J = 5.4 and 3.0 Hz), 7.14-7.41 (8 H, m), 8.10 (1 H, d, J = 8.4 Hz). Conducting the above reaction on a 2.88 mM scale gave **2** (1.037 g, 76% after recrystallization from MeOH). Anal. Calcd for $C_{33}H_{38}N_2O_3SSi$: C, 69.43; H, 6.71; N, 4.91. Found: C, 69.24, H, 6.74; N, 4.96. Further elution gave **3** (9 mg, 3%), whose ^1H NMR spectrum was identical with an authentic sample of **3**.[1]

Pummerer Reaction on 2 and the Formation of (±)-2,3,6,7-Tetrahydro-1-carbomethoxy-11-β-(phenylthio)-20,21-dinoraspidospermidin-8-one (6). A solution of MCPBA (17 mg, 83 μM) in CH_2Cl_2 (1 mL) was added over 0.5 h to a stirred solution of **2** (47 mg, 82.3 μM) in CH_2Cl_2 (1.5 mL) and 10% aqueous $NaHCO_3$ (1.5 mL) at 0 °C. The CH_2Cl_2 layer was separated and the aqueous phase extracted with CH_2Cl_2 (2 mL); the combined extracts were dried ($MgSO_4$) and evaporated to give the derived sulfoxide (58 mg, 100%) as a mixture of diastereoisomers (1:1). To a solution of the above sulfoxides in CH_2Cl_2 (1 mL) at 0 °C was added trifluoroacetic anhydride (26 μL, 184 μM), and the mixture was maintained at 20 °C for 1 h. The mixture was evaporated and toluene (2 mL) added to the residue. After the solution was heated at reflux (ca. 110 °C) for 1 h, the mixture was washed with saturated aqueous $NaHCO_3$, dried ($MgSO_4$), and evaporated in vacuo to give a brown glass (41 mg), which was chromatographed over silica gel (4 g) eluting with EtOAc to give **5** (7 mg, 15%): mp 174-176 °C (from EtOAc/hexane); IR ($CHCl_3$) 1710, 1615, 1440, and 1370 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ -0.10 (9 H, s), 1.06 (1 H, s), 2.01-2.06 (2 H, m), 2.49 (1 H, dd, J = 9.0 and 3.3 Hz), 2.94 (1 H, dd, J = 9.0 and 4.2 Hz), 3.07 (1 H, m), 3.08 (1 H, d, J = 12.0 Hz), 3.13 (1 H, d, J = 6.0 Hz), 3.17 (1 H, d, J = 12.0 Hz), 3.44 (1 H, br s), 3.89 (3 H, s), 4.09 (1 H, d, J = 5.0 Hz), 4.61 (1 H, dd, J = 10.8 and 5.6 Hz), 6.07 (1 H, dd, J = 5.5 and 3.0 Hz), 6.32 (1 H, br s), 7.11-7.17 (7 H, m), 7.37 (1 H, ddd, J = 8.0, 6.0, and 3.0 Hz), 7.84 (1 H, br d, J = 8.0 Hz). Anal. Calcd for $C_{33}H_{36}N_2O_3SSi$: C, 69.68; H, 6.38; N, 4.93. Found: C, 69.49; H, 6.34; N, 4.94. Further elution gave **6** (22 mg, 67%) identical with an authentic sample. The ratio of **5** to **6** varies with the reaction time and the reaction temperature. For example, conducting the Pummerer reaction in benzene at 70 °C for 1.5 h gave **5** (41%) and **6** (53%).

Retro-Diels-Alder Reaction of Adducts 2 and 5. A degassed (freeze-thaw, 0.1 Torr) solution of **2** (8.3 mg) in toluene (1 mL), contained in a resealable Carius tube, was heated at 180-190 °C for 7 h. Evaporation of the mixture gave **3** (ca. 100%), identical with an authentic sample. Similar treatment of **5** (8.0 mg) at 120 °C for 0.5 h gave **6** (ca. 100%), identical with an authentic sample.

Retro-Diels-Alder Reaction of 14 in the Presence of Maleic anhyride. A mixture of the adduct **14** (22 mg, 0.09 mM) and maleic anhydride (12 mg, 0.122 mM) in dry $CHCl_3$ (3 mL) was stirred at 70 °C for 3 h. The mixture was cooled and evaporated, and the residue was recrystallized from hexane/CH_2Cl_2 to give **15** (15 mg, 71%): mp 98-99 °C, NMR (90 MHz, $CDCl_3$) δ -0.05 (9 H, s), 1.24 (1 H, s), 3.62 (4 H, m), 6.26 (2 H, m).

Kinetics. The recrystallized adduct **14** (0.7-1.5 mM) and freshly sublimed maleic anhydride (2.0-4.3 mM) were dissolved in chlorobenzene (100 mL), and the solution was placed in a refluxing solvent bath (temp ±0.2 °C) and equilibrated while being magnetically stirred. Aliquots (3 mL) were removed and cooled in ice-water. Analysis of each aliquot was carried out with a Perkin-Elmer 330 spectrometer, observing the increase in absorbance at 435 nm for the benzoquinone chromophore.

Data were obtained over the first 3 to 5 half-lives, with infinity absorbance recorded after at least 10 half-lives. The reaction displayed clean first-order kinetics over 1 to 2 half-lives, and the slope of the log $(A_\infty - A_t)$ vs. time curve was obtained by least-squares analysis enabling the first-order rate constant to be calculated.

A control rate run was carried out to determine the effect, if any, of added maleic anhydride on the rate of cycloreversion of **13**. Data obtained at 78 °C were comparable to those obtained by Wasserman and Khambata [3.1×10^{-4} min^{-1}, 3.3×10^{-4} min^{-1} vs. 3.3×10^{-4} min^{-1} (lit.[4])].

