Multistep Reversible Redox Systems. 48.[1] 1,3-Bisquinone Methide Cyclobutanes and Related Bicyclo[1.1.0]butanes: Syntheses and Redox Properties

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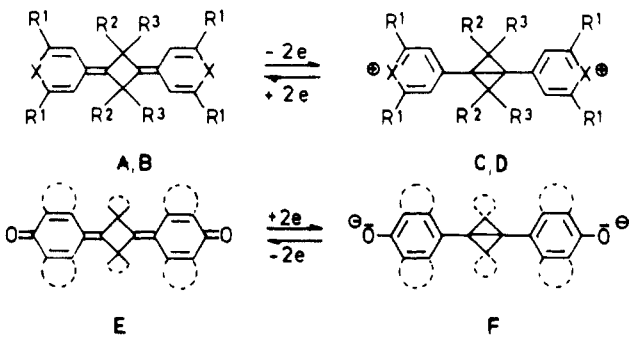
A new approach to quinone methides is presented, which starts from quinone diazides and thioketones. Together with some model compounds, 1,3-bisquinone methide cyclobutanes **23**, **25**, and **37** were synthesized. Reduction with sodium transforms these quinoid compounds into bicyclo[1.1.0]butanes with phenolate groups in the 1,3-positions. These phenolates can be trapped as silyl ethers **40–43**. After hydrolysis, reoxidation to the starting material readily occurs. These examples demonstrate that suitably substituted 1,3-bis(methylene)cyclobutanes and bicyclo[1.1.0]butanes constitute reversible redox systems of type E/F. Spectral properties, especially UV spectra of **23**, **25**, and **37** together with those of **40–43**, are discussed in terms of possible 1,3-interactions.

Recently we have demonstrated that 1,3-bis(methylene)cyclobutanes of type A and B are reversibly transformed into the corresponding bicyclobutanes C[3] and D[4] by removal of two electrons. In these unique reactions,



A and C, X = NCO_2R (ref 3); B and D, X = O (ref 4)

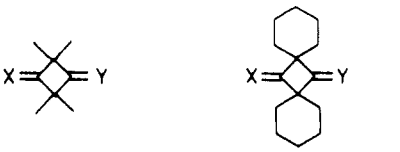
the resonance energy of the heteroaromatics formed pays at least partly for the higher strain energy of the bicyclobutane ring.

Subsequently, we looked for a system of similar energetic balance in which, however, the oxidation and reduction steps are reversed. According to the transformation E → F, 1,3-bisquinomethide cyclobutanes should serve as suitable examples, although bicyclobutanes F may rearrange rather easily into the corresponding butadienes due to their donor substituents.[5]

This paper describes the synthesis of type E cyclobutanes and related compounds, including also derivatives of F. Physical properties of series E and F are compared together with those of related compounds from the literature. Electrochemical data will be published elsewhere.

Results and Discussion

Synthesis of 1,3-Bisquinone Methide Cyclobutanes. Selection of the Synthetic Route. From the numerous approaches to 1,3-disubstituted cyclobutanes,[6] we selected the route starting with the readily accessible nonenolizable 1,3-diones **1** and **4**.[7] However, the seemingly straightforward reaction of **1** or **4** with **7** (Nu^-, e.g., (alkoxyphenyl)lithium) does not yield **9**, the precursor of the desired quinone methides. As in several other cases,[8] the intermediates **8** suffer ring opening to enolate **10** much faster than addition of a second nucleophile to give the diadduct **9**; double Schiff bases derived from **1** are known.[8]



1: X = Y = O
2: X = S, Y = O
3: X = Y = S

4: X = Y = O
5: X = S, Y = O
6: X = Y = S

As a nonnucleophilic approach to the two carbon–carbon double bonds needed for type E, a route was envisaged that capitalizes on the well-developed reaction sequence (Scheme I). The 1,3,4-thiadiazolines **13**, obtained from diazoalkanes **11** and thioketones **12**, decompose thermally, forming the sulfur ylide **15**, which can be trapped by dipolarophiles, dimerize, or collapse to thiiranes **16**,[9] as shown by Staudinger.[10] Extrusion of sulfur finally yields olefins **17**. The whole sequence has been turned into a powerful synthesis of tetrasubstituted olefins by Barton et al.[11] and Kellog et al.[12] Dipole **15** may also be produced by addition

(1) Paper 48 in the series "Multistep Reversible Redox Systems". Preceding paper, XLVII: Aumüller, A.; Hünig, S. *Liebigs Ann. Chem.* **1986**, 165.

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(4) Hesse, K.; Hünig, S. *Liebigs Ann. Chem.* **1985**, 740.

(5) The thermolability of substituted bicyclo[1.1.0]butanes parallels those of the corresponding cyclobutanes. Cf.: Willcott, M. R.; Cargill, R. L.; Sears, A. B. In *Progress in Physical Organic Chemistry*; Streitwieser, A., Jr., Taft, R. W., Eds.; Wiley-Interscience: New York, 1972; Vol. 9, p 25f.

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(7) Cf.: Brady, W. T. In *The Chemistry of Ketenes, Allenes and Related Compounds*; Patai, S., Ed.; Interscience: New York, 1980.

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(9) Schönberg, A.; König, B.; Singer, E. *Chem. Ber.* **1967**, *100*, 767. Huisgen, R.; Kalwinsch, I.; Xingya, L.; Gottstein, J. *J. Am. Chem. Soc.* **1981**, *103*, 7032 (cf.: Huisgen, R., et al. *Bull. Soc. Chim. Belg.* **1984**, *93*, 511). Kalwinsch, I.; Huisgen, R. *Tetrahedron Lett.* **1981**, *22*, 3941. Huisgen, R.; Xingya, L. *Tetrahedron Lett.* **1983**, *24*, 4185; *Heterocycles* **1983**, *20*, 2363 and earlier literature cited therein.

(10) Staudinger, H.; Siegwart, J. *Helv. Chim. Acta* **1920**, *3*, 833.

(11) Barton, D. H.; Guziec, F. S., Jr.; Shahak, J. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1794.

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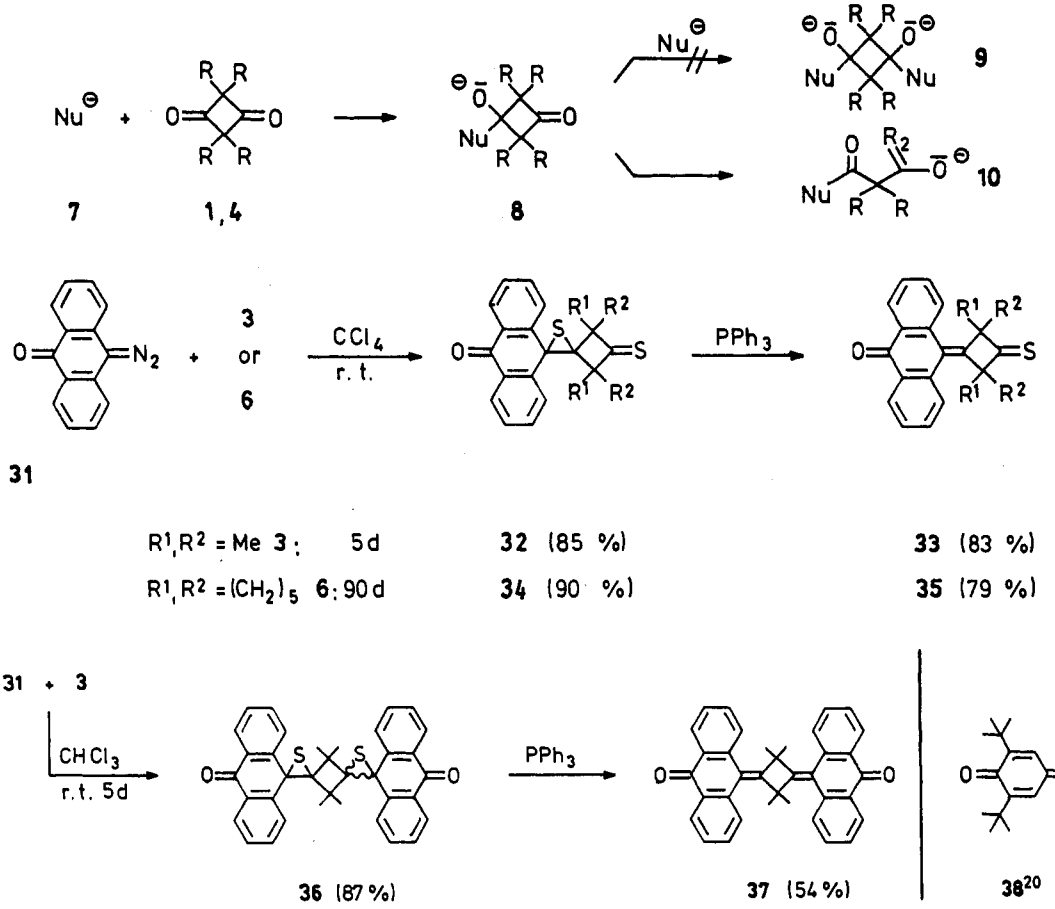

of carbene **14** (obtained from **11** by photolysis) to **12**.[13]

