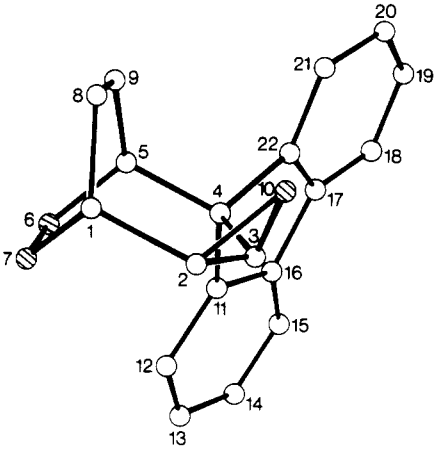
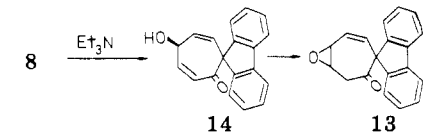


Figure 4. Perspective drawing of **12b** with the labeling of the atoms corresponding to Tables V and IX in supplementary material. White and hatched spheres represent carbon and oxygen atoms, respectively.

yield of 65%. These could be separated by means of thick-layer silica gel chromatography at ca. 25 °C, eluting with methylene chloride. After recrystallization from methylene chloride/hexane, the isomers were obtained as pure compounds in 17% and 22% yield. On the basis of the ^1H and ^{13}C NMR spectral data, which are perfectly consistent with this structure assignment, a definitive choice between these isomers was not possible. Attempts to isomerize them thermally or photochemically to the corresponding triepoxides,[15] in order to make a rigorous assignment of the stereochemistry, failed because a complex mixture of decomposition products (containing hydroxy and carbonyl functionalities) was formed. It was, however, possible to grow adequate crystals of isomer **12b** for X-ray analysis, which confirms the structure assignment (Figure 4).

Finally, base-catalyzed isomerization of the endoperoxide **8** was carried out with triethylamine in methylene chloride at ca. 25 °C, in the hope of converting the expected hydroxy dienone to the dienedione by means of manganese dioxide oxidation.[16] Instead, however, the epoxy enone **13** was isolated in 9% yield, after thick-layer silica gel chromatography and recrystallization from methylene chloride/pentane. The 400-MHz ^1H NMR permitted an unequivocal assignment in the form of the epoxy enone **13**. Thus, the methylene hydrogens $H_{1\text{-cis}}$ and $H_{1\text{-trans}}$ appear at δ 2.04 and 2.50 as a doublet of doublets. The epoxy hydrogens H_3 and H_4 are located at δ 3.44 (ddd) and 5.75 (dd). The olefinic hydrogens H_5 and H_6 occur at δ 6.40 (dd) and 5.80 (d), respectively. Decoupling experiments confirm these assignments. Also the 100.61-MHz ^{13}C NMR spectrum corroborates structure **13**. For example, the methylenic carbon C_3 is located at δ 32.66 as a triplet, the epoxy carbons C_3 and C_4 at δ 46.81 and 88.84 as doublets, the quarternary carbon C_7 at δ 66.60 as a singlet and the carbonyl carbon also as a singlet at δ 176.53. The olefinic carbons C_3 and C_4 are buried as doublets in the complex aromatic region.

As to its mode of formation, clearly the base-catalyzed isomerization initially must have afforded the expected hydroxy dienone **14** (eq 6). However, facile intramolecular Michael addition transforms **14** into **13**.



(6)

Experimental Section

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. A Beckman Acculab 4 or a Perkin-Elmer 157G spectrophotometer were used to record the infrared spectra. The ^1H NMR spectra were taken on a 90 MHz Varian EM 390 and the ^{13}C NMR spectra on a Bruker 100.61 MHz spectrometer. 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 and 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 workup 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.