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[4]Paracyclophane Intercepted

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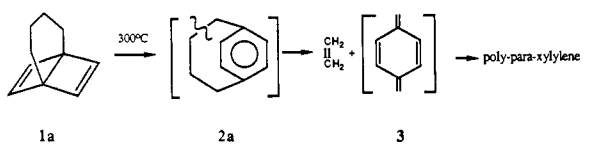
Abstract: Irradiation (254 nm) of 1,4-tetramethylene(Dewar benzene) (**1a**) at -20 °C in THF leads to [4]paracyclophane (**2a**). In the absence of acid, **2a** polymerizes immediately. In the presence of CF_3COOH, adducts **6** and **7** are formed by protonation of **2a** at a bridgehead carbon atom to give the benzenonium ion **9a**, followed by addition of a nucleophile, i.e., CF_3COO^- or THF, respectively, at the other bridgehead carbon, leading to a bridged 1,4-dihydrobenzene. The corresponding methanol adduct **8** is formed on irradiation of **1a** in methanol solution in the presence of CF_3COOH. The difference in behavior between **2a** and its higher homologue is discussed on the basis of calculated charge densities.

Small [n]cyclophanes[1] continue to receive considerable interest. It has been shown that reducing the length of their oligomethylene bridge forces the benzene ring into a nonplanar, boat-type geometry. Surprisingly, this change appears to hardly impair the aromatic delocalization.[2] On the other hand, the increasing strain clearly manifests itself in a rapid decrease of thermal stability. This is convincingly demonstrated by the instability of the shortest member of the homologous family of [n]paracyclophanes, the recently prepared [5]paracyclophane (**2b**).[3] This hydrocarbon

Scheme I



1a 2a 3

is thermally unstable above 0 °C and polymerizes;[3a] substitution of the aromatic ring by electron-withdrawing groups increases the thermal stability somewhat, but still the half-lives are not more than several hours at room temperature.[3b-d] Reasonable, though not complete stability is encountered only with the next higher homologue [6]paracyclophane (**2c**).[4] Extrapolating the homologous series in the opposite direction, one expects a dramatic decrease in stability for [4]paracyclophane (**2a**) for which MNDO

(1) For a review, see: Keehn, P. M.; Rosenfeld, S. M., Eds. *Cyclophanes*; Academic Press: New York, 1983.

(2) Van Zijl, P. C. M.; Jenneskens, L. W.; Bastiaan, E. W.; MacLean, C.; De Wolf, W. H.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1986**, *108*, 1415.

(3) (a) Jenneskens, L. W.; De Kanter, F. J. J.; Kraakman, P. A.; Turkenburg, L. A. M.; Koolhaas, W. E.; De Wolf, W. H.; Bickelhaupt, F.; Tobe, Y.; Kakiuchi, K.; Odaira, Y. *J. Am. Chem. Soc.* **1985**, *107*, 3716. (b) Tobe, Y.; Kaneda, T.; Kakiuchi, K.; Odaira, Y. *Chem. Lett.* **1985**, 1301. (c) Kostermans, G. B. M.; De Wolf, W. H.; Bickelhaupt, F. *Tetrahedron Lett.* **1986**, *27*, 1095. (d) Kostermans, G. B. M.; De Wolf, W. H.; Bickelhaupt, F., submitted for publication.

(4) (a) Kane, V. V.; Wolf, A. D.; Jones, M., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 2643. (b) Kammula, S. L.; Iroff, L. D.; Jones, M., Jr.; Van Straten, J. W.; De Wolf, W. H.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1977**, *99*, 5815.

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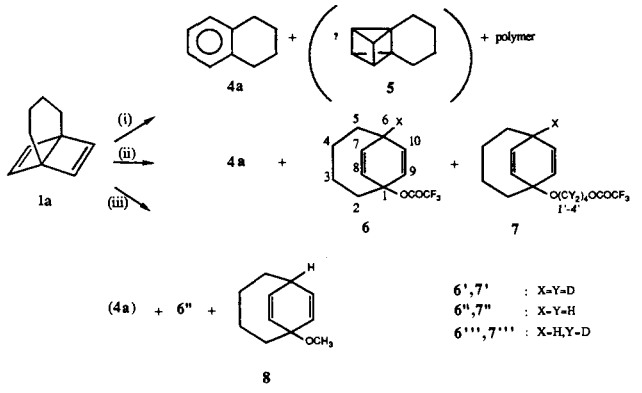
Scheme II



(*i*) [D_8]THF, -50°C, hv. (*ii*) [Y_8]THF, -20°C, 5-30 eq. CF_3COOX, hv.
(*iii*) CH_3OH, -20°C, 5 eq. CF_3COOH, hv.

calculations indicate a strain energy (about 88 kcal·mol^{-1})[5] which by far exceeds the estimated resonance energy of benzene (ca. 20–40 kcal·mol^{-1}).[6] Therefore the question may be raised whether **2a** is not beyond the limit of stability and thus not capable of existence. We wish to present chemical evidence that **2a** is formed at −20 °C in solution as an unstable intermediate which can be intercepted.