The desired thioketones **2**, **3**, **5**, and **6**, being stable because of peralkylation, are easily synthesized by treating diketones **1** and **4** with hydrogen sulfide/hydrogen chloride.[14]

The reaction sequence **11** + **12** → **13** → **16** has been successfully applied to diazomethane and dithioketones **2** and **3**, which cycloadd very rapidly at 0 °C.[14c]

For our purpose, diazoalkanes had to be replaced by diazoquinones, which to the best of our knowledge have not yet been reacted with thioketones. Only for 9,10-diazoanthraquinone (**31**) have 1,3-dipolar additions been performed with maleate esters[15] and benzyne[16] as dipolarophiles.

Reaction of Diazoquinones with Thiocyclobutanone Derivatives. Diazoquinones **18** and **31** (*tert*-butyl groups in **18** stabilize the expected quinone methide[17]) form solutions in carbon tetrachloride that are stable for several weeks under exclusion of light. Only after addition of thioketones **2**, **3**, or **6** is nitrogen gas slowly evolved. This behavior points to a [3 + 2] cycloaddition in which the product of type **13** rapidly loses nitrogen. With the exceptions of **32**, **34**, and **36** (cf. also **27** and **28**), even the thiiranes formed are thermally labile since from diazoquinone **18** only olefins **20**–**25** were isolated (Scheme II).

Thiones **2**, **3**, and **19** and even more so thione **6** react sluggishly with diazoquinone **18**. From **19** and **2** the expected monosubstitution products **20** and **21** are produced. With dithiones **3** and **6**, the addition of a second molecule of **18** proceeds more slowly than that of the first; in both cases monoquinone methides **22** and **24** can easily be isolated at shorter reaction times. In **6** the thiono groups are shielded so strongly that even after 5 months and with 2 equiv of **18** only a 3.7% yield of **25** was obtained despite its extremely low solubility. In refluxing hexafluorobenzene (avoids side products), the yield of **25** could be raised to 22%.

As expected from its reaction with **3**,[14c] diazomethane attacks **22** rapidly at 0 °C to form the 1,3-dipolar cycloadduct **26**. By thermal extrusion of nitrogen, thiirane **27** is smoothly formed, which through abstraction of sulfur by triphenylphosphine[17] provides the unsymmetrically substituted cyclobutane **30**. The related compound **29** is similarly produced from **22** and diphenyldiazomethane with thiirane **28** as a stable intermediate.

Even the bulky anthraquinone methide **31** adds to dithiones **3** and **6**. Here a 1:1 stoichiometry provides high yields of 1:1 products whereas a 2:1 stoichiometry furnishes equally well the 2:1 products. These products are mono- (**32**, **34**) or dithiiranes (**36**), which are easily transformed into quinone methides **33**, **35**, and **37**, respectively, by extrusion of sulfur.

As with dithiiranes derived from **3** or **6** and diazomethane,[14c] syn/anti isomers of **36** are to be expected. Whereas with the parent compounds syn/anti ratios of ca. 3:7 are reported,[14c,18] with **36** a ratio of 9:1 is observed. The

(12) Kellog, R. M.; Wassenaar, S.; Buter, J. *J. Org. Chem.* **1972**, *37*, 4045.
(13) McGimpsey, W. G.; Scaiano, J. C. *Tetrahedron Lett.* **1986**, *27*, 547.
(14) (a) Lipscomb, R. D. U.S. Patent 3 297 769, Jan. 10, 1967; *Chem. Abstr.* **1967**, *66*, 65180r. (b) Elam, E. U.; Davis, H. E. *J. Org. Chem.* **1967**, *32*, 1562. (c) Elam, E. U. Br. Patent 1 137 377 Dec. 18, 1968; *Chem. Abstr.* **1969**, *70*, 96253d. (d) Krapcho, A. P.; Rao, D. R.; Silvon, M. P.; Abegaz, B. *J. Org. Chem.* **1971**, *36*, 3885.
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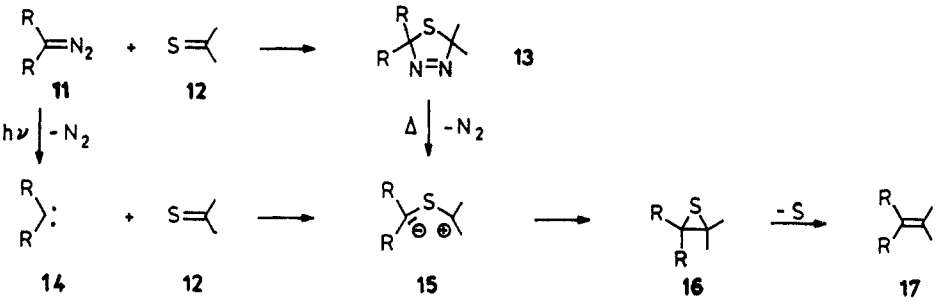
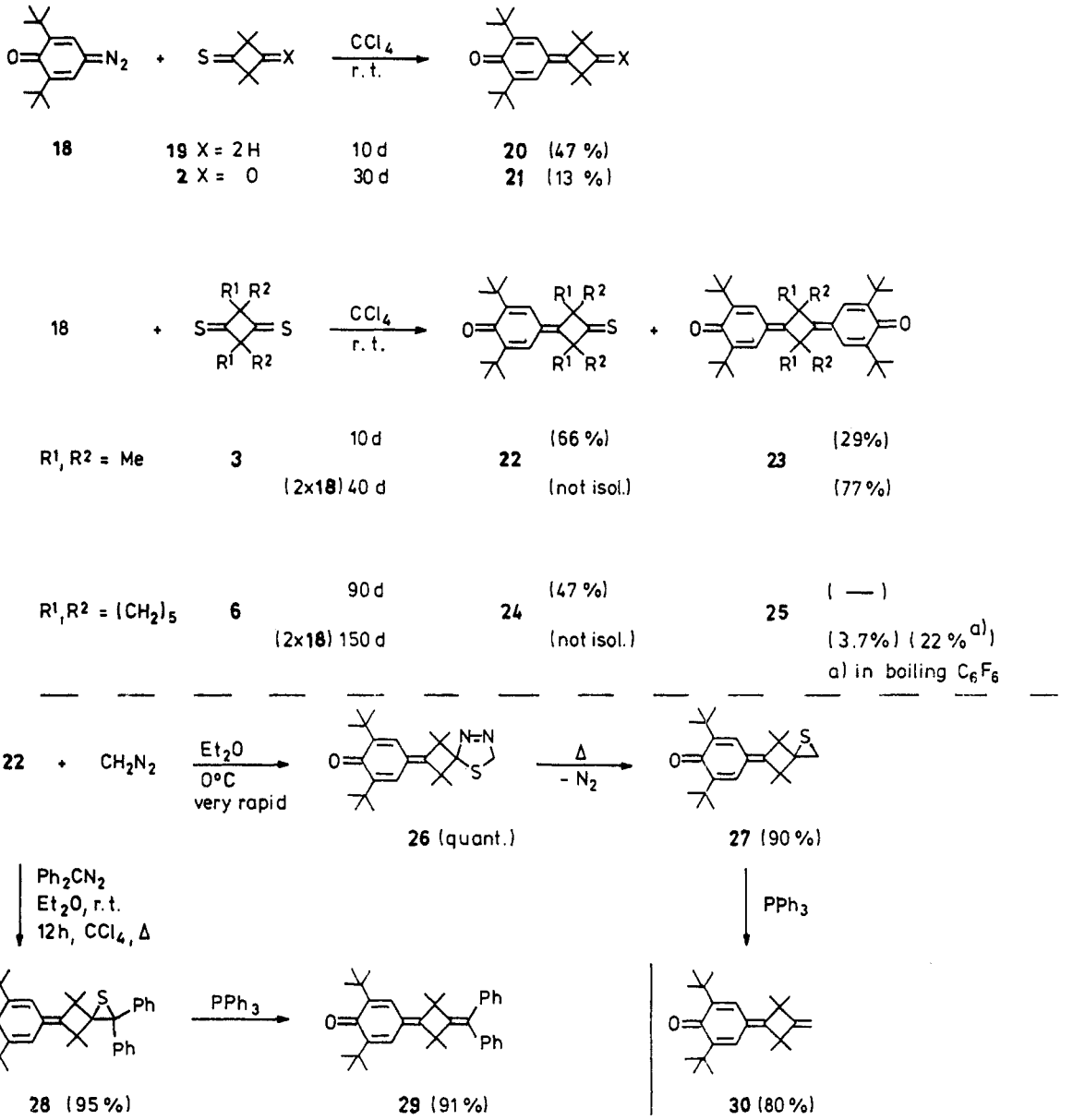
Scheme I



Scheme II



high preference of the sterically less favored isomer points to attractive (HOMO/LUMO?) interactions in the transition state for the addition of the second diazoquinone molecule **31**.