General Procedure for the Addition of 4-Substituted-1,2,4-triazoline-3,5-dione to the Spirocyclopentadienes 1a–c. A 50-mL round-bottomed flask was charged with 0.5 mmol of the spirocyclopentadienes **1a–c** in 20 mL of methylene chloride. While stirring at ca. 20–25 °C, 0.5 mmol of TAD was added portionwise over a period of 20 min. The mixture was stirred overnight, the solvent roto-evaporated, and the solid residue chromatographed, using a 9:1 ratio of dichloromethane and ether. Final recrystallization afforded the pure urazoles **3a–c**. The physical constants, yields, and spectral and analytical data are summarized below for the individual cases.

***N*-Phenylspiro[cycloheptatriene-7,7′-[2,3]-diazabicyclo-[2.2.1]hept]-2′-ene-2′,3′-dicarboximide (3a)**, mp 85 °C, was obtained in 22% yield after silica gel chromatography, eluting with methylene chloride: IR (CCl_4) 3050, 3010, 1775, 1720, 1610, 1510 cm^{-1}; ^1H NMR ($CDCl_3$) 60 MHz δ 4.75 (m, 2 H), 5.21 (m, 1 H), 5.80 (m, 1 H), 6.45 (m, 4 H), 6.78 (m, 2 H), 7.47 (m, 5 H). Anal. Calcd for $C_{19}H_{15}N_3O_2$ (317.3): C, 71.80; H, 4.73; N, 13.20. Found: C, 71.47; H, 4.63; N, 12.96.

***N*-Phenyl-1,4-diphenylspiro[cycloheptatriene-7,7′-[2,3]-diazabicyclo[2.2.1]hept]-5′-ene-2′,3′-dicarboximide (3b)**, mp 176–177 °C (granular solid from methylene chloride/*n*-pentane), was obtained in 88% yield: IR (KBr) 3040, 3010, 1790, 1730, 1600, 1500, 1450, 1400, 1245, 1145, 1050, 1020, 925, 875 cm^{-1}; ^1H NMR ($CDCl_3$) 90 MHz δ 5.13 (br d, 1 H, J = 11.1 Hz), 5.45 (t, 2 H, J = 3.6 Hz), 5.80 (br d, 1 H), 5.96–6.00 (m, 2 H), 6.7 (s, 2 H), 7.3–7.8 (m, 15 H); ^{13}C NMR ($CDCl_3$) 22.25 MHz δ 73.71 (s), 85.64 (s), 120.02, 122.43, 125.24, 127.68, 128.00, 128.36, 128.80, 129.06, 129.70, 129.87, 131.50, 132.05, 134.25, 157.37. Anal. Calcd for $C_{31}H_{23}N_3O_2$ (469.2): C, 79.29; H, 4.94; N, 8.95. Found: C, 79.24; H, 5.34; N, 8.88.

***N*-Phenyl-1,4,5,6-tetrachlorospiro[cycloheptatriene-7,7′-[2,3]-diazabicyclo[2.2.1]hept]-5′-ene-2′,3′-dicarboximide (3c)**, mp 165–167 °C (needles from methylene chloride/pentane), was obtained in 85% yield: IR (KBr) 3040, 3025, 1800, 1750, 1595, 1505, 1400, 1300, 1220, 1175, 1160, 1085, 1025, 990, 880, 860, 800 cm^{-1}; ^1H NMR ($CDCl_3$) 90 MHz δ 4.9 (m, 1 H), 5.6 (m, 1 H), 6.5 (m, 4 H), 7.4 (m, 5 H); ^{13}C NMR ($CDCl_3$) 22.25 MHz δ 92.42, 115.51, 119.95, 125.01, 125.71, 128.71, 129.33, 129.46, 130.24, 130.76, 131.05, 131.78, 132.13. Anal. Calcd for $C_{19}H_{11}Cl_4N_3O_2$ (453.0): C, 50.33; H, 2.45; N, 9.27. Found: C, 50.14; H, 2.55; N, 9.29.