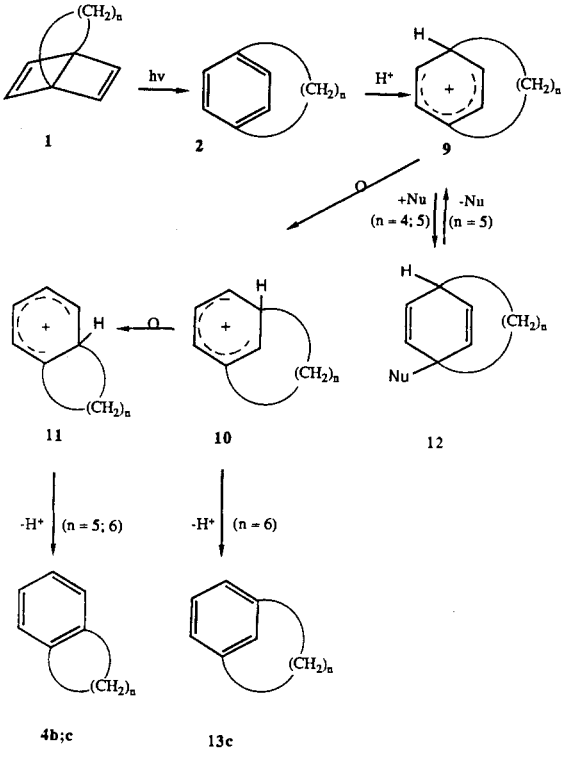
In this context it should be pointed out that the fleeting intermediacy of **2a** has been tentatively invoked as early as 1974[7] in order to explain the product formation on flow thermolysis at 300 °C of **1a**, the Dewar isomer of **2a** (Scheme I). The products *p*-xylylene (**3**) and ethylene could best be explained by postulating **2a** as an intermediate (vide infra).

Results and Discussion

It was obvious that the chances to isolate or even intercept **2a** under thermal conditions were extremely poor. On the one hand, the higher homologue **2b** was really stable only at −20 °C, so **2a** could be expected to decompose at or below that temperature. On the other hand, the precursor **1a** of **2a** did not react, at least under flow pyrolysis conditions,[7] below 300 °C, in contrast to **2b** (285 °C) and **2c** (60 °C).[8] The behavior of the latter is more or less typical for the aromatization of a normal Dewar benzene.[4b]

We therefore attempted the photolytic approach to **2a** which can be performed at much lower temperature and had proven successful in the case of **2b**.[3] However, the irradiation of **1a**[7,9] in [D_8]THF at −50 °C in a quartz NMR tube with a low-pressure mercury lamp (254 nm) did not give a clear indication for the formation of **2a**; instead, within 3 h a white polymer was formed together with some tetralin (**4a**; 3%); another minor product, which was not fully characterized, is probably the prismane **5** (2%), as indicated by a signal of the crude reaction mixture at $\delta(^1H)$ = 2.29 ppm which may be assigned to the four prismane protons[10] (Scheme II). In analogy to the polymerization of **2b**, especially on continued irradiation,[3a] it was conceivable that the predominant polymer formation was due to rapid polymerization of initially formed **2a**. If this assumption was correct, it seemed promising to attempt the interception of **2a** by acid; in analogy to the rapid acid catalyzed rearrangement of **2b** to cycloheptabenzene (**4b**) at −20 °C,[3a] it was expected that **2a** should quantitatively rearrange to tetralin (**4a**).

Scheme III



a : n = 4; b : n = 5; c : n = 6

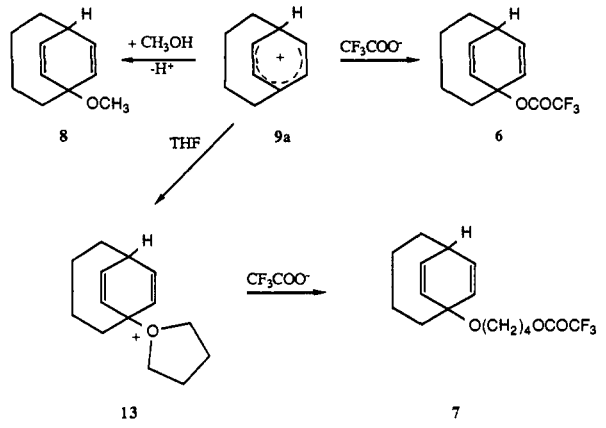
Compound **1a** was checked to be stable in THF at −20 °C with 5 equiv of CF_3COOH in the absence of light. On irradiation in [D_8]THF in the presence of various amounts of CF_3COOD, **1a** was completely consumed within 1–4 h depending on the amount of **1a** (1–90 mg). Polymer was not formed at all, but neither was the yield of **4a** (3%) increased. Instead, two new products **6'** and **7'** were formed in close to quantitative yield (Scheme II). The ratio of **6'**:**7'** varied from 1:4 to 4:1; it depends on the amount of acid, but also to some extent on temperature and concentration. The origin of X from CF_3COOX and of Y from [Y_8]THF was established by repeating the irradiation with CF_3COOH in THF or with CF_3COOH in [D_8]THF which yielded **6"** and **7"**, or **6'''** (=6") and **7'''**, respectively. Using methanol instead of THF as the solvent gave, under identical conditions, a trace of **4a** (<1%), **6'''** (3%), and the new product **8** (97%). All new products were isolated by preparative gas chromatography and identified by their spectral data (see Experimental Section).

We feel that these results present strong indirect evidence for the intermediacy of **2a**, even though final proof in the form of a direct, e.g., spectroscopic, detection is still missing. A rationalization is presented in Schemes III and IV, for which the following arguments can be advanced.