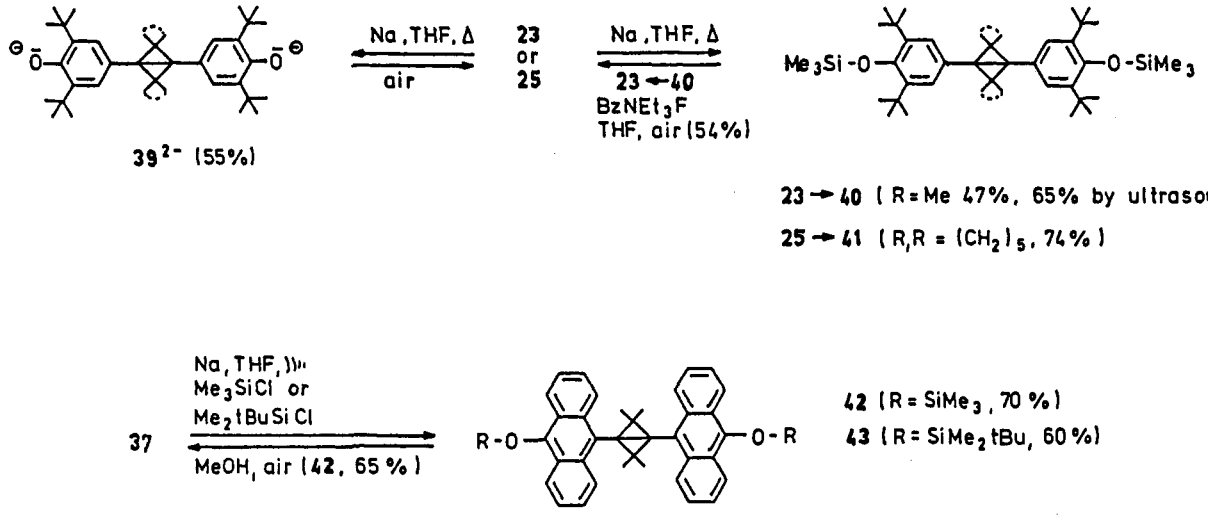
(18) The authors[14c] do not specify if 3:7 or 7:3 is correct although an anti isomer had been isolated in a pure state and the CH_3 NMR signals correctly assigned. Since with the corresponding 1,3,4-thiadiazolines the anti isomer always prevails and the geometry remains unchanged on nitrogen extrusion, a syn/anti ratio of 3:7 for the dithiiranes should be correct.

Because of its high symmetry, *anti*-**36** shows only one singlet (0.17 ppm) in the ^1H NMR spectrum for the methyl hydrogens. In the syn isomer, the two nonequivalent sets of methyl groups display signals at −0.54 and 1.00 ppm.

Bicyclo[1.1.0]butanes 39–42. By cyclic voltammetry in DMF, bis(methylene)cyclobutanes **23** and **37** show reduction peaks at −1.7 and −1.4 V, respectively.[2] Therefore alkali metals are expected to reduce **23** and **37** easily.

Treatment of **23** with a sodium suspension in refluxing THF affords colorless crystals of extremely low solubility

Scheme III



(no NMR spectra possible). In contact with air this solid turns yellow immediately and displays an IR spectrum that is identical with that of starting material **23**. The reduction product is therefore assumed to be the sodium salt of the anionic bicyclobutane 39^{2-} (Scheme III).

If Rühlmann conditions[19] (reduction of carbonyl compounds with sodium in the presence of trimethylsilyl chloride) are employed, both **23** and **25** yield phenolic silyl ethers which analyze for bicyclobutanes **40** and **41**.

Similar treatment of the anthraquinomethide **37** furnished the corresponding trimethylsilyl ether **42**. This oily substance is highly sensitive to protic solvents. Methanol hydrolysis of **42** in the presence of air rapidly produces **37**.

In contrast to **42**, the corresponding analogue **40** is surprisingly stable. It can be recrystallized from methanol or ethanol without decomposition. Removal of the silyl groups by fluoride ion, however, paves the way for air oxidation back to starting material **23**.

A stable derivative of reduced **37** can be produced if dimethyl-*tert*-butylsilyl chloride is used as a trapping agent. The crystalline bicyclobutane **43** can be stored over months without decomposition.

Spectral Properties of Quinone Methides 20–25, 29, 30, 33, and 37. ^{13}C NMR Spectra. All quinone methides in question display a signal for the carbonyl C atom at 185.7 ± 0.2 ppm close to that of the unstrained analogue **38** (186.3 ppm).[20] These similarities are not observed with the methylene C atoms incorporated into the cyclobutane ring. In contrast, these signals found for the benzoquinoid compounds **22–24** at 171 ± 1 ppm are shifted upfield by ca. 14 ppm for the quinoid derivatives **28**, **30**, and **32** (158 ± 1 ppm). In addition, anthraquinone methides have been shown to prefer a boat conformation for the central cyclohexadiene moiety[21] by which steric interaction between the peri hydrogen and the methylene substituent is minimized.

^{1}H NMR Spectra. Expectedly the hydrogen atoms of the four methyl groups linked to the cyclobutane ring in **20–23**, **29**, and **30** produce sharp singlets between 1.39 and 1.82 ppm. The singlet for **33** at 1.39 ppm results from rapid flipping of the nonplanar anthraquinoid moiety: at −60 °C the nonequivalence of the two methyl groups is documented by two singlets at 0.89 and 1.86 ppm. In the symmetrically substituted derivative **37**, the methyl hydrogens already at room temperature give rise to a broad singlet, which splits into three singlets at lower temperature: one singlet at 1.27 ppm, which can be assigned to be highly symmetrical *trans*-**37** in which one set of methyl groups is exposed to deshielding and the other one to shielding effects of the benzene rings at either side. According to Eyring,[22] from the coalescence temperature at 253 K for **33** and 288 K for **37** ($CDCl_3$, 90 MHz) one estimates $\Delta G^{\ddagger}$ = 50.5 ± kJ/mol for **33** and 56.2 ± kJ/mol for **37**. The lower transformation barriers for the two identical conformers of **33** can be attributed to twisting of the four methyl groups toward the thiono group in the transition state.

Table I. UV Maxima (>230 nm (log ε > 2)) of Quinone Methides and Bicyclobutane in *n*-Hexane

no.	UV max, nm (log ε)
38	313 (4.40)
20	322 (4.49)
30	322 (4.50)
29	324 (4.54)
21[a]	308 (4.46), 316 (sh) (4.45), 334 (4.32)
22[a]	298 (4.40), 312 (4.32), 324 (4.39), 338 (sh) (4.22)
26[a]	306 (4.32), 329 (4.16), 345 (4.04)
23[a,b]	313 (sh), 326, 337 (sh)
33[a]	270 (3.98), 345 (3.45)
37[a,c]	278 (4.48), 351 (5.14)
44[d]	239 (4.26), 312 (sh) (4.51), 329 (4.55), 344 (sh) (4.34)
40	253 (4.15)
41	253 (4.21)
45[d,e]	255 (5.10), 263 (5.15), 378 (3.93), 400 (4.08), 425 (4.27)
43	254 (5.16), 261 (5.10), 380 (4.11), 402 (4.33), 426 (4.34)

[a] In addition, a weak absorption (log ε = 10–50) at 415–525 nm is seen. [b] Very low solubility. [c] Solvent chloroform. [d] Solvent cyclohexane. [e] Cf. reference 35.