***N*-Methylspiro[fluorene-9,9′-[6,7]-diazatricyclo-[3.2.2.0^{2,4}]non]-8′-ene-6′,7′-dicarboximide (6)** was obtained in 70% yield as a thermally labile substance by running the cycloaddition at 0 °C for 25 min (fast decoloration of the TAD color) and silica gel chromatography at 0 °C, eluting with a 9:1 mixture of methylene chloride/ether: ^1H NMR ($CDCl_3$) 90 MHz at 0 °C, δ 2.55 (t′, 2 H), 2.95 (s, 3 H), 5.35 (m, 2 H), 6.53 (t′, 2 H), 6.8–7.9 (m, 8 H, J = 2.0, 4.0 Hz). ^{13}C NMR ($CDCl_3$) 100.61 MHz at −20 °C, δ 25.75 (d), 31.91 (q), 38.67 (s), 53.93 (d), 119.36, 120.23, 124.97, 125.60, 126.30, 127.16, 128.08, 129.36, 130.39, 135.70, 137.19, 140.31, 143.10, 148.05, 158.51.

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***N*-Methylspiro[fluorene-9,9′-[7,8]-diazabicyclo[4.3.0]nona]-2′,4′-diene-7′,8′-dicarboximide (7)**, mp 215–217 °C (granular solid from methylene chloride/pentane), was obtained in 70% yield by running the cycloaddition at 20–25 °C for 2 h. Alternatively, on allowing a solution of the urazole **6** in methylene chloride to stand at 20–25 °C for 2 h afforded the rearranged urazole **7**. Silica gel chromatography at 20–25 °C eluting with a 9:1 mixture of methylene chloride/ether gave the pure product: IR (KBr) 3020, 2990, 1750, 1725, 1445, 1375, 1305, 1260, 1040, 970, 950, 805 cm^{-1}; ^1H NMR ($CDCl_3$) 400 MHz δ 3.00 (s, 3 H), 3.95 (d, 1 H), 4.80 (d, 1 H), 5.25 (d, 1 H), 5.89 (ddd, 1 H), 6.19 (ddd, 1 H), 6.73 (d, 1 H, J = 2.0, 2.8, 4.0, 5.0, 9.7, 18.0 Hz); ^{13}C NMR ($CDCl_3$) 100.61 MHz δ 25.34 (q), 56.48 (d), 60.12 (d), 71.92 (s), 120.45, 120.75, 123.24, 124.24, 124.72, 126.24, 127.01, 127.21, 127.92, 128.55, 129.79, 139.88, 140.68, 141.68, 152.29, 156.89. Anal. Calcd for $C_{22}H_{17}N_3O_2$ (355.1): C, 74.34; H, 4.82; N, 11.83. Found: C, 74.09; H, 4.94; N, 11.96.

Spiro[fluorene-9,2′-[6,7]-dioxabicyclo[3.2.2]nona]-3′,8′-diene (8) via Singlet Oxygenation of Cycloheptatriene 1d. A 50-mL pear-shaped flask, provided with a rubber septum, was charged with 100 mg (0.41 mmol) of cycloheptatriene **1d** and 5 mg of tetraphenylporphine (TPP) in 15 mL of metal-free methylene chloride. While cooling at 0 °C by means of an ice bath, a vivid stream of dry oxygen gas was allowed to bubble through the solution via a syringe needle connected to a Teflon tube reaching to the bottom of the flask and another syringe needle as gas vent. Irradiation was performed externally with a 150-W sodium street lamp, monitoring the progress of singlet oxygenation by TLC and peroxide test. After ca. 4 h the cycloheptatriene **1d** was consumed, the solvent roto-evaporated, and the solid residue chromatographed, eluting with a 2:1 mixture of methylene chloride/*n*-pentane. Recrystallization from methylene chloride-pentane afforded colorless needles, mp 150–152 °C, in 80% yield: IR (KBr) 3050, 3025, 2925, 1600, 1450, 1360, 1340, 980, 910, 870 cm^{-1}; ^1H NMR ($CDCl_3$) 400 MHz δ 4.16 (d, 1 H), 4.90 (t, 1 H), 5.23 (d, 1 H), 6.36 (dd, 1 H), 6.43 (t, 1 H), 7.02 (t, 1 H), 7.2–8.0 (m, 8 H, J = 2.0, 7.0, 7.2, 9.0, 10.5 Hz); ^{13}C NMR ($CDCl_3$) 22.25 MHz δ 61.87 (s), 73.79 (d), 81.63 (d), 119.69, 120.16, 125.85, 126.96, 127.49, 128.12, 130.75, 135.57, 136.06, 140.08, 140.86, 142.65, 147.19. Anal. Calcd for $C_{19}H_{14}O_2$ (274.3): C, 83.19; H, 5.14. Found: C, 82.92; H, 5.22.