The first step in the sequence of reactions is the photochemical aromatization of the Dewar isomer **1a** to **2a**. This reaction is well-known in Dewar benzene chemistry;[13] in particular, a close analogy can be found in the conversion of **1b** to **2b**[3a] and of **1c** to **2c**.[4b] In the two latter examples, the aromatic component **2** can be observed directly; a photochemical equilibrium is established between **1** and **2**. In these equilibria, the ratios **1b**:**2b** = 93:7 and **1c**:**2c** = 75:25 reflect to some extent the amount of strain involved

(5) Jenneskens, L. W. Thesis, 1986, Vrije Universiteit, Amsterdam.
(6) (a) Lewis, D.; Peters, D. *Facts and Theories about Aromaticity*; MacMillan: London, 1975. (b) George, P.; Bock, C. W.; Trachtman, M. *Tetrahedron Lett.* **1985**, *26*, 5667 and references cited.
(7) (a) Landheer, I. J.; De Wolf, W. H.; Bickelhaupt, F. *Tetrahedron Lett.* **1974**, 2813. (b) Landheer, I. J. Thesis, 1976, Vrije Universiteit, Amsterdam.
(8) Van Straten, J. W.; Turkenburg, L. A. M.; De Wolf, W. H.; Bickelhaupt, F. *Recl. Trav. Chim. Pays-Bas* **1985**, *104*, 89, and references cited.
(9) Weinges, K.; Klessing, K. *Chem. Ber.* **1974**, *107*, 1915.
(10) The formation of prismanes has not been observed so far on irradiation of **2b**.[3a] However, a prismane isomeric to **5** with a tetramethylene bridge across a cyclopropane edge has been obtained in quantitative yield on analogous irradiation of 2,6-tetramethylene(Dewar benzene); its prismane protons resonate at δ 2.33–2.15 ppm.[11] Prismanes are also formed on irradiation of substituted 1,4-hexamethylene(Dewar benzenes).[12]
(11) Kostermans, G. B. M.; Hogenbirk, M.; De Wolf, W. H.; Bickelhaupt, F., submitted for publication.
(12) (a) Liebe, I.; Wolff, C.; Tochtermann, W. *Tetrahedron Lett.* **1982**, *23*, 171. (b) Tobe, Y.; Kakiuchi, K.; Odaira, Y.; Hosaki, T.; Kai, Y.; Kasai, N. *J. Am. Chem. Soc.* **1987**, *105*, 1776.
(13) Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978.

Scheme IV



in **2**. By extrapolation to the tetramethylene series, one may expect the steady-state concentration of **2a** in the photoequilibrium **1a** ⇄ **2a** to be far below the 7% observed for **2b**. Furthermore, as mentioned above, the observed rapid (photochemical?) polymerization of **2a** in the absence of an intercepting reagent parallels the behavior of **2b**. Both factors are obviously detrimental to the direct spectroscopic observation of **2a**.

In the presence of a moderately strong acid like trifluoroacetic acid, the next step is protonation of **2a** at a bridgehead carbon atom to form the benzenonium cation **9a**. This reaction will be extremely favorable, as the strain in **2a** (MNDO: about 88 kcal·mol^{-1})[5] is reduced to about 34 kcal·mol^{-1} in **9a**; it is therefore apparently quite rapid and competes successfully with the otherwise occurring polymerization. This protonation reaction has precedent for the higher homologues, too. However, both the ease of formation and the further chemical fate of **9** show gradual, but characteristic differences with increasing strain. Thus, the protonation of **2c**[14] occurs at ambient temperature and leads by Wagner–Meerwein rearrangement via **10c** and **11c** and deprotonation to a mixture of the meta and the ortho isomers **13c** and **4c**, respectively, in a ratio of 1:3 (Scheme III). In contrast, **2b** is protonated already at −20 °C to give **9b** which shows a mixed behavior. In our preliminary communication,[3a] we reported the rapid formation of **4b** from **2b** (the meta isomer **13b** was not observed and, in fact, is known to rearrange rapidly on acid treatment to give **4b**[8]). A recent closer scrutiny of this reaction revealed that under controlled conditions and at low temperatures, dihydrobenzene intermediates analogous to **6** and **7** are formed, apparently by a similar addition of a nucleophile (trifluoroacetate or THF) to **9b**. Contrary to **6** and **7**, the higher homologues are thermally unstable and have a high tendency to cleave off the nucleophile and revert to **9b** which eventually aromatizes via **10b** and **11b** to **4b**. Because of their instability, these intermediates have not yet been fully characterized.[15] The trend of exclusive aromatization for **2c** via dual behavior of **2b** continues for **2a**, which shows the other extreme of the reactivity pattern: on acid treatment in situ, **2a** does not lead to **4a**, as evidenced by the unchanged amount of **4a** (3%), but instead gives dihydrobenzenes such as **6**, **7**, and **8** exclusively. In other words, intermediate **9a** shows no inclination to give a Wagner–Meerwein rearrangement to **10a**, but it stabilizes itself by addition of whatever nucleophile it encounters to furnish **12**. We will return to this point later.

The reaction of **9a** with nucleophiles constitutes the third step in the reaction sequence of Scheme III. In Scheme IV, the different possibilities are analyzed in more detail. The solvolysis of **9a** with methanol to give, after deprotonation, **8** is perhaps not too surprising, although it is certainly without precedent for normal, flat benzene derivatives. A little less straightforward is the interception of **9a** by the weak nucleophile trifluoroacetate to furnish **6**. Quite exceptional, however, is the attack of **9a** on the otherwise quite unreactive tetrahydrofuran. It leads to the oxonium ion **13** which in a S_N2 reaction with trifluoroacetate anion gives the final product **7** under ring opening.