UV Spectra. These spectra merit a more detailed consideration because they should be rather indicative of any diagonal interaction in 1,3-bis(methylene)cyclobutanes. Indeed, through-space interactions of the p orbitals[6] (transannular interactions) but also through-bond interactions[23] (circumannular conjugation) have been postulated and experimentally[24] supported. Especially with **1** and **3**, it has been concluded both from experimental data[6,24–27]

(19) Rühlmann, K. *Synthesis* **1971**, 236.
(20) Lycka, A.; Snobl, D.; Koutek, B.; Pavlickova, L.; Soucek, M. *Collect. Czech. Chem. Commun.* **1981**, *46*, 2083.
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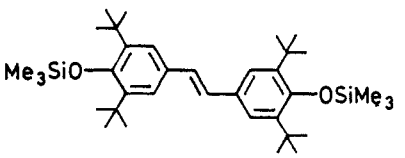

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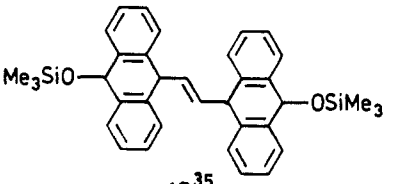

45[35]

and calculations (extended Hückel and CNDO/2)[28] that the HOMO *and* the LUMO are destabilized to about the same extent.

In comparing the UV data of the cyclobutanes in question, one must keep in mind the strong solvation shifts shown by quinone methides.[29] Therefore, these spectra have to be taken always in the same solvent of low polarity.

Structural influences of typical derivatives can be found in Table I. The known quinone methide **38**[20] can be considered as the parent system, especially for spectroscopic comparisons. A four-membered ring instead of the methyl groups as in **20** causes a slight bathochromic shift of 9 nm. A methylene group in the 3-position of the ring (**30**) shows no effect, and even a diphenylmethylene group (**29**) hardly influences the absorption maximum. It is noteworthy that **38**, **20**, **30**, and **29** in addition to an absorption band at 220–230 nm show only the one long-wavelength band discussed above. By contrast, substitution of the four-membered ring in a β-position by oxygen (**21**) or sulfur (**22**, **26**) produces 2–3 new absorption bands as well as a bathochromic shift. Interestingly, a second quinone methide moiety instead of the oxygen or sulfur (**23**) causes only a small spectral shift in spite of its large π-system. The same behavior holds true for the anthraquinoid system **33** compared to **37**.

Spectral Properties of Bicyclobutanes 40, 41, and 43. ^{13}C NMR Spectra. With bicyclobutanes **40**, **41**, and **43**, two ^{13}C signals are observed in the range of 42–57 ppm. All three compounds have the signal at 42–43 ppm in common, but only **40** and **43** show a signal around 49 ppm whereas with **41** the signal is shifted to 56.82 ppm. Since only **41** differs from **40** and **43** by its spirocyclohexane ring, the signals with the stronger chemical shift can be attributed to the two positions 2 and 4 of the bicyclobutane ring, whereas the high-field signals at 42–43 ppm are produced by the carbon atoms in positions 1 and 3. This assignment agrees well with the ^{13}C data of 2,2,4,4-tetramethylbicyclo[1.1.0]butane (52.0 ppm (C-2, C-4) and 25 ppm (C-1, C-3)).[30] Phenyl groups at the bridgehead position generally cause a low-field shift of 15–20 ppm,[30] in good agreement with the situation in **40**, **41**, and **43**. In different cyclobutanes a conjugative interaction with bridgehead phenyl groups cannot be derived from ^{13}C NMR data[30] although the symmetry properties of the Walsh HOMO orbitals[31] with the LUMO orbitals of the phenyl ether groups[32a] would allow these interactions; and π-conjugation has been evidenced by significant UV spectral shifts in the presence of two bridgehead phenyl groups.[32b] The appropriate geometry of the substituents is at least possible, as demonstrated by X-ray analysis of related examples.[33]

Unfortunately, single crystals of **40**, **41**, or **43** could not be obtained. The fact, however, that *exo*- and *endo*-methyl groups in **40** and **43**, respectively, give rise to one ^{13}C and ^{1}H singlet only is explained by the mirror symmetry in both **40** and **43**.

^{1}H NMR Spectra. Only the two singlets of the methyl groups displayed by both **40** and **43** are indicative of the bicyclobutane structure. The signal of the *exo*-methyl group in **43** shows a low-field shift of 0.4 ppm compared to **40** due to the anisotropy of the anthracene moiety.

UV Spectra. Reductive transformation of quinone methides **23** and **25** to bicyclobutanes **40** and **41** causes a strong hypsochromic shift of the long-wave absorption band. It appears now at 253 nm, the typical absorption region of a phenol ether. These findings again illustrate the lack of conjugative power of the bicyclobutane ring. Stilbene ether **44**, for comparison, shows a completely different behavior, with absorption bands up to 329 and 344 nm, respectively (Table I). By contrast, the pyridinium-substituted bicyclobutane C showed a definite effect of the central ring although substantially smaller than that of the corresponding di-4-pyridinioethylene.[3]

Anthracene derivative **43** behaves differently. Surprisingly, it shows the same UV spectrum as that of the ethylene derivative **45** reported in the literature.[34] Only the longest wavelength absorption at 425 nm is due to the conjugative effect of the bicyclobutane and vinylene moiety, since anthranol 9-trimethylsilyl ether already shows absorption bands at 378 nm ($\log \epsilon = 3.88$) and 400 nm ($\log \epsilon = 3.77$) in cyclohexane.[35] The reasons for the different effects from phenyl and anthranyl groups in bicyclobutanes **40** and **43**, respectively, are not yet understood.

Conclusions

By extending the well-known reaction between diazoalkanes and thiones for the formation of new C=C bonds to diazoquinones, a versatile method for the synthesis of quinone methides has been developed. Via this route several new bisquinone methides of type E were obtained. On chemical reduction they produce bicyclobutanes of type F, which can be isolated as the bis silyl ethers. By hydrolysis and air oxidation the quinone methides E are easily regenerated.

The discussed examples clearly demonstrate that 1,3-bis(methylene)cyclobutanes and bicyclo[1.1.0]butanes can be transformed into one another simply by transfer of two

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(26) Gleiter, R. *Top. Curr. Chem.* **1979**, *86*, 197.
(27) Spafford, R.; Baiardo, J.; Wrobel, J.; Vala, M. *J. Am. Chem. Soc.* **1976**, *98*, 5217.
(28) Martin, H.-D.; Eckert-Maksic, M.; Mayer, B. *Angew. Chem.* **1980**, *92*, 833.
(29) Grünanger, P. In *Methoden der Organischen Chemie*, 4th ed.; Thieme: Stuttgart, 1979; Vol. VII/3b, p 398. Freund, W. Diploma Thesis, Würzburg, 1980.
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electrons. A prerequisite for this transformation is the ability of the substituent at the methylene moieties to pay for the strain energy on forming the bicyclobutane ring.

Experimental Section

Corrected melting points were determined on a Kofler microscope. Infrared spectra were recorded on a Perkin-Elmer 157 G, a Beckman IR 33, or a Beckman Acculab 4 spectrophotometer. ^{1}H NMR spectra were obtained on a Varian T 60 (60 MHz), a Varian EM 390 (90 MHz), or a Bruker WM 400 (400 MHz) spectrometer. UV spectra were run on a Beckman DB-GT or Perkin-Elmer 330 spectrometer. Mass spectra were taken on a Varian MAT CH7 instrument. Microanalyses were performed at the Institute of Inorganic and of Organic Chemistry, University of Würzburg.

All solvents were purified according to literature procedures. Chromatography was carried out on silica gel 60 (Woelm, 63–200 μm).

14-Thioxodispiro[5.1.5.1]tetradecan-7-one (5) and Dispiro[5.1.5.1]tetradecane-7,14-dithione (6). A solution of 22.0 g (10 mmol) of dispiro[5.1.5.1]tetradecane-7,14-dione (**4**) was treated with HCl and H_2S in the presence of 7.50 g (55 mmol) of anhydrous zinc chloride as described for **2** and **3**[14] but in a mixture of 300 mL of ethanol and 100 mL of methanol. After chromatography (100 g of silica gel, petroleum ether), 16.4 g of the crude product yielded 12.8 g (51%) of **6** and 3.40 g of **5**, melting point and IR spectra identical with those reported in the literature.[36]

2,2,4,4-Tetramethylcyclobutanethione (19). A solution of 15.7 g (125 mmol) of 2,2,4,4-tetramethylcyclobutan-1-one[37,38] was treated in 150 mL of methanol as described for **2** and **3**.[14] After the addition of 200 g of ice, the mixture was extracted with dichloromethane to give 8.44 g (47%) of **19**, bp 140–142 °C (760 Torr), whose IR and ^{1}H NMR spectra were identical with those reported.[39]

General Procedure for the Reaction of Diazoquinones with Thiones. The two components were dissolved or suspended in the solvents given and stirred at room temperature in the dark. The reactions were monitored by ^{1}H NMR or IR spectroscopy.