***syn*-3,4:5,6-Diepoxyspiro[fluorene-9,7′-cycloheptene] (9)** was obtained in 80% yield by using the above singlet oxygenation procedure but employing the cobalt complex of TPP as sensitizer. Alternatively, this diepoxide can be obtained in ca. 100% yield by irradiating externally a solution of 500 mg (1.82 mmol) of endoperoxide **8** in methylene chloride and the cobalt complex of TPP at 0 °C with a 150-W sodium street lamp for 2 h, monitoring the consumption of the endoperoxide by TLC and peroxide test. The solvent is roto-evaporated and the dark residue submitted to preparative layer chromatography on silica gel, eluting with a 3:1 mixture of methylene chloride/hexane. Recrystallization from methylene chloride–hexane afforded the pure diepoxide **9**: mp 138–140 °C (needles); IR (KBr) 3080, 3025, 3000, 2975, 1475, 1450, 1390, 1290, 1150, 1120, 1000, 960, 915 cm^{-1}; ^1H NMR ($CDCl_3$) 90 MHz δ 2.80 (dd, 1 H), 3.45 (t, 1 H), 3.60 (t, 1 H), 3.75 (t, 1 H), 5.50 (dd, 1 H), 6.10 (dd, 1 H), 7.0–8.6 (m, 8 H, J = 1.3, 3.7, 3.8, 3.9, 4.0, 11.7 Hz); ^{13}C NMR ($CDCl_3$) 100.61 MHz δ 51.29 (d), 52.53 (d), 54.54 (d), 56.84 (s), 62.12 (d), 120.06, 120.41, 124.72, 124.90, 125.43, 128.06, 128.34, 128.61, 128.75, 133.83. Anal. Calcd for $C_{19}H_{14}O_2$ (274.1): C, 83.19; H, 5.14. Found: C, 82.98; H, 5.06.

Spiro[fluorene-9,4′-[6,7]-dioxabicyclo[3.2.2]non]-2′-ene (10) and 4-Spiro[fluorene-9,2′-[6,7]-dioxabicyclo[3.2.2]nonane] (11) via Diazene Reduction of Endoperoxide 8. A dry, 100-mL, one-necked, round-bottomed flask, provided with pressure-equalizing dropping funnel and nitrogen inlet and outlet, was charged with 300 mg (1.1 mmol) of endoperoxide **8** and 970 mg (5 mmol) of dipotassium azodicarboxylate in 25 mL of methylene chloride. Under a nitrogen atmosphere, while cooling by means of an ice bath and stirring rigorously, a solution of 594 mg (9.9 mmol) of acetic acid in 10 mL of methylene chloride was added slowly within 1 h. After an additional 30 min of stirring, the suspension was allowed to warm up to 20–25 °C and 10–20 mL of water was added. The contents were transferred into a separatory funnel and the organic layers were collected, washed with 10 mL of 5% aqueous sodium bicarbonate, and dried. Roto-evaporation of the solvent afforded a mixture of the endoperoxides **10** and **11**. These were separated with the help of thick layer chromatography on silica gel, eluting with a 2:1 mixture of methylene chloride–hexane. Endoperoxide **10** eluted before **11**. Final purification was achieved through recrystallization.