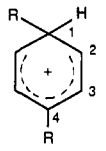
The course of events depicted in Schemes III and IV is tentative in so far as none of the postulated intermediates including **2a** has been observed directly. Nevertheless, this mechanism is by far the most simple and likely one. Alternative schemes may be envisaged; e.g., **1a** could be protonated reversibly and the protonated species be excited by irradiation and then converted to excited **9a**, etc.;[16] or **1a** might be photoexcited and then protonated, etc. However, these alternative schemes have drawbacks compared to the proposed mechanism. In the first place, they have no precedent, while the proposed scheme, as discussed above, does. In the second place, even though accurate kinetic measurements have not been performed, the rate of disappearance of **1a** is the same in the presence or absence of acid. This is a supportive and necessary requirement for the proposed mechanism, but it would be highly accidental and unlikely for other schemes in which the reaction with and without acid are uncorrelated. A third argument in favor of the intermediacy of **2a** is the following. There is no doubt that the protonation of **1a**, if relevant, is an equilibrium reaction which lies far on the side of unprotonated **1a**. Irradiation of **1a** in the presence of acid would therefore in fact come down to irradiation of a minute amount of protonated species and simultaneous irradiation of close to 100% of unprotonated species. Now the latter process has been demonstrated in a separate experiment to lead to immediate and nearly quantitative polymer formation; consequently, polymer should also be formed on irradiation of **1a** in the presence of acid. This is clearly in contradiction to experimental facts.

Finally, as mentioned in the introduction, there is support for the claim that **2a** is a molecule capable of (temporary) existence from the mechanistically unrelated flow pyrolysis of **1a**.[7] Again, extrapolation from the behavior of the higher homologues **1b** and **1c** furnishes strong, though circumstantial evidence. The temperature necessary for thermolysis increases with increasing strain of **2** from **1c** (60 °C) via **1b** (285 °C) to **1a** (300 °C). In support of this reasoning, the lower homologue of **1a**, 1,4-trimethylene (Dewar benzene), is stable on flow pyrolysis up to 300 °C and is recovered unchanged, obviously because the only unimolecular mode of reaction is aromatization to the [*n*]paracyclophane, with [3]paracyclophane being prohibitively strained and therefore inaccessible.[17] Returning to **1a**, its thermolysis gives **2a** which fragments by cleavage of a benzylic bond[18] as indicated in Scheme I, followed by β-cleavage of the resulting diradical to ethylene and **3**.[7] Taking all this evidence together makes the intermediacy of **2a** in thermolysis much more likely than the conceivable alternative of $[\sigma^2 + \sigma^2 + \sigma^2]$ fragmentation. Similarly, we feel that no other interpretation presents an equally consistent rationalization of all observations on photolysis of **1a** as does the intermediate formation of **2a**.

Two aspects of the presented mechanism need additional comment. In the first place, the question arises why **9** shows a chemical behavior which is so remarkably dependent on the bridge length *n*; in particular, why does **9a**, contrary to expectation, not rearrange rapidly and cleanly to **10a** and finally to **4a**? To answer this question, we performed MNDO[19] and MINDO/3[20] calculations on **9a–c** and on the dimethyl analogue **9d** (Table I); MINDO/3 calculations were included because they usually give better predictions of heats of formation and gross atomic charges for cations.[21] Even though the results may be expected to furnish not more than a qualitative indication, it is obvious that the charge distribution in the benzenonium cations **9** shows an interesting trend. With increasing strain and bending of the benzenonium

(14) Tobe, Y.; Ueda, K.; Kakiuchi, K.; Odaira, Y. *Chem. Lett.* **1983**, 1645.
(15) Preliminary results; to be published.
(16) This possibility has been suggested by a referee.
(17) Landheer, I. J.; De Wolf, W. H.; Bickelhaupt, F. *Tetrahedron Lett.* **1975**, 349.
(18) Jenneskens, L. W.; De Wolf, W. H.; Bickelhaupt, F. *Tetrahedron* **1986**, *42*, 1571, and references cited.
(19) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.
(20) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285.
(21) Clark, T. *Handbook of Computational Chemistry*; Wiley: New York, 1985; p 144.

Table I. Heats of Formation $\Delta H_f°$ and Gross Atomic Charges q of Benzenonium Ions **9**



9

		MNDO					MINDO/3				
			q^b					q^b			
compd	R + R	$\Delta H_f°$ [a]	C-1	C-2	C-3	C-4	$\Delta H_f°$ [a]	C-1	C-2	C-3	C-4
9a	$-(CH_2)_4-$	226.9	−0.08	0.09	−0.18	0.34	221.7	0.02	0.11	−0.13	0.38
9b	$-(CH_2)_5-$	212.2	−0.08	0.12	−0.18	0.30	206.4	0.01	0.13	−0.13	0.35
9c	$-(CH_2)_6-$	202.2	−0.08	0.13	−0.17	0.28	193.4	0.01	0.15	−0.12	0.33
9d	CH_3, CH_3	194.4	−0.10	0.14	−0.16	0.24	189.8	0.01	0.18	−0.12	0.32

[a] In kcal·mol^{-1}. [b] In Z.

ring, the positive charge at the ortho carbons (C-2) decreases, while that at the para carbon (C-4) increases. In terms of resonance structures this can be understood because the structure with the positive charge on C-2 has a double bond between C-3 and C-4 which violates Bredt's rule. It is, however, *this* structure which permits a 1,2-carbon shift from C-1 to C-2. Less charge at C-2 is therefore expected to decrease the driving force for the Wagner–Meerwein rearrangement **9** → **10**. The MINDO/3 results show that in **9c**, the charge at C-2 is reduced by only 17% relative to the model **9d**. In contrast, in **9a** the charge reduction is 39%, while **9b** occupies an intermediate position. We suggest that the strong reduction of charge at C-2 in **9a** retards the rearrangement sufficiently to give the alternative interception by a nucleophile a chance. Conversely, the increase of positive charge at C-4 from **9c** to **9b** and especially to **9a** favors the attack of nucleophiles to form **12** (Scheme III). Even though the overall pathway from **9a** to **4a** would be thermodynamically much more favorable, it loses kinetically to the solvolysis which leads to the dihydrobenzenes **6**, **7**, and **8**.