2,6-Di-*tert*-butyl-4-(2,2,4,4-tetramethylcyclobutylidene)-cyclohexa-2,5-dienone (20): 1.42 g (10.0 mmol) of **19**, 2.68 g (12.0 mmol) of **18**,[40] 3 mL of CCl_4, 30 days. The isolated crystals were dissolved in CS_2 and filtered through a short silica gel column. After evaporation, the residue was recrystallized from ligroin: 410 mg (13%) of **20**, yellow crystals, mp 192–192.5 °C; IR (KBr) 3015, 2962, 2870, 1636, 1618, 1582, 1381, 1362 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.28 (s, 18 H, $C(CH_3)_3$), 1.44 (s, 12 H, CH_3), 1.81 (s, 2 H, CH_2), 7.12 (s, 2 H, olefinic *H*); ^{13}C NMR ($CDCl_3$) δ 19.50 (q, C-8), 29.77 (q, C-5′,6′), 35.04 (s, C-7), 39.68 (s, C-2′,4′), 47.92 (t, C-3′), 126.76 (s, C-4), 127.88 (d, C-3,5), 146.33 (s, C-2,6), 180.17 (s, C-1′), 185.76 (s, C-1); UV (cf. Table I). Anal. Calcd for $C_{22}H_{34}O$ (312.5): C, 84.56; H, 10.97. Found: C, 84.87; H, 10.78.

2,6-Di-*tert*-butyl-4-(2,2,4,4-tetramethyl-3-oxocyclobutylidene)cyclohexa-2,5-dienone (21): 312 mg (2.00 mmol) of **2**, 603 mg (2.60 mmol) of **18**, 3 mL of toluene. After a 15-min reflux, 330 mg (50%) of **21** was isolated. Alternatively, 200 mg (1.30 mmol) of **2**, 300 mg (1.30 mmol) of **18**, and 5 mL of CCl_4 for 10 days at room temperature furnished 200 mg (47%) of **21**. Recrystallization from ligroin or sublimation at 150 °C (0.01 Torr) gave pale yellow crystals: mp 203–204 °C (sealed tube); IR (CCl_4) 1787, 1622, 1608, 1581, 1376, 1356 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.26 (s, 18 H, $C(CH_3)_3$), 1.49 (s, 12 H, CH_3), 7.02 (s, 2 H, olefinic H); ^{13}C NMR ($CDCl_3$) δ 23.55 (C-5′,6′), 29.47 (C-8), 35.18 (C-7), 63.22 (C-2′,4′), 127.02 (C-4), 128.26 (C-3,5), 147.88 (C-2,6), 166.30 (C-1′), 185.69 (C-1), 217.33 (C-3′); MS (70 eV), *m/e* 328 (13, M$^+$), 300 (27, M − CO), 243 (36, M − C_5H_9O), 57 (100, C_4H_9). Anal. Calcd for $C_{22}H_{32}O_2$ (328.5): C, 80.44; H, 9.82. Found: C, 80.30; H, 9.66.

2,6-Di-*tert*-butyl-4-(2,2,4,4-tetramethyl-3-thioxocyclobutylidene)cyclohexa-2,5-dienone (22): 3.45 g (20.0 mmol) of **3**, 4.64 g (20.0 mmol) of **18**, 30 mL of CCl_4. After 10 days, 1.50 g (29%) of **23** (vide infra) separated. The filtered solution was evaporated. The residue was chromatographed (5 cm, length 30 cm, CS_2). The second fraction afforded 4.69 g (66%) of **22** as orange crystals: mp 194–195 °C; IR (KBr) 1631, 1593, 1134 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.30 (s, 18 H, $C(CH_3)_3$), 1.58 (s, 12 H, CH_3), 7.07 (s, 2 H, olefinic H); ^{13}C NMR ($CDCl_3$) δ 27.26 (C-5′,6′), 29.47 (C-8), 35.18 (C-7), 65.69 (C-2′,4′), 127.09 (C-4), 128.06 (C-3,5), 147.72 (C-2,6), 170.78 (C-1′), 185.73 (C-1), 278.47 (C-3′); UV (methanol) λ_{max} (log ε) 302 (4.32), 316 (4.34), 327 (4.38), 404 (1.79), 492 nm (1.22); MS (70 eV), *m/e* 344 (70, M$^+$), 57 (100, $C(CH_3)_3$). Anal. Calcd for $C_{22}H_{32}OS$ (344.6): C, 76.69; H, 9.36; S, 9.31. Found: C, 76.84; H, 9.65; S, 9.24.

1,3-Bis(3,5-di-*tert*-butyl-4-oxocyclohexa-1,5-dienylidene)-2,2,4,4-tetramethylcyclobutane (23): 860 mg (5.00 mmol) of **3**, 2.32 g (10.0 mmol) of **18**, 10 mL of CCl_4. After 40 days, a precipitate was isolated, which was washed several times with CS_2 (removal of sulfur) to give 2.00 g (77%) of **23** as yellow crystals, mp >360 °C. The compound was twice recrystallized from *o*-dichlorobenzene and sublimed at 230 °C (3 × 10^{-5} Torr): IR (KBr): 3000, 2932, 2862, 1645, 1632, 1614, 1572, 1386, 1363, 1176 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.33 (s, 36 H, $C(CH_3)_3$), 1.82 (s, 12 H, CH_3), 7.15 (s, 4 H, olefinic H); ^{13}C NMR ($CDCl_3$) δ 28.44 (C-5′), 29.56 (C-8), 35.27 (C-7), 50.82 (C-2′,4′), 126.55 (C-1), 127.64 (C-2,6), 147.52 (C-3,5), 172.01 (C-1′,3′), 185.75 (C-4); UV (cf. Table I); MS (70 eV), *m/e* 516 (45, M$^+$), 501 (12, M − CH_3), 57 (100, C_4H_9). Anal. Calcd for $C_{36}H_{52}O_2$ (516.8): C, 83.67; H, 10.14. Found: C, 83.48; H, 10.48.

14-(3,5-Di-*tert*-butyl-4-oxocyclohexa-2,5-dienylidene)dispiro[5.1.5.1]tetradecane-7-thione (24): 1.25 g (5.00 mmol) of **6**, 2.32 g (10.0 mmol) of **18** in 10 mL of CCl_4, 90 days. From the mixture was isolated 1.40 g of orange crystals. By chromatography (5 cm, length 30 cm, CS_2), 990 mg (47%) of **24**, mp ca. 270 °C, was obtained. Recrystallization from ligroin and sublimation at 200 °C (0.01 Torr) produced **24** with mp 299–301 °C: IR (KBr) 2990, 1622, 1610, 1581 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.22–1.34, 1.59–1.67, 1.83–2.20 (m, total 20 H, CH_2), 1.33 (s, 18 H, $C(CH_3)_3$), 7.34 (s, 2 H, olefinic H); ^{13}C NMR ($CDCl_3$) δ 21.66 and 36.14 (each t, C-2′,6′,9′,13′, C-3′,5′,10′,12′), 25.82 (t, C-4′,11′), 29.55 (q, C-8), 35.36 (s, C-7), 68.55 (s, C-1′,8′), 126.87 (s, C-1), 127.88 (d, C-2,6), 157.22 (s, C-3,5), 170.50 (s, C-14′), 185.67 (s, C-4), 276.92 (s, C-7′). Anal. Calcd for $C_{28}H_{40}OS$ (424.7): C, 79.19; H, 9.49. Found: C, 79.33; H, 9.67.