Endoperoxide 10 was obtained in 60% yield: mp 142–143 °C (plates from methylene chloride/pentane); IR (CCl_4) 3080, 3050, 3000, 2950, 1480, 1450, 1215, 1075, 995, 930, 895 cm^{-1}; ^1H NMR ($CDCl_3$) 90 MHz δ 2.0–2.7 (m, 4 H), 3.7 (td, 1 H), 4.85 (m, 1 H), 5.45 (dd, 1 H), 6.2 (dd, 1 H), 7.2–8.1 (m, 8 H, J = 1.5, 6.3, 8.8 Hz); ^{13}C NMR ($CDCl_3$) 100.61 MHz δ 20.02 (t), 23.42 (t), 65.20 (s), 75.43 (d), 81.77 (d), 119.43, 120.29 (d), 125.50, 127.06, 127.65, 128.06, 128.30, 128.90, 133.40, 135.37, 139.61. Anal. Calcd for $C_{19}H_{16}O_2$ (276.3): C, 82.57; H, 5.84. Found: C, 82.36; H, 5.68.

Endoperoxide 11 was obtained in 36% yield: mp 119–120 °C (plates from methylene chloride/*n*-pentane); IR (KBr) 3050, 3025, 2970, 2960, 2930, 1475, 1450, 1440, 1345, 1300, 1245, 1210, 1155, 1100, 1065, 1040, 960, 930, 880 cm^{-1}; ^1H NMR ($CDCl_3$) 90 MHz δ 1.6–2.9 (m, 8 H), 3.60 (br s, 1 H), 4.8 (br t, 1 H), 7.1–8.3 (m, 8 H); ^{13}C NMR ($CDCl_3$) 100.61 MHz δ 19.11 (t), 20.04 (t), 30.93 (t), 33.40 (t), 59.99 (s), 76.50 (d), 81.46 (d), 119.45, 119.99, 124.48, 127.03, 127.21, 127.51, 127.88, 128.03, 139.37. Anal. Calcd for $C_{19}H_{18}O_2$ (278.3): C, 81.97; H, 6.51. Found: C, 82.05; H, 6.50.

***syn*- and *anti*-2,3-Epoxyspiro[fluorene-9,4′-[6,7]-dioxabicyclo[3.2.2]non]-8′-enes (12a,b) via Epoxidation of Endoperoxide 8.** A 50-mL, round-bottomed flask was charged with 300 mg (1.09 mmol) of endoperoxide **8** in 15 mL of chloroform and ca. 50 mg of solid sodium bicarbonate. While stirring, to the suspension was added over a period of 1 h 1.5 g (8.72 mmol) of *m*-chloroperbenzoic acid and the solution was allowed to stir for 48 h. The reaction mixture was transferred into a separatory funnel and washed twice with 10 mL of 10% aqueous sodium bicarbonate, the combined bicarbonate extracts were washed with 3 × 20 mL ether, and the combined organic layers were washed with 20 mL water and dried. On roto-evaporation of the solvent and thick layer chromatography on silica gel the epoxide **12a** eluted with methylene chloride before the epoxide **12b**. Final purification was achieved through recrystallization.

Epoxide 12a was obtained in 17% yield: mp 182–184 °C (granular solid from methylene chloride/pentane); IR (KBr) 3050, 2990, 2960, 1600, 1485, 1450, 1300, 1260, 1205, 1150, 1090, 1025, 995, 900, 845 cm^{-1}; ^1H NMR ($CDCl_3$) 400 MHz δ 2.93 (d, 1 H), 3.56 (t, 1 H), 3.95 (d, 1 H), 5.22 (br t, 1 H), 6.68 (ddd, 1 H), 6.90 (dd, 1 H), 7.25–8.20 (m, 8 H, J = 1.3, 2.0, 3.8, 7.0, 7.5, 9.0 Hz); ^{13}C NMR ($CDCl_3$) 100.61 MHz δ 55.34 (d), 55.92 (s), 57.74 (d), 72.39 (d), 80.89 (d), 119.47 (d), 120.32 (d), 125.92, 127.09, 127.78, 128.29, 128.47, 128.71, 129.59, 131.93, 139.76; exact mass by high-resolution MS, 290.09429; found, 290.0943.