A second minor point concerns the formation of tetralin (**4a**) from **1a**. As pointed out above, it cannot be derived from **2a** as its yield is unchanged on addition of acid. The formation of **4a** from the presumable prismane **5** is also questionable, as **5** does not rearrange to **4a** at −50 °C. The origin of **4a** is therefore at present unclear.

Experimental Section

^{1}H NMR spectra were recorded on a Bruker WM 250 spectrometer. Pairs of assignments indicated by *, **, or ***, respectively, are tentative and may have to be reversed. GCMS spectra were measured on a HP 5890 MSD and HRMS spectra on a Varian CH-5 DF operating at 70 eV.

The assignment of proton signals of **6**, **7**, and **8** is supported by the ^{1}H NMR spectrum of bicyclo[4.2.2]deca-7,9-diene (δ(H(1,6)) 2.92; δ(H-(7,8,9,10)) 5.87).[22]

Irradiation of [4.2.2]Propella-7,9-diene (1a) in THF in the Presence of CF_3COOH. A solution of **1a**[7] (90 mg, 0.6 mmol) and CF_3COOH (18 mmol) in THF (2 mL) in a quartz NMR tube was irradiated for 4 h at −20 °C with a low-pressure mercury lamp (254 nm). The conversion to **4a** (3%), **6″** (24%), and **7″** (73%) was quantitative on the basis of ^{1}H NMR (THF internal standard) and analytical GCMS analysis. Preparative GC (1.5 m, 15% SE-30, H_2, as carrier gas 60 mL/min, 170 °C) gave **6″** (35 mg, 0.14 mmol, 23%; retention time 1 min) and **7″** (10 mg, 0.03 mmol, 5%; retention time 7 min) as the first and second fraction, respectively. **1-Trifluoroacetoxybicyclo[4.2.2]deca-7,9-diene (6″)**: Colorless liquid; ^{1}H NMR (250 MHz, $CDCl_3$, 298 K) δ 6.07 (AB part of ABX system, δ(A) = 6.03, H(8,9), δ(B) = 6.11, H(7,10), J(AB) = 10 Hz, J(BX) = 5 Hz, 4 H), 3.07 (m, 1 H, H(6), X part of ABX system), 2.04 (m, 2 H, H(2)), 1.72 (m, 2 H, H(5)), 1.53 (m, 4 H, H(3,4)); ^{13}C NMR (62.89 MHz, $CDCl_3$, 298 K) δ 156.0 (q, ^2J(CF) = 42 Hz, *C*=O), 130.7 (d, ^1J(CH) = 162 Hz, C(8,9)*), 130.3 (d, ^1J(CH) = 170 Hz, C(7,10)*), 114.4 (q, ^1J(CF) = 287 Hz, *C*F_3), 85.9 (s, C(1)), 39.9 (t, ^1J(CH) = 129 Hz, C(2)), 35.6 (d, ^1J(CH) = 133 Hz, C(6)), 33.7 (t, ^1J(CH) = 127 Hz, C(5)), 24.6 (t, ^1J(CH) = 128 Hz, C(3)**), 24.1 (t, ^1J(CH) = 129 Hz, C(4)**); MS, m/z (relative intensity) 246 (38) M•$^+$, 203 (81) [M− C_3H_7]$^+$, 107 (58), 91 (71), 84 (100); HRMS calcd for $C_{12}H_{13}F_3O_2$ 246.0867, found 246.0852. **1-(4′-Trifluoroacetoxybutoxy)-bicyclo[4.2.2]deca-7,9-diene (7″)**: colorless liquid; ^{1}H NMR (250 MHz, $CDCl_3$, 298 K) δ 5.96 (AB part of ABX system, δ(A) = 5.86, H(8,9), δ(B) = 6.05, H(7,10), J(AB) = 10 Hz, J(BX) = 5 Hz, 4 H), 4.39 (t, ^3J(HH) = 7 Hz, 2 H, H(4′)), 3.41 (t, ^3J(HH) = 6 Hz, 2 H, H(1′)), 2.93 (m, 1 H, H(6), X part of ABX system), 1.85 (m, 2 H, H(3′)), 1.65 (m, 6 H, H(2′) and H(2,5)), 1.47 (m, 4 H, H(3,4)); ^{13}C NMR (62.89 MHz, $CDCl_3$, 298 K) δ 157.7 (q, ^2J(CF) = 42 Hz, C=O; tentative assignment), 134.2 (d, ^1J(CH) = 162 Hz, C(8,9)*), 131.7 (d, ^1J(CH) = 160 Hz, C(7,10)*), 114.3 (q, ^1J(CF) = 286 Hz, CF_3), 76.7 (s, C(1)), 68.2 (t, ^1J(CH) = 149 Hz, C(4′)), 63.5 (t, ^1J(CH) = 141 Hz, C(1′)), 41.4 (t, ^1J(CH) = 129 Hz, C(2)), 35.7 (d, ^1J(CH) = 129 Hz, C(6)), 34.2 (t, ^1J(CH) = 127 Hz, C(5)), 26.6 (t, ^1J(CH) = 125 Hz, C(3′)**), 25.4 (t, ^1J(CH) = 125 Hz, C(2′)**), 25.0 (t, ^1J(CH) = ca. 125 Hz, C(3)***), 24.7 (t, ^1J(CH) = 127 Hz, C(4)***); MS, m/z (relative intensity) 318 (22) M•$^+$, 275 (33) [M − C_3H_7]$^+$, 107 (96), 91 (52); HRMS calcd for $C_{16}H_{21}O_3F_3$ 318.1442, found 318.1450.