7,14-Bis(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dienylidene)dispiro[5.1.5.1]tetradecane (25). A solution of 2.52 g (10.0 mmol) of **6** and 5.81 g (25.0 mmol) of **18** in 10 mL of hexafluorobenzene was refluxed for 2 h. After recovery of the solvent, the very fine precipitate was refluxed in 80 mL of *o*-dichlorobenzene for 30 min. After cooling, the precipitated **25** (1.30 g (22%)) was collected and washed several times with CS_2 to provide yellow crystals of extremely low solubility (no ^{1}H and ^{13}C NMR spectra), mp >360 °C. Alternatively, 1.25 g (5.00 mmol) of **6** and 2.32 g (10.0 mmol) of **18** were reacted in 5 mL of $CHCl_3$ for 150 days. After the precipitate was treated with CS_2, 110 mg (3.7%) of **25** was isolated: IR (KBr) 3010, 2970, 2895, 1605, 1629, 1560 cm^{-1}; UV (cf. Table I); MS (70 eV), *m/e* 596 (26%, M$^+$), 57 (100%, C_5H_9). Anal. Calcd for $C_{42}H_{60}O_2$ (597.0): C, 84.51; H, 10.13. Found: C, 84.21; H, 10.06.

2,6-Di-*tert*-butyl-4-(1,1,3,3-tetramethyl-8-thia-5,6-diazaspiro[3.4]oct-5-en-2-ylidene)cyclohexa-2,5-dienone (26). A solution of diazomethane in ether was slowly added to 1.03 g (3.00 mmol) of **22** at 0 °C until the orange color changed to yellow. Evaporation of the solvent at −40 °C left 1.15 g (100%) of **26** as yellow crystals, mp 102–102.5 °C dec. At room temperature **27** is slowly formed. **26**: IR (CCl_4) 1621, 1588 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.27 (s, 18 H, $C(CH_3)_3$), 1.37 (s, 6 H, CH_3), 1.44 (s, 6 H, CH_3), 5.70 (s, 2 H, CH_2), 7.05 (s, 2 H, olefinic H). Anal. Calcd for $C_{23}H_{34}N_2OS$ (386.6): C, 71.46; H, 8.86; N, 7.25. Found: C, 70.94; H, 8.83; N, 7.03.

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2,6-Di-*tert*-butyl-4-(4,4,6,6-tetramethyl-1-thiaspiro[2.3]-hex-5-ylidene)cyclohexa-2,5-dienone (27). A solution of 386 mg of **26** in 5 mL of CCl_4 was refluxed until N_2 evolution ceased. From ethanol was obtained 320 mg (94%) of **27** as pale yellow crystals: mp 162–163 °C; IR (CCl_4) 1627, 1582 cm^{-1}; ^1H NMR (CCl_4) δ 1.27 (s, 18 H, $C(CH_3)_3$), 1.35 (s, 6 H, CH_3), 1.42 (s, 6 H, CH_3), 2.48 (s, 2 H, CH_2), 7.05 (s, 2 H, olefinic H); UV (*n*-hexane) λ_{max} (log ϵ) 231 (3.52), 322 nm (4.52). Anal. Calcd for $C_{23}H_{34}OS$ (358.6): C, 77.04; H, 9.56. Found: C, 77.04; H, 9.22.

2,6-Di-*tert*-butyl-4-(4,4,6,6-tetramethyl-2,2-diphenyl-1-thiaspiro[2.3]hex-5-ylidene)cyclohexa-2,5-dienone (28). To a solution of 344 mg (1.00 mmol) of **22** in 5 mL of ether was slowly added 194 mg (1.00 mmol) of diphenyldiazomethane[41] in 5 mL of ether. From the orange solution nitrogen gas evolved slowly, and a yellow color appeared. After 24 h, the solvent was removed and the oily residue chromatographed (2 cm, length 20 cm, CCl_4). **28**, yellow crystals, 470 mg (95%): mp 218–221 °C; IR (CCl_4) 3090, 3063, 1636, 1620, 1584 cm^{-1}; ^1H NMR (CCl_4) δ 1.24 (s, 18 H, $C(CH_3)_3$), 1.28 (s, 6 H, CH_3), 1.37 (s, 6 H, CH_3), 7.02 (s, 2 H, olefinic H), 7.10–7.85 (m, 10 H, Ar H); ^{13}C NMR ($CDCl_3$) δ 28.65 and 30.83 (each q, C-7, C-8), 29.43 (q, C-8′), 35.09 (s, C-7′), 51.62 (s, C-4,6), 65.79 (s, C-3), 76.86 (s, C-2), 124.81 (s, C-4′), 127.38 and 130.82 (each d, C-3′,5′, C-10,11), 128.16 (d, C-12), 139.59 (s, C-9), 146.68 (s, C-2′,6′), 176.40 (s, C-5), 185.50 (s, C-1′). Anal. Calcd for $C_{35}H_{42}OS$ (510.8): C, 82.30; H, 8.29. Found: C, 82.11; H, 8.34.

4′,4′,6′,6′-Tetramethyl-10-oxospiro[anthracene-9,2′-[1]-thiaspiro[2.3]hexane]-5′-thione (32). A solution of 860 mg (5.00 mmol) of **3** and 1.11 g (5.00 mmol) of 9,10-diazaanthrone (**31**)[42] in 5 mL of CCl_4 was reacted for 5 days. The solvent was removed from the orange suspension. Chromatography (3.5 cm, length 35 cm, CCl_4) yielded 1.65 g (86%) of **32** as orange needles: mp 202–204 °C; IR (KBr) 3065, 2965, 2860, 1670, 1599, 1080, 796, 704 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.41 (s, 6 H, CH_3), 1.23 (s, 6 H, CH_3), 7.43–7.65, 7.70–8.03, and 8.13–8.40 (m, 8 H, Ar H); ^{13}C NMR ($CDCl_3$) δ 25.52 and 28.68 (each q, C-7, C-8), 56.52 (s, C-3), 66.92 (s, C-4,6), 77.80 (s, C-2), 127.48, 127.59, 128.55, and 132.61 (each d, C-1′,8′, C-2′,7′, C-3′,6′, C-4′,5′), 135.16 and 140.85 (each s, C-4a′,10a′, C-8a′,9a′), 184.11 (s, C-9′), 279.62 (s, C-5); UV (*n*-hexane) λ_{max} (log ϵ) 501 nm (0.89). Anal. Calcd for $C_{22}H_{20}OS_2$ (364.5): C, 42.49; H, 5.53; S, 17.59. Found: C, 72.89; H, 5.69; S, 17.30.

10′-Thioxospiro[anthracene-9(10*H*),2′-[1]thiatrispiro-[2.0.5.1.5.0]hexadecan]-10-one (34). A solution of 1.25 g (5.00 mmol) of **6** and 1.11 g (5.00 mmol) of **31**[42] in 5 mL of CCl_4 was reacted for 90 days. Workup as for **32** yielded 270 mg (22%) of **6** and 1.56 g (90% based on consumed **6**) of **34** as pink crystals: mp 218–220 °C; IR (KBr) 3060, 2929, 2920, 2855, 1668, 1592, 931, 794, 692 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.6–2.5 (br m, 20 H, CH_2), 7.33–7.65, 7.70–8.03, and 8.07–8.33 (m, 8 H, Ar H); ^{13}C NMR ($CDCl_3$) δ 21.04, 22.52, 25.20, 33.02, 27.96 (each t, C-5,16, C-6,15, C-7,14, C-8,13, C-9,12), 55.24 (s, C-3), 68.36 (s, C-4,11), 76.97 (s, C-2), 127.50, 127.96, 128.57, 131.99 (each d, C-1′,8′, C-2′,7′, C-3′,6′, C-4′,5′), 135.85, 141.00 (each s, C-4a′,10a′, C-8a′,9a′), 184.60 (s, C-9′), 277.04 (s, C-10); UV (*n*-hexane) λ_{max} (log ϵ) 538 nm (0.96). Anal. Calcd for $C_{28}H_{28}OS_2$ (444.7): C, 75.63; H, 6.35. Found: C, 75.75; H, 6.56.

2″,2″,4″,4″-Tetramethyltetraspiro[anthracene-9(10*H*),2′-thiirane-3′,1″-cyclobutane-3″,2‴-thiirane-3‴,9⁗(10⁗*H*)-anthracene]-10,10⁗-dione (36). From 860 mg (5.00 mmol) of **3** and 2.22 g (10.0 mmol) of **31**[42] in 5 mL of $CHCl_3$ pale yellow crystals precipitated (2.41 g (87%) of crude **36**, mp 285–291 °C), which was directly transformed into **37**. The orange mother liquor contained **32** (IR). **36**: IR (KBr) 3060, 2989, 2928, 1666, 1594, 780, 711, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.54, 1.00 (syn), 0.17 (anti) (each s, CH_3), 7.20–7.90 (m, Ar H).