Epoxide 12b was obtained in 22% yield: mp 182–184 °C (granular solid from methylene chloride/pentane); IR (KBr) 3025, 3000, 2990, 2950, 1600, 1465, 1445, 1350, 1295, 1275, 1252, 1150, 960, 905, 890, 825 cm^{-1}; ^1H NMR ($CDCl_3$) 400 MHz δ 3.02 (dd, 1 H), 3.63 (dd, 1 H), 3.87 (m, 1 H), 5.40 (m, 1 H), 6.55 (ddd, 2 H), 7.2–8.1 (m, 8 H, J = 2.0, 2.5, 4.0, 6.0, 6.5, 7.8, 9.5 Hz); ^{13}C NMR ($CDCl_3$) 100.61 MHz δ 52.72 (d), 56.35 (s), 59.64 (d), 76.70 (d), 80.50 (d), 119.83 (d), 120.01 (d), 127.23, 127.51, 127.65, 127.79, 128.57, 128.72, 128.77, 140.00; exact mass by high-resolution MS, 290.09429; found, 290.0943.

6,7-Epoxyspiro[fluorene-9,3′-cyclohept]-1-en-4-one (13). A 25-mL, round-bottomed flask was charged with 150 mg (0.550 mmol) endoperoxide **8** in 20 mL dry methylene chloride. While stirring at 20–25 °C 61 mg (0.60 mmol) of dry (freshly distilled from potassium hydroxide) triethylamine in 5 mL of methylene chloride was added dropwise over a period of ~10 min. The dark reaction mixture was allowed to stir overnight. After roto-evaporation of the solvent the dark residue was submitted to preparative-layer chromatography on silica gel, eluting with a 3:1 mixture of methylene chloride/hexane. The pure epoxy enone **13** was obtained in 9% yield as colorless needles: mp 154–156 °C (after several recrystallizations from methylene chloride/*n*-pentane); IR (KBr) 3035, 3005, 2985, 2975, 1775, 1485, 1450, 1360, 1350, 1300, 1165, 1050, 1020, 995, 910, 893, 855 cm^{-1}; ^1H NMR ($CDCl_3$) 400 MHz δ 2.04 (dd, 1 H), 2.50 (dd, 1 H), 3.44 (ddd, 1 H), 5.75 (dd, 1 H), 5.80 (d, 1 H), 6.40 (dd, 1 H), 7.2–7.8 (m, 8 H, J = 2.4, 3.0, 5.5, 9.4, 10.2, 18.6 Hz); ^{13}C NMR ($CDCl_3$) 100.61 MHz δ 32.66 (t), 46.81 (d), 66.60 (s), 88.84 (d), 120.08, 120.38, 123.45,

126.00, 127.92, 128.03, 128.21, 128.69, 130.55, 140.34, 140.77, 176.53 (s). Anal. Calcd for $C_{19}H_{14}O_2$ (274.1): C, 83.19; H, 5.14. Found: C, 83.21; H, 5.10.

X-ray Crystallography of Urazoles 3b and 7 and Endoperoxides 8 and 12b. The crystals were optically centered on a Syntex $P\bar{1}$ four circle diffractometer. The intensities of all reflections were measured according to the ω technique (Mo Kα, graphite monochromator) using a scan range of 1° and a scan speed between 0.5 and 24.0 deg min^{-1} as a function of the intensities of the reflections. In the range between $3.0° \leq 2\theta \leq 55.0°$ 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. All structures were solved by the direct phase determination. The parameters of the complete structures could be refined by anisotropic least-squares cycles to the given R values. The positions of the hydrogen atoms were calculated geometrically and considered isotropically in all refinements. Special X-ray operations and results are listed in Table I, the positional and thermal parameters in Tables II–V, and the bond lengths and angles in Tables VI–IX, respectively (see supplementary material). We have omitted the presentation of the structure factors, which can be obtained upon request.