Irradiation of 1a in [D_8]THF in the Presence of CF_3COOD. The experiment was performed as described above with **1a** (13 mg, 0.087 mmol), CF_3COOD (0.45 mmol), and [D_8]THF (0.5 mL). According to ^{1}H NMR and GCMS, the ratio of **6′** to **7′** was 2:3. **6-[D]-1-Trifluoroacetoxybicyclo[4.2.2]deca-7,9-diene (6′)**: ^{1}H NMR spectrum was identical with that of **6″** except for the absence of the signal of H(6); MS, m/z (relative intensity) 247 (13) M•$^+$, 203 (45) [M − C_3H_6D]$^+$, 107 (33), 92 (100). **6,1′,1′,2′,2′,3′,3′,4′,4′-[D_9]-1(4′-Trifluoroacetoxybutyoxy)bicyclo[4.2.2]deca-7,9-diene (7′)**. The ^{1}H NMR spectrum was identical with that of **7″** except for the absence of the signals of H(6) and H(1′-4′); ^{2}H NMR (38.4 MHz, $CHCl_3$, 298 K) δ 4.36 (s, 2D, D(4′)), 3.38 (s, 2D, D(1′)), 2.90 (s, 1D, D(6)), 1.79 (s, 2D, D(3′)), 1.59 (s, 2D, D(2′)); the retention times on GCMS of **6′** and **6″** and of **7′** and **7″**, respectively, were identical; MS, m/z (relative intensity) 327 (40) M•$^+$, 283 (81) [M − C_3H_6D]$^+$, 203 (8), 177 (25), 108 (100), 92 (45).

Irradiation of 1a in [D_8]THF in the presence of CF_3COOH. The experiment was performed as described above with **1a** (ca. 2 mg, 0.013 mmol), CF_3COOH (0.4 mmol), and [D_8]THF (0.5 mL). According to ^{1}H NMR and GCMS, the reaction was quantitative, and the ratio of **6‴**:**7‴** = 3:7. The ^{1}H NMR spectrum of **6‴** = **6″** was identical; the ^{1}H NMR spectrum of **7‴** was identical with that of **7″** except for the absence of the signals of H(1′-4′). Incidentally, this experiment happens to be historically the first one in the series, and the nonvisibility of the incorporated [D_8]THF fragment initially caused considerable headache when ^{1}H NMR and mass spectra were compared. MS, m/z:**6‴** identical to **6″**; **7‴** 326 (25) M•$^+$, 283 (46) [M − C_3H_7]$^+$, 203 (6), 177 (25), 108 (100), 91 (41). The retention times on GCMS of **6‴** and **6″** and of **7‴** and **7″**, respectively, were identical.

Irradiation of 1a in Methanol in the Presence of CF_3COOH. A solution of **1a** (35 mg, 0.23 mmol) and CF_3COOH (1.17 mmol) in methanol (2 mL) in a quartz NMR tube was irradiated for 4 h at −20 °C with a low-pressure mercury lamp (254 nm). According to GCMS, the conversion to **4a** (trace), **6‴** (3%), and **8** (97%) was quantitative. Compound **8** was isolated by preparative GC (1.5 m, 15% SE-30, H_2 as carrier gas, 70 °C; retention time 0.9 min). **1-Methoxybicyclo[4.2.2]deca-7,9-diene (8)**: colorless liquid; ^{1}H NMR (250 MHz, CD_2Cl_2, 298 K) δ 5.98 (AB part of ABX system, δ(A) = 5.91, H(8,9), δ(B) = 6.08, H(7,10), J(AB) = 10 Hz, J(BX) = 5 Hz, 4 H), 3.22 (s, 3 H, OCH_3), 2.94 (m, 1 H, H(6), X part of ABX system), 1.68 (m, 4 H, H(2,5)), 1.48 (m, 4 H, H(3,4)); ^{13}C NMR (62.89 MHz, CD_2Cl_2, 298 K) δ 133.9 (d, ^1J(CH) = 160 Hz, C(8,9)*), 132.0 (d, ^1J(CH) = 160 Hz, C(7,10)*), 77.3 (s, C(1)), 51.4 (q, ^1J(CH) = 140 Hz, OCH_3), 41.1 (t, ^1J(CH) = 127 Hz, C(2)), 35.5

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(d, ^1J(CH) = 131 Hz, C(6)), 33.9 (t, ^1J(CH) = ca. 120 Hz, C(5)), 24.8 (t, ^1J(CH) = ca. 132 Hz, C(3)**), 24.4 (t, ^1J(CH) = 127 Hz, C(4)**); MS, m/z (relative intensity) 164 (10) $M^{\bullet+}$, 121 (100) $[M - C_3H_7]^+$, 108 (7), 91 (18); HRMS calcd for $C_{11}H_{15}O$ 164.1201, found 164.1203.

Treatment of 1a in THF with CF_3COOH. Under exclusion of light, a solution of **1a** (10 mg, 0.067 mmol) and CF_3COOH (0.33 mmol) in THF (1 mL) was kept for 3 h at −20 °C. According to GCMS, no **6** and **7** had been formed and **1a** appeared to be unchanged.

Irradiation of 1a in [D_8]THF in the Absence of Acid. A solution of **1a** (5 mg, 0.04 mmol) in [D_8]THF (0.5 mL) was irradiated at −50 °C with a low-pressure mercury lamp (254 nm). Polymer formation occurred almost instantaneously; signals of **1a** decreased in the ^{1}H NMR spectrum. After 3 h of irradiation **1a** was completely consumed and signals of **4** (3%) and **5** (2%) were found ([D_7]THF as internal standard).