General Procedure for Desulfuration of Thiiranes. Thiirane and triphenylphosphine (TPP) were refluxed in 2–8 mL of benzene under nitrogen, and the solvent was subsequently removed.

4-[3-Benzhydrylidene-2,2,4,4-tetramethylcyclobutylidene]-2,6-di-*tert*-butylcyclohexa-2,5-dienone (29). After 24 h, 200 mg (0.40 mmol) of **28** and 135 mg (0.50 mmol) of TPP yielded on recrystallization from *o*-dichlorobenzene 168 mg (88%) of **29** as pale yellow crystals: mp 296–298 °C dec: IR (CCl_4) 3080, 3060, 1647 (C=C), 1630, 1618, 1580 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26 (s, 18 H, $C(CH_3)_3$), 1.42 (s, 12 H, CH_3), 7.07 (s, 2 H, =C*H*), 7.26 (s, 10 H, Ar H); ^{13}C NMR ($CDCl_3$) δ 28.30 (q, C-5′,6′), 29.47 (q, C-8′), 35.09 (s, C-7′), 50.55 (s, C-2,4), 125.72 (s, C-4′), 126.83 (d, C-3′,5′), 128.00 and 128.74 (each d, C-9,10), 128.35 (d, C-11), 137.68 (s, C-3), 141.32 (s, C-8), 146.48 (s, C-2′,6′), 152.00 (s, C-7), 178.19 (s, C-1), 185.73 (s, C-1′); MS (70 eV), *m/e* 478 (55, M^+), 57 (100, $C(CH_3)_3$). Anal. Calcd for $C_{35}H_{42}O$ (478.7): C, 87.82; H, 8.84. Found: C, 87.23; H, 8.79.

2,6-Di-*tert*-butyl-4-(2,2,4,4-tetramethyl-3-methylidenecyclobutylidene)cyclohexa-2,5-dienone (30). The crude product obtained from 160 mg (0.45 mmol) of **27** and 118 mg (0.45 mmol) of TPP after 24 h was suspended in petroleum ether and filtered at −20 °C (removal of triphenylphosphine sulfide). The filtrate was evaporated and the residue chromatographed (2 cm, length 20 cm, CCl_4). **30** (110 mg (80%), pale yellow crystals): mp 161–162 °C; IR (KBr) 3020, 1631, 1625, 1585 cm^{-1}; ^1H NMR (CCl_4) δ 1.27 (s, 18 H, $C(CH_3)_3$), 1.49 (s, 12 H, CH_3), 4.94 (s, 2 H, $=CH_2$), 7.00 (s, 2 H, =C*H*); UV (cf. Table I). Anal. Calcd for $C_{23}H_{34}O$ (326.5): C, 84.68; H, 10.50. Found: C, 84.38; H, 10.37.

3-(10′-Anthronylidene)-2,2,4,4-tetramethylcyclobutane-1-thione (33). The product formed from 1.46 g (4.00 mmol) of **32** and 1.10 g (4.20 mmol) of TPP after 25 days was treated with a little CCl_4 and filtered. The filtrate was evaporated and the residue purified by flash chromatography on SiO_2 (4 cm, length 40 cm, CCl_4). **33** (1.11 g (83%), orange crystals): mp 142–143 °C; IR (KBr) 3065, 2970, 2860, 1667, 1662, 1600, 1596, 783, 712, 690 cm^{-1}; ^1H NMR ($CDCl_3$; *T* 303 K) δ 1.39 (s, 12 H, CH_3), 7.35–7.90, 8.02–8.28 (m, 8 H, Ar H), (*T* 213 K) δ 0.89, 1.86 (each s, CH_3), 7.33–7.86, 8.01–8.20 (br m, Ar H); ^{13}C NMR ($CDCl_3$; *T* 297 K) δ 27.2–29.4 (br s, C-5,6), 67.46 (s, C-2,4), 126.93, 128.00, 131.25 (each d, C-1′,8′, C-2′,7′, C-3′,6′, C-4′,5′), 131.07 (s, C-10′), 132.16, 139.96 (each s, C-4a′,10a′, C-8a′,9a′), 157.51 (s, C-3), 185.54 (s, C-9′), 280.86 (s, C-1), (*T* 213 K) δ 23.91, 31.29 (each s, C-5,6), 67.34 (s, C-2,4), 126.64, 126.71, 127.93, 131.53 (each d, C-1′,8′, C-2′,7′, C-3′,6′, C-4′,5′), 130.60 (s, C-10′), 131.36, 139.45 (each s, C-4a′,10a′, C-8a′,9a′), 156.91 (s, C-3), 186.25 (s, C-9′), 281.32 (s, C-1); UV (cf. Table I). Anal. Calcd for $C_{22}H_{20}OS$ (332.5): C, 79.48; H, 6.06; S, 9.64. Found: C, 79.53; H, 6.12; S, 9.46.

14-(10′-Anthronylidene)dispiro[5.1.5.1]tetradecane-7-thione (35). A mixture of 1.33 g (3.00 mmol) of **34** and 790 g (3.20 mmol) of TPP was treated after 7 days as described for **33**. **35** (1.08 g (79%), pink crystals): mp 250–251 °C; IR (KBr) 3052, 2935, 2840 (C–H), 1656, 1593, 931, 781, 702, 692 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.70–2.55 (br m, 20 H, CH_2), 7.33–7.61, 7.70–8.18 (m, 8 H, Ar H); ^{13}C NMR ($CDCl_3$) δ 21.44, 25.41 (each t), 31–41 (br) (C-2, C-3, C-4, C-5, C-6, C-9, C-10, C-11, C-12, C-13), 69.84 (s, C-1,8), 126.74, 127.49, 127.79, 130.55 (each d, C-1′,8′, C-2′,7′, C-3′,6′, C-4,5′), 131.14 (s, C-10′), 133.07, 140.92 (each s, C-4a′,10a′, C-8a′,9a′), 156.13 (s, C-14′), 185.97 (s, C-9′), 278.75 (S, C-7′); UV (cf. Table I). Anal. Calcd for $C_{28}H_{28}OS$ (412.6): C, 81.51; H, 6.84; S, 7.77. Found: C, 81.26; H, 6.80; S, 7.30.

2,4-Di-10′-anthronylidene-1,1,3,3-tetramethylcyclobutane (37). The crude product obtained from 2.80 g (5.00 mmol) of **36** and 3.41 g (13.0 mmol) of TPP after 6 days was recrystallized twice from *o*-dichlorobenzene to give 1.56 g (63%) of **37** as colorless crystals: mp >350 °C; IR (KBr) 3060, 3972, 3922, 2860, 1660, 1593, 729, 712 cm^{-1}; ^1H NMR ($CDCl_3$; *T* 333 K) δ 1.40 (s, 12 H, CH_3), 7.29–7.55, 7.60–7.84, 7.91–8.13 (each m, 16 H, Ar H), (*T* 213 K) δ 0.50, 2.42 (each s, 12 H, CH_3, syn isomer), 1.27 (s, CH_3, anti isomer), 7.20–8.15 (m, Ar H); ^{13}C NMR ($CDCl_3$; *T* 303 K) δ 55.06 (s, C-1,3), 126.79 (d, C-1′,8′), 127.52 (d, C-2′,7′, C-3′,6′), 130.64 (d, C-4′,5′), 133.04 (s, C-4a′,10a′), 141.26 (s, C-9a′,8a′), 159.93 (s, C-10′), 162.14 (s, C-2,4), 185.92 (s, C-9′); UV (cf. Table I). Anal. Calcd for $C_{36}H_{28}O_2$ (492.6): C, 87.78; H, 5.73. Found: C, 87.36; H, 5.63.

General Procedure for the Reduction of 1,3-Bis(methylene)cyclobutanes 23, 25, and 37. To a 50% suspension of sodium in Nujol (3–5 mmol) was added 5 mL of benzene under dry nitrogen gas, and after the mixture was stirred, the solvent was removed by a syringe. The procedure was repeated, the flask evacuated, and finally the sodium suspended in 5 mL of THF. After addition of 1.00 mmol of substrate and 3.0 mmol of chlorosilane (with the exception of the first experiment), the mixture was refluxed or treated with ultrasound. When the reaction starts,

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(42) Regitz, M. *Chem. Ber.* **1964**, *97*, 2742.

a violet or red color develops which remains on removal of the solvent after the reaction is over.