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Registry No. **T-1a**, 36673-54-8; **T-1b**, 36673-53-7; **T-1c**, 36677-51-7; **T-1d**, 33604-51-2; **3a**, 82238-71-9; **3b**, 82238-72-0; **3c**, 82238-73-1; **6**, 82238-75-3; **7**, 88980-94-3; **8**, 82238-76-4; **9**, 88969-12-4; **10**, 88969-13-5; **11**, 82238-77-5; **12a**, 88969-14-6; **12b**, 89015-99-6; **13**, 88969-15-7; PTAD, 4233-33-4; MTAD, 13274-43-6; O_2, 7782-44-7.

Supplementary Material Available: Crystal data of **3b**, **7**, **8**, and **12b**, atomic coordinates, thermal parameters, bond lengths, and bond angles in Tables I–IX (9 pages). Ordering information is given on any current masthead page.

Structures of Pyridines Obtained in the Aluminum Bromide Mediated Cyclocongregation of Acetylenes with Cyanoformates

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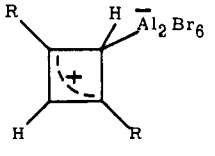
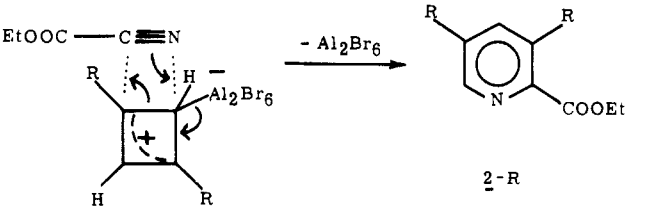
It is shown that the product of the title reaction with *tert*-butylacetylene and ethyl cyanoformate is not ethyl 3,5-di-*tert*-butyl-2-picolinate as reported in the recent literature but rather the 4,5-isomer. Varying yields of the 4,6-isomer are also obtained. The NMR spectra described for the 3,5-dimethyl analogue likewise suggest a misassignment of structure in that case. A revised mechanism is tentatively given for these reactions.

For reasons we hope to describe in a future publication, we have found ourselves in need of substantial quantities of 3,5-di-*tert*-butylpyridine. The recently described[1] facile synthesis of ethyl 3,5-di-*tert*-butyl-2-picolinate seemed to offer the best approach; it is one of a series of reports describing the multifaceted chemistry of aluminum bromide complexes of acetylenes. Thus, when *tert*-butylacetylene is treated with 1 equiv of aluminum bromide in methylene chloride at −85 °C, a 2:2 complex is produced, the ^1H and ^{13}C NMR spectra of which strongly suggest structure **1**-*t*-Bu. Complexes of this sort react with many

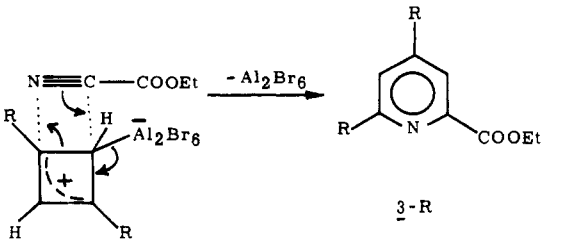


1-R

substrates to give rise to a remarkable variety of products; a summary of this chemistry was included in a recent publication.[2] In the case of activated nitriles such as ethyl cyanoformate, for example, cycloaddition to **1**-*t*-Bu occurs to give a product described as **2**-*t*-Bu. Under the same conditions, the propyne complex **1**-Me was reported to lead to the two cycloaddition products **2**-Me and **3**-Me. It was postulated that these two products were formed by the addition of the nitrile with, effectively, either the nitrogen or carbon atom displacing the aluminum:



2-R



3-R

The evidence offered for the structure of these products—obtained in analytical purity—was based on the

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