The Unexpected Regioselectivity in the Singlet Oxygen Cycloadditions to Electron-Rich 1,3-Butadienes

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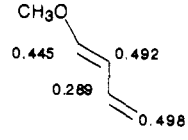
Abstract: The reactions of singlet oxygen with (*E*)- and (*Z*)-1-*tert*-butoxy-1,3-butadiene are compared to the reactions of these substrates with tetracyanoethylene and diphenylketene. Singlet oxygen unlike the other reagents exhibits an affinity for the most highly substituted olefinic linkage in these dienes. The reason for this unusual regiochemical preference of singlet oxygen is discussed. It is suggested that the relative stabilities of the two possible perepoxide regioisomers play a major role in determining the product distribution.

Frontier molecular orbital theory (FMO) has been utilized successfully to predict the regiochemistry of many cycloaddition reactions.[1] These exothermic reactions are ideally suited to such analyses because the interactions in their early transition states can still be justifiably described as perturbations of the HOMOs and LUMOs of the reaction partners.[2] The potent electrophilic nature of singlet oxygen[3] and the exothermicities of its cycloaddition reactions would at first glance appear to fulfill the requirements for the successful application of this powerful theory. We report here, however, that FMO theory fails to predict the regiochemistry of the singlet oxygen 2 + 2 cycloaddition. We also suggest possible explanations for this unexpected behavior.

Results

The isomeric (*E*)- (**1**) and (*Z*)-1-*tert*-butoxy-1,3-butadiene (**2**)[4] reacted rapidly with singlet oxygen at −78 °C in CD_2Cl_2 to give the dioxetane and endoperoxide products shown in Scheme I. In the reactions of both dienes the more highly substituted cis dioxetanes were the major products of the reactions. This is the opposite regiochemistry from that predicted from an analysis of the absolute values of the P_z coefficients[5] or of the proton reactivity surface[5b] of 1-methoxy-1,3-butadiene. Analysis of the electrostatic



potentials[5b] for the four carbon atoms in this diene suggests that reaction at C_3C_4 is 4.9 kcal/mol more favorable than reaction at C_1C_2.

The regiochemical assignments in both reactions were based on analyses of the proton NMR spectra of the dioxetanes taken at −78 °C. The spectral assignments (Table I) were made with the aid of single frequency decoupling experiments and computer simulations. The stereochemical arrangement of the vinyl and *tert*-butoxy groups on the dioxetane rings were established by using the previous observation[6] that δ_{H_2} in cis-substituted dioxetanes are significantly upfield of δ_{H_2} in their trans isomers.

The regiochemical preference for the 2 + 2 cycloaddition was also corroborated by the observation that decomposition of the dioxetanes produced acrolein and *tert*-butyl formate. Only in the decomposition of the reaction mixture from photooxidation of the *E* isomer **1** was a small amount of 3-*tert*-butoxyacrolein observed.

The reactions of **1** and **2** were also investigated in CD_2Cl_2/

Table I. NMR Data for the Oxidation Products

^{1}H NMR[a]	3	4	6	^{1}H NMR[a]	3	4	6
δ_{H_1}[c]	6.56	6.57	6.24	J_{12}	5.9	5.9	10.1
δ_{H_2}	5.64	5.94	5.88	J_{23}	9.3	9.9	2.2
δ_{H_3}	6.34	6.47	5.57	J_{34}	10.1	9.9	1.8
δ_{H_4}	5.51	5.48	4.66	J_{35}	17.2	17.2	1.8
δ_{H_5}	5.63	b	4.34	J_{45}	1.8		17.0
δ_{CH_3}	1.15	1.16	1.21	J_{13}			1.5
				J_{14}			1.5
				J_{15}			4.4
				J_{24}			4.0
				J_{25}			1.8

[a] All NMR were taken at −80 °C in acetone-d_6 immediately after photolysis. [b] Not observed buried under another peak. [c] ppm.

Table II. Product Distributions as a Function of Solvent in the Reactions of Dienes **1** and **2** with Singlet Oxygen[a]

		products, %				
diene	solvent[b]	3	4	5[c]	6	A[d]
***E*-1**	$(CD_3)_2CO$	23	10	2	54	11
	$(CD_3)_2CO/CD_2Cl_2$ (4)	32	13	1	43	9
	$(CD_3)_2CO/CD_2Cl_2$ (1)	32	13	3	41	9
	$(CD_3)_2CO/CD_2Cl_2$ (0.25)	36[e]	15[e]	3	35	11
	CD_2Cl_2	44[e]	18[e]	3	35	0
***Z*-2**	$(CD_3)_2CO$	8	5	0	83	4
	$(CD_3)_2CO/CD_2Cl_2$ (4)	11	7	0	79	3
	$(CD_3)_2CO/CD_2Cl_2$ (1)	13	8	0	77	2
	$(CD_3)_2CO/CD_2Cl_2$ (0.25)	16[f]	10[f]	0	74	g
	CD_2Cl_2	18	12	0	70	0

[a] Distributions measured by integration and cut and weighing of the proton NMR spectrum and are only good to ±5%. [b] The number in the parentheses after the solvent is the volume/volume ratio of the solvents in the mixture. [c] Detected by observing 3-*tert*-butoxyacrolein after reaction mixture decompostion. [d] Directly formed acrolein. [e] Estimate from a seriously overlapped NMR spectrum. [f] Not adjusted for directly formed acrolein. [g] Not determined.

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