Formation of the disodium salt of 2,2,4,4-tetramethyl-1,3-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)bicyclo[1.1.0]butane (39^{2-}): 50.8 mg (2.20 mmol) of Na, 517 mg of **23**, 15-h reflux. Colorless crystals, which are supposed to be 39^{2-}, were separated from the violet solution: 310 mg (55%), insoluble in Me_2SO and $CHCl_3$. On exposure to air, the crystals turn immediately yellow and show an IR spectrum identical with that of **23**.

2,2,4,4-Tetramethyl-1,3-bis[3,5-di-*tert*-butyl-4-(trimethylsiloxy)phenyl]bicyclo[1.1.0]butane (40): 69.0 mg (3.00 mmol) of Na, 517 mg of **23**, 326 mg of Me_3SiCl, 7 h ultrasound. The blue violet residue was treated with 5 mL of CH_2Cl_2 and 5 mL of $NaCO_3$ (10%), the aqueous layer extracted twice with CH_2Cl_2, and the solvent removed from the organic phase. The yellow oil became crystalline on adding some methanol. Recrystallization from methanol yielded 390 mg (65%) of **40** as colorless crystals: mp 135–137 °C; IR (KBr) 3020, 2950, 2915, 2860, 1594, 1268, 1255, 1120, 917, 842 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.40 (s, 18 H, OSiMe_3), 1.02 (s, 6 H, endo-CH_3), 1.39 (s, 36 H, C(CH_3)$_3$), 1.52 (s, 6 H, exo-CH_3), 7.13 (s, 4 H, Ar H); ^{13}C NMR ($CDCl_3$) δ 3.84 (q, C-7′), 23.52, 25.16 (both q, C-5, C-6), 31.06 (q, C-9′), 35.08 (s, C-8′), 41.94 (s, C-1,3), 48.52 (s, C-2,4), 127.44 (s, C-1′), 128.02 (s, C-2′,6′), 139.84 (s, C-3′,5′), 151.37 (s, C-4′); UV (cf. Table I); MS (70 eV); *m/e* 665, 664, 663, 662 (4, 14, 36, 63, M^+), 319 (17), 73 (100, C_3H_9Si), 57 (71, C(CH_3)$_3$). Anal. Calcd for $C_{42}H_{70}O_2Si_2$ (663.2): C, 76.07; H, 10.64. Found: C, 75.92; H, 10.92.

Through a stirred suspension of 333 mg (0.50 mmol) of **40** and 540 mg (2.00 mmol) of benzyltrimethylammonium fluoride in 5 mL of THF was bubbled air for 10 h. The color changed rapidly from colorless to yellow. The isolated precipitate, washed with THF/H_2O, CH_3OH, and CH_2Cl_2, consisted of 140 mg (54%) of **23**. All spectral data were identical with data of authentic **23**.

Cyclohexane-1-spiro-1′-[2,4-bis[3,5-di-*tert*-butyl-4-(trimethylsiloxy)phenyl]bicyclo[1.1.0]butane]-3′-spiro-1″-cyclohexane (41): 115 mg (5.00 mmol) of Na, 597 mg of **25**, 326 mg of Me_3SiCl, 11-h reflux. To the violet residue was added 10 mL of petroleum ether, and after filtration the solvent was evaporated. The oily residue, treated as described for **40**, afforded 540 mg (76%) of **41** as colorless crystals: mp 148–150 °C; IR (KBr) 3040, 2930, 2850, 1592, 1256, 1227, 1121, 929, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.37 (s, 18 H, OSiMe_3), 1.39 (s, 36 H, C(CH_3)$_3$), 1.05–1.65 and 2.07–2.12 (m, 2 H, –CH_2–), 7.27 (s, 4 H, Ar H); ^{13}C NMR ($CDCl_3$) δ 3.58 (q, C-7′), 24.61, 26.62, 26.90, 33.08, 35.26 (all t, C-1″, C-2″, C-3″, C-4″, C-5″), 31.59 (q, C-9′), 35.08 (s, C-8′), 42.98 (s, C-1,3), 56.82 (s, C-2,4), 127.96 (s, C-4′); UV (cf. Table I); MS (70 eV), *m/e* 745, 744, 743, 742 (4, 14, 34, 53, M^+), 685 (10, M – $SiMe_3$), 464 (14), 371 (23), 305 (18), 73 (100, C_3H_9Si), 57 (88, C(CH_3)$_3$). Anal. Calcd for $C_{48}H_{78}O_2Si_2$ (743.2): C, 77.56; H, 10.58. Found: C, 77.69; H, 10.73.

2,2,4,4-Tetramethyl-1,3-bis[9-(trimethylsiloxy)-anthronyl]bicyclo[1.1.0]butane (42): 80.5 mg (3.50 mmol) of Na, 493 mg of **37**, 326 mg of Me_3SiCl, 9 h ultrasound at 10 °C. Workup according to that described for **40** yielded crude **42** (~80%) as yellow oil, which could not be crystallized without decomposition. By comparison with **43** (vide infra), the following ^1H NMR signals ($CDCl_3$) support the given structure: δ 0.31 (s, OSiMe_3, cf. 0.30 in **40**), 1.05 (s, CH_3), 1.96 (s, CH_3), 6.85–7.70 and 8.15–8.60 (m, Ar H). On treatment of the oil with methanol, 320 mg (62%) of **37** (IR, ^1H NMR) was recovered.

2,2,4,4-Tetramethyl-1,3-bis[9-(*tert*-butyldimethylsiloxy)-10-anthryl]bicyclo[1.1.0]butane (43): 80.5 mg (3.50 mmol) of Na, 493 mg of **37**, 452 mg of *t*-BuMe_2SiCl, 5.5 h ultrasound at room temperature. Workup according to that described for **40** furnished 435 mg (60%) of **43** as pale yellow crystals: mp 158–161 °C; IR (KBr) 3095, 3060, 2965, 2942, 2910, 2875, 1629, 1562, 1525, 1269, 1263, 1116 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.24 (s, 12 H, OSi-*t*-BuMe_2), 1.06 (s, 6 H, endo-CH_3), 1.22 (s, 18 H, OSi-*t*-BuMe_2), 1.94 (s, 6 H, exo-CH_3), 6.93–7.46 and 8.24–8.49 (m, 16 H, Ar H); ^{13}C NMR ($CDCl_3$) δ –2.97 (q, C-11′), 18.93 (s, C-12′), 25.12, 25.48 (both q, C-5, C-6), 26.24 (q, C-13′), 43.63 (s, C-1,3), 49.29 (s, C-2,4), 123.48, 124.09, 128.77 (all d, C-1′,8′, C-2′,7′, C-3′,6′, C-4′,5′), 123.20, 123.90 (both s, C-4a′,10a′, C-8a′,9a′), 133.32 (s, C-10′), 147.26 (s, C-9′); UV (cf. Table I); MS (70 eV), *m/e* 725, 724, 723, 722 (6, 18, 41, 68, M^+), 361 (30), 73 (100). Anal. Calcd for $C_{48}H_{58}O_2Si_2$ (732.2): C, 79.72; H, 8.08. Found: C, 79.32; H, 8.02.

1,2-Bis[3,5-di-*tert*-butyl-4-(trimethylsiloxy)phenyl]ethene (44). The reaction was run according to the general procedure for **23**, **25**, and **37**, except that trimethylchlorosilane was added prior to workup. To a suspension of 97 mg (4.2 mmol) of sodium in 5 mL of THF was added 869 mg (2.0 mmol) of 3,5,3′,5′-tetra-*tert*-butylstilbene-4,4′-quinone, in 15 mL of THF. After a 5-h treatment with ultrasound, 478 mg (4.4 mmol) of trimethylchlorosilane in 3 mL of THF was slowly added. Thereby the green blue color of the solution turned to orange. After 1 h, the solvent was evaporated and the residue treated with 50 mL of petroleum ether and again evaporated after filtration, yielding 1.14 g (98%) of crude **44** as yellow-orange crystals. After three recrystallizations from ligroin/2-propanol (1:3), 386 mg (33%) of **44** was obtained as colorless crystals: mp 204–206 °C; IR (KBr) 3039, 2960, 2920, 2870, 1423, 1268, 1255, 1240, 1230, 1140, 970, 845, 770 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.42 (s, 18 H, SiMe_3), 1.45 (s, 36 H, C(CH_3)), 6.91 (s, 2 H, olefinic *H*). Anal. Calcd for $C_{36}H_{60}O_2Si_2$ (581.1): C, 74.42; H, 10.41. Found: C, 74.67; H, 10.62.

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